Centre for
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NATURAL ENVIRONMENT RESEARCH COUNCIL

Ozone Pollution:
Impacts on ecosystem services and biodiversity

Report prepared by
the ICP Vegetation
April 2013

Editors:
Gina Mills, Serena Wagg
and Harry Harmens

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Working Group on Effects
of the
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[1] International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops.

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Executive summary

In this report we provide a review of the state of current knowledge on the effects of ozone pollution on ecosystem services including consideration of effects on biodiversity. Although considered separately, all of the ecosystem services and underlying processes are interlinked, with for example, ozone impacts on root growth contributing to supporting services (primary productivity), provisioning (crop and timber production), regulating (C sequestration and impacts on climate) and cultural services (reduced growth of sensitive species influencing aesthetic qualities of vegetation), and reducing economic value of products such as crop yield. Until recently, much of the research on ozone impacts has focussed on quantifying effects on ecological processes rather than considering the implications for ecosystem services. This report, for the first time, places current process-based knowledge within the context of ecosystem services and thus reports on the potential for impacts of ozone on ecosystem services and biodiversity. The report has been prepared by the Coordination Centre of the ICP Vegetation, an International Cooperative Programme reporting on air pollution impacts on vegetation to the Working Group on Effects of the Convention on Long-Range Transboundary Air Pollution.

Impacts of ozone on ecological processes and supporting services

Ozone pollution impacts directly or indirectly on many of the fundamentally important ecological processes that underpin almost all ecosystem services, these include:

Primary productivity and carbon cycling Ozone reduces whole plant photosynthesis by directly impacting on the photosynthetic machinery (Rubisco and chlorophyll content), reducing leaf area by promoting early senescence and leaf abscission, diverting carbon (C) use into detoxification and/or repair metabolism, changing stomatal conductance (both increases and decreases have been noted, see below) and altering C allocation in favour of the above ground parts rather than below ground parts. Carbon flux to and from the soil is also altered by changes in leaf litter quality, altered rhizodeposition of C, changes in soil microbial community composition, and altered soil processes.

Nutrient cycling Tropospheric ozone has the capacity to impact on nutrient cycling by both direct and indirect mechanisms: by altering the chemical composition of plant tissue and the quantity (and quality) of litter fall, impacting on below-ground plant biomass and root exudates, indirectly altering microbial community composition(s) and functioning, and soil processes and the chemical properties. All of these have the capacity either, independently or in concert, to ultimately reduce the long-term sustainability of ecosystems.

Stomatal functioning and water cycling Tropospheric ozone is known to alter stomatal responses to environmental stimuli and in the short term (at higher concentrations) can cause stomata to close, however, under prolonged chronic exposure (at lower concentrations) many reports document ozone-induced stomatal opening or loss of stomatal sensitivity to closing stimuli, such as drought, light and humidity. In a review of 49 papers covering 68 species conducted for this report, 22% of species showed no change in stomatal conductance, 10% showed a slowed (sluggish) stomatal response to elevated ozone, 23.5% showed an increased stomatal opening under elevated ozone and 44% displayed stomatal closure in response to ozone. No clear patterns emerged for the ozone concentration range for the different responses, except perhaps a tendency for stomatal opening to occur at lower concentrations than stomatal closure.

Impacts of ozone on biodiversity and species balance

In the simplest interpretation, to impact on biodiversity, ozone pollution would need to exert sufficient toxic effect on an individual species for that species to be lost from a habitat. In reality, however, in most natural or (semi-)natural communities, plants are growing in a highly competitive environment - a slight loss of vitality of one species due to ozone can result in a more vigorously growing but less ozone-sensitive species outcompeting the affected species for light, nutrients and water resulting in a shift in species balance and potential loss of the more sensitive species at a sub-lethal ozone concentration. All of the component species of the plant community would potentially be impacted, including the animals, fungi, bacteria and insects that live in close association with plants or in nearby soils.

Effects on species balance have been widely reported from controlled exposure experiments conducted in open-top chambers and solardomes, but a less clear picture emerges from field-based studies with long established communities and from field surveys. Although more studies are needed, it is clear that impacts of ozone are of particular concern for global biodiversity hotspots that experience relatively high ozone concentrations such as the Mediterranean basin.

Impacts of ozone on provisioning services

In this report we described effects on two key provisioning services that are impacted on by ozone effects on primary productivity and associated processes:

Crop production Effects of ozone on primary productivity are especially relevant for crop plants. With the world population predicted to increase to 9 billion by 2050, security of food supplies is one of the most important challenges for this century. Ozone damages crop plants by, for example, reducing photosynthesis, causing a yellowing of leaves and premature leaf loss, decreased seed production and reduced root growth, in turn resulting in reduced yield quantity and/or quality and reduced resilience to other stress such as drought. As a consequence, the key components of the food system that ozone interferes with are the productivity of crops, the nutritional value and the stability of food supplies as ozone concentrations and therefore impacts vary from year to year. Some of the world's most important staple food crops are sensitive (wheat, soybean and other pulses) or moderately sensitive (maize, rice, potato) to ozone and effects on the yield of these crops are of global significance. A recent state of knowledge report by the ICP Vegetation (Mills and Harmens, 2011), for the first time, quantified ozone impacts on wheat yield in Europe using the stomatal flux-based methodology and predicted that losses would remain at 9% in 2020 amounting to €2 billion in EU27 (+ Norway and Switzerland). Current ambient ozone levels in South Asia are also considered to be reducing crop yield and quality for a range of important crops in the region, commonly within the range of 10 to 20%.

Timber production A recent meta-analysis has suggested that the increase in ozone since the industrial revolution has been responsible for a reduction in photosynthesis of approximately 11% in trees, which may have reduced tree productivity by approximately 7%. In general, deciduous trees tend to be more sensitive to ozone than coniferous trees, with ozone sensitive species present across most of Europe. Using National forest age class statistics, ozone response relationships for different species and ages, a model of stem increment growth and national mean AOT40 values, it was estimated that losses in C stocks averaged 10% across 10 northern European countries, with the highest losses predicted for the Czech Republic, Germany and Poland.

Impacts on Regulating Services

By impacting on carbon sequestration, nutrient cycling, land-atmosphere exchanges and biodiversity, ozone impacts on many beneficial regulatory functions of ecosystems, including:

C sequestration and global warming If ozone concentrations are high enough to reduce photosynthesis (i.e. CO_2 fixation) and/or above-ground plant growth, then less CO_2 and ozone will be absorbed by the leaves of vegetation, leading to a positive feedback to atmospheric CO_2 and ozone concentrations and therefore more global warming. The ICP Vegetation recently conducted the first flux-based assessment of effects of ozone on C sequestration in the living biomass of trees in Europe focussing on 2000 and 2040 effects. This study showed that applying the flux-based methodology using a climate-region specific parameterisation for 2000 revealed C reductions of 14% in the living biomass of trees. Predictions for 2040 indicated that the reduction of C storage is expected to decrease considerably compared to the reduction in 2000, mainly as a result of a predicted reduction in atmospheric ozone concentrations across Europe.

Air quality Globally, it has been estimated that ozone deposition to vegetation (by reaction with plant surfaces and uptake through the stomata) reduces tropospheric ozone concentrations by as much 20%. This is an especially significant function of vegetation given that ozone is the third most important greenhouse gas causing global warming. Under drought conditions, however, plants close stomata to conserve water and stomatal uptake of ozone is substantially reduced, with one study indicating that the European summer heatwave in August, 2013 led to 20 – 30 ppb increase in ozone concentration. A further level of complexity involves ozone-induced emission of biogenic volatile organic compound (BVOCs) from plants - these can either react with ozone to reduce concentrations or lead to ozone formation.

Methane emissions There is evidence that ozone may influence emissions of the greenhouse gas, methane, from wetlands although the results are less conclusive than for CO_2 effects. Global estimates of carbon sequestration in peatlands are in the region of 20-30 gC m^{-2} yr^{-1}, and thus any effects of increasing ozone are of global significance for climate regulation. Results from experiments are rather mixed, with some studies indicating methane increases whilst others show a decrease. The inconsistencies in these effects are most probably due to differences in species present and concentration and duration of ozone exposure.

Water cycling As described above, there are two main stomatal responses to ozone, each potentially having an opposite effect on the water cycle: ozone induced stomatal closure will preserve water within soils whilst ozone induced stomatal opening will increase water loss from vegetation and soils. Global climate modellers have until recently assumed the former mechanism is dominant, but very recently the implications of increased water loss as a result of chronic ozone exposure are beginning to be considered within such models. Extensive measurements of a Southern Appalachian forest in the USA have indicated an almost linear increase in average daily sap flows and enhancement of the amplitude of daily water–loss from native trees with increasing ambient ozone exposure, suggesting an ozone-induced disruption to the whole-tree water balance, not only as a result of increased day-time transpiration but also due to increased night-time stomatal conductance.

Flowering, pollination and insect signalling Reported ozone – induced changes in the number and timing of flowering will play an important role in the reproductive success of plants, particularly for species in which flowering is closely synchronized with pollinating species. Floral scent trails, important in pollinator attraction and plant defenses against herbivorous insects, have also been shown to be destroyed or transformed by ozone. These ozone-induced changes in flowering timing and signaling could have large ecological impacts.

Impacts of ozone on cultural services including leisure, recreation and amenity

The potential for impacts of ozone on cultural services has attracted very little attention so far even though ozone can have both subtle and profound influences over some, if not all, aspects of cultural services by impacting on the visual appearance and quality of the natural environment, including potentially impacting on the tourist industry. Ozone impacts on leaf colour may be the most visually noticeable effect, as ozone induces early senescence in leaves and visible injury such as stippling and bronzing on sensitive species. Approximately 80 species of (semi-)natural vegetation have been recorded with symptoms attributed to ozone in Europe over the period 1990 – 2006, with records of injury being widespread across Europe and found in 16 countries. Furthermore changes in the species balance of natural ecosystems might make some natural areas less visually attractive.

Valuing ozone impacts on ecosystem services

There is an explosion of interest globally in placing and economic value on ecosystem services. This is seen as a useful way to communicate the benefits provided by the natural environment to policy makers, and to capture in a systematic way many of the unintended consequences of policy actions or management decisions. It is also facilitates comparisons of effects of different drivers of change. Examples of approaches are discussed in the report, including: estimating the impact of ozone on a product or service compared with assumed zero impact under no or low ozone; scenario analysis, estimating marginal cost of a change in a level of ozone and cost-benefit analysis.

Research Recommendations

Whereas there is a wealth of information on ozone impacts on natural- and agri-ecosystems, almost all studies were not originally conducted in the context of ecosystem services, and a comprehensive quantitative assessment of ozone effects on ecosystem services, including an economic valuation, is not currently possible for most services. We therefore recommend that the following further research is conducted:

- A systematic review and data mining exercise for each ecosystem service to derive generic response functions for calculation of effects.

- Use this review to identify those services for which there is insufficient experimental information available for derivation of response functions and make recommendations for further experimental work. Examples of experimental research would include:

    - Further quantification of below-ground impacts of ozone on carbon sequestration in roots and soils
    - Further studies of the effects of ozone on stomatal conductance and the potential uncoupling from photosynthesis
    - Experimental studies on the responses of vegetation to ozone in representative future climates and CO_2 concentrations
    - Large-scale field ozone exposure experiments on intact ecosystems
    - Epidemiological analysis of field measurements to detect spatial and temporal trends in ecosystem processes and functions
    - In association with proof of concept ozone exposure experiments, surveys to show the extent of occurrence of visible injury, early senescence and changes in expression of autumn colour.

- Identification of appropriate spatial data, including land-use, ozone, species distribution, ecosystem functions and products (for example, carbon stocks and yield), to facilitate a spatial analysis of impacts on ecosystem services.

- Further research on economic valuation methods, especially for those ecosystem services provided by natural ecosystems that are difficult to value without large uncertainty.

- Using the above, conduct a comprehensive quantitative assessment of past, current and predicted future effects of ozone on ecosystem services, and where possible a cost-benefit analysis for future scenarios.

Contents

1. Introduction

Gina Mills and Serena Wagg

1.1 Ecosystem services – an introduction

Earth’s ecosystems provide an array of services upon which humans depend for food, fresh water, disease management, climate regulation, aesthetic enjoyment and spiritual fulfilment (Millennium Ecosystem Assessment, 2003). Such ‘Ecosystem Services’ are currently grouped according to the benefits they provide to humans, distinguishing between provisioning, regulating, supporting and cultural services (**Figure 1.1**). Although humans are an integral part of ecosystems, the increased global population along with increased standards of living and other socio-political, economic, technological and societal changes, mean that our interventions can have profound negative effects on the quality of the services provided by ecosystems. Because ecosystems are complex systems comprising animal, plant and microorganism communities together with the non-living environment (Millennium Ecosystem Assessment, 2005), these systems are inherently dynamic whilst maintaining some intrinsic resilience to natural disturbances. However, human-driven changes (principally over the last 50 years) have become increasingly worrying, and thus many of the World’s ecosystems and the services they provide are now degraded, or vulnerable to degradation. In this report we provide an assessment of the state of current knowledge on the effects of ozone pollution on ecosystem services including consideration of effects on biodiversity.

Global toxification (including air pollution) is one of the “savage sextet” (Aguirre, 2009) of direct drivers of ecosystem degradation, with the others being over-exploitation of species, introduction of novel exotic species, land use changes (principally habitat destruction, fragmentation and degradation), pathogen pollution and global warming (Mantyka-Pringle et al., 2012). Indirect drivers of ecosystem change are associated with demographic, economic, socio-political and cultural or religious changes, and advancements in science and technology. Stressed or degraded ecosystems do not have the resilience or re-bound capacity of pristine/unstressed systems (Rapport and Maffi, 2009). Furthermore, there is often a substantial time-lag between a change in a driver and the time taken to realize the full consequences of that change in any given system. Even more worrying is that once a threshold is crossed, a system may alter to a distinctly changed and sometimes irreversible new state. Careful management of our ecosystems and the benefits and services we derive from them are therefore vital for future prosperity and general human well-being.

Human influence extends into even the remotest landscapes and more often than not has a pervasive influence on the ecosystems they support, frequently irreversibly changing biodiversity. Whilst extinction rates of species are now estimated to be 1,000 times greater than historical background levels (Millennium Ecosystem Assessment, 2005; Mantyka-Pringle et al., 2012), recent studies have identified linkages between changes in biodiversity and ecosystem functioning, highlighting the importance of adopting a multi-sectoral approach to policy and decision making (e.g. Maestre et al., 2012; Mace et al., 2012). Such an approach fully evaluates changes in ecosystem services and their impacts on humans and examines the supply and condition of each ecosystem service, as well as the interactions among them. Society needs to make difficult decisions regarding its use of biological resources and environmental valuation techniques provide useful evidence to support polices by quantifying both the monetary and non-monetary value associated with the protection of resources. To support this drive, the Intergovernmental Platform on Biodiversity and Ecosystem Services (IPBES) was established in April 2012 by 90 governments and acts as a global mechanism for gathering, analyzing and synthesizing information to advise decision-making on biodiversity and ecosystem services (Redford et al., 2012). Further, possibilities for introducing human manufactured substitutions are limited for many ecosystem services, especially for supporting services. Therefore, preservation of functioning, and restoration of degraded systems is paramount at this time in history.

As shown in **Figure 1.1**, ecosystem services can be classified into provisioning, regulating, supporting and cultural services. When considering impacts of one driver of change (in this case ozone pollution), it immediately becomes clear that impacts on one service are linked to several and sometimes all of the other services. For example, negative effects of ozone on root growth would impact on provisioning services (crop foods, wood production, water uptake), regulating services (climate and water regulation), supporting services (nutrient cycling, primary production, water cycling) and possibly cultural services by impacting on the aesthetics of a natural ecosystem. Because of such complexities and the growing desire to add an economic value to ecosystem services, the final ecosystem services that provide goods of value to humans can be considered to be linked by "stocks and flows" to the underpinning ecological processes (**Figure 1.2**, adapted from Mace et al., 2012). For example, ozone reduces primary productivity in forest trees (i.e. impacts on an ecological process), influencing the final ecosystem service of tree production which can be used for a variety of goods such as timber, fuel, carbon sequestration and recreational value. The final value of these goods is dependent on the inputs to the forest system such as management costs, fertilizer etc. all of which may be influenced by the negative effects of ozone on productivity.

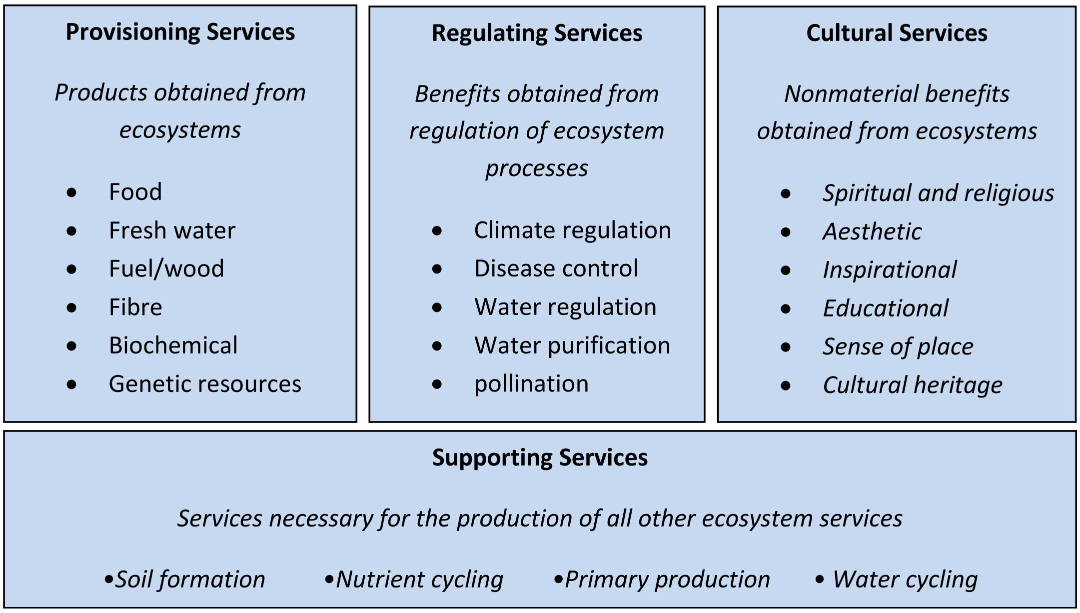

Figure 1.1 Ecosystems services are the benefits people obtain from ecosystems. These include provisioning, regulating, and cultural services that directly affect people and supporting services needed to maintain the other services (Millennium Ecosystem Assessment, 2005).

1.2 Biodiversity as an ecosystem service

The role of biodiversity in ecosystem services is often rather unclearly stated – biodiversity is sometimes considered as a separate service and yet is implicit in most ecosystem services. Mace et al. (2012) addressed this issue and showed how biodiversity is involved throughout the ecosystem hierarchy: "as a regulator of underpinning ecosystem processes, as a final ecosystem service and as a good that is subject to valuation." They described biodiversity contributions as being from both an "ecosystem services perspective", measured in simplest terms by ecosystem service flows, and from a "conservation perspective", where higher value is given to conserving charismatic species.

There are many drivers of loss in biodiversity, with the increase in human population, especially in the last century, having a profound influence by, for example, increasing the need for biomass for fuel and construction, changes in land-use towards food and fodder production, industrial and residential developments, introduction of invasive species, pollution and climate change. Species losses are currently outpacing background rates calculated from fossil records (Millennium Ecosystem Assessment, 2005) and it is widely recognised that the earth is facing its sixth mass extinction (Barnosky et al., 2011). Some ecosystems are more resilient to change than others, with for example, primary forests being more resistant to change than modified natural forests or plantations (Thompson et al., 2009).

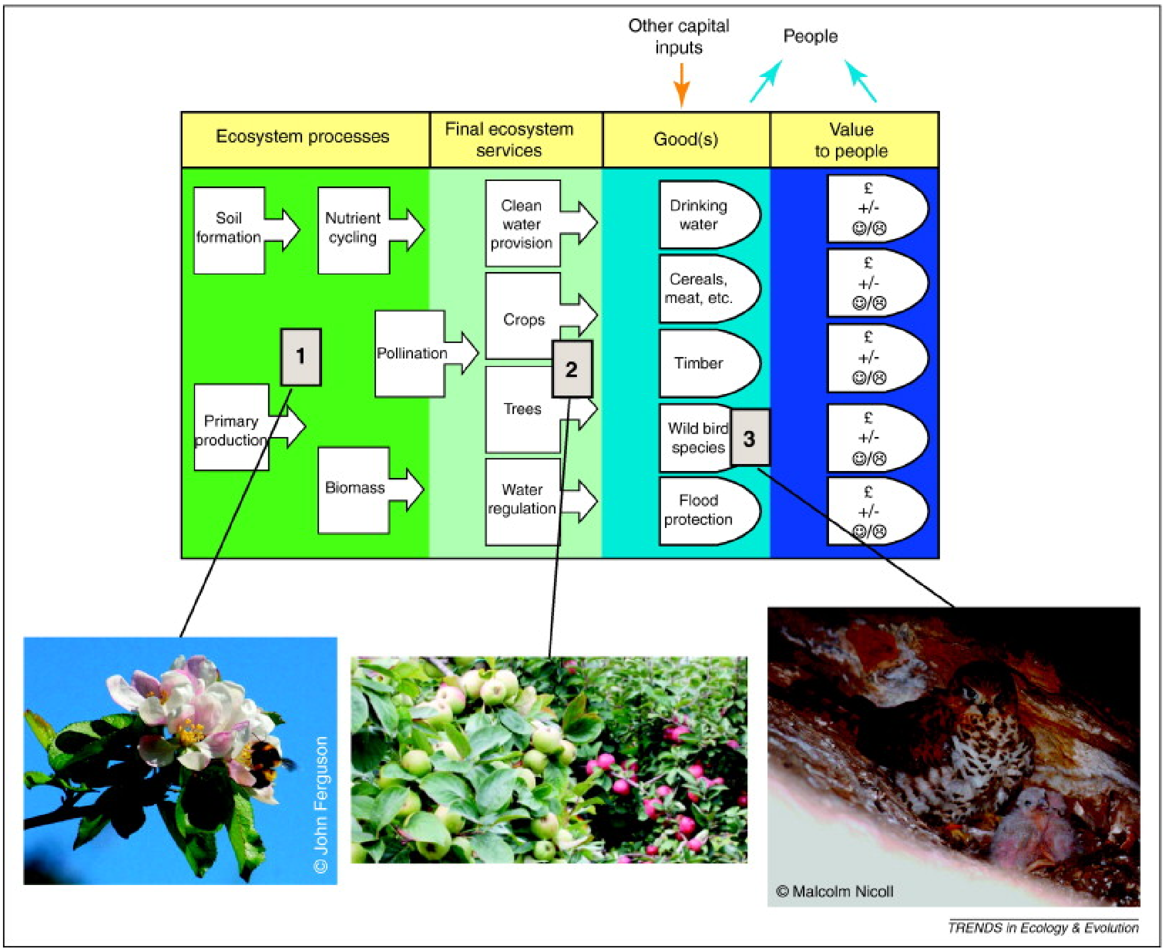

Figure 1.2 Schematic diagram of a selection of ecosystem processes and services that illustrates how ecosystem processes are linked to final ecosystem services and the goods and values they generate for people. The final ecosystem services are the outcomes from ecosystems that directly lead to good(s) that are valued by people. The full value is not only from the ecosystem but depends on the addition of inputs from society (other capital inputs) and the value is often context dependent. The final value of the good(s) is therefore attributable to both the ecosystem and human inputs. Values might be monetary (£), quantitative and nonmonetary (1/+) and/or qualitative. Biodiversity might have a role as: (1) a regulator of ecosystem processes (e.g. a bee pollinator); (2) a final ecosystem service (e.g. cultivated apples), or (3) a good that has value of its own (e.g. Mauritius kestrel). Images reproduced, with permission, from John Ferguson (bee pollinator) and Malcolm Nicoll (kestrel). Diagram reproduced from Mace et al. (2012).

Meta-analyses of published data on effects of species loss on the key ecosystem processes of productivity and decomposition have shown how important species loss is in ecosystem service delivery (Hooper et al., 2012). For example, species losses of 21 – 40% reduced plant productivity by 5 – 10%, an equivalent amount of reduction as that estimated for effects of UV light and global warming. The study also indicated that species losses of 41 – 60%, as projected for global extinctions by the end of this century, is predicted to result in a 13% biomass loss, a similar amount to that predicted for ozone effects alone. In a similar study, Mantyka-Pringle et al. (2012), investigated the synergies between climate change and habitat loss for explaining biodiversity loss. They showed that habitat loss and fragmentation were highest in areas where the maximum temperature of the warmest month has increased the most. Although not included in their meta-analysis, globally, ozone concentrations tend to be relatively high in many high temperature areas (e.g. southern USA, the Mediterranean, South East Asia), and it is possible that ozone may also be a contributory driver in habitat loss and fragmentation.

1.3 Examples of the global significance of ecosystem services

1.3.1 Carbon cycle and primary productivity

Annual net primary productivity (NPP) is the net amount of carbon (C) captured by land plants through photosynthesis. It is of fundamental importance to humans because the largest proportion of our food supply is from plant productivity. Recent estimates of the global NPP range from 19.6 g C m^{-2} yr^{-1} to 43.5 g C m^{-2} yr^{-1} (Prieto-Blanco et al., 2009). Total global CO_2 emissions were estimated to be approximately 8.7 ± 0.5 Pg C yr -1 in 2008 and were shown to have increased at a rate of 3.4% per year between 2000 to 2008 (Le Quere et al., 2009). Most of the CO_2 emissions increase is from developing countries (non-Annex B countries) where emissions have more than doubled over the last decade. Shockingly, tropical deforestation is estimated to have released between 1-2 billion tonnes of CO_2 per year during the 1990s (i.e. 15 – 25% of annual global emissions) (Gibbs et al., 2007). Despite the pressing need to reduce CO_2 emissions, Le Quere et al. (2009) report a rapid increase in fossil fuel CO_2 emissions since the 1990s and a dramatic increase in per-capita emissions since the early 2000s. Although around 55% of all anthropogenic CO_2 emissions are absorbed by land and ocean sinks (Friedlingstein and Prentice, 2010), a large quantity remains in the atmosphere.

World forests are a vital component in the global C cycle as they sequester and store more C than any other terrestrial ecosystem and are therefore an major natural sink for anthropogenic emissions (Gibbs et al., 2007). For example, total global forests sequester 14000Mt CO_2 annually, with temperate and boreal ecosystems sequestering 5000Mt CO_2 of this amount (Pan et al., 2011) (**Figure 1.3**). European forests contribute around 10% of the global sequestration of C with Norway, Finland, Germany and Sweden having the greatest potential for CO_2 capture due to the large forested areas. Further, managed forests generally sequester C at a faster rate than natural forests (Pingoud et al., 2010). Any factor that increases primary productivity in temperate and boreal forests is likely to increase forest C sequestration; conversely any factor that negatively affects primary productivity (including ozone pollution) will reduce CO_2 sequestration. As a major part of C sequestration goes into the living biomass the most important aspect of forest management for C sequestration is, therefore, the rate of harvest relative to rate of forest growth; the greater the forest growth the greater the C sequestration potential. Estimated decreases in current living biomass stock due to ozone pollution are approximately 10% (Wittig et al., 2009). Hanson et al. (2005) have estimated that co-occurring climate factors, increased CO_2, increasing temperate, decreased soil water availability and ozone will amount to a 20% reduction in net ecosystem exchange (NEE) by 2100.

The CO_2 taken up by vegetation will be sequestered in the shorter or longer term in plant material or soils. Soils are the largest C reservoir of the terrestrial C cycle. Worldwide, they contain three to four times more organic C (1500 Gt to 1m, 2500 Gt to 2m depth) than vegetation (610 Gt) and twice or three times as much C as the atmosphere (750 Gt; Batjes and Sombroek, 1997). C storage in soils is the balance between the input of dead plant material (leaf and root litter, decaying wood) and losses from decomposition and mineralization of organic matter (heterotrophic respiration). Under aerobic conditions, most of the C entering the soil returns to the atmosphere by autotrophic root respiration and heterotrophic respiration (together called soil respiration). The mineralization rate is a function of moisture levels and chemical environment with factors such as temperature, pH, redox potential, nitrogen level and the cation exchange capacity of the minerals in the soil affecting the mineralization rate of soil organic C (e.g. Li et al., 1994; Kätterer et al., 1998; Heimann and Reichstein, 2008). Under anaerobic conditions, resulting from constantly high water levels, part of the C entering the soil is not fully mineralized and accumulates as peat.

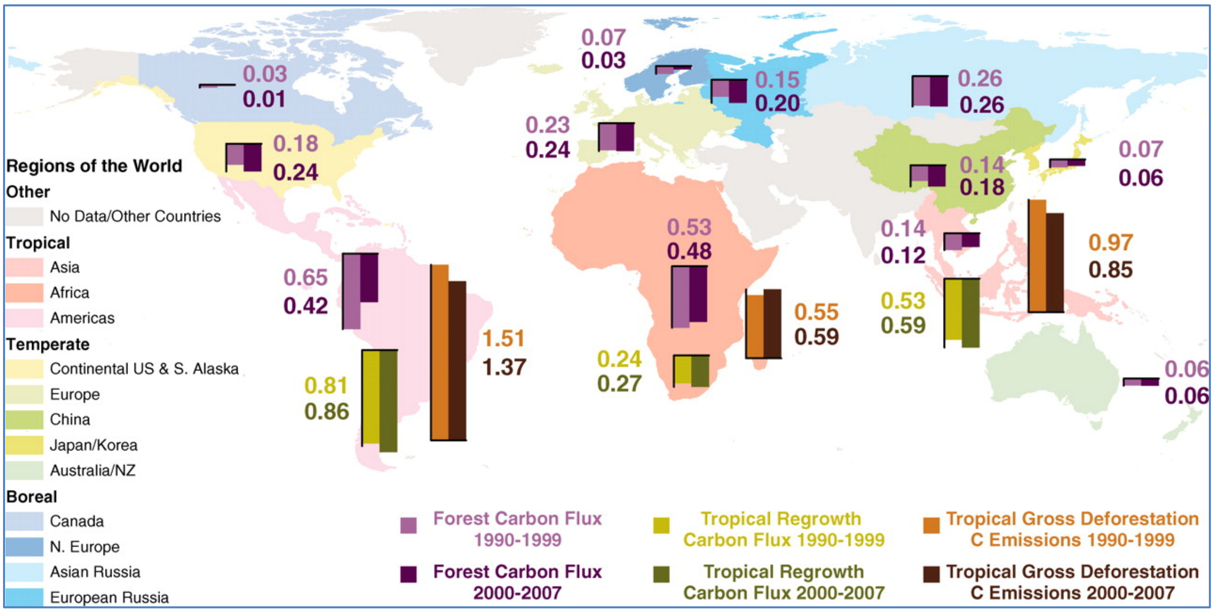

Figure 1.3 Carbon sinks and sources (Pg C year $^{-1}$) in the world's forests. Coloured bars in the down facing direction representing C sinks, whereas bars in the upward-facing direction representing C sources. Light and dark purple, global established forests (boreal, temperate and intact tropical forests); light and dark green, tropical re-growth forests after anthropogenic disturbances; and light and dark brown, tropical gross deforestation emissions (Reproduced from Pan et al., 2011)

1.3.2 Water cycling

Water is essential for life on Earth and supports all other ecosystem processes. Human water use has increased drastically over the last 50 years and is now double pre-1960 values; most of this water (70% worldwide) is used for irrigation of crops. Estimated mean annual global land-surface evapotranspiration from vegetation is approximately 65 ± 3 x 10^3 km^3 per year, with forests, grasslands and crops accounting for 29 x 10^3 km^3, 21 x 10^3 km^3, and 7.6 x 10^3 km^3 respectively (Jung et al., 2010; Oki and Kanae, 2006). Any factor that acts to alter evapotranspiration will have potential effects on local/regional microclimate/climate and soil water status/hydrology (Blyth and Harding, 2011). Most of the water transpired by plants passes through the stomatal pores, the diameter of which is in turn modified by external climatic and edaphic conditions such as light, temperature, soil moisture, and carbon dioxide (CO_2). Consequently, transpiration processes impact on the global hydrological cycle (Lombardozzi et al., 2012b); effects of ozone on transpiration can be either positive or negative depending on species, episodic/background ozone characteristics and soil water availability.

