Chapter 4

Tropospheric ozone: A continuing threat to global forests?

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Abstract

   Ozone (O_3) has a critical role in tropospheric chemistry. It absorbs radiation in
the infrared and ultraviolet regions and is very reactive and biologically toxic at
appropriate levels of exposure. At the earth's surface, O_3 is subject to long-range
transport and is the most pervasive air pollutant affecting the world's forests to-
day. The existence of O_3 has been known since 1840 and smog-induced foliar
injury on plants was first identified in the 1950s. Levels were $\sim$ 10–15 ppb during
the second half of the 1800s, compared with 30–40 ppb measured as the global
background today. By 2100, fully 50% (17 million km^2) of world forests are pre-
dicted to be exposed to O_3 at concentrations > 60 ppb. Ozone induces a variety
of symptoms and pattern of injury that are dependant upon species, genotype,
leaf position on the plant, leaf age, exposure dynamics, and meteorological fac-
tors or growth conditions. It is absolutely essential to have knowledge on species
sensitivities, O_3 profiles and toxicity concentrations for the species under investi-
gation before diagnosis can be confirmed. Ozone is generally detrimental to tree
growth and ecosystem productivity, often through induced changes in patterns
of carbon allocation or pre-disposition to insects and disease. The development
of ozone exposure–forest response relationships that are scientifically defensible
and applicable in air quality regulation has been difficult due to serious limita-
tions encountered in scaling-up experimental data. In terms of air quality reg-
ulations, North America and Europe have adopted different approaches toward
ambient ozone standard setting, with Europe opting for an approach that protects
vegetation. The US and Canada, in their individual countries, implement separate
or identical standards to protect both human health and the environment.

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1. Introduction

The earth's atmosphere is highly dynamic and very complex (Finlayson-Pitts and Pitts, 2000). In the troposphere, temperature decreases with increasing altitude due to the heating effect near the earth's surface, where incoming solar radiation is absorbed. The troposphere is separated from the stratosphere above (there, the temperature increases with altitude) by the tropopause. These characteristics result in the trapping of air pollutants within the troposphere and their chemical transformation, destruction, scavenging or deposition onto vegetation and other surfaces (Finlayson-Pitts and Pitts, 2000). Ozone (O_3) is the most pervasive, and one of the most damaging air pollutants to forests (Sandermann et al., 1997) worldwide. It is also somewhat unique in its presence both within the troposphere (0–15 km, $\sim$ 10% of the total column) and the stratosphere (15–50 km, $\sim$ 80% of the total column). In the stratosphere, O_3 (so-called "good ozone") is essential for life on earth, as it absorbs biologically damaging UV-C radiation $<$ 290 nm (Krupa, 2000). However, in the troposphere, O_3 (so-called "bad ozone") is extremely phytotoxic to plants at appropriate exposures (US EPA, 1996).

1.1. Historical aspects of surface-level ozone

The existence of tropospheric O_3 has been known since 1840. The German scientist Schönbein noted the presence of an electrical odor during thunderstorms and proposed the name ozone for it (Schönbein, 1840). By the mid 1850s, routine O_3 measurements were being conducted at more than 300 locations in Europe (Houzeau, 1858). However, it was not until the late 1940s that O_3 was confirmed as a major constituent of smog then impinging on the Los Angeles region. Unlike London during the 1950s, the Los Angeles smog was found to contain strongly oxidizing, eye-watering, and plant-killing pollutants (Finlayson-Pitts and Pitts, 2000).

Following the identification of smog-induced foliar injury on plants by Middleton et al. (1950), Haagen-Smit and co-workers conducted a classic series of laboratory experiments that confirmed that the injury reported under ambient conditions could be reproduced by concurrently exposing plants under sunlight to polluted air containing nitrogen dioxide (NO_2) and alkenes (hydrocarbons), primary pollutant precursors to catalytic O_3 formation (Haagen-Smit et al., 1952). Later, Richards et al. (1958) demonstrated that O_3 was the smog constituent that caused foliar injury to California grapes, and Heggestad and Middleton (1959) reported extensive crop damage in the eastern United States. Today, O_3 is a human health concern and is damaging vegetation in much of the industrialized world, and increasingly, in the rapidly industrializing world as well (Mauzerall and Wang, 2001).

### 1.2. *Source and formation of surface-level ozone*

Ozone has a critical role in tropospheric chemistry. It absorbs radiation in the infrared and ultraviolet regions and at the same time is very reactive and biologically toxic at appropriate levels of exposure (Finlayson-Pitts and Pitts, 2000). In its former role, O_3 is a major contributor to the global greenhouse effect. Tropospheric O_3 ($+0.40$ W m^{-2}) is estimated to be the third largest contributor to global mean radiative forcing, after carbon dioxide (CO_2; $+1.56$ W m^{-2}) and methane (CH_4; $+0.47$ W m^{-2}) (Ramaswamy et al., 2001).

There are natural and anthropogenic sources for surface level O_3 (Guenther et al., 2000; Trainer et al., 2000). Natural sources include: (1) lightning activity during thunderstorms; (2) downward intrusions of naturally produced O_3 from the stratosphere; and (3) biological processes that emit two key precursor pollutant groups, volatile organic compounds (VOC) and nitrogen oxides (NO_x). In urban areas, natural sources of VOCs and NO_x are less important than man-made sources. With the significant expansion of city centers and the resultant rise of urban conurbations, many former rural forests are now exposed to the photochemical products of urban VOC and NO_x emissions.

Sillman (1999), Kley et al. (1999) and Jenkin and Clemitshaw (2000) have provided detailed summaries of O_3 formation at the surface. The general mechanisms for catalytic O_3 formation from the oxidation of VOCs and NO_x by sunlight are well characterized. Oxides of nitrogen are emitted into the atmosphere mainly as NO (nitric oxide) from the combustion of fossil fuels. Nitric oxide is converted rapidly (reaction (1)) during daytime to NO_2 (nitrogen dioxide) via reaction with O_3 already present at the surface.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

Nitrogen dioxide is then converted back to NO by photolysis (reaction (2)). Overall, this reaction generates no net flux in chemistry and a photo-stationary state is reached where concentrations of NO and NO_2 are related to O_3:

$$NO_2 + h\nu(\text{wavelength} < 420 \text{ nm}) \rightarrow O(^3P) \tag{2}$$

$$O(^3P) + O_2(+M) \rightarrow O_3(+M) \tag{3}$$
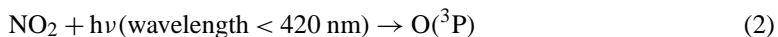
However, other daytime processes (Jenkin and Clemitshaw, 2000) convert NO_x and those are the result of the photo oxidation of carbon monoxide (CO) and VOCs. The intermediate compounds produced during those processes generate highly reactive free radicals, including the hydro-peroxy radical (HO_2) and organo-peroxy radicals (RO_2). These radicals also convert NO to NO_2 (reactions (4) and (5)), but in so doing, do not consume O_3. Hence, the photolysis of NO_2 (reaction (2)) followed by reaction (3) results in a net source
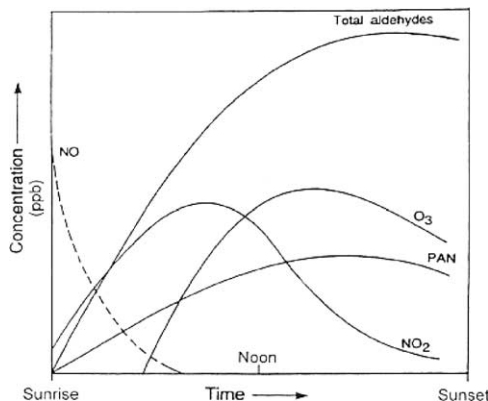
Figure 1. Idealized diurnal pattern of reactants (NO_2, and total aldehydes or hydrocarbons) and products (i.e., O_3 and PAN) in photochemical air pollution (from Krupa, 1997).

of O_3.

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{5}$$

Although other reactions occur during the daytime, under certain conditions, night-time conversion of NO_x to secondary aerosols (including nitric acid, HNO_3) at some geographic locations and their subsequent transport and deposition are of considerable importance (Takemoto et al., 2001).

Krupa (1997) provided an idealized daily pattern of urban O_3 and its precursors to highlight the predominance of daytime O_3 formation. Nitric oxide emissions and VOCs are high during the early morning due to heavy traffic (Fig. 1). These emissions scavenge some of the O_3 present (reaction (1)) leading to the production of NO_2. The NO concentrations reach a peak later in the day when the atmosphere is able to oxidize NO without completely consuming O_3. This process is maintained due to the increased presence of hydrocarbons (aldehydes) in the atmosphere, leading to a much greater NO_2: NO ratio and a peak in O_3 concentrations in mid to late afternoon. Subsequently during the day, NO_2 conversion decreases (lower sunlight) and new emissions of NO deplete the existing O_3. The cycle may then repeat itself the following day.

1.3. Transport of surface ozone

There is clear evidence for O_3 formation and/or transport at regional (NAR-STO, 2000), continental (Chameides et al., 1994) and inter-continental scales

(Derwent et al., 2002)). The presence of high O_3 concentrations is governed by the occurrences of stagnant air masses on one to several days at different spatial scales. Stagnant conditions are characterized by sufficient sunlight, high air temperature, low wind speeds and abundant precursor emissions at the local and regional scales. In addition, O_3 concentrations at the surface are governed by thermally driven meteorological phenomena: (a) up-slope, down-slope air flow in mountainous areas (e.g., Fortress Mountain, Alberta, Canada (Legge and Krupa, 1990)), (b) land–sea or land–lake circulation (e.g., Lake Michigan, (LADCO, 1995)), (c) nocturnal jets or eddy circulation (e.g., Mexico City, (Jáuregui, 2002; Bravo and Torres, 2000)), and (d) convergence zones of two air masses flowing in the opposite directions (e.g., NE US (see Solomon et al., 2000)).

Examples of long-range transport of O_3 and related pollutants include SE Canada, NE US, along the Mexico–US border (Guinnup and Collom, 1997; Roberts et al., 1996) and much of Europe (Borrell et al., 1997). Long-range transport is also important in western North America, sometimes exceeding 500 km (Blumenthal et al., 1997). Similarly, transport from Western Europe has been suggested to be partially responsible for some of the elevated O_3 concentrations in Norway (Schjoldager, 1981). Many geographically specific studies in North America and Europe show that O_3 concentrations > 100 ppb are observed when NO_x–VOC and/or O_3-laden air is transported into or downwind from an urban area, or derived from recirculation of polluted air during more than one dial cycle (Beck and Grennfelt, 1994; Blumenthal et al., 1997; Reid et al., 1996; Thuillier, 1997). It is important to note that peak concentrations of O_3 and other oxidants usually occur when a relatively high regional background level is augmented by additional O_3 by plume transport from urban areas and even from rural point sources rich in NO_x (Blumenthal et al., 1997). Normally hydrocarbons are the limiting factor in the photochemical O_3 production in the city centers, and NO_x is the limiting factor away from urban centers (Sillman, 1999). Therefore, NO_x-rich point source plumes in the rural areas downwind from urban centers are very important.

Ozone concentrations aloft are higher than the levels measured at the surface (Blumenthal et al., 1997; Hidy, 1994; Pisano et al., 1997; Reid, 1994). Evidence shows that O_3 can be carried over aloft from one day to the next and be brought to the ground when the night-time atmospheric inversion breaks up the next day (Beck and Grennfelt, 1994; Blumenthal et al., 1997; McKendry et al., 1997; Niccum et al., 1995; Roussel et al., 1996). Estimates from some of the studies indicate that carry over can account for up to 100 ppb and for nearly 50–100% of the surface O_3 in rural areas.

