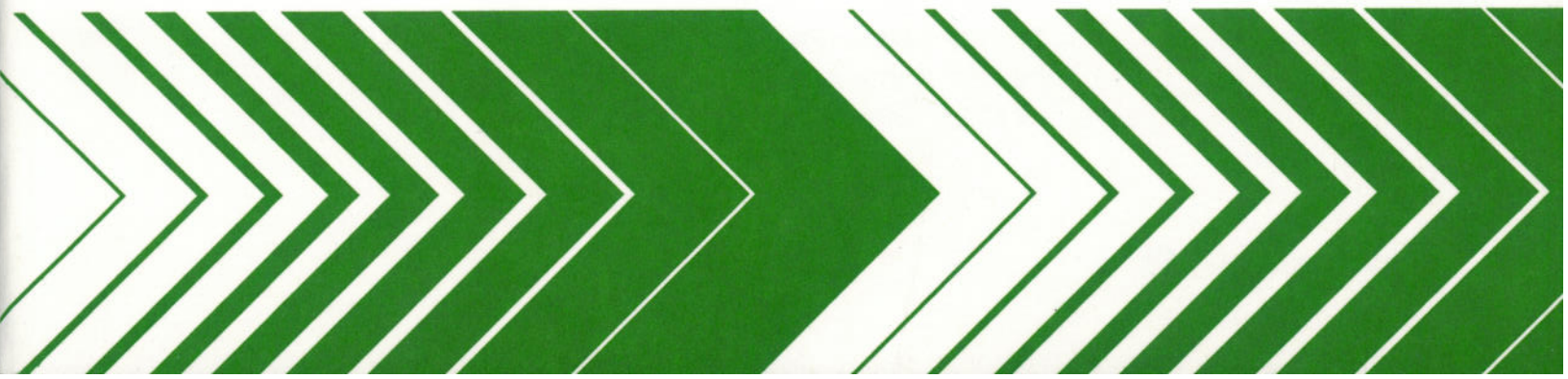




# **Air Quality Criteria for Ozone and Related Photochemical Oxidants**

## **Volume II of III**



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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# Air Quality Criteria for Ozone and Related Photochemical Oxidants

## Volume II of III

National Center for Environmental Assessment  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711



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## Preface

In 1971, the U.S. Environmental Protection Agency (EPA) promulgated National Ambient Air Quality Standards (NAAQS) to protect the public health and welfare from adverse effects of photochemical oxidants. In 1979, the chemical designation of the standards was changed from photochemical oxidants to ozone ( $O_3$ ). This document focuses primarily on the scientific air quality criteria for  $O_3$  and, to a lesser extent, on those for other photochemical oxidants such as hydrogen peroxide and the peroxyacyl nitrates.

The EPA promulgates the NAAQS on the basis of scientific information contained in air quality criteria issued under Section 108 of the Clean Air Act. The previous  $O_3$  criteria document, *Air Quality Criteria for Ozone and Other Photochemical Oxidants*, was released in August 1986 and a supplement, *Summary of Selected New Information on Effects of Ozone on Health and Vegetation*, was released in January 1992. These documents were the basis for a March 1993 decision by EPA that revision of the existing 1-h NAAQS for  $O_3$  was not appropriate at that time. That decision, however, did not take into account some of the newer scientific data that became available after completion of the 1986 criteria document. The purpose of this revised air quality criteria document for  $O_3$  and related photochemical oxidants is to critically evaluate and assess the latest scientific data associated with exposure to the concentrations of these pollutants found in ambient air. Emphasis is placed on the presentation of health and environmental effects data; however, other scientific data are presented and evaluated in order to provide a better understanding of the nature, sources, distribution, measurement, and concentrations of  $O_3$  and related photochemical oxidants and their precursors in the environment. Although the document is not intended to be an exhaustive literature review, it is intended to cover all pertinent literature available through 1995.

This document was prepared and peer reviewed by experts from various state and Federal governmental offices, academia, and private industry and reviewed in several public meetings by the Clean Air Scientific Advisory Committee. The National Center for Environmental Assessment (formerly the Environmental Criteria and Assessment Office) of EPA's Office of Research and Development acknowledges with appreciation the contributions provided by these authors and reviewers as well as the diligence of its staff and contractors in the preparation of this document at the request of the Office of Air Quality Planning and Standards.



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# 5

## Environmental Effects of Ozone and Related Photochemical Oxidants

### 5.1 Introduction

Analyses of photochemical oxidants in the ambient air have revealed the presence of a number of phytotoxic compounds, including ozone ( $O_3$ ), peroxyacyl nitrates (PANs), and nitrogen dioxide ( $NO_2$ ). Ozone, the most prevalent photochemical oxidant, has been studied the most, and its effects are understood better than those of other photochemically derived oxidants. Ozone affects vegetation throughout the United States, impairing crops, native vegetation, and ecosystems more than any other air pollutant (Heck et al., 1980). The phytotoxicity of nitrogen oxides has been assessed in Air Quality Criteria for Oxides of Nitrogen (U.S. Environmental Protection Agency, 1993) and will not be discussed here. On the basis of concentration, the PANs are more toxic than  $O_3$ , with peroxyacetyl nitrate (PAN) being about 10 times more phytotoxic than  $O_3$  (Darley et al., 1963; Taylor and MacLean, 1970; Pell, 1976). Although more phytotoxic than  $O_3$ , PANs generally occur at significantly lower ambient concentrations and are distributed less widely than those of  $O_3$ . Ambient concentrations of  $O_3$  and PAN, as well as their concentration ratios, are discussed in detail in Chapter 4.

The effects of photochemical oxidants were observed first as foliar injury on vegetation growing in localized areas in Los Angeles County, CA (Middleton et al., 1950). In these early reports, foliar injury was described as glazing, silvering, and bronzing of the lower leaf surface of leafy vegetables and as transverse bands of injury on monocotyledonous species. Subsequent studies showed that these symptoms of photochemical oxidant injury were caused by PAN (Taylor et al., 1960). The characteristic  $O_3$  stipple on grape (*Vitis labruscana*) leaves reported in the late 1950s was the first observation of  $O_3$  injury to vegetation in the field (Richards et al., 1958). Subsequent studies with tobacco (*Nicotiana tabacum*) and other crops confirmed that  $O_3$  was injuring vegetation at sites near urban centers (Heggstad and Middleton, 1959; Daines et al., 1960). It now is recognized that vegetation at rural sites may be injured by  $O_3$  transported long distances from urban centers (Edinger et al., 1972; Heck et al., 1969; Heck and Heagle, 1970; Wolff et al., 1977a,b,c, 1980; Wolff and Liroy, 1980; Kelleher and Feder, 1978; Miller et al., 1972; Skelly et al., 1977; Skelly, 1980; Garner et al., 1989; see also Chapters 3 and 4). Concentrations of  $O_3$  in polluted air masses often remain high for prolonged periods in rural areas, increasing the concern over possible effects on agriculture, forests, and native ecosystems.

Exposure to tropospheric  $O_3$  can cause injury and premature mortality of plant tissues after entering the plant because  $O_3$  has strong oxidizing properties and reacts with

cellular components. The effects of O<sub>3</sub> on terrestrial ecosystems begin with the responses of individual plants (Figure 5-1). Effects are initiated within the plant by reactions between O<sub>3</sub> or its metabolites and cellular constituents that influence biochemical and physiological processes and alter plant growth. Plant sensitivity to O<sub>3</sub> varies widely among individuals and among species. Sensitivity is determined both by genetic composition of the plant and environmental conditions. Plant response also is influenced by factors such as pollutant concentration, duration of exposures, plant nutrition, developmental stage, climate, insects, and diseases (See Sections 5.3 and 5.4).

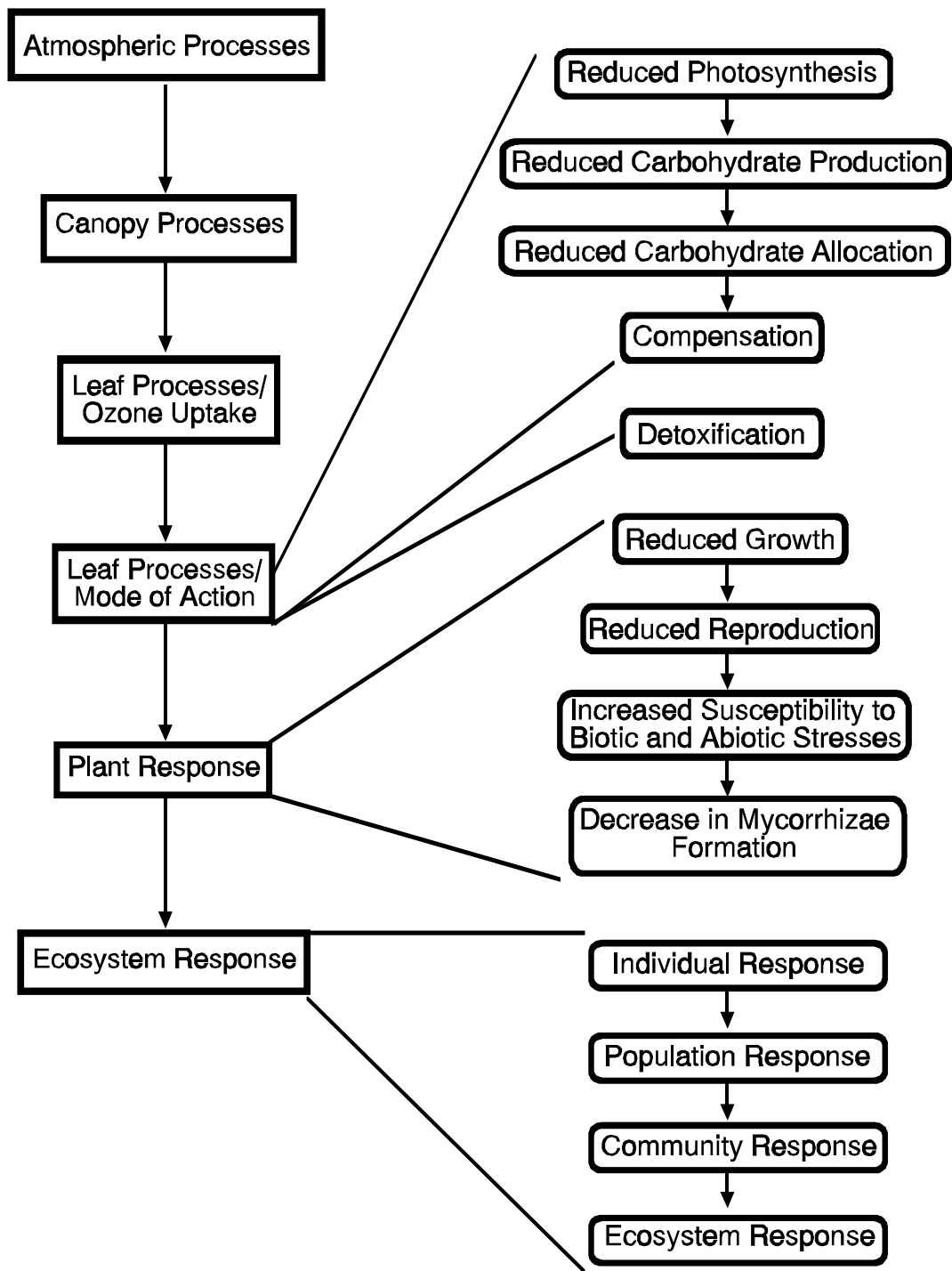
Changes in foliar pigmentation and development of injured tissues are usually the first visible sign of injurious O<sub>3</sub> exposures and indicate impairment of physiological processes with the leaves. To affect metabolic processes within the cell, sufficient amounts of O<sub>3</sub> from the atmosphere must be able to enter the plant through the leaf stomata and dissolve in the aqueous layer lining the air spaces. Ozone and its decomposition products then diffuse through the cell membrane, where they can react with cellular components (unless the plant is able to detoxify or metabolize O<sub>3</sub> or its metabolites) (Section 5.3; Tingey and Taylor, 1982).

Ozone can affect all aspects of plant growth (Figure 5-1). Plants accumulate, store, and use carbon compounds to build their structure and maintain physiological processes (Waring and Schlesinger, 1985). Within the leaf, carbon dioxide (CO<sub>2</sub>) absorbed from the atmosphere is converted to carbohydrates during the process of photosynthesis. The water and minerals necessary for growth are absorbed by plants from the soil. Growth and seed formation depend not only on the rate of photosynthesis and uptake of water and nutrients, but also on the subsequent metabolic processes and the allocation of the carbohydrates produced during photosynthesis. Most plants require a balance of resources (i.e., energy, water, mineral nutrients) to maintain optimal growth, but these are seldom available in natural environments (Chapin et al., 1987). Plants compensate for injury or stress by allocating their available resources to the point of injury or stress (McLaughlin et al., 1982; Miller et al., 1982; Tingey et al., 1976b). Altering the allocation of carbohydrates has been shown to decrease plant vigor, to increase susceptibility to insect pests and fungal pathogens, to interfere with mycorrhizal formation, and to reduce plant growth and reproduction (McLaughlin et al., 1982; Miller et al., 1982; U.S.Environmental Protection Agency, 1986; Garner et al., 1989).

Most of the available information concerning the effects of O<sub>3</sub> on vegetation is the result of exposure-response studies of important agricultural crops and some selected forest tree species, usually as seedlings. Through the years, crop plants, because of human food demand, usually have been selected for their productivity. They are grown as monocultures, fertilized, weeded, and frequently irrigated. In other words, competition for water nutrients, space, and light is minimized greatly when compared with plants growing in natural conditions, particularly in ecosystems. Trees for timber and paper also are grown on plantations under conditions favoring the greatest production.

Some O<sub>3</sub> exposures (concentration and duration) result in visible foliar injury to the plant without growth reduction; other exposures result in growth reduction and decrease in productivity without visible injury, whereas some exposures result in both. Data is presented in Section 5.6 that deals with the impact of different concentrations and exposure durations from many different experimental exposure-response studies on the growth of a variety of cultivated crops, ornamental species, and natural vegetation.





*Figure 5-1. Leaf absorption and possible functional changes that may occur within the plant. Ecosystem response begins at the level of the individual and is propagated to the more complex level of organization.*

The number of crop species and cultivars for which information regarding O<sub>3</sub> effects exists encompasses a mere fraction of the total of those cultivated as crops or found growing in natural communities. It is not possible to predict the sensitivity of the species and cultivars that have not been investigated, except in very general terms, because of the wide range of sensitivities to O<sub>3</sub> known to exist among crop cultivars and species that have been studied. Attempts to develop a general framework of response covering a range of species using the fragmented knowledge available have not been successful.

For many years, attempts have been made to develop mathematical equations that quantify the relationship between pollutant exposure and agricultural crop yield. The advantages and limitations of the various indices that have been developed to aid in predicting the effects of O<sub>3</sub> on crop yield are discussed in Section 5.5.

Organisms, not ecosystems, respond to O<sub>3</sub> exposure (Sigal and Suter, 1987). The only well-documented study of ecosystem change is that of the San Bernardino Mixed Forest ecosystem in Southern California where the impact of O<sub>3</sub> on the keystone species, ponderosa and Jeffrey pine (*Pinus jeffreyi*), resulted in the reversion of the forest to a simpler stage (Miller et al., 1982; Miller, 1984; U.S. Environmental Protection Agency, 1978, 1986). In other regions of the United States, most of the data available for assessing ecosystem responses deals with the responses of individuals to experimental O<sub>3</sub> exposures. Studies within the forests of the eastern United States, have dealt chiefly with the response in the field of eastern white pine (*Pinus strobus*) (McLaughlin et al., 1982; Skelly, 1980; Skelly et al., 1984). No long-term studies exist that deal with the impacts of O<sub>3</sub> on the various ecosystems components and how and whether these impacts alter ecosystem structure and functions. Therefore, the determination of the impact of O<sub>3</sub> on eastern forest ecosystems is difficult, if not impossible (see Section 5.7).

Plant populations are affected if they include many sensitive individuals. Removal of sensitive individuals within populations, or stands, if large in number, ultimately can change community and ecosystem structure (Figure 5-1). Structural changes that alter the ecosystem functions of energy flow and nutrient cycling can arrest or reverse ecosystem development (Odum, 1985).

The sequential organization of this chapter begins first with the methodologies (Section 5.2) that have been used to obtain the information presented and discussed in this chapter. Next, Section 5.3 explains the known biochemical and physiological changes that occur within the leaf cells after O<sub>3</sub> entry into the plants and how these chemical responses affect plant vigor, growth, and reproduction. Factors within and external to plants influence their response to O<sub>3</sub> and other stresses. These factors, as observed during experimental exposures and in the field, can modify functional growth responses of plants to O<sub>3</sub> (see Section 5.4). The development of indices or exposure statistics that may be used in quantifying and predicting crop responses to O<sub>3</sub> exposures are found in Section 5.5. Data obtained from many experimental exposure-response studies using methodologies presented in Section 5.2 and the basis for the development of the indices discussed in Section 5.5 are presented in Section 5.6. The information available on the ecosystem effects of O<sub>3</sub> and the data needed for more definitive assessments are found in Section 5.7. The costs to the nation of O<sub>3</sub> exposure of crops and ecosystems is discussed in Section 5.8. The scientific names of the plants cited in this chapter are presented in Appendix B. Section 5.10 discusses the effects of O<sub>3</sub> on nonbiological materials.

## 5.2 Methodologies Used in Vegetation Research

### 5.2.1 Fumigation Systems

The methodologies used in vegetation research have become more sophisticated over the years as new technology has developed. New exposure systems have been devised with pollutant dispensing systems that make it possible to more nearly duplicate the exposures plants receive in the field. These systems and their good points and shortcomings are discussed below.

Ozone fumigation plant-response studies require the fumigation of well-characterized vegetation to varying  $O_3$  regimes. The variation in  $O_3$  regimes may be achieved by controlled fumigation, chemical/mechanical exclusion or natural gradients of  $O_3$ . Controlled  $O_3$  fumigation systems are designed to maintain a modified gaseous atmosphere around a plant for a period of exposure, for the purpose of monitoring plant responses to that modified gaseous atmosphere. All fumigation systems share some common features: general plant growth conditions (light, temperature, humidity,  $CO_2$ , and soil moisture) must be met, and differential concentrations of  $O_3$  generated either artificially or naturally must be supplied to the vegetation and maintained during the exposure period. Exposure systems have been established in controlled environments, greenhouses, and the field. Many of these were described in the earlier criteria document, *Air Quality Criteria for Ozone and Other Photochemical Oxidants* (U.S. Environmental Protection Agency, 1986). More recent reviews of wet and dry deposition exposure systems have refined the knowledge of the strengths and limitations of experimental approaches for studying the effects of  $O_3$ , alone or in combination with other pollutants, on crops and trees (Hogsett et al., 1987a,b; Grünhage and Jäger, 1994a; Manning and Krupa, 1992). Controlled fumigation systems may range from cuvettes, which enclose leaves or branches (Bingham and Coyne, 1977; Legge et al., 1978), to a series of tubes with calibrated orifices spatially distributed over a field to emit gaseous pollutants to a plant canopy (Lee et al., 1978). Systems that exclude  $O_3$  by mechanical or chemical means have been used, as have natural gradients of  $O_3$ , to evaluate vegetation response to ambient  $O_3$ .

#### 5.2.1.1 Methodologies Discussed in the *Air Quality Criteria for Ozone and Other Photochemical Oxidants* (U.S. Environmental Protection Agency, 1986)

##### *Controlled Environment Exposure Systems*

Controlled environment fumigation systems are those in which light sources and control of temperature and relative humidity are artificial. Light quality and quantity are likely to be lower than in ambient environments, usually resulting in lower photosynthetically active radiation (PAR). Temperature and relative humidity likely will be more consistent in a controlled environment than in ambient air. Controlled environment exposure systems are typified by the widely used continuous stirred tank reactor (CSTR), a system originally designed for mass balance studies of  $O_3$  flux to vegetation. The CSTR chambers have distinct advantages for gas exchange studies because fluxes can be calculated readily when controlling for environmental and pollutant conditions. The rapid air mixing minimizes horizontal and vertical gradients within chambers as well as leaf boundary layer resistance. Disadvantages of CSTR chambers include the following: the artificial pollution and growing conditions may not represent natural exposure conditions, the rapid air movement may cause wind injury to sensitive plants, the size of chambers restricts the study of large plants, and lighting systems are problematic and provide subambient levels of PAR. Although CSTR

chambers are useful for evaluating O<sub>3</sub> effects on physiological processes, it is not possible to extrapolate the data to field situations.

Greenhouse system designs are similar to those found in controlled environments, except that light, temperature, and relative humidity conditions fluctuate with those occurring in the greenhouse. Thus, greenhouse system designs are related more closely to field studies than are controlled environments, but plant culture and environmental conditions are still quite different from those of field exposure chambers, making direct extrapolation difficult. These studies are, however, more applicable to phytotoxicity of O<sub>3</sub> to greenhouse grown ornamental and floriculture crops (U.S. Environmental Protection Agency, 1986). Some greenhouse exposure systems use activated charcoal filtration to remove pollutants from the incoming air prior to the addition of experimental O<sub>3</sub> and either vent directly to the outside or use charcoal filtration of the outgoing air to prevent contamination of the greenhouse air supply. Other greenhouse exposure systems filter neither incoming nor outgoing air.

### ***Field Exposure Systems***

Fumigation of plants with O<sub>3</sub> in the field is most frequently carried out using open-top chambers (OTCs). There are many designs, each produces an environment that differs in some degree from the ambient air (Unsworth et al., 1984a,b). The most widely utilized design (U.S. Environmental Protection Agency, 1986) consists of a cylindrical aluminum frame, covered with transparent film. The bottom half of the transparent covering is double layered, with the inside panel perforated. Charcoal- and particulate-filtered air, nonfiltered air, or O<sub>3</sub>-supplemented air is blown into the bottom layer, forced through the perforations into the plant canopy, and then escapes through the top of the chamber. The positive pressure maintained by the forced movement of air up through the chamber minimizes influx of ambient air into the chamber through the open top. The design of these chambers has been modified with frusta to reduce such incursions by ambient air, making the chambers more viable under windy conditions. Moveable canopies have been added so that rain exclusion studies can be carried out. Finally, these chambers have been modified in shape or increased in size so that species such as mature trees and grapevines can be enclosed. The OTC exposure system was employed in the National Crop Loss Assessment Network (NCLAN) from 1980 to 1988, and a description and discussion of the chambers is provided in Section 6.2.4 of the 1986 criteria document (U.S. Environmental Protection Agency, 1986).

The main advantage of OTCs is the ability to provide an enclosed environmental area for an increased range of treatments at near-ambient environmental conditions, while excluding ambient pollutants. Most current OTC designs have been used widely and successfully for studying the impact of O<sub>3</sub> on crops over a growing season (e.g., NCLAN program), but have diameters and heights that limit their use for larger plants. Although the OTCs provide for the least amount of environmental modification of any outdoor chamber, the OTC still may alter the microclimate sufficiently to have a significant effect on plant growth under pollutant stress. The OTC effects on the microclimate include reductions in light intensity, wind velocity, rainfall, and dew formation and persistence, and increases in air temperature and possibly relative humidity (Hogsett et al., 1987a; Heagle et al., 1988a; McLeod and Baker, 1988; Heck et al., 1994). For plants taller than 120 cm, there is more air movement near the bottom of the plant canopy than near the top during calm periods (Heagle et al., 1979c; Weinstock et al., 1982).

Exhaustive comparisons have been made among plants grown in carbon-filtered (CF) chambers, NF chambers, and similarly sized and located ambient air (AA) plots. Much attention has been paid to the potential for differences in productivity between AA and NF plants because of the modification of microclimate in OTCs (Manning and Krupa, 1992). For NCLAN studies, plants in NF chambers were frequently taller than AA plants (Albaugh et al., 1992; Olszyk et al., 1980; Heagle et al., 1979b). However, height was the only variable that was consistently different between AA and NF (Heagle et al., 1988a). Krupa et al. (1994) demonstrated that of 73 comparisons between NF and AA plants (NCLAN data), 56 showed no statistical significance, due either to lack of chamber effect or to random compensation. A more relevant question, whether OTCs change plant response to  $O_3$ , has been addressed. A comparison of plant growth and plant response to  $O_3$  exposure in OTCs, closed-top chambers, and air-exclusion systems has been carried out (Olszyk et al., 1986a). The authors discovered that there was interaction between plant response to  $O_3$  and type of exposure system for less than 10% of the growth parameters measured in California, suggesting that plant response to  $O_3$  was the same regardless of exposure system. Plants from exclusion systems were shorter than those grown in OTCs and generally weighed more. Of the three groups of plants, those in the control plots of the exclusion system (i.e., receiving ambient  $O_3$  exposure) were most similar in size to plants grown in field plots. Although this and another study (Olszyk et al., 1992) indicate that environmental modification caused by chambers will affect plant growth and yield, there is no evidence that there is a large effect of chambers on plant response to  $O_3$ . It is assumed that, because of the decreasing relative effects on plant environment caused by controlled environment, greenhouse, closed-top field chambers, OTCs, open-air systems, and ambient gradients, the system effects on plant response to  $O_3$  will decrease in the same order. Microclimatic differences within an OTC can cause significant differences in yield, but rarely were there significant interactions between position effect and plant response to  $O_3$  (Heagle et al., 1989a).

Considerable concern has been raised about plant response to trace pollutants in OTCs, specifically nitrogen pentoxide ( $N_2O_5$ ) and nitric oxide (NO) in chambers receiving  $O_3$  generated from dry air, and  $NO_2$  in chambers receiving AA. These trace pollutants may have a direct effect (positive or negative) on plant processes or may change how plants respond to  $O_3$ , and, without careful evaluation, these effects may go undistinguished from those of  $O_3$ . A comparison of alfalfa (*Medicago sativa*) response to the same  $O_3$  exposure, generated either electrostatically from air or through nonfiltration of AA, indicated that the generated  $O_3$  treatment was more phytotoxic than the ambient  $O_3$  treatment, probably due to the co-generation of  $N_2O_5$  and NO, along with  $O_3$  from dry air (Olszyk et al., 1990a). Open-top chamber studies that use filtered versus NF ambient  $O_3$  have been proposed to avoid the problems of generating  $O_3$ . The drawback of this or any two treatment approaches is that such plant responses to low ambient levels of  $O_3$ , such as might occur in many years, is quite subtle. To detect statistically significant differences between filtered- and NF-chamber-grown plants when responses are subtle requires a high number of replications (Rawlings et al., 1988a). This fact is illustrated in Heagle's own two-chamber work; as described in Heagle (1989), some of the two-chamber studies had differences between AA and NF of greater than 10%. Such large differences reduce the number of replications needed to detect a significant difference at  $p = 0.05$ . In any event, the differences either were not treated nor tested, or were tested but were not significant, except in one case at Beltsville, MD, with soybean (*Glycine max*). Heagle (1989) discussed the calculation of power and reviewed two-chamber studies in great detail.

Limited use (for O<sub>3</sub> studies) has been made of chamberless field exposure systems, which rely on ambient wind conditions to move O<sub>3</sub> across an open-field canopy. The O<sub>3</sub> is emitted from vertical pipes, which are spaced in a circle around the experimental plot of plants. The amount of O<sub>3</sub> emitted from each vertical pipe, as well as the number and compass direction of emitting pipes, depends on the wind direction and speed; this whole process is usually being computer controlled.

#### **5.2.1.2 Methodologies Referenced Since the Air Quality Criteria for Ozone and Other Photochemical Oxidants (U.S. Environmental Protection Agency, 1986)**

##### ***Branch and Leaf Chambers***

Most of the developments in exposure systems since 1986 have been modifications of existing systems. The tremendous interest in evaluation of mature tree response to O<sub>3</sub> has prompted the development of large branch chambers for estimating O<sub>3</sub> flux to trees. These branch chambers share many of the design characteristics of a CSTR. The chamber walls are transparent film spread over a supporting frame. There is a fan to reduce boundary layer resistance across the foliar surface, and an air inlet and outlet so that differential O<sub>3</sub>, CO<sub>2</sub> (photosynthesis), and water vapor (leaf diffusive resistance) measurements can be taken (Ennis et al., 1990; Houpis et al., 1991; Teskey et al., 1991). The advantages of this system include the ease with which the Teflon® bag can be replaced; uniform light transmission can be maintained; and the branch chamber can be moved from plant-to-plant, can be used in situ, and can be modified for different sized branches. One of the disadvantages of the branch chamber, and indeed of any such cuvette that isolates one part of the plant under different environmental conditions than the rest of the plant, is that the isolation may lead to a response different from that which would have been observed if the branch was under the same environmental conditions as the rest of the plant. In addition, total tree growth cannot be estimated using branch chambers because only part of the plant is treated with O<sub>3</sub>.

##### ***Flux Measurement***

Estimation of O<sub>3</sub> flux to foliage can be made directly by measuring the difference in O<sub>3</sub> concentration between air going into a leaf chamber and the same air stream exiting the chamber after passing over the leaf. This estimation also can be inferred from measurements of leaf diffusive resistance during exposure of a leaf to O<sub>3</sub>. The former method requires a chamber or cuvette fumigation system with uptake of O<sub>3</sub> that is quite small or extremely nonvariable relative to the amount being taken up by the leaf. Otherwise, it is difficult to detect O<sub>3</sub> flux to a leaf with good precision. Such cuvettes can be adapted from those commercially available for portable photosynthesis meters (Graham and Ormrod, 1989) or constructed from a novel design, such as that developed by Fuentes and Gillespie (1992) to estimate the effect of leaf surface wetness on O<sub>3</sub> uptake of maple leaves. The criteria for flux cuvette design include good light transmissibility, ease of leaf manipulation, minimal reaction of chamber wall surface with O<sub>3</sub>, and good air mixing within the chamber. Good mixing of air is necessary to avoid a gradient in pollutant concentration and to maintain a boundary layer resistance, which is much less than stomatal resistance. Maintenance of leaf temperature close to that of the surrounding air, so that transpiration rates are not abnormally high, is another benefit of good air mixing. The physical design of the Fuentes and Gillespie chamber was simple, consisting of two glass hemispheres that were clamped together and separated by a Teflon® O-ring over the petiole of the leaf under investigation. Inlet and outlet

air attachments were on opposite sides of the cuvette. Other cuvette designs have been used to estimate leaf gas-exchange responses to  $O_3$ ; their principals of operation are similar, but there are differences in materials and design (Amiro et al., 1984; Freer-Smith and Dobson, 1989; Laisk et al., 1989; Moldau et al., 1991a; Skarby et al., 1987).

Compared to the CSTR, which has been used for mass balance measurement of gas flux by whole plants during fumigation (Le Sueur-Brymer and Ormrod, 1984), cuvette systems usually determine flux to one leaf at a time. This results in a more precise understanding of the interaction among leaf age, diffusive resistance, illumination and  $O_3$  flux. However, these data are not particularly well adapted to estimating flux of  $O_3$  to a large vegetated surface. Finally, regardless of the methodology used to determine  $O_3$  flux to foliage, there exist only very sketchy mechanistic-process models that would link  $O_3$  fluxes to decreases in growth and productivity of plants. These data primarily are useful for developing a relationship between *internal*  $O_3$  dose and plant response and in estimating the strength of vegetation as sinks for  $O_3$  flux on a large scale. Recent studies have estimated fluxes of  $O_3$  to plant canopies by indirect methods. Ozone flux to oat (*Avena sativa*) in OTCs (using mass balance principles and a resistance analogue model) was compared to that for oat growing in the field, using an aerodynamic gradient method (Pleijel et al., 1994). Vertical flux density calculations for  $O_3$  uptake by grassland vegetation ( $O_3$  based on radiometric measurements) estimated exchange between the atmosphere close to the ground and the ecosystem (Grünhage et al., 1994; Dämmgen et al., 1994). Although fluxes of  $O_3$  to vegetation cannot imply growth or  $O_3$  physiological responses, techniques such as these can suggest whether plant responses to  $O_3$  in OTCs might differ from those in ambient field culture because of micrometeorological-induced differences in  $O_3$  flux.

### ***Pollutant-Dispensing Systems***

Although exposure chambers have changed little in design in the last several years, the profile characteristics and method of dispensing pollutant profiles have. Whereas early studies utilized static or square-wave exposures, usually controlled by hand-set flowmeters, many more recent systems expose plants with so-called dynamic exposures during which the  $O_3$  concentration gradually reaches a maximum, thus simulating diurnal variation in  $O_3$  concentration (Hogsett et al., 1985a). These profiles may be achieved by mass flow controllers that are themselves computer controlled. Proportional-add systems such as that used in NCLAN usually achieve ambient type profiles using rotameters instead of mass flow controllers. The  $O_3$  concentration in each of the chambers is logged at preset intervals, so that the integrated exposure for the entire fumigation period can be calculated. Deviations from the planned  $O_3$  episode can occur, due to failure in dispensing or monitoring equipment, as well as incursions of air through the tops of the chambers. The length of the interval between determinations of  $O_3$  concentration in the chambers can be an important contribution to the control of  $O_3$  profile. In general, longer intervals lead to less well-controlled and well-characterized  $O_3$  exposure profiles (Lefohn et al., 1993). These deviations from the expected profiles can be mathematically quantified and monitored among treatments and replications (Hale-Marie et al., 1991).

### ***Open-Air Field-Fumigation Systems***

Open-air field-fumigation systems have the potential to estimate most closely field losses due to  $O_3$ , as the plants are grown and exposed under ambient field environmental conditions. However, of all the fumigation systems, this is the least controllable and

repeatable. It has been used in the past to expose plants to "static" concentrations (i.e., desired concentration is the same throughout the exposure period) of such pollutants as sulphur dioxide (SO<sub>2</sub>) or hydrogen fluoride (HF) (Hogsett et al., 1987a). The Zonal Air Pollution System (ZAPS) has been modified vastly and improved on to enable fumigation of plants with a diurnally varying pattern of concentration (Runeckles et al., 1990). The system represents a significant advancement over earlier open-air field fumigation systems in that 12 discrete seasonal treatments that simulate ambient patterns are achieved, rather than the usual two or three. Ozone was supplied to 4-m plots, which were laid out in groups of four, through a manifold suspended over the plant canopy. The wind speed and direction determined the actual seasonal O<sub>3</sub> exposures, although the O<sub>3</sub> was released in concentrations proportional to that observed at the time in the ambient environment. Although the 12 treatments are not repeatable over time, a regression relationship between pollutant exposure and plant response can be established for each growing season.

The Liphook study in England of long-term responses of *Picea sitchensis*, *Picea abies*, and *Pinus sylvestris* to SO<sub>2</sub> and O<sub>3</sub> in combination consisted of seven growth plots, 50 m in diameter, five of which were surrounded by 64 vertical pipes from which pollutant gasses were emitted (McLeod et al., 1992). The 64 pipes were divided into four quadrants of 16 adjacent pipes, and each quadrant had diluted pollutant gases supplied to it from a computer controlled mass flow controller. The emitting quadrants, as well as the rate at which the gases were supplied to the quadrants, depended on wind speed and direction. The gases were emitted from the vertical pipes into the plant canopy at two heights, 0.5 and 2.5 m above a reference height, which was approximately two-thirds of tree height. This pattern of gas dispersion resulted in a uniform horizontal distribution of hourly mean gas concentration across each central 25-m diameter experimental plot. This exposure system, like all open-air exposure systems, clearly simulates field plant growth conditions far better than open- or closed-top chambers, and, with five enclosures and two nonenclosed ambient plots, this is by far the largest of the very few of these systems that are in operation. Measured over a winter wheat canopy, SO<sub>2</sub> concentration differed by less than 1 nL.L<sup>-1</sup> over a 5-h period of measurement; measurement of consecutive 2-min mean values at five locations across the plots demonstrated high uniformity (McLeod et al., 1985). The usefulness of the data is limited, however, by the low number of treatments and lack of replication of those treatments.