1.3.3 Nutrient cycling

Nitrogen (N) is a vital element determining the diversity, dynamics and functioning of many ecosystems. Numerous natural ecosystems have relatively low levels of N availability, for example, N deposition in the absence of human influence is typically ~ 0.5 Kg N ha^{-1} yr^{-1}, whereas in many areas of the world N deposition rates now exceed 10 Kg N ha^{-1} yr^{-1}, and are often higher. Alarmingly, by 2050 N deposition rates could reach 50 Kg N ha^{-1} yr^{-1} in some regions (Galloway et al., 2008). The two main anthropogenic drivers of N loading into natural (eco)systems are agriculture practices and combustion of fossil fuels. Estimations surmise that more than half of all synthetic N fertilizer ever used on the planet has been used since 1985, and as such, humans have doubled the flow of reactive nitrogen (Nr) within natural and man-made ecosystems. Worryingly, this N burden is anticipated to increase by a further 66% by 2050 (Millennium Ecosystem Assessment, 2005). Oxidized nitrogen (N, NO) concentrations in the atmosphere have also increased dramatically during the last 100 years, largely arising from combustion sources. Total Nr is now estimated to be > 187Tg yr^{-1} (formally 15Tg yr^{-1} in the late 1800's), with about 70% arising from food production (fertilizers) (Galloway et al., 2003; Galloway et al., 2008). Unsurprisingly, both these anthropogenic sources have increased the cycling of fixed/reactive N through ecosystems and changed species composition and ecosystem dynamics globally.

1.4 Ozone pollution – a growing threat to ecosystem service provision

Ozone is a secondary air pollutant formed, and destroyed, by a series of complex photochemical reactions involving nitrogen oxides ($NOx = NO + NO_2$), methane (CH_4), carbon monoxide (CO) and non-methane volatile organic carbons (NMVOC) (Avnery et al., 2011; Royal Society, 2008). Although tropospheric (ground-level) ozone is a natural phenomenon, since the industrial revolution ozone concentrations in the troposphere have substantially increased from around 10-15 parts per billion (10-15 ppb), to present day values of 30-40 ppb (Simmonds et al., 2004; Sitch et al., 2007) with the steepest rise being from 1950 to 2000 (Vingarzan, 2004; Parrish et al., 2012). Future projections of ozone concentrations are closely coupled to levels of anthropogenic precursor emissions (Dentener et al., 2006). With the global population estimated to reach 9.2 billion by 2050, associated increased demand for resources such as fossil fuels, energy production, transport and agriculture is likely to further increase precursor emissions (Oltmans et al., 2006). Tropospheric ozone pollution is, therefore, a major concern at a local, regional and global (hemispheric) scale (Jenkin, 2008; Van Dingenen et al., 2009) with several projections indicating concentrations reaching 75 ppb over much of Europe by 2100 (Fiscus et al., 2005; Hollaway et al., 2012; IPCC, 2007; Sitch et al., 2007). Future ozone trends will not only depend on the anthropogenic emission levels of precursors, but also on trends in temperature, humidity and solar radiation. A multi-model study of impacts of climate change alone on ozone concentrations in Europe predicts increases in the mean ozone concentration in the range 0.9 to 3.6 ppb for 2040-49 climates compared to 2000-09 climates (Langner et al., 2012).

As well as these steady increases in background ozone concentrations across Europe, it is also of concern that ozone episodes frequently occur in which the ozone concentration exceeds 60 ppb, sometimes for several days at a time. In recent hot, dry years, ozone episodes have been widespread across Europe. For example, in July 2006, two significant ozone episodes occurred between 17 – 22 July and 25 – 28 July. During these episodes, ozone concentrations in excess of 90 ppb were experienced in countries such as the UK, Belgium, Netherlands, France, Germany, Switzerland and Italy with the highest one hour value recorded being over 180 ppb in Italy (EEA, 2007). Even in a cooler, wetter year such as 2011, the EU's information threshold (one hour at 180 $\mu g\ m^{-3}$ (or 90 ppb) was exceeded in 16 Member States whilst the alert threshold of 240 $\mu g\ m^{-3}$ (or 120 ppb) was exceeded in Bulgaria, France, Greece, Italy, Portugal and Spain.

Within the context of effects on ecosystem services, it is important to remember that ozone concentrations are usually highest in rural and upland areas downwind of major conurbations, where unlike in cities, fewer other pollutants are present to react with ozone to reduce the concentration. These rural/upland areas are where many of the ecosystems occur that provide essential services for man (agricultural production, forest production, water catchments etc.). Here, ozone impacts on ecosystems will vary from direct toxicity and cell damage, to indirect effects mediated by changes in individual organisms and their ecological interactions, and in the rate and nature of chemical and biological processes (Ainsworth et al., 2012; Ashmore, 2005).

Excessive uptake of ozone by vegetation in the short-term can cause altered physiology (photosynthesis, respiration, C allocation and stomatal functioning), reduced growth (both above– and below-ground), altered phenology and increased senescence (see **Figure 1.4**). In the long-term, it may lead to changes in species and genetic composition and functioning of (semi-)natural plant communities (hence, ecosystems), and to changes in water economy and C stocks (ICP, 2012; McLaughlin et al., 2007a; Sun et al., 2012). Thus, ozone acts primarily on the processes which underlie the functioning of ecological systems whilst the benefits we derive from ecosystems are often many steps removed from these functional processes.

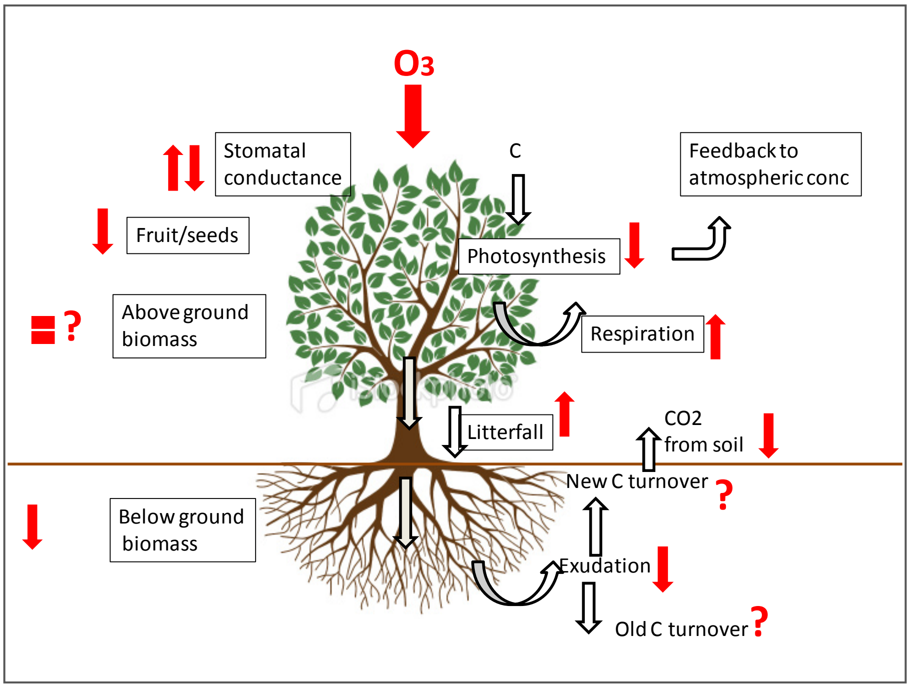

Figure 1.4 A schematic of the effects of ozone on C cycling in vegetation. Clear black arrows represent carbon flows and filled red arrows represent decreases (down arrow) or increases (up arrow) in processes, unknown effects are represented by '?' and no effect by '='.

1.5 ICP Vegetation – coordinated assessment of ozone impacts on vegetation, ecosystems and ecosystem services

Over the last 25 years, the ICP Vegetation[2] has reported to the Working Group on Effects of the Convention on Long-Range Transboundary Air Pollution (LRTAP) on impacts of ozone pollution on vegetation in Europe. Other pollutant impacts are also included in the ICP Vegetation work programme, including nitrogen, heavy metals and POPs. The programme is coordinated from the UK and involves ozone experts from 35 European countries plus the USA. Recent reports have shown that:

(1) Ozone effects are widespread, with effects reported on over 110 species of crops, shrubs and grasslands in 16 European countries (Hayes et al., 2007b; Mills et al., 2011c),

(2) Ozone impacts on wheat production are costing over € 3 billion annually (Mills et al., 2011a), and

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[2] The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops

(3) Ozone is negatively impacting on C sequestration in the living biomass of trees in many areas of Europe (Harmens and Mills, 2012).

The ICP Vegetation has been instrumental in developing ozone risk methodology for application at the European scale. Initially, ozone exposure indices based on accumulated exposure above a threshold concentration (e.g. AOT40) were recommended for use across Europe. In the last decade, a method has been developed that takes into account the instantaneous effects of climatic factors (temperature, humidity, light), soil factors (soil moisture) and plant factors (growth stage) on the amount of ozone that is taken up by the stomatal pores on the leaf surface (ozone flux or phytotoxic ozone dose over a threshold flux of Y, POD_Y). Ozone effects detected in the field are better correlated with ozone flux than AOT40 (Mills et al., 2011c), and the flux-based methodology has now been accepted by the LRTAP Convention as the preferred approach within the revised Gothenburg Protocol (Mills et al., 2011d).

Previous research by the ICP Vegetation has focussed on the effects of ozone on vegetation alone. Here we take a broader view by investigating the implications of negative effects of ozone on vegetation within dynamic ecosystems by considering the consequences for the many inter-related processes taking place and subsequent effects on ecosystem services and biodiversity.

1.6 Aims and structure of this report

As indicated, vegetation plays a critically important role in ecosystems, sustaining the cycling of water, nutrients and C between the biosphere, atmosphere, hydrosphere and lithosphere. In this report we draw attention to the many ways in which current and future ozone pollution is (likely to be) interfering with these roles of vegetation and the implications for ecosystem service provision and biodiversity. The current state of knowledge is reviewed for ozone effects on ecological processes associated with supporting services (Chapter 2), and we consider the implications of these changes for final ecosystem services, goods and values associated with provisioning processes including crop production (Chapter 3), regulating services including climate and water regulation (Chapter 4) and biodiversity (Chapter 5). We also speculate on the potential effects of ozone on cultural services (Chapter 6) and in Chapter 7, we briefly describe methods for assigning an economic value to effects of ozone on ecosystem services. Conclusions and research recommendations are provided in Chapter 8. In Annex 1, we provide contributions from participants in the ICP Vegetation, including research on effects on selected ecosystem services in Germany, Italy, Sweden, Switzerland and the UK, and in Annex 2 a synthesis of data on ozone effects on stomatal conductance.

2 Effects of ozone on ecological processes and supporting ecosystem services

Gina Mills, Serena Wagg, Harry Harmens, Jürgen Bender, Elke Bergmann

Supporting services are necessary for the effective functioning and production of all other ecosystem services. These include the interlinked underlying ecological processes that determine primary production, nutrient and water cycling. For simplicity of presentation, we consider ozone effects on each of these supporting services separately. The consequences of impacts for provisioning, regulating and cultural services and biodiversity are considered in separate chapters.

2.1 Impacts of ozone on primary productivity and C cycling

The rate of carbohydrate production in plants is determined by the rate of CO_2 entry via the stomatal pores which in turn is determined by atmospheric and edaphic conditions including temperature, humidity, light, soil moisture, CO_2 and air pollutant concentration. Carbon fixation on the other hand, is controlled by the carbon-fixing enzymes, ribulose bisphosphate carboxylase (RuBisCo) or phosphoenol pyruvate carboxylase (Darrall, 1989), which in turn is driven by the supply of electrons from light-harvesting processes in the chloroplasts. Any factor that acts to cause a change in any of the above processes will influence plant growth and partitioning of photosynthates between sources and sinks. Ozone has the potential to reduce the amount of C sequestered into plants and soil by various routes in isolation or in combination (**Figure 2.1**):

- Reduction in photosynthesis per unit leaf area (e.g. Morgan et al., 2003; Ainsworth., 2008; Wittig et al., 2007), either directly via effects on the photosynthetic machinery such as a reduction in Rubisco and chlorophyll content (Dizengremel, 2001; Fiscus et al., 2005; Wittig et al., 2009; Kobayakawa and Imai, 2011), and/or indirectly by closing the stomatal leaf pores (Torsethaugen et al., 1999; Evans et al., 2005; Overmyer et al., 2008; Wittig et al., 2009), results in a reduction in whole plant photosynthesis (see also Section 2.3). On the other hand, mechanisms by which ozone might stimulate the opening of stomatal leaf pores transiently and hence affect whole plant photosynthesis and water balance have been discussed in more detail by Wilkinson and Davies (2010). Other studies have shown that ozone induces stomatal sluggishness, limiting CO_2 uptake and increasing water loss (Mills et al., 2009; Paoletti and Grulke, 2010).

- Reduction in whole plant photosynthesis due to ozone-induced damage of leaves, early senescence and abscission, and hence a reduction in total green leaf area and leaf area index (Morgan et al., 2003; Ainsworth; Wittig et al., 2009).

- As more C is required for secondary plant metabolism to detoxify ozone and/or repair ozone-induced cell damage (Betzelberger et al., 2010), less C will be available for plant growth (Dizengremel, 2001) and C allocation below-ground. In addition, the production of biogenic volatile organic compounds (BVOCs) might be stimulated by elevated ozone concentration, which is energetically expensive, although contrasting results have been reported in the literature (see Section 2.2).

- Although increases in respiration per unit leaf area have been reported in response to high ozone exposure (e.g. Volin and Reich, 1996; Dizengremel, 2001), decreases (Wittig et al.,

2009) have been reported too. However, in case of the latter, there seems to be a trend that the reduction in foliar respiration is less than the reduction in photosynthesis. Hence, relatively more of the C fixed at elevated ozone levels during daylight will be lost again to the atmosphere at night in response to ozone exposure.

- Another major effect of ozone on plants is to accelerate phenological development (e.g. Gelang et al., 2000). Maturity can be advanced by days or weeks, causing early flowering (Shi et al., 2009; Hayes et al., 2012b), and early leaf senescence (Feng et al., 2011).

- A significant decline in the root to shoot ratio has been observed at elevated compared to either current ambient or pre-industrial ozone levels (Wittig et al., 2009). Hence, root biomass appears to be more sensitive to adverse effects of ozone than shoot biomass. In addition, increased ethylene formation, a common response to ozone pollution, tends to reduce root growth directly (Wilkinson and Davies, 2010). As a consequence, total C allocation to the soil is likely to be reduced.

Open-air exposure to elevated ozone resulted in an increase in soil respiration (the sum of root and microbial respiration) due to a stimulation of fine root production in a beech and spruce forest (Nikolova et al., 2010). However, for spruce this was dependent on soil water availability as the ozone effect was observed in a wet year but not in a dry year. Microbial biomass and respiration were not significantly affected by elevated ozone in the aspen open-air exposure study (Larson et al., 2002). Mycorrhizal associations are generally enhanced by elevated ozone (Gorissen et al., 1991; Scagel and Andersen, 1997; Matyssek et al., 2010a,b). Elevated ozone can increase ectomycorrhizal colonization of host species, and alter the relative abundance of species within the ectomycorrhizal community despite having a generally negative impact on primary productivity (Andersen, 2003).

Although open-air exposure to elevated ozone affected litter quality, this had little impact on microbial respiration. In contrast, litter quantity affected microbial respiration (Hillstrom et al., 2010). Litter from ponderosa pine trees with severe symptoms of ozone damage (chlorotic mottle) decomposed at the same rate as litter from adjacent trees with no visible chlorotic mottle (Fenn, 1991). Chapman et al. (2005) concluded that if changes in soil C cycling occur, they will most likely be brought about by changes in litter production. Holmes et al. (2006) showed that elevated ozone could reduce nitrogen availability in the soil via changes in litter production. As the effects of ozone on plant chemistry and ecological interactions are highly context- and species-specific, it difficult to identify general, global patterns.

In a meta analysis, Wittig et al. (2009) analysed 263 peer reviewed papers and reported that current ambient ozone (approximately 40ppb) relative to charcoal filtered air significantly reduced total tree biomass by an average of 7%, with leaf area alone being reduced by 4%. This analysis also showed that background ozone at concentrations between 81- 101 ppb (predicted by some models to occur by the end of this century) decreased total biomass by an average of 17% and significantly altered root:shoot ratios by 6%, thus indicating a decrease of photosynthates partitioning to below ground sinks (with important consequences for C sequestration, see Section 5.1). At these higher ozone concentrations (average 93 ppb), height was also significantly decreased along with a 20% decrease in leaf area and an 18% reduction in leaf photosynthesis. Decreased chlorophyll content and very significantly decreased Rubisco content (28%) and activity (21%) was also reported by these authors.

Carbon-limiting stressors, such as ozone, can have rapid and significant effects on root growth, often visible within one growing season (Wagg et al., 2012; Wittig et al., 2007), and decreased C pools can lead to carry-over effects on root growth over time as has been shown for ozone exposed cuttings or seedlings of *Populus tremuloides* (Coleman et al., 1996) and *Fagus sylvatica* (Kelting et al., 1995). However, a stimulation of fine-root production has been observed in these species, when examining mature trees within established communities (Pregitzer et al.; 2008, Nikolova et al., 2010). Sensitivity screening or competition studies using grassland species have revealed ozone-induced reductions in root growth for single species such as *Lotus corniculatus* and *Anthyllis vulneraria*, (calcareous grassland, Warwick & Taylor, 1995), *Achillea ptarmica*, *Cirsium dissectum*, *Lythrum salicaria,* and *Molinia caerulea* (fen-meadows, Franzaring et al., 2000), and *Medicago sativa* (Johnson et al., 1996, Renaud et al., 1997), as well as a reduction of the total community root biomass of meadow mesocosms (Manninen et al., 2005; Kaneva et al., 2008).

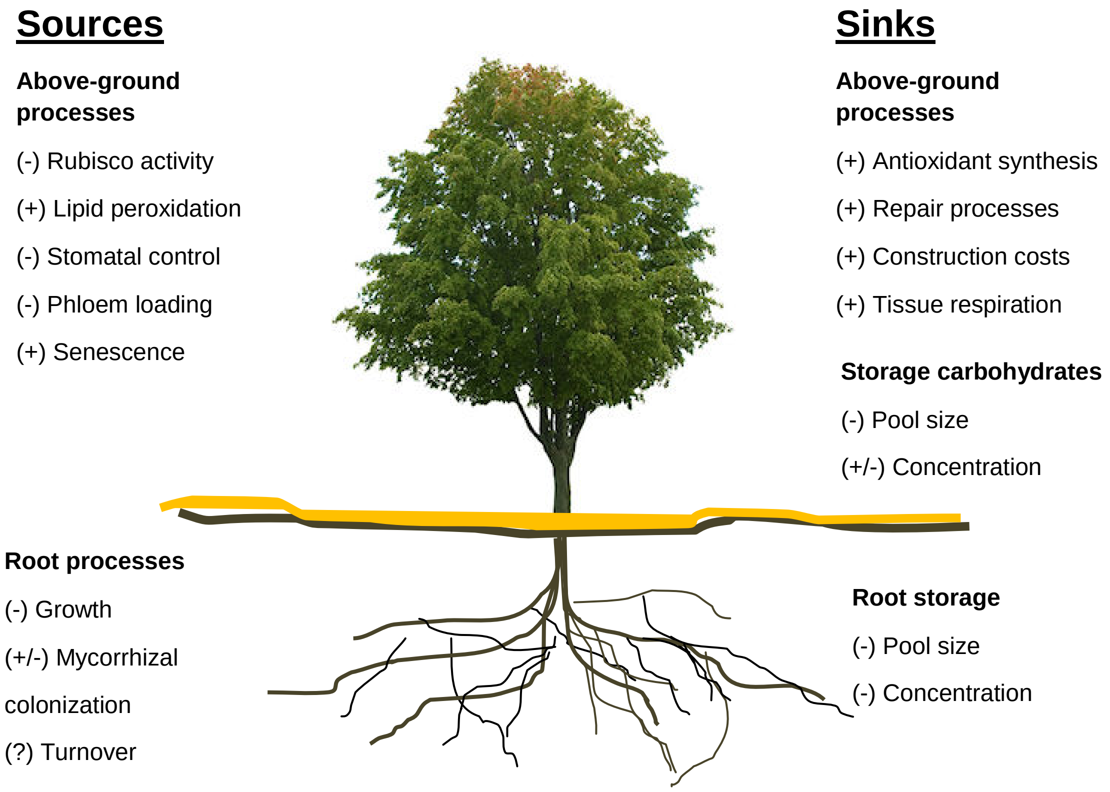

Figure 2.1 A conceptual diagram of processes and storage pools in sources and sinks that are affected by ozone exposure. A plus (+) denotes an increase in process rate or pool size, a minus (-) denotes a decrease in processes or pool size, and a plus-minus (+/-) denotes that both increases and decreases have been reported in response to ozone. Primary effects in the shoots are distinguished from secondary effects in roots since the primary site of ozone action occurs in the leaves (Adapted from Andersen, 2003).

Ozone tends to have greatest impact on the older leaves, and as it is these that preferentially allocate photosynthates to below ground sinks, any ozone-induced premature senescence and/or leaf loss will reduce root growth. Although effects on the roots are considered secondary/indirect responses to ozone, such effects may be more critical than above ground effects in determining the long-term consequences of ozone on ecosystem processes and services (Andersen, 2003). Current levels of ozone are capable of altering the timing and quality of C flux to soils, and therefore are likely to have a profound influence on root stock and root exudates and therefore, interactions among soil foodweb organisms (Andersen, 2003), potentially by altering C retention, mineralization and other important soil properties (**Figure 2.1**).

Three primary ways in which ozone alters C flux into and out of soils, in addition to changes in leaf litter quality or quantity are, altered rhizodeposition, changes in soil microbial community composition, and altered soil processes. Processing of plant-derived C compounds by organisms is a basic requirement for a functional stable below-ground ecosystem, as processing of C residues influences the chemical and physical properties of the soil, such as water holding capacity, porosity and aggregate structure etc. Soil organisms are essential for the recycling of nutrients. The high degree of interdependence amongst soil organisms comprising food webs suggests that any change in the quantity/quality of N/C movement from plants to soils resulting from ozone stress would be transmitted through other levels of the food web (de Ruiter et al., 1998).

2.2 Impacts of ozone on nutrient cycling

Tropospheric ozone has the capacity to impact on nutrient cycling by both direct and indirect mechanisms, namely by (1) altering the chemical composition of plant tissue, (2) altering the quantity (and quality) of litter fall, (3) impacting on below-ground plant biomass and root exudates, (4) indirectly altering microbial community composition(s) and functioning, and (5) indirectly influencing soil processes and the chemical properties of soils. All of these have the capacity either, independently or in concert, to reduce the long-term sustainability of ecosystems (Lindroth et al., 2001).

Leaf litter is a significant contributor to nutrient cycling and soil C. Changes in quantity and quality of leaf litter are important once it reaches the litter layer because the chemical composition of plant tissue is a primary determinant of their decomposition rates (Baldantoni et al., 2011) and therefore, by controlling soil organic C inputs, can alter microbial composition, activity and processes in a way that might feedback to effects on N and other nutrient availability (Holmes et al., 2006; Liu et al., 2005). However, research on the effects of ozone on below-ground processes has mainly focused on agro-ecosystems or forest soils with only a few studies having been published about grassland ecosystems. It is therefore, important to gain greater understanding of the implications of ozone in all ecosystems and how interactions between systems may be modified.

An important mechanism by which conditions for soil organisms may be changed could be modification in the quality of litter released from plants exposed to ozone. Kasurinen et al. (2007a) reviewed existing information about ozone effects on leaf litter and concluded that ozone effects on litter chemistry were more obvious at high ozone concentrations. For instance, effects of ozone on litter quality have been described for *Betula pendula* (Kasurinen et al., 2006, 2007b) but could not be detected on *Fagus sylvatica* (Schloter et al., 2005). In the course of the Aspen-FACE experiments, it has been demonstrated that ozone-induced changes in litter quality of *Populus tremuloides* and *Betula papyrifera* communities led to reduced inputs of hemicellulose and lignin (Liu et al., 2005, Meehan et al., 2010) and caused a decrease in nutrient flux into soil (Liu et al., 2007). In contrast, Stoelken *et al.* (2010) detected additional N incorporation into the soil down to 30 cm depth within *Fagus sylvatica* lysimeter experiments.


Photo: G Mills

Further, work by Holmes et al. (2006) document that elevated ozone decreased gross N mineralization by 16% in temperate forest species, probably due to decreased organic substrate inputs. Lui et al. (2005) have shown a 14.2% and 20.5% reduction in above-ground litter production in ozone treated aspen-birch and aspen communities respectively compared to control treatments. Plants exposed to elevated ozone have also been shown to contain a greater proportion of foliar N than control plants. For example, ozone was found to consistently increase nitrogen concentrations in wheat (Pleijel et al., 1999); increased foliar N often means that leaf litter decays more rapidly. Conversely, Weigt et al. (2012) report a significant decrease in leaf N concentrations in

European beech (*Fagus sylvatica*) when exposed to 2 x ambient ozone regimes. Reduced N uptake under 2 x ambient ozone has been previously found in beech by Haberer and colleagues (2007). Lui et al. (2005) and Lindroth et al. (2001) also report significantly reduced foliar N by up to 6.6% in response to elevated ozone.

The effects of ozone on secondary metabolites, lignifications and/or carbon: nitrogen (C: N) ratio of above- and below-ground plant parts can also alter the biodegradability of litter and thus the rate of decomposition which may, in turn, impact on detritivore and herbivore trophic pathways (Lindroth et al., 2001). Boerner and Rebbeck, (1995) have shown that ozone altered the structure, nutrient status and deposition of secondary metabolites in leaves of forest trees, whereby ozone lowered soluble carbohydrate concentrations and increased lignin content, the consequences of which were reduced decay rates of litter fall. Lui et al. (2005) observed increased concentrations of C-based defence compounds in *Populus tremuloides* and *Betula papyrifera* in response to elevated ozone and proposed that altered concentration of C-based compounds can modify C:N ratios, which again negatively impacts on decay rates. In support of this, Baldantoni and colleagues (2011) report that in *Quercus ilex* L. plants exposed to elevated ozone, decomposition rates of fallen leaves were altered due to slower C release, and higher C:N ratios. In the above study by Baldantoni et al. (2011), ozone exposure again significantly slowed litter fall decomposition rates, indicating a negative effect of ozone on nutrient cycling. Changes in the C: N ratios are also reported by Scherzer et al. (1998) amongst others.

Nitrogen allocated to synthesis of secondary metabolites, or lost in litter due to incomplete remobilization, is not available for internal recycling and therefore represents a significant cost to the plant. In some plant species this means that additional N uptake is require to maintain plant N balance (Andersen, 2003). It is apparent from the above studies that the effects of ozone on plant and residue quality may translate into long-lasting changes in soil chemistry and microbial properties. Relevant in the global change context is the effect of increasing background ozone on C pools in forest and grassland soils as changes in root growth and mycorrhizal status of the plant may be impacted early in the plant-ozone interaction and may actually condition other plant responses to ozone stress. Ozone is also anticipated to impair the mycorrhizae-induced protection of root stock from pathogen attack (Fuhrer and Booker, 2003).

The effects described for C and N above will influence the long-term chemical properties and stability of soils (Gregg et al., 2006). Other nutrients are also likely to be influenced by ozone such as potassium and phosphates, but more research is needed before generalisations can be made.

2.3 Impacts of ozone on stomatal functioning and water cycling

Tropospheric ozone is known to alter stomatal response(s) to environmental stimuli and in the short term (at higher concentrations) can cause stomata to close (Minnocci et al., 1999; Pollastrini et al., 2010; Roberts, 1990). However, under prolonged chronic exposure (at lower concentrations) many reports document ozone-induced stomatal opening or loss of stomatal sensitivity to closing stimuli, such as drought (Hayes et al., 2012a; Maier-Maercker, 1999; McLaughlin et al., 2007a, b; Sun et al., 2012; Wagg et al., 2012; Wilkinson and Davies, 2009), light (Paoletti and Grulke, 2010) and vapour pressure deficit (Grulke et al., 2007; Wagg et al., 2013). An example of such a response, taken from Wagg et al., 2013, is provided in **Figure 2.2**. In this experiment, the grass species *Dactylis glomerata* (Cock's foot grass) was exposed to a high background, low peak ozone exposure regime in the CEH Bangor, UK, solardomes for 14 weeks at two soil moisture levels: near field capacity (20 – 40% v/v) and reduced watering (7.5 – 20% v/v). By detaching leaves from the plant, severe water stress is simulated. Healthy leaves, as shown for the 16 ppb ozone treatment would lose some weight initially as the stomata are closing and then gradually lose less and less weight until a near steady state is achieved. Those leaves from the reduced watering treatment in 16 ppb followed a similar trajectory but were better adapted to water shortage. In contrast, although the leaves from the 89 ppb ozone treatment showed no visible signs of damage, their weight loss was much more rapid indicating more wide open stomata that were much slower closing. Leaves from the 89 ppb reduced watering treatment showed a similar trend to those from the well-watered 89 ppb treatment, but had a lower initial rate of water loss.

For this report, we conducted a comprehensive review of the published literature on ozone effects on stomatal functioning to determine if generalisations can be made based on species, genotype, duration and intensity of ozone exposure, climatic conditions and soil water availability. The detailed results of this analysis of data from 49 papers published over the last 25 years are provided in Annex 2, including for each paper, the direction of stomatal responses to ozone taking into account species type, ozone fumigation method, ozone concentration, and additional treatments such as drought and fluctuations in light.

In **Table 2.1** we summarise the stomatal response data from Annex 2. The results suggest that of the 68 species examined (including trees, crops and (semi-)natural grassland species), 22% showed no change in stomatal conductance, 10% showed a slowed (sluggish) stomatal response to elevated ozone, 23.5% showed an increased stomatal opening under elevated ozone and 44% displayed stomatal closure in response to ozone. Tree species were the most adversely affected with 73% of species showing an altered stomatal response, with 13 species showing stomatal opening and 15 showing stomatal closure in response to ozone. Crops tended to respond to ozone stress with stomatal closure (occurring in 75% of the species), whilst increased, or "sluggish" stomatal response was only reported in 19% of the species. For the 8 grassland species included, responses were more or less evenly spread across the four categories of stomatal response.

The proportions of species showing different responses should be interpreted with some caution as there were large variations in exposure facilities, the magnitude and duration of ozone exposure, climatic conditions (i.e. differences in light, temperature, soil moisture etc.), as well as inherent differences in response of species/genotypes to elevated ozone. No clear patterns emerged for the ozone concentration range for the different responses (**Table 2.1**), except perhaps the tendency for stomatal opening to occur at lower concentrations. Further analysis is needed to understand the complexities of ozone exposure duration, concentration and climate effects in the stomatal responses to ozone. The implications of effects of ozone on stomatal functioning for water cycling, including under drought conditions are considered in Section 5.4.

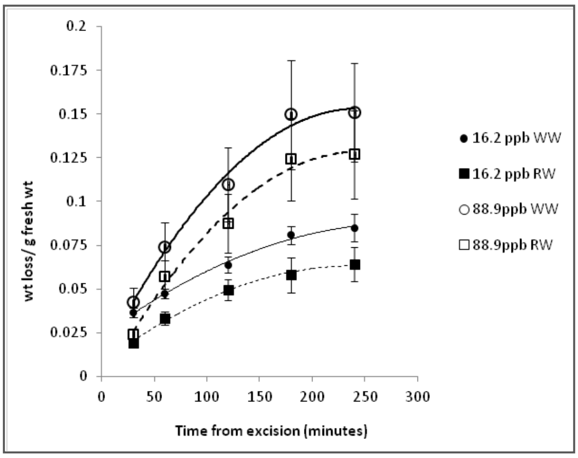

Figure 2.1 Response of leaves developing in ozone to severe water stress, simulated by excision from the plant. Data is the weight loss of upper canopy excised *Dactylis glomerata* (Cock's foot grass) leaves, with enhanced water loss indicating loss of stomatal closure after 14 weeks exposure to either 16.2 ppb (black symbols) or 88.9 ppb (clear symbols) ozone under well-watered (WW, circle) and reduced-watered (RW, square) conditions. N= 4, bars represent ± SE (Wagg et al., 2013); p =0.007 for ozone effect, ozone x watering and watering were n.s.

Table 2.1 Summary of effects of ozone on stomatal conductance in trees, crops and grassland species (data obtained from 49 peer reviewed publications, for details, see Annex 2).

	Total number	No effect	Sluggish control	Increased opening	Stomatal Closing
Crops (no. of species)	16	1	2	1	12
Crops (no. of experiments)	22	2	2	1	17
Trees (no. of species)	44	12	4	13	15
Trees (no. of experiments)	60	12	10	17	21
Grasslands (no. of species)	8	2	1	2	3
Grasslands (no. of expts.)	11	2	1	5	3
Total (no. of species)	68	15	7	16	30
Total (no. of experiments)	93	16	13	23	41
Ozone range (25th to 75th percentile)		35 – 80 ppb	70 – 120 ppb	50 – 90 ppb	59 – 100 ppb
Mean ozone concentration		59 ppb	91 ppb	67 ppb	89 ppb

3 Impacts of ozone on provisioning services

Gina Mills, Harry Harmens, Karine Vandermeiren, David Simpson, Håkan Pleijel and Per Erik Karlsson

In this Section, we describe how ozone effects on primary productivity and associated processes impact on the quantity and quality of crop yield and spatially assess the potential losses in crop value for wheat and tomato. In a second case study, we show how ozone effects on tree biomass production and C sequestration have been quantified for different age classes for northern European forests, affecting timber production.