2. Ozone distribution at the surface and trends

2.1. Global ozone distribution

Tropospheric O_3 is the most pervasive air pollutant affecting global forests. Levels were $\sim$ 10–15 ppb more than a century ago, compared with 30–40 ppb measured as the global background today (Finlayson-Pitts and Pitts, 2000). Taking a concentration of 60 ppb as likely to be phytotoxic to sensitive forest vegetation, Fowler et al. (1999) have used a global model (STOCHEM) to simulate exposure of forests for the years 1860, 1950, 1970, 1990 and 2100. Model results show no exposure to $O_3 > 60$ ppb in 1860 and only 6% exposed by 1950 (Fig. 2). Of those forests, 75% were in temperate latitudes (parts of south-western/eastern North America, Mexico, central/eastern Europe) and 25% in the tropics.

The area of global forests exposed to $O_3 > 60$ ppb expanded threefold between 1950 and 1970 (Fig. 2). Most of Europe, eastern and parts of western North America, southern Scandinavia, parts of central/eastern Asia, South America and Africa were affected, with greatest increases (2.9–12% of forests) in tropical and subtropical forests. By 1990, some 24% of global forests were exposed to $O_3 > 60$ ppb. Fowler et al. (1999) predict that by 2100, 50% (17 million km^2) of the world's forests will be exposed to $O_3 > 60$ ppb. Large increases in the affected forest areas are calculated for both temperate–subpolar and tropical–subtropical forests.

Maximum daily surface O_3 concentrations are lowest over remote marine areas (20–40 ppb O_3) and remote tropical forests (20–40 ppb O_3). However, rural areas are exposed to daily maximums between 50–120 ppb O_3. In comparison, highest daily maximum concentrations of 100–400 ppb O_3 occur over urban–suburban areas (Krupa et al., 2001). For most of the year, a country (UK) may be a net sink for O_3, with production only exceeding losses in the photochemically active months (Coyle et al., 2003).

2.2. Trends in surface ozone concentrations

Three types of trends in surface O_3 concentrations are apparent: (1) a huge increase in the extent of O_3 and the forest areas at risk; (2) a decrease in maximum 1-hour O_3 concentrations, at least in the northern hemisphere countries having O_3 precursor control programs in place; and (3) an increase in background O_3 concentrations over much of the world. In the United States, trends in surface O_3 are based upon both 1-hour and 8-hour data. Over the past 20 years (379 sites; 1982–2001), national ambient O_3 levels decreased by 18% based on 1-hour data and by 11% based on 8-hour data (US EPA, 2002). For the period 1981–2001, the downward trend ($> 10\%$) in 1-hour maximum O_3
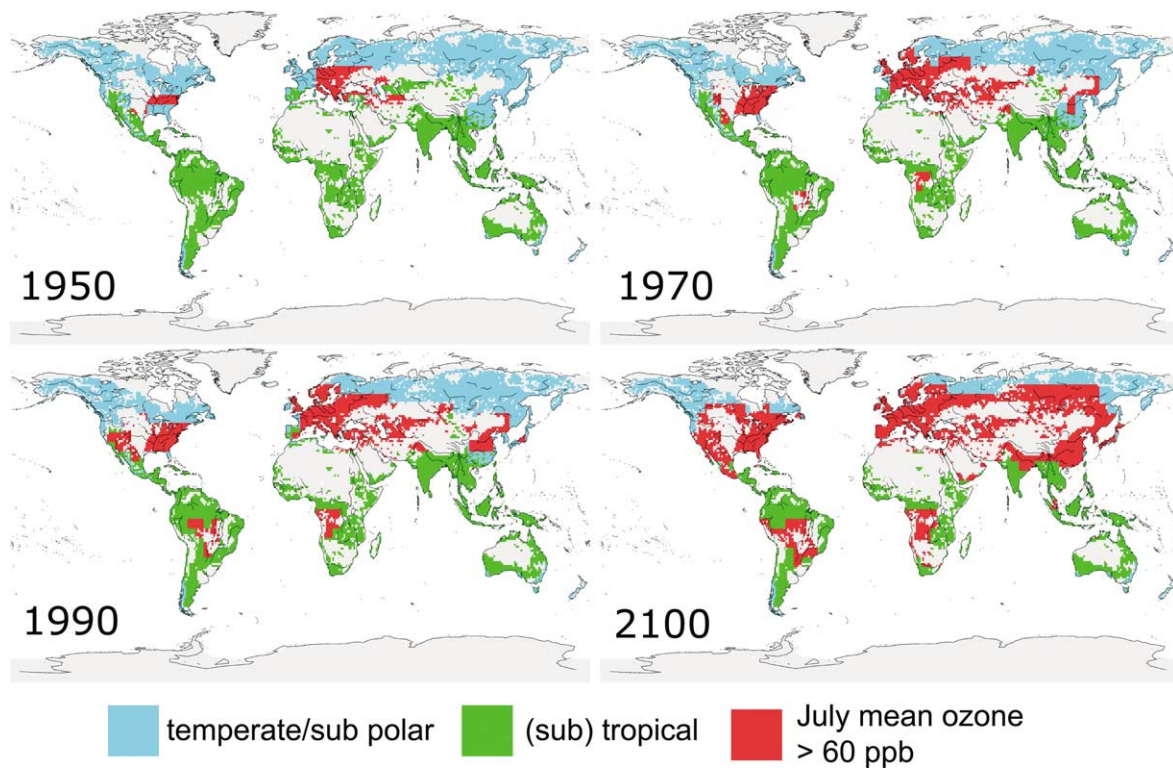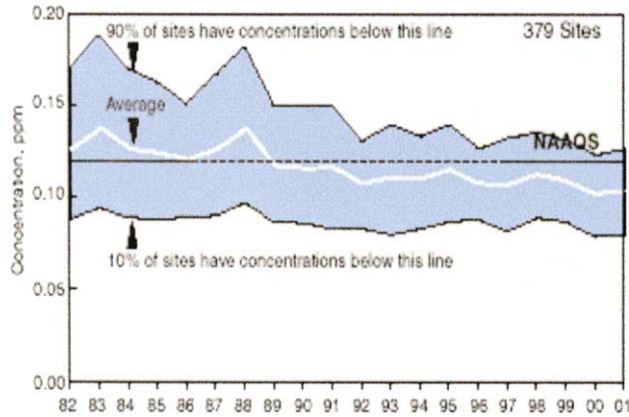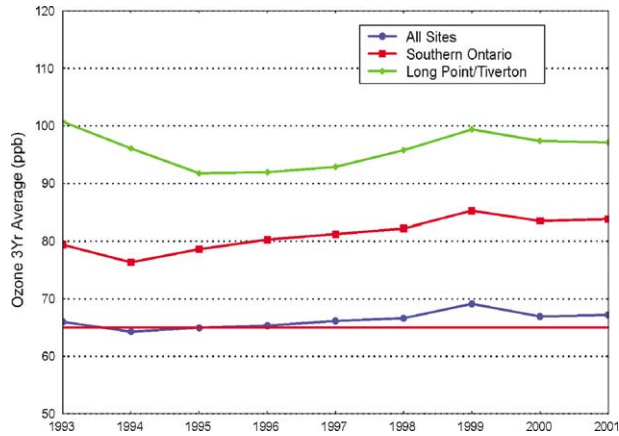
Figure 2. Global forest area where July peak surface O_3 concentration exceeds 60 ppb (from Fowler et al., 1999).

(a)

(b)

Figure 3. Comparison of surface-level O_3 trends and concentrations in North America and Europe. (a) Twenty-year trend in annual 4th highest 8-hour average O_3 at 379 ground locations in the United States (US EPA, 2002); (b) Ten-year trend in running 3-year annual 4th highest 8-hour average O_3 at 126 ground locations in Canada (from Dann, 2001); (c) Number of exceedances of the threshold value of 150 μg m^{-3} (75 ppb) O_3 in Europe during 2000 (from Hjellbrekke and Solberg, 2002). (*Continued on next page*)

levels occurred in every geographic area (Fig. 3(a)). Nearly all regions experienced improvement in 8-hour O_3 levels between 1981–2001 except the north central region, which showed little change. The west and northeast exhibited the most substantial reductions as measured by both 1-hour and 8-hour data (US EPA, 2002).
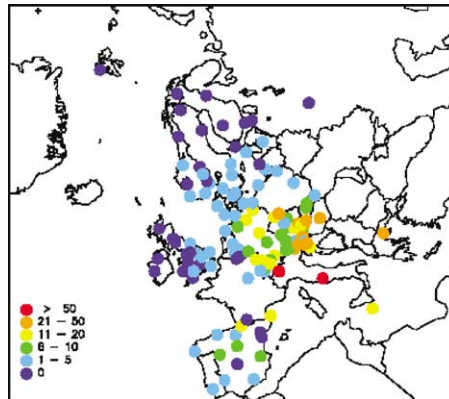
(c)

Figure 3. (*Continued*)

Across the US, highest 1-hour O_3 concentrations are typically found at suburban sites and concentrations there have decreased by 20% since 1982. However, national improvements at rural monitoring locations have been slower. One-hour O_3 levels in 2001 were 11% below those in 1982 but $< 1\%$ lower than levels in 1991 (US EPA, 2002). Since 1996, 1-hour rural O_3 concentrations have been greater than the corresponding values at urban sites. Between 1992 and 2001, the average 8-hour O_3 level in 33 national parks actually increased nearly 4%.

These trends mirror the patterns in other northern countries and regions. In Canada, trends in surface O_3 are tracked using the 3-year running average of 4th highest 8-hour daily maximum O_3 (ppb) concentration. National ambient O_3 levels averaged across all locations showed a decrease from 70 ppb in 1991 to 62 ppb in 1993 (Dann, 2001). Since 1993, the trend, except for the years 1996 and 2000, has shown increasing levels (70 ppb) through 2001 (Fig. 3(b)). Parallel trends have been observed for locations in southern Ontario. Levels decreased from 88 ppb in 1991 to 74 ppb in 1993, followed by an increase to 88 ppb in 1999 and 87 ppb in 2001.

Systematic O_3 monitoring throughout Europe began in the late 1980s and the corresponding trends are less certain than in North America (Matyssek and Innes, 1999). There are no clear trends in the alpine regions, with episodes occurring downwind of industrialized areas in northern and central regions. Nevertheless, O_3 episodes occur over the entire continent every summer. During 2000, surface-level O_3 concentrations were monitored at 124 ground locations in 26 countries (Hjellbrekke and Solberg, 2002). The 1-hour critical level for O_3 formulated by the Economic Commission for Europe (ECE) for the protection of vegetation, 150 µg m^{-3} ($\sim$ 75 ppb), was exceeded in 2000 at 95 (77%)

of European ground-level monitoring sites (Fig. 3(c)). Exceedance was considerable in the central parts of Europe. Highest hourly mean values were reported for two Italian locations (126, 128 ppb) and > 100 ppb O_3 were recorded at locations in Germany, Austria, Switzerland, Poland, Slovenia, Sweden and Denmark during a continental-scale episode around June 20. The lowest maximum hourly concentration measured was 47 ppb (Spitsbergen, Norway).

In the most recent years, some of the highest surface O_3 concentrations recorded have been in the Valley of Mexico (Mexico city urban metro-plex), representing a unique situation that deserves a brief explanation. At night and during early morning (especially during the dry season), the down slope winds from surrounding mountains and the converging circulation induced by the heat island combine to restrict the lateral dispersion of pollutants. The vertical dilution of urban gases is further restricted by the frequent (more than 70%) surface inversions observed during that period. Once the stable layer is heated from below by abundant insolation, turbulent mixing dilutes the pollutants in the vertical plane, while the regional winds, that descend to the ground (usually with a northerly component), transport pollutants to the southern suburbs, where usually the highest levels of O_3 (average 1-hour concentrations of 0.3–0.5 ppm) are observed (Jáuregui, 2002; Bravo and Torres, 2000). The Mexican O_3 Air Quality Standard (MOAQS) is a 1-hour mean of 0.11 ppm, not to be exceeded more than once per year. According to Bravo and Torres (2000), as a gross average, the MOAQS is exceeded during more than 4–5 hours per day on at least 300 days per year.