### ***Field Chamber Exposure Systems***

Open-top field chambers are used in most field studies of plant response to gaseous pollutants. The OTCs first were designed for studies on annual herbaceous crop plants (Mandl et al., 1973), but enlarged versions also have been used successfully in tree seedling and sapling studies (Adams et al., 1990a,b; Chappelka et al., 1990; Qiu et al., 1992; Kress et al., 1992; Hogsett et al., 1989; Andersen et al., 1991; Karnosky et al., 1992a,b; Wang et al., 1986a,b; Temple et al., 1992). Because the results from these studies using tree species are extrapolated to predict the effects of O<sub>3</sub> on forests, these studies require good exposure control in order to replicate ambient O<sub>3</sub> profiles characteristic of many low-elevation, rural areas of eastern North America. This condition could have been met using an open-field exposure system. Open-top chambers large enough for mature trees have been developed but are expensive (Mandl et al., 1989; Albaugh et al., 1992).

Microclimatic modification by OTCs, as well as O<sub>3</sub> exposure schedules that are disconnected from typical O<sub>3</sub> episode meteorology, have been addressed in a seasonal study



of tree response to O<sub>3</sub> in the United Kingdom (Wiltshire et al., 1992). This study uses OTCs with roll-up sides, but, except for fumigation days, the plants are maintained in ambient climatic conditions. The exposure episodes number between 27 and 30 throughout the growing season and occur on days with ambient meteorology associated with naturally occurring O<sub>3</sub> episodes (i.e., high incident radiation and temperature, with little air movement) (Wiltshire et al., 1992). The maintenance of near-ambient meteorological conditions during both growth and exposure periods is an effort to make this study better represent field-grown plant responses to O<sub>3</sub>, while maintaining control of O<sub>3</sub> exposure.

Several designs of field fumigation chambers have been developed to overcome some of the disadvantages of the OTCs, namely small plot size and incursion of ambient air. Closed-top chambers first were developed in the 1950s; generally, their use diminished in favor of OTCs. However, closed-top chambers smaller in dimension than the open-top design have been constructed more recently in California to assess crop loss to O<sub>3</sub>. Closed-top chambers were chosen because the authors wished to characterize the pollutant dose to the plants very precisely; pollutant gradients within the chamber were minimal (Musselman et al., 1986a). The chambers were octagonal in shape and covered with Teflon® film; the soil was completely replaced with standard greenhouse mix. Temperatures in the chamber were higher (2 to 4 °C at midday, 1 to 2 °C at night) than in the ambient air, and light levels were reduced by 11% (spectral quality of the light in the chambers was not reported). The authors concluded that, although the chambers were not suitable for studies destined for extrapolation to plant response under field conditions, the chambers were very useful when tight control over soil moisture and pollutant concentration was needed.

Closed-top chambers were constructed and installed in the United Kingdom to study responses of shrubs and large herbaceous species to long-term, low (chronic) concentrations of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> (Rafarel and Ashenden, 1991). These chambers were a smaller version of an earlier design, because the larger chambers required pure gas sources of NO<sub>2</sub> and SO<sub>2</sub> to be diluted into the ventilating air stream, which resulted in highly variable exposure concentrations. The flow rate of the smaller chambers meant that premixed gases were sufficient to maintain steady control of treatment concentrations. Because the gases were discharged from the source at constant concentrations, different treatments were achieved by placing one or more pollutant supply tubes in the fumigation chambers. Good air circulation and moderate ambient temperatures maintained the chambers at near ambient conditions; however, results cannot be extrapolated to predict plant response to O<sub>3</sub> under ambient air conditions.

### ***Ambient Gradients for Evaluation of Plant Response to Ozone***

The exposure system that utilizes ambient conditions of O<sub>3</sub> exposure, temperature, humidity, soils, and soil moisture is the ambient gradient system. By this method, plants are grown along a transect of known differential pollutant concentrations, usually downwind of a major point source or urban area. The concentration of pollutants is diluted as distance from the source increases. The most well-defined O<sub>3</sub> gradients exist in the Southern California Air Basin and have been used in studies by Oshima et al. (1976, 1977a,b); unfortunately, outside this region, few suitable gradients exist. A study using four different cultivars of red clover (*Trifolium praetense*) and spring barley (*Hordeum vulgare*), each differing in sensitivity to SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub>, was conducted along such a transect of gradient SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> concentrations in the United Kingdom (Ashmore et al., 1988). Ozone concentration was inferred from injury to Bel W3 and Bel B cultivars of tobacco but was found to have very

little relationship to cultivar performance. The authors cautioned that these results must be interpreted with an understanding that differences among sites in other environmental parameters could contribute to the detection of (or the failure to detect) O<sub>3</sub> effects on the crops. For ambient gradient studies to be interpretable, good characterization of site parameters (rainfall, temperature, radiation, and soil type) is needed. Additionally, the modeler needs to know how these factors should be used to adjust the apparent plant response. In order to know that, a good knowledge base is needed of how all of these factors modify plant response to O<sub>3</sub>.

Although Manning and Krupa (1992) assert that natural gradients are the "ideal way to conduct O<sub>3</sub>/plant response studies in ambient air in field plots," they concede that few gradients that meet statistical requirements for intermediate O<sub>3</sub> concentrations exist outside Southern California. It is possible, however, that more gradients will be identified as rural air monitoring increases. They also concede that, although using artificial soils removes a significant source of variation in plant response to O<sub>3</sub>, pot-grown plants do not closely simulate the rooting environment found in the field (Manning and Krupa, 1992). Although plants using gradients are commonly considered to be easily replicable in large numbers, they should probably be considered as "repeats" rather than "replicates" in the conventional sense. If treatments are replicated by locating them very close together at the same location in the gradient, then they may better be considered as "sub-samples" of one replicate, if the climatic and edaphic conditions are very similar, or as repeats of a study, if the conditions are not. This argument is not just semantic; in data analysis, repeats and replicates should be handled differently, because the sum of squares for repeats is likely much larger than for replicates and may be composed significantly of plant response factors other than O<sub>3</sub> concentration.

At this time, although some information is available, the relationships still are incompletely understood. Many investigators consider that ambient gradients are impossible to find without major differences in environmental conditions that may affect plant response to O<sub>3</sub> and, therefore, confound interpretation of the results.

### ***Cultivar Comparisons***

The comparison of isogenic lines of a particular species that differ only in their tolerance to O<sub>3</sub> is "the ideal way to determine the effect of ambient O<sub>3</sub> on plants in the field ...." (Manning and Krupa, 1992). Heagle et al. (1994) report on the use of a white clover (*Trifolium repens* L.) system to estimate the effects of O<sub>3</sub> on plants. A field experiment conducted in 1984 and 1985 using white clover revealed a wide range of sensitivity among the genotypes present in the commercial line "Regal" (Heagle et al., 1991a, 1993). Plants were screened for relative sensitivity to O<sub>3</sub>. Two clones were selected: one ozone-sensitive (NC-S) and another ozone-resistant (NC-R). Subsequent studies suggested that these clones could be useful as indicators of O<sub>3</sub> sensitivity, if they routinely displayed measurable differences in response to O<sub>3</sub>, while responding similarly to other factors (e.g., biotic, climatic, soil, chemical, and other pollutants). Experimentation indicated that the white clover system can be used to indicate where and when ambient O<sub>3</sub> concentrations cause foliar injury and decrease growth. Hence, it can be inferred that other plant species sensitive to O<sub>3</sub> also may be affected (Heagle et al., 1994).

### ***Protective Chemicals***

Chemicals that protect plants from O<sub>3</sub> have been in use since the 1970s to evaluate plant response to O<sub>3</sub>. Ethylene diurea (EDU) has been used in studies to modify the

O<sub>3</sub> sensitivity of several species (see Section 5.4.7). Ethylene diurea (and perhaps other undetermined chemicals) has potential as a tool to evaluate field crop losses to O<sub>3</sub> in the absence of chambers, with their inherent modification of microclimate. A low-cost, simple technique, EDU can be applied to larger plot sizes than currently are possible with OTCs, thus reducing some of the uncertainty of extrapolating experimental results to a large scale. Field protocols for the use of EDU have not been well established. Frequency and rate of application that protects plants vary with species and edaphic and atmospheric conditions. Depending on the method of application, EDU may have little effect on field-grown plant response to O<sub>3</sub> (Kostka-Rick and Manning, 1993). The basis for the year-to-year variation in degree of protection of plants by EDU is not well understood, so drawing conclusions from multi-year studies, which is the situation most relevant to evaluation of plant community responses to ambient O<sub>3</sub>, is difficult. Two-treatment studies of EDU and plant response to O<sub>3</sub> (Kostka-Rick and Manning, 1992a,b) indicate that protection is variable, suggesting that the experimental system under investigation (soil, plant, and climate) would have to be extremely well characterized and understood for interpretation of EDU studies to be complete. Manning and Krupa (1992) point out that EDU is probably more useful in conjunction with OTCs so that a factorial range of O<sub>3</sub> can be administered to the plants. It is not clear that EDU protection can be fine-tuned sufficiently into a range of discrete levels suitable for regression analysis (Kostka-Rick and Manning, 1993). The mechanism by which EDU protects plants, beyond being a systemic antioxidant, is unknown; understanding this mechanism has the potential to contribute to the broader understanding of the mechanisms of O<sub>3</sub> injury at the cellular/metabolic level of the plant.

### 5.2.2 Experimental Design and Data Analysis

Experimental design strategies, including the number, kind, and levels of pollution exposure; patterns of randomization; number of replicates; and experimental protocol are crucial to the ability of the statistical approaches to test and model the effects of O<sub>3</sub> on plant response and to extrapolate experimental results to real world conditions. The experimental design focuses an experiment on the specific objectives of the study and, so, may limit the application of the data to other research goals. The various experimental design and analyses for exposure-response data from controlled exposure studies have been well reviewed in the 1986 criteria document (U.S. Environmental Protection Agency, 1986) and will not be repeated here. In summary, most field studies involving OTCs have used randomized block or split-plot designs and pollution levels appropriate for regression analysis. These exposure-response relationships generalize the mathematical relationship between the plant parameter of interest and O<sub>3</sub> exposure. Plant response to concentrations other than those used in the experiment can be interpolated from these relationships, and thresholds of plant response can be determined (Ormrod et al., 1988). In the latter half of the NCLAN program, the Weibull model was chosen to characterize yield response to O<sub>3</sub> because of its flexibility to describe a wide range of data patterns (Rawlings and Cure, 1985) and, consequently, to allow a common model to be fit when pooling data across years and sites (Lesser et al., 1990).

Experimental designs for exposure-response relationships can be expanded easily so that plant response to O<sub>3</sub> and another factor at multiple levels can be determined. Because of the need to contain each O<sub>3</sub> treatment by a chamber, incomplete factorial designs are more efficient approaches to multi-factor studies, leading to exposure-response surfaces (Allen et al., 1987). Choosing the appropriate incomplete factorial design for a response surface

study requires forethought on whether all areas of the surface are of equal interest. For many O<sub>3</sub> plant response studies, this is not so because extremely high concentrations, although increasing the precision with which plant response to lower concentrations is estimated, are not as likely to occur in the ambient environment (see Chapter 4).

Because the U.S. Environmental Protection Agency (1986) decided to place greater emphasis on damage (i.e., effects that reduce the intended human use of the plant) than on injury, studies more frequently have used experimental designs that generate data suitable for regression and treatment mean separation analyses for the purposes of modeling and testing the impact of O<sub>3</sub> on plant response. Although the impact at current O<sub>3</sub> levels is of primary interest and can be studied effectively using two O<sub>3</sub> levels generated by CF and NF treatments, the development of exposure-response models necessitates the use of additional treatments at above ambient concentrations (Heagle et al., 1989a; Rawlings et al., 1988a). The optimal number, range, and spacing of treatment levels depends on the anticipated exposure-response model, but, in the case of the Weibull and polynomial models, greater precision for estimation of relative yield loss at ambient O<sub>3</sub> concentration is obtained when the lowest treatment level is near zero and the highest treatment level is well above the ambient concentration. For the Weibull model, the highest treatment should correspond to a concentration for which yield loss is at least 63% of the yield at zero exposure (Dassel and Rawlings, 1988; Rawlings et al., 1988b).

When studying the impact of mixtures of pollutants on plant processes in chambers, response surfaces can be generated from complete or incomplete factorial designs. These designs have been shown to increase the precision and efficiency of estimating relative yield loss at ambient concentrations (Allen et al., 1987). The optimal design cannot be specified a priori and necessitates the use of treatment levels from near zero to well above the ambient concentration for each pollutant. However, response surface designs have not been used widely in pollutant mixture studies, nor have these designs been used extensively to study the interaction between pollutant exposure and quantitative environmental parameters, such as light, temperature, and soil moisture. The interaction between O<sub>3</sub> and phytotoxic concentrations of other pollutants, in particular SO<sub>2</sub>, has not been studied extensively because instances of co-occurrence of O<sub>3</sub> and other pollutants are not common in the United States. An analysis of pollution monitoring data showed fewer than 10 periods of co-occurrence between O<sub>3</sub> and phytotoxic concentrations of SO<sub>2</sub> during the growing season at the sites where the two pollutants were monitored (Lefohn and Tingey, 1984; U.S. Environmental Protection Agency, 1986).

Design and analysis of pollutant effects studies have used various characterizations of exposure to determine optimum spacings of treatment levels and to relate exposure to response. Most notably, the daytime mean concentration index (i.e., either M7 or M12) was adopted by the NCLAN program to determine the effects of O<sub>3</sub> on plant response. However, there has been considerable debate over the use of the mean index in exposure-response modeling; the variety of ways to compute the characterizations of plant exposure will be discussed in Section 5.5. When plant yield is considered, plant response is affected by the concentration of exposure and by other exposure-dynamic factors (e.g., duration, frequency, threshold, respite time), in combination with physiological, biochemical, and environmental factors that may mask treatment effects over the growing period. Research goals to understand the importance of exposure dynamic factors have utilized experimental designs that apply two or more different patterns of exposure that are equal on some scaling (e.g., total exposure). Experiments designed specifically to address the importance of components

of exposure may require the use of exposure regimes that are not typical of the ambient environment.

The majority of chambered field studies use regression-based designs that focus on developing exposure-response models but have limited application for testing the importance of exposure dynamics (e.g., exposure duration) for evaluating exposure indices based on statistical fit. When data from replicate studies of equal or varying duration are available, the ability to test for duration effects on plant response may be enhanced using regression analysis to combine data. The regression approach has been used to fit a common model to combined data from replicate studies of the same species when it is reasonable to assume that the primary cause of biological response is pollutant exposure, and that differences in environmental, edaphic, or agronomic conditions among sites do not significantly change the shape of the regression relationships. When pooling data across sites and years, additional terms for site and year effects often are included in the model as either fixed or random components, depending on the population of interest. Inferences over random environments implies that the environments sampled by the experiments are representative of the population of regions of interest under a variety of environmental conditions. In this case, site and year effects are incorporated as random components when fitting a common model. The appropriate analysis is to use a mixed model to fit an exposure response model with variance components. This analysis has been used recently to combine data from replicate studies of varying durations to test the importance of length of exposure in influencing plant response (see Section 5.5).

### **5.2.3 Mechanistic Process Models**

In addition to regression type models of plant response to  $O_3$ , which are empirical and statistical in nature, there are mechanistic-process models (Luxmoore, 1988; Kickert and Krupa, 1991; Weinstein et al., 1991). The key difference between these two types of models is how the changes are handled in the dependent variable over time. Empirical models treat a time period (e.g., a growing season) as a single point and report the response of the dependent variable as a single point as well. Regression models also may oversimplify the characteristics of an  $O_3$  exposure, in that the description of the  $O_3$  exposure is compressed over time to a single number. The variety of ways to compute this single number will be discussed in Section 5.5.

Mechanistic-process models on the other hand describe the rate of change of a variable in response to the treatment (such as  $O_3$ ) with change in time. The latter type of model has the potential to capture the interaction among plant age or stage of development, variability of ambient exposure concentrations, and plant response to  $O_3$ . For this reason, mechanistic-process models have been rated much more highly than regression models for their realism, scientific value, and applicability to other locations (Kickert and Krupa, 1991). However, compared to regression models, mechanistic-process models require more input data, and the input data are less accessible. The mechanistic-process models are more complex than regression models, requiring more computer time and memory to develop. The precision of the output regression models is greater than mechanistic-process models (for interpolative examinations only), as is their ability to estimate response probabilities. The authors conclude that the popularity of single-equation, time-lumped models is related to the fact that the studies of plant responses to  $O_3$  are oriented more to air quality standard setting as an endpoint, rather than the physiological processes underlying plant responses. The

problems with process-based models are the necessity for some large assumptions (in place of real data) and the lack of validation. Without validation, using estimates from these models is questionable; if the estimations are used, then the uncertainties associated with them must be identified and quantified.

#### 5.2.4 Summary

Each type of fumigation system is suited particularly well to certain types of studies of plant response to  $O_3$ ; no one system is appropriate for all types of studies of plant responses to  $O_3$  (Table 5-1). Each system has advantages and limitations that must be evaluated in terms of the research objectives that it was designed to meet. Table 5-1 lists the characteristics of the various exposure systems as they relate to experimental objectives, including simulation of field conditions, replication, range of treatment levels possible, and the ability to control extraneous environmental factors that may influence plant growth. Controlled-environment chambers are well suited for mechanistic type studies at the molecular or cellular level. Most plant cellular processes, as well as the equipment that measures them, are quite sensitive to temperature and light, so good control and definition of these factors are needed. Growth responses to  $O_3$  determined from controlled-environment chamber studies cannot be extrapolated to the prediction of field losses to  $O_3$  because the culture conditions in the two systems are just too dissimilar. Open-top chamber systems, although a compromise in ability to simulate field conditions, have major advantages over other fumigation systems for developing exposure-response functions (to develop a statistically robust surface requires at least three or, better yet, five treatment levels) because (1) a range of pollution levels at near-ambient environmental conditions can be generated to optimize the precision in empirical modeling; (2) extrapolation of experimental results to probable field responses to ambient exposure is possible to a certain extent because OTCs, although modifying microclimate, appear not to affect relative plant response to  $O_3$ ; and (3) a semi-controlled environment is created for plant growth with only  $O_3$  exposure level varied, thus it is valid to assume that the primary cause of response is due to  $O_3$  exposure. Exclusion methods, particularly those using chemicals such as EDU, are the least disruptive of ambient culture conditions in the field, so these approaches most closely estimate real crop losses to  $O_3$ . However, their application is limited by the availability of ambient  $O_3$  in any particular year or location, as well as by confounding by climatic and edaphic conditions. They are not well suited for establishing exposure-response relationships because it is difficult to quantify the degree of protection actually offered by the exclusion method in the field (Ashmore and Bell, 1994). In general, open-field exposure systems or natural gradients are not replicable, nor can a range of treatments be imposed to enable construction of a response function, which is necessary for interpolation of  $O_3$  concentrations that cause plant response.

At the current time, OTCs represent the best technology for determination of crop yield responses to  $O_3$ ; concentration and duration of the gas are well controlled, and the plants are grown under near-field-culture conditions. There are several limitations and uncertainties associated with the collected data: (1) the plot size is small relative to a field, (2) microclimate differences may influence plant sensitivity to  $O_3$ , and (3) air quality after

**Table 5-1. Comparison of Fumigation Systems for Ozone Exposure-Plant Response Studies**

Fumigation System	Simulation of Field Losses	Replication of Experimental Unit	Range of Treatment Levels	Likelihood of Extraneous Factors Affecting Response
Controlled-environment chambers	Low	Low	High	Medium
Greenhouse chambers	Low	Medium	High	Medium
Closed-top field chambers	Medium	High	High	Medium
Open-top field chambers	Medium to high	High	High	Medium
Mechanical field exclusion	High	Low to medium	Low	Medium
Open-field fumigation	High	Low	Low	High
Natural gradients	High	Low	Low	High

passage through a charcoal filter has not been widely characterized. These uncertainties are not quantified, although there are preliminary data establishing their existence. There is concern that these uncertainties are forgotten in the scaling of the plant response data to national yields and their integration into larger cost-benefit models. However, because the uncertainties are not yet quantified, they cannot be incorporated into the national estimates of losses to  $O_3$ . There is an urgent need to estimate these uncertainties so that the OTC data can be used fully, with little doubt as to how well the data represents real crop losses. Further comparisons of OTC and chemical exclusion plant responses, expanding the range of environmental conditions and species for which they are compared, would help determine the extent of the role of microclimate in modifying plant response to  $O_3$ . Large scale exclusion studies also could contribute to quantifying the uncertainty of extrapolating plot response to field scale. Analysis of the atmospheric chemistry inside OTCs under various scenarios of light, temperature, and humidity would address the question of what additional pollutants may influence plant growth or plant responses to  $O_3$ . Once these uncertainties are fully characterized and quantified, existing models of crop loss can be constructed more precisely and then incorporated into the national scale models with greater confidence.

## **5.3 Species Response/Mode of Action**

### **5.3.1 Introduction**

Plant adaptation to changing environmental factors or to stresses involves both short-term physiological responses and long-term physiological, structural, and morphological modifications. These changes help plants to minimize stress and to maximize the use of internal and external resources. A great deal of information is available on the physiology of single leaves; however, relatively little is known about whole-plant systems and whether the physiological mechanisms involved are initiated wholly within the leaf or are the result of whole-plant interactions (Dickson and Isebrands, 1991).

The many regulatory systems contained in leaves change both as a function of leaf development and in response to different environmental stresses. Leaves function as the major regulators of anatomical and morphological development of the shoot and control the allocation of carbohydrates to the whole plant (Dickson and Isebrands, 1991). This section discusses the movement of  $O_3$  into plant leaves and what is known about their biochemical and physiological responses.

Movement of  $O_3$  into plant leaves involves both a gas and a liquid phase. The phytotoxic effects of air pollution on plants appear only when sufficient concentrations of the gas diffuse into the leaf interior and pass into the liquid phase within the cells. Therefore, to modify or degrade cellular function,  $O_3$  must diffuse in the gas-phase from the atmosphere surrounding the leaves through the stomata into the air spaces and enter into the cells after becoming dissolved in the water coating the cell walls (U.S. Environmental Protection Agency, 1986). The exact site or sites of action are not known. Biochemical pathways are closely interrelated, and sufficient knowledge of all the control and regulatory mechanisms does not exist (Heath, 1988). The previous criteria document summarized the overall processes controlling plant response to  $O_3$ .

"The response of vascular plants to  $O_3$  may be viewed as the culmination of a sequence of physical, biochemical, and physiological events. Ozone in the ambient air does not impair processes or performance, only the  $O_3$  that diffuses



into the plant. An effect will occur only if a sufficient amount of  $O_3$  reaches the sensitive cellular sites within the leaf. The  $O_3$  diffuses from the ambient air into the leaf through the stomata, which can exert some control on  $O_3$  uptake to the active sites within the leaf. Ozone injury will not occur if (1) the rate of  $O_3$  uptake is sufficiently small that the plant is able to detoxify or metabolize  $O_3$  or its metabolites; or (2) the plant is able to repair or compensate for the  $O_3$  impacts (Tingey and Taylor, 1982). The uptake and movement of  $O_3$  to the sensitive cellular sites are subject to various physiological and biochemical controls" (U.S. Environmental Protection Agency, 1986).

Responses to  $O_3$  exposure that have been measured include reduced net  $CO_2$  exchange rate (photosynthesis minus respiration), increased leaf/needle senescence, increased production of ethylene, and changes in allocation patterns. Overall understanding of the response of plants to  $O_3$  has been refined since the last criteria document (U.S. Environmental Protection Agency, 1986). Increased emphasis has been placed on the response of the process of photosynthesis to  $O_3$ , on identification of detoxification mechanisms, and on changes in biomass (sugar and carbohydrate) allocation.

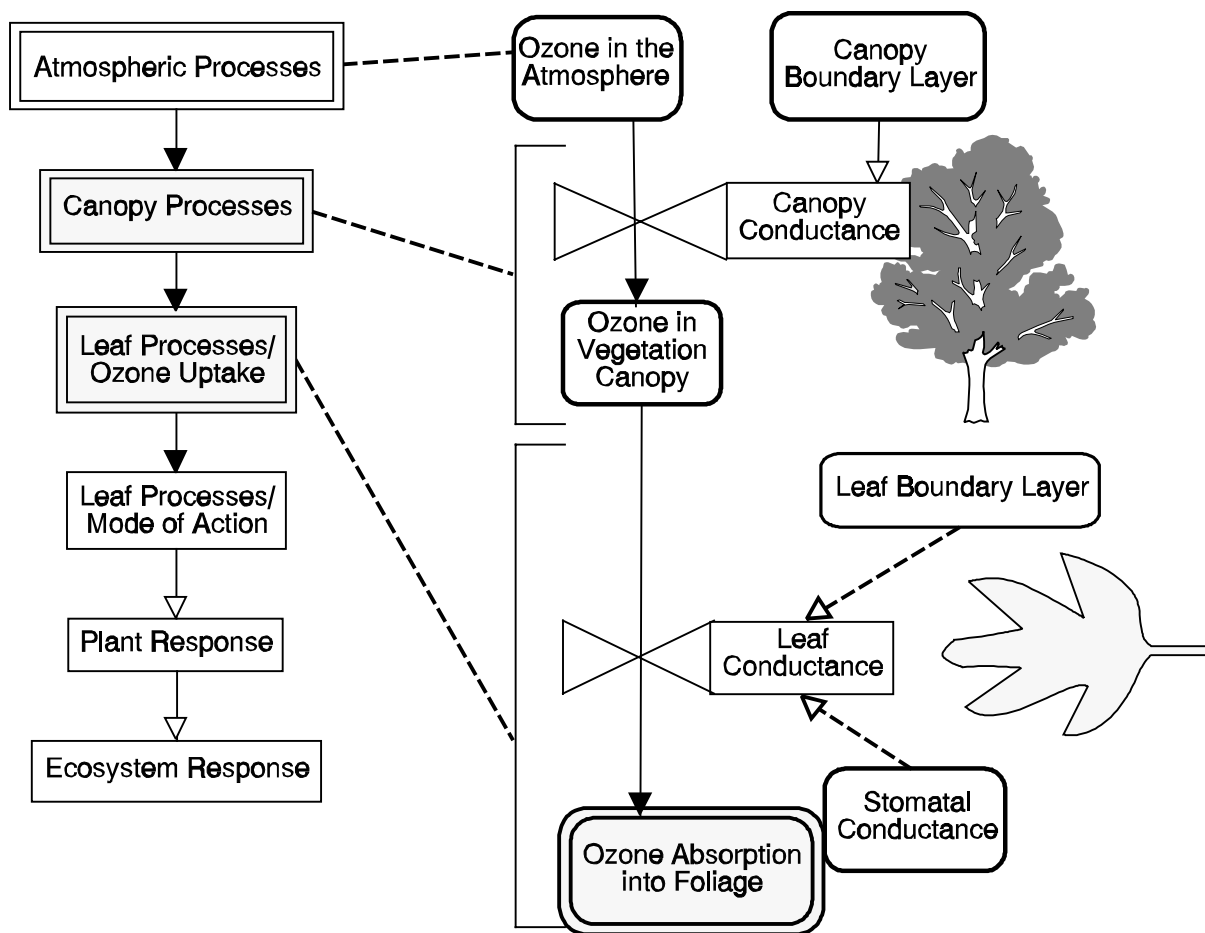
As indicated above, entry of  $O_3$  into leaves involves the gas-phase external to the plant and the liquid-phase within the leaf cells. A precondition for  $O_3$  to affect plant function is that it be absorbed into the tissues. Ozone uptake will be divided into two components: adsorption to surfaces and absorption into tissues. Adsorption will affect surface materials (e.g., cuticles) but have little direct effect on physiological processes, whereas  $O_3$  absorption can affect physiological function if  $O_3$  is not detoxified. In the following section, the processes that control movement of  $O_3$  into the plant canopy and then into the leaf will be examined.

### **5.3.2 Ozone Uptake**

Uptake of  $O_3$  in a plant canopy is a complex process involving adsorption of  $O_3$  to surfaces (stems, leaves, and soil) and absorption into tissues, primarily in the leaves (Figure 5-2). Movement of  $O_3$  from the atmosphere to the leaf involves micrometeorological processes (especially wind) and the architecture of the canopy (including the leaves). Within the canopy,  $O_3$  can be scavenged by chemicals in the atmosphere (Kotzias et al., 1990; Gäb et al., 1985; Becker et al., 1990; Yokouchi and Ambe, 1985; Bors et al., 1989; Hewitt et al., 1990); however, the products of these reactions themselves may be phytotoxic (Kotzias et al., 1990; Gäb et al., 1985; Becker et al., 1990; Hewitt et al., 1990). The extent to which these scavenging processes affect  $O_3$  absorption by leaves is not well known. Uptake of  $O_3$  by leaves is controlled, in large part, by the complex of microclimate and canopy architecture, which control movement of  $O_3$  from the atmosphere to the leaf. Leaf conductance is determined by leaf boundary layer conductance and stomatal conductance. In this section, the theoretical and empirical studies on  $O_3$  uptake at the canopy and leaf levels will be examined.

#### **5.3.2.1 Ozone Uptake by Plant Canopies**

Integration of  $O_3$  uptake at the stand level requires attention to several levels of organization (Enders et al., 1992; Hosker and Lindberg, 1982) because uptake at this level



**Figure 5-2. Uptake of ozone ( $O_3$ ) from the atmosphere.** *Ozone is moved from the atmosphere above the canopy boundary layer into the canopy primarily by turbulent flow of air. Canopy conductance, controlled by the complexity of the canopy architecture and the wide distribution within the canopy, is a measure of the ease with which gases move into the canopy. Within the canopy,  $O_3$  can be adsorbed by surfaces as well as being absorbed into the foliage. Foliage absorption is controlled by two conductances, leaf boundary layer and stomatal, which together determine leaf conductance. The solid black arrows denote  $O_3$  flow; dotted arrows indicate processes affecting uptake or response to  $O_3$ . Boxes at the left with double borders are those processes described in the figure. The rounded box with a double border is the end of pathway on this figure.*

includes not only uptake by leaves but also adsorption by stems, the soil, and other structures with which  $O_3$  can react. Although the actual pathway, and therefore conductance, will vary within the canopy, depending on position and wind profile, an integrated average conductance is frequently used to describe canopy conductance (Monteith and Unsworth, 1990). For most tree species, canopy conductance tends toward high values, whereas, for crops, it tends to be low.

Two general approaches have been used to estimate  $O_3$  uptake by a plant stand: (1) measurement of gradients over the canopy using micrometeorological methods and (2) simulation of canopy conductance. The results of the two methods generally are different because the micrometeorological techniques include  $O_3$  uptake by all surfaces, whereas simulation accounts only for  $O_3$  absorbed by the surfaces simulated, primarily the foliage.

Two micrometeorological methods, (1) Bowen ratio and (2) eddy correlation, have been used to calculate canopy  $O_3$  uptake. The Bowen ratio assumes a constant relationship between heat and water vapor fluxes (i.e., sensible and latent heat), then calculates  $O_3$  uptake assuming a constant relation between water vapor and  $O_3$  fluxes (Leuning et al., 1979a). The eddy correlation technique requires more elaborate instrumentation for measurement of variation in temperature, water vapor, and  $O_3$  concentration over time and has stringent site requirements (Wesely et al., 1978).

Wesely et al. (1978), using eddy correlation, found a strong diurnal variation in the deposition velocity (the inverse of canopy conductance) and  $O_3$  flux over a corn canopy. They also found evidence that 20 to 50% of the flux was to the soil and to the surface of the canopy. Ozone flux to a dead corn canopy also had a diurnal variation, but a lower magnitude, probably reflecting the absence of uptake through the stomata. Single time measures of deposition velocity, or canopy resistance, have been taken in a Gulf Coast pine forest ( $54 \text{ s m}^{-1}$ ; Lenschow et al., 1982) and in a New Jersey pine forest (120 and  $300 \text{ s cm}^{-1}$ ; Greenhut, 1983). Ozone uptake in a maple forest varied diurnally in a pattern explainable by variation in leaf conductance and  $O_3$  concentration (Fuentes et al., 1992). Ozone flux below the tree canopy at 10 m was about 10% of the flux above the canopy at 33 m. Measurements in specially constructed chambers showed that  $O_3$  uptake, as well as photosynthesis, could occur when the foliage was wet (Fuentes and Gillespie, 1992). The fact that wet leaves could take up significant  $CO_2$  is evidence that the stomata were not blocked by the water on the leaf surface. This result is counter to assumptions made in earlier work (Baldocchi et al., 1987) in which water on the surface of the leaf was presumed to interfere with  $O_3$  uptake.

Simulation of canopy conductance requires scaling uptake from individual leaves to individual trees to that of a stand using a combination of canopy models (one for each species) and a stand model to handle interactions among individuals. Several assumptions are required for this approach: the primary sink for  $O_3$  is the foliage, variation in stomatal conductance can be simulated through the canopy using either direct measurements or models, and canopy and plant models adequately simulate response when competition is occurring.

Leuning et al. (1979a,b) used a simple model to estimate canopy uptake in corn (*Zea mays*) and tobacco. Comparison of the results of these simulations with estimates using the Bowen ratio technique indicated that about 50% of the  $O_3$  absorbed by the stands entered the leaves. Baldocchi et al. (1987) presented a model for canopy uptake of  $O_3$  that incorporated stomatal function, some aspects of canopy architecture, and soil uptake. The results of the simulation of  $O_3$  uptake by a corn canopy correlated well with estimations using the Bowen ratio, but tended to overestimate the magnitude. These authors point out that results of model simulation are quite sensitive to the assumptions used. As part of a series of simulations, Reich et al. (1990) explored the effects of different  $O_3$  exposures (daily average  $O_3$  concentrations of 0.035, 0.05, 0.065, and 0.080 ppm) on canopy carbon gain in a mixed oak-maple forest. Depending on the response function and  $O_3$  exposure used, reductions in carbon gain were between 5 and 60%. An important result of these simulations is that the effect of  $O_3$  was strongest in the upper layer of the canopy, where most of the photosynthesis occurred. Although all these simulations provide some interesting insights into how

O<sub>3</sub> uptake (and response) varies with time and exposure, data for validating the models are still needed.

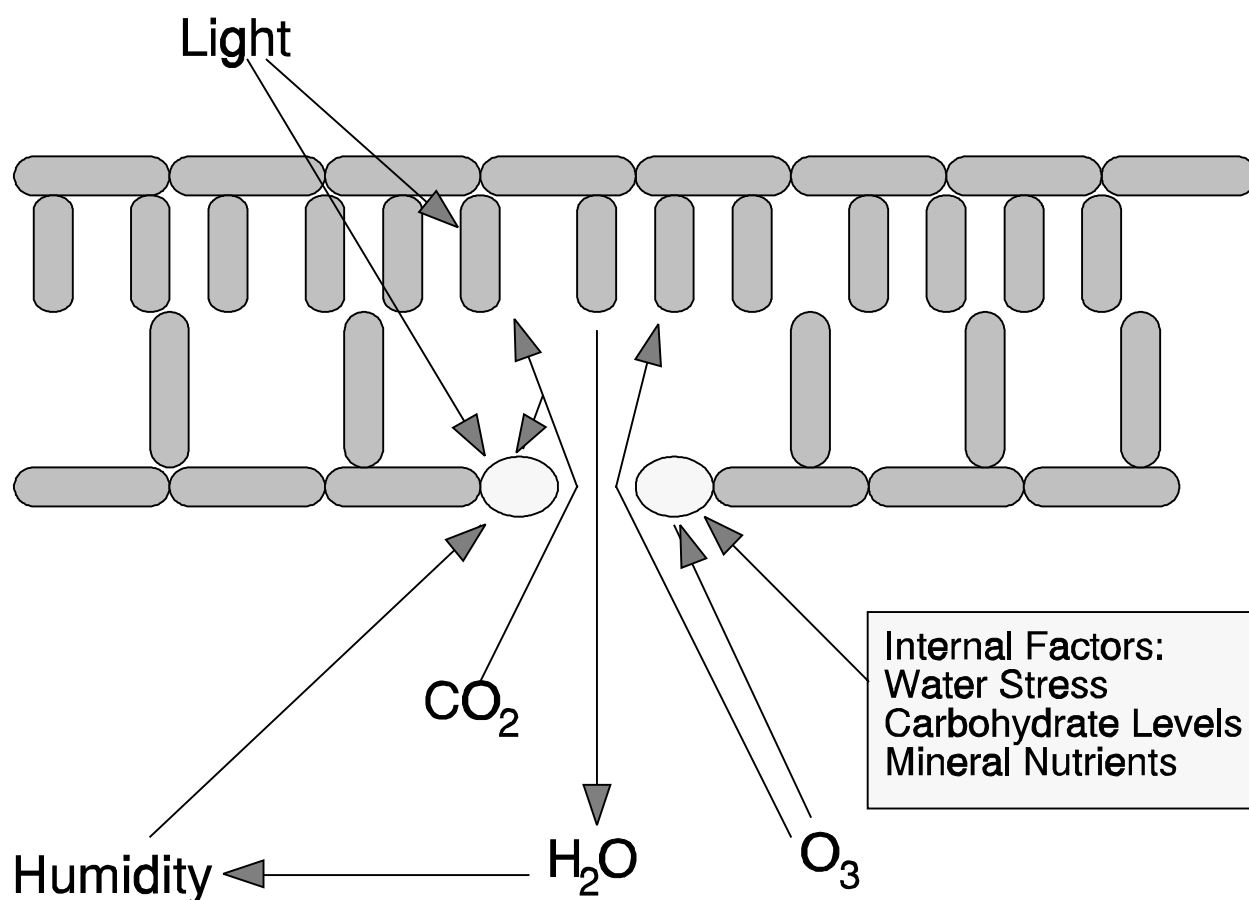
Grünhage and Jäger (1994a,b), using information gathered from a micrometeorological study of O<sub>3</sub> flux observations above a natural grassland in Germany, developed a mathematical model to describe the flux and to estimate the potential injury to the grassland. The aim of the paper was to explain how both vertical flux and stomatal conductance changed during the day and influenced the uptake of air pollutants. For this reason, under ambient conditions, exposures cannot be expressed as a simple function of the pollutant concentration in air.