3.1 Crop production

Effects of ozone on primary productivity (see Section 2.1) are especially relevant for crop plants. With the world population predicted to increase to 9 billion by 2050, security of food supplies is one of the most important challenges for this century. Ozone damages crop plants by, for example, reducing photosynthesis, causing a yellowing of leaves and premature leaf loss, decreased seed production and reduced root growth, resulting in reduced yield quantity and/or quality and reduced resilience to other stress such as drought. As a consequence, the key components of the food system that ozone interferes with are the productivity of crops, the nutritional value and the stability of food supplies as ozone concentrations and therefore impacts vary from year to year. Some of the world's most important staple food crops are sensitive (wheat, soybean and other pulses) or moderately sensitive (maize, rice, potato) to ozone and effects on the yield of these crops are of global significance (**Table 3.1**, Mills et al., 2007a).

Table 3.1 The range of sensitivity of agricultural and horticultural crops to ozone (From Mills et al., 2007a).

Sensitive	**Moderately sensitive**	**Moderately resistant**	**Insensitive**
Cotton, Lettuce, Pulses, Soybean, Salad Onion, Tomato, Turnip, Watermelon, Wheat	Potato, Rapeseed, Sugarbeet, Tobacco	Broccoli, Grape, Maize, Rice	Barley, Fruit (Plum & Strawberry)

Using concentration-based indices, current global yield losses are estimated to be between 4 - 15% for wheat, 6 - 16% for soybean, 3 - 4% for rice and 2.2 - 5.5% for maize, with global economic losses estimated to be in the range $11 - $26 billion (Van Dingenen et al., 2009; Avnery et al., 2011a; Royal Society, 2008). Under the IPCC SRES[3] A2 Scenario, global yield losses for the year 2030 due to ozone are predicted to range from 5.4 - 26% for wheat, 15 - 19% for soybean, and 4.4 - 8.7% for maize, with total global agricultural losses in the range $17 - $35 billion annually (Avnery et al., 2011b). Even under the lower emission scenario B1, less severe impacts will nevertheless be in the range $12 - $21 billion annually. In areas of the world where demand already outweighs supply, the "hidden" threat from ozone impacts on crop production will add to the many threats to food security in areas of rapidly increasing population. So far no global evaluation is available on the impacts of ozone on food and feed quality, thus the total impacts of ozone on food security might be even higher than those described here.

In a detailed meta-analysis of published data from ozone effects of wheat experiments, Feng et al. (2009) indicated that elevated ozone (mean of 77 ppb) decreased grain yield of wheat by 26%. Light-

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[3] The Intergovernmental Panel on Climate Change Special Report on Emissions Scenarios

saturated photosynthetic rate, stomatal conductance and chlorophyll content were also decreased by 40%, 31% and 46% respectively relative to ambient air (35 ppb). In a previous meta-analysis Feng et al. (2008) report reductions in above- and below ground biomass in wheat (*Triticum aestivum* L.) of 18% and 27% respectively alongside reductions in wheat yield of 29% exposed to ozone concentrations in the range of 31-200ppb (average 72 ppb). Furthermore, elevated ozone in the 31 ppb to 59 ppb range (average 43 ppb) also significantly decreased grain yield and above-ground biomass by 18% and 16% respectively compared to charcoal-filtered air, indicating that current ambient ozone is already negativity impacting wheat production. Losses in biomass productivity were attributed to significant ozone-induced decreases in photosynthetic rates, chlorophyll content, stomatal conductance and RuBisCo activity of 20%, 40%, 22% and 19% respectively.

A recent state of knowledge report by the ICP Vegetation (Mills and Harmens, 2011), for the first time, quantified ozone impacts on wheat yield in Europe using the stomatal flux-based methodology. Using the national emissions projections scenario for 2000, ozone pollution in EU27 (+ Norway and Switzerland) was predicted to be causing an average of 13% yield loss for wheat, with an economic loss of €3.2 billion predicted if soil moisture is not limiting (**Table 3.2**). Economic losses per grid square in 2000 were greatest for wheat in the highest producing areas in France, Germany, Belgium, Denmark and the UK, indicating that ozone flux was high enough in these central and northern areas to have an impact on wheat production (**Figure 3.1**). Effects were also predicted for more southern countries such as Italy and Bulgaria. Impacts on tomato, a moderately ozone sensitive crop were investigated as a representative horticultural crop for southern Europe. Using the flux-based method, economic losses of €1.02 billion, representing 9.4% of the production value, were estimated for 2000, with the highest total losses predicted for Italy, Spain, Greece and the Netherlands. Predicted effects for 2020 were generally lower than those in 2000. For both wheat and tomato, economic impacts were predicted to decrease by 38% to €1.96 billion and €0.63 billion respectively. However, for wheat, critical level exceedance remained high at 82% for the wheat growing areas. Critical level exceedance reduced from 78% of tomato growing areas in 2000 to 51% in 2020.

Food security of many countries of South Asia is under threat due to the rapidly increasing population, industrialisation and economic growth. This has resulted in an increase in the emission of ozone precursors and hence atmospheric ozone concentrations. Asia is now the world's biggest emitter of NO_x, a major ozone precursor, and its NO_x emissions are predicted to further increase over the coming decades. Studies with a chemical protectant against ozone damage, and ozone filtration experiments using open-top chambers, have shown that current ambient ozone levels in South Asia are reducing crop yield and quality for a range of important crops in the region, commonly within the range of 10 to 20%, but sometimes considerably more (see Emberson et al., in Mills and Harmens, 2011, for further details). Comparison of the Asian data with European and North-American dose-response relationships show that, almost without exception, Asian crops appear to have a higher sensitivity to equivalent ozone concentrations (Emberson et al., 2009). Hence, Asian crop yield and economic loss assessments made using North-American or similar European based dose-response relationships may underestimate the damage caused by ozone. As such, there is an urgent need for co-ordinated experimental field campaigns to assess the effects of ozone across Asia to allow the development of dose-response relationships for Asian cultivars and growing conditions leading to improved quantification of current and future impacts.

Of further concern for global food security is the growing evidence that ozone impacts on yield quality as well as yield quantity. These effects are much less documented (see review by Vandermeiren and Pleijel, in Mills and Harmens, 2011), but are considered to be equally as important as effects on yield quantity. In wheat (*Triticum aestivum*), the most important effects of ozone include increases in grain protein concentration (but decreases the protein yield per plant or ton of seeds) and results in changes in baking quality (Fuhrer et al., 1992; Pleijel et al., 1999; Piikki et al., 2008; Rudorff et al., 1996; Vandermeiren et al., 1992). The “CHIP” study, covering seven different sites across Europe, reported positive effects of ozone on potato tuber quality by decreasing the content of reducing sugars (i.e. glucose and fructose) and increasing the vitamin C content; reduction of the starch content on the other hand, had a negative impact on the quality (Pell et al., 1988; Vorne et al., 2002; Vandermeiren et al., 2005). These effects may be due to reduced assimilate allocation from leaves to tubers (Plessl et al., 2007). Seed quality of oilseed rape, the third most important world source of vegetable oil (Lühls and Friedt, 1994), in terms of crude protein and oil content, was reduced by elevated ozone, which represents an additional economic loss to the decrease in seed yield (Ollerenshaw et al., 1999). De Bock et al. (2011) confirmed the decrease in oil percentage in spring oilseed rape, however there was an increase in the percentage of protein (Vandermeiren et al., unpublished). Early-season ozone exposure has been shown to decrease the relative feed value of *Poa pratensis*, a common perennial pasture grass in Europe, by an average of 8%. This is sufficient to have nutritional implications for its utilization by herbivores as a result of predicted decreases in voluntary intake and digestibility (Bender et al., 2006).

Table 3.2 Predicted impacts of ozone pollution on wheat and tomato yield and economic value, together with critical level exceedance in EU27+Switzerland+Norway in 2000 and 2020 under the current legislation scenario (NAT scenario). Analysis was conducted on a 50 x 50 km EMEP grid square using crop values in 2000 and an ozone stomatal flux-based risk assessment.

	Wheat		**Tomato**	
	2000	**2020**	**2000**	**2020**
Total production, million t	133.53		17.68	
Total economic value of wheat in 2000, billion Euro	15.87		6.85	
Mean % yield loss per grid square	13.7[1]	9.07[1]	9.4[2]	5.7[2]
Total production loss, million t	26.89	16.45	2.64	1.62
Total economic value loss, billion Euro	3.20	1.96	1.02	0.63
Percentage of EMEP grid squares exceeding critical level	84.8[1]	82.2[1]	77.8[2]	51.3[2]

[1]based on all grid squares with wheat production, [2] based on grid squares with > 1 tonne of production

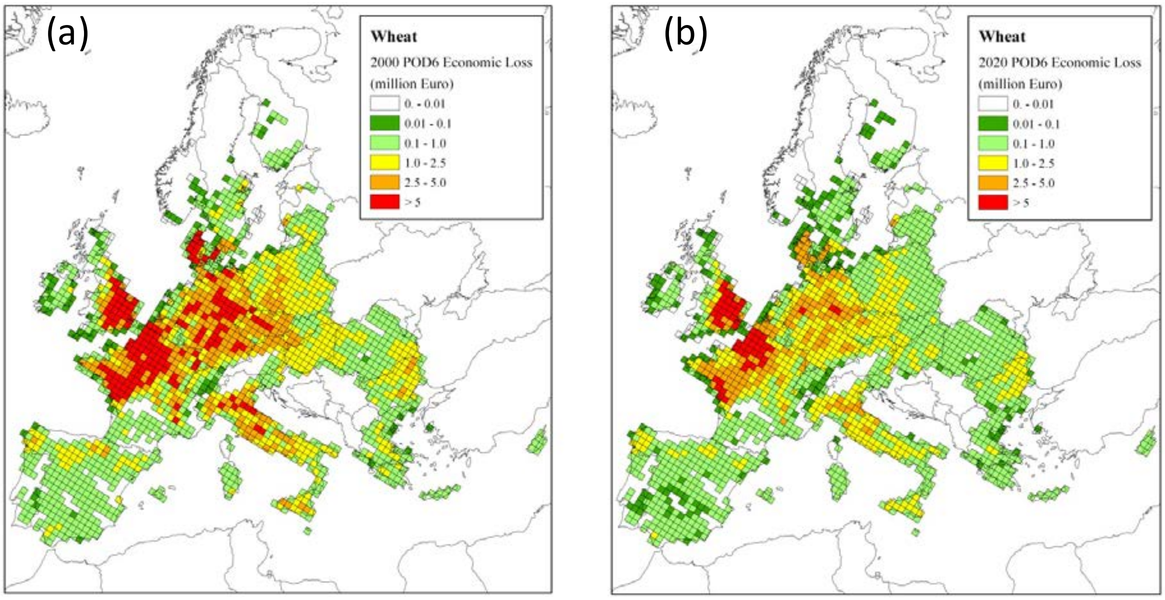

Figure 3.1 Predicted economic losses for ozone effects on wheat in million Euro per 50 x 50 km grid square in (a) 2000 and (b) 2020 for the wheat growing areas of EU27+CH+NO as indicated by the NAT scenario and flux-based methodology.

3.2 Timber production

A recent meta-analysis has suggested that the increase in ozone since the industrial revolution has been responsible for a reduction in photosynthesis of approximately 11% in trees (Wittig et al., 2007), which may have reduced tree productivity by approximately 7% (Wittig et al., 2009). Some ozone-sensitive forest tree species are present in large areas of Europe: birch, Scots pine and Norway spruce are particularly important in central and northern Europe; beech and deciduous oaks are frequent across several European regions, in particular in central and southern areas; Holm oak and Aleppo pine are frequent in Mediterranean Europe (see, for example, Karlsson et al., 2007). In general, deciduous trees tend to be more sensitive to ozone than coniferous trees. There is evidence that negative effects of ambient ozone on forest trees are already occurring all over Europe. For example, visible injury has been detected in ICP Forests surveys (Ferretti et al., 2007a,b), reduced stem growth has been reported in Sweden (Karlsson et al., 2005), reduced stem (Braun et al., 1999) and shoot growth in Switzerland (Braun et al., 2010) and leaf loss occurs in Greece (Velissariou, pers. com.). Karlsson recently quantified effects of ozone on production in northern European forests (in Harmens and Mills, 2012), and we use this as an example here to show the potential effects of ozone on timber production in parts of Europe. A spatial flux-based assessment of current and future effects on C sequestration is provided in Section 5.1.

The forested areas of northern Europe are largest in Germany, Finland, Norway and Sweden (**Table 3.3**). Whereas the fraction of young forests was relatively similar between the countries, the fraction of highly productive coniferous forests was particularly high for Denmark and Sweden, whilst Estonia and Lithuania had a relatively high fraction of productive broadleaved forests (data not presented). The fraction of forests characterized as mixed was generally low for these countries. The most important factor that determines the changes in the forest living biomass C stock is the gap between growth and harvest rates. If this gap is small, then a certain growth reduction caused by ozone will have a relatively large impact on the C stock change, and vice versa. By far the most important countries for C sequestration in the living biomass C stocks in northern and central Europe are Sweden, Finland, Poland and Germany. Ozone-induced growth reductions will also result in an economic loss for forest owners.

Table 3.3 Forested areas, growing stocks and C stocks for ten major, northern and central European countries. The four highest values for each parameter are given in bold; n.a.: data not available. Source: FAO statistics, State of the World Forests, 2009.

	Extent of forest		Growing stock			C in biomass	
Country	Forest area 2005 (1000 ha)	Annual change 2000-2005 (%)	Per hectare (m^3 ha^{-1})	Total (Million m^3)	Com-mercial (%)	Tonnes ha^{-1}	Total (Mt)
Czech Rep.	2648	0.1	**278**	736	**97**	**123**	326
Estonia	2284	**0.4**	**196**	447	**94**	73	167
Latvia	2941	**0.4**	**204**	599	85	**79**	231
Lithuania	2099	**0.8**	190	400	**86**	61	128
Poland	9192	0.3	**203**	**1864**	**94**	**97**	**896**
Germany	**11076**	n.a.	n.a	n.a.	n.a.	**118**	**1303**
Denmark	500	**0.6**	153	77	76	52	26
Finland	**22500**	0.0	96	**2158**	84	36	**816**
Norway	**9387**	0.2	92	**863**	78	37	344
Sweden	**27528**	0.0	115	**3155**	77	43	**1170**
All	90155						

Calculations were based on national mean AOT40 values (**Table 3.4**). However, it should be noted that the AOT40 approach might underestimate the risk of ozone impacts on vegetation in northern European countries in particular (e.g. Hayes et al., 2007b; Mills et al., 2011c; see also Chapter 5). The response variable used for calculating the ozone effects in this study was the relative increment of either stem volume or total biomass, i.e. the increment during a period relative to the value at the start of the period. Unfortunately, many studies report only the percentage reduction of biomass caused by ozone at the end of the experiment and do not provide information on the biomass at the start of the experiment, so that impacts on growth rates cannot be calculated. For example, the results of the study by Wittig et al. (2009) could not be used in the current case study.

Table 3.4 Estimated national mean values for annual, daylight AOT40 accumulated during the growing season for trees; the values are annual means for the time period 2000-2005. Source: EMEP model (David Simpson, 27-09-2011).

Country	AOT40 (ppm h)	Country	AOT40 (ppm h)
Czech Rep.	28	Latvia	10
Denmark	13	Lithuania	12
Estonia	7	Norway	4
Finland	3	Poland	21
Germany	24	Sweden	5

In this study ozone impacts were assessed differently for proportions of trees per country in each of the following age classes: young trees before canopy closure (age <10 years), productive age classes (age 10-60 years) and old forests (age >60 years). It was assumed that trees in the productive age classes were equally affected by ozone as juvenile trees, and that old trees (>60 years) have a lower ozone sensitivity due to overall reduced growth rates, here assumed to 50% of the growth rate of younger age classes .

Ozone exposure – response relationships for young coniferous and broad-leaved trees (**Table 3.5**) were derived from Karlsson et al. (2005). The forest stem increment growth for the baseline scenario, i.e. the low ozone exposure, was calculated as:

$y = h/(100+(i*j)/100)$

where y = annual increment growth (m^3 y^{-1}), h = annual increment growth under current ozone exposure levels (m^3 y^{-1}), i = AOT40 (ppm h), j = the slope for the correlation between AOT40 and the per cent growth reduction (% $(ppm\ h)^{-1}$, negative values imply growth reductions).

Table 3.5 Relationships for ozone impacts on the annual stem volume increment growth rates of coniferous and broadleaved tree species separated into three different age classes, as related to the annual mean daylight AOT40, accumulated from 1 April to 30 September and expressed as ppm h. Ozone impact on the relative stem volume increment rates is expressed as % change.

Forest type	Age class ≤10 years	Age class 11-60 years	Age class >60 years
Conifers	-0.26 * AOT40	-0.26 * AOT40	-0.13 * AOT40
Broadleaved	-0.49 * AOT40	-0.49 * AOT40	-0.25 * AOT40

The differences between the changes for the living biomass C stocks in the current ozone exposure and the pre-industrial ozone exposure scenario are shown in **Table 3.6**, in absolute values for the different forests types and age-classes as well as the total forests in each country and as percentage change for the total forests. The estimated percentage reduction in the change of the living biomass C stock across total forests in all ten countries was 10%. For different countries these values ranged between 2 - 32%. The differences depended on the size of the gap between growth- and harvest rates, as discussed in the following section.

The calculated C stock changes of 56 Mt CO_2e yr^{-1} in the living biomass in Finland, Norway and Sweden is in the same range as that presented by Pan et al. (2011) for the boreal forest C stock increase for the three countries since the Industrial Revolution, i.e. 77 Mt CO_2e yr^{-1}. Although the value calculated in the current study also included temperate forests, temperate forests cover a relatively small part of these countries. Hence, the assumptions made in this study were reasonable regarding forest types and age-class distributions, as well as the conversions between stem volume increments and C stock changes, at least for these three Nordic countries. Although percentage changes in tree biomass at the end of an experiment due to ozone cannot directly be translated into changes in C stocks, the meta-analysis by Wittig et al. (2009) indicated a similar reduction in biomass (7%) as found in this study for C stocks (10%) when comparing current ambient levels with pre-industrial levels of ozone. The highest losses in C stocks were predicted to be in the Czech Republic, Germany and Poland. Uncertainties associated with this approach are discussed in Karlsson (in Harmens and Mills, 2012).

Table 3.6 Estimated reductions in annual C sequestration (Mt CO_2e yr^{-1}) due to current ozone exposure as compared to pre-industrial ozone levels for different forest types and age-classes as well as for total forests. Also presented is the percentage reduction due to ozone exposure, for the total forest in each country.

Age (years)	**≤10**			**11-60**			**>60**				
Country	**Coniferous**	**Broadleaved**	**Mixed**	**Coniferous**	**Broadleaved**	**Mixed**	**Coniferous**	**Broadleaved**	**Mixed**	**Total forest**	**Reduction (%)**
Czech Rep.	0.02	0.01	0.01	0.65	0.26	0.23	0.22	0.09	0.05	1.55	32.0
Denmark	0.00	0.01	0.00	0.13	0.07	0.00	0.00	0.02	0.00	0.24	5.8
Estonia	0.00	0.01	0.00	0.05	0.14	0.06	0.01	0.01	0.01	0.28	4.5
Finland	0.01	0.00	0.00	0.32	0.07	0.10	0.10	0.01	0.02	0.64	2.2
Germany	0.10	0.29	0.03	3.49	2.42	0.14	0.86	1.30	0.05	8.69	12.3
Latvia	0.00	0.01	0.00	0.11	0.23	0.05	0.04	0.03	0.02	0.51	8.8
Lithuania	0.00	0.01	0.00	0.10	0.23	0.06	0.02	0.02	0.01	0.46	13.8
Norway	0.00	0.01	0.00	0.07	0.06	0.05	0.03	0.02	0.01	0.24	1.8
Poland	0.04	0.06	0.03	1.37	1.73	0.64	0.41	0.22	0.14	4.64	12.8
Sweden	0.04	0.01	0.01	0.77	0.12	0.25	0.12	0.01	0.02	1.34	8.6
All										**18.6**	**9.8**

4 Impacts of ozone on biodiversity

Gina Mills, Jürgen Bender, Elke Bergmann, Ignacio González-Fernández, Giacomo Gerosa, Victoria Bermejo, Riccardo Marzuoli, Héctor Calvete-Sogo, Angelo Finco, Héctor García-Gómez, Rocío Alonso

Over recent decades, there have been numerous ozone exposure experiments to investigate the possibility of ozone-induced shifts in species balance using simulated communities, transplanted turves and open field ozone exposure systems. Here, we review current knowledge of ozone effects on biodiversity, including an assessment of evidence for effects in the field. As a case study, we summarise current evidence for effects of ozone on biodiversity in southern Europe, a globally important biodiversity "hotspot".

4.1 How ozone might affect biodiversity or species balance?

In the simplest interpretation, to impact on biodiversity, ozone pollution would need to exert sufficient toxic effect on an individual species for that species to be lost from a habitat. In reality, however, in most natural or (semi-)natural communities, plants are growing in a highly competitive environment - a slight loss of vitality of one species due to ozone can result in a more vigorously growing but less ozone-sensitive species outcompeting the affected species for light, nutrients and water resulting in a shift in species balance and potential loss of the more sensitive species at a sub-lethal ozone concentration. As described earlier in this report, typical effects of ozone on sensitive species include visible injury, premature and enhanced senescence, and changes in biomass, resource allocation and/or seed production. Each of these effects can impact on the vitality of component species of plant communities, potentially altering plant biodiversity as well as that of the animals, fungi, bacteria and insects that live in close association with plants (see schematic in **Figure 2.1**). For example, changes in leaf chemistry will impact on herbivorous insects and plant pathogens, whilst changes in root exudation will impact on mycorrhizal associations and microbial soil processes. In so doing, ozone-induced changes in species diversity or shifts in species balance will impact on many ecological processes, thereby impacting on ecosystem services, flows, goods and values.

4.2 Identifying plant communities potentially at risk of species changes

Recent attempts to predict the sensitivity of ecosystems to biodiversity loss as a result of ozone exposure have concentrated on compiling data from experiments involving exposure of plants to ozone pollution in solardomes, open top chambers or open field exposure systems. In three related studies, data were collated for 83 species from over 60 papers where the following criteria were met: biomass measurements were made; data were from field-based experiments (open-top chambers, field release systems, solardomes); the exposure duration was at least three weeks and did not exceed a mean maximum hourly ozone concentration of 100 ppb (Hayes et al., 2007a; Jones et al., 2007; Mills et al., 2007b). AOT40 over the duration of the exposure period was used as the measure of ozone exposure. Using linear regression, ozone dose-response functions were derived for those species that had three or more data points, and the relative sensitivity was calculated by dividing the relative biomass at 15 ppm h by that at 3 ppm h (Hayes et al., 2007a). A species was categorised as sensitive to ozone if the sensitivity index was less than 0.9 (33% of species), insensitive to ozone if the sensitivity index was between 0.9 and 1.06 (49% of species), or stimulated by ozone if the sensitivity index was greater than 1.06 (18 % of species, **Figure 4.1**). The geographical coverage of the database reflected the available sources of published data, with over 95% of the data from experiments conducted in Sweden, Denmark, UK, Netherlands, Germany and Switzerland.

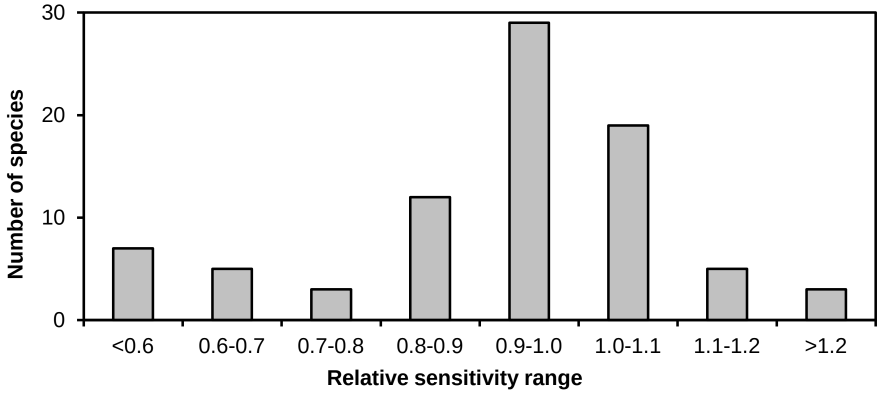

Figure 4.1 Range of relative sensitivity to ozone for the 83 species of grasslands, wetlands, heaths and forest margins/understory included in the analysis by Hayes et al. (2007a).

The three studies investigated characteristics that might allow ozone-sensitive communities to be identified. Hayes et al. (2007a), found that species with a therophytic life form were quite sensitive to ozone as were those from the *Fabaceae* family, but there was no correlation between ozone sensitivity and leaf longevity, flowering season, stomatal density or maximum altitude. An investigation of the relationship between relative sensitivity to ozone and Grime's CSR strategy, based on a species' competitiveness (C), stress tolerance (S) and ruderal (R) characteristics (Grime, 1988), showed no significant correlation with ozone sensitivity for each species (Hayes et al., 2007a). However, comparison of relative sensitivity to ozone with Ellenberg ecological values (Ellenberg et al., 1991) showed that light-loving plants tend to be more sensitive to ozone than plants that normally occur in the shade (Jones et al., 2007) although species representing the most shade-tolerant Ellenberg values (1 - 4) were not represented in the database. Plants of Ellenberg moisture value 3 (dry site indicator) tended to be more sensitive to ozone than those found in more moist soils. Plants which can tolerate moderately saline conditions (Ellenberg salt value of 1) are more sensitive to ozone than those of non-saline habitats. There were no relationships between Ellenberg nutrient, 'reaction' (pH) or temperature value and ozone sensitivity.

Jones et al. (2007) developed a method of identifying ozone sensitive species and communities from the Ellenberg Light and Salinity values and successfully applied this to predictions of ozone sensitive communities in the UK. For more general application across Europe, Mills et al. (2007b) used the same data to determine the habitats with the highest proportion of ozone-sensitive communities using the EUNIS (European Nature Information System) habitat classification system used by the LRTAP Convention. These habitats were found to be: Dry grasslands (E1), Mesic grasslands (E2), Seasonally-wet and wet grasslands (E3) and Woodland fringes (E5) (**Table 4.1**). This study also showed that Alpine and subalpine grasslands (E4) and Temperate shrub heathland (F4) should also be considered to be potentially ozone-sensitive as these tended to include a high proportion of species stimulated by ozone. Thus, by studying the responses of individual component species of different vegetation types, it is possible to predict how a community might respond to ozone. For example, in **Figure 4.2** the sensitivity of 23 species of EUNIS E2.11 grassland (unbroken pasture) are shown.

Many tree species are also sensitive to ozone, responding with for example, decreased growth, reduced photosynthesis, reduced leaf area and reduced root production. Wittig et al. (2009) conducted a meta-analysis of tree biomass and growth responses and found that angiosperms were more sensitive to ozone than gymnosperms. Overall, current ambient ozone of 40 ppb reduced biomass by 7% compared to charcoal filtered controls whilst a mean ozone concentration of 64 ppb reduced biomass by 17% compared to current ambient. The angiosperm genus' *Populus, Prunus* and *Quercus* all showed significant reductions in biomass in response to elevated ozone (compared to ambient concentrations) whilst *Betula* did not. In compiling data for the derivation of critical levels

Table 4.1 Ozone sensitivity at EUNIS level 2 determined from the relative sensitivity of component species (From Mills et al., 2007b).

EUNIS Category	Abbreviated name	Mean no. of spp. in habitat	No. of level 4 communities included	Mean no. of spp. Tested for O_3 sensitivity	No. of OS[1] spp.	% OS[2]
B1	Coastal dunes and sandy shores	80.9	3	16.6	6.7	41.6
B3	Rock cliffs and shores	73.5	1	15.5	6.5	42.0
D1	Raised and blanket bogs	81.5	2	7.5	6.0	80.4
D2	Valley and transition mires	119.0	1	10.0	6.0	60.0
D4	Calcareous mires	98.3	4	10.8	6.3	59.8
D5	Sedge and reed beds	60.0	1	9.0	6.0	66.7
E1	Dry grasslands	91.9	6	20.5	9.8	48.6
E2	Mesic grasslands	78.8	4	25.6	7.9	30.7
E3	Seasonally wet grasslands	79.4	6	15.6	6.8	45.0
E4	Alpine and sub-alpine grasslands	72.7	3	13.6	9.1	68.1
E5	Woodland fringes	101.8	4	17.9	9.4	51.6
F2	Arctic, alpine and sub-alpine scrub	78.9	3	12.8	8.6	72.4
F3	Temperate and Mediterranean – montane scrub	94.7	3	15.7	7.7	49.8
F4	Temperate shrub heathland	67.9	4	13.4	6.8	51.7
F9	Riverine and fen scrubs	112.0	1	7.0	6.0	85.7
G1	Broadleaved deciduous woodland	126.6	4	11.4	6.4	56.4
G3	Coniferous woodland	70.0	1	8.0	6.0	75.0
H1	Cave systems	99.0	1	17.0	9.0	52.9
I1	Arable land and market gardens	76.0	2	17.0	6.5	38.2

[1] OS = Ozone-sensitive, [2] Percentage of ozone sensitive species within the community

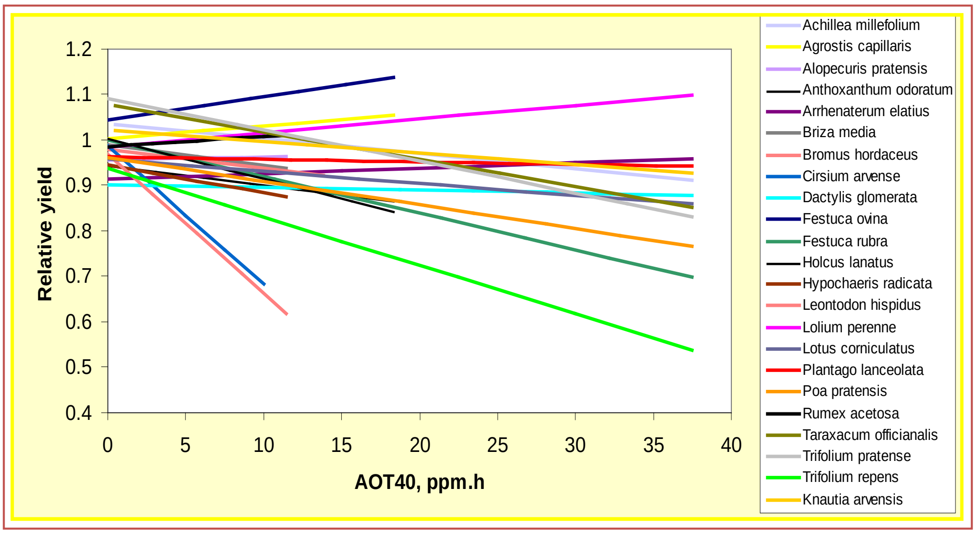

Figure 4.2 Dose-response functions (from the data included in Hayes et al., 2007a) for species present in EUNIS E2.11 (Unbroken pastures)

for trees, Karlsson et al. (2007), also showed that gymnosperms were less sensitive to ozone than angiosperms, with the slopes of AOT40-based and flux-based regression lines for beech and birch being ca. twice that for Norway spruce (LRTAP Convention, 2010). There is also evidence that pioneer species may be more sensitive to ozone than climax species (Matyssek et al., 2010a). Surveys by the ICP Forests have shown widespread occurrence of visible injury on forest margin and understory species in Europe (Ferretti et al., 2007a,b), with similar effects also reported by Manning and Godzik (2004) and in the USA (for example, Allen et al., 2007) . Within each genus, however, there is genotypic variation in ozone sensitivity and a future challenge lies in understanding the relationship between genes, physiological plasticity and sensitivity to ozone for forest species (Paoletti et al., 2010).

4.3 Experimental evidence of ozone-induced changes in species balance or biodiversity

4.3.1 Effects above ground

Based on the responses of individual species within unbroken pasture (**Figure 4.2**), one would predict that very sensitive species such as *Leontodon hispidus* (Rough hawkbit) and *Cirsium arvense* (creeping thistle) might be out-competed by less sensitive grass species such as *Festuca ovina*, *Lolium perenne* or *Dactylis glomerata*. There is some experimental evidence to support this prediction. In two-species mixtures exposed to ozone in solardomes, the more resistant grass species *Dactylis glomerata* increased in cover whilst the sensitive species *Leontodon hispidus* decreased in cover (**Figure 4.3**). Similar effects have been shown for other species mixtures exposed to ozone in open-top chambers or solardomes. For example, ozone sensitive clover has been shown to be gradually replaced by less sensitive grass species (Fuhrer et al., 1994; Nussbaum et al., 1995; Hayes et al., 2009), there was a decrease in the forb:grass ratio in grassland mesocosms (e.g. Hayes et al., 2010) and a shift in species balance in calcareous grassland mesocosms (Thwaites et al., 2006). However, such effects are by no means consistent, with reductions in total biomass occurring in some communities without a shift in species balance (e.g. Ramo et al., 2006, Pleijel et al., 1996).