Emberson et al. (2001) have summarized some historical O_3 data for developing countries and regions. In India, maximum hourly concentrations up to 166 ppb O_3 have been reported in Delhi, with northern and western parts of the country exposed to higher concentrations. In Pakistan, surface O_3 levels increased away from Lahore, with 6-hour weekly means in peri-urban areas reaching 72 ppb during 1993–1994. In Taiwan, daily mean O_3 concentrations > 120 ppb frequently occurred between 1994 and 1997. Similarly hourly mean O_3 concentrations > 100 ppb have been recorded in Cairo and Alexandria, Egypt.

2.3. Natural surface-level ozone

Knowledge of O_3 dose and flux-uptake dynamics is essential to fully understand cause–effect relationships. Also, policy makers are required to establish and regularly review ambient O_3 (and other air pollutants) air quality standards and critical levels or loads to protect human health and vegetation (welfare). As noted previously, there is a natural background O_3, produced primarily from precursor pollutants originating from non-anthropogenic processes (Finlayson-Pitts and Pitts, 2000; Trainer et al., 2000). The levels of such back-

ground O_3 concentrations influence the maxima observed at any geographic location (Derwent et al., 2002). Thus, among the key questions being asked is the nature of the background O_3 concentrations and their significance in more remote forested areas.

To address the atmospheric portion of this issue, three different approaches have been used in determining the so-called background ambient O_3 concentrations: (a) examining historical measurement records from the late 1800s (pre-industrial times); (b) measuring current ambient O_3 concentrations at pristine geographic locations; and (c) application of photochemical models. In the context of approach (b), it is highly questionable whether there are any truly pristine locations in the world today that are not being influenced by human activity, and frequently criteria used to select such sites are not well described (see also Section 2.2).

Typical annual variations in tropospheric O_3 at Moncalieri, Italy from 1868 to 1893, Montsouris, France from 1876 to 1886 and Zagreb and Croatia in 1900 show peak values around 10 ppb (Marenco et al., 1994; Sandroni et al., 1992). In contrast, recent O_3 concentrations in the most unpolluted parts of Europe averaged between 20 and 45 ppb (Volz and Kley, 1988; Janach, 1989). A typical average tropospheric O_3 concentration of 30–40 ppb is found essentially everywhere in the world today (Finlayson-Pitts and Pitts, 2000; Derwent et al., 2002). Data from relatively remote European sites indicate a 1–2% annual increase in average O_3 concentrations during the period 1960–1990 (Janach, 1989). Such increases were attributed to greater emissions of NO_x associated with fossil fuel combustion (Volz and Kley, 1988; Janach, 1989).

Our future understanding of the issue of background O_3 concentrations is expected to improve considerably with the rapidly increasing use of passive samplers in ecological effects research (Krupa and Legge, 2000; Bytnerowicz et al., 2001). Passive samplers are inexpensive, relatively easy to use if deployed properly in the field, and do not require electrical power to operate. It is most interesting to note that some 150 years ago measurements of ambient O_3 levels were made through the use of passive samplers (Houzeau, 1858). Although passive samplers can be used over wide geographic areas, unattended for prolonged periods (1 week to a month), they provide average or total O_3 concentrations for the sampling duration. Mazzali et al. (2002) used krieging and iterative procedures based on the functional dependence of O_3 on the elevation above sea level and time of day to map vegetation exposures in a complex terrain of 80×40 km area in the southern side of the European Alps. Tuovinen (2002) achieved a rather simple model formulation to predict AOT40 (Accumulated dose Over a Threshold of 40 ppb, the European definition of exposure, Fuhrer and Achermann, 1999), by approximating the frequency distributions of hourly O_3 concentrations by their Gaussian proba-

bility. He concluded that it is possible to obtain reasonable AOT40 values even in the absence of continuous measurement data.

However, in many cases hourly ambient O_3 concentrations do not exhibit a frequency distribution that is Gaussian (Nosal et al., 2000). Furthermore, weekly or bi-weekly means or seasonal concentration summation (e.g., AOT40) methods cannot capture the dynamic changes of the atmosphere and the plant biology (Krupa and Kickert, 1997). To address that issue, Krupa and Nosal (2001) used a stochastic, Weibull probability model to predict hourly ambient O_3 concentrations from single weekly passive sampler data (weekly averages) to simulate the corresponding continuous measurements. More recently, Krupa et al. (2003) have developed a multi-variate statistical model for achieving the same purpose, but with the inclusion of meteorological variables (global radiation, air temperature, relative humidity and wind speed, variables that also influence plant O_3 uptake through stomata). If such efforts are coupled to multi-point plant response measurements, meaningful cause–effect relationships can be derived regarding the nature of the so-called background O_3 concentrations and their significance in more remote forested areas.

3. Effects of ozone on forest trees

Ozone is generally detrimental to tree growth and forest productivity. Numerous studies have been conducted on the impacts of O_3 on plant growth and biomass accumulation (see reviews by Chappelka and Samuelson, 1998; Matyssek and Innes, 1999). However, many of those studies are confounded by the artificial conditions imposed by exposure chambers and limited by the available space in such chambers to allow only single trees or small numbers of largely young, immature trees or saplings. Therefore, it is unlikely that such investigations can be used to assess risk at the landscape level.

3.1. Ozone symptomatology and species sensitivity

The symptomatology of O_3 injury on plants was first described in the 1950s (Richards et al., 1958; Heggestad and Middleton, 1959). At the present time, there is a large literature base on the development and recognition of O_3-induced foliar injury symptoms in forest trees (ICP Forests, http://www.ozone.wsl.ch). A comprehensive description, along with images of visible injury and a listing of species sensitivity, has also been provided by Krupa et al. (1998). There are a large number of tree species that are relatively sensitive to O_3 and some of these are listed in Table 1. After long-term, chronic exposure to relatively low concentrations, common symptoms of O_3 injury in broadleaf plants include changes in pigmentation or bronzing, chlorosis and

premature senescence of leaves or flowers. After short-term, acute exposure to relatively high concentrations, symptoms may include bleaching on the upper or lower leaf surface, flecking and stippling on the upper surface or bifacial necrosis (Krupa et al., 1998). On conifers, chronic exposure results in flecking and mottling of needles and often, premature loss of needles, and clear bands of chlorotic tissue (banding) and reddish-brown tip burn are common following acute exposure.

Several factors should be considered when attempting to determine O_3 injury. Ozone causes a variety of symptoms on many plants and the pattern of injury can depend on species, genotype, foliar position on the plant, leaf age, exposure dynamics and meteorological factors or growth conditions. It is essential to have knowledge about species sensitivities, O_3 profiles and toxicity concentrations for the species in question. Other stressors may also induce visible symptoms that mimic those of O_3. The use of native or transplanted indicator plants having a range of sensitivity and for which O_3 symptoms are clearly defined is extremely useful in diagnosis, especially if indicator plants are co-located with surface-level passive O_3 sampling or continuous monitoring systems. Another approach is the use of clonal field plantations containing genotypes of varying O_3 sensitivity such as trembling aspen (*Populus tremuloides* Michx.) co-located with continuous ground-level O_3 monitoring in which biomass growth, morbidity and mortality are measured over a multi-season period (Karnosky et al., this volume).

3.2. Biochemical action of ozone

The first interface between surface-level O_3 and the forest is the tree canopy. The main pathway of entry of O_3 into the leaf is through the stomata, although there is evidence for limited trans-cuticular movement. As O_3 is extremely soluble in water (although it is pH dependent), leaf surface dissolution may also be important, particularly in the late summer when a thin film of water (dew) may be present on the upper leaf surface. Once inside the leaf interior, O_3 dissolves in the fluids of the sub-stomatal cavity. However, the concentration of ozone within the leaf is essentially zero. It is the free radicals that are considered to be the initiators of cellular response. Enzymatic response within the leaf is extremely rapid, and can occur within minutes (Noormets et al., 2000). The movement and biochemical action of O_3 in the plant is well described and three major metabolic events induced by O_3 have been identified: (1) increased turnover of antioxidant systems; (2) production of symptoms similar to wounding, especially ethylene production; and (3) decline in photosynthesis (Heath, 1999).

These events have led Heath (1999) to present the following hypothesis for the induction of injury: (1) rapid entry of O_3 overwhelms the plant's antiox-

Table 1. List of some tree species that are relatively sensitive to O_3. Modified from Krupa et al. (1998) and ICP-Forests (http://www.ozone.wsl.ch)

Common name	Latin name
Ailanthus	*Ailanthus altissima* (Mill.) Swingle
Alder	*Alnus* spp., *Alnus viridis* DC.
European Alder	*Alnus glutinosa* (L.) Gaertner
Aleppo Pine	*Pinus halepensis* Miller
Ash	*Fraxinus* spp., *Fraxinus angustifolia* Vahl subsp. *angustifolia*
Aspen	*Populus tremula* L., *Populus tremuloides* Michx.
Austrian Pine	*Pinus nigra* Arnold
Beech	*Fagus sylvatica* L.
Birch	*Betula pendula* Roth
Black Poplar	*Populus nigra* L.
Cluster Pine	*Pinus pinaster* Aiton
Black Locust	*Robinia pseudoacacia* L.
Cornicabra	*Pistacia terebinthus* L.
Dogwood	*Cornus sanguinea* L.
Eastern White Pine	*Pinus strobus* L.
Field Maple	*Acer campestre* L.
Grey Alder	*Alnus incana* (L.) Moench
Green Ash	*Fraxinus pennsylvanica* Marshall
Hawthorn	*Crataegus* spp.
Hornbeam	*Carpinus betulus* L.
Italian Maple	*Acer granatense* Boiss.
Italian Stone Pine	*Pinus pinea* L.
Larch	*Larix* spp.
Mastic	*Pistacia lentiscus* L.
Narrow-leaved Ash	*Fraxinus angustifolia* Vahl subsp. *angustifolia*
Norway Maple	*Acer platanoides* L.
Norway Spruce	*Picea abies* (L.) Karst.
Plane-trees	*Platanus* spp.
Ponderosa Pine	*Pinus ponderosa* Laws.
Poplar	*Populus* spp.
Rowan, Rowan Tree, European Mountain-Ash	*Sorbus aucuparia* L.
Wild Black Cherry	*Prunus serotina* Ehrh.
Sassafras	*Sassafras albidum* (Nutt.) Nees.
Small-leaved Lime	*Tilia cordata* Miller
Smooth-leaved Elm	*Ulmus minor* Miller
Snowberry	*Symphoricarpos alba* (L.) S.F. Blake
Sweet Cherry, Wild Cherry	*Prunus avium* L.
Sweetgum	*Liquidambar styraciflua* L.
Sycamore Maple	*Acer pseudoplatanus* L.
Yellow Poplar	*Liriodendron tulipifera* L.
English Walnut	*Juglans regia* L.
White Mulberry	*Morus alba* L.
White Willow	*Salix alba* L.
Willow	*Salix* spp.
Wych Elm	*Ulmus glabra* Miller

idant response; (2) the membrane is altered such that permeability, transport and triggering mechanisms are no longer correct for the state of the cell, and the rate of ion movement and sensitivities to messages becomes either too slow, too fast or too reactive to maintain homeostasis; (3) stress-induced ethylene is transformed into a toxic product; (4) a decline in m-RNA (messenger-Ribonucleic acid) leads to a reduction in the level of Rubisco (Ribulose biphosphate carboxylase), a lowered rate of CO_2 fixation and lowered productivity; (5) the stomata close and limit CO_2 fixation; and (6) transport of sugar occurs from the source to the sinks. Carbon costs to the plant may include increased antioxidant and ethylene production as well as translocation of sugars out of source cells to sinks.