In summary, O<sub>3</sub> uptake (absorption to surfaces and absorption by tissues) by plant canopies has been measured only a few times. The results are consistent with the hypothesis that stomatal conductance plays a major role in the process. Modeling of O<sub>3</sub> absorption by leaves provides a means of assessing the understanding of the processes controlling O<sub>3</sub> absorption. Combining direct measurements over canopies with modeling will provide a means for assessing the dynamics of O<sub>3</sub> uptake in a canopy.

### **5.3.2.2 Ozone Absorption by Leaves**

The importance of stomatal conductance for the regulation of O<sub>3</sub> uptake by a canopy has been hypothesized for some time (Heck et al., 1966; Rich et al., 1970). Uptake of O<sub>3</sub> by leaves is controlled primarily by stomatal conductance, which varies as a function of stomatal aperture (Figure 5-3). Kerstiens and Lenzian (1989) found that the permeability of cuticles by O<sub>3</sub> from several species was about 0.00001 that of open stomata. Movement of guard cells, which control stomatal opening, are affected by a variety of environmental and internal factors, including light, humidity, CO<sub>2</sub> concentration, and water status of the plant (Zeiger et al., 1987; Kearns and Assmann, 1993). Air pollutants, including O<sub>3</sub>, also may affect stomatal function (U.S. Environmental Protection Agency, 1986). The pattern of diurnal stomatal conductance is produced by the integrated response of guard cells to a variety of factors.

As the primary "gate keepers" for gas exchange between the atmosphere and the leaf, stomata perform the vital function of controlling the movement of gases, including air pollutants such as O<sub>3</sub>, to and from the leaf. The complexity of the response of stomata to environmental (microclimatic and edaphic) factors is indicated by the large amount of research on stomatal physiology and response to changing conditions (for reviews, see Zeiger et al., 1987; Schulze and Hall, 1982) and on developing models to simulate stomatal response (Avisar et al., 1985; Ball et al., 1987; Collatz et al., 1991; Eamus and Murray, 1991; Friend, 1991; Gross et al., 1991; Johnson et al., 1991; Küppers and Schulze, 1985). The magnitude and diurnal pattern of stomatal conductance depends on both internal, species-specific factors and on the external environment, including soil fertility and nutrient availability, as well as microclimate (Schulze and Hall, 1982; Beadle et al., 1985a,b). Mid-day stomatal closure is observed frequently under conditions of high temperature and low water availability (Helms, 1970; Tenhunen et al., 1980; Weber and Gates, 1990). As an example of the variability in diurnal gas exchange, Tenhunen et al. (1980) present nine graphs of diurnal photosynthesis for apricot (*Prunus armeniaca*) measured from July to September 1976. Although there is a general pattern of increase in the morning and of decline in the evening, the path of photosynthesis and conductance are quite different among



**Figure 5-3.** *Movement of gases into and out of leaves is controlled primarily by the stomata (small openings in the leaf surface whose aperture is controlled by two guard cells). Guard cells respond to a number of external and internal factors, including light, humidity, carbon dioxide (CO<sub>2</sub>), and water stress. In general, the stomata open in response to light and increasing temperature and close in response to decreasing humidity, increased CO<sub>2</sub>, and increasing water stress. They also may close in response to air pollutants, such as ozone.*

of days. The inherent variability in stomatal opening makes using a set time period for O<sub>3</sub> exposure problematic. This variability makes determining the effects of a given diurnal O<sub>3</sub> exposure pattern difficult without reference to physiological, meteorological, and edaphic information, as well as to the sensitivity of individual species exposed.

To be absorbed, O<sub>3</sub> must be present in the atmosphere surrounding the leaf and the stomata must be open. Any factor that affects stomatal opening affects O<sub>3</sub> absorption (Figure 5-3). Under drought conditions, when stomatal conductance is reduced, the relative effect of O<sub>3</sub> is less when compared with well-watered controls (Tingey and Hogsett, 1985; Flagler et al., 1987; Temple et al., 1993, also see Section 5.4). Low humidity has been shown to modify plant response to O<sub>3</sub> (McLaughlin and Taylor, 1981), presumably due to reduced O<sub>3</sub> absorption (Wieser and Havranek, 1993).

To calculate  $O_3$  absorption, some estimate of the internal  $O_3$  concentration must be made. In earlier work, a finite  $O_3$  concentration was assumed to exist in the intercellular air space of the leaf (Bennett et al., 1973; Tingey and Taylor, 1982; Lange et al., 1989). Estimating this concentration is difficult because the rate of  $O_3$  absorption into the leaf must be known. Recently Laisk et al. (1989) presented evidence that this concentration is near zero, a result that is consistent with the highly reactive nature of  $O_3$ . Further studies on other species must be made to test the hypothesis that internal  $O_3$  concentration is negligible in leaves.

The other component of absorption,  $O_3$  concentration outside the leaf, may vary greatly with time of day and season (Chapter 4). Data on the effect of variations in  $O_3$  profile (from constant concentrations to equal daily peaks to variable [episodic] peaks), based on greenhouse and OTC chamber studies using simulated exposures, suggest that those profiles that have periodic high concentrations have a greater effect than those with low peaks even though the exposure is equivalent (Hogsett et al., 1985a; Musselman et al., 1986b; see Section 5.6). Taylor and Hanson (1992) show how variations in conductance can affect  $O_3$  absorption and conclude that conductances in and near the leaf surface have a major influence on absorption of  $O_3$ . Figure 5-4 shows a simulation of the effect of diurnal variation in stomatal conductance and  $O_3$  concentration on the  $O_3$  absorbed into the leaf. Amiro and Gillespie (1985) found that cumulative  $O_3$  absorption correlated with visible injury in soybean. Weber et al. (1993) found that rate of uptake may play an important role in the response of ponderosa pine (*Pinus ponderosa*). The roles of cumulative uptake versus uptake rate have not been clarified and need further study.

Absorption of  $O_3$  by leaves depends on variations in both stomatal conductance and  $O_3$  concentration. The highly reactive nature of  $O_3$  makes measuring its absorption difficult; therefore, models of stomatal conductance are used, along with  $O_3$  concentrations, to estimate  $O_3$  absorption. The relative importance of absorption rate versus cumulative absorption is not known at present.

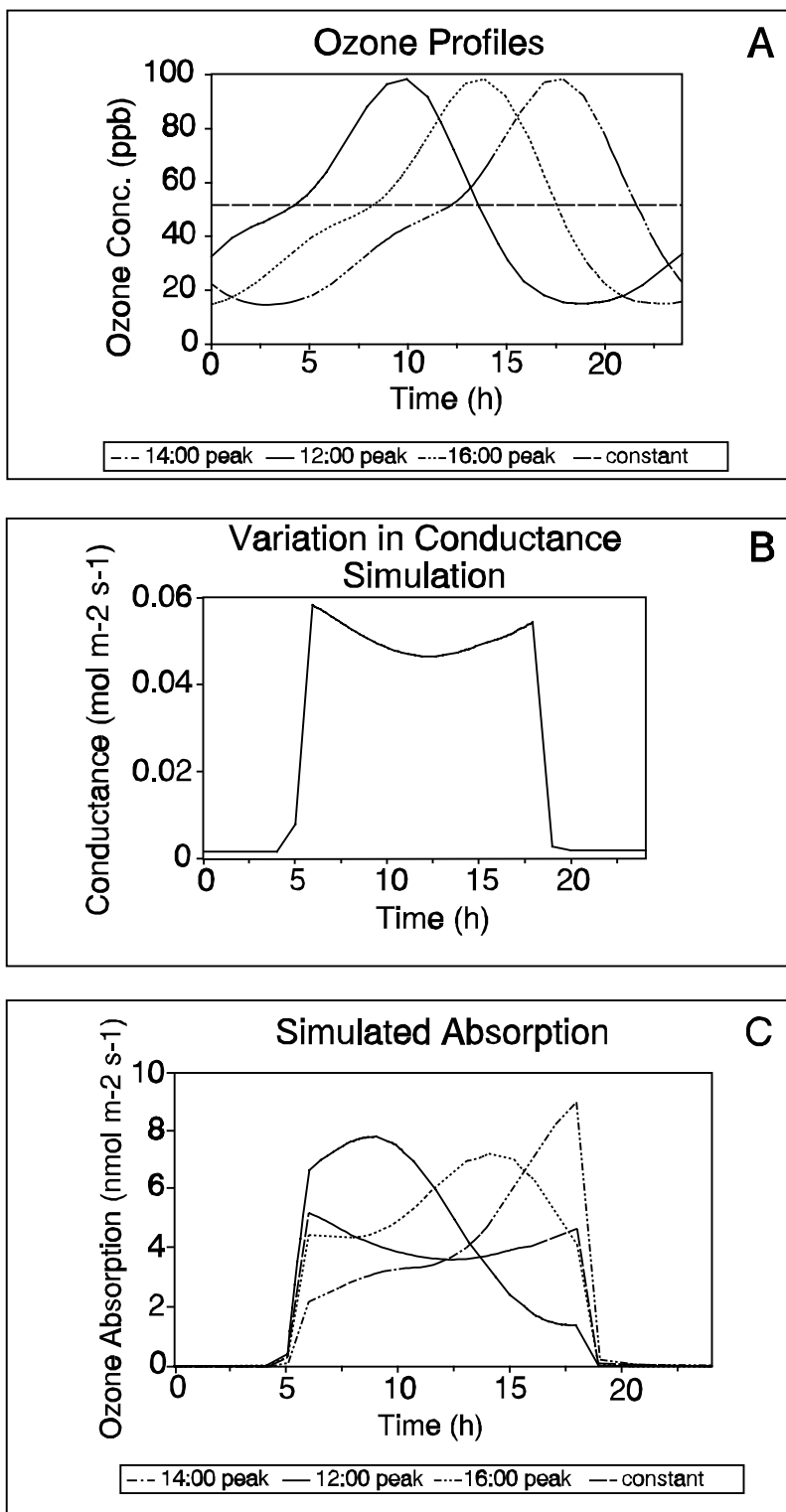
### 5.3.3 Resistance Mechanisms

Resistance mechanisms can be divided into two types: (1) exclusion from sensitive tissue and (2) detoxification near or in sensitive tissue. For leaves, the former involve response and cuticles, and the latter involve various potential chemical and biochemical reactions that chemically reduce  $O_3$  in a controlled manner. Although these systems potentially provide protection against  $O_3$  injury to tissue physiology, they come at some cost, either in the reduction in photosynthesis, in the case of stomatal closure, or in carbohydrate used to produce detoxification systems.

Injury to leaf and needle cuticles does not appear to have a major effect on leaf function, based on the inconsistent data. Barnes et al. (1988a) found that  $O_3$  exposure could damage leaf cuticles; however, Lütz et al. (1990) found no consistent changes in cuticle structure in Norway spruce (*Picea abies*).

#### 5.3.3.1 Stomatal Limitation

As noted above, stomata can be affected by a wide variety of environmental factors (Section 5.3.2.2), by occurrences of stress (Section 5.4), and by age. In addition,



**Figure 5-4.** Simulation of the effects of diurnal variation in stomatal aperture and in ozone ( $O_3$ ) concentration on  $O_3$  uptake: (A) diurnal  $O_3$  concentrations, (B) simulated conductance, and (C)  $O_3$  uptake.

stomatal response can vary among species. These multiple interactions make accurate prediction of uptake under field conditions difficult. Some early research showed a decrease in leaf conductance (Figure 5-3), with O<sub>3</sub> exposure implying a direct effect of O<sub>3</sub> on stomatal conductance (U.S. Environmental Protection Agency, 1986). In studies at high O<sub>3</sub> concentrations (>0.3 ppm), stomatal response was rapid (Moldau et al., 1990). In other studies, reduction in conductance in response to O<sub>3</sub> required hours to days of exposure (Dann and Pell, 1989; Weber et al., 1993). Several studies have shown that discrimination against C<sub>13</sub> in C<sub>3</sub> plants decreases with O<sub>3</sub> fumigation (Okano et al., 1985; Martin et al., 1988; Greitner and Winner, 1988; Saurer et al., 1991; Matyssek et al., 1992). These data are consistent with an increased restriction of diffusion of CO<sub>2</sub> into the leaf (Farquhar et al., 1989). However, Matyssek et al. (1992) and Saurer et al. (1991) found that internal CO<sub>2</sub> increased with O<sub>3</sub> exposure, and that water-use efficiency decreased, both the opposite of expectation, indicating that photosynthesis decreased relatively more than conductance. Although stomata limit O<sub>3</sub> uptake and may respond directly to high O<sub>3</sub> concentrations (e.g., >0.2 ppm, U.S. Environmental Protection Agency, 1986; Moldau et al., 1990), the relative importance of this response, compared to indirect effects induced by reductions in photosynthetic performance, has not been fully assessed.

### 5.3.3.2 Detoxification

When O<sub>3</sub> enters a cell, several highly reactive compounds can be produced (e.g., superoxide, free radicals, peroxides) (Heath, 1988). The effects of these compounds depends on their reactivity, mobility, and half-life. For detoxification to occur, oxidant and antioxidant must occur proximately. In addition, the rate of production of antioxidant must be a significant portion of the rate of oxidant entry into the system for effective detoxification to occur. Two general kinds of detoxification systems have been reported in plants: (1) those that utilize reductants (e.g., ascorbate) to reduce O<sub>3</sub> and (2) those that utilize enzymes (superoxide dismutase). In either case, excess oxidizing power is dissipated in a controlled manner, effectively protecting the tissue from damage. These protective systems probably developed in response to photooxidation, which can occur, for example, at low temperatures (Powles, 1984).

Several antioxidants have been reported, the most studied being ascorbate and glutathione (GSH). Much of this work has occurred since the 1986 criteria document (U.S. Environmental Protection Agency, 1986). Alscher and Amthor (1988) reviewed the literature in this area. In the chloroplast, the process requires dihydronicotinamide adenine dinucleotide phosphate and may be a cause for the transient reduction in photosynthesis observed in some studies (Alscher and Amthor, 1988).

Evidence for the participation of antioxidants in protecting cells from O<sub>3</sub> injury is primarily indirect (i.e., changes in levels of antioxidants or of associated enzymes). In red spruce (*Picea rubens*), GSH levels increased in year-old needles in response to O<sub>3</sub>, but not in current-year needles (Hausladen et al., 1990; Madamanchi et al., 1991). Dohmen et al. (1990) found increased concentrations of reduced glutathione in Norway spruce in response to long-term O<sub>3</sub> fumigation. In a poplar hybrid (*Populus maximowiczii* x *P. trichocarpa*), total GSH increased with O<sub>3</sub> fumigation; however, the ratio of reduced forms to oxidized forms declined, indicating that oxidation of GSH possibly was stimulated by O<sub>3</sub> (Gupta et al., 1991). Mehlhorn et al. (1986) found that both GSH and ascorbic acid (AH<sub>2</sub>) increased with O<sub>3</sub> fumigation in silver fir (*Abies alba*) and Norway spruce. The potential for AH<sub>2</sub> to protect cells from O<sub>3</sub> damage was explored by Chameides (1989), who concluded that such protection



was possible if  $\text{AH}_2$  occurred in the apoplast at sufficient concentrations and production rates; however, experimental data are needed to test this hypothesis.

The response of enzymes involved in detoxification is not clear. Activities of enzymes involved in antioxidant production increased in response to  $\text{O}_3$  in one study (Price et al., 1990); however, in several others, no effect was found (Madamanchi et al., 1992; Pitcher et al., 1991; Anderson et al., 1992; Nast et al., 1993). Activity of superoxide dismutase (SOD), an enzyme that can reduce one of the products of  $\text{O}_3$  interaction with the cytoplasm, can be increased by  $\text{O}_3$  fumigation (Alscher and Amthor, 1988; Gupta et al., 1991). There are both cytosolic and chloroplastic forms of this enzyme, but the role the different forms play in detoxification of  $\text{O}_3$  is not clear. Teppermann and Dunsmuir (1990) and Pitcher et al. (1991) found that increased production of SOD had no effect on resistance to  $\text{O}_3$  in tobacco.

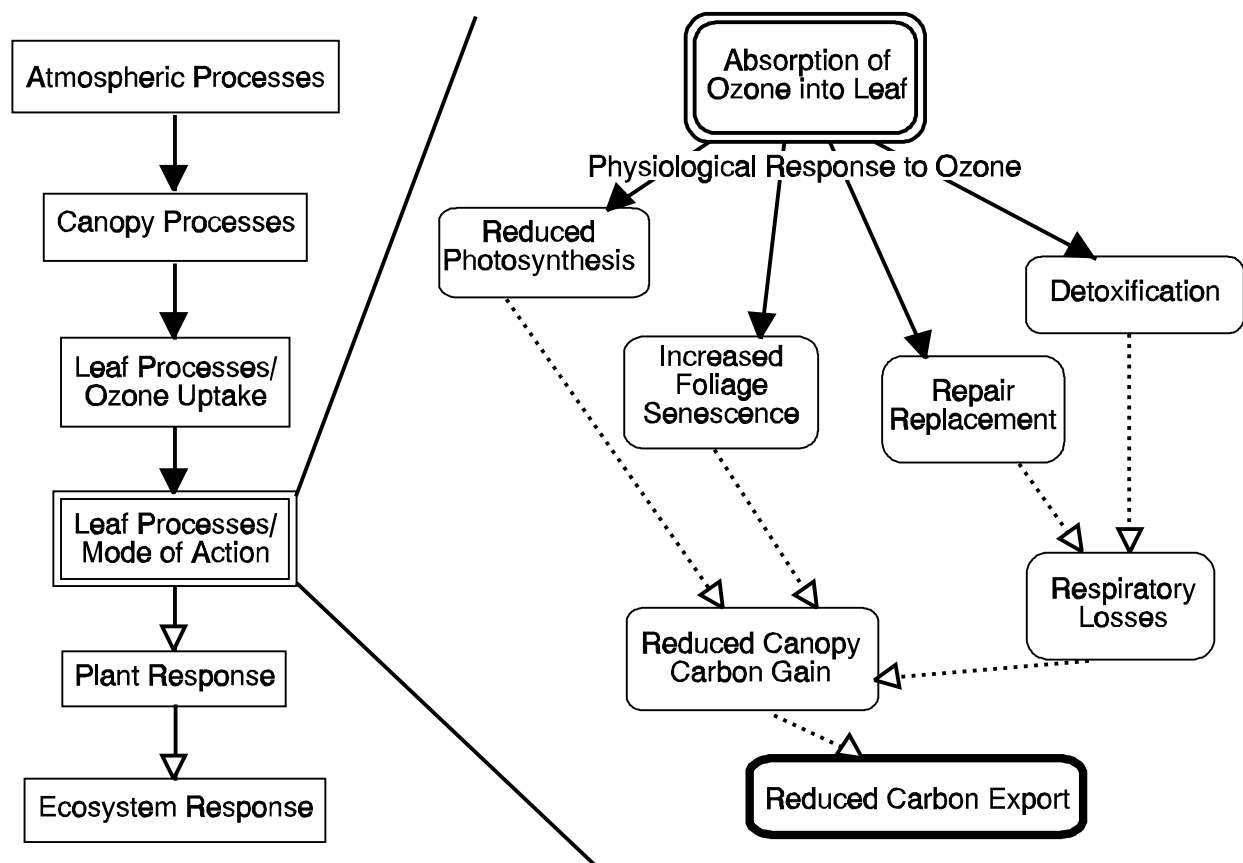
The extent to which these detoxification systems can protect tissue from  $\text{O}_3$  damage is unknown. However, "if plants have detoxification mechanisms which are kinetically limited, the rate of  $\text{O}_3$  uptake may be important, so that even an integrated absorbed dose may be insufficient to account for observed responses" (Cape and Unsworth, 1988). Potential rates of detoxification for given tissues are needed to estimate the importance of these systems to overall  $\text{O}_3$  response. In addition, the sites in which the detoxification systems occur need to be identified.

#### **5.3.4 Physiological Effects of Ozone**

The initial reactions of  $\text{O}_3$  with cellular constituents are not known. The high reactivity and nonspecificity of  $\text{O}_3$  reactions, coupled with the absence of a useful isotopic tag for  $\text{O}_3$ , make studies of the initial reactions difficult at best. The data on changes in biochemical function resulting from  $\text{O}_3$  exposure probably represent effects one or more steps beyond the initial reactions. Nonetheless, data is available that indicate the wide range of cellular processes that can be affected by  $\text{O}_3$ .

Ozone that has not been neutralized by one of the detoxification systems (Figure 5-5) acts first at the biochemical level to impair the functioning of various cellular processes (Tingey and Taylor, 1982; U.S. Environmental Protection Agency, 1986). The result of these impairments are reflected in integrated changes in enzyme activities, membrane function, and energy utilization (Queiroz, 1988). Several related papers have shown that the activity of the primary carboxylating enzyme (RuBP-carboxylase) is reduced by  $\text{O}_3$  exposures in the range of those measured at some sites (Dann and Pell, 1989; Enyedi et al., 1992; Pell et al., 1992; Landry and Pell, 1993). Membrane injury has been found in some experiments using acute levels of  $\text{O}_3$  (Heath, 1988). Chronic exposure can lead to changes in lipid composition and in cold resistance (Brown et al., 1987; Davison et al., 1988; DeHayes et al., 1991; Lucas et al., 1988; Wolfenden and Wellburn, 1991). Recently, Floyd et al. (1989) have shown that  $\text{O}_3$  can affect nuclear deoxyribonucleic acid (DNA).

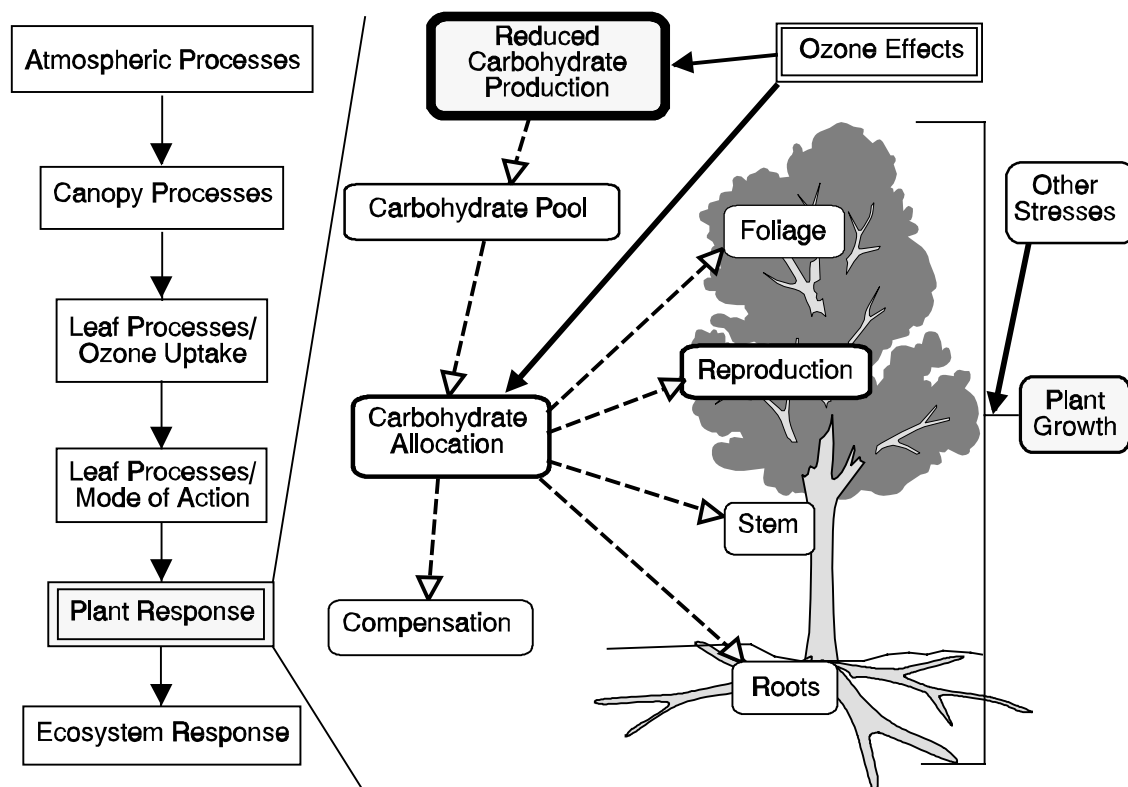
Changes in the in vivo concentrations of various growth regulators in response to  $\text{O}_3$  exposure could have important consequences for plant function. However, the effects of  $\text{O}_3$  on levels and activities of growth regulators have not been studied extensively. Ozone has been shown to stimulate ethylene production, and inhibitors of ethylene production have been found to reduce the effects of  $\text{O}_3$  in short-term experiments (Pell and Puente, 1986; Rodecap and Tingey, 1986; Taylor et al., 1988b; Mehlhorn et al., 1991; Telewski, 1992; Langebartels et al., 1991; Mehlhorn and Wellburn, 1987; Kargiolaki et al., 1991; Reddy



**Figure 5-5. Effects of ozone ( $O_3$ ) absorption into a leaf.** Once inside the leaf,  $O_3$  can have a number of effects, all of which affect carbohydrate production and utilization. Reduced photosynthesis, increased leaf senescence, production of detoxification systems, and increased respiration (both maintenance and growth) reduce the amount of carbohydrate available for allocation. Compensation through production of new leaves, for instance, can counter some or all of these effects, depending on the  $O_3$  exposure, the physiological state of the plant, and the species. Integration of these processes leads to changes in the amount of carbohydrate available for allocation from the canopy. Solid black arrows denote  $O_3$  flow, and dotted arrows show the cascade of effects of  $O_3$  absorption on leaf function. Boxes at the left and at the top with double borders indicate leaf processes; the box at the bottom with a dark border indicates the impact.

et al., 1993). Ethylene is produced during ripening of fruit, during periods of stress, and during senescence (Abeles et al., 1992). Increased levels of ethylene in the leaves could play a role in the early senescence of foliage. In some cases, there is a correlation between ethylene production and  $O_3$  sensitivity; however, the relationship is complex and makes use of ethylene production as an index of sensitivity problematic (Pell, 1988).

Abscisic acid (ABA) plays an important role in stomatal function (Davies et al., 1980). Atkinson et al. (1991) found that stomata from O<sub>3</sub> fumigated leaves were less sensitive to ABA than control leaves. Maier-Maercker and Koch (1991a,b; 1992a,b) found that exposure to ambient pollutants, including O<sub>3</sub> and SO<sub>2</sub>, caused histological changes in guard cells and resulted in some loss in stomatal control. Results from studies on European white birch (*Betula pendula*) also indicate some change in stomatal function (Matyssek et al., 1992). These data could explain the observation that stomatal function may be impaired by long-term O<sub>3</sub> exposure (Walmsley et al., 1980). Kobriger et al. (1984) found no effect of O<sub>3</sub> on whole-leaf content of ABA, but changes in compartmentation could not be ruled out.



**Figure 5-6.** *Effect of ozone ( $O_3$ ) on plant function and growth. Reduction in carbohydrate allocation affects the pool of carbohydrates available for growth. Changes in relative growth rate of various organs as a function of  $O_3$  exposure suggest that allocation patterns of carbohydrate are affected. Solid black arrows denote where  $O_3$  absorption affects the allocation processes of the plant; dotted arrows show the cascade to plant growth. Boxes with dark borders indicate site of impact. The box with a double border, at left, indicates the location of response.*

Ozone-induced reduction in net photosynthesis has been known for some time (U.S. Environmental Protection Agency, 1986). Changes in stomatal conductance, photosynthetic capacity, carbohydrate allocation, and respiration have been documented. The relationship between O<sub>3</sub> exposure and photosynthesis is not well known. Photosynthesis provides plants with the energy and structural building blocks necessary for their existence. The photosynthetic capacity of a plant is an important aspect of plant response to stresses in natural environments and is strongly associated with leaf nitrogen content and with water movement. Both resources are essential if the process is to occur and involves the allocation of carbohydrates from the leaves to the roots for nitrogen acquisition and water uptake. Leaf photosynthetic capacity is also age dependent. As the plant grows, the canopy structure changes altering the amount and angle of light hitting a leaf. Allocation of carbohydrates and nutrients to new leaves is especially important in stimulating growth production (Pearcy et al., 1987). Reductions in photosynthesis are likely to be accompanied by a shift in growth pattern that favors shoots and by an increase or decrease in leaf life span (Winner and Atkinson, 1986). Therefore, alteration of the processes of photosynthesis and carbohydrate allocation affects plant response to stresses such as O<sub>3</sub>. Reduction in photosynthesis (reduced carbohydrate formation and allocation to leaf repair or to new leaf formation decreases the availability of carbohydrates) potentially alters the normal allocation pattern and, therefore, all aspects of plant growth and reproduction (Figure 5-6). The effects of a reduction in photosynthesis on growth and reproduction was discussed in the previous criteria document (U.S. Environmental Protection Agency, 1986).

Carbohydrate production by a single plant is controlled not only by photosynthetic capacity of the foliage but also by the amount and distribution of that foliage. Stow et al. (1992) and Kress et al. (1992) found that O<sub>3</sub> exposure affected needle retention in loblolly pine (*Pinus taeda*). Similar data have been reported for slash pine (*Pinus elliotti*) (Byres et al., 1992a). Keller (1988) and Matyssek et al. (1993a,b) reported increased senescence with increased O<sub>3</sub> exposure in trembling aspen, as did Wiltshire et al. (1993) in apple (*Malus spp*). Replacement of injured leaf tissue has been reported for some species when they are exposed to low O<sub>3</sub> concentrations (Held et al., 1991; Temple et al., 1993). Temple et al. (1993) also found increased photosynthetic capacity of new needles in O<sub>3</sub> treatments compared to controls.

Few direct effects of O<sub>3</sub> have been found outside leaves. Kargiolaki et al. (1991) found that intumescences (lesions) appear on stems of three species of poplar (*Populus*) after 72 days of O<sub>3</sub> fumigation (70 to 80 ppb). Ozone probably enters the stem through the lenticles that occur on the surface of the stem and allow direct exchange of gases between the stem and the air. The consequence of this response to O<sub>3</sub> is not clear; however, it may be related to the reduction in phloem transport rate observed in loblolly pine (Spence et al., 1990).

#### **5.3.4.1 Carbohydrate Production and Allocation**

The importance of photosynthesis and carbohydrate allocation in plant growth and reproduction has been pointed out previously. The patterns of carbohydrate allocation directly affect growth rate. Plants require a balance of resources to maintain optimal growth; however, in natural environments optimal conditions seldom occur. Therefore, some plants compensate for differences in resource availability and for environmental stresses. They do this by changing the way they allocate carbohydrates (Chapin et al., 1987). Each response to stress affects the availability of carbohydrates for allocation from the leaves (Figure 5-5).

The carbohydrate pool is affected both by a reduction in the carbohydrate produced and by a shift of carbohydrate to repair and replacement processes. The effect is particularly noticeable in the roots where O<sub>3</sub> exposure significantly reduces available carbohydrate (Andersen et al., 1991; Andersen and Rygielwicz, 1991). Effects on leaf and needle carbohydrate content have varied from a reduction (Barnes et al., 1990b; Miller et al., 1989c) to no effect (Alscher et al., 1989) to an increase (Luethy-Krause and Landolt, 1990). Cooley and Manning (1987) reviewed the literature on carbohydrate partitioning and noted that "storage organs ... are most affected by O<sub>3</sub>-induced partitioning changes when O<sub>3</sub> concentrations are in the range commonly observed in polluted ambient air." Friend and Tomlinson (1992) found that O<sub>3</sub> exposure increased retention of <sup>14</sup>C-labeled photosynthate in needles of loblolly pine, and modified the distribution of labels among starch, lipids, and organic acids (Edwards et al., 1992b; Friend et al., 1992).

The above discussion supports the information in the previous criteria document (U.S. Environmental Protection Agency, 1986), which pointed out that roots usually were affected more by O<sub>3</sub> exposures than were the shoots. Studies by Miller et al. (1969), Tingey et al. (1976b), McLaughlin et al. (1982), and Price and Treshow (1972) were cited in support of this view. Miller et al. (1969) noted that reduction in photosynthesis was accompanied by decreases in sugar and polysaccharide fraction in injured needles of ponderosa pine seedlings, as well as by altered allocation of carbohydrates. Exposures were for 30 days, 9 h/day, to concentrations of 0.15, 0.30, or 0.40 ppm. These exposures reduced photosynthesis by 10, 70, and 85%, respectively. The observations of Tingey et al. (1976a) indicated that O<sub>3</sub> exposures differentially affected metabolic pools in the roots and tops of ponderosa pine seedlings grown in OTCs. Further, this study indicated that the amounts of soluble sugars, starches, and phenols tended to increase in the tops and decrease in the roots of ponderosa pine seedlings exposed to 0.10 ppm O<sub>3</sub> for 6 h/day for 20 weeks. The sugars and starches stored in the tree roots were significantly less than those in the roots of controls. In another study cited in the 1986 document, McLaughlin et al. (1982) also observed the reduced availability of carbohydrate for allocation to the roots and stated that the result was reduced vigor and enhanced susceptibility of trees to root diseases. Loss of vigor was due to a sequence of events that was associated with exposure to O<sub>3</sub>, including premature senescence, loss of older needles, lower gross photosynthetic productivity, and reduced photosynthate (carbohydrates) available for growth and maintenance. Carbon-14 transport patterns also indicated changes in carbon allocation. Older needles were found to be the source of photosynthate for new needle growth in the spring and were storage sinks in the fall. Retention of <sup>14</sup>C-photosynthate by foliage and branches of sensitive trees indicated that allocation to the trunks and roots was reduced.