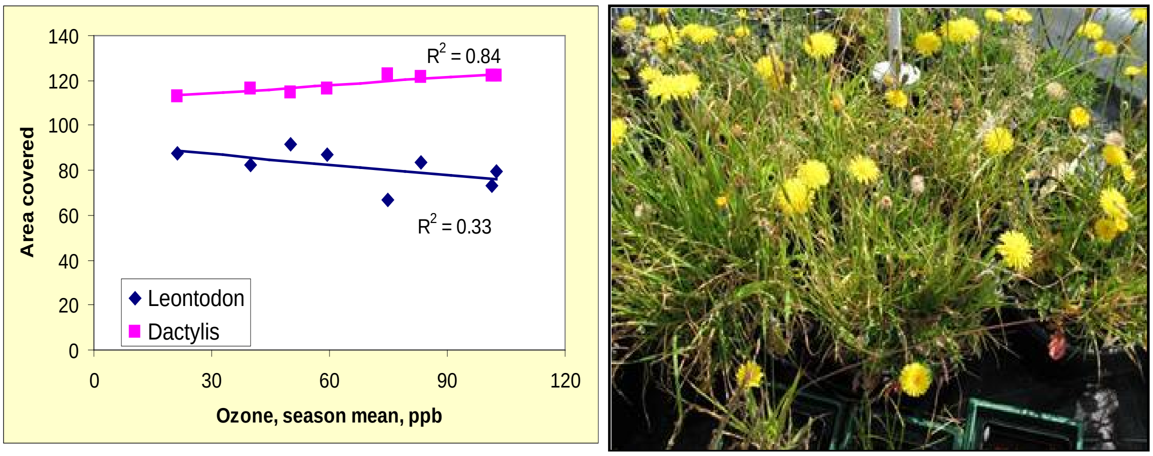

Figure 4.3 (a) Shifts in species balance between the ozone-sensitive forb *Leontodon hispidus* and the grass species *Dactylis glomerata* in (b) solardome experiments exposing the two species to ozone (Photo: G Mills).

In older or mature grassland communities there is greater resilience to stress and disturbance (Grime et al., 2002; Bassin et al., in press; Leuzinger et al., 2011), and there are many factors that influence whether a sensitive species is actually impacted by ozone. These include the number of other species present, plant age, genetic variability within the species, it's location within a canopy with taller species being exposed to higher ozone concentrations than low-growing species, the number of mutualistic interactions with surrounding species and the management regime, including grazing density (Bassin et al., 2007a). Proof of concept comes ultimately from field-based exposure of established communities using a free-air ozone exposure system. Four such studies have been conducted in recent years in Europe: species-rich upland meadow at Le Mouret, Switzerland (Volk et al., 2006, Stampfli and Fuhrer., 2010, see review in Annex 1 of this report), alpine pasture at Alp Flix, Switzerland (**Figure 4.4a**, Bassin et al., 2007b and in press, see also review in Annex 1 of this report); conservation-grade upland meadow at Keenley, UK (Wedlich et al., 2012, **Figure 4.4b**) and peat microcosms at Kuopio, Finland (Mörsky et al., 2011).

Figure 4.4 Examples of experiments investigating ozone effects on pasture using free air exposure systems (a) At Alp Flix, Switzerland (Photo: S Bassin) and (b) at Keenley, UK (Photo: G Mills).

The results from these European grassland field exposure experiments have been rather mixed. Wedlich et al. (2012) reported that an episodic ozone exposure that elevated the annual 24h mean by 4-10 ppb decreased herb biomass but not grass or legume biomass in a UK meadow being managed for conservation with a low grazing regime (**Figure 4.4b**). An important result from that study was that ozone reduced the growth of the hemi-parasitic species *Rhinanthus minor* (yellow rattle), a species used to reduce the productivity of grasses and open-up the canopy allowing conservation-value forbs to thrive. Thus, elevated ozone was interfering with the management regime and potentially reducing the conservation value of the grassland. In contrast, results from the field exposure experiments in Switzerland (**Figure 4.4a**) have indicated the resilience of long-established communities to ozone. Reductions in the overall yield and legume fraction biomass at le Mouret at the end of the 5 year exposure to elevated ozone (Volk et al., 2006) were unable to be separated from nutrient gradient effects found following extensive statistical analysis (Stampfli and Fuhrer, 2010). Similarly, after 7 years of exposure at Alp Flix, elevated ozone did not have a significant effect on the biomass of functional groups (grasses, forbs, sedges, legumes) but did increase the proportion of dead plant material; an increase in the growth of ozone-resistant *Nardus stricta* (mat grass) was detected (Bassin et al., in press).

Exposure of oligotrophic (low nutrient) pine fen microcosms to elevated ozone for three years in an open field exposure system for four growing seasons in Finland showed that the sedge *Eriophorum vaginatum L*. and the moss *Sphagnum papillosum* could tolerate ozone better than expected with few significant effects being observed (Morsky et al., 2011). However, methane release from the microcosms was initially reduced but eventually increased by prolonged ozone exposure and there were some changes in the microbial communities of the peat (Morsky et al., 2008).

Field release studies have also been conducted for trees in the USA (Aspen-FACE) with genotypes of trembling aspen (*Populus tremuloides*), paper birch (*Betula papyrifera* Marsh.), and sugar maple (*Acer saccharum* Marsh.) (e.g. Karnosky et al., 2007b) and in Germany (Kranzberg Forest) with 60 year old European beech (*Fagus sylvatica* Ehrh.) (Matyssek et al., 2007). These studies have confirmed many of the growth reduction effects of ozone measured in chamber-based systems with younger trees. Although these effects may well not be sufficient to change tree species biodiversity, *per se,* there is substantial experimental evidence of ozone effects on trees affecting associated organisms and ecological processes. A meta-analysis conducted by Valkama et al. (2007) showed that elevated ozone significantly increased relative growth rate of tree chewing insects whilst that of tree sucking insects tended to decrease under elevated ozone. Increases in phenolics and terpenes may have contributed to these differing insect herbivore responses, as concentrations of nutrients or carbohydrates in leaves were not be affected by ozone.

There is also substantial evidence of ozone affecting tree-fungi associations. For example, Olbrich et al. (2010) performed a controlled infection of mature beech trees being exposed to elevated ozone in a field release study in the Kranzberg forest with an endophytic fungus *Apiognomonia errabunda*. Elevated ozone was found to reduce both natural and controlled infection by the fungus. In contrast, Aspen trees were more susceptible to the rust pathogen (*Melampsora medusa*, Karnosky et al., 2002) which may have been due to ozone damaging the surface waxes (Karnosky et al., 2007a). Although ozone does not penetrate below ground, increases in fine root growth and soil respiration of the ozone-exposed mature beech trees of the Kranzberg forest were associated with increased diversity of mycorrhizal associations (Nikolova et al., 2010; Mattyssek et al., 2010a,b).

4.3.2 Effects detected below-ground

Ozone effects on the soil microbial community composition have been investigated both in the rhizosphere as influenced by root exudates and in the bulk soil close to leaf litter. Total bacterial biomass was decreased by ozone in the soil of the N_2-fixing legume *Lathyrus pratensis* but not in the soil of the grass *Agrostis capillaris* (Manninen et al., 2010). Changes in the ratio of fungal to bacterial biomass induced by plant's exposure to ozone have been described for *Pinus ponderosa* (Scagel & Andersen, 1997; Olszyk et al., 2001) and for blue wildrye (*Elymus glaucus,* Yoshida et al., 2001). For *Fagus sylvatica* a shift in the overall community structure (PLFA) in response to ozone (Pritsch et al., 2009) has been found to be associated with a reduction in the potential nutrient turnover (Schloter et al., 2005) and a higher abundance of plant-C utilising microbes (Esperschutz et al., 2009).

Aneja et al. (2007) characterised the diversity of microbial communities colonising control and ozone-exposed litter from *Fagus sylvatica* / *Picea abies* and provided evidence that changed litter quality due to elevated ozone influenced the structure of litter-colonizing microbial communities. In their review on microbial functioning in the soil, Kasurinen et al. (2007a) stated that the onset of these microbial responses may take years. For example, Morsky et al. (2008) found an ozone induced increase in microbial biomass at the end of a three-year experiment with peatland microcosms dominated by *Eriophorum vaginatum*.

Dohrmann & Tebbe (2005) studied the rhizosphere bacterial community composition of five low-managed grassland species using genetic profiling of PCR amplified 16S rRNA gene sequences based on single-strand conformation polymorphism (SSCP). They found that a five-week exposure to elevated ozone did not select for a different bacterial community composition as neither bacteria-specific profiles nor those with a more narrow phylogenetic range changed significantly. Because these plant species did not express any symptoms of ozone injury above-ground (Bender et al., 2002) they extended their study to four herbaceous species which were known to be more sensitive to ozone. Excepting some minor variations in the case of *Sonchus asper*, after a six-week treatment with ozone SSCP profiles did not reveal differences in community composition (Dohrmann & Tebbe, 2005), even when the plants (e.g. *Malva sylvestris*) were severely damaged by ozone (Dohrmann & Tebbe, 2006).

In a longer lasting experiment conducted over three years, Kanerva et al. (2008) provided evidence that elevated ozone is able to modify the structure of the microbial community in a meadow soil, while bacterial, actinobacterial, and fungal PLFA biomass was decreased simultaneously. Thus, these studies clearly indicate, that long-term observations are necessary to understand the effects of ozone on biodiversity and functional changes of soil processes in ecosystems as a whole.

Because of its implication for nitrogen acquisition, the degree of mycorrhization and its modification by ozone is of high importance for ecosystem function. Several studies described effects on mycorrhizal abundance for tree species when exposed to ozone (reviewed by Andersen, 2003). More recently this was shown for example for *Betula pendula* (Kasurinen et al., 2005), hybrid aspen *(Populus tremula L. x Populus tremuloides Michx.* (Haikio et al., 2009) and *Fagus sylvatica* (Pritsch et al., 2009, Grebenc & Kraigher, 2007a). Moreover, there is evidence that ozone impacts the microbial diversity in terms of mycorrhizal species composition as shown for *Pinus taeda* (Edwards & Kelly, 1992), *Betula pendula* (Kasurinen et al., 2005), *Fagus sylvatica*, (Haberer et al., 2007, Grebenc & Kraigher, 2007b), and recently in the Aspen-FACE community (Edwards & Zak, 2011). Currently, data about ozone effects on the mycorrhization of grassland species are limited. The mycorrhizal colonization of blue wild rye (*Elymus glaucus)* was reduced in response to ozone, and it has been demonstrated that this effect depends on the genotype of the grass tested (Yoshida et al., 2001).

To understand the implications of changes in ecosystem structure and function, consideration of the productivity of detritivore invertebrate communities is important. Unfortunately though, there are only a few published studies that show direct effects of elevated ozone on soil mesofauna composition. In a temperate forest soil (Aspen FACE) the individual density of soil mites (*Acari*) was reduced by nearly 50% under elevated ozone conditions, whereas the abundances of *Collembolans* remained unchanged (Loranger et al., 2004). Feeding experiments with litter altered in quality because of its production under ozone exposure conditions were able to demonstrate that growth rates were reduced for earthworm fed with birch litter (Kasurinen et al., 2007b) or springtail fed with aspen litter (Meehan et al., 2010). Schrader et al. (2009) observed a decrease in the individual density of enchytraeids, collembolans, and soil mites in the rhizosphere of ozone-exposed wheat plants and Chang et al. (2011) found a reduction in the abundance and diversity of *Collembolans* associated with cotton plants exposed to ozone.

As already indicated for root growth, results of below-ground microbial and mesofauna processes are rather inconsistent. In spite of the small number of studies, for microbial and invertebrate communities an influence of ozone on both the dynamic of nutrient cycling processes and the community composition is indicated.

4.4 Is there evidence of changes in species balance or biodiversity from field surveys?

Some of the strongest evidence for ozone effects on biodiversity in the field originate from field-based assessments made in the highly polluted San Bernardino National Forest, California. During the 1970s, ozone concentrations frequently exceeded 100ppb for 10h per day in this region. Multivariate analysis conducted by Miller et al. (1973) concluded that the San Bernardino National Forest had been influenced by increasing levels of air pollutants in the following ways: (1) the more ozone sensitive species, ponderosa pine (*Pinus ponderosa*), had in part been replaced by the more ozone-tolerant species white fir (*Abies concolor*); (2) ozone-induced decreased crown vigour had predisposed ponderosa pine to western bark beetle attack and (3) reduced cone and seed production indicated a loss of plant vigour and may have contributed to shift in dominance towards white fir and incense cedar (*Librocedrus decurrens*). A re-evaluation of the same sites 20 years later showed some improvement in crown condition in ponderosa pine, reflecting in part a decrease in ambient ozone in the area to 10h means in the range 50 – 60 ppb (Temple et al., 2005). Nevertheless, in high ozone areas, the basal stem diameter of trees > 30 cm was lower in all trees, with effects being more pronounced in ponderosa pine than incense cedar and white fir. Although there are many confounding factors, including moisture and nitrogen gradients in the San Bernandino forest, there were fewer native species present in the most polluted locations by 2003, leading Allen et al. (2007) to conclude that ozone pollution is likely to have contributed to a decline in biodiversity in this region.

In the UK, Payne et al. (2011) selected 64 calcifuge grassland sites along a gradient from SW England to N Scotland and statistically analysed species diversity against numerous drivers of change including climate, pollutant deposition (base cations, sulphur, nitrogen), ozone, soil chemistry and stocking density. Ozone (as AOT40) emerged as the third strongest driver of community composition, behind inorganic nitrogen deposition and mean annual potential evapotranspiration.

In the next section, González-Fernández and colleagues review evidence for effects of ozone on biodiversity in southern Europe.

4.5 A case study: Ozone effects on vegetation biodiversity in a biodiversity “hotspot” (southern Europe)

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4.5.1 Introduction

The Mediterranean Basin is one of the world’s richest places and is recognized as one of the top 25 Global Biodiversity Hotspots for conservation priorities (Myers et al., 2000). The Mediterranean is particularly noted for plant biodiversity with about 25,000 vascular plant species which represents more than four times the number found in all of the rest of Europe. More than half of these are endemic, representing 4.3% of world plant species. The biodiversity of countries such as Spain or Italy is higher than expected based on surface area (**Figure 4.5**). In Spain alone, the biodiversity of fungi, lichens, mosses and vascular plants represents 80% of the EU biodiversity and almost 60% of that of the European continent. The unique conjunction of a location in a transitional nature between subtropical deserts and temperate forests, together with a heterogeneous geography and climate, provides a mosaic of geology, biology and meteorological conditions explaining this high biodiversity. This region also presents a long history of human alteration and ecosystems management contributing to create additional ecological opportunities for adaptation and coexistence. However, current land use changes are considered the biggest threat for biodiversity in southern European countries (e.g. Cuttelod et al., 2008; Pereira et al., 2009). Particularly, agricultural intensification, disappearance of traditional stock-farming and agricultural uses, crop and pasture abandonment, urbanisation and infrastructure growth, are the main drivers causing degradation, fragmentation and habitat loss.

Air pollution represents an important additional threat for biodiversity in the Mediterranean area where high ozone concentrations and nitrogen deposition rates are frequently recorded (Dentener et al., 2006). Ozone pollution is especially relevant for the Mediterranean region where climatic conditions favor ozone photochemical formation and persistence (Millán et al., 1996; Cristofanelli & Bonasoni, 2009). In fact, ozone concentrations in this area frequently exceed the limits established to protect vegetation (Paoletti, 2006; Ferretti et al., 2007; EEA 2010). Ozone can potentially affect the biodiversity of Southern European ecosystems through both direct effects on natural vegetation, and indirectly, sensitizing plants to other environmental and biotic stresses, or altering biogeochemical cycling, processes subjected to future variations under global change scenarios.

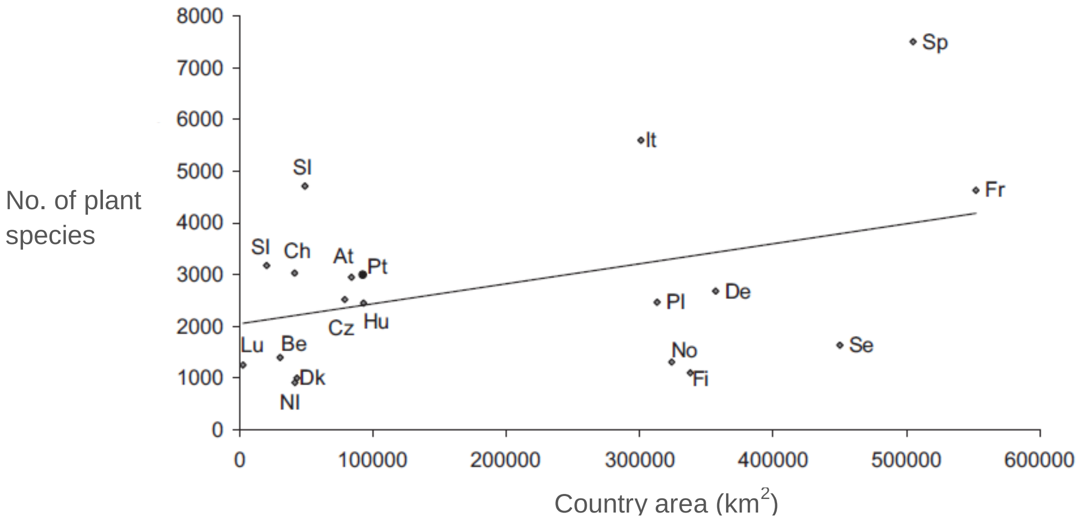

Figure 4.5 Relationship between richness of vascular plant species and country surface area in Europe. At – Austria, Be – Belgium, Ch – Switzerland, Cz – Czech Republic, De – Germany, Dk – Denmark, Fi – Finland, Fr – France, Hu – Hungary, It – Italy, Lu – Luxemburgo, Nl – Netherlands, No – Norway, Pl – Poland, Pt – Portugal, Se – Sweden, Sk – Slovakia, Sl – Slovenia, Sp – Spain (From Pereira et al., 2009).

4.5.2 Ozone sensitivity of Mediterranean vegetation

Very limited information is available on the ozone sensitivity of individual species or communities taking into account the huge plant biodiversity present in this area. Ozone-induced effects can be variable across different ecosystems and also across species and genotypes within the ecosystem. Due to the ecological and economical importance, field research and experimental studies have been focused on dominant tree species of some representative forests.

The most widely studied species of the Mediterranean vegetation with regards to ozone sensitivity has been Aleppo pine (*Pinus halepensis* Mill.). This coniferous species is considered as moderately sensitive to ozone (LRTAP Convention, 2010) showing ozone-induced visible symptoms in several areas of southern Europe (Gimeno et al., 1992; Velissariou et al., 1992; Sanz et al., 2000). Studies performed with seedlings under experimental conditions found ozone-induced effects on growth, biomass accumulation and physiology, with ozone sensitivity being strongly modified by environmental conditions (Elvira et al., 1998; Barnes et al., 2000; Alonso et al., 2003; Inclán et al., 2011). Interestingly, ozone might be impairing the ability of this species to withstand other environmental stresses such as those triggered by drought, high temperature and solar radiation, all characteristic of Mediterranean climatic conditions (Elvira et al., 1998; Barnes et al., 2000; Alonso et al., 2001, 2003). In this sense, it has been proposed that ozone might be one factor contributing to the reported reduction in vitality of Aleppo pine forests (Sanz et al., 2000) and could be altering the important role that Aleppo pine plays in soil stabilization in the dry areas where it is present.

Other conifer species dominant in some mountain areas are considered more sensitive to ozone, such as *Picea abies*, *Pinus sylvestris*, *Abies alba*, *Larix decidua or Pinus cembra* (Paoletti, 2006). However, little information is available about the response to ozone of populations of these species. Recently, ozone has been recognized as one of the factors that could be contributing to the observed processes of decline in *Pinus uncinata* forests of the Pyrenees, since ozone-induced visible injury and root biomass reduction have been described under experimental conditions (Díaz de Quijano et al., 2012). Reductions in roots growth would result in lower productivity and imply long-term effects on nutrient, C, and water cycles of the ecosystem.

Evergreen broadleaf Mediterranean woody species are assumed to be tolerant of air pollution due to their sclerophyllic adaptations (Manes et al., 1998; Bussotti and Gerosa, 2002; Nali et al., 2004;

Paoletti, 2006). Leaf morphology and anatomy, with packed mesophyll cells and sunken and protected stomata well adapted to reduce water loss, diminish gas exchange and pollutant uptake. Moreover, this vegetation type is a strong emitter of volatile organic compounds (VOCs) that can play a key role in protecting plant membranes against the oxidative stress induced by ozone (Loreto et al., 2004, see also Section 5.2). Also the high foliar concentration of antioxidant compounds normally present in many Mediterranean plants, and/or the ability to increase antioxidant status when needed, might protect plant tissues from the oxidative damage caused by ozone. Ozone tolerance is likely to further increase under field conditions, when summer drought stress limits gas exchange and hence ozone flux into the leaves. Despite these characteristics, both foliar visible symptoms and effects on growth and plant physiology caused by ozone have been described for some evergreen broadleaf species (Bussotti and Gerosa, 2002; Elvira et al., 2004; Nali et al., 2004; Ribas et al., 2005a,b; Vitale et al., 2008; Mereu et al., 2011; Calatayud et al., 2010, 2011). Studies comparing ozone sensitivity among different evergreen broadleaf species have shown that *Quercus ilex* was more sensitive than *Ceratonia siliqua*, while *Olea europea* showed no overall effects on C assimilation or biomass accumulation (Ribas et al., 2005b). Similarly, other studies have described the higher ozone tolerance of *A. unedo* to ozone with respect to *Q. ilex* within Mediterranean xerophytic ecosystems (Mereu et al., 2011).

With regards to Mediterranean deciduous species, it has been found that related deciduous species are more sensitive to ozone than evergreen broadleaf species (Calatayud et al., 2010, 2011). In this sense, *Q. ilex* was more resistant than related deciduous species (*Q. pyrenaica*, *Q. faginea*, *Q. robur*), with *Q. pyrenaica* being the most ozone sensitive based on visible injury, gas exchange, chlorophyll content and biomass accumulation (Calatayud et al., 2011). Another study reported that based on visible injury and growth, an ozone-sensitive clone of *Populus nigra* showed more effects than *Fraxinus excelsior*, *Fagus sylvatica* and even lower ozone sensitivity was observed in *Q. robur* (Gerosa et al., 2009a; Pollastrini et al., 2010). Ozone induced effects on the photosynthetic physiology and foliar structure of these species have also been described (Gerosa et al., 2003, 2008a, 2009a; Bussotti et al., 2007, 2011; Marzuoli et al., 2009; Desotgiu et al., 2010, 2012). Most of these deciduous species are representative of more temperate-thermophilous forests, and can grow in other areas of Europe.

A number of natural Mediterranean tree and shrub species have shown ozone-induced visible injury, both under experimental conditions and in the field (Orendovici et al., 2003; Bussotti et al., 2003; Bussotti and Ferretti, 2009; Gottardini et al., 2010a; Sanz and Calatayud, Ozone injury in European Forest Species, http://www.ozoneinjury.org.). Although clearly showing the pressure of an oxidative stress, it is difficult to relate visible injury development with ozone concentrations and further effects on growth, ecology and biodiversity, since other biological and ecological factors are involved (Bussotti and Ferretti, 2009).

Annual pasture in late spring, Spain (Photo: V. Bermejo)

Relatively little is known about the effects of ozone on annual, perennial and woody understory plants of Mediterranean ecosystems. Under experimental conditions, some species characteristics of the annual grasslands associated with *Quercus ilex* open forests “dehesas” have shown high ozone sensitivity. These annual communities present a remarkably high species richness. Interestingly, nitrogen-fixing legumes, with high nutritive quality for herbivorous feeding, are more ozone sensitive than grasses, based on visible injury and biomass production (Bermejo et al., 2003; Gimeno et al., 2004a). Moreover, ozone can strongly reduce flower and seed production of some sensitive legumes (Gimeno et al. 2004b; Sanz et al., 2007; **Figure 4.6**). Since plant composition of these prevailing therophyte systems is greatly dependent on the belowground seed pool, ozone could interfere with species perpetuation and competitive fitness. Thus, the different ozone sensitivity among species of the same community might potentially affect the structure and community composition, driving changes in the biodiversity of the herbaceous layer in a much shorter time than would be expected for the tree layer. An ozone induced reduction of the forage quality and the consumable food value in these communities has also been reported (Sanz et al., 2005, 2011). These annual pastures are traditionally used for extensive cattle feeding and the presence of legumes has been habitually promoted by means of land management. Therefore, ozone represents an additional risk factor for the conservation of these communities together with the abandonment of pasture traditional management.

The ozone sensitivity of other grassland or scrubland communities of southern Europe has not been assessed yet. This lack of information is particularly important in the case of plant communities of Mediterranean high-mountain pastures, ecosystems considered among the most vulnerable to global change and with a high presence of endemic species.

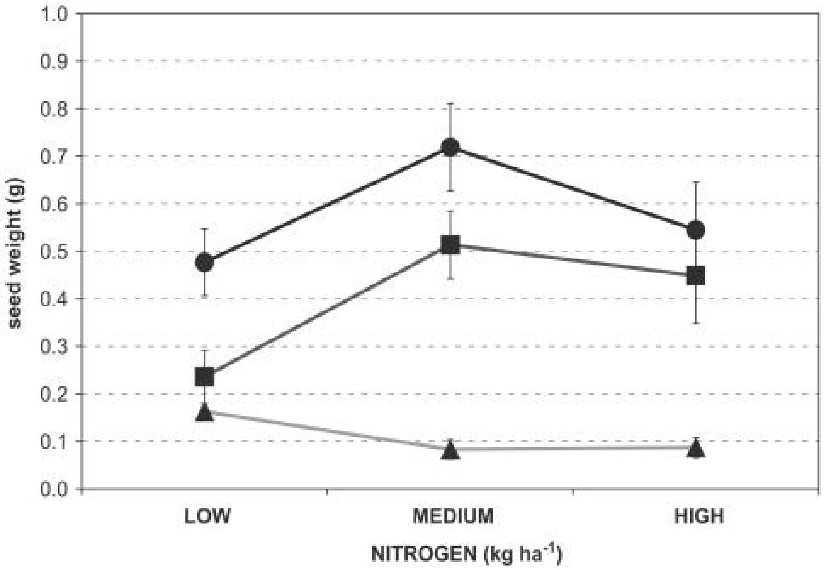

Figure 4.6 Seed production per plant in *Trifolium striatum* exposed to different ozone exposure and nitrogen fertilization treatments. Values are mean dry weight ± S.E. charcoal filtered air (circles); non-filtered air (squares); non-filtered air supplemented with 40 ppb ozone (triangles) (From Sanz et al., 2007).

4.5.3 Implications for biodiversity

Although available information under experimental conditions supports the conclusion that ozone could be affecting plant growth and vitality of some representative species of Mediterranean ecosystems, field validation of ozone effects on growth and biodiversity is still lacking in Mediterranean Europe. Different ozone sensitivity could be related to changes in the community composition, like those observed in some forests of southern California attributed to air pollution (Arbaugh et al., 2003). One important aspect is that the high ozone concentrations frequently registered in the Mediterranean Basin, together with co-occurring environmental factors such as high light, temperature and drought, could have already favoured the selection of populations with increased ozone tolerance (Paoletti, 2006; Bussotti, 2008). Paludan-Müller et al. (1999) tested the ozone sensitivity of *Fagus sylvatica* seedlings from different provenances in Europe, showing that photosynthesis, but not growth, was less affected in southern European than in northern European plants.

Some studies have also reported that previous exposure to elevated ozone can increase the tolerance to the pollutant of grasslands communities (Davison and Barnes, 1998). The evolution and geographic distribution of ozone tolerance is difficult to prove and it has not been described yet for many plant species common in southern European ecosystems, but an ozone-induced loss of genetic biodiversity within species cannot be discarded (Bassin et al., 2007a and references therein). This fact is especially important when it comes to project future ozone effects on species composition and structure based on currently available information. Long-term and/or regional scale studies could help to disentangle the potential effect of population evolution related to ozone effects on genetic biodiversity.

Generally, the long-term effects of ozone on communities and on biogeochemical cycling are in general poorly understood (Ashmore, 2005). Ozone-induced reductions on nitrogen content and increase of C/N in needles of *Pinus halepensis* have been reported (Elvira et al., 1995; Inclán et al., 2011) and could alter litter decomposition (see also, Section 4.3.2). In this sense, Baldantoni et al. (2011) found that ozone reduced leaf decomposition rates of *Q. ilex,* and that this effect could be related to changes in leaf quality. On the other hand, it has been described that ozone accelerates plant senescence, shortening plant life span of annual grasslands, (Sanz et al., 2007, 2011), an effect that could involve temporal changes in nutrients inputs to the ecosystem. There is an urgent need to investigate how ozone affects biogeochemical cycling and the implications that this could represent for ecology and biodiversity in the Mediterranean.

Monitoring programs for ozone and other pollutants in highly biodiverse natural areas is still scarce in Mediterranean countries (Sanz et al., 2007). Long-term monitoring networks of forest condition within the ICP-Forests framework provide some ozone risk assessment but it is difficult to relate ozone levels with the selected response parameters such as tree radial growth or crown defoliation (Bussotti and Ferretti, 2009). Other environmental variables and intrinsic structural or genetic features can mask or sometimes increase ozone effects, therefore complicating response interpretation. Further investigation is needed for determining more meaningful indicators of ozone effects. Numerous ozone measurements campaigns specifically aimed at assessing ozone risk for vegetation have been conducted in Italy (e.g. Finco et al., 2013; Gottardini et al., 2010b; Gerosa and Ballarin-Denti, 2003) or Spain (Ribas and Peñuelas, 2006; Alonso et al., 2009; Díaz de Quijano et al., 2009), but no stable monitoring network has been established yet. Ozone flux measurements have been taken only in a few ecosystems and not in a continuous way: in two *Quercus ilex* coastal ecosystems for two years (Gerosa et al., 2005, 2007, 2009b), over a coastal maquis ecosystem (Gerosa et al., 2009c) for a few summer months, over an high elevation alpine *Larix decidua* forest for two consecutive summers (Gerosa et al., 2013), over a poplar plantation for few months (Gerosa et al., 2008b), and over a mature *Quercus petraea-Carpinus betulus* forest in the Po Valley (ongoing).

In summary, current knowledge on direct ozone effects on biodiversity in Mediterranean European countries is still too limited for quantification and to draw firm conclusions. Importantly, field validation of effects observed under experimental conditions is still lacking for many species and plant communities. Also indirect effects remain mostly unknown, despite the fact that they are probably of great importance in terms of assessing ozone effects on ecosystem biodiversity.

5. Impacts of ozone on regulating services

Gina Mills, Serena Wagg, Harry Harmens, Laurence Jones, David Simpson, Patrick Büker, Lisa Emberson, Sally Power, Stephen Sitch, Elke Bergmann and Jürgen Bender

By impacting on carbon sequestration, nutrient cycling, land-atmosphere exchanges and biodiversity, ozone impacts on many beneficial regulatory functions of ecosystems. We describe here the impacts of ozone on climate, water, air quality regulation together with effects on flowering and pollination.

5.1 Impacts on C sequestration and global warming

5.1.1 Interactions with climate change

Depending on emission control scenario, projected changes in climate include a warming of ca. 0.2 °C per decade, increased evapotranspiration and changes in amount and distribution of rainfall leading to a greater risk of drought, especially in mid-continental areas (IPCC, 2007). Together with projected increases in CO_2 concentration, each of these will modify stomatal conductance and therefore flux of ozone into plants, potentially impacting on the extent of effects of ozone on C sequestration. We briefly consider here how these combined changes might impact on plant physiology and soil processes.

In principle, increases in CO_2 are expected to increase the capacity of vegetation to act as a C sink through greater productivity, however, recent field studies using Free Air CO_2 Enrichment (FACE) systems indicate that the positive effect of elevated CO_2 on C sequestration might be overestimated using data from shorter term CO_2 exposures (Long et al., 2005; Bernacchi et al., 2006). Given that concentrations of CO_2 and ozone in our atmosphere are predicted to increase in parallel over the coming decades, through anthropogenic sources, it is implicit for understanding and predicting high CO_2 effects on the land C sink that we consider effects of both gases together (Sitch et al., 2007). Current knowledge of the combined effects of CO_2 and ozone on plant physiology and soil processes were reviewed by Harmens and Mills (2012) and are summarised in **Table 5.1**. As elevated ozone and CO_2 often have effects that are in opposite directions (e.g. ozone reduces photosynthesis whilst CO_2 increases photosynthesis) the overall direction and magnitude of response is finely balanced dependent on the relative concentrations of both gases.