3.3. Evolution of ozone tolerance or resistance

In many industrialized regions, surface-level O_3 concentrations are high enough to cause subtle shifts in composition of natural (and semi-natural) plant communities. As such, O_3 is thought to constitute a novel evolutionary challenge for natural and managed ecosystems. In fact, there is a growing consensus that O_3 levels in many industrialized and industrializing regions are high enough to drive selection for resistant individuals within wild plant communities (Barnes et al., 1999). In the case of trembling aspen, the most widely distributed tree species in North America, there is new evidence from managed stands that rapid selection may occur over a very few years near major urban areas (Karnosky et al., 2003). That work also provides important new field evidence for the previously described (McDonald et al., 2002) competitive interaction among genotypes in the presence of elevated O_3.

The role of competitive status within a stand is a strong cofactor determining tree-growth response to O_3. It is very important, however, to remember that, depending upon genotype, negative O_3 effects in aspen may be stronger with competitive advantage or competitive disadvantage (McDonald et al., 2002). What is of concern is that in some tree species, sensitive individuals exhibit a higher genetic multiplicity and diversity. The decline of pollution sensitive tress, therefore, may result in a partial genetic depletion of forest stands through the loss of frequent alleles with potential adaptive significance to altered stress regimes of the future (Longauer et al., 2001).

In sensitive genotypes, acute O_3 injury, usually observed as the development of foliar lesions, resembles the hypersensitive response of plants to pathogens (Sandermann, 1996). An oxidative burst occurs as the initial reaction to both O_3 exposure and pathogen infection and similar signal molecules have been implicated in induction of the hypersensitive response and O_3 injury (Schraudner et al., 1998). In O_3-tolerant genotypes, either the oxidative burst is suppressed or oxidative damage is highly localized, thereby restricting the ex-

tent of foliar lesions (Koch et al., 2000). The plant antioxidant system, which scavenges naturally occurring reactive oxygen compounds, could function as a primary mechanism to alleviate the oxidative burden resulting from O_3 exposure. The ascorbate (vitamin C)–glutathione (a tripeptide) cycle has been the most intensively studied and generally there is a positive correlation of O_3 tolerance with levels of antioxidants and antioxidant enzyme activities (Conklin and Last, 1995). However, transgenic plants that have been engineered to overproduce ascorbate-glutathione antioxidant enzymes have provided mixed results regarding O_3 tolerance, depending upon the species, the cellular compartment in which the enzyme is expressed and the isozyme chosen (Mullineaux and Creissen, 1999). Numerous other antioxidant compounds are found in plants and their role in O_3 tolerance requires attention. In addition to signaling processes and biochemical protective mechanisms, plants may express differential tolerance depending upon the rate of influx of O_3 into the leaf interior. Uptake may be affected by stomatal density or by guard cell response to oxidative conditions. It appears that O_3 does not directly affect stomatal closure (Torsethaugen et al., 1999; Karnosky et al., 2003), but acts indirectly, perhaps by influencing CO_2 "fixation" or altering hormone levels. In any case, the role of stomates in influencing O_3 tolerance has not been fully characterized.

4. Case studies of forest ecosystem response to ozone

4.1. North America

McLaughlin and Percy (1999) provided a retrospective analysis of the four most prominent case studies on air pollution and forest responses in North America. They concluded that changes in depth and vigor of root systems, shifts in pool sizes and allocation patterns of carbon, and changes in supply rates of nitrogen and calcium, caused by O_3 and acidic deposition (singly or combined), represent important shifts in ecological function in diverse forest types across a large geographic area in North America. The authors predicted that the influence of those process-level changes on future health of North American forests could be greatly increased by changes in climate. Chappelka and Samuelson (1998) reported that O_3 repeatedly induces foliar injury on a number of tree species throughout much of the eastern US. However, as symptom expression is influenced by a number of endogenous and exogenous factors, it has proven difficult to confirm cause and effect at the routine biomonitoring level.

Apparent growth declines in unmanaged southeastern pines were reported in the early 1980s by Sheffield and Cost (1987). Process research conducted

through the Southern Commercial Forest Research Cooperative has been summarized in Fox and Mickler (1996). Those authors have compiled a summary of forest characteristics, biotic and abiotic stresses along with the results from a large number of integrated field and experimental research projects. Studies at ambient levels have provided evidence that moderate O_3 levels can increase water stress and reduce growth in larger trees. McLaughlin and Downing (1995, 1996) evaluated seasonal growth patterns of mature loblolly pine (*Pinus taeda* L.) trees growing in eastern Tennessee for O_3 effects. Although levels of O_3, rainfall and temperature varied widely over the period, they identified significant influences of O_3 on stem growth patterns using regression analysis. Effects of ozone exposures interacted with soil moisture and high air temperatures to reduce short-term rates of stem expansion (McLaughlin and Downing, 1995). Observed O_3 responses were rapid, occurring within 1–3 days of exposure to average O_3 concentrations at > 40 ppb.

Since the mid 1950s, much of the mixed conifer forests in Southern California has been exposed to some of the highest concentrations of O_3 in North America. Long-term exposure to high levels of O_3 and oxidants in the San Bernardino forest has produced the classic example of hierarchical forest response to O_3 (Miller and McBride, 1999). Effects from foliar level to succession stages have been documented. Average concentrations of 50–60 ppb O_3 were sufficient to cause foliar injury, early needle loss, decreased nutrient availability, reduced carbohydrate production, lower vigor, decreased height/diameter growth and increased susceptibility to bark beetles (Miller et al., 1989). The concurrence of drought, long-term reduction in precipitation and high O_3 (Arbaugh et al., 1999) has contributed to a period of growth decline in ponderosa (*Pinus ponderosa* Laws.) and Jeffrey (*Pinus jeffreyii* Grev. and Balf.) pines and bigcone Douglas fir (*Pseudotsuga macrocarpa* (Vasey) Mayr.). Decreases in radial basal area growth rates during 1950–1975 were 25–45% (ponderosa and Jeffrey pines) and 28% (bigcone Douglas fir). Other factors such as high nitrogen deposition (Bytnerowicz et al., 1999) and stand developmental changes due to fire suppression have also contributed. Older trees are the most vulnerable and additional stress imposed by high O_3 may render these trees more vulnerable to bark beetle attack (Arbaugh et al., 1999). It is interesting that, under diminishing annual average O_3 concentrations, Miller et al. (1989) have reported an improvement (1974–1988) in the foliar injury index. This recovery is not expected to prevail indefinitely due to changing precipitation patterns.

4.2. Valley of Mexico studies

Early reports of O_3 damage to forests in Mexico date from the mid 1970s when O_3-induced chlorotic mottle and premature needle senescence was observed

Table 2. A comparison of surface-level, O_3-related characteristics of Mexico City and the Los Angeles area. From Krupa (1997), modified originally from Miller (1993)

Characteristic	Mexico City	Los Angeles
Latitude	25°19′N	00°34′N
Elevation	2250 m MSL	104 m MSL
Topography	Mountain valley	Ocean front, inland mountain range
Rainfall period	Mainly summer	Mainly winter
Periods of high concentra-tions	Summer, between rains and even higher in winter	Summer
UV-A (320–400 nm)[a]	Relatively high	Lower than Mexico City
Vegetation	No respite from O_3	Respite during winter from O_3
Impact on natural ecosystems (area) (sensitive, major tree species)	Ajusco, Desierto de los Leones (approximately >80 km downwind from Mexico City) (*Pinus hartwegii*)	San Bernardino National Forest (approximately >120 km downwind from Los Angeles) (*Pinus ponderosa*)

[a]The peak wavelength for the photolysis of NO_2 is ~ 398 nm (UV-A band), a requirement for photochemical O_3 production.

on Hartweg pine (*Pinus hartwegii* Lindl.), Chihauha pine (*Pinus leiophylla* (Engelm) Shaw.), and Montezuma pine (*Pinus montezumae* var. *lindleyi*) near Mexico city (Krupa and de Bauer, 1976). In the early 1980s, a sudden decline of sacred fir (*Abies religiosa* (H.B.K.) Schdl. and Cham.) was observed in a national park situated southwest of Mexico City (Desierto de los Leones). This was thought to be due to O_3 (deBauer et al., 1985). Further investigation revealed an ongoing reduction in ring width since the early 1970s. The overall problem, including visible foliar injury, appears to be the product of complex interactions between chronic O_3 exposures and other growth-regulating factors.

Table 2 provides a comparison of surface-level, O_3-related characteristics of Mexico City (an area with some of the highest concentrations in the world at the present time) and the Los Angeles area (the area where O_3-induced vegetation injury was first reported in the 1950s). The main difference between the two cities is that, although high O_3 concentrations persist throughout the year in Mexico City, the winter season is a period of respite for O_3 levels in Los Angeles. In the Valley of Mexico, nine different native pine species represent 43% of the total forested land cover. Based on foliar injury, several of these species exhibit moderately high to very high sensitivity to O_3 (Miller et al., 2002). Of concern are the reductions in their normal growth rates, an issue that requires a detailed study.

4.3. European forest health monitoring

One-third of Europe is covered in forest. Despite concerns (Ferretti et al., 1999), annual crown condition surveys remain the main tool in the overview of European forest condition. In the most recent (2001) assessment, 22.4% of 132 000 trees assessed were classified as moderately or severely defoliated (UN-ECE and EC, 2002). In 2000, exceedance of the European critical level for O_3 was considerable over large parts of central and Eastern Europe (Hjellbrekke and Solberg, 2002). Although O_3 may adversely affect tree growth, unequivocal evidence for O_3-induced foliar injury has only been found at few locations. Research suggests that risks exist for European forests, but that those risks need to be validated at the stand level (Matyssek and Innes, 1999).

The impact of O_3 on European forests has been reviewed in Skarby et al. (1998). Evidence for O_3 stress was at that time inferred and was derived in the main from controlled fumigation experiments using young saplings. In the late 1990s, no relationship existed between needle loss in the field and O_3 levels. In comparison with the effects of extended drought or nutrient stress, the effects of O_3 were stated to be much milder with respect to tree growth. Therefore, Skarby et al. (1998) concluded that a link between the occurrence of O_3 and forest damage had not at that time been unequivocally established.

Although accelerated growth trends (attributed to excess nitrogen) have been found in parts of northern (EFI, 2002), most of central, and some parts of southern Europe, decreasing trends have been found where exposure to pollutants (including O_3) or exceptional climatic conditions prevailed. In 2001, visible injury assessments were carried out on 53 intensive monitoring plots located in 9 countries. Ozone injury was reported on the main tree species growing at 18 of those plots. In central Europe, visible ozone damage on European beech (*Fagus sylvatica* L.) was reported on 27% of the plots (UN-ECE and EC, 2003). However, by 2002, the precise role of O_3 in those declining growth trends remains to be elucidated.