Lost carbohydrate production has effects throughout the plant (Figure 5-6). The roots and associated mycorrhizal fungi are especially susceptible to reduced carbohydrate availability and, quite frequently, show the greatest decline in growth (Adams and O'Neill, 1991; Edwards and Kelly, 1992; McQuattie and Schier, 1992; Meier et al., 1990; Taylor and Davies, 1990). However, in some cases, increased mycorrhizal formation has been reported (Gorissen et al., 1991b; Reich et al., 1985). It might be expected that reduced allocation to roots would affect shoot growth through increased susceptibility to water stress, reduced nutrient availability (Flagler et al., 1987), and reduced production of growth factors (Davies and Zhang, 1991; Letham and Palni, 1983). Effects on production and retention of leaves and needles were described above. Effects on stem growth have been found in tree species (Hogsett et al., 1985b; Mudano et al., 1992; Pathak et al., 1986; Matyssek et al., 1992;

Matyssek et al., 1993b). Changes in canopy density, root/shoot ratio, and stem growth will affect the functioning of the plant and may make plants more susceptible to environmental stresses, such as drought and nutrient limitation, that are characteristic of many ecosystems.

#### **5.3.4.2 Compensation**

Compensatory responses occur as plants attempt to minimize the effects of stress. Responses include adjustments to changes in physiological processes (e.g., photosynthetic performance and foliage production) that tend to counteract the effects of O<sub>3</sub> absorption by the leaves. Pell et al. (1994) have reviewed the extensive literature produced in the Response of Plants to Interacting Stresses (ROPIS) experiment (Goldstein and Ferson, 1994). A wide range of compensatory responses have been identified, especially reallocation of resources leading to increased relative growth in the shoot compared to the root (see above). Compensation can take the form of production of new tissue (e.g., leaves) to replace injured tissue or of biochemical shifts, including increased photosynthetic performance in new foliage.

Changes in respiratory rate have been attributed to such repair processes (U.S. Environmental Protection Agency, 1986). Recent studies have found stimulation of dark respiration in Norway spruce (Barnes et al., 1990b; Wallin et al., 1990) and pinto bean (Amthor, 1988; Amthor and Cumming, 1988; Moldau et al., 1991b). Repair of membranes (Sutton and Ting, 1977; Chevrier et al., 1988, 1990) and replacement of impaired enzymes are two probable reasons for increased respiration. Ozone has been shown to increase the adenosine triphosphate/adenosine diphosphate (ATP/ADP) ratio, which is consistent with increased respiratory activity (Weidmann et al., 1990; Hampp et al., 1990). As in the case of detoxification, the importance of repair processes in the overall carbohydrate budget of the plant and of their influence of apparent threshold is unknown.

Recovery of photosynthetic performance after O<sub>3</sub> exposure has been noted in some studies. Early work indicated that recovery of photosynthetic capacity could occur after exposure of high concentrations (>0.25 ppm) of O<sub>3</sub> (e.g., Botkin et al., 1971, 1972). Dann and Pell (1989) found that photosynthetic rate, but not Rubisco activity, recovered within a few days in potato (*Solanum tuberosum*) after exposure to 0.2 ppm O<sub>3</sub>. In ponderosa pine, photosynthetic rates in O<sub>3</sub> treated needles recovered to that of controls within 40 to 50 days (Weber et al., 1993). To what extent this recovery can offset losses in carbohydrate gain is not known, nor is the mechanism.

Replacement of injured foliage (see Section 5.3.4) is another method to counteract the effects of O<sub>3</sub> exposure. The extent to which increased leaf and needle production and increased photosynthetic performance in the new foliage compensates for O<sub>3</sub> injury is not known.

The importance of various compensatory mechanisms is not sufficiently well known to allow an estimate of the degree to which they might mitigate the effect of O<sub>3</sub>. The fact that increases in photosynthesis and in leaf production have been measured indicates that these processes, at least, may be important.

#### **5.3.5 Role of Age and Size Influencing Response to Ozone**

Plant age, physiological state, and frequency of exposure play important roles in plant response to O<sub>3</sub>. In annual species, effects of O<sub>3</sub> on production will occur through changes in allocation of carbohydrates over the years, resulting in reduced seed production.

In perennial species, plant growth will be affected by reduction in storage of carbohydrates, which may limit growth the following year (carry-over effects). Carry-over effects have been documented in the growth of tree seedlings (Hogsett et al., 1989; Sasek et al., 1991; Temple et al., 1993) and roots (Andersen et al., 1991). Accumulation of these effects will affect survival and ability to reproduce. Data on cumulative effects of multiple years of  $O_3$  exposures have been, for the most part, the result of 2- to 3-year studies.

A tacit assumption in much of the research on  $O_3$  effects on trees is that seedling response to  $O_3$  is a good predictor of large-tree response. This assumption has been necessitated by the difficulty in exposing large trees to  $O_3$  for long periods. Pye (1988) reviewed the problems of extrapolation from seedling/sapling experiments to large trees and noted several areas of difference between seedling/saplings and large trees: (1) microclimate (especially radiation), (2) transport distances, (3) ratio of photosynthetic to respiratory tissue, and (4) potential for storage. Cregg et al. (1989) also argued that these differences in scale can affect growth responses seen. Some studies have indicated that seedlings may be more sensitive (i.e., greater visible injury) than large trees (Kozlowski et al., 1991); however, Samuelson and Edwards (1993) found that leaves on large red oak trees (*Quercus rubra*) are more sensitive than those on seedlings. It is likely that a variety of factors determines sensitivity to  $O_3$ , including stomatal function and presence of detoxification systems, so that, in some cases, seedlings will be more sensitive and, in others, large trees will be. Although each of the four differences between small and large trees mentioned above can be supported on theoretical grounds, little direct information is available to evaluate the importance of these differences, especially with respect to  $O_3$ .

The microclimate of the canopy of mature trees is quite different from that of seedlings, as is that of a stand of trees compared to a single tree in a field. Light intensity through the multilayer canopy can vary by an order of magnitude or more (Jones, 1992). In addition, gradients of other important microclimatic variables (temperature, humidity, and wind speed) exist within the canopy. These will all affect stomatal conductance, and some (e.g., wind speed) will affect canopy conductance. In addition, leaf development will be affected by these microclimatic variables (especially light intensity), leading to leaves with different physiological capacity and sensitivity to  $O_3$  (Samuelson and Edwards, 1993; Waring and Schlesinger, 1985).

The effect of plant size on transport processes and the subsequent response to  $O_3$  is unknown. The simple fact of greater distance over which transport must occur will affect the timing of response of organs distant from the primary site of  $O_3$  impact, the foliage. Studies using methods that integrate functions over the whole tree could provide useful information. For example, combinations of porometer measurements on foliage and whole-plant water use measured (Schulze et al., 1985) on individuals of different sizes could provide very useful information on the coupling of leaf-level processes to whole-canopy and whole-plant response. Greater evaporative demand in large trees as the result of greater leaf area and different microclimate than in small trees could lead to transient water stress and stomatal closure because of insufficient water transport capacity.

As a tree grows from a seedling to a large tree, the ratio between photosynthesis and respiration declines as a greater portion of the plant tissue becomes nonphotosynthetic. It is reasonable to assume that such a change could result in less resource being available for detoxification and repair as the plant grows. How this change affects the ability of a plant to survive  $O_3$  (or any other stress) is not known. Recently, Samuelson and Edwards (1993) presented data on northern red oak that show  $O_3$  decreased photosynthetic performance more

on lower leaves within the canopy of large trees than on leaves near the top of the canopy (a result apparently counter to the model results of Reich et al., 1990). Seedling photosynthesis was not affected by the same  $O_3$  exposure. A more interesting result of this work is the reduction in total canopy biomass found in large trees exposed to  $O_3$ . It is not possible to assess directly the relative importance of reduced photosynthesis versus loss of canopy from these data, but the data do show that differences may exist between large trees and seedlings in their response to  $O_3$ . These differences may be due to changes in carbon budgets, stomatal characteristics, microclimate, and flushing patterns that develop as seedlings become trees. The ability of northern red oak seedlings to produce three flushes and thus replace injured foliage may be an important defense mechanism in the seedling stage. The physiological basis of these findings need further investigation.

In evergreen perennial plants, foliage must be maintained from one year to the next, frequently through periods unfavorable to growth. In evergreen species that retain a few to several years of leaves, increased susceptibility to stress (e.g., frost) could further reduce potential canopy photosynthesis in subsequent years (Brown et al., 1987; Davison et al., 1988; DeHayes et al., 1991; Lucas et al., 1988). Fincher (1992) found that  $O_3$  decreased frost tolerance in red spruce in both seedlings and trees; the consequences of this change in seedlings and large trees needs of further study.

The effect of  $O_3$  on storage of carbohydrates in large compared to small trees is not known. Changes in storage could affect the ability of the plant to withstand other stresses or to produce adequate growth during each growing season.

Dendrochronology (tree-ring analysis) provides the opportunity to do retrospective studies over the life of large trees. Reduction in annual radial growth has been found in the southern Sierra Nevada for Jeffrey pine but not for ponderosa pine (Peterson et al., 1987, 1989, 1991; Peterson and Arbaugh, 1988). One difficulty with using tree-ring data to estimate  $O_3$ -related effects is that it is not always possible to separate reductions due to  $O_3$  from other effects (e.g., drought).

Development of reliable methods for scaling from small to large trees is crucial to the prediction of the long-term effects of  $O_3$  on forest function. Measurement of the response of different size trees to  $O_3$  could provide useful data on the relative responses of small and large trees. However, problems exist in giving similar exposures to trees of widely different sizes. The most direct method is to fumigate trees over a significant portion of their life span. Time is the primary obstacle to these studies because they would require decades to complete. Whatever methods are used must be based on a good understanding of the physiological changes that occur as trees grow.

#### **5.3.5.1 Summary**

In the previous criteria document, it was concluded that the "critical effects, including reduction in photosynthesis and a shift in the assimilation of photosynthate, will lead to reduced biomass, growth, and yield" (U.S. Environmental Protection Agency, 1986). In addition, changes in carbohydrate allocation patterns and effects on foliage were noted as important. Since that report, additional information has been developed, especially on the effects of  $O_3$  on photosynthetic performance. However, at present there is still no clear understanding of the initial biochemical changes resulting within the leaf cells after the entry of  $O_3$  and how these changes interact to produce the observed responses. Much of the earlier research used very high ( $\geq 0.25$  ppm)  $O_3$  concentrations, which produced what could be characterized as acute responses. More recent research has used lower concentrations, usually



including near ambient (0.04 to 0.06 ppm) O<sub>3</sub> levels, so that the observed responses may be more relevant to field conditions. One characteristic of these more recent data is that a longer exposure (days to weeks, instead of hours) is needed to show a response.

As a result of the research since the last criteria document (U.S. Environmental Protection Agency, 1986), the way in which O<sub>3</sub> exposure reduces photosynthesis, especially its effects on the central carboxylating enzyme (ribulose-6-P-carboxylase/oxygenase), is better understood. The rate of senescence of leaves has been shown to increase as a function of increasing O<sub>3</sub> exposure. At near-ambient exposures, leaf production has been shown to increase in some species, thereby off-setting the increased loss to due senescence. The mechanism of the increase in senescence is not known, hence deserves further study. Finally, the role that changes in allocation of resources play in plant response to O<sub>3</sub> is now better understood. Most studies have shown that allocation of photosynthate to roots is decreased by O<sub>3</sub>. In some cases, allocation to leaf production has increased. Whether these changes are driven entirely by changes in carbohydrate availability or are controlled by other factors (e.g., hormones) is not known.

Some potentially significant processes have been investigated since the last criteria document, especially detoxification and compensatory processes. The role of detoxification in providing a level of resistance to O<sub>3</sub> has been investigated; however, it is still not clear to what degree these processes can provide protection against O<sub>3</sub> injury. Data are needed especially on the potential rates of antioxidant production and on the subcellular localization of the antioxidants. Potential rates of antioxidant production are needed to assess whether they are sufficient to detoxify the O<sub>3</sub> as it enters the cell. The localization is needed to assess whether the antioxidants are in a location (cell wall or plasmalemma) that permits contact with the O<sub>3</sub> before it has a chance to damage subcellular systems. Ozone exposure has been shown to decrease cold tolerance of foliage in some species. This response could have a major impact on long-lived evergreen species that retain leaves for several years. Various forms of compensation, especially stimulation of production of new leaves and higher photosynthetic performance of new leaves, have been reported. Although these processes divert resources away from other sinks, compensation may counteract the reduction in canopy carbon fixation caused by O<sub>3</sub>. The quantitative importance of these processes is still in need of investigation.

The major problem facing researchers trying to predict long-term O<sub>3</sub> effects on plants is how the plant integrates all of the response to O<sub>3</sub> into the overall response to the environment, including naturally occurring stresses. Little is now known about how response to O<sub>3</sub> changes with increasing age and size. This information is crucial to predicting the long-term consequence of O<sub>3</sub> exposure in forested ecosystems.

## **5.4 Factors That Modify Plant Response**

### **5.4.1 Modification of Functional and Growth Responses**

Plant response to oxidants may be modified by various biological, physical, and chemical factors. Biological factors that modify plant response include those within the plant, as well as those external to the plant. The genetic makeup and the developmental stage play critical roles in the way individual plants respond to O<sub>3</sub> and other external stresses. For example, different varieties or cultivars of a particular species are known to differ greatly in their responses to a given exposure to O<sub>3</sub>, whereas the magnitude of the response of a

particular variety, in turn, depends on environmental factors such as temperature and humidity, soil moisture and nutrition, the presence of pests or pathogens, and exposure to other pollutants or agricultural spray chemicals. In other words, response will be dictated by the plant's present and past environmental milieu, which also includes the temporal pattern of exposure and the plant's stage of development. The corollary is also true: exposure to oxidants can modify response to other environmental variables. For example, exposure to O<sub>3</sub> reduces the ability of trees to withstand winter injury caused by exposure to freezing temperatures (Davison et al., 1988) and influences the success of pest infestations (Hain, 1987; Lechowicz, 1987). Hence, both the impact of environmental factors on response to oxidants and the effects of oxidants on responses to environmental factors have to be considered in determining the impact of oxidants on vegetation in the field. These interactions are summarized as the involvement of "other stresses" in the scheme shown in Figure 5-6 (Section 5.3). In the following review, the environmental factors are grouped into three categories: (1) biological (including genetic and developmental components), (2) physical, and (3) chemical.

Runeckles and Chevone (1992) have provided a general review of the interactive effects of environmental factors and O<sub>3</sub>. The subject also is treated in a National Acid Precipitation Assessment Program (NAPAP) report (Shriner et al., 1991). The numbers of publications that have appeared since the previous criteria document and supplement vary widely among the different environmental factors reviewed. As a result, in several sections, material covered in these earlier documents has been repeated in order to provide comprehensive coverage and to place new findings into context.

#### 5.4.2 Genetics

The response of an individual plant within a species and at a given age is affected both by its genetic makeup and the environment in which it grows. This section examines the role of genetics in plant response to O<sub>3</sub> and its implication for both managed and natural ecosystems. In addition, major knowledge gaps in the understanding of genetic aspects of O<sub>3</sub> responses are pointed out.

The responses of plants to O<sub>3</sub> are strongly influenced by genetics, as was summarized in the air quality criteria document for O<sub>3</sub> (U.S. Environmental Protection Agency, 1986). Thus, the plants of a given population or family will not respond to O<sub>3</sub> in the same way, even if they are grown in a homogenous environment. This has been demonstrated amply through intraspecific comparisons of O<sub>3</sub> sensitivity as determined by foliar sensitivity of ornamental plants, the aesthetic value of which is decreased by visible foliar injury, and of woody plants that are important components of natural ecosystems (Table 5-2). Ornamental plants and plants growing in wilderness areas, for example, have an intrinsic worth, apart from any economic value related to growth (Tingey et al., 1990). Considerable genetic variation in O<sub>3</sub> sensitivity also has been demonstrated for growth responses of crop plants (Table 5-3). The range of responses displayed for visible foliar injury and growth, biomass, or yield vary from species to species and from study to study. However, it is not uncommon to have genotypes varying from no response to well over 50% leaf area injured or 50% growth or yield reductions in the same study. Additional examples of genetic variation in O<sub>3</sub> response are shown in Figure 5-7 for visible foliar injury and in Figure 5-8 for growth. From Figure 5-7, one can see that, depending on what population has been examined, white ash (*Fraxinus americana*) and green ash (*F. pennsylvanica*) could

**Table 5-2. Examples of Intraspecific Variation of Foliar Symptoms in Ozone Response**

Species	Genetic Unit <sup>a</sup>	Ozone Concentration	Duration	Range of Response <sup>b</sup>	Reference
<u>Ornamental, Non-woody Plants</u>					
<i>Petunia</i> sp. (Petunia)	Cultivars	400 ppb 4 h/day	4 days	20 to 60% (3)	Elkiey and Ormrod (1979a,b), Elkiey et al. (1979)
<i>Poa pratensis</i> L. (Kentucky bluegrass)	Cultivars	400 ppb 300 ppb	2 h 4 h	0 to 90% (3) 30 to 60% (3)	Murray et al. (1975), Wilton et al. (1972)
<u>Trees</u>					
<i>Acer rubrum</i> L. (Red maple)	Populations	750 ppb 7 h/day	3 days	19 to 34% (2)	Townsend and Dochinger (1974)
<i>Fraxinus americana</i> L. (White ash)	Half-sib families	500 ppb 250 ppb	7.5 h 6 h	0 to 50% (3) 2 to 33% (2)	Karnosky and Steiner (1981), Steiner and Davis (1979)
<i>Fraxinus pennsylvanica</i> Marsh. (Green ash)	Half-sib families	500 ppb 250 ppb	7.5 h 6 h	0 to 40% (3) 2 to 39% (2)	Karnosky and Steiner (1981), Steiner and Davis (1979)
<i>Gleditsia triacanthos</i> L. (Honeylocust)	Cultivars	Ambient	1 growing season	0 to 34% (3)	Karnosky (1981a)
<i>Pinus ponderosa</i> Dougl. ex P. Laws and C. Laws (Ponderosa pine)	Half-sib families	1.5 × ambient	3 growing seasons	0 to 28% (2)	Temple et al. (1992)
<i>Pinus strobus</i> L. (Eastern white pine)	Clones	300 ppb	6 h	0 to 60% (3)	Houston (1974)
<i>Pinus taeda</i> L. (Loblolly pine)	Half-sib families	250 ppb ambient + 60 ppb	8 h 1 growing season	3 to 29% (2) 1 to 42% (1)	Kress et al. (1982a), Adams et al. (1988)
<i>Populus tremuloides</i> Michx. (Trembling aspen)	Clones	200 ppb 150 ppb	3 h 6 h	7 to 56% (1) 10 to 91% (1)	Karnosky (1977), Berrang et al. (1991)

<sup>a</sup>Cultivars = a variety of agricultural or horticultural crops produced by selective breeding or a vegetatively propagated tree selection; Half-sib = seedlings with one parent in common; Clones = vegetatively propagated individual genotypes; and Populations = seedlings derived from a common gene pool.

<sup>b</sup>Range of response is expressed as (1) percentage of leaves showing visible symptoms, (2) percentage of leaf area injured, or (3) percentage from a leaf injury rating scheme.

**Table 5-3. Examples of Intraspecific Variation in Growth Responses Following Ozone Exposures**

Species	Genetic Unit <sup>a</sup>	Ozone Concentration	Duration	Range of Response <sup>b</sup>	Reference
<u>Crops and Non-woody Plants</u>					
<i>Agrostis capillaris</i> L. (Bentgrass)	Populations	60 ppb	4 weeks	-45 to +20% (2)	Dueck et al. (1987)
<i>Begonia semperflorens</i> Hort. (Bedding begonia)	Cultivars	500 ppb 4 h/day 250 ppb 4 h/day	2 days 4 days	-59 to 0% (2) -16 to +10% (2)	Reinert and Nelson (1979), Reinert and Nelson (1980)
<i>Festuca arundinacea</i> Schreb. (Fescue)	Cultivars	400 ppb 6 h/day	7 days	-53 to -35% (2)	Flagler and Younger (1982)
<i>Lycopersicon esculentum</i> L. (Tomato)	Cultivars	400 ppb 1.5 × ambient	2 h 1 growing season	-50 to -4% (2) -54 to -17% (3)	Reinert and Henderson (1980), Temple (1990a)
<i>Phaseolus vulgaris</i> L. (Snapbean)	Cultivars	60 ppb 7 h 72 ppb 7 h 80 ppb 7 h/day	mean - 44 days mean - 54 days 42 days	-26 to -2% (3) -73 to -44% (3) -68 to -50% (3)	Heck et al. (1988), Temple (1991), Eason and Reinert (1991)
<i>Plantago major</i> L. (Common plantago)	Populations	70 nL/ 1-7 h/day	2 weeks	-24 to 0% (1)	Reiling and Davison (1992a)
<i>Raphanistrum sativus</i> L. (Radish)	Within cultivar	0.1 µL/ 1-4 h/day 3 days/week	3 weeks	-40 to -5% (2)	Gillespie and Winner (1989)
<i>Silene cucubalus</i> (Bladder campion)	Populations	35 ppb 12 h/day	4 weeks	-75 to -48% (2)	Ernst et al. (1985)
<i>Solanum tuberosum</i> L. (Potato)	Cultivars	150 ppb 6 h/day	8 days	-10 to 0% (2) -40 to 0% (2)	Pell and Pearson (1984), Ormrod et al. (1971)
<i>Spinacia oleracea</i> L. (Spinach)	Cultivars	130 ppb 7 h/day	38 days	-56 to -28% (2)	Heagle et al. (1979a)
<u>Trees and Other Woody Plants</u>					
<i>Acer rubrum</i> L. (Red maple)	Populations	750 ppb 7 h/day	3 days	-36 to -17% (1)	Townsend and Dochinger (1974)
<i>Abies alba</i> Mill. (Silver fir)	Populations	250 ppb 7 h/day	10 days	-18 to +3% (1)	Larsen et al. (1990)
<i>Pinus elliotii</i> Engelm. (Slash pine)	Half-sib families	3 × ambient	3 growing seasons	-20 to 0% (1)	Dean and Johnson (1992)

**Table 5-3 (cont'd). Examples of Intraspecific Variation in Growth Responses Following Ozone Exposures**

Species	Genetic Unit <sup>a</sup>	Ozone Concentration	Duration	Range of Response <sup>b</sup>	Reference
<i>Pinus taeda</i> L. (Loblolly pine)	Full-sib families	50 ppb 6 h/day 1.9 × ambient	28 days 2 growing seasons	–18 to 0% (1) –19 to 0% (2)	Kress et al. (1982b), Shafer and Heagle (1989)
<i>Pinus taeda</i> L. (Loblolly pine)	Half-sib families	Ambient + 60 ppb 2.5 × ambient 250 ppb	1 growing season 1 growing season 8 h	–27.5 to +3% (2) –19 to –2% (2) –22 to +30% (2)	Adams et al. (1988), Qiu et al. (1992), Winner et al. (1987)
<i>Populus tremuloides</i> Michx. (Trembling aspen)	Clones	26.4 ppm-h ambient	92 days 3 growing seasons	–74 to –5% (2) –24 to –12% (2)	Karnosky et al. (1992a), Wang et al. (1986a,b)
<i>Rhododendron obtusum</i> (Lindl) Planch. (Azalea)	Cultivars	250 ppb - 3 h/day	6 days	–43% to 0% (2)	Sanders and Reinert (1982)

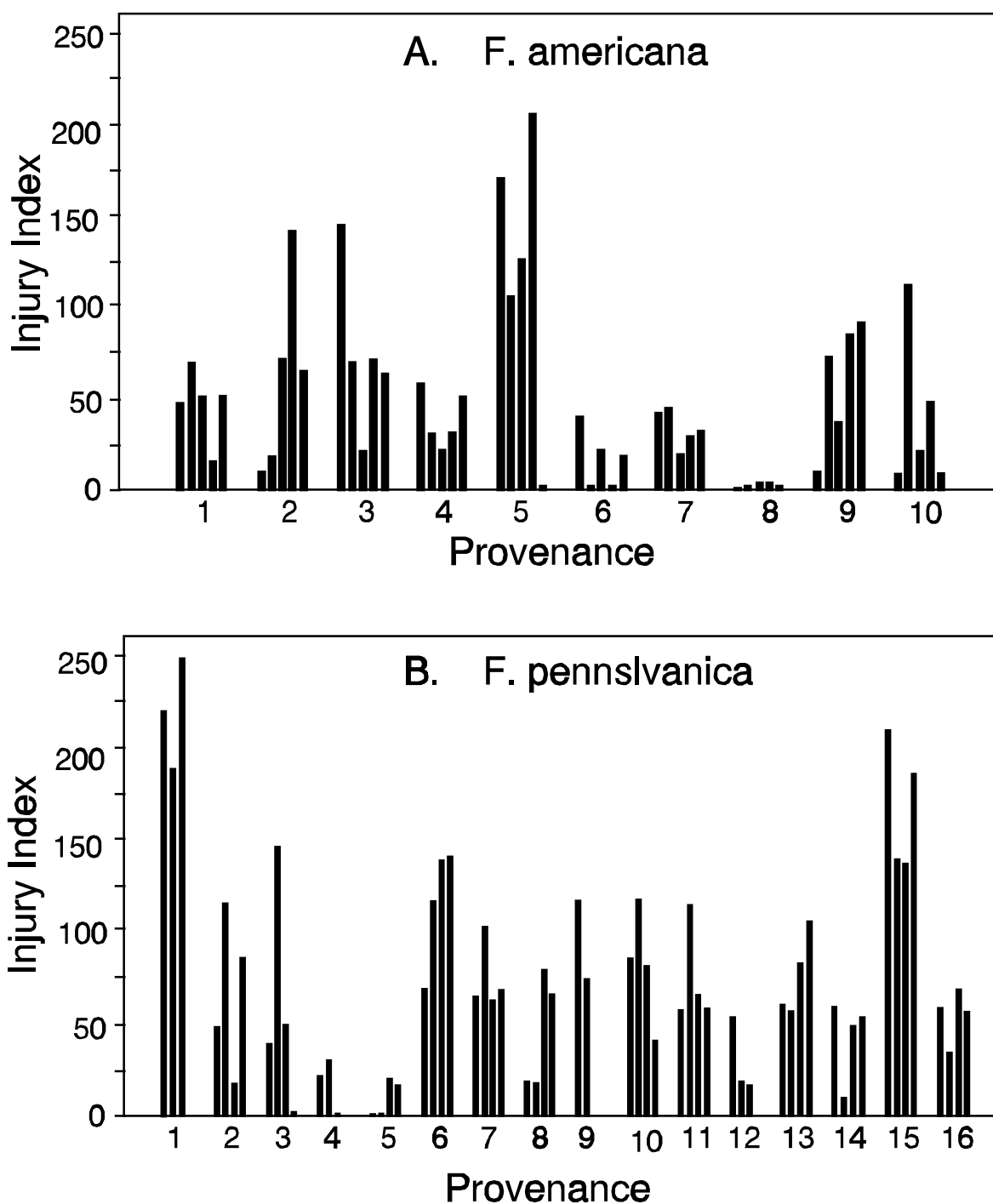
<sup>a</sup>Cultivars = a variety of agricultural or horticultural crops produced by selective breeding or a vegetatively propagated tree selection; Half-sib = seedlings with one parent in common; Clones = vegetatively propagated individual genotypes; and Populations = seedlings derived from a common gene pool.

<sup>b</sup>Range of response is expressed as (1) decrease compared to charcoal-filtered-air control plants in terms of growth, (2) biomass, or (3) yield.

have been classified as either O<sub>3</sub> sensitive or O<sub>3</sub> tolerant. Also noticeable from this figure is the large amount of variation in O<sub>3</sub> tolerance of individual half-sib (one parent in common) families from a given population. From Figure 5-8, the heterogeneity within a given loblolly pine half-sib family in terms of growth is displayed. This variability has some interesting implications. First, because plants of a given species vary widely in their response to O<sub>3</sub> exposure, response relationships generated for a single genotype or small group of genotypes may not represent adequately the responses of the species as a whole (Temple, 1990a). Second, because of the genetic variability and differential fitness extant among different genotypes in a population of plants, O<sub>3</sub> imposes a selective force favoring tolerant genotypes over sensitive ones (Roose et al., 1982; Treshow, 1980). Each of these implications will be discussed in this section.

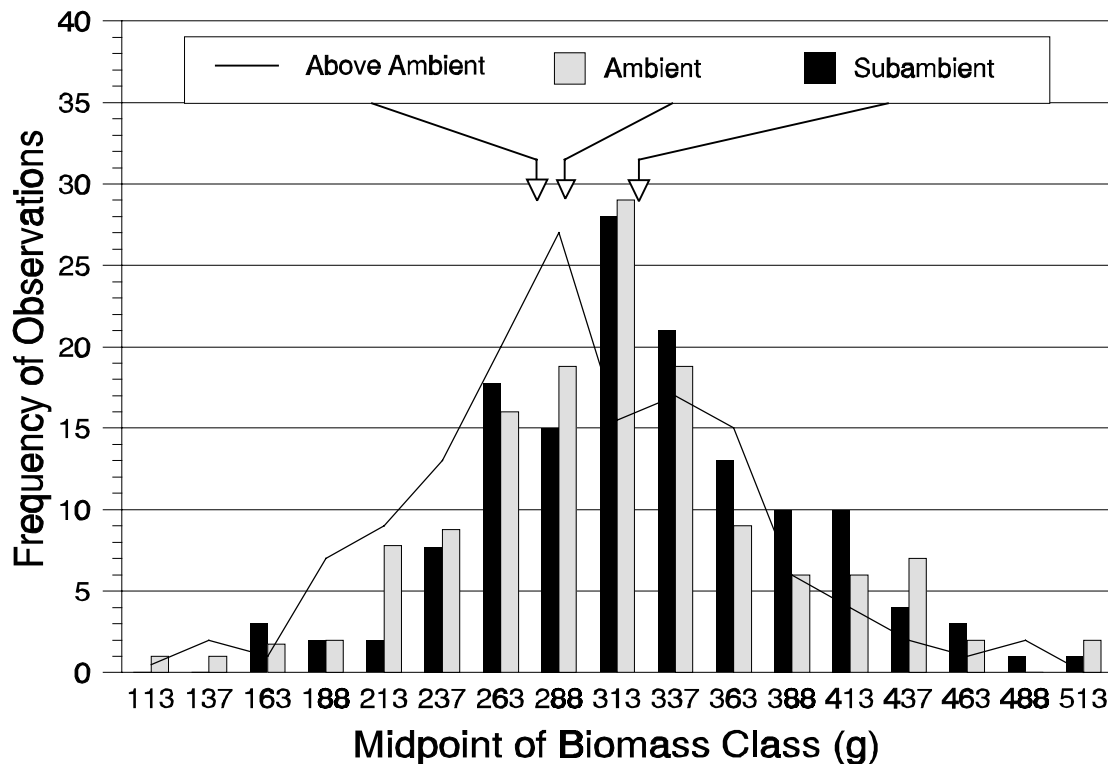
### ***Mechanisms and Gene Numbers***

Little is known about the genetic bases for O<sub>3</sub> resistance mechanisms or about the numbers of genes involved in these mechanisms (Pitelka, 1988). Most O<sub>3</sub> resistance mechanisms involve a physiological cost that will result in decreased growth and productivity of resistant plants grown under O<sub>3</sub> stress. Partial or complete stomatal closure in the presence of O<sub>3</sub> is an example of a mechanism of resistance that has been demonstrated for several plants (Engle and Gabelman, 1966; Thorne and Hanson, 1976; Reich, 1987;



**Figure 5-7.**

*The average injury index for visible foliar injury after exposure of 1-year-old seedlings to 50 pphm ozone for 7.5 h. Each mean shown represents the average of five trees per family. There were either four or five half-sib families for each white ash (*Fraxinus americana* L.) provenance (geographic location) and either three or four families for each green ash (*F. pennsylvanica* Marsh.) provenance. The specifics of the experimental design are reported in Karnosky and Steiner (1981).*



**Figure 5-8.**

***Frequency distribution showing the variability in ozone ( $O_3$ ) response (midpoint of whole-plant biomass) within one half-sib family of loblolly pine (*P. taeda* L.) exposed to increasing levels of  $O_3$  under chronic-level field conditions over several growing seasons (Adams et al., 1988). The arrows show the mean response for each of the three  $O_3$  treatments (subambient, ambient, and above-ambient  $O_3$ ). The specifics of the experimental design are reported by Adams et al. (1988). This figure was developed by Taylor (1994).***

Sumizono and Inoue, 1986; Tingey and Taylor, 1982) and that involves a high physiological cost because plants that have reduced stomatal conductivity also will have reduced carbon assimilation for growth (Ehleringer, 1991). Tolerance of internal leaf tissues to  $O_3$  may involve the production of antioxidant defense compounds (Lee and Bennett, 1982; Gupta et al., 1991) or other types of biochemical defense systems. The extent to which these internal tolerance mechanisms have physiological costs associated with them is not yet understood, but it is likely that increased defense compound production, triggered by  $O_3$ , will impact the amount of carbon available for growth (Ehleringer, 1991). The genetic regulation of these or other  $O_3$  resistance mechanisms has not yet been characterized thoroughly.

Whether or not  $O_3$  resistance is due to single gene or multi-gene control will affect the rate and extent of resistance development (Roose, 1991). Rapid stomatal closing in the presence of  $O_3$  appears to be under the control of either a single gene or a few genes in onion (*Allium cepa*) (Engle and Gabelman, 1966), some bean (*Phaseolus vulgaris*) cultivars

(cultivated varieties) (Knudson-Butler and Tibbitts, 1979), soybean (Damicone et al., 1987b), and petunia (*Petunia* spp.) (Elkiey and Ormrod, 1979a,b; Elkiey et al., 1979). Generally, resistance mechanisms appear to be more complex (Karnosky, 1989a) and seem to involve multiple gene control as has been demonstrated in tobacco (Aycock, 1972; Huang et al., 1975; Povilaitis, 1967), some bean cultivars (Mebrahtu et al., 1990a,b,c), corn (Cameron, 1975), tall fescue (*Festuca arundinacea*) (Johnston et al., 1983), potato (De Vos et al., 1982; Dragoescu et al., 1987), and loblolly pine (Weir, 1977; Taylor, 1994).

### ***Genetic Implications of Ozone Effects: Managed Ecosystems***

Because of the high cost involved in conducting long-term growth studies to determine O<sub>3</sub> effects on plants, only a small proportion of the total number of commercial crop cultivars and important tree seed sources, families, clones, and cultivars have been examined adequately for O<sub>3</sub> sensitivity. Still, a tremendous amount of variation has been found, as was described in the previous O<sub>3</sub> criteria document (U.S. Environmental Protection Agency, 1986) and in Tables 5-2 and 5-3.

Plant breeders and nurserymen working in locations with high O<sub>3</sub> concentrations have inadvertently developed selections more tolerant to O<sub>3</sub> than those developed in locations with low O<sub>3</sub> exposures (Reinert et al., 1982; Roose et al., 1982). The cultivars Team alfalfa and Kennebec, Pungo, and Katahdin potatoes were developed at the U.S. Department of Agriculture Research Center at Beltsville, where 0.120 ppm O<sub>3</sub> frequently is exceeded (Lefohn and Pinkerton, 1988; Ludwig and Shelar, 1980). These cultivars have proven to be more O<sub>3</sub> tolerant than cultivars developed elsewhere (Reinert et al., 1982). Similarly, cotton (*Gossypium* spp.) and sugar beet (*Beta* spp.) cultivars developed in Southern California, where O<sub>3</sub> levels are among the highest in the country, are more O<sub>3</sub> tolerant than cultivars developed in low O<sub>3</sub> areas (Reinert et al., 1982).

Nurserymen, Christmas tree growers, and seed orchard managers all routinely have discarded pollution-sensitive chlorotic dwarf and tip-burned white pine trees because of their slow growth in areas with high O<sub>3</sub> exposures (Umbach and Davis, 1984). Thus, they have contributed to the selection of more O<sub>3</sub>-tolerant commercial forests.

Although these examples suggest that selection of O<sub>3</sub>-tolerant genotypes is possible, the general consensus of the scientific community is that top priority should be given to solving pollution problems at their source (Karnosky et al., 1989) and not in selecting pollution-tolerant cultivars.