Table 5.1 Ozone and CO_2 impacts on plant physiology and other processes are often in opposite directions (From Harmens and Mills, 2012).

Parameter	Ozone	CO_2
Photosynthesis	-	+
Stomatal conductance*	-/+	-
Leaf area index	-	+
Ratio photosynthesis:respiration	-	+
Phenology	+	-/+
Ratio root:shoot biomass	-	-/+
Isoprene emissions**	-/+	-
Soil respiration	-/+	+

* ‘-’ reduces, ‘+’ enhances susceptibility to drought stress
** warming enhances isoprene emissions

If ozone concentrations are high enough to reduce photosynthesis (i.e. CO_2 fixation) and/or above-ground plant growth, then less CO_2 and ozone will be absorbed by the leaves of vegetation, leading to a positive feedback to atmospheric CO_2 and ozone concentrations and therefore more global warming. In a recent global climate modelling study, Sitch et al. (2007), using a modified version of the MOSES-TRIFFID land-surface scheme, show that increases in tropospheric (ground-level) ozone concentrations (using the SRES A2 scenario, IPCC, 2007) impact on gross primary productivity (GPP) with large reductions anticipated in North America, China, India and Europe for both the "low" and "high" ozone plant sensitivity (see **Figure 5.1**). Such reductions in GPP for the period 1900-2100 are anticipated to reduce land-carbon storage accumulation by between 143 Pg C and 263 Pg C, which is approximately equivalent to a reduction of between 17% to 31% (Sitch et al., 2007).

More recent simulations conducted by Sitch and colleagues (in Harmens and Mills, 2012, and reproduced here in **Table 5.3**), indicate that the consequences for C fixation were relatively similar whether the model simulated direct negative effects of ozone on photosynthesis (leading indirectly to reduced stomatal conductance, GPP was reduced by 15.4%) or directly negatively affected photosynthesis without a stomatal effect (GPP was reduced by 17.9%). Sitch et al. (2007) concluded that the global warming effect of ozone due to this positive feedback could be at least as high as the direct global warming effect of ozone as a greenhouse gas.

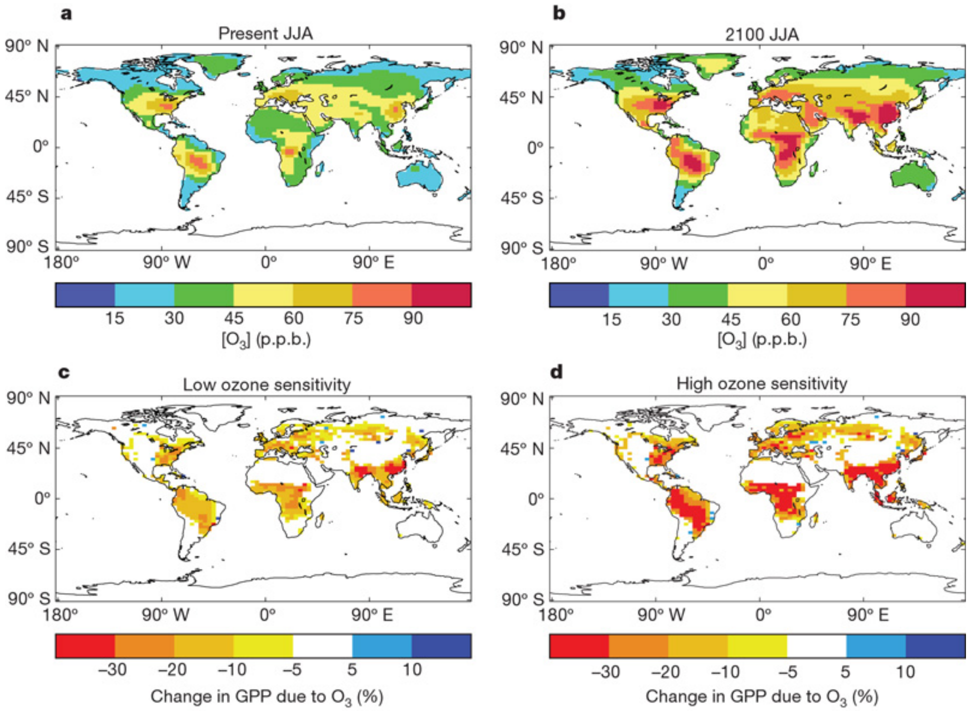

Figure 5.1 Temporal changes of modelled ozone concentrations and gross primary productivity (GPP). a, b, Modelled diurnal (24-h) mean surface ozone in p.p.b. averaged over June, July and August (JJA) for present day (a) and the year 2100 under the SRES A2 emissions scenario (b). c, d, Simulated percentage change in GPP between 1900 and 2100 due to ozone effects at fixed pre-industrial atmospheric (CO_2) for "low" (c) and high (d) ozone plant sensitivity (Sitch et al., 2007).

The complexity of the interactions between the factors involved in climate change is well illustrated by consideration of the impacts of global warming on the canopy uptake of ozone. When considered as a single factor, increased temperature is likely to increase stomatal uptake of ozone providing the optimum temperature for stomatal conductance has not been reached (Emberson et al., 2000), e.g. in temperate climates. However, the response to warming will also be affected by the following indirect effects of increased warming: added stimulation of tropospheric ozone formation, an increase in vapour pressure deficit, a decrease in soil water potential (soils will dry out faster due to enhanced soil evaporation and enhanced canopy transpiration), and earlier and enhanced plant development, resulting in a forward shift of the period within the year when plants are absorbing ozone. Thus, the overall impact of warming on the canopy flux of ozone is difficult to predict and will depend on the severity and timing (e.g. summer or winter) of warming and changes in precipitation together with any changes in seasonal patterns in the occurrence of peak episodes of ozone. Little is known about the impacts of a few degrees rise in temperature on the antioxidant status of leaves and thus on ozone detoxification.

At the same time, global warming will also affect photosynthesis and plant and soil respiration. The impact of warming on C sequestration will depend on the change in balance between plant photosynthesis and ecosystem respiration. Few studies have been conducted on vegetation responses to the combined impacts of ozone and warming. Kasurinen et al. (2012) showed that elevated temperature increased above- and below-ground growth and soil respiration rates in silver birch. However, for some of these variables the temperature effect was modified by tree genotype and prevailing atmospheric ozone concentration. Although warming has the potential to increase silver birch growth and hence C accumulation in tree biomass, the final magnitude of this C sink strength is partly counteracted by temperature-induced increase in soil respiration rates and simultaneous ozone stress. Silver birch populations' response to climate change will also largely depend on their genotype composition (Kasurinen et al., 2012).

Since ozone episodes frequently co-occur with climatic conditions associated with drought and an increased frequency of drought is predicted for the coming decades (IPCC, 2007), it is important to understand how vegetation will respond to the combined stresses of ozone and drought in order to predict future impacts on C sequestration. As described in Section 5.2, drought does not necessarily protect plants from the damaging effects of ozone as chronic exposure to ozone can lead to loss of stomatal control, with consequences for C sequestration.

5.1.2 Spatial assessment of impacts in Europe

The ICP Vegetation recently conducted the first flux-based assessment of effects of ozone on C sequestration in the living biomass of trees in Europe (Harmens and Mills, 2012) focussing on effects in 2000 and 2040. The following input data were used:

- Ozone and meteorological data provided by EMEP for the year 2000, and ii) ozone and climate data provided by the Rossby Centre regional Atmospheric climate model (RCA3) for current (2000) and future (2040) years.

- Land cover data to identify the distribution of forest tree species: i) for EMEP data the species-specific JRC land cover data and for ii) RCA data the UNECE Long-Range Transboundary Air Pollution (LRTAP) Convention harmonised land cover data were used

- Forest C stock data were derived from the European forests inventory dataset.

In addition, for the year 2000 using EMEP ozone and meteorological data, the application of generic parameterisations for trees in DO_3SE (POD_1) were compared with the application of climate region specific parameterisations (a mixture of POD_1 and $POD_{1.6}$) and a deactivated soil moisture deficit (SMD) module (POD_1), i.e. no limitation of soil moisture on stomatal conductance and hence ozone flux (no influence of drought). Finally, the flux-based results were compared with concentration-based results (AOT40[4]) to highlight the differences.

This study showed that applying the flux-based methodology and a generic parameterisation for deciduous and conifer trees resulted in a reduction of C sequestration in the living biomass of trees by 12.0 (EMEP input data) to 16.2% (RCA input data) compared to pre-industrial ozone (**Table 5.2**). The

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[4] The accumulated hourly mean ozone concentration above 40 ppb, during daylight hours

flux-based approach indicates a high risk of ozone impacts on forests in Atlantic and Continental Central Europe, and also a considerable risk in northern Europe (in comparison with the concentration based approach) (**Figure 5.2**) . Using a climate-region specific parameterisation for 2000 revealed higher C reductions (13.7%) due to ozone compared to the generic parameterisation (12.0%) for calculating POD_Y. The deactivation of the soil moisture deficit module of the DO_3SE model, which simulates drought-free stomatal ozone uptake conditions throughout Europe, led to an increase in C reduction, especially in the warmer and drier climates in Central and Mediterranean Europe. Predictions for 2040 indicated that the reduction of C storage in the living biomass of trees due to ozone is expected to decrease considerably compared to the reduction in 2000, mainly as a result of a predicted reduction in atmospheric ozone concentrations across Europe for the applied emission scenario.

Whilst the spatial patterns and temporal trends indicated above can be postulated with a considerable degree of certainty, the absolute figures of C reductions given in the Harmens and Mills (2012) report have to be interpreted very carefully. It should be remembered that these are for effects on living tree biomass only, and do not take into account any effect on soil C processes, including any direct or indirect ozone effects on below-ground processes that affect the rate of C turnover in the soil. Furthermore, the response functions used were derived for young trees (up to 10 years of age). However, there is some scientific evidence from epidemiological studies that the functions are applicable to mature trees within forests (Braun et al., 2010).

Table 5.2 Estimated total reduction of C storage (Mt C) in the living biomass of trees due to ozone in 2000 and 2040 compared to pre-industrial atmospheric ozone levels. Values in brackets show the percentage of estimated reduction. Key: Cl. Specific = climate specific, SMD_{off} = soil moisture deficit module switched off (see text for further details), NE = Northern Europe, ACE = Atlantic Central Europe, CCE = Continental Central Europe, ME = Mediterranean Europe (From Harmens and Mills, 2012).

Input data	Year	DO_3SE parameteri-sation	POD_Y or AOT40	NE	ACE	CCE	ME	Total
EMEP	2000	Generic	POD_1	256 (8.5)	40.3 (14.3)	735 (14.1)	218 (11.9)	1249 (12.0)
	2000	Cl. specific	$POD_{1/1.6}$	553 (14.5)	44.3 (15.0)	877 (14.8)	215 (10.7)	1689 (13.7)
	2000	SMD_{off}	POD_1	268 (8.8)	43.1 (15.1)	1034 (19.7)	437 (23.4)	1782 (17.3)
	2000	Generic	AOT40	29.7 (1.3)	10.5 (2.8)	499 (10.3)	253 (14.2)	792 (8.2)
RCA	2000	Generic	POD_1	317 (10.4)	60.6 (21.2)	1247 (21.4)	305 (14.7)	1929 (16.2)
	2000	Generic	AOT40	41.8 (2.1)	13.2 (5.0)	483 (10.4)	254 (14.1)	791 (8.4)
	2040	Generic	POD_1	271 (9.3)	52.9 (19.8)	821 (15.7)	184 (10.2)	1330 (12.6)
	2040	Generic	AOT40	-0.9 (-0.3)	4.4 (2.3)	68.5 (2.1)	57.1 (4.1)	129 (2.1)

5.2 Impacts of ozone on air quality via effects on vegetation

Globally, it has been estimated that ozone deposition to vegetation (by reaction with plant surfaces and uptake through the stomata) reduces tropospheric ozone concentrations by as much 20% (Royal Society, 2008). This is an especially significant function of vegetation given that ozone is the third most important greenhouse gas causing global warming (IPCC, 2007). Reductions are greatest in the spring and summer when climatic conditions are highly conducive to ozone uptake. Under drought conditions, however, plants close stomata to conserve water and stomatal uptake of ozone is substantially reduced. Vieno et al. (2010) estimated that this effect resulted in 20 – 30 ppb increases in ozone concentration during the European summer heatwave in August, 2013. Similarly, Emberson

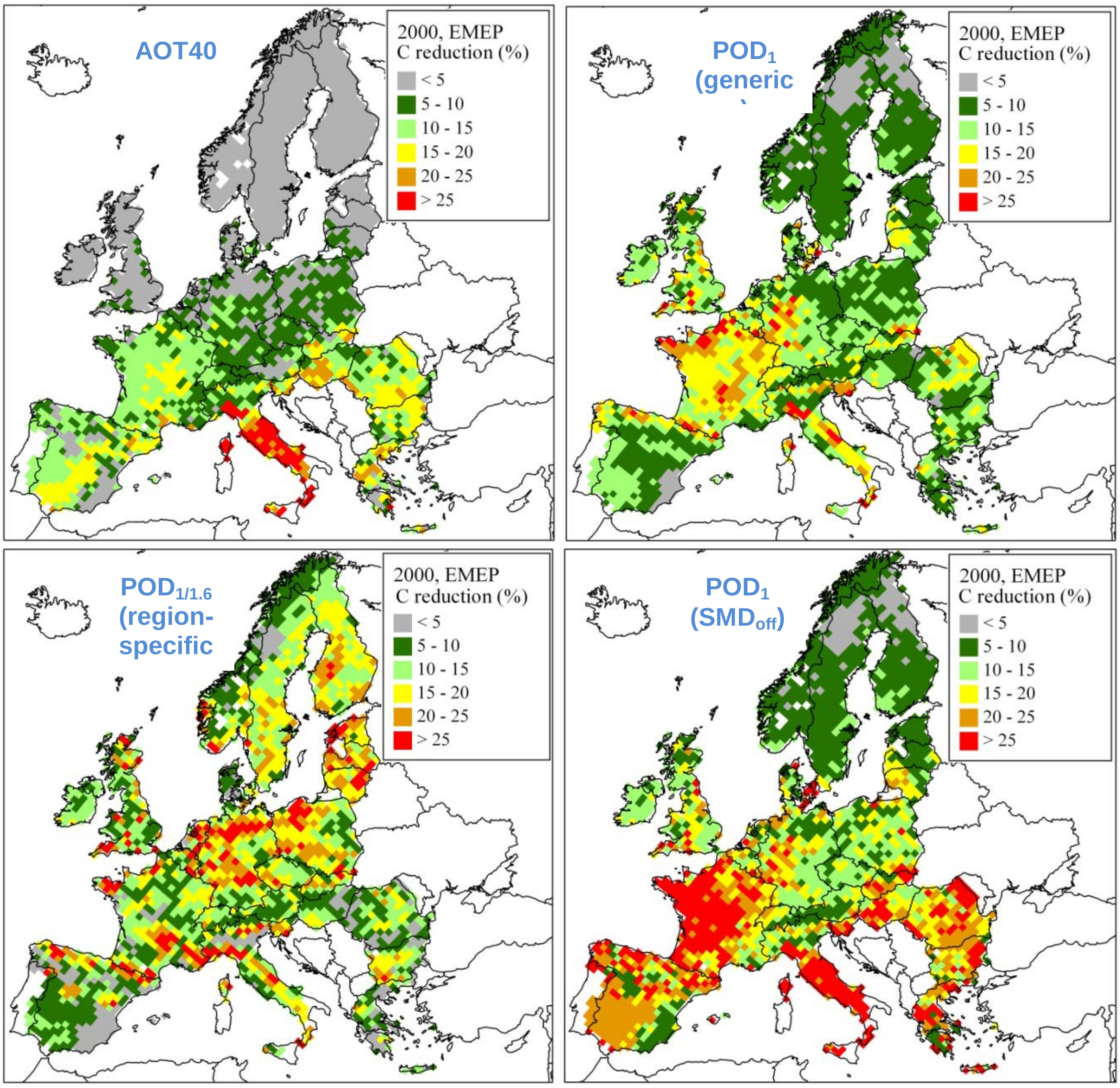

Figure 5.2 Relative reduction (%) in C storage in the living biomass of trees due to ozone in 2000, applying (a) AOT40 and (b) – (d) POD_Y calculated from EMEP input data and applying the following parameterisations in DO_3SE: (b) generic parameterisation ($Y = 1$ nmol m^{-2} PLA s^{-1}), (c) climate region specific parameterisation (Y is a mixture of 1 and 1.6 nmol m^{-2} PLA s^{-1}), and (d) generic parameterisation with soil moisture module switched off (i.e. no soil water limitations. From Harmens and Mills, 2012).

et al. (2012) estimated that the extended drought in the UK in June and July, 2006 heatwave increased the number of exceedances of the 8h mean ozone concentration of 50 ppb (EU health indicator) from 8 days under perfect ozone deposition conditions to 24 days , potentially resulting in 460 more premature deaths. In their calculations, Emberson et al. (2012) found that the extended drought reduced impacts of ozone on vegetation due to reduced stomatal uptake. Their analysis has not, as yet, taken into account the damaging effects of ozone on stomatal functioning (see Chapter 2). It is also important to remember that ozone itself causes premature senescence, further reducing ozone uptake.

A further level of complexity involves the emission of biogenic volatile organic compound (BVOCs) from plants - these can either react with ozone to reduce concentrations or lead to ozone formation - and ozone effects on plants can lead to an increase in BVOC emissions. Plants emit over 1700 BVOCs from almost all plant parts including stems, leaves and flowers, with emissions varying throughout their lifecycle (Loreto and Schnitzler, 2010). Abiotic factors such as light temperature,

CO_2 and ozone as well as wounding and feeding by herbivorous insects all stimulate BVOC formation. The main pathways involved include synthesis of terpenes (=isoprenoids), oxylipins, shikimate and benzoic acid, methanol, ethanol, formaldehyde and acetaldehyde, methane and ethylene. Of these, the terpenes constitute more than half, with some plant species emitting isoprene at rates of 50 – 100 nmol m^{-2} s^{-1} (Guenther et al., 1995, In Loreto and Schnitzler, 2010*)*. Terpenes, and other BVOCs to a lesser extent, have a very important role in photochemical production and destruction of ozone depending on the presence or absence of NO_X respectively. In assessing current evidence, Penuelas and Staudt (2010) showed that there are far more studies showing that ozone induces increases in BVOCs than decreases in emissions. Variations in response were due to ozone concentration, species, climatic conditions, phenology and chemical type of BVOCs.

The role of trees in removing air pollutants, including ozone from urban areas has been reviewed recently by Escobedo et al. (2011), and is described in the contribution by Salvatori et al. in Annex 1 of this report. This can be a cost–effective way of reducing urban concentrations of ozone (e.g. Nowak et al., 2006) but has to be balanced against problems of spatial heterogeneity and BVOC emissions. Manes et al. (2012) and summarised in Annex 1, considered the effects of trees on ozone removal in Rome, Italy for the main three functional groups of urban trees (evergreen broadleaves, deciduous broadleaves, conifers). The results showed that the majority of ozone removal by urban trees occurred in the southern coastal area of the metropolitan area of Rome, where the largest urban (Castel Fusano) and peri-urban (Castelporziano Presidential Estate) forests are located, and where tree diversity is highest (Manes et al., 1997). However, also the urban forest patches in the city centre played an important role, by improving air quality in the most urbanized sites. The beneficial ecosystem service of ozone removal by the urban forests of Rome was prudently valued at approximately $2 to $3 million/yr.

5.3 Effects of ozone on methane emissions

There is evidence that ozone may influence emissions of the greenhouse gas, methane, from wetlands although the results are less conclusive than for CO_2 effects. Global estimates of C sequestration in peatlands are in the region of 20-30 gC m^{-2} yr^{-1} (Wieder et al., 2001), and thus any effects of increasing ozone are of global significance for climate regulation. Several studies have provided some evidence of ozone increasing methane emissions. These include a four-year study of ozone exposure of cores from boreal peatland in Finland to twice ambient ozone concentrations, indicating a small, non-significant, but consistent increase in methane emissions towards the end of the experimental period (Morsky et al., 2008), two shorter-term exposures (4 weeks and 5 months) of bog and fen cores from North Wales showing increases in emissions (Williamson, 2009), and a 6 week exposure of fen cores in Finland to 100 ppb ozone, showing methane emissions more than doubling (Niemi et al., 2002). However, measurements from wet hay-meadow mesocosms found no change in methane emissions with more moderate ozone exposure of 40-50ppb (Kanerva et al., 2007). Furthermore, mesocosms from a raised bog in northern England exposed to winter ozone concentrations of 10 ppb and summer concentrations of 49 ppb for two years indicated a 25% reduction in methane emissions in mid-summer (Toet et al., 2010). The inconsistencies in these effects are most probably due to differences in species present, for example, measurements of natural peatland systems have shown that methane emissions are patchy, being much higher in areas of plants such as cotton grass, sedges and rushes that act as “chimneys” facilitating transfer from lower peat levels to the atmosphere (e.g. Strack et al., 2006).

5.4 Impacts of ozone on water cycling

5.4.1 Climate modelling and field evidence

As described in Section 2.3, there are two main stomatal responses to ozone, each potentially having an opposite effect on the water cycle: ozone-induced stomatal closure will preserve water within soils whilst ozone-induced stomatal opening will increase water loss from vegetation and soils. Global climate modellers have until recently assumed that the former mechanism is dominant, but very recently the implications of increased water loss as a result of chronic ozone exposure are beginning to be considered within such models (e.g. Harmens and Mills, 2012). For example, in their initial study, Sitch et al. (2007) predicted that an indirect closing effect of ozone on stomatal conductance due to a reduction in photosynthesis would partially offset drought effects, i.e. ozone exposure would act to conserve soil moisture and increase river runoff thereby increasing fresh water availability. Recently, however, these co-workers have acknowledged the growing evidence that this might not always be the case for all vegetation types under all environmental conditions.

Using the Joint UK Land Environment Stimulator (JULES), Sitch and colleagues were able to demonstrate that by “fixing” (switching off) the stomatal response (considering the effect of elevated ozone on vegetation over the 2000-2040 period) there was a 0.6% increase in river runoff, whereas, in the control situation, with ozone effects on photosynthesis inducing a decrease in stomatal response, there was a 4.5% increase in river run off (see **Table 5.3**, reproduced from Harmens and Mills, 2012). These co-workers also confirm that if ozone has adverse impacts on stomatal functioning, reducing their responsiveness to environmental stimuli, it is possible that under drought conditions this would exacerbate plant water loss and decrease soil moisture/river runoff and accordingly, fresh water availability (Harmens and Mills, 2012).

Table 5.3 Simulated future percentage changes (% Δ) in carbon (C) and water cycle (runoff) variables globally for three time periods: 1901-2040, 1901-2000, and 2000-2040. GPP = Gross Primary Productivity, Veg = vegetation, Gs = stomatal conductance (From Harmens and Mills, 2012).

	% Δ GPP	% Δ VegC	% Δ SoilC	% Δ TotalC	% Δ Runoff	% Δ Gs
1901-2040						
Control	-15.4	-10.9	-9.7	-10.0	12.6	-13.3
Fixed stomata	-17.9	-11.8	-10.5	-10.9	1.4	-1.6
2000-2040						
Control	-6.9	-5.0	-4.1	-4.4	4.5	-5.0
Fixed stomata	-8.1	-5.5	-4.6	-4.8	0.6	-0.5
1901-2000						
Control	-9.2	-6.2	-5.8	-5.9	7.7	-8.7
Fixed stomata	-10.7	-6.7	-6.2	-6.4	0.8	-1.1

Other studies that document reduced transpiration/photosynthesis, and therefore, water conservation in the presence of increasing tropospheric ozone, include Felzer et al. (2009) and Lomardozzi et al. (2012b). Felzer et al. (2009) reported that elevated ozone leads to reduced stomatal conductance, and thereby increased soil water availability/content and enhanced runoff. Since chronic ozone, however, often causes stomatal conductance and photosynthesis to decrease at different rates (Calatayud et al., 2007; Gregg et al., 2006), Lombardozzi and colleagues (2012a) incorporated independent/uncoupled responses of stomatal conductance and photosynthesis of tulip poplar to ozone in the Community Land Model (CLM) and predicted decreasing conductance with increasing ozone uptake. As such, transpiration rates were shown to be reduced by more than 50% in many areas when stomatal conductance was changed indirectly (i.e. due to changes in photosynthesis). However, when conductance was directly altered a smaller decrease in transpiration resulted. The work by Lombardozzi et al. (2012b) is pertinent in that, by decoupling stomatal and photosynthetic responses to ozone they are able to more accurately elicit vegetation type responses to ozone and therefore, have greater confidence in extrapolating leaf response to determine regional and global changes in stomatal driven modifications in soil water availability. These authors, however, recognized that the studies they used to determine this outcome were limited and there is acknowledgement of variation in stomatal response to ozone stress.

Extensive measurements of a Southern Appalachian forest in the USA by McLaughlin and colleagues (2007a,b) provide evidence to support the concept of ozone-induced increases in transpiration rather than the ozone decreasing transpiration theory. These authors document an almost linear increase in average daily sap flows and enhancement of the amplitude of daily water–loss from native trees with increasing ozone exposure, suggesting an ozone-induced disruption to the whole-tree water balance, not only as a result of increased day-time transpiration but also due to increased night-time stomatal conductance. In one of the regions in the study, soil moisture and canopy conductance analyses revealed that elevated ozone contributed to a rapid loss of water from the rooting zone of native trees and exacerbated water-stress in the area. Water stress has important physiological effects on cell division and expansion, and may be more important in limiting tree growth in the Southern Appalachian forests than ozone-induced reductions in photosynthesis. Furthermore, McLaughlin et al. (2007a,b) anticipate that ozone uptake by vegetation in the Appalachian region will be increased indirectly by increased canopy conductance during high ozone episodes and directly by the higher ozone exposures. These authors also speculate that the increased water use of over-story trees would likely be even more detrimental to under-story vegetation.

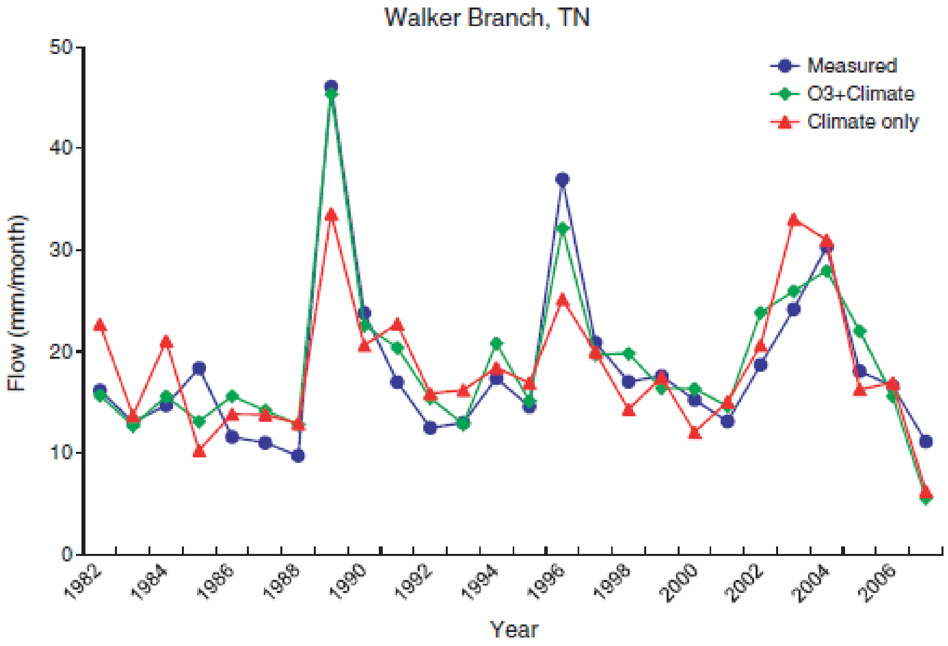

Figure 5.3 Empirical models of annual variations in later season streamflow were significantly improved for the 94ha Walker Branch catchment, Tennessee USA when climate and ozone were included ($R^2 = 0.78$) compared to a climate only model ($R^2 = 0.51$). Reproduced from Sun et al. (2012).

In a more recent study of the same Appalachian region, Sun et al. (2012) reported that, based on analysis of 18-26 year data records, ambient ozone concentration accounted for up to 23% of the variation in late season stream-flow from six forested watersheds in the South Eastern United States. Reductions in stream flow (**Figure 5.3**) were attributed to increased transpiration inferred by an ozone-induced loss of stomatal control and increased sap flow together with ozone-induced secondary changes in root biomass and associated altered moisture holding capacity of soils. These findings indicate that ozone and climate interactions are likely to increase plant water use, reduce soil moisture, diminish plant growth and weaken stream flow, therefore, significantly altering forest water use efficiency. Sun et al. (2012) suggest that loss of stomatal sensitivity will not only increase drought frequency and severity in the region, thus affecting ecosystem hydrology and productivity, but it will also have negative implications for flow-dependent aquatic biota.

5.4.2 Implications of effects for a drier climate

Drought linked to climate change and increasing ozone pollution are both becoming increasingly frequent co-occurring problems. Drought is generally regarded to induce stomatal closure, primarily through increased abscisic acid (ABA) biosynthesis in the roots of vegetation and its mobilization and perception at the stomatal guard cells (Davies and Zhang, 1991; Wilkinson and Davies, 2002). Reduced soil water availability has until recently been considered to have a protective mechanism against ozone damage by limiting its uptake into leaves (Bungener et al., 1999; Manes et al., 2001; Mills et al., 2009; Tingey and Hogsett, 1985). However, this is not always the case as ozone has also been shown to reduce or prevent drought-induced stomatal closure in some species or under some circumstances (Jiang and Hartung, 2008; McLaughlin et al., 2007a,b; Paoletti, 2005; Pearson and Mansfield, 1993; Wilkinson and Davies, 2009). For example, work by Hayes et al. (2012a) has shown that stomatal flux of ozone into a common grassland species is increased under reduced soil water availability (as predicted with climate change in many regions of Europe in the coming decades) because the stomata remain more open. Thus increased water is lost at a time of water stress, leaving plants more vulnerable to dehydration/desiccation. Wagg et al. (2013), Paoletti & Grulke (2010) and Grulke et al. (2007) have also demonstrated that elevated ozone can reduce the closing response of stomata to water-stress and other environmental stimuli (e.g. water stress (See **Figure 2.1**), changing light, increased vapour pressure deficit, and increased temperature), effectively increasing transpiration rates and thus plant water use. Such losses of stomatal control over transpiration rates can occur in one (or more) of several ways:

- Ozone may lead to alterations in the permeability of the guard cell plasma membrane, leading to a loss of cell turgor in the subsidiary cells, thus preventing complete stomatal closure (Manes et al., 2001).

- Disruption to guard cell osmoregulation and impairment of the sensory mechanism of the stomata (Maier-Maercker, 1999).

- Ozone has been shown to lead to the destruction of lignin in the intermicellar spaces, which again may have negative effects on osmoregularity (Maier-Maercker, 1999).

- Ozone has also been shown to impact on the capacity of stomata to response to the drought hormone abscisic acid (ABA). This has been demonstrated experimentally with exogenous ABA supplied to the plant either via a foliar spray (Wilkinson and Davies, 2009) or via the cut petiole (Mills et al., 2009; Wilkinson and Davies, 2009). Wilkinson and Davies (2009) proposed that the loss of stomatal response to ABA may be due to an ozone-induced increased ethylene generation and its antagonistic effect on the ABA signalling pathway, possibly downstream of reactive oxygen species (ROS) generation, such that as ethylene biosynthesis increases it prevents ABA acting to close the stomata with a concurrent increase in stomatal conductance.

5.5 Impacts of ozone on flowering, pollination and insect signalling

Studies conducted during recent decades have demonstrated that various stages of the reproductive development of plants are clearly sensitive to ozone. A recent meta-analysis of ozone effects on plant reproductive growth and development indicated that current ambient ozone concentrations significantly reduced seed number, fruit number and fruit weight, while there was a trend towards increasing flower number and flower weight at elevated ozone (Leisner & Ainsworth, 2012). Negative effects on the reproductive performance in response to ozone may result from a reduction in plant growth, a decreased reproductive allocation, or from direct effects on reproductive structures (Black et al., 2000). Bender et al. (2006) observed contrasting effects on resource allocation to the vegetative and reproductive organs of 17 herbaceous species that were exposed to different ozone regimes from the seedling stage to the flowering stage. Although ozone caused comparable reductions in both vegetative and reproductive growth in the majority of the investigated species, three species (*Chenopodium album, Matricaria discoidea, Stellaria media*) showed a greater vegetative growth and reduced reproductive allocation. The germination ability of the seeds was affected by ozone such that germination rate was up to 30% lower in ozone-treated plants compared to control plants (Bender et al., 2006). Similarly, Darbah et al. (2008) investigated the effects of elevated ozone on reproductive fitness in paper birch (*Betula papyrifera*) at the Aspen FACE site in Rhinelander, Wisconsin. Elevated ozone increased flowering, but decreased seed weight and germination rate. These results suggest that ozone can significantly affect resource allocation patterns and reproductive fitness which may have significant implications for the establishment and survival of the progeny and hence for plant productivity and composition of plant communities.