5. Ozone air quality standards in North America and critical levels in Europe

Ambient air quality standards in North America are based on the best available scientific knowledge and understanding which is balanced by social, economic and political considerations at the time they are set. These air quality standards provide policy makers and regulators with a measure of air quality for air contaminants for the purpose of compliance with legislation (IUAPPA, 1995). Ambient air quality standards do not assume the existence of a concentration threshold for receptor response and, therefore, target values are often

substituted for the regulatory purposes. In Europe, the United Nations Economic Commission for Europe (UN-ECE) has taken an approach to managing ambient air quality that is quite different from North America, with the concept of critical levels being applied. Critical levels are defined as concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials, may occur according to present knowledge (UN-ECE, 1988; Tema Nord, 1994). Critical levels are set based solely on the best available scientific knowledge and understanding and acknowledgement that a threshold concentration for receptor response exists. They are not used directly for air quality compliance purposes but rather as an integral part of emission control/abatement strategies (Bull, 1991). That being said, the critical levels concept implicitly assumes that all adverse effects should be prevented regardless of the economic costs of reducing pollutant emissions. A more in-depth discussion of these matters is provided in Legge et al. (1995) and Ashmore (2002).

5.1. North American standards for ozone

In the United States, the Clean Air Act requires the Environmental Protection Agency (US EPA) to propose and promulgate the form and level of National Ambient Air Quality Standards (NAAQS) for selected ubiquitous pollutants that are known to endanger public health and welfare and to issue primary and secondary standards for them. A primary standard is defined as one of attainment and maintenance that allows an adequate margin of safety for sensitive population groups to protect the public health. A secondary standard is one of attainment and maintenance which protects the public welfare from any known or anticipated adverse effects associated with the presence of the pollutant in ambient air (US EPA, 1996). Welfare effects relate to impacts on vegetation, crops, ecosystems, visibility, climate and man-made material to name a few. Primary and secondary NAAQS can be different or they can be the same. The previous primary O_3 standard which was set in 1979, is currently being phased out and is the maximum hourly O_3 concentration of 0.12 ppm (120 ppb) not be exceeded more than 1 day per calendar year. The US EPA has replaced the 1979 primary O_3 NAAQS with a new primary O_3 NAAQS set at 0.08 ppm (80 ppb) calculated as the 3-year average of the annual fourth highest daily maximum 8-hour O_3 concentrations measured at each monitor within an area (Federal Register, 1997).

Before setting a new NAAQS, the US EPA conducts an open and rigorous scientific assessment process. First, a criteria document for the pollutant in question is prepared by the US EPA's National Center for Environmental Assessment (NCEA) that summarizes the current state of the science in the peer-reviewed scientific literature as it relates to public health and welfare. Based

on the science in the criteria document, the US EPA's Office of Air Quality Planning and Standards (OAQPS) develops a 'staff paper' that includes recommendations to either retain and/or revise the current NAAQSs. Both documents undergo rigorous scientific peer review by the US EPA's Science Advisory Board's Clean Air Scientific Advisory Committee (CASAC), as well as comment from the public, industry and other interest groups. Based on all of the above, the US EPA Administrator then decides whether or not to maintain or revise the current NAAQSs.

In 1998, Canada began development of a new ambient O_3 air quality standard under the Canada-wide Accord on Environmental Harmonization under the leadership of the Canadian Council of Ministers of the Environment (CCME). The fundamental concepts accepted as prerequisites for a new standard were as follows: (1) a numerical target value; (2) a time line by which the target is to be achieved; and (3) a reporting protocol. Canada adopted a Canada-Wide Standard (CWS) for ozone in 2000 (CCME, 2000). The CWS for O_3 has been set at 65 ppb with an 8-hour averaging time with achievement based upon the fourth highest annual measurement, averaged over 3 consecutive years. This target is to be achieved by 2010. Community-oriented monitoring sites in census metropolitan areas with greater than 100 000 people will be included, but rural and source-specific sites will be excluded for CWS achievement determination.

5.2. European critical levels for ozone

Critical levels for vegetation for ground-level ozone in Europe have evolved through a series of UN-ECE workshops: Bad Harzburg, Federal Republic of Germany, 1988 (UN-ECE, 1988); Egham, United Kingdom, 1992 (Ashmore and Wilson, 1992); Bern, Switzerland, 1993 (Fuhrer and Achermann, 1994); Kuopio, Finland, 1996 (Kärenlampi and Skärby, 1996); Gerzensee, Switzerland, 1999 (Fuhrer and Achermann, 1999); and Göteborg, Sweden, 2002 (Karlsson et al., 2003). Based on the available scientific literature at the time, the UN-ECE (1988) provisionally defined the critical levels for short-term O_3 exposures as 75 ppb (150 $\mu g\,m^{-3}$) for a 1-hour mean and 30 ppb (60 $\mu g\,m^{-3}$) for an 8-hour mean and for longer-term O_3 exposures as 25 ppb (50 $\mu g\,m^{-3}$) for a 7-hour daily mean (0900–1600) averaged over the vegetation growing period.

As scientific knowledge and understanding advanced and the workshop process proceeded, however, a new two-stage approach to critical levels was proposed by the UN-ECE called Level I and Level II (Fuhrer and Achermann, 1994). The recommendation was made for critical levels for O_3 for forests, agricultural crops and semi-natural vegetation to be based on the accumulated mean hourly exposure of vegetation to ozone over an O_3 concentration

threshold of 40 ppb expressed as ppbh or ppmh and was called AOT40. The first-stage or Level I approach was not to consider any biotic or abiotic factors that might modify the response of vegetation to ozone. Level I was to be used to assess maximum potential risk to vegetation from ozone exposure. The second-stage or Level II approach, however, was to incorporate the modifying influence of biotic factors, as well as abiotic factors, on the responses of vegetation to ozone. Level II was to be used to more realistically quantify impacts of ozone exposure and their economic consequences to vegetation.

The provisional Level I AOT40 value for forests has been set at 10 000 ppbh (10 ppmh) and is calculated for daylight hours with global clear-sky radiation greater than 50 W m^{-2} during a six-month period (April–September). The long-term provisional Level I AOT40 value for semi-natural vegetation and agricultural crops has been set at 3000 ppbh (3 ppmh) calculated for daylight hours with global clear-sky radiation greater than 50 W m^{-2} for the appropriate 3-month growing season (Kärenlampi and Skärby, 1996). No Level II values have been established at this time as the underlying science for Level II is a work in progress.

The UN-ECE reported in Göteborg, Sweden (Karlsson et al., 2003) that one of the main difficulties in establishing O$_3$ critical levels at Level II is to determine the impact of ambient ozone on mature trees under field conditions. Data from Scandinavia suggest that a lower AOT40 value is required to protect the most sensitive tree species growing in northern Europe, under long-day, low vapor pressure deficit (VPD) conditions and short growing seasons. It was concluded that a stepwise procedure to enable a Level II estimate of ozone critical levels for forests is needed. The first step was the development of ozone uptake–biomass response relationships from experimental data using young trees. The following three approaches were suggested as possibilities: (1) modification of AOT with response factors; (2) MPOC (Maximum Permissible Ozone Concentration); and (3) flux-based concept. The final consensus from the Göteborg workshop indicated that the effective dose to forest trees based upon stomatal uptake should be implemented for future ozone critical levels for forests and that the AOT approach should be retained as a provisional measure.

North America and Europe have clearly taken different approaches in ambient ozone standard setting, with the latter opting for an approach to specifically protect vegetation. European research is now focused on incorporating the ozone uptake metric into the next generation of Level II, flux-based critical levels for ozone. It is clear that this process will serve as a useful guide for an equivalent standard-setting approach in North America (Mauzerall and Wang, 2001; Karlsson et al., 2003).

6. Uncertainties in current scientific understanding on ozone and forests

6.1. Uncertainties due to experimental methodologies

Much of our knowledge of tree species responses to O_3 is largely derived from experimental exposure in continuous stir-tank reactors, growth chambers and open-top chambers (Manning and Krupa, 1992; Chappelka and Samuelson, 1998), although a few studies relate to ambient field observations, e.g., the San Bernardino Mountains of Southern California (Miller and McBride, 1999). However, some recent field studies include chamber-less, free air O_3 enrichment (Karnosky et al., 2003). For instance, the exposure of tree communities to O_3 in Free Air Carbon Dioxide Enrichment (FACE) facilities has created an opportunity to study multi-trophic, long-term (5–10 years) responses of stand-level forest ecosystems under inter-annual climate variability and relatively unaltered experimental microclimate. At Aspen FACE (Wisconsin, USA), O_3 effects are being studied in terms of carbon sequestration, physiological processes, growth and productivity, competitive interactions and stand dynamics, and interactions with pests and ecosystem processes, such as foliar decomposition, mineral weathering, and nutrient cycling. Overall during 1998–2002, the response to O_3 exposure at growing season, daytime hourly average concentrations between 46–56 ppb (max. AOT40 25 000 ppbh; max CWS 96 ppb) has been remarkably consistent from leaf to ecosystem levels in pure aspen (five genotypes) and aspen/birch stands (Karnosky et al., 2003). Feedbacks to growth include a large reduction in both height and diameter growth at the population level (Percy et al., 2002). When averaged across five clones ranging from tolerant to highly sensitive to O_3, height growth began to diverge following 3 years of fumigation and was 12% reduced from growth in controls (Fig. 4(a)). Diameter growth, however, diverged between treatments almost immediately after year 2 of fumigation and was 13% reduced from that in the controls at year 4 (Fig. 4(b)). Physiological and genetic responses are cascading through the ecosystem, leading to a large reduction in stand net primary productivity and biomass (Karnosky et al., 2003).

Feedbacks to plant growth have also been shown in free-air O_3 exposure due to alteration of chemical plant defenses leading to a "bottom up" driven increased performance of some important herbivores (Percy et al., 2002). Trembling aspen normally accumulates high concentrations of phenolic glycosides (PG) that have important roles as protective agents against pests. Significantly, PG concentrations decreased following aspen exposure to O_3 leading to a large increase in forest tent caterpillar female pupal mass (Fig. 5), a surrogate for insect performance in the most important defoliator of deciduous forest trees in North America. It is important to emphasize that only through studies such as the Aspen free-air, field, stand-level, multitrophic studies can longer-term
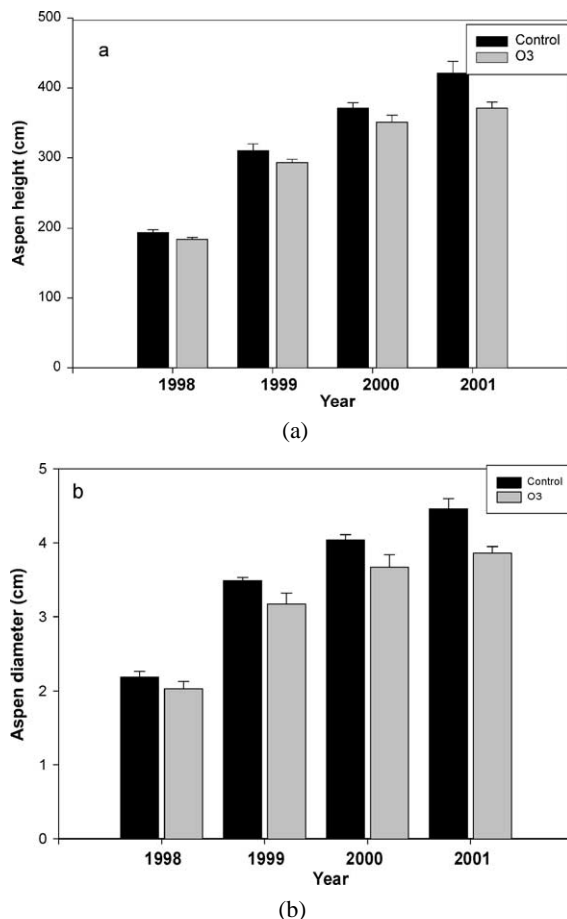
(a)

(b)

Figure 4. Effect of 4 years of free-air exposure at Aspen FACE on growth of trembling aspen (*Populus tremuloides* Michx.) averaged across five clones varying in sensitivity to O_3. (a) Trend in trembling aspen height growth; (b) trend in trembling aspen diameter growth. Data are means and 1 SE averaged across three FACE rings. Modified from Percy et al. (2002).

changes in forest function be studied and, importantly, forest-dose response relationships better defined.