An interesting set of experiments by Barnes et al. (1990c) and Velissariou et al. (1992) have described a concern about the modern crop varieties that have been developed in clean-air environments but are being grown routinely in areas with elevated O<sub>3</sub> exposures. These authors speculated that breeders of spring wheat (*Triticum aestivum*) grown in Greece inadvertently had selected varieties with increased O<sub>3</sub> sensitivity due to their higher rates of stomatal conductivity (Velissariou et al., 1992). Velissariou et al. (1992) found a significant correlation between year of introduction and stomatal conductance, with stomatal conductance, increasing with the more modern introductions. The authors suggested that the selection for higher yields had resulted in a higher O<sub>3</sub> uptake for the modern spring wheat cultivars, contributing to their increased O<sub>3</sub> sensitivity. When they compared the relative growth rates of spring wheat cultivars released over the period from 1932 to 1980, the modern cultivars had more foliar injury and more growth decrease when grown in the presence of O<sub>3</sub> (Barnes et al., 1990c; Velissariou et al., 1992).



### ***Genetic Implications of Ozone Effects: Natural Ecosystems and Biodiversity***

Air pollutants can affect the genetics of plant populations in two ways: (1) they may increase mutation rates or (2) they may apply selection pressures that eventually may lead to adaptive responses (Cook and Wood, 1976). The issue of O<sub>3</sub>-induced changes in mutation rate has not been studied adequately, but recent evidence by Floyd et al. (1989) suggests that DNA may be affected by O<sub>3</sub> to induce mutation in plants. However, there is evidence that O<sub>3</sub> may be affecting plant populations via natural selection. According to Bradshaw and McNeilly (1991), there are three stages of selection-driven population change: Stage I, elimination of the most sensitive genotypes; Stage II, elimination of all genotypes except the most resistant; and Stage III, interbreeding of the survivors.

The first report of O<sub>3</sub> as a selective force in plant populations was that involving lupine (*Lupinus bicolor*) populations in the greater Los Angeles area (Dunn, 1959). Local Los Angeles area populations were more O<sub>3</sub> resistant than populations originating from cleaner-air areas. Berrang et al. (1986, 1989, 1991) have presented evidence for population change in trembling aspen (*Populus tremuloides*). Aspen clones from across the United States were sampled randomly from populations in polluted and nonpolluted areas. Aspen from areas with high ambient O<sub>3</sub> concentrations were injured visibly to a lesser extent by experimental O<sub>3</sub> exposures than clones from areas with low O<sub>3</sub> concentrations (Berrang et al., 1986, 1991). Similar results were seen for field trials of O<sub>3</sub> injury (Berrang et al., 1989). More recently, growth rate and biomass differences have been reported for aspen clones differing in O<sub>3</sub> tolerance (Karnosky et al., 1992b). Berrang et al. (1989) suggest that sensitive genotypes are not killed directly by O<sub>3</sub>, but are eliminated through intraspecific competition for light, nutrients, and water with their resistant neighbors. Spatial (population) variation in O<sub>3</sub> resistance that is related to background O<sub>3</sub> pollution also has been demonstrated in British populations of plantago (*Plantago major*) (Reiling and Davison, 1992a,b).

There have been three concerns raised regarding the spatial variation studies of O<sub>3</sub> resistance. First, because O<sub>3</sub> generally does not show steep concentration gradients, spatial studies must involve populations that are great distances from one another, so it is difficult to determine whether geographical differences in O<sub>3</sub> resistance are related primarily to local O<sub>3</sub> exposures or to other environmental factors (Reiling and Davison, 1992a). Second, spatial studies are limited by the general absence of historical records of ambient O<sub>3</sub> concentrations at the sites where the populations were sampled (Bell et al., 1991). Third, no O<sub>3</sub> study has collected plants from the same population over time to demonstrate O<sub>3</sub>-induced population change over time (Bell et al., 1991), as has been demonstrated for other pollutants. However, Karnosky (1981b, 1989b) studied the O<sub>3</sub> symptom expression and survival of over 1,500 eastern white pine trees growing in southern Wisconsin and found that O<sub>3</sub>-sensitive genotypes had a 10-times-higher rate of mortality than did the O<sub>3</sub>-resistant genotypes over a 15-year study (Table 5-4). This is direct evidence of the occurrence of Stage I natural selection. Further evidence of this type was presented by Heagle et al. (1991a), who found a population change in O<sub>3</sub> sensitivity over 2 years with white clover (*Trifolium repens*) exposed to O<sub>3</sub> in OTCs. A high O<sub>3</sub> dose at the end of the study caused significantly less foliar injury in plants that survived two seasons of exposure to high O<sub>3</sub> concentrations than in plants that had survived low O<sub>3</sub> concentrations.

The rate of evolution is dependent on the selection pressure, the magnitude of the genetically controlled variability, and the number of genes involved (Roose, 1991). Long-lived species, such as trees, will evolve more slowly than annuals or biennials

**Table 5-4. Mortality of Three Ozone Sensitivity Classes of Eastern White Pine (*Pinus Strobus* L.) Trees During 1971 to 1986**

Sensitivity Class <sup>a</sup>	Number Trees	Number Trees Dead	Percent Mortality
Resistant	1,386	34	2.4%
Intermediate	98	3	3.1%
Sensitive	57	14	24.6%

<sup>a</sup>Resistant = not showing visible foliar injury during the study; Intermediate = showing visible injury, including foliar tip burn during 1 or 2 years; Sensitive = showing visible injury, including foliar tip burn, short needles, and poor needle retention for 3 or more years of the study.

Source: Karnosky (1989b).

(Barrett and Bush, 1991). Gillespie and Winner (1989) found O<sub>3</sub> to be a strong and rapid selective force with radish (*Raphanus sativus*). Ozone resistance was expressed within one generation following a series of artificial pollinations with various populations from the radish cultivar "Cherry Belle".

Whether or not the loss of some genotypes from plant populations is important is a debatable question. However, it is likely that sensitive genotypes are being lost from natural ecosystems with current O<sub>3</sub> exposures. Field studies documenting differential growth rates of O<sub>3</sub>-sensitive and tolerant genotypes of eastern white pine in natural ecosystems influenced by O<sub>3</sub> were summarized in the previous air quality criteria document for O<sub>3</sub> (U.S. Environmental Protection Agency, 1986). Similar findings subsequently have been reported for O<sub>3</sub>-sensitive and tolerant Jeffrey pine trees in California (Peterson et al., 1987). It is likely that these growth-rate differences affect the competitive ability of O<sub>3</sub>-sensitive genotypes and increase their mortality rate (Karnosky, 1989b).

Although some loss of rare alleles (one of a series of genes that are alternative in inheritance) and change in gene frequency is likely with loss of sensitive genotypes, the significance of these effects on biodiversity is unknown (Barrett and Bush, 1991). If the remaining population of O<sub>3</sub>-resistant plants is less adaptable to subsequent change due to a reduced redundancy, as has been predicted by Gregorius (1989), or if O<sub>3</sub> sensitivity is linked to other traits such as rapid growth or high productivity, as has been suggested because of the inherently higher gas-exchange rates of some O<sub>3</sub>-sensitive genotypes (Barnes et al., 1990c; Thorne and Hanson, 1976; Turner et al., 1972; Velissariou et al., 1992), then losing these sensitive genotypes is both biologically and economically important. This remains a point of scientific debate. Although the evolution of resistance to air pollution is hypothesized to contribute to the loss of genetic variability (Scholz et al., 1989; Karnosky, 1991), other scientists suggest that there is little experimental evidence for concluding that genetic diversity is actually threatened by air pollution and that air pollution has less important implications for plant populations than do factors such as global climate change and habitat fragmentation (Parsons and Pitelka, 1991; Taylor and Pitelka, 1992). Clearly, there is a need for additional research in this area of O<sub>3</sub> effects in plant biodiversity (Karnosky et al., 1989).

### ***Reproductive Aspects and Related Genetic Implications***

In the previous discussion in this section, only natural selection at the whole-plant level has been mentioned. This type of selection occurs as plants compete with their neighbors for survival and the ability to reproduce. Selection is thought to occur also during the reproductive process (Feder and Sullivan, 1969; Krause et al., 1975), and this is referred to as gametophytic selection (Mulcahey, 1979; Wolters and Martens, 1987) or fertility selection (Venne et al., 1989). The ability of gametophyte (haploid part of the plant-life cycle) selection to modify the sporophytic generation depends on two critical issues: (1) pollen genes should be expressed after meiosis (cell divisions leading to production of gametes), and (2) those same genes also should be expressed in the sporophytes (diploid part of the plant-life cycle) (Mulcahey and Mulcahy, 1983). This genetic overlap has been demonstrated in some species (Mulcahy, 1979; Searcy and Mulcahy, 1985; Walsh and Charlesworth, 1992). Indirect evidence for O<sub>3</sub>-induced gametic selection was presented for Scot's pine (*Pinus sylvestris*) by Venne et al. (1989). Based on their studies of the effects of O<sub>3</sub> on the pollen germination and tube elongation of some 30 Scots pine clones, they found that O<sub>3</sub> could change markedly the relative male contribution to successful fertilization. However, this study did not actually examine offspring, as would be needed to positively prove O<sub>3</sub>-induced gametophytic selection.

Studies of O<sub>3</sub> effects on pollen germination and tube elongation generally have found a negative impact of O<sub>3</sub> on this critical element of reproduction (Table 5-5). Whether or not selection is occurring at the pollen level because of a selective disadvantage of the pollen from sensitive genotypes is a debatable issue. Feder (1986) and Krause et al. (1975) found that the pollen from O<sub>3</sub>-sensitive genotypes of petunia and tomato (*Lycopersicon esculentum*) was more severely affected by O<sub>3</sub> than pollen from tolerant genotypes, suggesting that gametophytic selection could be occurring. Similar results were found for Scots pine clones by Venne et al. (1989). These authors found that the relative male contribution for charcoal-filtered air versus O<sub>3</sub>-treated conditions was very different and potentially could lead to a strong gametophytic selection response caused by O<sub>3</sub>. However, Hanson and Addis (1975) did not see any differences in the effect of O<sub>3</sub> on the pollen from sensitive and tolerant petunia (*Petunia hybrida*) genotypes, and Benoit et al. (1983) found no apparent differences in the susceptibility of eastern white pine pollen from O<sub>3</sub>-sensitive or tolerant genotypes. Clearly, the question of whether O<sub>3</sub>-induced gametophytic selection is occurring has not been resolved.

Reduced flowering as the result of prolonged fumigation with O<sub>3</sub> has been shown in bladder campion (*Silene cucubalus*) (Ernst et al., 1985). Decreased floral initiation and decreased floral productivity under long-term O<sub>3</sub> exposures also have been reported in geranium (*Pelargonium* spp.) and carnation (*Dianthus caryophyllus*) (Feder, 1970). Ozone-induced impairment of flowering will reduce the fitness of the affected genotypes, populations or species and may result in the eventual loss of these genetic units from the O<sub>3</sub>-stressed ecosystem. Reduced eastern white pine fecundity in air-pollution-stressed ecosystems has been reported by Houston and Dochinger (1977).

### ***Genetic Summary***

Plant species, cultivars, populations, and individuals within populations display variable responses to O<sub>3</sub>. Variability in O<sub>3</sub> responses among and within species was described in the previous O<sub>3</sub> criteria document (U.S. Environmental Protection Agency, 1986). An important component of this variation is genetically controlled. The specific

**Table 5-5. Examples of Ozone Effects on Pollen Germination and Tube Elongation**

Species	Pollen Germination	Pollen Tube Elongation	Reference
<i>Nicotiana tobacum</i> L. (Tobacco)	Decrease	Decrease	Feder (1968) Feder and Shrier (1990)
<i>Petunia hybrida</i> (Petunia)	Not tested	Decrease	Feder and Shrier (1990)
<i>Pinus strobus</i> L. (Eastern white pine)	No effect	Decrease	Benoit et al. (1983)
<i>Zea mays</i> L. (Corn)	Decrease	Not tested	Mumford et al. (1972)

genes controlling O<sub>3</sub> response and involved in mechanisms of O<sub>3</sub> tolerance are largely unknown. However, control of stomatal conductance and internal biochemical defense systems are among the most commonly described tolerance mechanisms. Ozone tolerance is generally thought to be controlled by multiple genes.

There are implications of genetic variation in O<sub>3</sub> response, both for managed and natural ecosystems. These are summarized below along with the relative degree of uncertainty attached to each.

It is known, with a great deal of certainty, that plants have a high degree of genetic variation in O<sub>3</sub> response. Thus, exposure-response equations and yield-loss equations developed for a single or small number of cultivars, genotypes, families, or populations may not represent adequately the response of the species as a whole.

The issue of O<sub>3</sub> effects on biodiversity via natural selection is a topic of debate within the scientific community. The potential for natural selection for O<sub>3</sub> tolerance and associated loss of sensitive genotypes is regional in nature, unlike well-known, point-source pollution impacts that occur on local plant populations. However, the intensity of O<sub>3</sub> selection generally is thought to be quite low, 0.3 or less (Taylor and Pitelka, 1992), in the majority of the United States. The extent that germplasm has been, or continues to be, affected, in terms of allele loss or gene frequency changes by O<sub>3</sub>, and how this might be impacting the genetic adaptability of populations, are open and important research questions.

Although it is well known that individual plants within a species vary in their O<sub>3</sub> tolerance, the physiological costs to tolerant plants are not known in terms of carbon assimilation and allocation. Tolerance mechanisms based on reduced stomatal conductivity in the presence of O<sub>3</sub> would likely reduce growth of tolerant plants. Similarly, tolerance mechanisms based on the productivity of antioxidant compounds likely will shunt plant resources away from growth to the production of the defense compounds. The characterization of the extent and types of physiological costs involved in O<sub>3</sub> tolerance remains an important research question.

### 5.4.3 Environmental Biological Factors

The previous criteria document (U.S. Environmental Protection Agency, 1986) discussed pollutant-plant-pest and pollutant-plant-pathogen interactions together, and provided a tabular summary of pathogen effects. However, in light of the numerous studies of insect and pathogen interactions that have appeared in recent years, the topics are dealt with separately below. Nevertheless, it is worth reiterating several points made in the previous criteria document.

- Pests and diseases are natural components of managed and natural ecosystems.
- Significant crop and timber losses result from pests and pathogens.
- The establishment of disease and pest infestations and their subsequent development involve complex interactions among the host plant, the environment, and the causal organism.
- The generalized disease (or pest infestation) cycle involves the arrival of the pathogen or pest on the host plant surface or its introduction into the host plant tissues through wounds or as a result of insect feeding activity.
- Growth and development or propagation of the pathogen or pest only occurs if all environmental conditions are favorable.
- Such development leads to various degrees of host tissue destruction or malfunction, and usually culminates in the causal organism entering a reproductive stage and producing propagules (e.g., spores or eggs) that facilitate its spread.

Ozone may modify any stage of the disease cycle directly, by affecting the causal organism itself, or indirectly, by effects on the host plant (Lechowicz, 1987). Conversely, the plant-pest interaction may modify the sensitivity of the host plant to O<sub>3</sub>.

The roots of many members of the pea family (including many important crops such as soybeans, beans, and peas [*Pisum sativum*]) are infected by symbiotic nitrogen-fixing bacteria (*Rhizobium spp.*), leading to the formation of bacteria-rich nodules that contribute to the nitrogen economy of the plant through their ability to fix and convert atmospheric nitrogen to biologically useful forms. Other nitrogen-fixing microorganisms are associated with the roots of several species, and, in many cases, roots are invaded by species of soil fungi to form mycorrhizal symbioses that assist in root functioning. These symbioses constitute micro-ecosystems and are discussed more fully in Section 5.7 as they relate to forest tree species.

Biological interactions also affect the growth of plants in populations (pure stands) and communities (mixtures of species) through the individual plants' competition for available resources (light, CO<sub>2</sub>, water, and nutrients). Such plant-plant interactions are features of all managed and natural ecosystems, but they operate at the individual plant level. Hence, the effects of oxidants on these interactions are discussed in this section, as well as in Section 5.7, which deals with ecosystem responses.

#### 5.4.3.1 Oxidant-Plant-Insect Interactions

The previous criteria document (U.S. Environmental Protection Agency, 1986) concluded that little was known at that time about O<sub>3</sub>-insect interactions. Since then, the topic has been covered in several reviews: Fluckiger et al. (1988), Hughes (1988), Manning and Keane (1988), and Hain (1987). Relevant studies of the effects of O<sub>3</sub> on the feeding preference of herbivorous insects and on their growth, fecundity, and survival are presented in

Table 5-6. As can be seen readily in this summary, the information is scattered widely among a wide range of host plants and pests. Nevertheless, there appears to be a general trend in the observations suggesting that O<sub>3</sub>-induced changes in the host plants frequently result in increased feeding preference of a range of insect species, although this may or may not be reflected in effects on the growth of the insect.

However, in most studies, the effects have been far from clear-cut. For example, variable responses were observed with the aphid, *Aphis fabae*, on broad bean (*Vicia faba*) (Brown et al., 1992); with the aphids, *Acyrtosiphon pisum* and *Aphis rumicis*, on pea and dock (*Rumex obtusifolius*), respectively; with the beetle, *Gastrophysa viridula*, on dock (Whittaker et al., 1989), with the Mexican bean beetle, *Epilachna varivestis*, on Corsoy soybean (Endress and Post, 1985); and with the gypsy moth, *Lymantria dispar*, on white oak (*Quercus alba*) (Jeffords and Endress, 1984). Although statistically significant effects were observed frequently, they did not provide any consistent pattern of insect growth response to different levels or patterns of exposure.

Brown et al. (1992) observed that the response of *Aphis fabae* depended on the dynamics of exposure: growth was stimulated in short-term (<24 h) continuous exposures or in episodic exposures over several days, whereas longer continuous exposures caused decreased growth. Chappelka et al. (1988c) found that O<sub>3</sub> consistently enhanced the feeding preference and larval growth of the Mexican bean beetle on soybean, leading to increased defoliation. Although the cultivar Forrest was significantly more sensitive to O<sub>3</sub> than Essex, this difference did not lead to any differences in insect behavior and development. Similarly, clear stimulatory responses were observed with pinworm, *Keiferia lycopersicella*, on tomato (*Lycopersicon esculentum*) (Trumble et al., 1987); with an aphid, *Phyllaphis fagi*, and a weevil, *Rhynchaenus fagi*, on European beech (*Fagus sylvatica*) (Braun and Fluckiger, 1989; Hiltbrunner and Fluckiger, 1992); with the monarch butterfly, *Danaus plexippus*, on milkweed (*Asclepias syriaca*) (Bolsinger et al., 1991, 1992); and with infestation by the willow leaf beetle, *Plagioderia versicolora*, on cottonwood (*Populus deltoides*) (Coleman and Jones, 1988). However, there was less egg-laying by *Plagioderia* on O<sub>3</sub>-treated foliage, and treatment had no effect on beetle growth rates and survival (Jones and Coleman, 1989).

In view of previous experiments in which it was demonstrated clearly that aphid growth was stimulated significantly by ambient pollutant mixtures containing O<sub>3</sub>, SO<sub>2</sub>, and NO<sub>2</sub> and, in light of other reports of O<sub>3</sub>-induced stimulations of insect growth, the inhibitory effects of O<sub>3</sub> on the growth of *Aphis fabae* on broad bean (Dohmen, 1988) or kidney bean (Braun and Fluckiger, 1989) may be anomalous. The inhibitory effects on broad bean were observed only at low O<sub>3</sub> levels; exposure to higher concentrations resulted in a stimulation of aphid growth, which Dohmen (1988) attributed to the increased rate of leaf senescence of the host plant. The effects observed on kidney bean could not be accounted for by differences in the amino acid composition of the plant sap, although differences in other constituents or direct effects of O<sub>3</sub> on the pea aphid itself could not be ruled out (Braun and Fluckiger, 1989).

A well-established indirect stimulatory effect is the predisposition to bark beetle attack of ponderosa pine injured by exposure to O<sub>3</sub>. However, the infested trees do not favor good brood production; O<sub>3</sub> injury results in a more susceptible but less suitable host (Hain, 1987).

In all of these studies, the focus was on direct or indirect effects of O<sub>3</sub> on the insect. With the exception of the work of Braun and Fluckiger (1989), any effects on the

**Table 5-6. Ozone Effects on Insect Pests**

Host Plant/Insect	Exposure <sup>a</sup>	Experimental Conditions <sup>b</sup>	Effect of Ozone on Insect	Reference
<u>CROP SPECIES</u>				
Broad bean/aphid	3 day, 0.085 ppm <24 h, 0.1 ppm >24 h, 0.1 ppm 8 h/day, episodic	Chamber, whole plant Chamber, whole plant Chamber, whole plant Chamber, whole plant	3-13% decreased growth rate 17% increased growth rate 12% decreased growth rate 15% increased growth rate	Dohmen (1988), Brown et al. (1992)
Pea/aphid	4-8 day, var.	Chamber, whole plant	Variable effects on growth	Whittaker et al. (1989)
Kidney bean/aphid	14 day, var.	OTC	15-50% reduction in growth of insect	Braun and Fluckiger (1989)
Soybean/beetle (cv. Corsoy) (cvs. Essex, Forrest)	16 day, var. 21 day, 7 h/day, var.	Chamber OTC	Variable feeding preference 0.11>0.0>0.05>0.03 ppm; feeding preference increased and greater larval growth	Endress and Post (1985), Chappelka et al. (1988c)
Tomato/pinworm	2-4 day, 3 h/day 0.28 ppm	Chamber, detached leaf Chamber, whole plant	80% increase in larval development; no effect on fecundity	Trumble et al. (1987)
<u>NATURAL VEGETATION</u>				
Milkweed/monarch butterfly	17-19 day, 7 h/day 0.150-0.178 ppm	Chamber, whole plant	No feeding preference but greater larval growth rate	Bolsinger et al. (1991, 1992)
Dock/aphid	15 day, var.	Chamber, whole plant	10% increased growth rate	Whittaker et al. (1989)
Dock/beetle	15 day, var.	Chamber, whole plant	10% larger egg batches; fourfold greater larval survival	Whittaker et al. (1989)
<u>TREES SPECIES</u>				
European beech/aphid	2 mo, var.	OTC	75% increase in number	Braun and Fluckiger (1989)
European beech/weevil	72 h, var.	OTC	Twofold increase in feeding preference	Hiltbrunner and Fluckiger (1992)

**Table 5-6 (cont'd). Ozone Effects on Insect Pests**

Host Plant/Insect	Exposure <sup>a</sup>	Experimental Conditions <sup>b</sup>	Effect of Ozone on Insect	Reference
<u>TREE SPECIES</u> (cont'd)				
Cottonwood/beetle	5 h, 0.2 ppm	OTC	22-60% greater consumption of foliage but decreased fecundity	Jones and Coleman (1988), Coleman and Jones (1988)
Ponderosa pine/bark beetle	Natural	None, field	Increased infestation but decreased survival	Hain (1987)
White oak/gypsy moth	11 day, 7 h/day, var.	Chamber, leaf disks	Variable feeding preference 0.15 > 0.03 > 0.09 ppm	Jeffords and Endress (1984)

<sup>a</sup>var. indicates a range of exposures.

<sup>b</sup>Chamber indicates closed chamber; OTC indicates open-top field chamber.



host plant that were reported were confined to observations on visible symptoms of foliar injury. The only report of an O<sub>3</sub>-insect interaction affecting the response of the host plant appears to be that of Rosen and Runeckles (1976). This study showed that exposure to subacute levels of O<sub>3</sub> and infestation with the greenhouse whitefly, *Trialeurodes vaporariorum*, acted synergistically (i.e., more than additively) in causing leaf injury and accelerated senescence of kidney bean. However, the extent to which other insects with sucking mouthparts, such as aphids, might be involved in similar interactive responses is unknown, as is the nature of any interactions that involve pests that ultimately invade and develop within the host plant, such as those that cause the formation of galls.

The reports of O<sub>3</sub>-insect-plant interactions are thus scattered among a wide range of host plant and insect species, and represent only a minute fraction of the plant-insect interactions that involve crop and native species. Although there appears to be a trend in the limited data available that suggests that exposures to moderate O<sub>3</sub> levels may increase the likelihood of insect attack and its consequences, there is insufficient information to decide whether extrapolation of this generalization is warranted or not. Even if the generalization is valid, it is not possible to generate any quantitative measure of response. Before such estimates will be possible on a broad scale, studies of a much wider range of plant insect-systems will be needed, together with systematic, in-depth studies of individual systems, aimed at determining the long-term effects on both the host plant and the insect. Such studies should include investigations of biological control systems employing beneficial insects, which are used increasingly as alternatives to chemical insecticides and herbicides.

#### **5.4.3.2 Oxidant-Plant-Pathogen Interactions**

Plant disease is the result of infection by fungi, bacteria, mycoplasmas, viruses, and nematodes. Recent reviews of pathogen-plant-O<sub>3</sub> interactions have been published by Dowding (1988) and Manning and Keane (1988) and extend the coverage of the previous criteria document (U.S. Environmental Protection Agency, 1986), in which the results of published studies of the effects of O<sub>3</sub> on disease development were summarized in tabular form. Interactions involving fungal pathogens occupied most of that review, and more recent studies have maintained this emphasis.

The previous criteria document concluded that it was "impossible to generalize and predict effects in particular situations" (U.S. Environmental Protection Agency, 1986). However, Dowding (1988) has concluded that pathogens that can benefit from injured host cells or from disordered transport mechanisms are enhanced by pollution insult to their hosts, whereas those that require a healthy mature host for successful invasion and development are depressed by pollutant stress to their host.

This conclusion is supported by evidence that the development of diseases caused by obligate parasites such as the rust fungi and bacterial pathogens usually is reduced by O<sub>3</sub>. As shown by the observations summarized in Table 5-7, reductions in disease development were observed in five of the nine studies of obligate fungal parasites listed, whereas increases were observed in all but four of the studies of facultative fungal pathogens. Similarly, in four of the five bacterial systems, O<sub>3</sub> reduced infection or disease development. It should be noted that, in three of the four studies of obligate fungi on which exposure to O<sub>3</sub> either had no effect or that resulted in stimulated fungal growth, the pathogen was a powdery mildew (*Erysiphe*, *Microsphaera*). As discussed by Tiedemann et al. (1991), these species constitute a special case because they are ectoparasites whose hyphae merely penetrate the surface epidermal cells of the host plant's leaves rather than the mesophyll

**Table 5-7. Ozone-Plant-Pathogen Interactions<sup>a</sup>**

Host Plant	Pathogen	Effect of O <sub>3</sub> on Disease	Effect of Disease on O <sub>3</sub> Response	Reference
<u>OBLIGATE FUNGI</u>				
Kidney bean	<i>Uromyces phaseoli</i>	Increased number of smaller pustules	Reduced injury on severely diseased leaves	Resh and Runeckles (1973)
Barley	<i>Erysiphe graminis</i>	Reduced infection but greater spore production	Not reported	Heagle and Strickland (1972)
Cottonwood	<i>Melampsora medusae</i>	Reduced infection and development	Not reported	Coleman et al. (1987)
Lilac	<i>Microsphaera alni</i>	No effect	Not reported	Hibben and Taylor (1975)
Oats	<i>Puccinia coronata</i>	Reduced infection and development	No effect	Heagle (1970)
Wheat	<i>Erysiphe graminis</i>	Increased infection and development	Not reported	Tiedemann et al. (1991)
	<i>Puccinia graminis</i>	Reduced infection and development	Reduced leaf injury	Heagle and Key (1973a,b)
	<i>Puccinia graminis</i>	Reduced development	Not reported	Heagle (1975)
	<i>Puccinia recondita</i>	Reduced infection and development	Not reported	Dohmen (1987)
<u>FACULTATIVE FUNGI</u>				
Barley	<i>Drechslera teres</i>	Increased infection	Not reported	Tiedemann et al. (1990)
	<i>Gerlachia nivalis</i>	Increased infection	Not reported	Tiedemann et al. (1990)
	<i>Helminthosporium sativum</i>	No effect	Not reported	Tiedemann et al. (1990)
Cabbage	<i>Fusarium oxysporum</i>	Decreased development	Not reported	Manning et al. (1971a)
Corn	<i>Helminthosporium maydis</i>	Increased development	Not reported	Heagle (1977)

**Table 5-7 (cont'd). Ozone-Plant-Pathogen Interactions<sup>a</sup>**

Host Plant	Pathogen	Effect of O <sub>3</sub> on Disease	Effect of Disease on O <sub>3</sub> Response	Reference
<u>FACULTATIVE FUNGI (cont'd)</u>				
Cottonwood	<i>Marssonina brunnea</i>	Increased infection	Not reported	Coleman et al. (1988)
Geranium	<i>Botrytis cinerea</i>	Decreased infection	Not reported	Krause and Weidensaul (1978)
Onion	<i>Botrytis</i> (3 spp.)	Increased infection and development	Not reported	Wukasch and Hofstra (1977a,b)
Potato	<i>Botrytis cinerea</i>	Increased infection and development	Not reported	Manning et al. (1969)
	<i>Alternaria solani</i>	Increased infection	Not reported	Holley et al. (1985)
	<i>Alternaria solani</i>	Increased infection	Not reported	Bisessar (1982)
Soybean	<i>Fusarium oxysporum</i>	Increased infection	Increased leaf injury	Damicone et al. (1987a)
Wheat	<i>Gerlachia nivalis</i>	Increased infection	Not reported	Tiedemann et al. (1990)
	<i>Helminthosporium sativum</i>	No effect	Not reported	Tiedemann et al. (1990)
	<i>Helminthosporium sativum</i>	Increased infection	Not reported	Tiedemann et al. (1991)
	<i>Septoria</i> (2 spp.)	Increased infection	Not reported	Tiedemann et al. (1990)
	<i>Septoria</i> (2 spp.)	Increased infection	Not reported	Tiedemann et al. (1991)
Jeffrey pine	<i>Heterobasidium annosum</i>	Increased development	Not reported	James et al. (1980a)
Ponderosa pine	<i>Heterobasidium annosum</i>	Increased development	Not reported	James et al. (1980b)
White pine	<i>Verticicladiella procera</i>	Slightly increased incidence	Not reported	Costonis and Sinclair (1972)
	<i>Lophodermium pinastre</i>	Slightly increased incidence	Not reported	Costonis and Sinclair (1972)

**Table 5-7 (cont'd). Ozone-Plant-Pathogen Interactions<sup>a</sup>**

Host Plant	Pathogen	Effect of O <sub>3</sub> on Disease	Effect of Disease on O <sub>3</sub> Response	Reference
<b><u>BACTERIA</u></b>				
Alfalfa	<i>Xanthomonas alfalfae</i>	Reduced development	Reduced leaf injury	Howell and Graham (1977)
Soybean	<i>Pseudomonas glycinea</i>	Reduced incidence	No effect	Laurence and Wood (1978a)
	<i>Pseudomonas</i> spp.	Reduced infection	Reduced leaf injury	Pell et al. (1977)
White bean	<i>Xanthomonas phaseoli</i>	No effect	Reduced leaf injury	Temple and Bisessar (1979)
Wild strawberry	<i>Xanthomonas fragariae</i>	Reduced incidence	No effect	Laurence and Wood (1978b)
<b><u>NEMATODES</u></b>				
Begonia	<i>Aphelenchoides fragariae</i>	Reduced nematode reproduction	Reduced leaf injury	Weber et al. (1979)
Soybean	<i>Belonolaimus longicaudatus</i>	Stimulation or no effect	Not reported	Weber et al. (1979)
	<i>Heterodera glycines</i>	Reduced nematode reproduction	Not reported	Weber et al. (1979)
	<i>Paratrichodorus minor</i>	Reduced nematode reproduction	Reduced leaf injury	Weber et al. (1979)
	<i>Pratylenchus penetrans</i>	No effect	Not reported	Weber et al. (1979)
Tobacco	<i>Meloidogyne hapla</i>	Possible stimulation <sup>b</sup>	Increased leaf injury	Bisessar and Palmer (1984)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Based on studies using the protectant EDU (see Section 5.2.1.2).

tissues within the leaves. They noted that Heagle and Strickland (1972) observed greater pustule development of *Erysiphe* on exposed barley once infection was established, although the pathogen was sensitive during the early stages of infection. Tiedemann et al. (1991) suggest that the observed stimulations result from a differential weakening of the host's resistance response to the pathogen.

In a few of the studies summarized in Table 5-7, effects of disease development on the sensitivity of the host plant to O<sub>3</sub> were noted. Heagle and Key (1973b) and Resh and Runeckles (1973) confirmed the earlier observation of Yarwood and Middleton (1954) that infection with obligate rust fungi could reduce the severity of acute injury caused by exposure to O<sub>3</sub>. However, with *Uromyces* on bean, the "protection" was noted only on severely infected leaves (Resh and Runeckles, 1973), and Heagle (1970) observed no such effect with crown rust, *Puccinia coronata*, on oats.

Infection with bacterial pathogens and nematodes also tends to reduce the impact of O<sub>3</sub>, and almost all studies of the interactions of O<sub>3</sub> with virus infections appear to do so. The previous criteria document (U.S. Environmental Protection Agency, 1986) reviewed the supporting evidence from numerous studies with a range of host plants and viruses, and noted only two studies in which O<sub>3</sub> injury was apparently increased by virus infection (Ormrod and Kemp, 1979; Reinert and Gooding, 1978). However, with tomato infected by mosaic viruses, injury was reduced in the leaves of plants in which viral infection was well established (Ormrod and Kemp, 1979). Two more recent studies have indicated either no effect or variety-dependent increased sensitivity to relatively high O<sub>3</sub> levels. Heagle et al. (1991a, 1992) found no effects of infection with several viruses on the response of two clonal strains of white clover. On the other hand, Reinert et al. (1988) reported that three cultivars of burley tobacco responded differently to O<sub>3</sub> when infected with either tobacco etch virus or tobacco vein mottling virus (TVMV). Although tobacco etch virus infection resulted in the protection of cultivars from O<sub>3</sub>-induced growth suppression, TVMV infection enhanced the suppression of the growth of two cultivars, Burley 21 and Greenville 131, but had no effect on the third, Burley 49.

With the exception of one field study demonstrating the suppression of O<sub>3</sub> injury on tobacco infected with tobacco mosaic virus (Bisessar and Temple, 1977), the other investigations of virus interactions all have been conducted in laboratory or greenhouse chambers, which raises the question of the relevance of these investigations to field conditions. As noted in the previous criteria document (U.S. Environmental Protection Agency, 1986), with few exceptions, the reports of viral protection are probably of little commercial significance but may provide information at the mechanistic level of plant response. The same caveat is equally applicable to the significance of protective effects of other obligate pathogens.

No studies appear to have been conducted of interactions involving disease-causing mycoplasmas.

As in the case of plant-insect interactions, much more systematic study is needed before it will be possible to provide any quantitative estimates of the magnitude of the interactive effects. The patterns of pollutant modification of plant-pathogen relations suggested by Dowding (1988) are supported partly by the limited evidence available for O<sub>3</sub>, but studies of a wider range of plant-pathogen systems will be needed before it will be possible to provide quantitative generalizations.

#### 5.4.3.3 Oxidant-Plant-Symbiont Interactions

Exposure to O<sub>3</sub> can modify the symbiotic relationships between plants and microorganisms. In the case of *Rhizobium*, the important nitrogen-fixing symbiont of many leguminous species, the adverse effects of exposure of the host plant reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986) all were observed at O<sub>3</sub> levels of 0.3 ppm or greater. However, Flagler et al. (1987) observed a consistent decline in total nitrogen-fixing activity of nodulated soybean roots with increasing O<sub>3</sub> concentrations up to 0.107 ppm (7-h/day seasonal average), with no effect on specific nodule activity. In a greenhouse study of soybean plants exposed at three different growth stages to a 12-h treatment in which the peak O<sub>3</sub> concentration (at 6 h) was 0.2 ppm, Smith et al. (1990) observed a 40% decrease in specific nodule activity. Hence, there is limited evidence to indicate adverse effects on Rhizobial nitrogen-fixation at O<sub>3</sub> levels experienced in polluted air.