Any impact of ozone exposure on the timing of flowering may also play an important role in reproductive success, particularly for species in which flowering is closely synchronized with pollinating species (Black et al., 2000; Hayes et al., 2012b). However, the impact of ozone on the timing of flowering varies markedly between species. For example, ozone exposure has been reported to delay flowering in two species (*Campanula rotundifolia* and *Vicia cracca*) of simulated meadow community mesocosms (Rämö et al., 2007). In mesocosms representing ‘calcareous grassland’, ozone has been found to accelerate the timing of the maximum number of flowers in *Lotus corniculatus* (Hayes et al. 2012). By contrast, Bergmann et al. (1996) showed that the timing of flowering and seed set in 17 wild plant species were not significantly influenced by season-long exposure to 1.5 x ambient ozone concentration in open top chambers.

Floral volatile hydrocarbons play an important role in pollinator attraction and, additionally, serve as indirect plant defenses against herbivorous insects. These floral scent trails in plant-insect interactions can be destroyed or transformed by ozone (McFrederick et al., 2008). Signals may travel shorter distances before being destroyed by chemical reactions with ozone, thus losing their specificity (McFrederick et al., 2008). Pollinators that rely on scents to orient to flowers are likely to spend more time searching for forage, which could affect their reproductive fitness, but could also affect plant reproduction as reduced pollinator efficiency could result in greater pollinator limitation (McFrederic et al., 2008). The implications of a loss or modification of scent signals by ozone pollution for both pollinators and signaling plants may be even greater in patchy or fragmented habitats because pollinators may be spending more time searching for flowers.


Photo: A-C Le Gall

In summary, ozone-induced changes in flowering timing and signaling could have large ecological impacts, affecting plant pollination, the food supply of nectar feeding insects or defense against herbivorous insects.

6 Impacts of ozone on cultural services including leisure, recreation and amenity

Gina Mills and Serena Wagg

Quantifying the potential impacts of ozone on cultural services has attracted very little attention so far even though ozone can have both subtle and profound influences over some, if not all, aspects of cultural services by impacting on the visual appearance and quality of the natural environment. In this Section, we speculate on what those impacts might be, with the main focus being on impacts on people's experience of the natural environment.

6.1 Introduction

Cultural services are the nonmaterial benefits that humans obtain from ecosystems through cognitive development, recreation, reflection, spiritual enrichment, and aesthetic experiences (Millennium Ecosystems Assessment, 2003). Further, cultural diversity is influenced by ecosystems and can profoundly shape knowledge systems developed by different indigenous peoples/cultures. Equally so, ecosystems and their components and processes provide the basis of both informal and formal education. Many societies place high value on historically important landscapes or culturally significant species. However, often the importance of certain ecosystems is only appreciated by the indigenous people who have an intrinsic understanding of their landscape. More importantly, ecosystems and the species they harbour (including indigenous people) are becoming increasingly threatened by land use change, fragmentation/destruction of habitats, and pollution of habitats. Tropospheric ozone can have both subtle and profound influences over some, if not all, of these aspects. Many such effects have already been described in this report. In this Chapter, we focus on ozone effects on the visual appearance and quality of the natural environment via effects on leaf colour and appearance, changes in species composition and flowering. The importance of vegetation in absorbing ozone thereby reducing health effects is also noted.

6.2 Impacts of ozone on the visual appearance of natural ecosystems

6.2.1 Impacts through effects on leaf colour

By reducing photosynthesis and promoting early senescence, areas of outstanding natural beauty may be less visually attractive in a "high" ozone year. Leaves will turn yellow early (see example oF premature senescence in **Figure 6.1**) and there is some evidence that ozone changes the expression of autumn colour in trees by accelerating the senescence process e.g. Pell et al. (1999), Karnosky et al. (2007a). Although not, to our knowledge, quantified yet, such effects could potentially impact on the tourist industry, especially in areas renowned for autumn colour e.g. eastern USA, SE Canada and the Caucasus region.

In addition to accelerated senescence, ozone episodes can cause visible injury to the leaves of a wide range of species. For the ICP Vegetation evidence report (Hayes et al., 2007b; Mills et al., 2011), records of visible ozone injury (see examples in **Figure 6.2**) were collated in Europe for the period 1990 – 2006. Although recorded in every year, the number of records per year was very variable (**Figure 6.3**). However, much of this variation reflected the number of surveys conducted in a particular year, rather than there being more symptoms in some years than others. Generally, there were more records per year from 2001 onwards than for earlier years. However, it is not possible to distinguish whether this is due to an increased occurrence of visible injury symptoms or whether there was increased effort in looking for (and identifying) symptoms.

Figure 6.1 Ozone induced senescence in a simulated grassland community exposed to (a) a low ozone ambient regime, mean concentration 33 ppb, and (b) a high ozone regime, mean ozone concentration 89 ppb.

Figure 6.2 Ozone injury on (a) *Ranunculus acr*is (meadow buttercup), (b) *Trifolium repens* (white clover) and (c) *Viola riviniana* (dog violet).

Approximately 80 species of (semi-)natural vegetation have been recorded with symptoms attributed to ozone (listed in Mills et al., 2011c). These include ‘stippling’ and those where the symptoms have subsequently been confirmed in exposure studies. A further thirteen species have shown symptoms that may be due to ozone, although the symptoms were either non-specific or unconfirmed, and these records were not used in subsequent analysis. Of the species with ‘ozone-type’ injury symptoms, a wide variety of plant families are included, from both forbs and grasses. There are several records for some species, e.g. *Centaurea jacea* (brown knapweed) and *Epilobium angustifolium* (fireweed/rosebay willowherb) but just a single record for others (data not presented).

The distribution of records of visible injury symptoms attributed to ozone shows that the observations of visible injury are widespread across Europe (**Figure 6.4a**). Generally speaking, the records of ozone injury symptoms are clustered around research groups that work on effects of ozone on vegetation, which is probably because these researchers may actively look for symptoms in natural areas around their institute and can recognise ozone injury symptoms when they occur. Nevertheless, this analysis clearly showed that visible injury occurs in areas with moderate to high ozone flux (**Figure 6.4b**, for further details see Mills et al., 2011c).

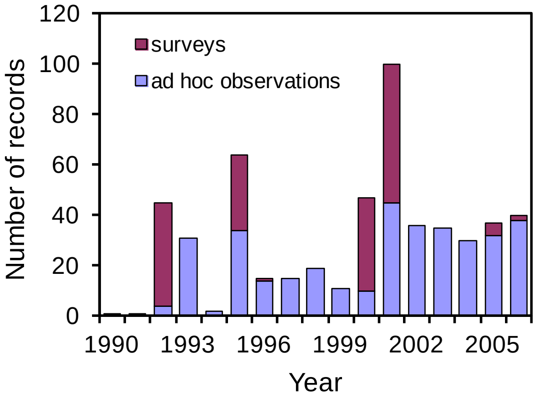

Figure 6.3 Number of records of visible leaf injury symptoms attributed to ambient ozone per year (Hayes et al., 2007b).

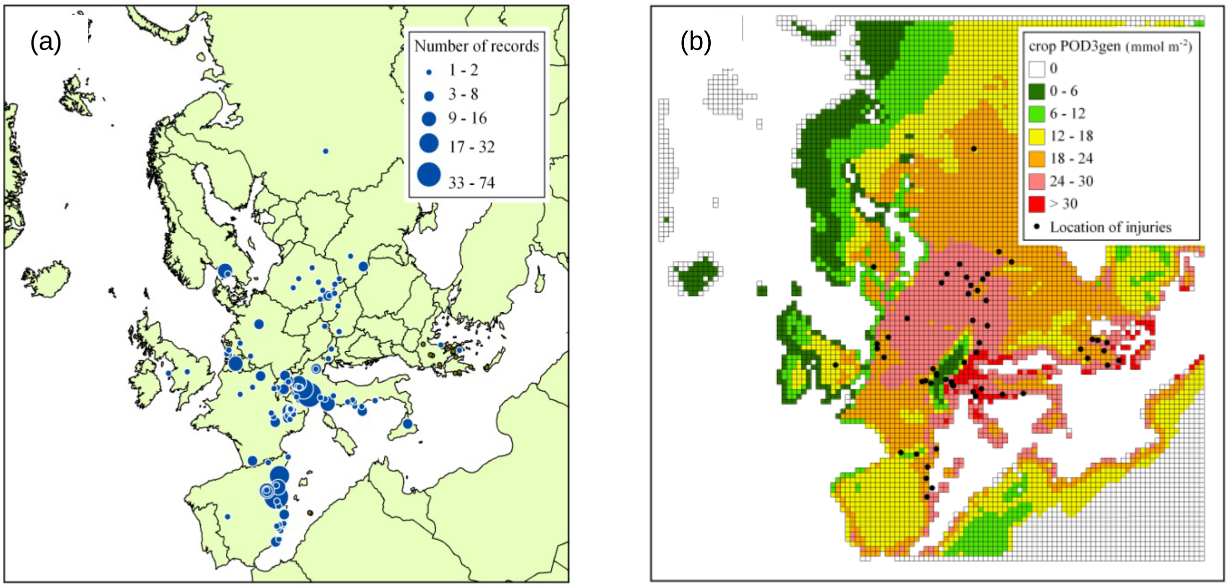

Figure 6.4 (a) Locations of records of visible injury attributed to ozone on crops, shrubs and semi-natural vegetation species (Hayes et al., 2007b) and (b) Locations of injury superimposed on EMEP modelled ozone flux (POD_3gen for crops) averaged over the period 1995 – 2004 (Mills et al., 2011c).

Similarly, ozone exposure can also increase the susceptibility of vegetation to pathogen attack therefore spoiling the aesthetics of vegetation. The outcome of environment-plant–pathogen or plant-pest interactions may strongly vary with timing, stage of plant development and environmental conditions. An important role is played by the early onset of senescence in ozone-exposed leaves and the declining quality of the leaves, for example pests that depend on a high quality diet will decline whilst those primarily affecting plant weaknesses will increase (Fuhrer, 2009).

6.2.2 Impacts by changing species balance in natural ecosystems

In Chapter 4, we described how ozone can impact on species balance in natural ecosystems with less sensitive species potentially outcompeting ozone sensitive species in experimental ozone exposures. The net effect of such competition can be a lessening of the visual attractiveness of, for example, upland grassland areas, with fewer of the attractively flowering forbs present. For example, in the UK, Payne et al. (2011) found that ozone (using the AOT40 index) was the third most important driver of change in species composition for calcifuge grassland. A decline in ozone-sensitive species and an increase in ozone-tolerant species such as the grass *Festuca ruba* was detected. A further example, described in more detail in Section 4.4, comes from the San Bernandino National Forest, California USA where there has been a shift towards the more ozone tolerant white fir (*Abies concolor* Gord. and Glend.) away from ozone-sensitive Ponderosa pine (*Pinus ponderosa*) (Miller et al., 1973; Allen et al., 2007).

6.2.3 Impacts by changing timing and number of flowers

Also impacting on the visual appearance of natural spaces would be the ozone-induced changes in flowering described in Section 5.5. For example, a delay or reduction in flowering of iconic species such as harebell (*Campanula rotundifolia,* see **Figure 6.5** and Hayes et al., 2012b) in moderate - high ozone areas could potentially reduce the enjoyment of visiting natural areas.

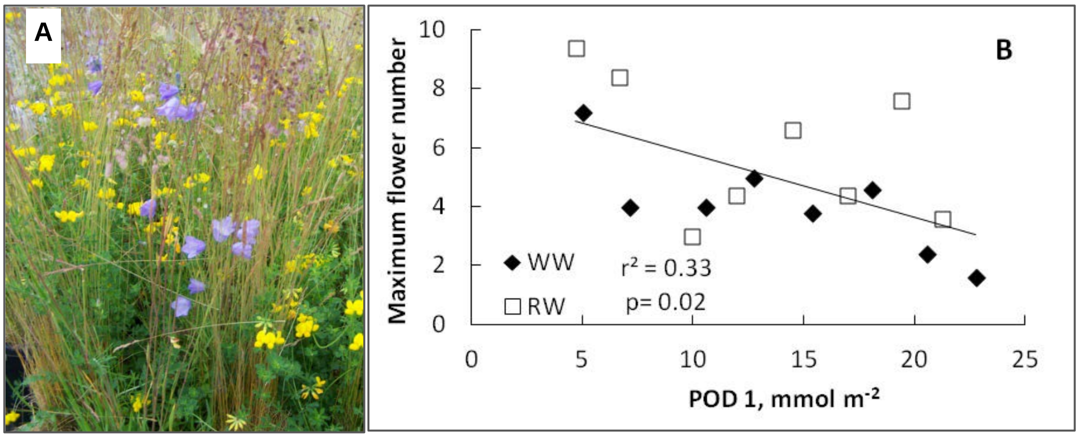

Figure 6.5 (a) *Campanula rotundifolia* (harebell) growing in a mixed species mesocosm in solardome experiments and (b) reduction in flower number for *Campanula rotundifolia* with increasing ozone flux (POD_1) from the same experiments (From Hayes et al., 2012b).

6.3 Impacts on air quality - a health effect

Ozone is known to cause respiratory problems in humans, triggering oxidative stress as it enters the airways (WHO, 2008). Effects depend on the concentration and duration of exposure with both acute and chronic respiratory responses noted. It has been estimated that ca. 21,000 premature deaths are associated with ozone exposures over 35 ppb (maximum 8h mean average) and 14,000 respiratory hospital admissions as a result of ozone episodes occur annually in EU25 (WHO, 2008). For example, in a recent study, Pehnec et al. (2011) with a group of untrained male volunteers walking in the Medvednica Mountain Nature Park, Croatia at approximately 1000m above sea level found a statistically significant influence of short-term ozone exposure on lung functioning, which was exacerbated in volunteers that smoked. As described in Section 5.2, vegetation is a critically important sink for ozone, reducing annual concentrations by 20% (Royal Society, 2008). Ozone-induced senescence can reduce the rate of ozone absorption, thereby reducing the ability of vegetation to indirectly reduce health impacts by decreasing the ozone concentration. Such effects would be more pronounced in rural or upland areas, especially if ozone pollution is accompanied by drought, with the potential to impact on recreation.

7 Approaches for valuing ozone impacts on ecosystem services

Laurence Jones, Felicity Hayes and Gina Mills

Policy makers are increasingly interested in the economic value of effects of drivers of change in ecosystem services and biodiversity. For those ecosystem services that have an easily valued product e.g. crop or timber production, this is relatively straight forward. However, for other ecosystem services, including biodiversity, placing a monetary value on effects is far more complex and considerably less certain. In this section, we describe three approaches for valuing ozone impacts on ecosystem services.

7.1 Introduction

In recent decades, the majority of ozone-effects research has concentrated on quantifying the impacts of ozone on plant parameters such as growth, visible injury, and physiology. The reasons for this have been varied, linked partly to ability to observe and measure responses over time (e.g. visible injury), but also to the different applications of the findings including quantifying impacts on plant growth, understanding ecological processes, the implications for ecosystem function and risk assessment methodology. There is an explosion of interest globally in viewing the world through the framework of ecosystem services. This is seen as a useful way to communicate the benefits provided by the natural environment to policy makers, and to capture in a systematic way many of the unintended consequences of policy actions or management decisions. Within this emerging field, there is also a strong interest in estimating a value associated with the increase or decrease in a particular service, or the effects of different trade-off options between multiple ecosystem services (TEEB, 2009). This value is usually, but not exclusively, a financial value, as it is assumed that policy makers are most influenced by monetary considerations. Assigning financial values to air pollution impacts has been applied in a number of examples, e.g. human health impacts (Watkiss, 2008) and more recently within the European Nitrogen Assessment as a cost-benefit analysis of nitrogen in the environment (Sutton et al., 2011). Ironically, although most early ozone impacts research arose due to considerations of commercial damage to crops (e.g. Treshow and Bell, 2002), there have been relatively few attempts to upscale ozone impacts to larger areas, or to estimate a financial value of large-scale ozone impacts. In this short section we summarise some of the approaches that have been taken so far to value ozone impacts, discussing their advantages and disadvantages, using case studies to illustrate these ideas.

The main approaches can be summarised as

- Studies which estimate the impact of ozone compared with assumed zero impact under no or low ozone.
- Estimating marginal cost of a change in level of ozone.
- Cost-benefit analysis.

7.2 Estimating costs relative to zero ozone effect

Impacts on ecosystem services are calculated against a reference. For the total impact studies reported in chapters 3 and 5, the reference is a level of ozone that has no effect such as zero ozone flux (POD_1 = 0 for trees or POD_6 = 0 for crops) or zero AOT40. Thus, these studies provide an estimate of what the full effects of ozone are likely to be worth in a given year or averaged over a series of years, compared with the potential yield or biomass in the absence of damaging levels of ozone. This approach allows the varying effect of annual fluctuations in ozone to be quantified. For example, Mills and Harmens (2012) showed that the effects of ozone on wheat in an “average” year (2008) with more soil moisture available but moderate ozone were almost the same as those for a hotter, drier year (2006) with higher ozone (**Figure 7.1**). Interestingly, the distribution of the highest economic losses was different in the two years. The largest effects in 2006 were in the cooler, more moist north east where conditions were conducive to high ozone flux whilst in 2008, the largest effects were in central England and East Anglia where wheat yields per grid square are highest.

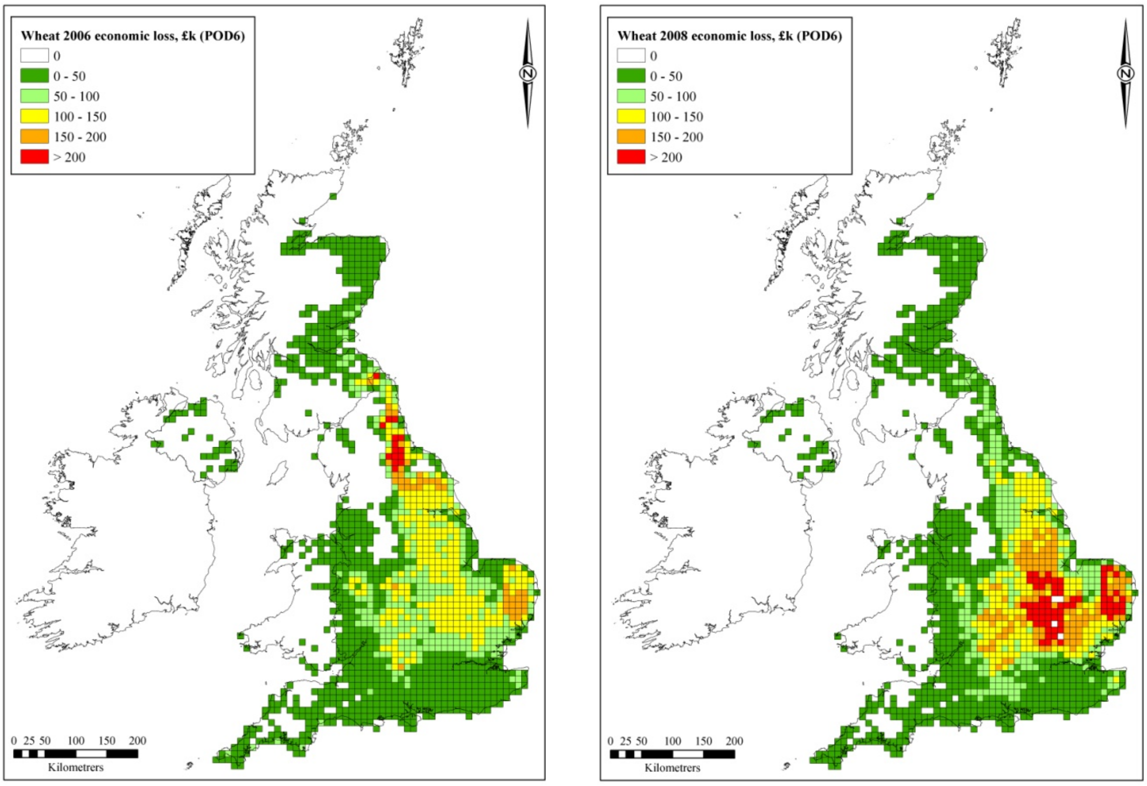

Figure 7.1 Spatial distribution of the impacts of ozone on wheat yield loss as predicted using POD$_6$ and presented as economic loss in thousand £UK for grid squares where wheat was grown on >100ha (1%). Reproduced from Mills et al. (2012).

7.3 Estimating marginal cost for a change in ozone concentration

Application of the “total value” of an ecosystem service is increasingly being questioned by economists since the unit value of some ecosystem services is dependent on how much of the service there is. For example, the value per unit area of an urban park is likely to be higher for a small park in the middle of a large urban area compared with a very large park in the same location. Similarly, the perceived biodiversity value is usually much higher for rare species than it is for common species (s Bateman et al. (2011) for further discussion of these issues). For these reasons, economists prefer marginal cost analysis, in other words the cost of moving from one state to another where we are reasonably confident of the value across that range of states, and the nature of the response function.

This approach has been applied in a study looking at impacts of ozone, nitrogen and sulphur pollution on six ecosystem services in the UK (Jones et al., 2012). One of the ozone impacts they evaluated was ozone impact on grassland C sequestration.The study was primarily a proof-of-concept for applying an Ecosystem Services Approach to valuing air pollution. It derived a simple dose-response function based on ozone impacts on plant growth in grassland, making assumptions about the effect of changes in above-ground plant growth on long-term C allocation below-ground. Ozone impacts were evaluated against two scenarios: The financial impact of historical increases in ozone concentrations over the period 1987 to 2005 against a reference position assuming no change in ozone since 1987, and a future scenario comparing the effect of projected changes in ozone from 2005 to 2020 compared with a reference position of no change in concentrations over the same period. Valuation of these impacts was conducted by calculating the value (positive or negative) of change in C allocation in each year, applying discounting procedures, and calculating Equivalent Annual Value (EAV) of that ozone damage. Carbon was valued using the non-traded shadow price of C at £51.70 per tonne (2010 price, DECC 2010). Based on the mean ozone concentration for the UK, the estimate of damage due to historical increases in ozone 1987 – 2005 was a loss in value of C sequestration of €2.8million (€1.7m to €3.8m, 95% confidence interval) and the projected scenario of damage due to future increases in ozone amounted to €11.9million (€7.3m to €16.2m, 95% confidence interval).

A more-or-less similar approach was applied by Karlsson et al. (2005) to evaluate ozone impacts on forest production in Sweden. They ran a forest growth model at 5-year time steps, coupled with an economic forestry model to calculate economic impact, discounted into the future at 3%. They ran two scenarios 100 years into the future, in which a scenario including adverse ozone effects at current concentrations (11-year average concentrations 1993-2003, modelled spatially) on tree growth was compared against a reference scenario assuming near-zero AOT40 in which adverse ozone effects were not included. Whether this can be strictly interpreted as a marginal cost approach, depends on the assumption of historically near-pristine ozone conditions in the period 1973-1977 which was used to calibrate the forest growth model parameters for the reference run, and whether the unit damage cost is likely to change within the range of ozone concentrations compared in the study. However, the study usefully serves to illustrate the potential cumulative effects of ozone over time on forest growth and its value, and moreover valuation estimates were calculated on a spatially explicit basis using an economic model.

The main advantage of this marginal cost approach is that it can be used to provide an estimate of damage per unit ozone. This allows policy makers to apply that unit damage cost figure to obtain estimates of the value of likely damage under different ozone concentration scenarios. A disadvantage of the approach applied in Jones et al. (2012) was that it calculated impact at a national scale using average ozone concentrations across the UK. Therefore, the calculations did not take account of either the spatial pattern of ozone across the UK, nor the spatial co-location with the target ecosystem service (in this case, the location of grassland). Ongoing work is seeking to improve on this methodology, including quantifying impacts of ozone on three ecosystem services: C sequestration, pasture quality and biodiversity (see Annex 1).

7.4 Cost benefit analysis

The ability to quantify, in monetary terms, ozone effects on ecosystem services would facilitate cost-benefit analysis. Such an analysis was completed for nitrogen impacts in the European Nitrogen Assessment, using the “willingness to pay” principle for environmental goods and services that do not have a market price (Sutton et al., 2011). For ozone, previous cost-benefit analysis has tended to use crop yield response functions, allowing a market value to be used. Examples include Holland et al. (2005), a cost-benefit analysis of policy option scenarios for the EU Clean Air for Europe programme, in which costs were presented as total damage per year, benefits as a change in valuation over baseline and incremental benefits as a change in valuation for each policy step for four scenarios including maximum feasible reduction. This and earlier studies used AOT40 as the dose metric for ozone. As already explained in this report, the preferred option is to use the flux-based methodology for economic impact assessment. The ozone flux method has very recently been incorporated into GAINS by IIASA under the EU ECLAIRE project, and following further development it will shortly be possible to conduct a flux-based cost-benefit analysis for the scenarios considered in the recent revision of the Gothenburg Protocol.

8 Conclusions and recommendations

Gina Mills and Harry Harmens

In this report we have provided a review of the state of current knowledge on the effects of ozone pollution on ecosystem services including consideration of effects on biodiversity. To provide information in an easily accessible form we have followed the commonly applied structure of considering impacts on supporting services and biodiversity, followed by provisioning, regulating and cultural services together with a brief overview of some methods used to add an economic value to impacts on ecosystem services. We have considered impacts on biodiversity separately whilst acknowledging that biodiversity is integral to many ecosystem services and is also subject to valuation. Indeed, all of the ecosystem services and underlying processes are interlinked, with for example, ozone impacts on root growth contributing to supporting services (primary productivity), provisioning (crop and timber production), regulating (C sequestration and impacts on climate) and cultural services (reduced growth of sensitive species influencing aesthetic qualities of vegetation), and reducing economic value of products such as crop yield (Illustrated in **Figure 8.1**). Until recently, much of the research conducted on ozone impacts has focussed on quantifying effects on ecological processes rather than considering the implications for ecosystem services. This report, for the first time, places current process-based knowledge within the context of ecosystem services and thus reports on the potential for impacts of ozone on ecosystem services and biodiversity.

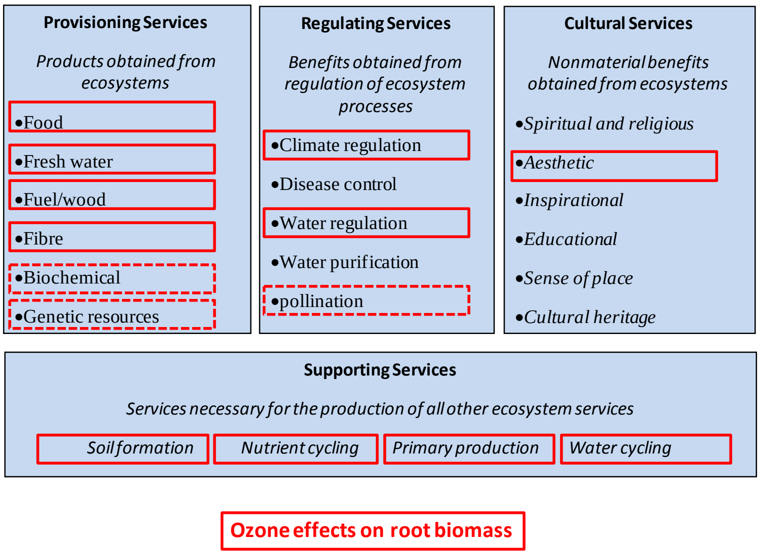

Figure 8.1 Schematic showing how impacts of ozone on root growth and biomass affects a variety of ecosystem services. Red outline indicates direct effect on ecosystem service whilst dotted red outline indicates indirect effects. Original figure from Millennium Ecosystem Assessment (2005).

8.1 Conclusions

8.2.1 Impacts of ozone on ecological processes and supporting services

As illustrated in **Figure 8.1**, these effects underpin impacts on all other ecosystem services. The many processes impacted include:

Primary productivity and carbon cycling Ozone reduces whole plant photosynthesis by directly impacting on the photosynthetic machinery (Rubisco and chlorophyll content, e.g. Wittig et al., 2007), reducing leaf area by promoting early senescence and leaf abscission (e.g. Ainsworth, 2008), diverting C use into detoxification and/or repair metabolism (e.g. Betzelberger et al., 2010), changing stomatal conductance (both increases and decreases have been noted, see below) and altering C allocation in favour of the above ground parts rather than below ground parts (e.g. Wittig et al., 2009). Carbon flux to and from the soil is also altered by changes in leaf litter quality (Holmes et al., 2006), altered rhizodeposition of C, changes in soil microbial community composition, and altered soil processes (Andersen, 2003).

Nutrient cycling Tropospheric ozone has the capacity to impact on nutrient cycling by both direct and indirect mechanisms, by altering the chemical composition of plant tissue and the quantity (and quality) of litter fall, impacting on below-ground plant biomass and root exudates, indirectly altering microbial community composition(s) and functioning, and soil processes and the chemical properties. All of these have the capacity either, independently or in concert, to ultimately reduce the long-term sustainability of ecosystems (Lindroth et al., 2001).

Stomatal functioning and water cycling Tropospheric ozone is known to alter stomatal response(s) to environmental stimuli and in the short term (at higher concentrations) can cause stomata to close (Matyssek et al., 1991; Minnocci et al., 1999; Pollastrini et al., 2010; Roberts, 1990), however, under prolonged chronic exposure (at lower concentrations) many reports document ozone-induced stomatal opening or loss of stomatal sensitivity to closing stimuli, such as drought (Hayes et al., 2012; Maier-Maercker, 1999; McLaughlin et al., 2007b; Sun et al., 2012; Wagg et al., 2012; Wilkinson and Davies, 2009), light (Paoletti and Grulke, 2010) and vapour pressure deficit (Grulke et al., 2007a; Wagg et al., 2013). In a review of 49 papers covering 68 species conducted for this report, 22% of species showed no change in stomatal conductance, 10% showed a slowed (sluggish) stomatal response to elevated ozone, 23.5% showed an increased stomatal opening under elevated ozone and 44% displayed stomatal closure in response to ozone. No clear patterns emerged for the ozone concentration range for the different responses, except perhaps a tendency for stomatal opening to occur at lower concentrations than stomatal closure.

8.2.2 Impacts of ozone on biodiversity and species balance

In the simplest interpretation, to impact on biodiversity, ozone pollution would need to exert sufficient toxic effect on an individual species for that species to be lost from a habitat. In reality, however, in most natural or (semi-)natural communities, plants are growing in a highly competitive environment - a slight loss of vitality of one species due to ozone can result in a more vigorously growing but less ozone-sensitive species outcompeting the affected species for light, nutrients and water resulting in a shift in species balance and potential loss of the more sensitive species at a sub-lethal ozone concentration.

Typical effects of ozone on sensitive species include: premature and enhanced senescence and changes in biomass, resource allocation and/or seed production. Each of these can impact on the vitality of component species of plant communities, potentially altering plant biodiversity as well as that of the animals, fungi, bacteria and insects that live in close association with plants or in nearby soils. In so doing, ozone-induced changes in species diversity or shifts in species balance will impact on many ecological processes, thereby impacting on ecosystem services, flows, goods and values.

Effects on species balance have been widely reported from controlled exposure experiments conducted in open-top chambers and solardomes, but a less clear picture emerges from field-based studies with long established communities and from field surveys. Although more studies are needed, it is clear that impacts of ozone are of particular concern for global biodiversity hotspots that experience relatively high ozone concentrations such as the Mediterranean basin.

8.2.3 Impacts of ozone on provisioning services

In this report we described effects on two key provisioning services that are impacted on by ozone effects on primary productivity and associated processes:

Crop production Effects of ozone on primary productivity (see Section 2.2) are especially relevant for crop plants. With the world population predicted to increase to 9 billion by 2050, security of food supplies is one of the most important challenges for this century. Ozone damages crop plants by, for example, reducing photosynthesis causing a yellowing of leaves and premature leaf loss, decreased seed production and reduced root growth, resulting in reduced yield quantity and/or quality and reduced resilience to other stress such as drought. As a consequence, the key components of the food system that ozone interferes with are the productivity of crops, the nutritional value and the stability of food supplies as ozone concentrations and therefore impacts vary from year to year. Some of the world's most important staple food crops are sensitive (wheat, soybean and other pulses) or moderately sensitive (maize, rice, potato) to ozone and effects on the yield of these crops are of global significance.

A recent state of knowledge report by the ICP Vegetation (Mills and Harmens, 2011), for the first time, quantified ozone impacts on wheat yield in Europe using the stomatal flux-based methodology. Using the national emissions projections scenario for 2000, ozone pollution in EU27 (+ Norway and Switzerland) was predicted to be causing an average of 13 % yield loss for wheat, with an economic loss of €3.2 billion predicted if soil moisture is not limiting. Economic losses per grid square in 2000 were greatest for wheat in the highest producing areas in France, Germany, Belgium, Denmark and the UK, indicating that ozone flux was high enough in these central and northern areas to have an impact on wheat production (**Figure 3.1**). Effects were also predicted for more southern countries such as Italy and Bulgaria. Economic impacts on wheat yield were predicted to decrease by 38% to €1.96 billion in 2020.