Independent of the various experimental methods used, there are a number of uncertainties associated with our current understanding. In most investigations, saplings rather than mature tree responses were examined. Although efforts are being made to scale the results to mature trees (Samuelson and Kelly, 2001; Kolb and Matyssek, 2001), there are other issues: (1) Use of inadequate number of O_3 exposure treatments to fully define the response surface (Khuri
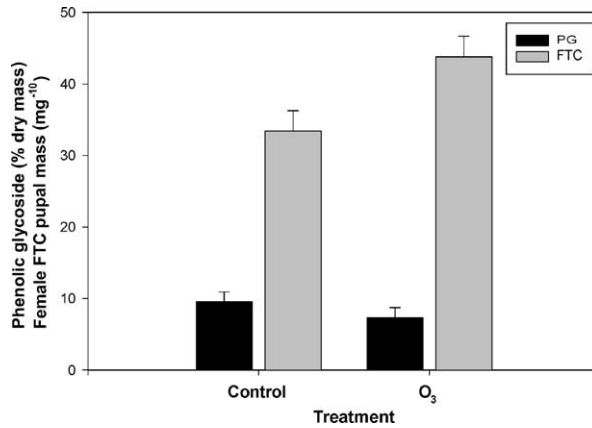
Figure 5. The effect of O_3 exposure at Aspen FACE on trembling aspen (*Populus tremuloides* Michx.) foliar susceptibility to herbivorous insects. Change in chemical leaf defence as manifested by concentrations of the important defensive metabolites, phenolic glycosides (PS); consequential change in performance of the important lepidopteran, leaf-chewing insect, the forest tent caterpillar (FTC) as assessed by female pupal mass. Modified from Percy et al. (2002).

and Cornell, 1996; Myers, 1971), (2) Use of O_3 treatments that do not simulate the stochasticity of the ambient fluxes and thus, realism, (3) Use of uni- or bi-variate systems and lack of emphasis on multi-variate systems, and (4) Use of monocultures, thus eliminating interspecies competition. Individuals growing in multi-species assemblages may respond differently to O_3 than individuals of the same species growing alone. For example, response of ponderosa pine to O_3 was greater when growing in the presence of a grass competitor than in its absence (Andersen and Grulke, 2001).

6.2. Definition of ozone exposure–forest response relationships

Kickert and Krupa (1991) provided a comprehensive review of the literature on modeling plant response to tropospheric O_3. In that context, cause–effect relationships have been established through the use of empirical or statistical and mechanistic or process models. Each approach has its advantages and disadvantages. Much of the effort in the US during the last decade has been directed to statistical models that have relied heavily on correlations. However, correlation does not necessarily mean causality (Snedcor and Cochran, 1978) and should have an underlying meaning. Furthermore, many such empirical models have not performed equally well every time. They are single-point models using season end biomass as the dependent variable. Such efforts cannot account for the dynamics of the atmosphere and the corresponding plant physiological

phenology-dependent processes of avoidance, compensation or stress repair and the consequent stochastic cause–effect relationships (Krupa and Kickert, 1997). The associated uncertainty can be addressed by the use of multi-point models that use response measurements as a time series.

Another source of uncertainty is the definition of the O_3 concentrations. Using average values for non-normally distributed populations of data such as the ambient O_3 concentrations is inappropriate (Krupa and Kickert, 1997). More importantly, average values cannot explain the temporal or spatial dynamics in the O_3 concentrations and their flux. Similarly summation methods rely on a single threshold value (e.g., SUM06, sum of all hourly concentrations equal to or above 60 ppb, US EPA (1996)). In ecological research a single threshold is inappropriate, as opposed to a range of such values (Woodwell, 1975).

Until now, numerous studies have relied on the use of measured air concentrations of O_3 at some height in establishing cause–effect relationships (US EPA, 1996). In reality, it is the actual O_3 concentration at the canopy level and absorbed by the plant that results in an effect. In recent years, a great deal emphasis has been directed by scientists within the European Community to adapt an ozone flux-based approach to protect vegetation (see Karlsson et al., 2003). However, concerted efforts in that direction have not taken place in North America.

At the field monitoring scale, large and well-coordinated programs have attempted to relate forest condition/health at national or supra-national scales to O_3 exposure. Despite a large incidence of foliar injury (27% of plots) in a given year due to O_3, cause–effect linkage is rarely achieved (UN-ECE and EC, 2003). It is clear, however, that in some cases air pollutants (including O_3) have been successfully linked with changes in forest condition/health. Retrospective analysis (Percy, 2002) indicates that if spatial/temporal scales of the stressor (including O_3) are considered, appropriate indicators are measured, ecosystem function is investigated and if there is continuity of investigation such as described in Section 4.1 and summarized in Table 3, then the role of O_3 in relation to other man-made and natural stresses can be elucidated.

One important factor that must be remembered when cause–effect relationships are studied or when dose–response functions are being developed is the fact that plants are seldom exposed to one air pollutant singly, but usually a number of pollutants together. Although a simultaneous occurrence of air pollutants like SO_2, NO, NO_2, O_3 or NH_3 at phytotoxic levels is unusual (Fangmeier et al., 2002), co-exposure of forests to pollutant mixtures does occur even if the patterns of exposure differ spatially and temporally by pollutant. Although our knowledge of the effects of pollutant mixtures is far from satisfactory owing to experimental constraints imposed in running the required multifactorial experiments, the combined effect of O_3 and SO_2 has been shown to be either synergistic or antagonistic (Fangmeier et al., 2002) and the interac-

Table 3. Retrospective analysis of degree of success in documenting the role of air pollution as an important factor in forest health. Modified from Percy (2002)

Successful when:	Unsuccessful when:
Network-level monitoring is succeeded by process-oriented research across spatial and temporal scales of stressors	Systematic monitoring is disconnected from process-oriented research
Appropriate indicators of ecosystem function are investigated at an intensity/extent appropriate to stressors and ecosystem	Endpoints measured are inappropriate or unresponsive to stressors
Systematic monitoring is not stratified on stressor distribution patterns	System protocols are not developed for single agents and integrated into multi-variant systems
Investigations in essential processes/cycles are integrated with investigations in ecosystem resilience through pests, genetics, succession, etc.	Hierarchical nature of forest response is not recognized
There is continuity of investigation as in long-term San Bernardino Mountain Forest-Oxidant Case Study	Dominant role of air pollutants in predisposition to other stressors is not recognized

tion of these two important globally distributed pollutants must be considered, particularly given the predicted increase in geographic co-occurrence of sulfur and O_3 during this century. Area of the world's forests at risk from S is predicted to increase 114% by 2050, with the largest proportional increases, as for O_3, being in tropical and subtropical forests (Fowler et al., 1999).

7. Conclusions

Ozone is a natural constituent of the surface layer in which the world's forests grow. However, man-made emissions of the O_3 precursors NO_x and VOCs have led to a large increase in average surface-level O_3 in the northern hemisphere during the past 100 years. In many regions of the world, O_3 concentrations are now damaging to vegetation, materials and human health. Between 1990 and 2100, the percentage of world forests exposed to damaging O_3 levels is expected to increase from 24% to fully 49%, or 17 million km^2 (Fowler et al., 1999).

The underlying processes responsible for the formation and deposition of O_3 are reasonably well understood. Despite some remaining uncertainties, the rate of O_3 deposition onto a given forest area can be calculated once ambient concentrations are known and information on key environmental variables such as wind velocity, air temperature, solar radiation and degree of leaf surface wetness is available. Indeed, recent progress in scientific understanding

has led to the development of O_3 mass budgets at the country level (Coyle et al., 2003). Yet, true risk assessment remains problematic due to scientific uncertainty around the magnitude of O_3 flux into the plant. Indeed, standards and critical levels currently used by regulators remain based upon some index of O_3 exposure alone.

New approaches employing passive O_3 samplers are providing valuable data on the patterns of exposure in forested regions. Case studies have documented O_3 damage to health and function across diverse forest types and over a wide geographic range. New evidence from free-air experiments is pointing to the multi-trophic nature of forest ecosystem response to longer-term, lower levels of O_3 and to the important role of O_3 in predisposition to pests and environmental change. When assessing risk to forests from O_3, one must remember that North American ambient air quality standards that are set for compliance regulation purposes, do not in fact assume the existence of a concentration threshold for receptor response. In contrast, European critical levels are set based solely upon the best available scientific knowledge and understanding and the presumption that a threshold concentration for receptor response exists. The future development of new flux-based critical levels in Europe and biologically based dose–response functions in North America will allow policy makers for the first time to more accurately predict O_3 risk to the world's forests in the future.

References

Andersen, C.P., Grulke, N.E., 2001. Complexities in understanding ecosystem response to ozone stress. Human Ecol. Risk Assess. 7, 1169–1182.

Arbaugh, M.J., Peterson, D.L., Miller, P.R., 1999. Air pollution effects on growth of ponderosa pine, jeffrey pine and bigcone Douglas-fir. In: Miller, P.R., McBride, J.R. (Eds.), Oxidant Air Pollution Impacts in the Montane Forests of Southern California. A Case Study of the San Bernardino Mountains. Springer-Verlag, New York, pp. 179–207.

Ashmore, M.R., 2002. Air quality guidelines and their role in pollution control policy. In: Bell, J.N.B., Treshow, M. (Eds.), Air Pollution and Plant Life, 2nd Edition. Wiley, Chichester, England, pp. 417–429.

Ashmore, M.R., Wilson, R.B., 1992. Critical Levels of Air Pollutants for Europe. Background papers prepared for the United Nations Economic Commission for Europe Workshop on Critical Levels, Egham, United Kingdom, March 23–26, 1992. Air Quality Division, Department of the Environment, London, United Kingdom.

Barnes, J.D., Bender, J., Lyons, T., Borland, A., 1999. Natural and man-made selection for air pollution resistance. J. Exp. Bot. 50, 1423–1435.

Beck, J.P., Grennfelt, P., 1994. Estimate of ozone production and destruction over northwestern Europe. Atmos. Environ. 28, 129–140.

Blumenthal, D.L., Lurmann, F., Kumar, N., Dye, T., Ray, S., Korc, M., Londergan, R., Moore, G., 1997. Transport and mixing phenomena related to ozone exceedances in the Northeast US. Report STI-996133–1710, Sonoma Technology, Santa Rosa, CA.

Borrell, P., Builtjes, P.J.H., Hov, Ø., Grennfelt, P. (Eds.), 1997. Photo-oxidants, Acidification and Tools: Policy Applications of EUROTRAC Results. In: Transport and Chemical Transformation of Pollutants in the Troposphere, Vol. 10. Springer-Verlag, Berlin, Heidelberg.

Bravo, A.H., Torres, J.R., 2000. The usefulness of air quality monitoring and air quality impact studies before the introduction of reformulated gasolines in developing countries. Mexico City: a real case study. Atmos. Environ. 34, 499–506.

Bull, K.R., 1991. The critical loads/levels approach to gaseous pollutant emission control. Environ. Pollut. 69, 105–123.

Bytnerowicz, A., Krupa, S., Cox, R. (Eds.), 2001. Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research. In: The Scientific World, Vol. 1, pp. 461–462 (Preface).

Bytnerowicz, A., Fenn, M.E., Miller, P.R., Arbaugh, M.J., 1999. Wet and dry pollutant deposition to the mixed conifer forest. In: Miller, P.R., McBride, J.R. (Eds.), Oxidant Air Pollution Impacts in the Montane Forests of Southern California. A Case Study of the San Bernardino Mountains. Springer-Verlag, New York, pp. 235–269.