The effects of O<sub>3</sub> on mycorrhizal fungal symbioses have been reviewed by Manning and Keane (1988) and McCool (1988). Seasonal exposures averaging 0.079 ppm O<sub>3</sub> resulted in a 40% reduction in the growth of the vesicular-arbuscular endomycorrhizal fungus, *Glomus fasciculatus*, on soybean roots; however, mycorrhizal infection lowered the O<sub>3</sub>-induced reduction in pod yield from 48 to 25% (Brewer and Heagle, 1983). Once-weekly exposures of tomato plants to 0.3 ppm for 3 h retarded the early development of the same fungus on tomato seedling roots, leading to reduced seedling growth (McCool et al., 1982). Greitner and Winner (1989) reported that the increased availability of nitrogen to alder (*Alnus serrulata*) seedlings resulting from the presence of root nodules containing the nitrogen-fixing actinomycete, *Frankia*, enabled plants to recover their photosynthetic integrity rapidly after exposure to O<sub>3</sub>; however, they did not investigate effects on symbiont.

In spite of the inconsistencies in the available evidence, it appears that rhizobial and mycorrhizal growth is likely to be impaired as a consequence of long-term exposure to oxidant stress, probably because of reduced allocation of photosynthate to the root system (Chapter 7, U.S. Environmental Protection Agency, 1986). However, the implications of such effects on mycorrhizae are particularly difficult to predict because of an inadequate understanding of the functioning of the tree root-mycorrhiza-soil system.

#### 5.4.3.4 Oxidant-Plant-Plant Interactions—Competition

In the field, the growth of any plant is to some extent dependent on its ability to compete for resources with its neighbors. Some are better competitors than others for light, water, nutrients, and space. Grime (1979) characterized as "competitors" those with a rapid growth rate associated with a capacity to adjust to rapidly changing conditions. Factors such as light or soil nutrients are not available *ad libitum*, because of the mutual shading of leaves within the canopy and root competition. Competition may be either intra- or interspecific, (i.e., the interference may be caused by neighboring members of the same or other species). The planting densities and row spacings adopted for agricultural crops represent compromises between maximizing the number of plants per unit area and the adverse effects of intraspecific competition. Weeds are typical interspecific competitors; interspecific competition also occurs in mixed plantings, such as grass-clover forage and pasture plantings and is an important feature of natural ecosystems.

Although competition from weeds may contribute more to crop losses on a global scale than any other factor, no studies appear to have been conducted on the effects of oxidant pollution on such competition. On the other hand, a few crop mixtures have been studied. A consistent finding with grass-clover mixtures has been a significant shift in the

mixture biomass in favor of the grass species (Bennett and Runeckles, 1977; Blum et al., 1983; Kohut et al., 1988a; Rebbeck et al., 1988; Heagle et al., 1989b).

As the number of competing species increases, the interactions more appropriately are dealt with at the ecological level, but, as demonstrated by the work of Evans and Ashmore (1992), it is important to recognize that, because of the differential stresses imposed by competition, the impact of O<sub>3</sub> on the components of a mixture may not be predictable on the basis of knowledge of the responses of the individual species grown in isolation. A similar caution must be stated about extrapolating to field conditions the results obtained in laboratory studies in which competition may be minimal. However, the development and use of field exposure systems have permitted many recent studies of crop species to be conducted at normal planting densities and, hence, have incorporated interspecific competition as an environmental factor. On the other hand, most forest tree studies have tended to be "artificial" in their use of individual seedlings or saplings or spaced trees, even when exposed in open-air systems (McLeod et al., 1992).

The significance of the effects of competitive interactions on the O<sub>3</sub> response of the competing species is thus largely unknown except for a few cases involving grass-legume mixtures. However, these are far from typical because they only involve two species, one of which is a legume with unique nitrogen nutrition conferred by the nitrogen-fixing capabilities of Rhizobial symbionts. Hence, the lack of knowledge of the effects of O<sub>3</sub> on competitive interactions leads to considerable uncertainty in attempting to assess the impact of O<sub>3</sub> on both managed and natural ecosystems by extrapolation from effects on individual species.

#### **5.4.4 Physical Factors**

The physical components of the plant's aerial environment are light, temperature, humidity, air turbulence, and surface wetness, whereas the physical, edaphic components affecting the plant roots are temperature, soil moisture, and soil salinity. The previous criteria document (U.S. Environmental Protection Agency, 1986) also included soil fertility under this heading; in the present review, this topic is dealt with separately in Section 5.4.5, which deals with chemical factors. The effects of the physical climatic factors (light, temperature, atmospheric turbulence, and the availability of water) on plant growth and survival are major determinants of the geographic distribution of the earth's natural vegetation and of the distribution of agricultural lands and the suitability of the crops grown on them. Because of the control that these factors exert over plant growth, their variation, especially in the short term, can be expected to influence the magnitude of plant responses to oxidants. As in the previous criteria document, the factors are discussed individually, although their actions on plant growth and sensitivity are interrelated closely. Ozone uptake and the effect of air turbulence on boundary layer processes is discussed in Section 5.3.2. A brief integration of their effects is presented in Section 5.4.8, which discusses the effects of global climate change.

At the time of the previous criteria document, much of the knowledge of the effects of these factors came from laboratory and greenhouse experimentation that focused the foliar injury response of high exposures to O<sub>3</sub>, which exceeded those likely to be encountered in ambient air. Since then, more information has become available on growth effects, especially with regard to the key area of the interactions involving drought stress.

##### **5.4.4.1 Light**

Light influences plant growth through its intensity, quality (i.e., the distribution of wavelengths), and duration (i.e., daylength or photoperiod). Much of the early work on light-oxidant interactions is largely of academic interest because light intensity and daylength are uncontrolled in natural field situations. However, reduced intensities are needed for the production of shade-grown cigar wrapper tobacco and in many commercial greenhouse floriculture operations, in which photoperiod also may be controlled in order to induce flowering. The general conclusion reported previously (U.S. Environmental Protection Agency, 1986) is that susceptibility to foliar injury is increased by low intensities and short photoperiods, although unpredictable responses had been observed when plants were subjected to increased or decreased intensities during and after exposure to  $O_3$ . One aspect of increased susceptibility to low light intensities that needs to be emphasized concerns the fact that many studies of oxidant effects have been conducted in controlled-environment chambers in which the light intensities used have rarely approached those of natural sunlight and, hence, may have magnified the observed responses. Significant differences in the amounts of foliar injury were observed on soybean plants grown in a growth chamber, a shaded greenhouse, or in an OTC in the field, when subsequently treated with a standard  $O_3$  exposure, although the growing conditions other than light intensity and quality were comparable (Lewis and Brennan, 1977). Factors other than light intensity must have contributed to the observed differences because the descending order of sensitivity was greenhouse-growth chamber-field chamber, although the average light intensities in the greenhouse and growth chamber were 81 and 18%, respectively, of those in the field chamber.

Reduced light intensities have been measured in OTCs in the field, resulting from the build-up of dust on the walls. However, Heagle and Letchworth (1982) could detect no significant effects on soybean growth and yield in a comparison of plants grown in unshaded OTCs and chambers to which shading cloth was applied.

At the mechanistic level, Darrall (1989) has reviewed the effects of light intensity and suggests that, at high intensities, the potential for endogenous oxyradical production is greatest, and that this, combined with the production of oxyradicals from  $O_3$ , might exceed the leaf's detoxification ability. However, at lower intensities, decreased carbon assimilation would limit the availability of energy for use in cellular repair.

In most species, light indirectly plays a major role in the opening and closing of stomata. Because stomata, therefore, tend to close at night and open during the day, light duration, to some extent, dictates whether or not  $O_3$  can be taken up by foliage from the ambient air.

#### **5.4.4.2 Temperature**

Temperature affects almost all physical processes and chemical reactions within the plant. Hence, it is the temperature within the plant tissues that is important. Although air temperature dictates the overall heat balance in the surrounding air, the temperature of the leaf also is determined by the absorption of infrared radiation during the photoperiod (which increases the leaf temperature) and the loss of water vapor through transpiration (which provides evaporative cooling). Hence, the effects of air temperature per se must be viewed in the context of these other physical factors. It therefore is not surprising that the few early studies of the effects of air temperature alone, using controlled environment chambers, led to variable and conflicting results, as noted in the previous criteria document (U.S. Environmental Protection Agency, 1986). In most of these studies, the RH and light intensity were held constant. In water-saturated air with a RH of 100%, the absolute humidity (or



water vapor pressure) increases with temperature. Such increases occur at all RHs. Therefore, at constant RH, the increase in absolute humidity, or vapor pressure with temperature, in turn, increases the vapor-pressure deficit (VPD) (i.e., the difference between the absolute humidity, or vapor pressure) and that of completely saturated air at the same temperature. Because VPD controls the rate of evaporation of water, at constant RH, the effects of temperature are unavoidably confounded with effects on VPD. In a recent study with tomato seedlings, in which differences in VPD at different temperatures were minimized, Todd et al. (1991) showed that, out of 11 growth variables measured, the only significant modifications of the effects of O<sub>3</sub> caused by temperature were on stem fresh weight and specific leaf area (leaf area/leaf dry weight). The authors suggest that VPD probably plays a more important role in determining sensitivity to O<sub>3</sub> than temperature.

Although transpiration rate is dependent on VPD, it also is regulated by the opening and closing of stomata on the leaf surface, vertical wind velocities, and factors, such as O<sub>3</sub>, that cause stomatal closure indirectly will cause leaf temperature to rise. Such stomatal and temperature changes have been observed during exposure to O<sub>3</sub> (Matsushima et al., 1985; Temple and Benoit, 1988).

An important O<sub>3</sub>-temperature interaction affecting trees and other woody perennials is winter hardiness. Several studies have shown that exposures to O<sub>3</sub> at realistic levels may reduce the cold- or frost-hardiness of plants, as reviewed by Davison et al. (1988). Using the pea plant as a laboratory model, Barnes et al. (1988b) showed that daily 7-h exposures to 0.075 or 0.09 ppm O<sub>3</sub> for 7 days significantly reduced plant survival after exposure to night-time temperatures that fell from 2 to -4 °C over a 2-h period and then were held at -4 °C for a further 4 h.

Various responses of coniferous trees to the exposure to O<sub>3</sub> during the growing season and freezing temperatures during the following winter have been reported. With Norway spruce, Eamus and Murray (1991) found that the recovery of photosynthetic rates after freezing was slower in O<sub>3</sub>-treated seedlings. Brown et al. (1987) and Barnes and Davison (1988) observed severe necrosis of the older needle classes of seedlings of some Norway spruce clonal saplings exposed to O<sub>3</sub> and then to freezing temperatures, although other clones showed no effect. Increased winter injury on plants exposed to O<sub>3</sub> also was observed with Sitka spruce (*Picea sitchensis*) (Lucas et al., 1988) and red spruce (Fincher et al., 1989). With loblolly pine, Edwards et al. (1990a) observed variable results, but Chappelka et al. (1990) reported that a late winter frost resulted in severe tip die-back of the youngest needles of seedling trees exposed to 1.7 (350 ppm·h) and 2.5 (433 ppm·h) times the ambient (272 ppm·h) O<sub>3</sub> concentration during the previous growing season (in contrast to the effects observed on Norway spruce). The response also varied with plant genotype. A reason for the difference may be that, in the study with Norway spruce, the freezing period occurred soon after exposure to elevated O<sub>3</sub> levels, whereas in the loblolly pine study, the frost occurred in late winter. The diversity of results led Eamus and Murray (1991) to develop a conceptual framework that recognizes that, even in severe winters, there are brief periods of mild temperatures that induce partial dehardening. Ozone decreases frost hardiness, per se, and it also increases the trees' predisposition to dehardening during winter; such dehardening puts O<sub>3</sub>-exposed trees at greater risk from subsequent low temperatures.

In a greenhouse study with 1-year-old red spruce seedlings, Neighbour et al. (1990) reported that decreasing the level of NO at the time of exposure to O<sub>3</sub> prevented the appearance of O<sub>3</sub>-induced frost injury. They suggest that the effects attributed to O<sub>3</sub> are

probably due to the combination of O<sub>3</sub> with traces of NO above a critical level. However, this effect apparently has not been investigated further.

In a study of the subtropical trees, Volkamer lemon (*Citrus volkameriana*) and avocado (*Persea americana*), in Florida, Eissenstat et al. (1991a) found that, although O<sub>3</sub> could reduce frost hardiness, the effects were subtle, and the authors concluded that the likelihood that frost resistance is adversely affected by current O<sub>3</sub> levels is slight.

The general consequences of global warming on O<sub>3</sub> responses are discussed in Section 5.4.8.

#### **5.4.4.3 Humidity and Surface Wetness**

A review of early investigations led to the conclusion that, in general, high RH tends to sensitize plants to O<sub>3</sub> (U.S. Environmental Protection Agency, 1986). Such a conclusion is supported on mechanistic grounds. A study by McLaughlin and Taylor (1981) indicated that measured O<sub>3</sub> uptake by bush bean plants (*Phaseolus vulgaris*) increased with RH, and there are several reports that, at high RH, the rapid decrease in stomatal conductance caused by O<sub>3</sub> at lower RHs is inhibited (Otto and Daines, 1969; Rich and Turner, 1972; Elkiey and Ormrod, 1979a; Elkiey et al., 1979). However, stomatal responses to O<sub>3</sub> show considerable variability among species and even among cultivars of the same species (Elkiey and Ormrod, 1979a; Elkiey et al., 1979), and, hence, it is to be expected that the patterns of the O<sub>3</sub>-RH interaction may not always be as clear. Thus, with yellow poplar (*Liriodendron tulipifera*), five consecutive daily exposures to 0.15 ppm for 7 h at either 40 or 80% RH revealed considerable variation in stomatal conductance (Jensen and Roberts, 1986). At 40% RH, there was a tendency for O<sub>3</sub> to cause a decrease in conductance during the later exposures. Nevertheless, at 80% RH, the conductances generally were greater and tended to increase during the later exposures.

Surface wetness also influences the foliar uptake of O<sub>3</sub>, although there appear to have been no studies undertaken to investigate the consequences of such uptake. Until recently, it has been suggested that O<sub>3</sub> uptake is reduced when foliage is wet because the stomata may be covered with water (Hicks et al., 1987). However, Fuentes and Gillespie (1992) reported that both wetness from dew or raindrops on the upper surface of red maple leaves can increase O<sub>3</sub> uptake significantly. Although this may be due partly to a stomatal response to resulting increases in RH, the fact that increased uptake occurred in darkness, when the stomata largely were closed led the investigators to suggest that direct uptake into the surface water is the more important mechanism. However, no information is available as to the consequences of such deposition.

#### **5.4.4.4 Drought and Salinity**

Short- and long-term variations in the availability of soil water have a profound influence on plant growth. In some agricultural situations, the use of irrigation may eliminate drought stress. However, the growth of crops and natural vegetation in many areas will be affected adversely by the varying degrees of water shortage that occur, both during a growing season and from year to year. The previous criteria document (U.S. Environmental Protection Agency, 1986) summarized earlier studies and concluded that drought stress reduced the magnitude of adverse effects of O<sub>3</sub>, including injury and growth and yield reductions. The effect was attributed to an increased rate of stomatal closure in drought-stressed plants in response to O<sub>3</sub> that effectively reduced uptake of the pollutant. These conclusions were based almost exclusively on studies with crop species. Since then, a number of studies with tree

seedlings and further studies with crops species have shown that the interaction between drought and O<sub>3</sub> is more complex and variable than originally thought.

Heagle et al. (1988a) summarized the results of investigations into the drought-O<sub>3</sub> interaction in six soybean studies, three cotton studies, one study each of alfalfa and a clover-fescue mixture. These studies were undertaken as part of NCLAN (Heck et al., 1984). The results of these investigations are included in Table 5-8. Significant interactions between O<sub>3</sub> and drought stress (soil moisture deficit, [SMD]) were reported only in three soybean studies, two cotton studies, and the alfalfa study. The interaction was usually revealed by the fact that the clear negative relationships between yield and O<sub>3</sub> exposure observed with watered plants were either much reduced or could not be demonstrated with drought-stressed plants, bearing in mind that, in most of these situations, the yields already were depressed by the SMD. As a result, the lack of any significant response to O<sub>3</sub> in some cases with such stressed plants reflects the decreased range of yield responses within which an O<sub>3</sub> effect could operate. However, as shown in Table 5-8, Heggstad et al. (1988) found with Forrest soybean that SMD significantly enhanced the effects of low O<sub>3</sub> exposures. Heagle et al. (1988a), therefore, concluded that the suppression of the response to O<sub>3</sub> caused by drought appeared to be dependent on the severity of the SMD-induced stress.

Brennan et al. (1987) suggested that the normal experimental protocols used in most NCLAN studies, which called for the use of irrigation to avoid possible complications due to drought, might have biased the yield loss data for soybean because it increased plant sensitivity to O<sub>3</sub>. However, Heggstad and Lesser (1990) found no evidence to support this suggestion, in view of the comparable estimates of yield losses predicted by the O<sub>3</sub>-response curves.

Bytnerowicz et al. (1988) found no interaction between SMD and O<sub>3</sub> in 18 desert annual species. However, moderate SMD rendered the tropical fiber plant, kenaf (*Hibiscus cannabinus*), less sensitive to O<sub>3</sub>, although sensitivity was enhanced by severe water stress (Kasana, 1992). A field survey of milkweed plants in two areas in the mid-Ohio River Valley revealed much less foliar injury attributable to O<sub>3</sub> in 1988, a dry year in which the maximum concentration recorded nearby reached 0.2 ppm, than in 1989, a year with ample precipitation and a nearby maximum of 0.12 ppm (Showman, 1991).

Although there have been several recent studies of the effects of O<sub>3</sub> exposure and drought stress on tree species, they have little in common with respect to the treatments applied or the measurements made. However, clear demonstrations of significant interactions have been obtained with beech, poplar, and loblolly pine seedlings. Davidson et al. (1992) found that, although O<sub>3</sub> reduced root growth in well-watered plants, SMD reversed this inhibition and led to slight O<sub>3</sub>-induced stimulations. Drought reduced foliar injury caused by O<sub>3</sub> to poplar (Harkov and Brennan, 1980), ponderosa pine (Temple et al., 1992), and loblolly pine (Meier et al., 1990). In poplar, the effect was attributed to the reduced stomatal conductance observed, which reduced O<sub>3</sub> uptake. Similar effects on stomatal conductance were observed in Norway spruce and sitka spruce (Dobson et al., 1990). In ponderosa pine, SMD also countered the inhibitory effects of O<sub>3</sub> on needle growth and retention (Temple et al., 1993). Tseng et al. (1988), however, observed no effects of O<sub>3</sub> on Fraser fir (*Abies balsamea*) grown under three levels of SMD. No consistent patterns were found with various physiological measurements made on red spruce seedlings subjected to both O<sub>3</sub> and drought (Roberts and Cannon, 1992). Lee et al. (1990b) observed reduced root conductivity in the second drought cycle following exposure to O<sub>3</sub>. Thus, there is some

**Table 5-8. Field Studies of Ozone-Drought Stress Interactions in Crop Species<sup>a</sup>**  
**(Adapted in part from Heagle et al., 1988a)**

Crop/Cultivar	Year	Response	Significant Interaction <sup>c</sup>	Estimated Yield Loss (%) per Seasonal Mean O <sub>3</sub> Concentration (ppm) <sup>b</sup>					Reference	
				0.04	0.05	0.06	0.07	0.08		
<u>Soybean</u>										
Williams	1982	Yield	No	7	13	19	24	30	Heggestad et al. (1985) Heggestad and Lesser (1990)	
Williams and Corsoy 79	1983	Yield	WW	7	13	18	24	30	Heggestad and Lesser (1990)	
		Yield	DS	6	11	15	19	23		
Williams		Root length	WW	No significant O <sub>3</sub> effect					Heggestad et al. (1988)	
		Root length	DS	[33 36 52] <sup>d</sup>						
Forrest	1982	Yield	WW	3	9	21	39	60	Heggestad et al. (1985)	
		Yield	DS	13	21	28	35	41	Heggestad and Lesser (1990)	
Davis	1983	Yield	WW	4	7	12	16	21	Heagle et al. (1987a)	
		DS								
		Yield		No significant O <sub>3</sub> effect						
Davis	1984	Yield	No	4	7	12	18	24	Heagle et al. (1987a)	
Corsoy 79	1986	Yield	WW	2	4	8	13	21	Irving et al. (1988)	
		Yield	DS	0	0	0	0	1		
Young	1986	Yield	No	6	11	17	25	34	Miller et al. (1989b)	
<u>Cotton</u>										
Acala SJ-2	1981	Yield	WW	3	7	13	21	30	Temple et al. (1985)	
		Yield	DS	1	2	3	7	12		
Acala SJ-2	1982	Yield	No	6	15	26	40	55	Temple et al. (1985)	
McNair 235	1985	Yield	No	7	13	21	30	40	Heagle et al. (1988b)	
Acala SJ-2	1986	Shoot dry mass	WW <sup>e</sup>		[22	26	42] <sup>f</sup>		Temple et al. (1988b)	
		Shoot dry mass	DS <sup>e</sup>		[20	37	44] <sup>f</sup>			
		Shoot dry mass	DS (severe) <sup>e</sup>		[+14	+22	27] <sup>f</sup>			

**Table 5-8 (cont'd). Field Studies of Ozone-Drought Stress Interactions in Crop Species<sup>a</sup>**  
**(Adapted in part from Heagle et al., 1988a)**

Crop/Cultivar	Year	Response	Significant Interaction <sup>c</sup>	Estimated Yield Loss (%) per Seasonal Mean O <sub>3</sub> Concentration (ppm) <sup>b</sup>					Reference
				0.04	0.05	0.06	0.07	0.08	
<u>Alfalfa</u>									
WL-514	1984	Yield	No	6	9	13	17	20	Temple et al. (1988a)
WL-514	1985	Yield	No <sup>g</sup>	4	7	10	14	18	
<u>Tall Fescue-Ladino Clover</u>									
Kentucky 31	1984	Yield	No	5	8	12	17	22	Heagle et al. (1989b)
and Regal	1984	Yield	No	6	11	17	24	32	

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Where a significant interaction was observed, separate responses are listed for well-watered (WW) and drought-stressed (DS) plants; otherwise, the pooled response is listed.

<sup>c</sup>Based on Weibull model estimates (Heagle et al., 1988a)

<sup>d</sup>Data presented are percent reductions in root length per soil core at seasonal mean O<sub>3</sub> exposures of 0.074, 0.107, and 0.132 ppm relative to 0.052 ppm. Increased root lengths in DS treatments ranged from 136 to 11% with increasing O<sub>3</sub> exposure.

<sup>e</sup>Interaction not significant by analysis of variance, but significant suppression of O<sub>3</sub> response in DS (severe).

<sup>f</sup>Weibull model data not available. Data presented are actual percent yield losses at seasonal mean O<sub>3</sub> exposures of 0.074, 0.094, and 0.111 ppm relative to 0.015 ppm.

<sup>g</sup>Polynomial regression analysis showed slightly greater response in WW than DS plots.

evidence from tree species to support the view that drought stress may reduce the impact of  $O_3$ . However, the work with trees provides no additional information to help in resolving the quantitative nature of the drought- $O_3$  interaction.

Although drought stress may be the result of insufficient rainfall, conditions of effective SMD also may be induced by excessive soil salinity. Laboratory studies reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986) showed that increased salinity could reduce the impact of  $O_3$  on injury and yield of various crops. However, in a more recent field study with alfalfa, Olszyk et al. (1988) found no overall interaction between  $O_3$  and salinity on growth or yield. Although salinity decreased the number of empty nodes caused by exposure to above-ambient levels of  $O_3$ , the effect was statistically significant only for the second of four harvests. In general, salinity was found to be more harmful to alfalfa growth than exposure to  $O_3$ , but, as pointed out by Olszyk et al. (1988), the amount of information available is insufficient to permit the development of models for estimating losses due to  $O_3$ -salinity combinations.

The bulk of the available evidence supports the view that drought stress may reduce the impact of  $O_3$  on plants. However, it must be emphasized that, in terms of growth and productivity, any "protective" benefit will be offset by the effects of SMD per se, as noted in the previous criteria document (U.S. Environmental Protection Agency, 1986).

The  $O_3$ -water interaction is not confined to the effects of SMD on direct plant response to  $O_3$ . Numerous studies have shown that  $O_3$  may affect various aspects of plant water status, including water-use efficiency (WUE), the ratio of the rates of photosynthetic carbon gain and transpirational water loss. For example, Reich et al. (1985) observed that daily exposures to 0.13 ppm  $O_3$  for 6.8 h resulted in a 25% reduction in WUE in well-watered Hodgson soybean, when compared to exposure to 0.01 ppm. Similar findings have been reported for alfalfa (Temple and Benoit, 1988) and radish (Barnes and Pfirrmann, 1992). However, WUE is a complex resultant of both stomatal conductance and the activity of the photosynthetic system, both of which may be independently affected by  $O_3$ . Genetic or environmentally induced difference in the relative sensitivities of the stomatal and photosynthetic components will dictate the nature and magnitude of any effect of  $O_3$  on WUE. Thus, with radish and soybean, Greitner and Winner (1988) observed effects on stomatal conductance and photosynthetic  $CO_2$  assimilation that translated into  $O_3$ -induced increases in WUE; however, they point out, that this advantageous increase far outweighed the adverse effects of  $O_3$  on growth.

However, these reports concern herbaceous weedy species, and there appears to be only one report concerning tree species. Johnson and Taylor (1989) reported that exposure to higher than ambient levels of  $O_3$  results in adaptation to a more efficient use of water by the foliage of loblolly pine seedlings. The corollary to this observation is that trees exposed continuously to low  $O_3$  levels may be more sensitive to recurrent drought stress than are those grown under higher exposure levels. As with most studies of tree species, these observations were made on tree seedlings, and the relevance to mature trees is still to be established.

It therefore is clear that not only does drought have a pronounced effect on the response of most species to  $O_3$ , but that  $O_3$  also may modify plant water relations, including conferring drought tolerance. However, more study will be needed before it will be possible to generalize about the implications of the latter effect and its importance to forest ecosystems.

### 5.4.5 Nutritional Factors

All land plants require an adequate supply of essential mineral elements from the soil in order to avoid adverse effects on growth and survival resulting from mineral deficiencies. Two of the essential elements needed for growth are nitrogen and sulfur, and although these are normally obtained from the soil through the root system, the plant's needs, at least in part, also can be met by the uptake of pollutant gases such as  $\text{NO}_2$  and  $\text{SO}_2$ . Other nutrients such as phosphorus, potassium, magnesium, and calcium generally are available only from the soil.

A supply of elements such as nitrogen, potassium, phosphorus, sulfur, magnesium, and calcium is essential for plant growth, but optimal growth requires that the supply be balanced; with insufficiency (or excess) of any of them, growth will be suboptimal. Not surprisingly, therefore, nutrient imbalance has been shown to affect response to  $\text{O}_3$ , although the previous criteria document (U.S. Environmental Protection Agency, 1986) concluded that work to that date had not clarified the relationship between soil fertility and sensitivity to  $\text{O}_3$ , largely because of the differences in nutrients and species selected for study and the experimental conditions used. This conclusion is still valid, in spite of the results of a limited number of more recent studies, and is not surprising in view of the vast number of possible permutations and combinations of nutrient elements and their levels that may exert effects on  $\text{O}_3$  response. A comprehensive summary of the relevant studies is presented in Table 5-9.

Most information concerns nitrogen. However, inspection of Table 5-8 shows that, in four of the 13 studies, increased nitrogen supply increased susceptibility to foliar injury or enhanced adverse effects on growth; two of the studies showed opposite effects; in three studies, injury was greatest at normal nitrogen levels and less at higher or lower levels; and, in one study, injury was least at normal nitrogen levels. No interactions were observed with soil nitrogen in three studies. Knowledge of the tissue nitrogen levels resulting from the fertilizer treatments, as recommended by Harkov and Brennan (1980), might resolve these contradictions, but these were not reported in most studies. The contradictory evidence for tobacco may reflect different responses of different cultivars, as suggested by Menser and Hodges (1967).

The possibilities of response to  $\text{O}_3$  being modified as a result of significant dry deposition of nitric acid ( $\text{HNO}_3$ ) vapor or of wet deposition of nitrate ion in acid precipitation are discussed in Sections 5.4.6.3 and 5.4.6.5, respectively.

The limited evidence for phosphorus, potassium, and sulfur consistently indicated a decrease in sensitivity with increased nutrient level. With respect to general fertility, both studies listed in Table 5-8 revealed decreased sensitivity to  $\text{O}_3$  at high levels of nutrient supply, although, with soybean, nutrient-deficient plants also showed decreased sensitivity. Heagle (1979) found that, although injury and growth reductions tended to be greatest at normal levels of fertility, the effects were dependent on the rooting medium used; in media containing peat, the impact of  $\text{O}_3$  on growth was least at the lowest fertility level.

Cowling and Koziol (1982) have suggested that, in spite of the apparent contradictory evidence regarding the effects of nutrition on  $\text{O}_3$  response, there is evidence to support the hypothesis that differences in sensitivity are ultimately linked to changes in the status of soluble carbohydrates in the plant tissues (Dugger et al., 1962). However, this hypothesis has yet to be tested systematically.

**Table 5-9. Ozone-Soil Nutrient Interactions  
(Based in part on Cowling and Koziol, 1982)<sup>a</sup>**

Species	Response to Increase in Nutrient Level	Reference
<u>Nitrogen</u>		
Loblolly pine	Decreased reduction of growth due to O <sub>3</sub>	Tjoelker and Luxmoore (1991)
Ponderosa pine	No injury or growth interactions	Bytnerowicz et al. (1990)
Poplar	Maximum injury in mid-range but no growth interaction	Harkov and Brennan (1980)
Yellow poplar	No growth interaction	Tjoelker and Luxmoore (1991)
Ladino clover/tall fescue	No growth interaction	Montes et al. (1982)
Mangel	Increased injury	Brewer et al. (1961)
Radish	Increased reduction of growth due to O <sub>3</sub>	Ormrod et al. (1973)
	Increased reduction of growth due to O <sub>3</sub>	Pell et al. (1990)
Spinach	Increased injury	Brewer et al. (1961)
Tobacco	Decreased injury	Menser and Street (1962)
	Minimum injury in mid-range	MacDowall (1965)
	Maximum injury in mid-range	Leone et al. (1966)
	Maximum injury in mid-range	Menser and Hodges (1967)
<u>Phosphorus</u>		
Radish	No growth interaction	Ormrod et al. (1973)
Tomato	Increased injury	Leone and Brennan (1970)
<u>Potassium</u>		
Norway spruce	Decreased reduction of CO <sub>2</sub> assimilation due to O <sub>3</sub>	Keller and Matyssek (1990)
Pinto bean	Decreased injury	Dunning et al. (1974)
Soybean	Decreased injury	Dunning et al. (1974)
<u>Sulfur</u>		
Bush bean	Decreased injury	Adedipe et al. (1972)
<u>Magnesium</u>		
Loblolly pine	No growth interaction	Edwards et al. (1992b)
<u>General Fertility (nitrogen, phosphorus, and potassium)</u>		
Bush bean	Decreased injury	Heck et al. (1965)
Soybean	Maximum injury and growth reduction in mid-range	Heagle (1979)

<sup>a</sup>See Appendix A for abbreviations and acronyms.



Nutritional nitrogen and sulfur also can be supplied directly to foliage in the form of nitrogen and sulfur oxides. The interactions of these gaseous pollutants with  $O_3$ , dealt with in the next section, focus on toxic rather than nutritional effects. However, one example of a beneficial effect concerns  $N_2O_5$ . Because  $N_2O_5$  is produced in trace amounts by high-voltage, corona-discharge  $O_3$  generators, it may contaminate  $O_3$  produced from air by such generators for use in studies of effects of  $O_3$  on vegetation, unless the  $O_3$  stream is passed first through a water scrubber. Brown and Roberts (1988) reported that deposition of the nitrate formed by hydration of trace amounts of  $N_2O_5$  in unscrubbed  $O_3$  significantly increased the nitrogen status of the exposed plants, which may have confounded the effects attributed to  $O_3$ .

#### **5.4.6 Interactions with Other Pollutants**

The concurrent or sequential exposure of vegetation to different gaseous air pollutants has been found to modify the magnitude and nature of the response to individual pollutants. Some of the early work reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986) on the effects of gaseous pollutant combinations is of academic interest, with little relevance to the present review because of the levels of exposure and the exposure profiles used and the fact that the experimental regimes usually involved concurrent exposures to two or more pollutants repeated daily. Lefohn and Tingey (1984) and Lefohn et al. (1987b) reviewed the patterns of co-occurrence of  $O_3$ ,  $SO_2$ , and  $NO_2$  in urban, rural, and remote sites in the United States for the years 1978 to 1982 and found that co-occurrences were usually of short duration and occurred infrequently. They noted that the most frequent types of co-occurrence were either purely sequential or a combination of sequential and overlapping exposures of short duration. Accordingly, the present review will focus on the evidence from experiments that simulated these naturally occurring patterns of combined exposure or, at least, that used exposure levels in the ranges of those occurring in polluted air. An exception is the co-occurrence of  $O_3$  and PAN, which are both components of photochemical oxidant.

Over the past decade, the effects of pollutant mixtures have been reviewed by Wolfenden et al. (1992), Shriner et al. (1991), Mansfield and McCune (1988), Torn et al. (1987), Lefohn and Ormrod (1984), Reinert (1984), and Runeckles (1984).

##### **5.4.6.1 Oxidant Mixtures**

Because of their photochemical origins, elevated levels of  $O_3$  and PAN can occur simultaneously. There appear to have been no further investigations of the effects of simultaneous or sequential exposures since the limited number of studies reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986). Hence, there is no reason to question the general conclusion, based on the work of Tonneijck (1984) and Nouchi et al. (1984), that the two gases tend to act antagonistically in both concurrent and sequential exposures. Hydrogen peroxide ( $H_2O_2$ ) is also a component of photochemically polluted atmospheres. Although Ennis et al. (1990) reported reduced stomatal conductances in red spruce needles exposed to a mixture of  $O_3$ ,  $SO_2$ , and  $H_2O_2$ , no studies have been made of  $O_3/H_2O_2$  interactions.

#### 5.4.6.2 Sulfur Dioxide

Because SO<sub>2</sub> originates from point sources of combustion, the occurrence of high ambient concentrations at a given location is usually episodic because of its dependence on wind speed and direction and the distance from the source. However, aggregations of point sources can lead to more widespread but less marked increases in ambient SO<sub>2</sub> levels. Thus, the potential exists for elevated O<sub>3</sub> exposures to be superimposed on patterns of SO<sub>2</sub>, ranging from severe fluctuations to almost steady low-level concentrations. Concern over the importance of O<sub>3</sub>-SO<sub>2</sub> interactions dates from the observations of Menser and Heggstad (1966) that simultaneous exposures of tobacco to SO<sub>2</sub> and O<sub>3</sub> acted synergistically (i.e., the effects of the mixture were greater than the sum of the responses to either pollutant alone). Indeed, in the Menser and Heggstad study, foliar injury was found to result from exposure to mixtures, although exposures to either gas alone at the same concentrations as in the mixtures did not result in injury.

Although much of the early work was concerned with foliar injury responses to simultaneous exposures to high levels of O<sub>3</sub> and SO<sub>2</sub>, more recent studies have tended to focus on the consequences of growth and yield of repeated exposures to lower level mixtures or sequences. Several studies have been aimed at obtaining statistical evidence for the existence of interactions. For example, Ashmore and Onal (1984), studying six cultivars of barley, found that SO<sub>2</sub> at 0.065 ppm for 6 h, an exposure that induced no adverse effects, acted antagonistically to a 6-h exposure to 0.18 ppm O<sub>3</sub>, causing significant decreases in foliar injury, ranging from 46% to as much as 95%. However, only one cultivar, Golden Promise, showed a significant interaction on yield, with SO<sub>2</sub> completely reversing the decrease caused by O<sub>3</sub> alone. The results could not be explained by effects on stomatal uptake because stomatal conductances were found to be highest in the mixture. In contrast, with pea, Olszyk and Tibbitts (1981) reported that O<sub>3</sub> + SO<sub>2</sub> caused the same degree of stomatal closure as SO<sub>2</sub> alone. An antagonism similar to that observed on Golden Promise also was observed in field studies of Arena barley (Adaros et al., 1991a) and spring rape (*Brassica napus*) (Adaros et al., 1991b). However, with Tempo spring wheat, a synergistic interaction was observed: the adverse effect of O<sub>3</sub> on yield (−26%) was increased to −38% by SO<sub>2</sub>, which, by itself, only reduced yield by 7% (Adaros et al., 1991a). On the other hand, neither Amundson et al. (1987) nor Kohut et al. (1987) observed any interaction in a field study with Vona winter wheat. Irving et al. (1988) observed no interaction on field corn.