Current ambient ozone levels in South Asia are also considered to be reducing crop yield and quality for a range of important crops in the region, commonly within the range of 10 to 20%, but sometimes considerably more (see Emberson et al., in Mills and Harmens, 2011, for further details). Almost without exception, Asian crops appear to have a higher sensitivity to equivalent ozone concentrations that European and American crops and cultivars (Emberson et al., 2009). Of further concern for global food security is the growing evidence that ozone impacts on yield quality as well as yield quantity. These effects are much less documented (see review by Vandermeiren and Pleijel, in Mills and Harmens, 2011), but are considered by many to be equally as important as effects on yield quantity.

Timber production A recent meta-analysis has suggested that the increase in ozone since the industrial revolution has been responsible for a reduction in photosynthesis of approximately 11% in trees (Wittig et al., 2007), which may have reduced tree productivity by approximately 7% (Wittig et al., 2009). Some ozone-sensitive forest tree species are present in large areas of Europe: birch, Scots pine and Norway spruce are particularly important in central and northern Europe; beech and deciduous oaks are frequent across several European regions, in particular in central and southern areas; Holm oak and Aleppo pine are frequent in Mediterranean Europe (see, for example, Karlsson et al., 2007). In general, deciduous trees tend to be more sensitive to ozone than coniferous trees. There is evidence that negative effects of ambient ozone on forest trees are already occurring all over Europe. For example, visible injury has been detected in ICP Forests surveys (Ferretti et al., 2007a,b), reduced stem growth has been reported in Sweden (Karlsson et al., 2005), reduced stem growth in Switzerland (Braun et al., 2010) and leaf loss occurs in Greece (Velissariou, pers. com.). Karlsson recently quantified effects of ozone on production in northern European forests (in Harmens and Mills, 2012). Using National forest age class statistics, ozone response relationships for different species and ages, a model of stem increment growth, national mean AOT40 values, it was estimated that losses in C stocks averaged 10% across 10 countries, with the highest losses predicted for the Czech Republic, Germany and Poland.

8.2.4 Impacts on Regulating Services

By impacting on C sequestration, nutrient cycling, land-atmosphere exchanges and biodiversity, ozone impacts on many beneficial regulatory functions of ecosystems, including:

C sequestration and global warming If ozone concentrations are high enough to reduce photosynthesis (i.e. CO_2 fixation) and/or above-ground plant growth, then less CO_2 and ozone will be absorbed by the leaves of vegetation, leading to a positive feedback to atmospheric CO_2 and ozone concentrations and therefore more global warming. For example, Sitch et al. (2007) estimated that reductions in gross primary productivity for the period 1900-2100 are anticipated to reduce land-C storage accumulation by between 143 Pg C and 263 Pg C, which is approximately equivalent to a reduction of between 17% to 31% (Sitch et al., 2007). The ICP Vegetation recently conducted the first flux-based assessment of effects of ozone on C sequestration in the living biomass of trees in Europe (Harmens and Mills, 2012) focussing on 2000 and 2040 effects. This study showed that applying the flux-based methodology and a generic parameterisation for deciduous and conifer trees resulted in a reduction of C sequestration in the living biomass of trees by 12 (EMEP input data) to 16% (RCA input data) compared to pre-industrial ozone (See Section 5.1 for details). The flux-based approach indicates a high risk of ozone impacts on forests in Atlantic and Continental Central Europe, and also a considerable risk in northern Europe. Using a climate-region specific parameterisation for 2000 revealed higher C reductions (14%) due to ozone compared to the generic parameterisation (12%) for calculating POD_1. Predictions for 2040 indicated that the reduction of C storage in the living biomass of trees due to ozone is expected to decrease considerably compared to the reduction in 2000, mainly as a result of a predicted reduction in atmospheric ozone concentrations across Europe.

Air quality Globally, it has been estimated that ozone deposition to vegetation (by reaction with plant surfaces and uptake through the stomata) reduces tropospheric ozone concentrations by as much 20% (Royal Society, 2008). This is an especially significant function of vegetation given that ozone is the third most important greenhouse gas causing global warming (IPCC, 2007). Under drought conditions, however, plants close stomata to conserve water and stomatal uptake of ozone is substantially reduced. Vieno et al. (2010) estimated that this effect resulted in 20 – 30 ppb increases in ozone concentration during the European summer heatwave in August, 2013. Their analysis has not, as yet, taken into account the damaging effects of ozone itself on leaf functioning in that ozone-induced premature senescence may reduce ozone uptake and stomatal conductance may be modified by ozone. A further level of complexity involves ozone-induced emission of biogenic volatile organic compound (BVOCs) from plants - these can either react with ozone to reduce concentrations or lead to ozone formation. In assessing current evidence, Penuelas and Staudt (2010) found that there are far more studies showing that ozone induces increases in BVOCs than decreases in emissions. Variations in response were due to ozone concentration, species, climatic conditions, phenology and chemical type of BVOCs.

Methane emissions There is evidence that ozone may influence emissions of the greenhouse gas, methane, from wetlands although the results are less conclusive than for CO_2 effects. Global estimates of C sequestration in peatlands are in the region of 20-30 gC m^{-2} yr^{-1} (Wieder, 2001), and thus any effects of increasing ozone are of global significance for climate regulation. Results from experiments are rather mixed, with some studies indicating methane increases (e.g. Williamson, 2009; Niemi et al., 2002) whilst others show a decrease (e.g. Toet et al., 2010). The inconsistencies in these effects are most probably due to differences in species present and concentration and duration of ozone exposure.

Water cycling As described above, there are two main stomatal responses to ozone, each potentially having an opposite effect on the water cycle: ozone induced stomatal closure will preserve water within soils whilst ozone induced stomatal opening will increase water loss from vegetation and soils. Global climate modellers have until recently assumed the former mechanism is dominant, but very recently the implications of increased water loss as a result of chronic ozone exposure are beginning to be considered within such models (e.g. Harmens and Mills, 2012). Extensive measurements of a

Southern Appalachian forest in the USA by McLaughlin et al. (2007 a,b), and Sun et al. (2012) provide field evidence to support the concept of ozone-induced increases in transpiration, rather than decreases. These authors document an almost linear increase in average daily sap flows and enhancement of the amplitude of daily water–loss from native trees with increasing ambient ozone exposure, suggesting an ozone-induced disruption to the whole-tree water balance, not only as a result of increased day-time transpiration but also due to increased night-time stomatal conductance.

Flowering, pollination and insect signalling A recent meta-analysis of ozone effects on plant reproductive growth and development indicated that current ambient ozone concentrations significantly reduced seed number, fruit number and fruit weight, while there was a trend towards increasing flower number and flower weight at elevated ozone (Leisner & Ainsworth, 2012). Any impact of ozone exposure on the timing of flowering may also play an important role in reproductive success, particularly for species in which flowering is closely synchronized with pollinating species (Black et al., 2000; Hayes et al., 2012b). Floral volatile hydrocarbons (VOC's) play an important role in pollinator attraction and, additionally, serve as indirect plant defenses against herbivorous insects. These floral scent trails in plant-insect interactions can be destroyed or transformed by ozone (McFrederic et al., 2008). In summary, ozone-induced changes in flowering timing and signaling could have large ecological impacts, affecting plant pollination, the food supply of nectar feeding insects or defense against herbivorous insects.

8.2.5 Impacts of ozone on cultural services including leisure, recreation and amenity

Quantifying the potential impacts of ozone on cultural services has attracted very little attention so far even though ozone can have both subtle and profound influences over some, if not all, aspects of cultural services by impacting on the visual appearance and quality of the natural environment. Ozone impacts on leaf colour may be the most visually noticeable effect, as ozone induces early senescence in leaves and visible injury such as stippling and bronzing on sensitive species. Approximately 80 species of (semi-)natural vegetation have been recorded with symptoms attributed to ozone in Europe over the period 1990 – 2006 (listed in Mills et al., 2011), with records of injury being widespread across Europe and found in 16 countries. Ozone can also affect the visible appearance of leaves by making them more susceptible to insect attack. All of these effects could impact on the tourist industry, especially in areas of outstanding natural beauty that are renowned for autumn leaf colour.

For "biodiversity", we described how ozone can impact on species balance in (semi-)natural ecosystems with less sensitive species potentially outcompeting ozone sensitive species in experimental ozone exposures. The net effect of such competition can be a lessening of the visual attractiveness of, for example, upland grassland areas, with fewer of the attractively flowering forbs present. Also impacting on the visual appearance of natural spaces would be the ozone-induced changes in flowering described above.

Lastly, ozone effects on the ozone concentration by altering deposition to vegetation could have a health impact on those visiting natural areas.

8.2.6 Valuing ozone impacts on ecosystem services

There is an explosion of interest globally in placing and economic value on ecosystem services. This is seen as a useful way to communicate the benefits provided by the natural environment to policy makers, and to capture in a systematic way many of the unintended consequences of policy actions or management decisions (TEEB, 2009). It is also facilitates comparisons of effects of different drivers of change. Examples of approaches are:

- Studies which estimate the impact of ozone compared with assumed zero impact under no or low ozone, such as the crop loss assessments presented in Section 3.1.

- Scenario analysis, estimating marginal cost of a change in a level of ozone. Valuation can be conducted by calculating the value (positive or negative) of a change in ecosystem service in each year, applying discounting procedures, and calculating Equivalent Annual Value (EAV) of that ozone damage.

- Cost-benefit analysis including both the (change in) costs attributed to reducing ozone pollution and also the costs of implementing a policy to reduce precursor emissions of ozone, conducted within a scenario comparison against a baseline.

8.3 Research Recommendations

As described above, quantifying the impacts of pollutants, including ozone, in a form that allows direct comparison with effects of other drivers of change will provide an invaluable tool for policy makers. This review has shown that whereas there is a wealth of information on ozone impacts on natural- and agri-ecosystems, almost all studies were originally conducted for a different purpose and drawing the data together for a comprehensive quantitative assessment of ozone effects on ecosystem services, including an economic valuation, is not currently possible for most services. We therefore recommend that the following further research is conducted:

- A systematic review and data mining exercise for each ecosystem service to derive generic response functions for calculation of effects.

- Use this review to identify those services for which there is insufficient experimental information available for derivation of response functions and make recommendations for further experimental work. Examples of experimental research would include:

    - Further quantification of below-ground impacts of ozone on C sequestration in roots and soils
    - Further studies of the effects of ozone on stomatal conductance and the potential uncoupling from photosynthesis
    - Experimental studies on the responses of vegetation to ozone in representative future climates and CO_2 concentrations
    - Large-scale field ozone exposure experiments on intact ecosystems
    - Epidemiological analysis of field measurements to detect spatial and temporal trends in ecosystem processes and functions
    - In association with proof of concept ozone exposure experiments, surveys to show the extent of occurrence of visible injury, early senescence and changes in expression of autumn colour.

- Identification of appropriate spatial data, including land-use, ozone, species distribution, ecosystem functions and products (for example, C stocks and yield), to facilitate a spatial analysis of impacts on ecosystem services.

- Further research on economic valuation methods, especially for those ecosystem services provided by natural ecosystems that are difficult to value without large uncertainty.

- Using the above, conduct a comprehensive quantitative assessment of past, current and predicted future effects of ozone on ecosystem services, and where possible a cost-benefit analysis for future scenarios.

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Annex 1 Contributions from participants

In this Annex, we have included five contributions from participants in the ozone effects work programme of the ICP Vegetation. The following short reports summarise aspects of their research on effects of ozone on ecosystem services; the responsibility for their content lies with the participants.

- **Effects of tropospheric ozone on the bioenergy plants *Sida hermaphrodita* L. Rusby and *Silphium perfoliatum* L. (Germany)**
- **Ecosystem service of air quality improvement provided by urban and natural vegetation in Latium region, Italy**
- **Economic evaluation of ozone impacts on crop yields and forest growth in Sweden**
- **Impacts of ozone on (sub-)alpine grasslands in Switzerland**
- **Valuing ozone impacts on carbon sequestration, livestock yield and biodiversity in the UK**

Effects of tropospheric ozone on the bioenergy plants *Sida hermaphrodita* L. Rusby and *Silphium perfoliatum* L.

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Objectives

Novel bioenergy plants are currently being introduced into European agro-ecosystems but their responses to climate change, the CO_2 fertilisation effect and tropospheric ozone have not been studied to date. While the biomass of Virginia Fanpetals (*Sida hermaphrodita* L. Rusby, Malvaceae) is used for power generation in Poland, Cup Plant (*Silphium perfoliatum* L., Asteraceae) is used in Germany to complement the excessively grown maize in biogas production. Both perennial plant species originate from floodplains in the Great Lakes Basin in Northern America. While Virginia Fanpetals is a rare plant in the US and Canada, Cup Plant is still a widespread tall herb in the remaining prairies. Due to their preference of moist habitats and their high relative growth rates both taxa might be subjected to high ozone fluxes and potential damage. However, in Poland and Germany both plant species are cultivated on drier sites. It is thus unclear whether the European biotypes which have been selected for cultivation over decades still exhibit the same ecological behavior than the North American ancestors.

Materials and methods

In order to test the sensitivity of these species to ozone, an experiment with potted plants was performed in May and June 2012 in mini-greenhouses which were supplied with charcoal-filtered (CF), unfiltered (NF) and ozone enriched (NF+20) air. Sowing and pre-culture of plants commenced in a greenhouse in mid February 2012 and in the end of April one seedling per pot was transplanted into 1.7 L rectangular pots. On 3rd of May 2012 pots were moved to the mini-greenhouses and once a week treatments and plants were rotated between the greenhouses to avoid placement effects. Plant development, vitality, leaf greenness (SPAD) and the occurrence of visible injury were determined using non-destructive methods, while treatment effects on growth and allocation patterns (shoot:root ratio) were determined at three harvests.

Results

Due to frequent randomization and rotation of plants and treatments between greenhouses temperatures and relative humidity did not differ between the ozone treatments. Mean ozone concentrations were 13, 23 and 43 ppb in the CF, NF and NF+20 treatments while after two months of exposure AOT40 reached 62, 2437 and 13518 ppb.h, respectively. Daily profiles of the three ozone treatments are shown in **Figure 1**.

Foliar injuries were observed on the first true leaves, i.e. the oldest leaves, two weeks after the onset of the fumigation (**Figure 2**). In *Sida,* white stipples were recorded while the symptoms in *Silphium* turned out as white-brownish lesions. Foliar injuries were only seen in plants that were grown in NF+20 treatments and did not occur in any of the leaves that were formed later in the experiment. Prior to the detection of injuries, maximum ozone concentrations did not exceed 90 ppb.

In *Silphium*, leaf greenness (SPAD values) was significantly higher in the CF treatments throughout the experiment (**Figure 3**), while in *Sida* SPAD values were significantly higher in NF air at the fourth assessment date. During the experiment only low numbers of senescent leaves were recorded and the dry mass allocated to senescent leaves was unrelated to the ozone treatment.

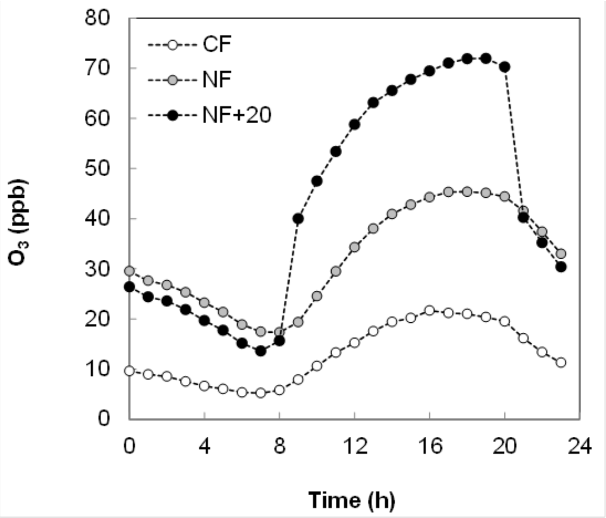

Figure 1 Mean daily ozone profiles realized in the ozone fumigation experiment lasting from 3rd of May to 26th of June 2012.

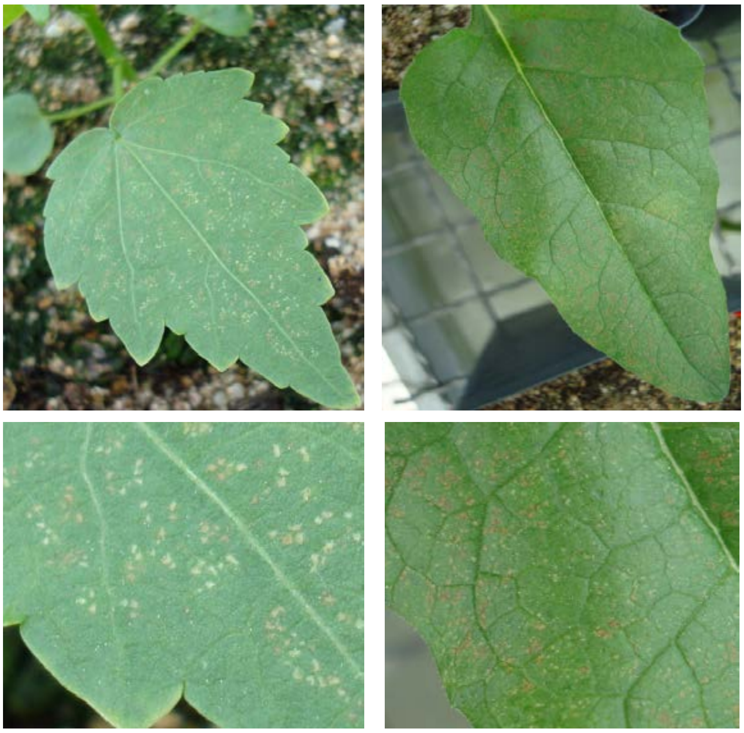

Figure 2 Foliar symptoms recorded on first true leaves of *Sida hermaphrodita* (above left, close-up below) and *Silphium perfoliatum* (above right, close-up below). Photographs were taken on 19 May 2012, i.e. 15 days after the onset of fumigation when AOT40 had reached 3600 ppb.h. Foliar injury was only observed in the NF+20 treatments.

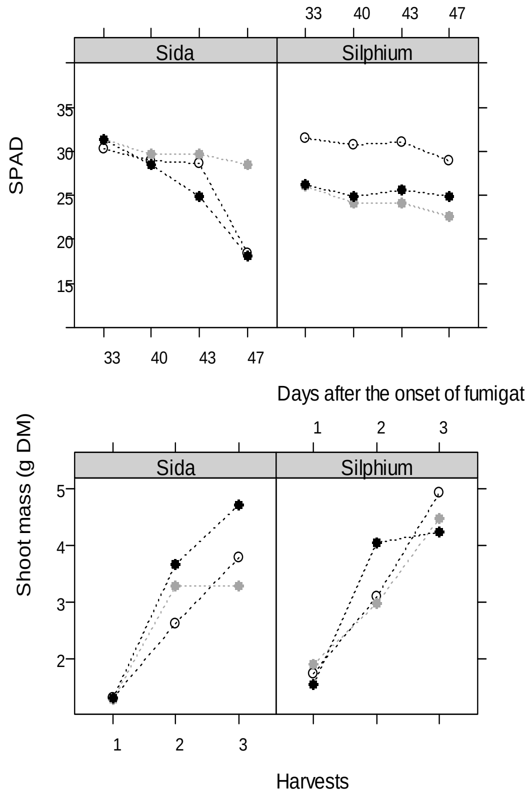

Figure 3 Effects of different treatments of ozone on leaf greenness (SPAD, above) and on shoot growth (below) of *Sida* and *Silphium* determined at three consecutive harvests (21, 35 and 49 days after the onset of fumigation. Treatments represent: ○ CF, ● NF and ● NF+20.

Although shoot masses of the two species were not significantly different in the ozone treatments, results may indicate a slight hormetic effect of ozone. As can be seen in **Figure 3** shoot mass at harvest 2 was slightly higher in *Sida* and *Silphium* in the NF+20 than in the CF treatments. In *Sida,* the insignificant positive effect remained until harvest 3, while *Silphium* plants grown at elevated ozone showed a lower shoot mass than the plants grown in CF.

Conclusion

Preliminary findings on potential damage of ozone to bioenergy crops suggest that Cup Plant and Virginia Fanpetals may show ozone related foliar injury in first true leaves but not in leaves developing later. In *Silphium* ozone exposure may significantly reduce leaf greenness and insignificantly reduce shoot growth. In contrast, shoot growth of *Sida* appeared to be not significantly favoured by ozone. We conclude that in early life stages Cup Plant has a higher sensitivity to ozone than Virginia Fanpetals. However, longer and multiple season experiments would have to be performed to study the effects of ozone on these perennial plant species. Additional research should be performed to address ozone-related changes in crop quality, e.g. energy contents and methane production potential, as well as the interactions between ozone exposure and carbon sequestration efficiencies of perennial bioenergy crops.

Acknowledgements

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Ecosystem service of air quality improvement provided by urban and natural vegetation in Latium region, Italy

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Introduction

Tropospheric ozone is dominant in the photochemical air pollution mixture during summer periods, particularly in Mediterranean areas (Millán et al., 2000), with negative effects on public health (Bell et al., 2006; Martuzzi et al., 2006), natural vegetation and crops (Manes et al., 2007; Mills et al., 2011). The increasingly evident detrimental effects of ozone on human health and ecosystems have underlined the need to develop environmental policies to reduce the air concentrations of this oxidizing agent. In this context, the study of the ozone exchange between the atmosphere near the ground and the vegetation is of particular interest, not only because ozone causes damages to vegetation, but also because it is an important process affecting the ozone concentration in the troposphere. In fact, plants contributes to the tropospheric ozone budget through three components of ozone fluxes: stomatal uptake, non-stomatal deposition, and gas-phase reactions (Gerosa et al., 2005; Cape et al., 2009). The sum of these three components is usually referred as “total ozone flux”. The ozone flux to vegetation is controlled by complex interactions of meteorological and biological processes in the soil-plant-atmosphere continuum (Mereu et al., 2009). Basic parameters, regulating the effects of vegetation on air quality, are the physiology of the main woody vegetation types, as well as the spatial distribution of green areas. In this context, the role of the forests to reduce ozone levels appears to be an important aspect to be considered in the global evaluation of their economic value in terms of ecosystem services provision.

Regulating services of urban forests: tree diversity stabilizes ozone removal in Rome, Italy

According to a recent review by Escobedo et al. (2011), focused on air pollution mitigation by urban forests, ecosystem services are considered as the components (including functions) of urban forests that are directly enjoyed, consumed, or used to produce specific and measurable human benefits. The role of urban forest in providing ecosystem services has been investigated in many papers, considering both basic ecosystem functions, like primary productivity (Pataki et al., 2011) and emerging services, such as the improvement of air quality (Nowak et al., 2006, Escobedo and Nowak, 2009). The reduction of air pollution by urban trees has been recognised as a cost effective component of pollution reduction strategies in several urban areas, such as Washington DC, New York, Baltimore, Atlanta and Chicago in the United States (Nowak et al., 2000, Nowak et al., 2006, Yang et al., 2008, Morani et al., 2011), Beijing (Yang et al., 2005), Santiago de Chile (Escobedo and Nowak, 2009), London (Tiwary et al., 2009), and Toronto (Millward and Sabir, 2011). However, while considering the temporal changes of air pollution concentration, most of these studies did not account for the spatial heterogeneity of vegetation within the urban environment, nor they considered the link between the site-specific pollution dynamics and the removal rates by vegetation, determined by plant physiological processes.

In the city of Rome, Italy, the effects of tree diversity on the ecosystem service of ozone removal has been quantified and valued, by means of a spatial analysis integrating system dynamic modelling and geostatistics. In particular, the seasonal and annual ozone removal by the main three functional groups of urban trees (evergreen broadleaves, deciduous broadleaves, conifers), has been estimated under two climatically different years: the extremely dry year 2003, and the year 2004, which is more representative of the average long-term climatic pattern of the city of Rome (Manes et al., 2012a). The results showed that the majority of ozone removal by urban trees occurred in the southern coastal area of the metropolitan area of Rome, where the largest urban (Castel Fusano) and peri-urban (Castelporziano Presidential Estate) forests are located, and where tree diversity is highest (Manes et al., 1997). However, also the urban forest patches in the city centre played an important role, by improving air quality in the most urbanized sites. Moreover, the functional differences (such as response to drought and length of the leaf-growing seasons) among the tree groups, together with their spatial distribution across the city of Rome, stabilized the ecosystem service of ozone removal under very different climatic conditions, in spite of the seasonal and inter-annual fluctuations in ozone uptake of the different groups. Finally, from an economic viewpoint, the ecosystem service of ozone removal by urban forests of Rome has been prudentially valued to roughly $2 and $3 million/yr, based on published unitary costs of externalities (Nowak et al., 2006), and of mortality associated with ozone, respectively.

In general, the results of this study could have important implications for development of future management strategies, like for targeted tree planting in selected locations, or for evaluating the potential benefits to the stabilizing effect on ozone uptake that could derive from the replacement of native plant species with ornamental exotic ones.

Regulating services of natural vegetation: ozone removal by evergreen and deciduous forests in Latium (Italy)

The role of the main natural woody vegetation classes of the CORINE Land cover Classification System in the whole Latium Region (Central Italy) in removing ozone during the growing season of the year 2005, has been estimated (**Figure 1**; Manes et al., 2012b). Cumulated ozone fluxes data allowed to estimate the externality value of this ecosystem service provided by deciduous and evergreen forests in the Latium region, using the ecoregion concept at the landscape level (Blasi and Frondoni, 2011; Capotorti et al., 2012). For the year 2005, this value should be around $57,248,000 and $2,286,000 in the Apennine Province for deciduous and evergreen forests, respectively, and 22,376,136 $ and 3,114,686 in the Tyrrhenian Province for deciduous and evergreen forests, respectively. This corresponds, for the growing season 2005, to a total value of $85,025,821 attributable to the ecosystem service of tropospheric ozone removal provided by the natural forests of the Latium region. On the basis of standard wood value estimation (INEA, 2012), it was calculated that the yearly rate return relative to the natural capital of two vegetation classes for ecosystem services of tropospheric ozone removal is about 0.6%.

This study takes into account only a process provided by forest ecosystems, related to the links between structure and functions of the two different vegetation classes examined. We acknowledge that there are some uncertainties in producing such estimates, however, these data are a first contribute to monetise ecosystem services of regional and national forests in Italy, and more in general, to promote the use of ecosystem service valuation in forest management and environmental policy-making, to highlight their intrinsic and utilitarian roles. Finally, the externality value used in our estimation does not take into account the positive effects on human health and well-being deriving from the ozone removal potential of forests in rural and peri-urban areas.

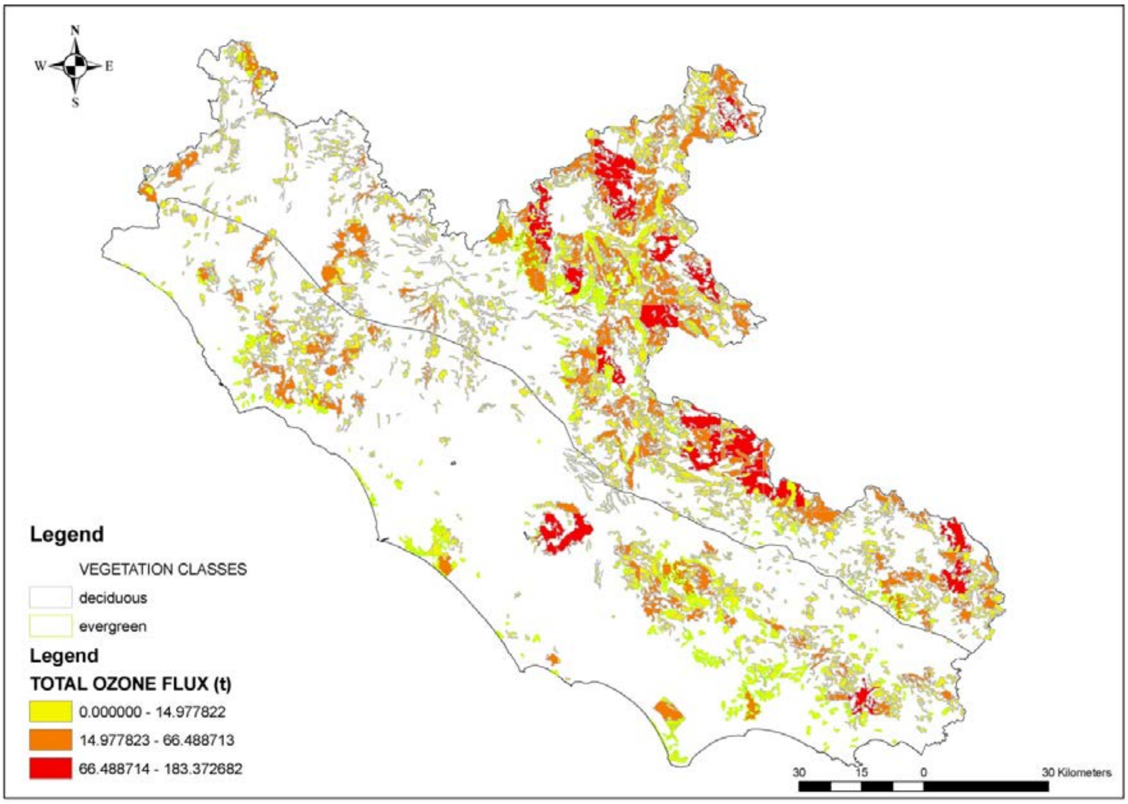

Figure 1 Total ozone flux (t) to deciduous and evergreen forests in the two Ecoregional Provinces of the Latium region (borderline in grey): Apennine Province (upper), Tyrrhenian Province (lower). (From: Manes et al., 2012b).

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Economic evaluation of ozone impacts on crop yields and forest growth in Sweden

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Introduction

An economic evaluation has been made of ozone impacts on crop yields and forest growth in Sweden (Karlsson et al., 2006). This was a further development of an earlier study by Karlsson et al. (2005) for the estate Östads Säteri. The assessments were made using dose-response relationships based on AOT40. This was justified since the experiments used to derive the dose-response relationships originated from Sweden or in some cases from other Nordic countries. At a yearly AOT40 value of 10 ppm h (Apr-Sep), the growth rates of coniferous trees were assumed to be reduced 2.6%. The corresponding value for deciduous trees was an 8 % reduction in the growth rates. For wheat, the assumed annual yield reduction was approximately 10% at an AOT40 (accumulation period 55 days) of 5 ppm h. The corresponding value for potato was a 13 % yield reduction at 5 ppm h (70 days accumulation period). The estimated impacts on pasture were relatively small.

Values for the ambient air ozone exposure were obtained from the EMEP model in 50 km x 50 km grids and they were obtained for the years 1995, 1996, 1997, 1999, 2000, 2001 and 2002. Ozone concentrations were estimated at 1 m above ground-level for crops and 20 m above ground-level for trees. As a mean value over the years the highest AOT40 values for trees (Apr-Sep, 20 m above ground) reached approximately 15 ppm h in southern Sweden and then decreased towards the north.

Information about land-use, forest growth- and harvest rates and prices as well as agricultural normal yields and prices were obtained from a database created within the major Swedish research programme ASTA, as well as from official Swedish sources for statistics. Estimates for forest production losses included Norway spruce, Scots pine, silver birch and other deciduous forests. Estimates for crop yield reductions included wheat, other cereals, potato (both for food and starch production, respectively) and pasture.

The annual economic costs due to ozone impacts in ambient air in Sweden were estimated to 160 MSEK (18 M€) for agricultural crop yield reductions and SEK 340M (€ 38M) for reduced forest production, as related to the reference scenario with the absence of the ozone problem.

The reduction in the annual forest growth rates summed up for the entire Sweden across all species was 1.6 M m^3 at ambient ozone exposure. The annual yield loss for wheat due to ambient ozone exposure was almost 80,000 tonnes when summed for the entire Sweden. The corresponding value for other cereals was 24,000 tonnes and for potato grown for food production close to 40,000 tonnes, for pasture it was 22,000 tonnes. No quality aspects were included when estimating the ozone impacts on crop yield. Neither were ozone impacts on the vitality and stress tolerance of trees considered, as were non-monetary values such as e.g. pre-mature shedding of the leaves for deciduous trees. No values were estimated for ozone impacts on semi-natural vegetation.

The estimated economic values for negative impacts of ambient ozone on crop yields and forest production in Sweden were of the same order of magnitudes as the estimated economic values of crop yield reductions due to pests and insect attacks in Sweden. Regarding forests, the ozone impacts corresponded to the economic values of the influence of root rot and to the economic value of the browsing of roe deer and moose on young plants.