Chameides, W.L., Kasibhatla, P.S., Yienger, J., Levi II, H., 1994. Growth of continental-scale metro-agro-plexes, regional ozone pollution, and world food production. Science 264, 74–77.

CCME (Canadian Council of Ministers of the Environment), 2000. Canada-Wide Standards for Particulate Matter (PM) and Ozone. Available at http://www.ccme.ca/assets/pdf/pmozone_standard_e.pdf.

Chappelka, A.H., Samuelson, L.J., 1998. Ambient ozone effects on forest trees of the eastern United States: a review. New Phytol. 139, 91–108.

Conklin, P.L., Last, R.L., 1995. Differential accumulation of antioxidant mRNAs in *Arabidopsis thaliana* exposed to ozone. Plant Physiol. 109, 203–212.

Coyle, M., Smith, R., Fowler, D., 2003. An ozone budget for the UK: using measurements from the national ozone monitoring network; measured and modelled metereological data, and a 'big-leaf' resistance analogy model of dry deposition. Environ. Pollut. 123, 115–123.

Dann, T., 2001 Trends and levels of CWS Pollutants, Presentation to an AWMA Speciality Conference on Canada Wide Standards, Toronto, March 7, 2001.

deBauer, M.L., Tejeda, T.H., Manning, W.J., 1985. Ozone causes needle injury and tree decline in *Pinus hartwegii* at high altitudes in the mountains around Mexico City. J. Air Pollut. Control. Assoc. 35, 838.

Derwent, R., Collins, W., Johnson, C., Stevenson, D., 2002. Global ozone concentrations and regional air quality. Environ. Sci. Technol. 36, 379–382.

Emberson, L.D., Ashmore, M.R., Murray, F., Kuylenstierna, J.C.I., Percy, K.E., Izuta, T., Zheng, Y., Shimizu, H., Sheu, H., Liu, C.P., Agrawal, M., Wahid, M., Abdel-latif, N.M., van Tienhoven, M.N., de Bauer, L.I., Domingos, M., 2001. Impacts of air pollutants on vegetation in developing countries. Water Air Soil Pollut. 130, 107–118.

EFI (European Forest Institute), 2002. Nitrogen deposition appears to be the main cause of increased forest growth in Europe, http://www.efi.fi/news/2002/recognition.html.

Fangmeier, A., Bender, J., Weigel, H.-J., Jäger, H.-J., 2002. Effects of pollutant mixtures. In: Bell, J.N.B., Treshow, M. (Eds.), Air Pollution and Plant Life, 2nd Edition. Wiley, Chichester, England, pp. 251–272.

Federal Register, 1997. National Ambient Air Quality Standards for Ozone, Rules and Regulations, Environmental Protection Agency, 40 CFR Part 50, Final Rule. 62(138), July 18, 1997, p. 38856.

Ferretti, M., Bussotti, F., Cenni, E., Cozzi, A., 1999. Implementation of quality assurance procedures in the Italian programs of forest condition monitoring. Water Air Soil Pollut. 116, 371–376.

Finlayson-Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego, CA.

Fowler, D., Cape, J.N., Coyle, M., Flechard, C., Kuylenstierna, J., Hicks, K., Derwent, D., Johnson, C., Stevenson, D., 1999. The global exposure of forests to air pollutants. Water Air Soil Pollut. 116, 5–32.

Fuhrer, J., Achermann, B. (Eds.), 1994. Critical Levels for Ozone – A UN-ECE Workshop Report. UN-ECE Convention on Long-Range Transboundary Air Pollution. Bern, Switzerland, November 1–4, 1993. Federal Research Station for Agricultural Chemistry and Environmental Hygiene, Liebefeld-Bern, Switzerland.

Fuhrer, J., Achermann, B. (Eds.), 1999. Critical Levels for Ozone – Level II, UN-ECE Workshop Report. UN-ECE Convention of Long-Range Transboundary Air Pollution. Gerzensee, Switzerland, April 11–15, 1999. Swiss Agency for the Environment, Forests and Landscape, Berne, Switzerland.

Fox, S., Mickler, R.A. (Eds.), 1996. Impact of Air Pollutants on Southern Pine Forests. Springer-Verlag, New York.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., Fall, R., 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. Atmos. Environ. 34, 2205–2230.

Guinnup, D., Collom, R., 1997. Final Report: Summary and Integration of Results. Air Quality Analysis Workgroup, Ozone Transport Assessment Group, Ozone Transport Commission. Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, NC.

Haagen-Smit, A.J., Brunelle, M.F., Haagen-Smit, J.W., 1952. Ozone cracking in the Los Angeles area. Rubber Chem. Technol. 32, 1134–1142.

Heath, R.L., 1999. Biochemical processes in an ecosystem: How should they be measured? Water Air Soil Pollut. 116, 279–298.

Heggestad, H.E., Middleton, J.T., 1959. Ozone in high concentrations as cause of tobacco leaf injury. Science 129, 208–210.

Hidy, G.M., 1994. Atmospheric Sulfur and Nitrogen Oxides. Academic Press, San Diego, CA.

Hjellbrekke, A.-G., Solberg, S., 2002. Ozone measurements 2000, EMEP/CCC Report 5/2002, Kjeller, Norway.

Houzeau, A., 1858. Preuve de la présence dans l'atmosphère d'un nouveau principe gazeux, l'oxygène naissant. C. R. Acad. Sci. Paris 46, 89–91.

IUAPPA (International Union of Air Pollution Prevention and Environmental Protection Associations), 1995. Clean Air Around the World—National Approaches to Air Pollution Control, 3rd Edition. IUAPPA, Brighton, England.

Janach, W.E., 1989. Surface ozone: trend details, seasonal variations, and interpretation. J. Geophys. Res. 94, 18289–18295.

Jáuregui, E., 2002. The climate of the Mexico City air basin: its effects on the formation and transport of pollutants. In: Fenn, M.E., de Bauer, L.I., Hernández-Tejeda, T. (Eds.), Urban Air Pollution: Resources at Risk in the Mexico City Air Basin. Springer-Verlag, New York, pp. 86–117.

Jenkin, M.E., Clemitshaw, K.C., 2000. Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer. Atmos. Environ. 34, 2499–2527.

Kärenlampi, L., Skärby, L., 1996. Critical Levels for Ozone in Europe: Testing and Finalizing the Concepts, UN-ECE Workshop Report. UN-ECE Convention on Long-Range Transboundary Air Pollution. Kuopio, Finland, April 15–17,1996. Department of Ecology and Environmental Science, University of Kuopio, Kuopio, Finland.

Karlsson, P.E., Selldén, G., Pleijel, H., (Eds.) 2003. Establishing Ozone Critical Levels II. UN-ECE Workshop Report. IVL Report B 1523. IVL Swedish Environmental Research Institute, Gothenburg, Sweden.

Karnosky, D.F., Pregitzer, K.S., Hendrey, G.R., Percy, K.E., Zak, D.R., Lindroth, R.L., Mattson, W.J., Kubiske, M., Podila, G.K., Noormets, A., McDonald, E., Kruger, E.L., King, J., Mankovska, B., Sober, A., Awmack, C.S., Callan, B., Hopkin, A., Xiang, B., Hom, J., Sober, J., Host, G., Riemenschneider, D.E., Zasada, J., Dickson, R.E., Isebrands, J.G., 2003. Impacts of interacting CO_2 and O_3 on trembling aspen: results from the aspen FACE experiment. Funct. Ecol. 17, 289–304.

Khuri, A.I., Cornell, J.A., 1996. Response Surfaces: Designs and Analyses, 2nd Edition. Marcel Dekker, New York.

Kickert, R.N., Krupa, S.V., 1991. Modeling plant response to tropospheric ozone: A critical review. Environ. Pollut. 70, 271–383.

Kley, D., Kleinmann, M., Sandermann, H., Krupa, S., 1999. Photochemical oxidants: state of the science. Environ. Pollut. 100, 19–42.

Koch, J.R., Creelman, R.A., Eshita, S.M., Seskar, M., Mullet, J.E., Davis, K.R., 2000. Ozone sensitivity in hybrid poplar correlates with insensitivity to both salicylic acid and jasmonic acid. The role of programmed cell death in lesion formation. Plant Physiol. 123, 487–496.

Kolb, T.E., Matyssek, R., 2001. Limitations and perspectives about scaling ozone impacts in trees. Environ. Pollut. 115, 373–393.

Krupa, S.V., 1997. Air Pollution, People and Plants. APS Press, St. Paul, MN.

Krupa, S.V., 2000. Commentary: Ultraviolet (UV)-B radiation, ozone and plant biology. Environ. Pollut. 110, 193–194.

Krupa, S.V., de Bauer, L.I., 1976. La Ciudad dana los Pinos del Ajusco. Panagfa 4, 5–7.

Krupa, S.V., Kickert, R.N., 1997. Ambient ozone (O_3) and adverse crop response. Environ. Rev. 5, 55–77.

Krupa, S.V., Legge, A.H., 2000. Passive sampling of ambient, gaseous air pollutants: an assessment from an ecological perspective. Environ. Pollut. 107, 31.

Krupa, S., Nosal, M., 2001. Relationships between passive sampler and continuous ozone (O_3) measurement data in ecological effects research. The Scientific World 1, 593–601.

Krupa, S., Nosal, M., Peterson, D.L., 2001. Use of passive ozone (O_3) samplers in vegetation effects assessment. Environ. Pollut. 112, 303–309.

Krupa, S.V., Tonneijck, A.E.G., Manning, W.J., 1998. Ozone. In: Flagler, R.B. (Ed.), Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas, 2nd Edition. Air and Waste Management Association, Pittsburg, PA, pp. 1–28.

Krupa, S., Nosal, M., Ferdinand, J.A., Stevenson, R.E., Skelly, J.M., 2003. A multi-variate statistical model integrating passive sampler and meteorology data to predict the frequency distributions of hourly ambient ozone (O_3) concentrations. Environ. Pollut. 124, 173–178.

LADCO, 1995. Lake Michigan Ozone Study: Lake Michigan Ozone Control Program, Vol. II-Technical Data Base. Lake Michigan Air Directors Consortium, Des Plaines, II.

Legge, A.H., Krupa, S.V. (Eds.), 1990. Acidic Deposition: Sulphur and Nitrogen Oxides. Lewis Publishers, Chelsea, MI.

Legge, A.H., Grunhäge, L., Nosal, M., Jäger, H.-J., Krupa, S.V., 1995. Ambient ozone and adverse crop response: An evaluation of North American and European data as they relate to exposure indices and critical levels. Angew. Bot. 69, 192–205.

Longauer, R., Gomory, D., Paule, L., Karnosky, D.F., Mankovska, B., Muller-Starck, G., Percy, K., Szaro, R., 2001. Selection effects of air pollution on gene pools of Norway spruce, European Silver fir and European beech. Environ. Pollut. 115, 405–411.

Marenco, A., Gouget, H., Nédélec, P., Pagés, J.P., Karcher, F., 1994. Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series: Consequences: Positive radiative forcing. J. Geophys. Res. Atmos. 99, 16617–16632.

Manning, W.J., Krupa, S.V., 1992. Experimental methodology for studying the effects of ozone on crops and trees. In: Lefohn, A.S. (Ed.), Surface Level Ozone Exposures and their Effects on Vegetation. Lewis Publishers, Chelsea, MI, pp. 93–156.

Matyssek, R., Innes, J.L., 1999. Ozone: a risk factor for trees and forests in Europe? Water Air Soil Pollut. 116, 199–226.