In a series of experiments in which exposure to O<sub>3</sub> or an O<sub>3</sub>/SO<sub>2</sub> mixture was preceded by exposures to SO<sub>2</sub> alone, an antagonistic response was observed on foliar injury to white bean (Hofstra and Beckerson, 1981). In contrast, the responses of cucumber (*Cucumis sativus*) and radish were synergistic, whereas there was no interaction on soybean or tomato. However, when followed by exposure to an O<sub>3</sub>/SO<sub>2</sub> mixture, SO<sub>2</sub> pretreatment resulted in an increase in injury to white bean, decreases in cucumber and tomato, and no effect on soybean and radish.

Field studies with soybean using an air-exclusion system to provide a range of exposures to O<sub>3</sub> and SO<sub>2</sub> at ambient and subambient levels revealed an antagonistic interaction on yield at low concentrations (Jones et al., 1988). However, Kress et al. (1986) found no interaction in a soybean field study using OTCs. No interactions were found with potato (Pell et al., 1988) or with a red clover-timothy (*Phleum pratense*) forage mixture (Kohut et al., 1988b).

From the foregoing, it is apparent that no clearer pattern of the interactive effects of O<sub>3</sub> and SO<sub>2</sub> on crops has emerged since the previous criteria document (U.S. Environmental Protection Agency, 1986). The same is true for the responses of tree species.

With tree seedlings, Chappelka et al. (1988a) observed no interaction on white ash. Although a synergistic interaction was found on root growth of yellow poplar (Chappelka et al., 1985), only additive interactions were found on the growth of other parts of the plant. In a unique study, Kargiolaki et al. (1991) noted that SO<sub>2</sub> reduced the accelerated leaf senescence caused by O<sub>3</sub> on two poplar clones, but had no effect on other clones. They also observed additive or less than additive interactions on the formation of intumescences, due to hypertrophy of the stems and bark cracking. They attributed the differences in clonal response to differences in the levels of pollutant-induced ethylene evolution.

Sulfur dioxide reversed the inhibition of photosynthesis caused by exposure to O<sub>3</sub> in two lichen species, *Flavoparmelia caperata* and *Umbilicaria mammulata* (Eversman and Sigal, 1987).

Several studies have attempted to quantify the magnitudes of joint responses to O<sub>3</sub> and SO<sub>2</sub>. The earliest (Macdowall and Cole, 1971) showed that the synergistic injury response of tobacco occurred at concentrations of SO<sub>2</sub> less than the threshold for SO<sub>2</sub> injury, but not less than the O<sub>3</sub> threshold. Oshima (1978), working with kidney bean, found that the synergistic reduction due to intermittent exposures to O<sub>3</sub> was linear through a range of O<sub>3</sub> concentrations achieved by varying degrees of filtration of ambient air (expressed as 10 to 90 ppm-h of concentrations greater than zero), although the threshold for an O<sub>3</sub> response was approximately 47 ppm-h.

A selection of statistical models of injury- or yield responses to O<sub>3</sub>/SO<sub>2</sub> is listed in Table 5-10. It is immediately apparent that the models reveal no consistent patterns of response. In part, this is because they were developed on the basis of individual experiments conducted under different environmental conditions at different locations in different years. Although each model was statistically significant, it was based on a unique data set. One study with soybean indicated an antagonistic interaction (Heagle et al., 1983b), but another indicated no interaction (Kress et al., 1986). Cucumber (Hofstra et al., 1985) and snap bean (Heggstad and Bennett, 1981) were reported to respond synergistically, whereas white bean responded antagonistically (Hofstra et al., 1985).

All that can be concluded from these studies is that the type of interaction, and whether or not one exists, is probably highly dependent on species and cultivar, and possibly dependent on other environmental variables. The available evidence is insufficient to be able to decide in which way, and to what extent, SO<sub>2</sub> exposure will influence the effects of O<sub>3</sub> on a particular species or cultivar at a particular location. The synergism originally observed (Menser and Heggstad, 1966) is not a general response.

#### **5.4.6.3 Nitrogen Oxides, Nitric Acid Vapor, and Ammonia**

As discussed in Chapter 3, the photochemical formation of O<sub>3</sub> involves a complex series of reactions in which NO, NO<sub>2</sub>, and HNO<sub>3</sub> participate as intermediates or reaction products. Of these, the limited number of reports of interactive effects with O<sub>3</sub> is confined to NO<sub>2</sub>. Some of the few studies of O<sub>3</sub>/NO<sub>2</sub> interactions that have utilized realistic concentrations have involved mixtures of the pollutants. Adaros et al. (1991a) found in a 2-year study of two cultivars each of barley and spring wheat that significant interactions could be detected only on wheat yield in one growing season. With both cultivars, the

**Table 5-10. Some Statistical Models of Combined Ozone and Sulfur Dioxide Responses<sup>a</sup>**

Species	Type of Interaction	Model	Reference
<u>Corn</u>			
Golden Jubilee	Synergistic	Injury = $-11.39 + 5.471 \ln(\text{IHT}) - 9.59[\text{O}_3] + 11.81[\text{SO}_2] - 86.63[\text{SO}_2]^2 + 428.95[\text{O}_3][\text{SO}_2]$ (IHT = initial plant height, used as a covariate; $[\text{O}_3]$ and $[\text{SO}_2]$ , ppm)	Deveau et al. (1987) <sup>b</sup>
<u>Cucumber</u>			
National Pickling	Synergistic	Injury = $2.70 + 1.95 n$ ; at $[\text{SO}_2] = 0.10$ ppm Injury = $2.40 + 0.21 n$ ; at $[\text{SO}_2] = 0.05$ ppm Injury = $2.39 + 0.39 n$ ; at $[\text{SO}_2] = 0.03$ ppm Injury = $1.86 + 0.166 n$ ; at $[\text{SO}_2] = 0.02$ ppm (n = number of daily 8-h $\text{SO}_2$ exposures; $\text{O}_3$ exposure, 0.15 ppm, 6 h)	Hofstra et al. (1985)
<u>Snap Bean</u>			
Maple Arrow	Additive; no interaction	Injury = $4.44 + 34.19[\text{O}_3] + 19.98[\text{SO}_2]$ ( $[\text{O}_3]$ and $[\text{SO}_2]$ , ppm)	Deveau et al. (1987) <sup>b</sup>
<u>White Bean</u>			
Seafarer	Antagonistic	Injury = $6.31 - 0.90 n$ ; at $[\text{SO}_2] = 0.10$ ppm Injury = $5.95 - 0.45 n$ ; at $[\text{SO}_2] = 0.05$ ppm (n = number of daily 8-h $\text{SO}_2$ exposures; $\text{O}_3$ exposure: 0.15 ppm, 6 h)	Hofstra et al. (1985)
<u>Potato</u>			
Norchip	Additive; no interaction	Yield = $1.27 - 0.0037[\text{O}_3] + 0.00092[\text{SO}_2]$ (Yield = number of Grade No. 1 tubers per plant; $[\text{O}_3]$ : ppm, 10 h/day seasonal mean; $[\text{SO}_2]$ , ppm, 3 h/day)	Pell et al. (1988)
<u>Soybean</u>			
Davis	Antagonistic	Polynomial model: Yield = $534.5 - 3988.6[\text{O}_3] - 479.7[\text{SO}_2] + 2661.0[\text{O}_3][\text{SO}_2] + 1,0960[\text{O}_3]^2$ Weibull model: Yield = $531 \times \exp[-([\text{O}_3]/0.133)] \times \exp[-([\text{SO}_2]/0.892)]$ (Yield = g/m of row; $[\text{O}_3]$ : ppm, seasonal 7 h/day mean; $[\text{SO}_2]$ : ppm, seasonal 4 h/day mean)	Heagle et al. (1983b)
Amsoy-71 and Corsoy-79 (pooled)	No interaction	Yield = $1934.4 \times \exp[-([\text{O}_3]/0.124)^{2.666}] \times \exp[-([\text{SO}_2]/1.511)^{1.044}]$ (Yield = kg/ha; $[\text{O}_3]$ : ppm, seasonal 7 h/day mean; $[\text{SO}_2]$ : ppm, seasonal 4 h/day mean)	Kress et al. (1986)

**Table 5-10 (cont'd). Some Statistical Models of Combined Ozone and Sulfur Dioxide Responses<sup>a</sup>**

Species	Type of Interaction	Model	Reference
<u>Tomato</u>			
New Yorker		Injury = $-75.78 + 20.48\ln[\text{PI}] - 29.16[\text{O}_3] + 1,016[\text{O}_3]^2 + 9.02[\text{SO}_2] - 17.29[\text{SO}_2]^2 + 258.76$ [O <sub>3</sub> ][SO <sub>2</sub> ] (PI = plastochron index, used as a covariate; [O <sub>3</sub> ] and [SO <sub>2</sub> ]: ppm)	Deveau et al. (1987) <sup>b</sup>

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Report includes models for other growth variables.

interaction was antagonistic. Nitrogen dioxide also reduced the adverse effect of O<sub>3</sub> on the yield of spring rape (Adaros et al., 1991b). Foliar injury to sunflower (*Helianthus annuus*) caused by daily exposures to O<sub>3</sub> (0.1 ppm, 8 h) was increased by continuous exposure to 0.1 ppm NO<sub>2</sub> (Shimizu et al., 1984). Plant dry weight was decreased by O<sub>3</sub> + NO<sub>2</sub> relative to growth in O<sub>3</sub> alone, but because O<sub>3</sub> exposure resulted in a slight increase in dry weight relative to the controls, the growth in the mixture and in the controls did not differ significantly.

The results of a study of seven tree species exposed to 0.1 ppm O<sub>3</sub> and/or 0.1 ppm NO<sub>2</sub> for 6 h/day for 28 days (Kress and Skelly, 1982) were reported in detail in the previous criteria document (U.S. Environmental Protection Agency, 1986). However, although several growth interactions were noted in the review, the only statistically significant effect was on top growth of pitch pine (*Pinus rigida*), in which NO<sub>2</sub> reversed a growth stimulation caused by exposure to O<sub>3</sub>. In contrast, although Yang et al. (1982) also observed an antagonistic interaction on the needle dry weights of two eastern white pine clones, in these cases NO<sub>2</sub> reversed the adverse effect of O<sub>3</sub>.

There appear to have been only three studies using sequential exposures of O<sub>3</sub> and NO<sub>2</sub>. Runeckles and Palmer (1987) exposed radish, wheat, bush bean, and mint (*Mentha piperita*) daily to 0.08 to 0.1 ppm NO<sub>2</sub> for 3 h (0900 to 1200 hours), to 0.08 to 0.1 ppm O<sub>3</sub> for 6 h (1200 to 1800 hours), or to the two gases in sequence. With each species except mint, pretreatment with NO<sub>2</sub> significantly modified the growth responses to O<sub>3</sub>. In radish and wheat, the two gases acted conjointly to reduce growth more than O<sub>3</sub> alone, whereas in bean NO<sub>2</sub> was antagonistic. In studies with tomato, Goodyear and Ormrod (1988) found that sequential exposure to 0.08 ppm O<sub>3</sub> for 1 h, followed by 0.21 ppm NO<sub>2</sub> for 1 h, significantly reduced growth. No significant effects were found when the sequence was reversed or the two gases were used as a mixture. However, because the study did not include a treatment with O<sub>3</sub> alone, no information was obtained as to how NO<sub>2</sub> may have influenced the response to O<sub>3</sub>. Bender et al. (1991) exposed kidney beans in OTCs in the field to the sequence: O<sub>3</sub> (0800 to 1600 hours, ambient + 0.50 ppm) followed by NO<sub>2</sub> (1600 to 0800 hours, ambient + 0.3 ppm), during two growing seasons. No significant treatment effects on growth were observed in 1988, but in 1989 a significant interaction on total plant biomass was noted after 48 days; the overnight NO<sub>2</sub> exposures negated the inhibition caused by O<sub>3</sub> with a change from -32 to +14%, relative to the controls. This type of response is similar to that observed on bean by Runeckles and Palmer (1987).

With such limited information, it is not possible to generalize, particularly because antagonistic and additive responses have been reported even for individual species. However, because, on a daily basis, changes in NO<sub>2</sub> levels tend to lead to maxima at times when O<sub>3</sub> levels are lowest, the evidence is sufficiently compelling to indicate that modifications of the O<sub>3</sub> response, as a result of increased NO<sub>2</sub>, are highly probable. Direct interactive effects of O<sub>3</sub> and NO<sub>2</sub> are virtually precluded because of their rapid reaction to form NO<sub>2</sub>.

In Southern California, O<sub>3</sub> levels have been correlated with levels of HNO<sub>3</sub> vapor (Fenn and Bytnerowicz, 1993). No studies of possible interactive effects between O<sub>3</sub> and HNO<sub>3</sub> have been reported. However, Taylor et al. (1988a) suggest that HNO<sub>3</sub> is largely deposited on foliar surfaces and, hence, may be leached to the soil by rainfall. Such leaching, together with rates of dry deposition to soil that have been conservatively estimated to range between 5.7 and 29.1 kg nitrogen ha<sup>-1</sup> year<sup>-1</sup>, would lead to nitrogen additions to the soil at rates considerably less than agricultural rates of nitrogen-application to crops. However, such

additions to forest soils could increase nitrogen levels significantly and lead to interactive effects with O<sub>3</sub> via changes in soil fertility, as discussed in Section 5.4.5.

Ammonia (NH<sub>3</sub>) can contribute significantly to total nitrogen deposition in some locations. However, virtually nothing is known of its interactive effects with O<sub>3</sub>. Tonneijck and van Dijk (1994) reported that, although NH<sub>3</sub> and O<sub>3</sub> showed a significant antagonism with regard to foliar injury of O<sub>3</sub>-sensitive bean cv. Pros, no interactions occurred with regard to growth effects.

#### **5.4.6.4 Hydrogen Fluoride and Other Gaseous Pollutants**

The adverse effects of HF released from the aluminum smelting process and superphosphate fertilizer manufacture are well documented, but information about possible HF/O<sub>3</sub> interactions are limited to a single study. MacLean (1990) reported that exposures of corn plants on alternate days to 4 h at 1 µg/m<sup>3</sup> fluorine as HF or 0.06 ppm O<sub>3</sub> showed reduced rates of senescence, compared with plants exposed only to O<sub>3</sub>.

#### **5.4.6.5 Acid Deposition**

Any impact that acid deposition has on crops or natural ecosystems occurs either through direct effects on foliage or indirectly through the soil. Soil effects may result from a change in pH or to the deposition of sulfate or nitrate onto the soil. The effects of acidic deposition have been reviewed extensively by Shriner et al. (1991). Although concerns over the possible role of exposures to acid rain or acid fog and O<sub>3</sub> in the forest-decline syndrome led to several studies with forest tree species, studies also have been conducted on crops. Of over 80 recent reports of studies on over 30 species, more than 75% of the reports indicated no significant interactions between O<sub>3</sub> and acidity of simulated acid rain (SAR) or acid fog. The reports are summarized in Table 5-10. In 63 studies, there was either no effect of one or other of the pollutants (usually acid rain) or the effects of both pollutant stresses were simply additive.

However, in other studies, statistically significant interactions have been reported for several species, as also shown in Table 5-11. For example, although a large number of studies of loblolly pine revealed no interaction, Qiu et al. (1992) reported significant interactions on foliar and stem and root biomass with seedling trees of an O<sub>3</sub>-sensitive family. However, because the study failed to show a significant main effect of acidity of the SAR, the authors question whether the interaction is meaningful.

With Norway spruce, antagonistic interactions were noted on stomatal conductance (Barnes et al., 1990a) and dark respiration (Barnes et al., 1990b). In contrast, Eamus and Murray (1991) reported greater than additive effects of O<sub>3</sub> and acid mist on photosynthetic rates. However, no interactions were noted in nine other investigations (Table 5-11).

Kohut et al. (1990) observed significant interactions on needle and shoot growth of red spruce. In both cases the inhibition caused by O<sub>3</sub> and SAR at pH 5.1 was reversed by more acidic rain at pH 3.1. However, there were unexplained inconsistencies in the trends because the combination of intermediate O<sub>3</sub> levels and low pH resulted in the greatest reductions in dry matter. Percy et al. (1992), also working with red spruce, observed an unexplained statistically significant interaction on the thickness of the needle epidermal cell cuticular membrane: at intermediate O<sub>3</sub> exposures, increased acidity led to reduced membrane thickness, whereas lower or higher O<sub>3</sub> levels led to thicker membranes.

Shelburne et al. (1993) reported that, in two growing seasons, needle biomass of shortleaf pine (*Pinus echinata*) was reduced significantly in tree seedlings receiving the

**Table 5-11. References to Reports of Interaction or No Interaction Between Ozone and Acid Rain or Acid Fog**

Species	No.	Interaction References	No.	No Interaction References
<b>Tree Species</b>				
CONIFERS				
Jeffrey pine	0	—	1	62
Loblolly pine	1	41	13	1, 10, 16-21, 26, 32, 43, 47, 49, 55
Ponderosa pine	0	—	2	65, 66
Shortleaf pine	1	52	1	8
Slash pine	2	9, 13	0	—
White pine	1	47	3	44, 46, 56
Douglas fir	0	—	1	25
Norway spruce	1	3, 4	9	2, 5-7, 15, 24, 30, 36, 50
Red spruce	2	31, 39	5	33, 34, 38, 40, 62
Sequoia	1	63	0	—
Totals	9		35	
HARDWOODS				
Green ash	0	—	1	23
White ash	0	—	1	23
European beech	1	14	1	35
Paper birch	1	29	0	—
Sugar maple	0	—	2	44, 45
Red oak	0		2	44, 45
Yellow poplar	3	11, 12, 27	1	48
Totals	5		8	
<b>Crop Species</b>				
FORAGES AND FIELD CROPS				
Alfalfa	1	59	4	42, 53, 59, 64
Sorghum	1	51	0	—
Soybean	1	67	4	28, 37, 53, 57
Wheat	0	—	1	53
Totals	2		5	
HORTICULTURAL CROPS				
Snap bean	0	—	1	53
Celery	0	—	1	60
Corn	0	—	1	60
Pepper	0	—	2	58, 60



**Table 5-11 (cont'd). References to Reports of Interaction or No Interaction Between Ozone and Acid Rain or Acid Fog**

Species	No.	Interaction References	No.	No Interaction References
<b>HORTICULTURAL CROPS (cont'd)</b>				
Strawberry	0	—	2	60, 61
Tomato	0	—	2	53, 60
Avocado	1	22	0	—
Citrus	1	22	0	—
Totals	2		9	
<b>Others</b>				
Ivy	0	—	1	30
Lichen (Lobaria)	0	—	1	54
Totals	0		2	
<b>TOTALS</b>	<b>19</b>		<b>63</b>	

**References:**

1. Adams and O'Neill (1991). 2. Barnes and Brown (1990). 3. Barnes et al. (1990a). 4. Barnes et al. (1990b). 5. Blank et al. (1990a). 6. Blank et al. (1990b). 7. Blaschke and Weiss (1990). 8. Boutton and Flagler (1990). 9. Byres et al. (1992a,b). 10. Carter et al. (1992). 11. Chappelka et al. (1985). 12. Chappelka et al. (1988b). 13. Dean and Johnson (1992). 14. Eamus and Murray (1991). 15. Ebel et al. (1990). 16. Edwards and Kelly (1992). 17. Edwards et al. (1990b). 18. Edwards et al. (1991). 19. Edwards et al. (1992a). 20. Edwards et al. (1992b). 21. Edwards et al. (1992c). 22. Eissenstat et al. (1991b). 23. Elliott et al. (1987). 24. Führer et al. (1990). 25. Gorissen et al. (1991b). 26. Hanson et al. (1988). 27. Jensen and Patton (1990). 28. Johnston and Shriner (1986). 29. Keane and Manning (1988). 30. Kerfourn and Garrec (1992). 31. Kohut et al. (1990). 32. Kress et al. (1988). 33. Laurence et al. (1989). 34. Lee et al. (1990b). 35. Leonardi and Langebartels (1990). 36. Magel et al. (1990). 37. Norby et al. (1986). 38. Patton et al. (1991). 39. Percy et al. (1992). 40. Pier et al. (1992). 41. Qiu et al. (1992). 42. Rebbeck and Brennan (1984). 43. Reddy et al. (1991a,b). 44. Reich and Amundson (1985). 45. Reich et al. (1986b). 46. Reich et al. (1987). 47. Reich et al. (1988). 48. Roberts (1990). 49. Sasek et al. (1991). 50. Senser (1990). 51. Shafer (1988). 52. Shelburne et al. (1993). 53. Shriner and Johnson (1987). 54. Sigal and Johnston (1986). 55. Somerville et al. (1992). 56. Stroo et al. (1988). 57. Takemoto et al. (1987). 58. Takemoto et al. (1988a). 59. Takemoto et al. (1988b). 60. Takemoto et al. (1988c). 61. Takemoto et al. (1989). 62. Taylor et al. (1986). 63. Temple (1988). 64. Temple et al. (1987). 65. Temple et al. (1992). 66. Temple et al. (1993). 67. Troiano et al. (1983).

highest O<sub>3</sub> exposures (2.5 × ambient) and SAR at pH 3.3. However, there were no effects at lower O<sub>3</sub> exposure levels or at higher pHs.

A 3-year study of slash pine revealed a significant interaction on stem volume increment in each year (Dean and Johnson, 1992). This was attributed to a high rate of increase observed with increasing acidity in trees exposed to an intermediate O<sub>3</sub> level (2 × ambient). In contrast, at higher or lower O<sub>3</sub> exposures, acidity of the SAR applied had little effect. Although another study with slash pine indicated a significant interaction on photosynthetic rates, no information was provided about its nature (Byres et al., 1992b).

The mineral status (potassium, calcium, and manganese) of white pine showed antagonistic interactions between O<sub>3</sub> and SAR (Reich et al., 1988). Increased acidity nullified

the increase in foliar potassium and the decreases in root calcium caused by O<sub>3</sub>, whereas increased O<sub>3</sub> nullified the increase in root manganese that resulted from increased acidity.

Temple (1988) reported a synergistic response to O<sub>3</sub> and SAR of root growth of giant sequoia. Yellow poplar showed no interactions in one study (Table 5-11), but a greater than additive response of root growth was observed by Chappelka et al. (1985). Chappelka et al. (1988b) found that, although neither O<sub>3</sub> nor the pH of SAR caused any significant effects on growth, at intermediate O<sub>3</sub> levels, increased acidity caused significant decreases in stem and leaf biomass. Jensen and Patton (1990), on the other hand, reported significant antagonistic interactions on yellow poplar leaf and shoot growth. Based on estimates from growth models derived from experimental data, increased acidity (pH 5.5 to 3.0) of SAR reduced the decreases caused by O<sub>3</sub> by almost 50%.

Adverse effects of O<sub>3</sub> on the leaf area and shoot, leaf, and root biomass of paper birch (*Betula papyrifera*) were reversed by increased acidity of SAR (Keane and Manning, 1988). Similarly, in both avocado and lemon (*Citrus volkameriana*) trees, Eissentstat et al. (1991b) found that increased acidity offset the negative effects of O<sub>3</sub> on leaf growth.

Although there are four reports of no interactions on alfalfa, Takemoto et al. (1988b) observed significant interactions on leaf drop. In charcoal-filtered air, leaf drop increased by a factor of 6 as the pH of the fog treatment changed from 7.24 to an extremely acid pH 1.68, the lowest level recorded in the field in Southern California. In unfiltered air, in contrast, leaf drop increased only 20%.

Several studies with soybean revealed no significant interactions. However, Troiano et al. (1983) reported a 42% reduction in seed yield between CF and unfiltered air with SAR at pH 2.8 versus a 6% reduction at pH 4.0. Increased acidity thus multiplied the effect of O<sub>3</sub>, due largely to a stimulation of seed yield caused by increased acidity. Shafer (1988) observed a stimulation of shoot growth of sorghum at pH 2.5 of SAR over growth at pH 5.5, as a result of which, greater growth occurred at low O<sub>3</sub> exposure levels, although there was no effect of acidity at the highest O<sub>3</sub> level (0.3 ppm).

In summary, although the majority of studies have not demonstrated the existence of interactions between O<sub>3</sub> and SAR, where statistically significant interactions on growth or physiology have been reported, the interactions were mostly antagonistic. The only synergistic interactions reported are in two studies of yellow poplar and single studies of sequoia and shortleaf and slash pines. In most cases where significant interactions were noted, the authors have had difficulty in providing any mechanistic explanation. It appears that, although the effects may have passed normally accepted tests of statistical significance, they may nevertheless have been spurious findings. Overall, it appears that exposure to acidic precipitation is unlikely to result in significant enhancement of the adverse effects of O<sub>3</sub> in most species. In the few cases of antagonistic interactions, the suggestion was made that these may have reflected a beneficial fertilizer effect due to the nitrate and sulfate present in the SAR applied.

The preceding review has focused on interactive effects of O<sub>3</sub> and wet hydrogen ion deposition. With regard to the anionic constituents of acid deposition, studies with SAR have tended to use dilute mixtures of nitric and sulfuric acids, together with other anions and cations, to achieve the desired pH levels. However, no studies appear to have been undertaken to separate any interactive effects of the individual cations (nitrates or sulfates) from those involving hydrogen ions. However, given the limited and variable information on interactive responses of O<sub>3</sub> and nitrogen and sulfur as soil nutrients, it is not possible to

predict the nature of any possible interactions of O<sub>3</sub> with the wet deposition of these elements.

#### 5.4.6.6 Heavy Metals

Interactions of O<sub>3</sub> with several heavy metal pollutants were reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986). The limited data for pollutants such as cadmium, nickel, and zinc almost invariably showed that they enhanced the adverse effects of O<sub>3</sub>, usually additively, but occasionally more than additively. To the results with cadmium, nickel, and zinc on garden cress (*Lepidium sativum*), lettuce (*Lactuca sativa*), pea, tomato, and aspen, reviewed at that time, should be added similar findings with zinc on pinto bean (McIlveen et al., 1975); increased zinc results in significantly increased foliar injury and decreased mycorrhizal infection. However, in a study of the effects of O<sub>3</sub>, nickel, and copper on tomato, Prokipcak and Ormrod (1986) found that, as the levels of both O<sub>3</sub> and nickel increased, the interaction changed from additive to less than additive. Complex interactions were observed when the treatments included both nickel and copper.

No information appears to be available about possible interactions with lead. Although qualitatively heavy metals appear to increase plant sensitivity to O<sub>3</sub>, the limited information available precludes defining any quantitative relationships.

#### 5.4.6.7 Mixtures of Ozone with Two or More Pollutants

Pollutant-pollutant interactions are not limited to mixtures or sequences of two pollutants. Several studies have been made of interactions of O<sub>3</sub> with various combinations of SO<sub>2</sub>, NO<sub>2</sub>, and acid rain. However, in some of these investigations, no treatment with O<sub>3</sub> was included in the experimental design, and, therefore, no information was obtained on effects in response to O<sub>3</sub>. Some studies using only repeated daily exposures to high levels (>0.3 ppm) of one or more pollutants are excluded from this review.

Adaros et al. (1991b), in a field study of spring rape using open-top chambers, found no significant interactions between O<sub>3</sub> and NO<sub>2</sub> (sequential exposures) and SO<sub>2</sub> (continuous exposures). In a 2-year study on spring barley and spring wheat, some statistically significant interactions were noted, but they were scattered through the different growth measurements, cultivars, and years with no consistent pattern (Adaros et al., 1991c). Additive effects with no interactions were observed in studies of shore juniper (*Juniperus conferta*) (Fravel et al., 1984), radish (Reinert and Gray, 1981), and azalea (*Rhododendron* spp.) (Sanders and Reinert, 1982). Yang et al. (1982) reported a less than additive interaction on injury to white pine.

No significant three-way interactions were found in studies of soybean (Norby et al., 1985), yellow poplar (Chappelka et al., 1985, 1988b), or any other hardwood species (Davis and Skelly, 1992a; Jensen and Dochinger, 1989; Reich et al., 1985) exposed to O<sub>3</sub>, SO<sub>2</sub>, and SAR.

No information was collected on interactions in the few published studies involving O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>, and SAR.

The limited data make it difficult to draw any firm conclusions, but, in general, the consequences of such exposures appear to be dictated largely by the dominant individual two-way interaction.

#### 5.4.7 Interactions with Agricultural Chemicals

Agricultural chemicals are used for the control of insect pests, diseases, and weeds and for the control of growth in specialized situations, such as the selective thinning of fruit on orchard trees. The potential for some agricultural chemicals to modify plant response to O<sub>3</sub>, first noted with certain fungicides on pinto beans (Kendrick et al., 1954), led to numerous field and laboratory studies. As noted in the previous criteria document (U.S. Environmental Protection Agency, 1986), protection against O<sub>3</sub> injury was found to be conferred by applications of numerous commercial fungicides, herbicides, and growth regulators.

The available information is derived from studies involving a number of different commercial chemicals and species. No comprehensive and systematic studies have been reported, but the weight of evidence indicates that certain fungicides are consistent in providing protection. In particular, there have been numerous reports of protection conferred by applications of benomyl (benlate; methyl-1-[butylcarbamoyl]-2-benzimidazolecarbamate). In addition to the studies reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986), benomyl protection of grape (Musselman and Taschenberg, 1985) and bean cultivars (Pell, 1976; Pellisier et al., 1972) also has been reported. It is of interest to note that, although several nematocides were found to increase sensitivity of tobacco and pinto bean to O<sub>3</sub>, applications of benomyl overcame this response and conferred resistance (Miller et al., 1976). However, benomyl was found to increase the injury caused by PAN (Pell and Gardner, 1979). It also should be noted that many of the effective fungicides are carbamates and have been used as antioxidants in other applications, such as rubber formulations.

The need to distinguish between protective action against O<sub>3</sub> injury and fungicidal activity per se is shown by a study of fentin hydroxide (Du-Ter; tetraphenyltin hydroxide) on potato (Holley et al., 1985). The fungicide reduced foliar injury in the field and also the colonization of injured leaf tissue by the early blight fungus, *Alternaria solani*. However, yield increases appeared to result from the reduction of disease rather than from diminished O<sub>3</sub> injury.

The triazoles are a family of compounds with both fungicidal and plant growth regulating properties. Fletcher and Hofstra (1985) reported on the protective action of triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone], and Musselman and Taschenberg (1985) found that triadimefon and the triazole, etaconazole (1-[(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl]methyl-1H-1,2,4-triazole), were as effective as benomyl in protecting grape from oxidant injury; cultivar differences were noted, with the fungicides being more effective on Concord than on Ives foliage. Seed treatment with triazole S-3307 ([E]-1-[4-chlorophenoxy]-3,3-dimethyl-2-[1,2,4-triazol-1-yl]-1-penten-3-ol) resulted in a 50% reduction in the size of wheat plants but provided complete protection from an excessive exposure to 0.5 ppm O<sub>3</sub> for 6 h that resulted in severe necrosis on the leaves of untreated plants (Mackay et al., 1987).

A range of commercial plant growth regulating compounds was studied by Cathey and Heggstad (1972). The plant growth retardants, CBBP (Phosfon-D; 2,4-dichlorobenzyltributyl phosphonium chloride) and SADH (Alar®; succinic acid, 2,2-dimethylhydrazide) and several of its analogs, were found to be more effective than benomyl in reducing O<sub>3</sub> injury on petunia.

Conflicting reports of the effects of herbicide-O<sub>3</sub> interactions were reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986). Recent studies of

metolachlor (2-chloro-*N*-[2-ethyl-6-methylphenyl]-*N*-[2-methoxy-1-methylethyl] acetamide) (Mersie et al., 1989) and atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) (Mersie et al., 1990) revealed species-dependent effects: metolachlor sensitized corn to O<sub>3</sub> but offered protection to bean and soybean. The effects of atrazine on corn were additive to those induced by exposure to 0.2 ppm O<sub>3</sub> for 6 h/day, twice weekly, for three weeks, but antagonistic to exposures to 0.3 ppm. Mersie et al. (1990) also observed a protective action of the commercial antioxidant, *n*-propyl gallate, on corn.

In spite of reports to the contrary (Teso et al., 1979), Rebbeck and Brennan (1984) found that the insecticide, diazinon (O,O-diethyl-O-[2-isopropyl-4-methyl-6-pyrimidinyl] phosphorothioate), did not protect alfalfa from O<sub>3</sub> injury in a greenhouse study.

The knowledge of the interactions of these different types of agricultural chemicals with O<sub>3</sub> is still too fragmentary to enable any general conclusions to be drawn, other than to note the general efficacy of the carbamate fungicides. As noted in the previous criteria document (U.S. Environmental Protection Agency, 1986), it is premature to recommend their use specifically for protecting crops from the adverse effects of O<sub>3</sub>, rather than for their primary purpose.

#### **5.4.8 Factors Associated with Global Climate Change**

This section focuses solely on the ways in which features of global climate change may be expected to affect the impact of oxidants on vegetation. It is not intended to provide a comprehensive review of the issues and components of climate change per se.

The magnitudes and causes of some of the changes in features of the global climate that have been observed or are predicted to occur are currently the subject of controversy. However, there is clear evidence of increases in mean CO<sub>2</sub> levels (Keeling et al., 1989), which, together with other anthropogenic emissions of radiatively active gases, may contribute to the upward trend in mean surface-level temperatures observed over the past century (Jones, 1989) and to changes in precipitation patterns throughout the world (Diaz et al., 1989). In addition, depletion of the stratospheric O<sub>3</sub> layer in the polar regions, caused by halofluorocarbons, results in increased penetration of the atmosphere by solar ultraviolet-B (UV-B) radiation (280- to 320-nm wavelengths). However, the intensity of UV-B radiation reaching the earth's surface may be attenuated by O<sub>3</sub>-pollution in the lower troposphere (Brühl and Crutzen, 1989). Differences in the degree of this attenuation probably contribute to the discrepancies between recently observed trends in surface-level UV-B intensities (Scotto et al., 1988; Blumenthaler and Ambach, 1990).

Independent of any effects of ambient temperature, CO<sub>2</sub> level affects plant-water relations through effects on stomatal aperture and conductance, leading to effects on leaf and canopy temperature and the uptake of gaseous pollutants. The effects of UV-B on numerous growth processes have been reviewed by Tevini and Teramura (1989) and Runeckles and Krupa (1994). Individual interactive effects of O<sub>3</sub> and several effects of global climate change have been reviewed in the previous sections. However, it is important to recognize that, because of the interactions among the different components of climate change themselves, a holistic approach is essential, which includes the potential of interactions for modifying plant response to oxidants. Overall reviews of the interactions involving the factors of climate change and O<sub>3</sub> have been presented by Krupa and Kickert (1989) and Ashmore and Bell (1991).

The effect of increased CO<sub>2</sub> in stimulating photosynthetic rates also may lead to increased leaf area, biomass, and yield (Allen, 1990). Increased CO<sub>2</sub> also leads to stomatal closure. However, with regard to water use, the result of decreased stomatal conductance in reducing transpiration is offset partly by the increase in leaf and canopy temperature, resulting from reduced evaporative cooling, and the increase in leaf area. The net result is that increased CO<sub>2</sub> may lead to only slight increases in water-use efficiency, which are attributable more to increased photosynthetic activity than to reduced transpiration (Allen, 1990). On the other hand, because the primary route of entry into the leaf of a gaseous pollutant such as O<sub>3</sub> is through the stomata, increased CO<sub>2</sub> levels would be expected to decrease the impact of O<sub>3</sub> by reducing uptake as a consequence of reduced stomatal conductance. The effects of increasing CO<sub>2</sub> levels discussed above relate to plants with the C<sub>3</sub> pathway of carbon fixation. These include the following major broad-leaved crops: wheat, rice (*Oryza sativa*), legumes, potato, and cole crops. Plants with the C<sub>4</sub> pathway tend to have greater water-use efficiencies (WUEs) than C<sub>3</sub> plants, but show less response to increased CO<sub>2</sub> levels. Major C<sub>4</sub> crops are corn and sorghum. However, no studies appear to have been conducted on O<sub>3</sub>/CO<sub>2</sub> interactions in C<sub>4</sub> species.