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Impacts of ozone on (sub-)alpine grasslands in Switzerland

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Introduction

Large areas in the mountainous and sub-alpine zones in the Swiss Alps are covered by semi-natural grasslands, mostly cattle pastures and hey meadows. At higher elevations, due to extensive management, low atmospheric nitrogen input, and high structural and climatic variability, these habitats are extraordinarily species-rich. This diversity is possibly endangered by still increasing concentrations of ozone and reactive nitrogen compounds in the atmosphere. However, considerable uncertainty remains concerning the sensitivity of (semi-)natural grassland to these pollutants, and about effects of a combination of the two (Fuhrer & Booker, 2003).

The majority of the available sensitivity assessment studies was carried out with mixtures of 1-4 species exposed to ozone for a few weeks during their establishment phase in open-top chambers (OTC) (i.e. Bungener et al., 1999). It is often assumed that the sensitivity of a community is determined by the ozone sensitivity of their component species. However, the community response is likely to be more than the sum of responses of individuals, since canopy structure, plant age, and complex interactions among individual plants might modulate effects of ozone. In addition, the ozone sensitivity of plants is often overestimated when tested in OTCs since ozone uptake is increased due to high air turbulence inside the chambers, and a microclimate that favors high stomatal conductance (Nussbaum & Fuhrer, 2000). These limitations can be overcome by using free-air exposure systems (Volk et al., 2003). However, up to now results from only two long-term experiments are available, which assessed effects of elevated ozone concentration on mature grassland communities by means of a free air-fumigation system.

Le Mouret experiment (1998-2003)

An extensively managed mountainous *Arrhenatherion elatioris* grassland was exposed for five years during the whole growing season to two levels of ozone concentrations (i.e. ambient and 1.5 x ambient concentration, simulating summer smog episodes) in a free-air fumigation system. Productivity and individual species abundance were measured three times annually. Although in the fifth year, yield as well as the fraction of legumes was significantly lower in the fumigated plots compared to the control (Volk et al., 2006), repeated-measure ANOVA with a covariable to account for productivity prior to the start of fumigation revealed effects on the temporal changes in total yield and yield of legumes that cannot be separated between ozone and pre-treatment nutrient status (Stampfli & Fuhrer, 2010). Although elevated ozone may have caused subtle physiological and genetic changes with possible longer term implications, the results suggested that this type of species-rich, mature grassland was more resilient to increasing ozone compared to productive grass/clover swards.

Alp Flix experiment (2004-2010)

Monoliths (180) of a species-rich subalpine *Geo-Montani-Nardetum* pasture were exposed for seven years during the growing season to five simulated nitrogen loads (0, +5, +10, +25, +50 kg N ha^{-1} yr^{-1}) in combination with three ozone levels (ambient, 1.2 or 1.6 x ambient concentration, simulating increased background concentrations) using a free-air fumigation experiment at 2000 m above sea level in the Central Alps (Bassin et al., 2007b). Above-ground biomass of the functional groups of grasses, forbs, sedges, and legumes, as well as individual species abundance was recorded once a year. Elevated ozone and the combined ozone x nitrogen exposure had no detectable effect on yield and functional group composition. However, an increase in dead plant material was observed in the highest ozone treatment. In contrast to earlier assumptions, this ozone-induced increase in leaf senescence caused no loss in productivity or shift in species abundance, with the exception of *Nardus stricta* which became more abundant. In contrast, nitrogen addition caused strong changes in community composition and Shannon diversity: sedges tripled their fractional biomass at the expense of the other functional groups. Compositional changes were significant with +5 kg ha^{-1} yr^{-1}; at all levels of nitrogen, however, these changes ceased after five years of treatment, thus indicating that a new equilibrium was reached. Overall, the results reveal high nitrogen sensitivity of this subalpine grassland, but low sensitivity to ozone, both singly and in combination with increasing nitrogen (Bassin et al., submitted).

Conclusions

Overall, after five or seven years under elevated ozone exposure, respectively, both the mountainous and the sub-alpine grassland community were only slightly affected by higher-than-ambient levels of ozone, irrespective of the level of nitrogen input. These findings contradict earlier assumptions that (sub-)alpine grassland should be classified among the most sensitive vegetation types (Mills et al., 2007) based on findings from pot experiments carried out under controlled conditions. When tested in field experiments, mature semi-natural grassland communities appear to be less ozone sensitive than previously expected. According to Bassin et al. (2007a) this could be due to:

a) Plant age and phenology: as the carbon demand and thus the dependency on a highly efficient photo-assimilation system differs between phenological phases, it is assumed that ozone sensitivity is highest during the establishment phase, while it is low in the vegetative phase, which dominates in mature communities.
b) Multiple co-limitations: In natural environments, photosynthetic capacity is rarely the limiting factor for productivity. Thus, ozone which predominantly affects the photosynthetic activity, is less effective. This is in contrast to pot experiments, where resources like water and nutrients are not limited.
c) Species richness: In agreement with the insurance theory, it is commonly assumed that higher species richness enhances both resistance and resilience of plant communities through functional redundancy.
d) Genetic variability: at the community level, ozone responses could be buffered through genetic variability.
e) Competitive and mutualistic interactions: species-specific ozone responses might be buffered or hidden by complex plant-plant or plant-microorganism interactions.

In view of the specific characteristics of sub-alpine grasslands, additional factors may be responsible for high ozone tolerance:

a) Alpine species typically contain high levels of antioxidants to cope with oxidative stress caused by high UV-radiation or naturally high ozone concentrations.
b) The chronic low-level exposure used in this experiment (simulating increasing background concentrations) might be less stressful because of the absence of peak ozone concentrations above 120 ppb that have been found to affect plants most effectively (Nussbaum et al., 1995).
c) Facilitative interactions among species, which play an important role in alpine habitats, could increase community resistance to ozone stress.

Overall, it is concluded that in Swiss mountainous and subalpine pastures, biodiversity and species composition is not endangered by projected higher future ozone concentrations. This has important implications for the definition of a critical level of ozone exposure/dose for this kind of vegetation. Also, in sub-alpine pastures a concomitant increase in nitrogen deposition is unlikely to increase the plant communities' sensitivity to ozone, but increasing deposition of anthropogenic nitrogen is a considerable threat for the biodiversity of these species-rich communities.

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Valuing ozone impacts on carbon sequestration, livestock yield and biodiversity in the UK

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Introduction

Current research funded by the UK department of the environment (defra) aims to estimate a financial value for ozone impacts on three ecosystem services:

- Carbon sequestration in grasslands, deciduous and coniferous woodland;
- Livestock yield via impacts on pasture quality;
- Appreciation of biodiversity via impacts on plant species richness.

The study follows an ecosystem services approach based on the impact pathway for ozone developed in a previous study (Jones et al. 2012). The chain of ozone impacts is identified starting from changes in ozone concentrations to calculating altered impact on ecosystem processes. The next step is to conceptually link changes in processes to a quantifiable impact on potential ecosystem service supply. Lastly, an estimate of the financial value of ozone impact is calculated by applying environmental economic analysis techniques including market values or benefit transfer valuation as appropriate. Uncertainty estimates are produced using Monte Carlo analysis.

Methodology

The approach taken calculates the marginal cost of changes in ozone using two scenario comparisons. The first looks at the cost due to historical changes in average UK ozone concentrations over the period 1987 to 2007, against a reference scenario of no change in concentrations since 1987. The second comparison estimates the cost of projected future changes in ozone concentrations over the period 2007 to 2020, against a reference scenario of no change in ozone concentrations from 2007.

The study uses the ozone metric of 24 hour mean (ppb), averaged over a 7 month growing season (1 March to 30 September). The 24 hour mean was selected instead of AOT40 because rising background ozone concentrations in the UK and Europe have made calculations based on a 40 ppb threshold an increasingly unrealistic measure of damage. While flux-based calculations are seen as the most reliable method for predicting ozone impact since they estimate the actual ozone uptake by the plant, they cannot be reduced to a common metric comparable across different species or environmental impacts because of an insufficient range of response functions. This common metric is necessary to be able to sum up impacts of ozone across multiple ecosystem services and thereby to calculate a damage cost, i.e. a financial cost per unit change in ozone concentration.

Exposure data from experiments used to derive dose-response functions were calculated as follows. Ozone exposure data were averaged over the seven-month growing season including periods of ambient exposure where applicable. For multi-year experiments the average was calculated between cutting dates i.e. for a multi-year experiment harvested in August 2010 and with a final harvest in August 2011, ozone exposure was summed as the exposure after harvest in August 2010 through to the harvest date in 2011, incorporating only those months within the 7-month growing season.

For quantifying impact of ozone over time, spatially explicit seven-month 24 hour mean ozone data for the historical scenario were obtained from a previous study (RoTAP 2012) at 1x1km resolution. Averages were calculated over a five-year average (1987-1991) for the start year 1987 and (2002-2006) for the end year 2007. These time periods were used because although ozone monitoring methods have changed over time in the UK, data over these time periods were recalculated using a consistent methodology (RoTAP 2012). Ozone data for future projections to 2020 were supplied by AEA Technologies, based on a spatial pattern of ozone concentrations in a single year 2007 and projected to the future based on altered precursor emissions under the UEP30 energy scenario. Ozone data for this scenario comparison were produced at 10x10km resolution (**Figure 2**). For each scenario, data were linearly interpolated between the two time points.

Ozone impacts on C sequestration

Dose response functions for ozone impacts on above-ground biomass in grassland were derived based on a meta-analysis of seven UK studies on grassland species mixes from the UK Defra Ozone Research consortium. Above-ground biomass data from each experiment were normalised relative to zero impact at zero ozone according to the method of Fuhrer (1994). The response function across all grassland experiments was fitted to obtain a slope at zero intercept. The slope coefficient was:

$$Y = -0.00407 \times \text{Ozone 24hr mean.}$$

Quantification of impact assumed that in grasslands above-ground biomass is approximately equivalent to annual net primary production, and that ~10 % of grassland NPP is converted to long-term soil C storage (Ciais et al. 2010). Grassland NPP data were obtained from MODIS satellite data averaged over the period 2002-2006. Projected historical and future changes in NPP were calculated using the dose response function based on this reference NPP value. In other words, under previous lower ozone concentrations, the NPP was calculated to be higher, but under the greater mean ozone concentrations in the future was calculated to be lower. All calculations were spatially explicit, applied over grid squares containing grassland, and changes in C sequestered were multiplied by the area of grassland in each grid square (LandCoverMap 2007). Only results for grasslands are presented here as calculations for woodland are ongoing.

On average over the UK, rising ozone concentrations have resulted in a net loss in C sequestration of -188,000 tonnes in the historic scenario and a further loss of -623,000 tonnes is projected for the future scenario. The spatial extent of changes in soil C in each scenario is shown in **Figures 1a,b**. The historical scenario shows a complex pattern of increases in C allocation in some areas, but decreases in C allocation in others. This is largely due to the changing pattern of ozone concentrations due to falling peaks versus rising background levels and their relative importance in the early 1990s. The future scenario reflects a more consistent increase in 24hr mean ozone concentrations, with a resulting negative effect on C sequestration.

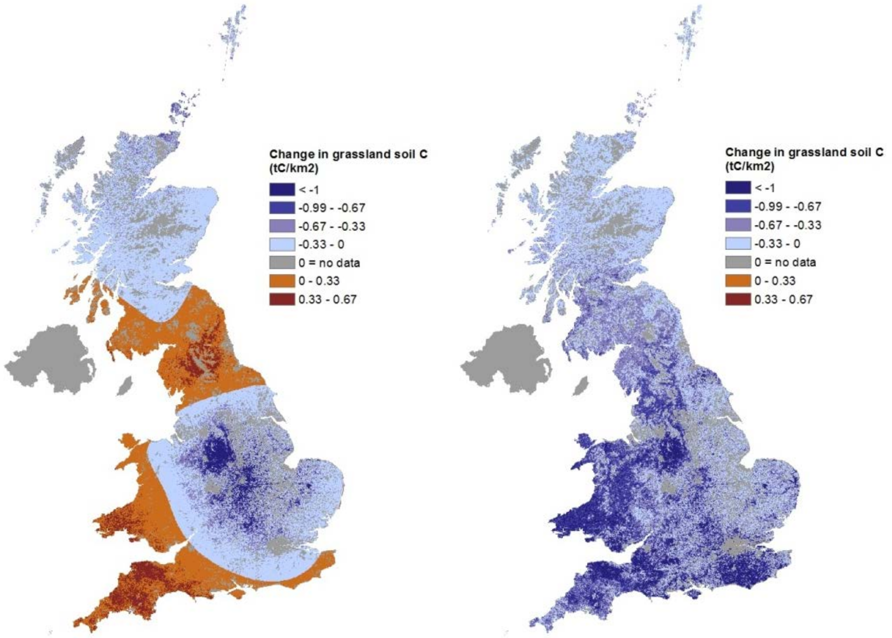

Figure 1 Changes in C sequestration (tC/km^2) due to ozone in the a) Historical ozone concentration comparison over the period 1987-2007, and b) Future ozone concentration comparison over the period 2007-2020.

Ozone impacts on livestock yield

Harvested plant material from a range of Defra funded UK studies of ozone impacts on grasslands, including calcareous grassland, mesotrophic grassland, sanddune grassland and haymeadow grassland (Keenley), was sent for analysis to a specialist laboratory (AUNIR, Towcester, UK). Each sample was individually ground, and near infrared reflectance spectroscopy was used for analysis of each sample for neutral detergent (NDF) and acid detergent (ADF) fractions, crude fibre, protein, sugar, lignin and fat. ‘Desirable’ quality parameters, which increase the nutritional value of forage (sugar, crude protein and fat), showed no statistically significant effects of increasing ozone concentration. In contrast, ‘undesirable’ quality parameters (ADF, crude fibre, lignin), which hinder digestibility of the pasture, showed an increase in concentration with increasing ozone exposure. Metabolisable energy (for sheep) was calculated for each sample and this decreased with increasing ozone concentration ($p=0.002$), with no differences in the slope of the regression line between the grassland types. Quality of forage has been shown to be an important factor influencing live weight gain of lambs. Relationships between metabolisable energy and potential liveweight gain exist in published literature and have been derived for lambs, cattle and milk production based on the maintenance metabolisable energy required. Using mapped data of 1km resolution for ozone concentration and distribution of lambs, pasture quality and therefore predicted liveweight gain of lambs was calculated. This showed that over the period 2007 to 2020, the total daily liveweight gain of lambs across the UK was reduced by approximately 4%. The monetary value of this change, considering the length of time of lamb rearing between weaning and slaughter and the proportion of the flock that is slaughtered is presented in the full Ozone and Ecosystem Services report.

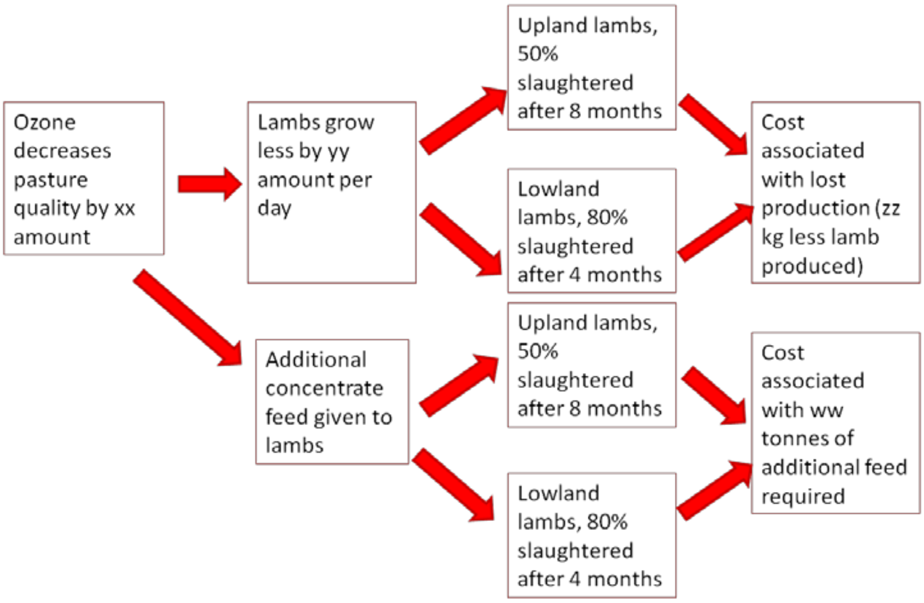

Figure 2 Pathway to economic impact for ozone impacts on livestock yield.

Ozone impacts on biodiversity

Ozone impacts on biodiversity were proxied by estimating dose response functions for ozone and plant species richness. This was the limit to which the assessments for biodiversity could be taken at this stage. Dose response relationships were based on spatial gradient analysis of national UK landscape surveys over 3 (approximately decadal) time intervals, and corresponding average ozone concentration data. The results were slightly counter-intuitive, in that some habitats suggested positive relationships with ozone (Fen, Marsh and Swamp) while others suggested negative relationships with ozone (Heathlands and Bogs) – see **Figure 3** below. Further work is required to better understand the outcomes of this gradient approach.

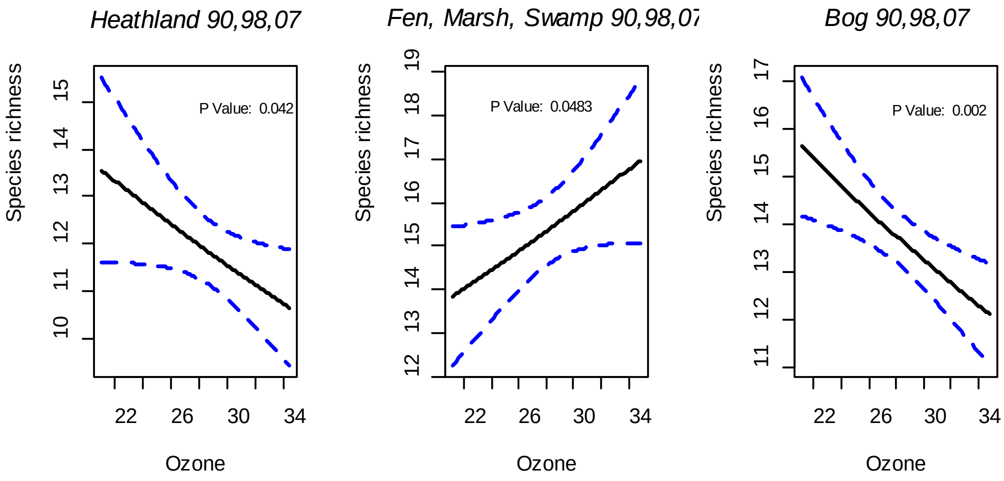

Figure 3 Gradient approach to determine ozone vs plant species richness relationships for three plant community types for survey years 1990, 1998 and 2007.

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Annex 2 Stomatal response to ambient and elevated ozone.

Papers are listed for trees and woody species, grassland species and crops, and grouped within these categories by type of response. An asterisk by author denotes assumptions made about the unreported ozone concentration: * ambient fluctuating conditions (assumed ozone concentration is 35 ppb), ** ambient x 1.3-1.5 (assumed ozone concentration 52.5 ppb), *** ambient x 1.8-2 (assumed ozone concentration 70 ppb).

A full reference list for the papers listed in this table is provided at the end of this Annex.

Trees and woody species

Author	Species	Length of exposure	Ozone concentration	Environment	Stomatal response	Additional treatment
Freer-Smith & Dobson 1989	*Sikka spruce*	2 days	80 ppb	chambers	increased gs	N/A
Gregg et al. 2006	*Populus deltoides*	11 weeks	98 ppb	open top chamber	increased gs	N/A
Mclaughlin et al. 2007	*forest trees*	23 yrs	natural flunctuating	natural	increased gs	N/A
Onandia et al. 2011	*Betula papyrifera*	10 years	1.5 x ambient	Aspen FACE	increased gs	CO2
Paakkonen et al. 1998	*Betula pendula*	11 weeks	1.5 x ambient	open field	increased gs	well-watered
Pearson & Mansfield 1993	*Fagus sylvaticum L*	18.2 weeks	60 - 120 ppb	Solardomes	increased gs	red.-watered
Pearson & Mansfield 1993	*Fagus sylvaticum* L	18.2 weeks	60 - 120 ppb	Solardomes	increased gs	well-watered
Roberts et al. 1990	*Liriodendron tulipifers*	14 weeks	50 ppb	chambers	increased gs	N/A
Sun et al. 2012	*Betula papyrifera* March.	12.8 weeks	80 ppb	Aspen FACE	increased gs	N/A
Sun et al. 2012	forest trees	18-24yr	natural flunctuating	natural	increased gs	N/A
Sun et al. 2012	*Populus tremuloides* Michx.	12.8 weeks	80 ppb	Aspen FACE	increased gs	N/A
Uddling et al. 2009	*Betula papyrifers*	2 growing seasons	ambient + 35%	Aspen FACE	increased gs	N/A
Uddling et al. 2009	*Populus tremuloides*	2 growing seasons	ambient + 35%	Aspen FACE	increased gs	N/A
Zhang et al. 2013	*Elaeocarpus balansae*	3 weeks	ambient	open-air	increased gs	N/A
Zhang et al. 2013	*Ficus microcarpa*	3 weeks	ambient	open-air	increased gs	N/A
Zhang et al. 2013	*Manglietia glauca*	3 weeks	ambient	open-air	increased gs	N/A
Tjoelker et al. 1995	*Acer saccharum* Marsh.	9.7 weeks	ambient x2 (approx 95 ppb)	free air exposure system	initial increase	N/A
Hoshika et al. 2012a	*Betula ermanii*	12 weeks	60 ppb	open top chamber	no change	N/A
Hoshika et al. 2012a	*Betula maximowicziana*	12 weeks	60 ppb	open top chamber	no change	N/A
Hoshika et al. 2012a	*Betula platyphylla* var. *japonica*	12 weeks	60 ppb	open top chamber	no change	N/A
Samuelson 1994	*Acer rubrum*	20 weeks	ambient x2 (60 - 120 ppb)	open-top chambers	no change	N/A
samuelson 1994	*Prunus serotina*	20 weeks	ambient x2 (60 - 120 ppb)	open-top chambers	no change	N/A
Zhang et al. 2013	*Aporusa dioica*	3 weeks	ambient	open-air	no change	N/A
Zhang et al. 2013	*Cinnamomum camphora*	3 weeks	ambient	open-air	no change	N/A
Zhang et al. 2013	*Litsea glutinosa*	3 weeks	ambient	open-air	no change	N/A
Zhang et al. 2013	*Sapium discolor*	3 weeks	ambient	open-air	no change	N/A
Zhang et al. 2013	*Schmima superba*	3 weeks	ambient	open-air	no change	N/A
Zhang et al. 2013	*Toxicodendron succedaneum*	3 weeks	ambient	open-air	no change	N/A
Hanson et al. 1994	*Quercus rubra* L	2 growing seasons	2x ambient	large open-top chambers	reduced gs	N/A
Hartikainen et al. 2012	*Betula pendula* Roth	2 growing seasons	ambient x 1.4	open field	reduced gs	incr. temp.
Hoshika et al. 2012b	*Fagus crenata*	12 weeks	56.7 ±10.5 ppb	free air exposure system	reduced gs	N/A
Lombardozzi et al. 2012	*Liriodendron tulipifers*	12 weeks	ambient + 70 ppb (100ppb app	open-top chambers	reduced gs	N/A
Matyssek et al. 1991	*Betula pendula*	5 weeks	100 ppb	field chambers	reduced gs	N/A
Minnocci et al. 1999	*Olea europaea* L. cv Frantoio	17.1 weeks	100 ppb	chambers	reduced gs	N/A
Minnocci et al. 1999	*Olea europaea* L. cv Moraiolo	17.1 weeks	100 ppb	chambers	reduced gs	N/A
Novak et al. 2005	*Fraxinus excelsior*	20 weeks	40.6 ppb	chambers	reduced gs	N/A
Novak et al. 2005	*Populus nigra* L	20 weeks	40.6 ppb	chambers	reduced gs	N/A
Novak et al. 2005	*Viburnum lantana*	20 weeks	40.6 ppb	chambers	reduced gs	N/A
Paakkonen et al. 1998	*Betula pendula*	11 weeks	1.5 x ambient	open field	reduced gs	red.-watered
Pollastrini et al. 2010	*Fagus sylvatiucm* L.	24 weeks	150 ppb	open-top chambers	reduced gs	red.-watered
Pollastrini et al. 2010	*Populus maximowiczii*	24 weeks	150 ppb	open-top chambers	reduced gs	red.-watered
Pollastrini et al. 2010	*Quercus robur* L	24 weeks	150 ppb	open-top chambers	reduced gs	red.-watered

Trees and woody species (continued)

Author	Species	Length of exposure	Ozone concentration	Environment	Stomatal response	Additional treatment
Roberts. 1990	*Liriodendron tulipifers*	14 weeks	200 ppb	chambers	reduced gs	N/A
Shan et al. 1996	*Pinus armandi* Franch	14 weeks	300 ppb	field chamber	reduced gs	N/A
Tjoelker et al. 1991	*Liriodendron tulipifers L.*	18 weeks	ambient + 60 ppb (approx 108	open-top field chambers	reduced gs	N/A
Tjoelker et al. 1991	*Pinus taeda* L.	18 weeks	ambient + 60 ppb (approx 108	open-top field chambers	reduced gs	N/A
Vandermeiren et al. 2002	*Solanum tuberosun* cv. Bintje	I growing season	ambient x 2	open-top chambers	reduced gs	N/A
Wullschleger et al. 1996	*Quercus rubra L*	I growing season	ambient x2	single tree chamber	reduced gs	nitrogen
Zhang et al. 2013	*Schefflera octophylla*	3 weeks	ambient	open-air	reduced gs	N/A
Dumont et al. 2013	*Populus deltoides x Populus nigra*	3 weeks	120 ppb	growth chambers	slowed response	blue light
Dumont et al. 2013	*Populus deltoides x Populus nigra*	3 weeks	120 ppb	growth chambers	slowed response	red light
Dumont et al. 2013	*Populus deltoides x Populus nigra*	3 weeks	120 ppb	growth chambers	slowed response	CO2
Dumont et al. 2013	*Populus deltoides x Populus nigra*	3 weeks	120 ppb	growth chambers	slowed response	VPD
Grulke et al. 2007b	*Quercus douglasii*	4 weeks	70 ppb	open top chamber	slowed response	light
Grulke et al. 2007b	*Quercus kelloggii*	4 weeks	70 ppb	open top chamber	slowed response	light
Paoletti & Grulke 2010	*Quercus douglasii*	8 weeks	70 ppb	open top chamber	slowed response	light
Paoletti & Grulke 2010	*Quercus kelloggii*	8 weeks	70 ppb	open top chamber	slowed response	light
Paoletti 2005	*Arbutus unedo*	13 weeks	110 ppb	greenhouse	slowed response	red.-watered
Paoletti 2005	*Arbutus unedo*	13 weeks	110 ppb	greenhouse	slowed response	reduced light

Grasslands

Hayes et al. 2012	*Dactylis glomerata*	20 weeks	70 -90 ppb	Solardomes	increased gs	red.-watered
Mills et al. 2009	*Dactylis glomerata*	20 weeks	101.3 ppb	Solardomes	increased gs	N/A
Mills et al. 2009	*Leontodon huspidus*	20 weeks	101.3 ppb	Solardomes	increased gs	N/A
Wagg et al. 2012	*Dactylis glomerata*	20 weeks	70-90 ppb	Solardomes	increased gs	red.-watered
Wilkinson & Davies 2009	*Leontodon huspidus*	5 weeks	70 ppb	growth cabinets	increased gs	red.-watered
Jaggi et al. 2005	*Trifolium prantense*	2 growing seasons	ambient x 1.5 (2002) ambient	free- air fumigation system	No change	red.-watered
Wagg et al. 2012	*Ranulculus acris*	20 weeks	70-90 ppb	Solardomes	No change	red.-watered
Zhang et al. 2012	*Chionanthus retusus* Lindl. & Paxt.	9.3 weeks	70 ppb	open top chambers	No change	N/A
Jaggi et al. 2005	*Holcus lanatus* L.	2 growing seasons	ambient x 1.5 (2002) ambient	free- air fumigation system	reduced gs	red.-watered
Jaggi et al. 2005	*Plantago lanceolata* L.	2 growing seasons	ambient x 1.5 (2002) ambient	free- air fumigation system	reduced gs	red.-watered
Neufeld et al. 1012	*Rudbeckia laciniata* L	16 weeks	natural fluctating	open field	reduced gs	N/A
Reiling and Davison 1995	*Plantago major* L. (28 populations	3 weeks	70 ppb	small chambers	reduced gs	N/A
Zhang et al. 2012	*Cornus alba L*	9.3 weeks	70 ppb	open top chambers	reduced gs	N/A
Zhang et al. 2012	*Euonymus bungeanus* Maxim	9.3 weeks	70 ppb	open top chambers	reduced gs	N/A
Zhang et al. 2012	*Photinia x fraseri*	9.3 weeks	70 ppb	open top chambers	reduced gs	N/A
Zouzoulas et al. 2009	*Gossypium allegria*	23 weeks	100 ppb	closed chambers	reduced gs	N/A
Zouzoulas et al. 2009	*Gossypium romanos*	23 weeks	100 ppb	closed chambers	reduced gs	N/A
Grulke et al. 2007a	*Rudbeckia laciniata var. digitata*	7 days	fluctuating ambient (25-80 pp	open air	slowed respsone	dynamic light

Crops

Author	Species	Length of exposure	Ozone concentration	Environment	Stomatal response	Additional treatment
Hassan et al. 1994	*Raphanus sativus* L. cv Baladey	8 days	80 ppb	chambers	increased gs	N/A
Bernacchi et al. 2006	*Glycine max* L	3 years	1.23x ambient	SoyFACE	no change	N/A
Betzelberger et al. 2012	*Glycine max*	2 growing seasons	38-120 ppb	open- field	no change	N/A
Biswas et al. 2011	*Triticum aestivum* L cv. Xiaoyan 22	3 weeks	83 ppb	open top chambers	no change	red.-watered
Flowers et al. 2007	*Phaseolus vulgaris L*	9 weeks	60 ppb	field chambers	no change	N/A
Biswas et al. 2011	*Triticum aestivum* L cv. Xiaoyan 22	3 weeks	83 ppb	open top chambers	reduced gs	well-watered
Biswas et al. 2011	*Triticum turgidum* ssp. *durum*	3 weeks	83 ppb	open top chambers	reduced gs	well-watered
Fernandez-bayon et al. 1993	*Citrullus lanatus*	3 weeks	70 ppb	chambers	reduced gs	N/A
Fernandez-bayon et al. 1993	*Cucumis melo*	3 weeks	70 ppb	chambers	reduced gs	N/A
Grantz et al. 2003	*Cucumis melo* cv. Ambrosia Hybrid	5 weeks	90ppb	open top chambers	reduced gs	N/A
Grantz et al. 2003	*Cucumis melo* cv. Ambrosia Hybrid	5 weeks	143 ppb	open top chambers	reduced gs	N/A
Grantz et al. 2003	*Gossypium barbadense* L	6 weeks	90ppb	open top chambers	reduced gs	N/A
Grantz et al. 2003	*Gossypium barbadense* L	6 weeks	143 ppb	open top chambers	reduced gs	N/A
Grulke et al. 2007	*Phaseolus vulgaris L*	l hr	120-250 ppb	curvette	reduced gs	N/A
Hassan et al. 1994	*Brassica rapa* L. cv. Sultani	8 days	80 ppb	chambers	reduced gs	N/A
Tiwari & Agrawal. 2011	*Raphanus sativus L.*	12 weeks	40.8 ppb	open- top chmabers	reduced gs	N/A
Tiwari & Agrawal. 2011	*Solanum melongena*	12 weeks	40.8 ppb	open- top chmabers	reduced gs	N/A
VanLoocke et al. 2012	*Glycine max* L	1 season	70.8 ppb	SoyFACE	reduced gs	N/A
Biswas et al. 2011	*Triticum turgidum* ssp. *durum*	3 weeks	83 ppb	open top chambers	slowed response	red.-watered
Paoletti & Grulke 2010	Phaseolus vulgaris L	4 weeks	70 ppb	open top chambers	slowed response	light

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Ozone pollution: Impacts on ecosystem services and biodiversity

This report provides a synthesis of current knowledge on the effects of ground-level ozone on ecosystem services and biodiversity. Ecosystems provide an array of services upon which humans depend for food, fresh water, climate regulation, aesthetic enjoyment and spiritual fulfilment. The increased global population along with increased standards of living and other socio-political, economic, technological and societal changes, mean that our interventions can have profound negative effects on the quality of the services provided by ecosystems. As well as having a direct impact on human health, ozone pollution also affects human well-being indirectly via effects on ecosystem services and biodiversity. This report provides a review of current knowledge of the impacts of ozone on biodiversity and supporting, provisioning, regulating and cultural services. Included are effects of ozone on primary production, carbon, nutrient and water cycling, air quality, crop and timber production, flowering and pollination, and aesthetics of the natural environment, together with the interactions with climate change. Approaches for valuing the cost of ozone pollution impacts on ecosystem services are also discussed.

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