Mauzerall, D.L., Wang, X., 2001. Protecting agricultural crops from the effects of tropospheric ozone exposure: reconciling science and standard setting in the United States, Europe and Asia. Annu. Rev. Energy Environ. 26, 237–268.

Mazzali, C., Angelino, E., Gerosa, G., Ballarin-Denti, A., 2002. Ozone risk assessment and mapping in the Alps based on data from passive samplers. Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research. The Scientific World 1, 1023–1035.

McDonald, E.P., Kruger, E.L., Riemenschneider, D.E., Isebrands, J.G., 2002. Competitive status influences tree-growth response to elevated CO_2 and O_3 in aggrading aspen stands. Funct. Ecol. 16, 792–801.

McKendry, I.G., Steyn, D.G., Lundgren, J., Hoff, R.M., Strapp, W., Anlauf, K.G., Froude, F., Martin, J.B., Banta, R.M., Oliver, L.D., 1997. Elevated ozone layers and vertical downmixing over the Lower Fraser Valley, British Columbia. Atmos. Environ. 31, 2135–2146.

McLaughlin, S.B., Percy, K.E., 1999. Forest health in North America: some perspectives on potential roles of climate and air pollution. Water Air Soil Pollut. 116, 151–197.

McLaughlin, S.B., Downing, D.J., 1995. Interactive effects of ambient ozone and climate measured on growth of mature forest trees. Nature 374, 252–254.

McLaughlin, S.B., Downing, D.J., 1996. Interactive effects of ambient ozone and climate measured on growth of mature loblolly pine trees. Can. J. Forest Res. 26, 670–681.

Middleton, J.T., Kendrick, J.B., Schwalm, H.W., 1950. Injury to herbaceous plants by smog or air pollution. Plant Disease Rep. 34, 245–252.

Miller, P.R., 1993. Response of forests to ozone in a changing atmospheric environment. J. Appl. Bot. (Angew. Bot.) 67, 42–46.

Miller, P.R., McBride, J.R. (Eds.), 1999. Oxidant Air Pollution Impacts in the Montane Forests of Southern California. A Case Study of the San Bernardino Mountains. Springer-Verlag, New York.

Miller, P.R., McBride, J.R., Schiling, S.L., Gomez, A.P., 1989. Trend in ozone damage to conifer forests between 1974 and 1988 in the San Bernardino Mountains in southern California. In: Olson, R.K., Lefohn, A.S. (Eds.), Transactions Air and Waste Management Association symposium, Effects of Air Pollution on Western Forests. Air & Waste Management Association, Pittsburgh, PA, pp. 309–323.

Miller, P.R., de Bauer, L.I., Hernández-Tejeda, T., 2002. Oxidant exposure and effects on pines in forests in the Mexico City and Los Angeles, California air basins. In: Fenn, M.E., de Bauer, L.I., Hernández-Tejeda, T. (Eds.), Urban Air Pollution and Forests: Resources at Risk in the Mexico City Air Basin. In: Ecol. Study Series. Springer-Verlag, New York, pp. 225–242.

Mullineaux, P., Creissen, G., 1999. Manipulating oxidative stress responses using transgenic plants: successes and dangers. In: Altman, A., Ziv, M., Izhar, S., Plant, S. (Eds.), Biotechnology and In Vitro Biology in the 21st Century. Kluwer Academic Publishers, Amsterdam, pp. 525–532.

Myers, R.H., 1971. Response Surface Methodology. Allyn and Bacon, Boston.

NARSTO (North American Research Strategy for Tropospheric Ozone), 2000. The Narsto Ozone Assessment—Critical Reviews. Atmos. Environ. 34, 1853–2332.

Niccum, E.M., Lehrman, D.E., Knuth, W.R., 1995. The influence of meteorology on the air quality in the San Luis Obispo County–Southwestern San Joaquin Valley Region for 3–6 August 1990. Special Issue for the Regional Photochemical Measurement and Modeling Studies Specialty Conference. J. Appl. Meteorol. 34, 1834–1847.

Nosal, M., Legge, A.H., Krupa, S.V., 2000. Application of a stochastic, Weibull probability generator for replacing missing data on ambient concentrations of gaseous pollutatants. Environ. Pollut. 108, 439–446.

Noormets, A., Podila, G.K., Karnosky, D.F., 2000. Rapid response of antioxidant enzymes to O_3-induced oxidative stress in *Populus tremuloides* clones varying in O_3 tolerance. For. Genet. 7, 339–342.

Percy, K.E., 2002. Is air pollution an important factor in forest health? In: Szaro, R.C., Bytnerowicz, A., Oszlanyi, J. (Eds.), Effects of Air Pollution on Forest Health and Biodiversity in Forests of the Carpathian Mountains. IOS Press, Amsterdam, pp. 23–42.

Percy, K.E., Awmack, C.S., Lindroth, R.L., Kubiske, M.E., Kopper, B.J., Isebrands, J.G., Pregitzer, K.S., Hendrey, G.R., Dickson, R.E., Zak, D.R., Oksanen, E., Sober, J., Harrington, R., Karnosky, D.F., 2002. Altered performance of forest pests under CO_2- and O_3-enriched atmospheres. Nature 420, 403–407.

Pisano, J.T., McKendry, I., Steyn, D.G., Hastie, D.R., 1997. Vertical nitrogen dioxide and ozone concentrations measured from a tethered balloon in the Lower Fraser Valley. Atmos. Environ. 31, 2071–2078.

Ramaswamy, V., Boucher, O., Haigh, J., Hauglustaine, D., Haywood, J., Myhre, G., Nakajima, T., Shi, G.Y., Solomon, S., 2001. Radiative forcing of climate change. In: Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Dai, X., Maskell, K., Johnson, C.A. (Eds.), Climate Change 2001: The Scientific Basis. Cambridge Univ. Press, New York, pp. 350–416.

Reid, N.W., 1994. The Southern Ontario Study (SONTOS): Data Report, Summer Field Campaign 1993 (13 July to 27 August 1993). Ministry of the Environment and Energy, Toronto, Ontario, Canada.

Reid, N.W., Niki, H., Hastie, D., Shepson, P., Roussel, P., Melo, O., Mackay, G., Drummond, J., Schiff, H., Poissant, L., Moroz, W., 1996. The Southern Ontario Study (SONTOS): Overview and case studies for 1992. Atmos. Environ. 30, 2125–2132.

Richards, B.L., Middleton, J.T., Hewitt, W.B., 1958. Air pollution with relation to agronomic crops. V. Oxidant stipple of grape. Agron. J. 50, 559–561.

Roberts, P.T., Coe, D.L., Dye, T.S., Ray, S.E., Arthur, M., 1996. Summary of Measurements Obtained during the 1996 Paso Del Norte Ozone Study, Final Report. Report STI-996191–1603-FR, Sonoma Technology, Santa Rosa, CA.

Roussel, P.B., Lin, X., Camacho, F., Laszlo, S., Taylor, R., Melo, O.T., Shepson, P.B., Hastie, D.R., Niki, H., 1996. Observations of ozone and precursor levels at two sites around Toronto, Ontario, during SONTOS 92. Atmos. Environ. 30, 2145–2155.

Samuelson, L., Kelly, J.M., 2001. Scaling ozone effects from seedlings to forest trees. New Phytol. 149, 21–41.

Sandermann, H., 1996. Ozone and plant health. Annu. Rev. Phytopathol. 34, 347–366.

Sandermann, H., Wellburn, A.R., Heath, R.L. (Eds.), 1997. Forest Decline and Ozone: A Comparison of Controlled Chamber and Field Experiments. Springer-Verlag, New York.

Sandroni, S., Anfossi, D., Viarengo, S., 1992. Surface ozone levels at the end of the nineteenth century in South America. J. Geophys. Res. Atmos. 97, 2535–2539.

Schjoldager, J., 1981. Ambient ozone measurements in Norway, 1975–1979. JAPCA 31, 1187–1190.

Schraudner, M., Moeder, W.V., Camp, W., Inzé, D., Langebartels, C., Sandermann, H., 1998. Ozone-induced oxidative burst in the ozone biomonitor plant tobacco W3. Plant J. 16, 235–245.

Schönbein, C.F., 1840. Recherches sur la nature de l'odeur qui se manifeste dans certaines actions chimiques. C. R. Acad. Sci. Paris 10, 706–710.

Sheffield, R.M., Cost, N.D., 1987. Behind the decline: why are natural pine stands in the Southeast growing slower? J. Forests 85, 29–33.

Sillman, S., 1999. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. Atmos. Environ. 33, 1821–1846.

Skarby, L., Ro-Poulson, H., Wellburn, F.A.M., Sheppard, L.J., 1998. Impacts of ozone on forests: a European perspective. New Phytol. 139, 109–122.

Snedcor, G.W., Cochran, W.G., 1978. Statistical Methods. Iowa State Univ. Press, Ames, IA, USA.

Solomon, P., Cowling, E., Hidy, G., Furiness, C., 2000. Special Issue: the NARSTO Ozone Assessment—Critical Reviews. Comparison of Scientific Findings from Major Ozone Field Studies in North America and Europe. Environ. Pollut. 34, 1885–1920.

Takemoto, B.K., Bytnerowicz, A., Fenn, M.E., 2001. Current and future effects of ozone and atmospheric nitrogen deposition on California's mixed conifer forests. Forest Ecol. Manag. 144, 159–173.

Tema Nord, 1994. Critical Levels for Tropospheric Ozone—Concepts and Criteria Tested for Nordic Conditions. L. Skärby (Coordinator). Nordic Council of Ministers, Copenhagen, Denmark.

Thuillier, R.H., 1997. Summary Description of Meteorological Conditions During SJ-VAQS/AUSPEX, Final Report. Research and Development, Report 005–97.7, Pacific Gas and Electric Company, San Ramon, CA.

Torsethaugen, G., Pell, E.J., Assmann, S.M., 1999. Ozone inhibits guard cell K^+ channels implicated in stomatal opening. Proc. Nat. Acad. Sci. USA 96, 13577–13582.

Trainer, M., Parrish, D.D., Goldan, P.D., Roberts, J., Fehsenfeld, F.C., 2000. Review of observation-based analysis of the regional factors influencing ozone concentrations. Atmos. Environ. 34, 2045–2061.

Tuovinen, J.-P., 2002. Assessing vegetation exposure to ozone: is it possible to estimate AOT40 by passive sampling? Environ. Pollut. 119, 203–214.

UN-ECE, 1988. ECE Critical Levels Workshop, Final Draft Report. Bad Harzburg, Federal Republic of Germany, March 14–18, 1988.

UN-ECE and EC 2002. The Condition of Forests in Europe: 2002 Executive Report, Federal Research Centre for Forestry and Forest Products (BFH), Germany.

UN-ECE and EC, 2003. 2003 Executive Report: The Condition of Forests in Europe. Federal Research Centre for Forestry and Forest Products (BFH), Germany (in press).

US EPA (United States Environmental Protection Agency), 1996. Air Quality Criteria for Ozone and Other Photochemical Oxidants, Vol. II. US EPA, National Center for Environmental Assessment, Research Triangle Park, NC, EPA-600/P-93/00bF. United States Environmental Protection Agency, Washington, D.C.

US EPA (United States Environmental Protection Agency), 2002. Ground-level ozone: nature and sources of the pollutant. Available at http://www.epa.gov/airtrends/ozone.html. United States Environmental Protection Agency, Washington, D.C.

Volz, A., Kley, D., 1988. Evaluation of the Montsouris series of ozone measurements made in the nineteenth century. Nature 332, 240–242.

Woodwell, G.M., 1975. The threshold problem in ecosystems. In: Levin, S.A. (Ed.), Ecosystem Analysis and Prediction. Society for Industrial and Applied Mathematics, Philadelphia, PA, pp. 9–21.