Allen (1990) provides a simulation of the effect of doubling the average ambient CO<sub>2</sub> level from 340 to 680 ppm on soybean yield, based on the Weibull response model to O<sub>3</sub> and SO<sub>2</sub> of Heagle et al. (1983b) and the model of stomatal conductance developed for soybean by Rogers et al. (1983):

$$g_s = 0.0485 - 7.00 \times 10^{-5}[\text{CO}_2] + 3.40 \times 10^{-8}[\text{CO}_2]^2,$$

where  $g_s$  is stomatal conductance (in meters per second), and  $[\text{CO}_2]$  is CO<sub>2</sub> concentration (in parts per million). According to this model, a doubling of the CO<sub>2</sub> level would reduce  $g_s$  by a factor of 0.69, effectively reducing the O<sub>3</sub> and SO<sub>2</sub> concentrations to 0.038 and 0.018 ppm, respectively. At the current 340 ppm CO<sub>2</sub> level, the Weibull model predicts a yield of 340.5 g/m of row. Reduced pollutant entry at 680 ppm CO<sub>2</sub> gives a predicted yield of 390.6 g/m of row, an increase of 14.7%. This is a conservative estimate because it ignores the direct effect of the increased CO<sub>2</sub> level on soybean growth.

Although the calculation makes numerous assumptions, it is supported qualitatively by evidence from the few studies published to date on CO<sub>2</sub>/O<sub>3</sub> interactions. Barnes and Pfirrmann (1992) reported that an increased CO<sub>2</sub> level of 765 ppm countered the adverse effects of O<sub>3</sub> on photosynthesis, shoot growth rate, leaf area, and water-use efficiency of radish. Protection against the adverse effects of O<sub>3</sub> on soybean by elevated CO<sub>2</sub> also was reported by Kramer et al. (1991). The yield loss due to O<sub>3</sub> at ambient CO<sub>2</sub> was 11.9%, whereas, in the presence of ambient + 150 ppm CO<sub>2</sub>, the loss was only 6.7%.

Although these studies support the prediction of Allen (1990), they were conducted in growth chambers (Barnes and Pfirrmann, 1992) or OTCs (Kramer et al., 1991; Mulchi et al., 1992), as were the studies on which Allen's model was based. Hence, the plants would not have been subjected to the environmental conditions typical of the open field, particularly with respect to wind speed and its effects on transpiration and temperature. Nevertheless, these studies support the view that increased CO<sub>2</sub> levels will reduce adverse effects of O<sub>3</sub> on crops.

It is unclear as to whether such CO<sub>2</sub>-induced reductions of the impact of O<sub>3</sub> also apply to the long-term growth of trees, and it is equally unclear as to how increased CO<sub>2</sub> will affect the impact of O<sub>3</sub> on ecosystems. These uncertainties arise because of the numerous

compensatory feedback mechanisms that play important roles in both long-term perennial growth and in the behavior of ecosystems. Such feedback includes changing demands for nutrients, increased leaf area and potential water loss, and changes in litter quality and quantity. For example, in terms of the effects of increased CO<sub>2</sub> alone, long-term studies of several species suggest that, although photosynthesis may be demonstrably stimulated, there may be little or no net response at the ecosystem level (Bazzaz, 1990).

The consequences of global warming as a feature of climate change are difficult to assess because, as discussed in Section 5.4.4, the information on the effects of temperature on O<sub>3</sub>-response is conflicting. However, as Ashmore and Bell (1991) point out, concerns over the effects of O<sub>3</sub> on sensitivity to freezing temperatures will become increasingly unimportant as warming occurs.

Various models of climate change scenarios have indicated that changed precipitation patterns will lead to increased drought in some mid-latitude regions of the world. The bulk of the evidence reviewed in Section 5.4.4 suggests that this would reduce the impact of O<sub>3</sub>. However, because of the major direct impact of drought per se, such protection would be of little practical significance.

Greater certainty surrounds the likelihood that global warming will increase the incidence and severity of losses caused by pests and diseases. Concurrent increases also may favor the competitiveness of many weed species. At present, it is not possible to quantify such changes or to determine how they would influence the interactions discussed in Section 5.4.3.

With regard to possible interactions of O<sub>3</sub> and UV-B, Runeckles and Krupa (1994) point out that, because of the episodic nature of O<sub>3</sub> pollution, including its typical diurnal pattern, surface-level exposures to UV-B also will be episodic. They have described various possible O<sub>3</sub>/UV-B scenarios that need to be considered. With low surface-O<sub>3</sub> levels and increased UV-B irradiation due to stratospheric O<sub>3</sub> depletion, effects of UV-B will predominate. On the other hand, elevated surface-O<sub>3</sub> levels will cause increased attenuation of UV-B resulting in reduced surface intensities. With no stratospheric O<sub>3</sub> depletion, this condition implies that surface effects of O<sub>3</sub> will predominate over the effects of UV-B; with stratospheric O<sub>3</sub> depletion, the resulting surface level irradiation will be dependent on the concentration and thickness of the surface O<sub>3</sub> layer, and both O<sub>3</sub> and UV-B effects may occur.

To date, there have been no experiments conducted specifically to simulate these different scenarios. However, Miller et al. (1994) exposed soybean in field OTCs, within which lamps were suspended to provide increased intensities of UV-B. The O<sub>3</sub> treatments were ambient and 1.5 × ambient. No significant O<sub>3</sub>/UV-B interactions were noted; the effects on growth were solely attributable to the O<sub>3</sub> exposure. However, increased UV-B irradiation resulted in increases in the foliar content of UV-absorbing constituents. In contrast, Miller and Pursley (1990) reported that a preliminary experiment revealed a less than additive interaction of O<sub>3</sub> and UV-B on soybean growth.

It is clear overall that the effects of O<sub>3</sub> on vegetation will be modified to some degree by various components of the complex mix of factors that constitute climate change. Considerably more research will need to be undertaken before quantitative assessments of the magnitudes of the changes will be possible.

#### **5.4.9 Summary—Environmental Factors**

Since the previous criteria document (U.S. Environmental Protection Agency, 1986), additional studies have been published on a wide range of biological, physical, and chemical factors in the environment that interact with plant response to O<sub>3</sub>.

Biological components of the environment of individual plants include pests, pathogens, and plants of the same or other species in competition. With regard to insect pests, although only a very limited number of plant-insect systems have been studied, there is a general trend in the observations that suggests that some pests have a preference for and grow better when feeding on plants that have been impacted by O<sub>3</sub>. Unfortunately, because there is no knowledge of how the vast majority of plant-insect systems will be affected by O<sub>3</sub>, it is not possible to offer any quantitative overall assessment of the consequences of such interactions on the growth of crops and natural vegetation. At best, there is a reasonable likelihood that some insect pest problems will increase as a result of increased ambient O<sub>3</sub> levels, but there is no evidence to suggest that O<sub>3</sub> may trigger pest outbreaks.

Plant-pathogen systems also are affected by O<sub>3</sub>, but, here too, the available evidence is far from representative of the wide spectrum of plant diseases. Nevertheless, the suggestion of Dowding (1988) that diseases caused by obligate pathogens tend to be diminished by O<sub>3</sub>, whereas those caused by facultative pathogens tend to be favored, generally is supported by the limited evidence available. In terms of its broader implications, this suggests that continued exposure to O<sub>3</sub> may lead to a change in the overall pattern of the incidence and severity of specific plant diseases affecting crops and forest trees. However, it is not possible, with the limited evidence currently available, to predict whether the net consequences of O<sub>3</sub> exposure would be more or less harmful.

A major level of uncertainty concerns the effects of O<sub>3</sub> at the population and community levels within natural ecosystems. Very few studies have been conducted on multi-species systems, and Woodward (1992) has pointed out the hazards of attempting to extrapolate from responses of the individual plant to responses of a population of such plants. This is borne out by the observations of Evans and Ashmore (1992) who showed that the behavior to O<sub>3</sub>-exposure of a species growing in mixture with other species is not predictable from its behavior when grown in isolation. This has serious implications with regard to complex natural ecosystems and identifies a serious gap in the knowledge of the effects of O<sub>3</sub> that can be filled only by a substantial research effort.

With regard to the physical environment, the combination of light, temperature, air turbulence, and water availability largely determines the success of plant growth because of the influence of these factors on the processes of photosynthesis, respiration, and transpiration. Air turbulence plays an important role in O<sub>3</sub> uptake because it determines the amount of O<sub>3</sub> to which a plant is exposed, as well as when exposure will occur. For agricultural crops, perhaps the most important of these potential interactions with O<sub>3</sub> concerns water availability and use. There is consistent evidence that drought conditions tend to reduce the direct adverse effects of O<sub>3</sub> on growth and yield. Conversely, the ready availability of soil water tends to increase the susceptibility of plants to O<sub>3</sub> injury. However, a lack of water should not be viewed as a potentially protective condition, because of the adverse effects of drought per se. The combination of drought conditions and exposure to O<sub>3</sub> is likely to result in adverse effects on growth and yield that are largely the result of lack of water. However, with perennial trees, there is evidence that prolonged exposures to O<sub>3</sub> may lead to greater water use efficiency, which would enable such trees to be better able to survive drought conditions.



In contrast with crop species, with tree species, the relative roles of light, temperature, and water are shifted somewhat because of the differences in plant form. In particular, the photosynthetic function of the leaves is carried out by a much smaller proportion of the plant's biomass. Conversely, a larger demand is placed on temperature-dependent respiratory processes to maintain and support the tissues of the stem and root systems. In addition, in temperate regions, the perennial habit brings with it the requirement for storage of carbohydrates and other reserves, in order to permit survival during the winter season and to facilitate renewed spring growth. Hence, with tree species it becomes important to distinguish between the immediate effects of exposure to  $O_3$  and the longer term consequences of these effects.

Of particular importance in northern latitudes and at higher elevations is the demonstrated role of  $O_3$  in adversely affecting cold hardiness by reducing carbohydrate storage. Independent of effects on winter hardiness, there is also evidence to indicate that adverse effects on storage also may be a component of changes in growth occurring in subsequent seasons (Hogsett et al., 1989; Andersen et al., 1991; Sasek et al., 1991). However, it is not yet possible to assemble these observations into a general quantitative model.

The plant's environment also contains numerous chemical components, ranging from soil nutrients and other air pollutants to agricultural chemicals used for pest, disease, and weed control. With regards to plant nutrients and their influence on plant response to  $O_3$ , the available evidence is highly fragmentary and frequently contradictory and, hence, does not permit the drawing of any general conclusions. A large number of studies have been conducted on the effects of  $O_3$  in conjunction with other gaseous air pollutants such as  $SO_2$  and  $NO_2$ , although the information obtained in several of the studies is of no more than academic interest because of the unrealistic exposure conditions used. Although there is clear evidence to show that  $O_3$  and  $SO_2$  may act synergistically in increasing foliar injury in some species, the available evidence indicates that this type of response is not universal. Several empirical models of the  $O_3$ - $SO_2$  interaction have been developed, but they have little in common and are highly specific to the crop and exposure conditions used. Furthermore, the frequently observed lack of interaction implies that in many cases the impact of  $O_3$  is probably best assessed on its own. The same is true of the situation with regard to combinations of  $O_3$  and acid rain or acid fog and of  $O_3$  and  $NO_2$ .

Numerous agricultural chemicals have been found to influence the responses of plants to  $O_3$ . In particular, several fungicides have been shown to provide protection against visible injury, although none has been adopted for commercial application for this purpose. On the other hand, the experimental chemical EDU has been found consistently to provide protection of a wide range of species, both in the laboratory and in the field.

Because increased tropospheric  $O_3$  is a component of global climate change, results from studies on the interactions of  $O_3$  with increased levels of  $CO_2$  and UV-B radiation are beginning to appear. Initial work with  $CO_2$  suggests that increased  $CO_2$  levels may ameliorate the effects of  $O_3$ . However, it is too soon to be able to generalize on the outcome of this interaction. At the present time, no investigations of the compound interactions involving  $O_3$ ,  $CO_2$ , UV-B, increased temperature, and changed soil-moisture status have been reported.

In conclusion, in spite of the amount of work carried out on the interactions of  $O_3$  with environmental factors, there exists only a very fragmented understanding from which to draw conclusions. This is probably inevitable in view of the vast scope of the possible

interactions between  $O_3$  and all the other environmental variables. It is also a result of the fact that most of the published work consists of studies resulting from personal interests of the investigators, rather than from coordinated programs of research that focus on systematic investigations. The consequence is that, although information has been reported about magnitudes of many interactions of  $O_3$  with environmental variables (or the lack thereof), the fragmented and nonsystematic nature of the information prevents the drawing of general conclusions and of defensible estimates of the uncertainties associated with these interactions.

## **5.5 Effects-Based Air Quality Exposure Indices**

### **5.5.1 Introduction**

#### **5.5.1.1 Biological Support for Identifying Relevant Exposure Indices**

The effects of  $O_3$  on individual plants and the factors that modify plant response to  $O_3$  are complex and vary with species, environmental conditions, and soil and nutrient conditions. Because of the complex effect of  $O_3$  and its interactions with physical and genetic factors that influence response, the development of exposure indices to characterize plant exposure and to quantify the relationship between  $O_3$  exposure and ensuing plant response has been, and continues to be, a major problem. At best, experimental evidence of the effect of  $O_3$  on biomass production can refine the knowledge of those factors of  $O_3$  exposure that affect the ability to predict plant response using exposure indices. The impacts of measured  $O_3$  concentrations on plant response are discussed and evaluated to determine the key factors of exposure that account for the variations in plant response and, if possible, to develop measures of pollutant exposure that relate well with plant response.

Considerable evidence of the primary mode of action of  $O_3$  on plants (e.g., injury to proteins and membranes, reduction in photosynthesis, changes in allocation of carbohydrate, early senescence), which eventually impacts biomass production, identifies  $O_3$  uptake as the measurement of plant exposure (Section 5.3). Ozone uptake is controlled by canopy and stomatal conductance and by ambient  $O_3$  outside the leaf (see Figure 5-3). Any factor that will affect stomatal conductance (e.g., light, temperature, humidity, soil and atmospheric chemistry, air turbulence, nutrients, time of day, phenology, biological agents) will affect  $O_3$  uptake and, consequently, plant response (i.e., yield or biomass). Biochemical mechanisms describe the mode of action of  $O_3$  on plants as the culmination of a series of physical, biochemical, and physiological events leading to alterations in plant metabolism. Ozone-induced injury is cumulative, resulting in net reductions in photosynthesis, changes in allocation of carbohydrate, and early senescence, which ultimately lead to reductions in biomass production. In most cases, increasing the duration of exposure increases the effect of  $O_3$  on plant response. Peak concentrations, when they occur during daylight (when stomatal conductance is high), can have more influence in determining the impact of  $O_3$  on plant response than lower concentrations or night concentrations because of a greater likelihood of intracellular impairment.

From a toxicological perspective, duration and peak concentrations above some level have value in determining plant response but interact with other factors such as respite time, temporal variation, phenology, canopy structure, physiological processes, environmental conditions, and soil and nutrient conditions in different fashions, depending on species. Effects occur on vegetation when the amount of pollutant absorbed exceeds the ability of the plant to detoxify  $O_3$  or to repair the initial impact (Tingey and Taylor, 1982).

Although O<sub>3</sub> uptake integrates the above factors with atmospheric conditions and relates well with plant response, it is difficult to measure. Several empirical models to predict stomatal conductance have been developed for particular species (Lösch and Tenhunen, 1981) but have not been used to estimate O<sub>3</sub> uptake or to develop exposure indices. Based on atmospheric measurements of deposition and diurnal patterns of O<sub>3</sub> and gas exchange in a natural grassland ecosystem, Grünhage and Jäger (1994a,b) and Grünhage et al. (1993a,b) proposed an ambient O<sub>3</sub> exposure potential for characterizing O<sub>3</sub> uptake and related it to the damaged-leaf area (DLA) of leaf No. 4 of Bel W3 tobacco (Grünhage et al., 1993a,b).

### 5.5.1.2 Historical Perspective on Developing Exposure Indices

For almost 70 years, air pollution specialists have explored alternative mathematical approaches for summarizing ambient air quality information in biologically meaningful forms that can serve as surrogates for dose for vegetation effects purposes. Some of the indices introduced have attempted to incorporate some of the factors (directly or indirectly) described above. Recognizing the importance of duration and peak concentrations in conjunction with stomatal conductance, the optimum exposure index can be written as

$$\text{Index} = \sum_{i=1}^n w_i \times f(C_i), \quad (5-1)$$

where  $C_i$  is the hourly mean concentration,  $f(C_i)$  is some function of  $C_i$ , and  $w_i$  is some weighting scheme that relates ambient condition and internal O<sub>3</sub> flux. The optimal weights are difficult to develop because of the complex relationship among exposure, environmental condition, and species.

Equation 5-1 represents a taxonomy of exposure indices that have been proposed as surrogates of dose in the literature. The exposure indices differ in the ways in which the values are assigned to  $w_i$ . Based on the weighting function, the exposure indices can be arranged into the categories described below (description from Lee et al., 1989).

- One Event:  $w_i = 0$  for all  $C_i$ , except for the few concentrations where  $w_i = 1$ . Examples of such indices are the second highest daily maximum 1-h concentration (2HDM), the maximum of 7-h (P7) and 1-h (P1) maximum daily averages, and the 90th or higher percentiles of hourly distribution.
- Mean:  $w_i = 0$  for all  $C_i$  outside the period of interest (P) and  $w_i = v_i / \sum_{i=1}^n v_i$  for all  $C_i$  inside the period P, where  $v_i$  is a function of  $C_i$  or some environmental variable. Examples are the seasonal mean of 7-h daily means (M7) (Heagle et al., 1979b); the effective mean ( $m_e$ ), where  $m_e^v$  is the index in Equation 5-1 with  $f(C_i) = C_i^{-1/v}$  and  $w_i = 1$  for some parameter  $v$  (Larsen and Heck, 1984); the solar-weighted mean where  $v_i$  is the hourly solar radiation value (Rawlings et al., 1988b).
- Cumulative:  $w_i = 1$  for all  $C_i$ . An example is the seasonal sum of all hourly concentrations (i.e., total exposure, denoted as SUM00).
- Concentration Weighting:  $w_i = g(C_i)$  where  $g()$  is a monotonically nondecreasing function. Examples are the seasonal sum of hourly concentrations at or above a threshold level such as 0.06 ppm (SUM06) or 0.08 ppm (SUM08); the seasonal sum of the difference between an hourly concentration above a threshold level, less the threshold value, such as 0.08 ppm (AOT08); the total impact with  $w_i = C_i^{(-1-1/v)}$  for some  $v$  (Larsen et al.,

1983); the index with the allometric function,  $g(C_i) = C_i^a$ ,  $a > 0$ ; the index with sigmoidal weighting function,  $g(C_i) = 1/[1 + M \times \exp(-Ax_i)]$ , where  $M = 4,403$  and  $A = 126$ , denoted as W126 by Lefohn et al. (1988a), and  $M = 500$  and  $A = 100$ , denoted SIGMOID by Lee et al. (1989); total hours with concentrations at or above a threshold level, such as 0.08 ppm (HRS08),  $g(C_i) = 0$  for  $C_i < 0.08$  ppm and  $w_i = 1/C_i$  for  $C_i \geq 0.08$  ppm.

- Multicomponent:  $w_i = g(C_i, i)$ . Examples are indices that incorporate several characteristics of exposure and crop development stage, including the phenologically weighted cumulative impact indices (Lee et al., 1987).

Oshima (1975) and Oshima et al. (1976) proposed an exposure index, where the difference between the value above 0.10 and 0.10 ppm was summed. This is referred to as the AOT10 exposure index with  $f(C_i) = C_i - 0.10$  and  $w_i = 0$  for  $C_i < 0.10$  ppm and  $w_i = 1$  for  $C_i \geq 0.10$  ppm in Equation 5-1. Alternatively, Lefohn and Benedict (1982) introduced an exposure index based on the hypothesis that, if the higher  $O_3$  concentrations had greater value in predicting adverse effects on agricultural crops than did the lower values, then the higher hourly mean concentrations should be given more weight than the lower values. This index summed all hourly concentrations equal to and above a 0.10-ppm threshold level. This index is referred to as the SUM10 exposure index, with  $f(C_i) = C_i$  and  $w_i = 0$  for  $C_i < 0.10$  ppm and  $w_i = 1$  for  $C_i \geq 0.10$  ppm. The SUM indices are not concentration weighting but threshold weighting, in that all concentrations at or above a threshold level have equal weight rather than increasing weight to higher concentrations.

A 6-h, long-term, seasonal mean,  $O_3$  exposure index was used by Heagle et al. (1974). Also, Heagle et al. (1979b) reported the use of a 7-h experimental period mean. The 7-h (0900 to 1559 hours) mean, calculated over an experimental period, was adopted as the statistic of choice by the U.S. Environmental Protection Agency's (EPA's) NCLAN program (Heck et al., 1982). The 7-h daily daylight period was selected by NCLAN because the index was believed to correspond to the period of greatest plant susceptibility to  $O_3$  pollution. In addition, the 7-h period of each day (0900 to 1559 hours) was assumed to correspond to the time that the highest hourly  $O_3$  concentrations would occur. However, not all monitoring sites in the United States experience their highest  $O_3$  exposures within the 0900 to 1559 hours 7-h time period (Lefohn and Jones, 1986; Lefohn and Irving, 1988; Logan, 1989). Toward the end of the program, NCLAN redesigned its experimental protocol and applied proportional additions of  $O_3$  to its crops for 12-h periods. The expanded 12-h window reflected NCLAN's desire to capture more of the daily  $O_3$  exposure. In the published literature, the majority of NCLAN's experiments were summarized using the 7-h experimental-period average.

Based on the concept that higher concentrations of  $O_3$  should be given more weight than lower concentrations (summarized in U.S. Environmental Protection Agency, 1986), concerns about the use of a long-term average to summarize exposures of  $O_3$  began appearing in the literature (Lefohn and Benedict, 1982; Tingey, 1984; Lefohn, 1984; Lefohn and Tingey, 1985; Smith et al., 1987). Specific concerns were focused on the fact that the use of a long-term average failed to consider the impact of peak concentrations. The 7-h seasonal mean contained all hourly concentrations between 0900 to 1559 hours; this long-term average treated all concentrations within the fixed window in a similar manner. A large number of hourly distributions within the 0900- to 1559-hours window could be used to generate the same 7-h seasonal mean, ranging from those containing many peaks to those containing none. Larsen and Heck (1984) pointed out that it was possible for two air

sampling sites with the same daytime arithmetic mean O<sub>3</sub> concentration to experience different estimated crop reductions.

In the late 1980s, the focus of attention turned from the use of long-term seasonal means to cumulative indices (i.e., exposure indices that sum the products of concentrations multiplied by time over an exposure period). As indicated previously, the cumulative index parameters proposed by Oshima (1975) and Lefohn and Benedict (1982) were similar. Both parameters gave equal weight to the higher hourly concentrations but ignored the concentrations below a subjectively defined minimum threshold (e.g., 0.10 ppm). Besides the cumulative indices proposed by Oshima (1975), Oshima et al. (1976), and Lefohn and Benedict (1982), other cumulative indices were suggested, including the number of occurrences of daily maximum hourly averaged concentrations greater than a threshold level (Ashmore, 1984) and the use of exponential functions (Nouchi and Aoki, 1979; Larsen and Heck, 1984) to assign unequal weighting to O<sub>3</sub> concentrations.

A possible disadvantage of applying an integrated exposure index, as defined by Oshima (1975) and Lefohn and Benedict (1982), is that the use of an artificial threshold concentration as a cutoff point eliminates any possible contribution of the lower concentrations to vegetation effects. Although this disadvantage may not be important when considering O<sub>3</sub> exposures that occur in the California South Coast Air Basin, where repeated high concentrations are experienced from day to day, and there are relatively short periods between episodes, it is important when assessing the typical exposures experienced in other parts of the United States.

Recognizing the disadvantage, Lefohn and Runeckles (1987) suggested a modification to the Lefohn and Benedict (1982) exposure index by weighting individual hourly mean concentrations of O<sub>3</sub> and summing over time. Lefohn and Runeckles (1987) proposed a sigmoidal weighting function that was used in developing a cumulative integrated exposure index. The index included the lower concentrations in the integrated exposure summation.

None of the exposure indices mentioned above fully characterize the potential for plant uptake of O<sub>3</sub> because the indices, being measures of ambient condition, ignore the biological processes controlling the transfer of O<sub>3</sub> from the atmosphere through the leaf and into the leaf interior (U.S. Environmental Protection Agency, 1986, 1992). Early studies with beans and tobacco, reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1986), showed that short-term, higher peak exposures induced more visible injury than longer term, lower peak exposures of the same total exposure, indicating that concentration has more value than exposure duration in eliciting a response, at least for short-lived species. Other studies with soybean, tobacco, and bean, conducted prior to 1983 and described in U.S. Environmental Protection Agency (1986), showed that the foliar injury response to subsequent peak exposures varies with temporal pattern. Predisposition to low levels of O<sub>3</sub> for a few days increases plant sensitivity to subsequent peaks (Johnston and Heagle, 1982; Heagle and Heck, 1974; Runeckles and Rosen, 1977). Tobacco plants exposed to 2 consecutive days of peak exposures showed greater injury on the first day (Mukammal, 1965). Plants exposed to a series of successive short exposures suffered more injury than did those plants that received a continuous uniform exposure, with all plants receiving equal total exposure (Stan and Schicker, 1982).

When yield or growth are considered, "not only are concentration and time important, but the dynamics of the O<sub>3</sub> exposure are also important" (U.S. Environmental Protection Agency, 1986). Musselman et al. (1983) were the first to demonstrate that plants

exposed to variable concentrations showed greater effect on plant growth than those exposed to a fixed or daily peak concentration of equal total exposure but lower peak concentrations. The Hogsett et al. (1985b) study also reported a greater effect on plant growth of variable concentrations; however, no plant response data is presented in the paper. Musselman et al. (1986b), in a subsequent experiment, exposed kidney bean plants to either a simulated ambient or a uniform concentration that had equal total exposure and peak concentration (at two levels of 0.30 and 0.40 ppm) and found that the effects of the two distributions did not differ significantly. Consequently, when peak concentrations and total exposures are equal, the diurnal distribution of concentrations appears to be unimportant.

More recent studies with bean (Kohut et al., 1988b), soybean (Heagle et al., 1986b), and tobacco (Heagle et al., 1987b) (reviewed in U.S. Environmental Protection Agency, 1992) showed conflicting evidence of no significant differences in response to different exposure patterns of equal total exposure but varying peak concentrations. The value of peak concentrations in influencing response was inconclusive. For the study with beans, plants exposed to peak exposures showed significant impairment in the early harvests, but, at the final harvest, O<sub>3</sub> effects on growth and yield were not statistically significant. For the NCLAN studies with soybean and tobacco, differences in yield between the constant and proportional 7-h O<sub>3</sub>-addition exposures were not significant, even though the proportional-addition treatments had greater peak concentrations. In reanalysis of the soybean and tobacco studies, Rawlings et al. (1988b) stated that the differences between the constant and proportional O<sub>3</sub> additions were relatively small, thus limiting the power of the comparison test. However, 12-h exposures caused greater effects than 7-h exposures, but the decrease in yield loss was not directly proportional to the increased length of exposure (Rawlings et al., 1988b).

Considerable research since the publication of the previous criteria document (U.S. Environmental Protection Agency, 1986) has been directed at developing measures of exposure that were consistent with then-current knowledge of the mode of action of O<sub>3</sub> on plants, as well as on factors such as concentration, duration, and temporal dynamics of exposure influencing response. A number of retrospective studies of existing data to evaluate and compare exposure indices based on statistical fit (Rawlings et al., 1988b; Adomait et al., 1987; Cure et al., 1986; McCool et al., 1986, 1987; Smith et al., 1987; Lee et al., 1987, 1988; Lefohn et al., 1988a; Tingey et al., 1989; Musselman et al., 1988) have been summarized in the literature between 1986 and 1988 and reviewed by the U.S. Environmental Protection Agency (1992). Studies using O<sub>3</sub> exposures in chambers suggest the following conclusions: O<sub>3</sub> effects are cumulative, peak concentrations may be more important than lower concentrations in eliciting a response, and plant sensitivity to O<sub>3</sub> varies with time of day and crop development stage. Exposure indices that cumulate the exposure and preferentially weight the peaks yield better statistical fits to response than do the mean and peak indices.

Because the mean exposure index treats all concentrations equally and does not specifically include an exposure duration component, the use of a mean exposure index for characterizing plant exposures appears to be inappropriate for relating exposure with vegetation effects (U.S. Environmental Protection Agency, 1992). In particular, the weighting of the hourly O<sub>3</sub> concentrations of the mean is inconsistent with the weighting function of plant exposure to O<sub>3</sub> in Equation 5-1, which attempts to relate O<sub>3</sub> flux to ambient condition. The total exposure index includes an exposure duration component but does not adequately relate pollutant exposure with plant response because the index weights all concentrations equally and focuses on the lower concentrations.

Evidence supporting the use of peak-weighted, cumulative indices in relating O<sub>3</sub> exposure and plant response is based on statistical reanalyses of NCLAN data. However, it is unlikely that the empirical modeling of plant response will determine the optimal weighting function of hourly O<sub>3</sub> concentrations for use in characterizing plant exposure, which varies with environmental factors and species. The development and comparison of exposure indices based on statistical fits is difficult because only a limited number of experiments have been designed specifically to test and evaluate the various exposure indices.

Although much research has been conducted on O<sub>3</sub> effects on crops and trees since 1988, the overall understanding of the mode of action of O<sub>3</sub> on plants and factors that modify plant response remains unchanged since the previous criteria document (U.S. Environmental Protection Agency, 1986) and its supplement (U.S. Environmental Protection Agency, 1992). Additional studies further support the value of concentration, duration, and temporal pattern of exposure in describing plant exposure and its relation to plant response. Studies that applied two or more different exposure patterns of equal exposure but possibly different peak concentrations are reviewed in Section 5.5.2.2 to substantiate the value of exposure structure in influencing the magnitude of plant response. Recent papers that report results from replicate studies over time and space are summarized in Section 5.5.2.3 to test the value of duration and its relation to plant response. In addition, a few recent studies that provide additional insight to those factors that modify plant response are reviewed in Sections 5.5.2.4 and 5.5.2.5.

## **5.5.2 Developing Exposure Indices**

### **5.5.2.1 Experimental Design and Statistical Analysis**

Controlled and field exposure-response studies, where extraneous factors influencing response are controlled or monitored, allow the study of concentration, duration, respite time, and temporal fluctuations at various stages of crop development in influencing response. These studies provide insight on the efficacy of exposure indices in explaining variation of response. A small number of experiments have been designed specifically to study the components of exposure and have applied two or more different patterns of exposure that measure the same SUM00 values. These designs provide the best evidence to determine whether plants respond differentially to temporal variations in O<sub>3</sub> concentrations; however, they may have limited application in developing a statistical relationship between O<sub>3</sub> exposure and plant response. Other design considerations, including the number, kind, and levels of O<sub>3</sub> exposure; the patterns of randomization; the number of replicates used in the experiment; and experimental protocol, determine the strength of the statistical analysis that is applied to the treatment mean comparison tests and the range of ambient and environmental conditions over which generalizations may be made. These designs have been used successfully to test the value of components of exposure, particularly concentration, in influencing response (Musselman et al., 1983, 1986b, 1994; Hogsett et al., 1985b). Different approaches that include either a mean separation procedure or a regression procedure have been used to identify those important components of exposure that influence response.

To identify the importance of exposure in contributing to variation of plant response, the majority of pollutant effects studies use regression-based designs that apply a single pattern of exposure at varying concentration levels. However, if these designs are used, the application of the results is limited; plant response (i.e., plant yield) with respect to exposure is unchanged with different measures of exposure. The relative position and spacing

between exposure levels is a function of how the exposure index weights the hourly O<sub>3</sub> concentrations and governs the statistical fit to response. The regression approach has been used to compare and evaluate various exposure indices, but the ability to discriminate among indices is low for these studies. By their nature, those studies that have used regression-based designs that utilize data from single patterns of exposure cannot distinguish between mean exposure indices and sums constructed from means (i.e., mean  $\times$  duration) and, consequently, cannot be used to test the value of duration in explaining the variation of response.

Evidence to substantiate the value of duration in explaining the experimental variation of plant response may be obtained when combining data from replicate studies of the same species and cultivar over time and space. Pooling of data from replicate studies of the same species to evaluate duration effects and to compare various exposure indices assumes that the primary cause of biological response is pollutant exposure. This assumption may or may not be valid, particularly when plants from replicate studies are grown under varying environmental, edaphic, and agronomic conditions that tend to mask the treatment effects during the growth of the plant (Section 5.3). Hence, it is more difficult to substantiate the importance of exposure-dynamic factors from retrospective analyses of combined data from replicate studies of the same species than from experiments designed specifically to address the components of exposure. The comparison of environmental conditions, as well as the yields of plants exposed to CF air over replicate studies, is a simple check of interaction but does not ensure that O<sub>3</sub> effects on response can be isolated. In addition, when the main effect of O<sub>3</sub> is insignificant, the data may be limited for determining the value of duration or other components of exposure in predicting response. Nonetheless, if an air pollutant is the primary source of variability in plant response, the relationship between exposure and response should be consistent when data sets for the same crop are combined over several years or locations.

Sets of replicate studies of equal and varying duration are readily available in the published literature, but only a few reports have combined the data to test specifically the value of duration in explaining variation of plant response or to evaluate exposure indices based on statistical fit. Lefohn et al. (1988a) were the first to fit a common response model to combined data from two replicate studies of varying duration using various exposure indices. Greater yield losses occurred when plants were exposed for the longer duration, indicating that the duration component of exposure was important in influencing response, and that a cumulative-type index was able to describe adequately the relationship between exposure and yield. More recent papers have reported results of the 2 years of replicate studies, and a few papers have used the regression approach, with and without variance components for sites and years, to evaluate various exposure indices based on the adequacy of fit of a common response model.

A number of the papers relevant to the study of components of exposure influencing plant response report only the mean and total exposure (SUM00) indices. Because exposure indices weight hourly O<sub>3</sub> concentrations differently, it is almost impossible to convert one index to another. The original data, which in many cases are not available, would be necessary to generate alternative exposure indices. Therefore, unless adequate information is given to allow calculation of exposure indices, the analysis of reported results from individual and combined data to evaluate different exposure indices is not possible, although it may be possible to perform retrospective evaluation of the structure of exposure in altering plant response.



Another concern relates to the experimental design, particularly the number, kind, and levels of exposure used in the study. Generalization of experimental results is largely dependent on the degree to which atmospheric and biospheric conditions mimic those of the target population when growing under ambient conditions. However desirable the need to mimic the real world, understanding the relationship between exposure and the ensuing response (i.e., plant yield) and identifying those components of exposure that influence response may require the use of exposure regimes with temporal pattern, concentration, or structure that are not observed in nature. Such data requires the comparison of exposure levels between CF and near-NF conditions, but the mathematician who attempts to model an experiment requires higher than NF levels of O<sub>3</sub> to better determine the nature of plant response to O<sub>3</sub>. A discussion of the advantages and disadvantages of OTCs and the types of NCLAN exposures is discussed in the section on methodologies (Section 5.2.1.1). The O<sub>3</sub> exposures utilized by the NCLAN program have been described as producing artificial regimes that do not mimic actual conditions.

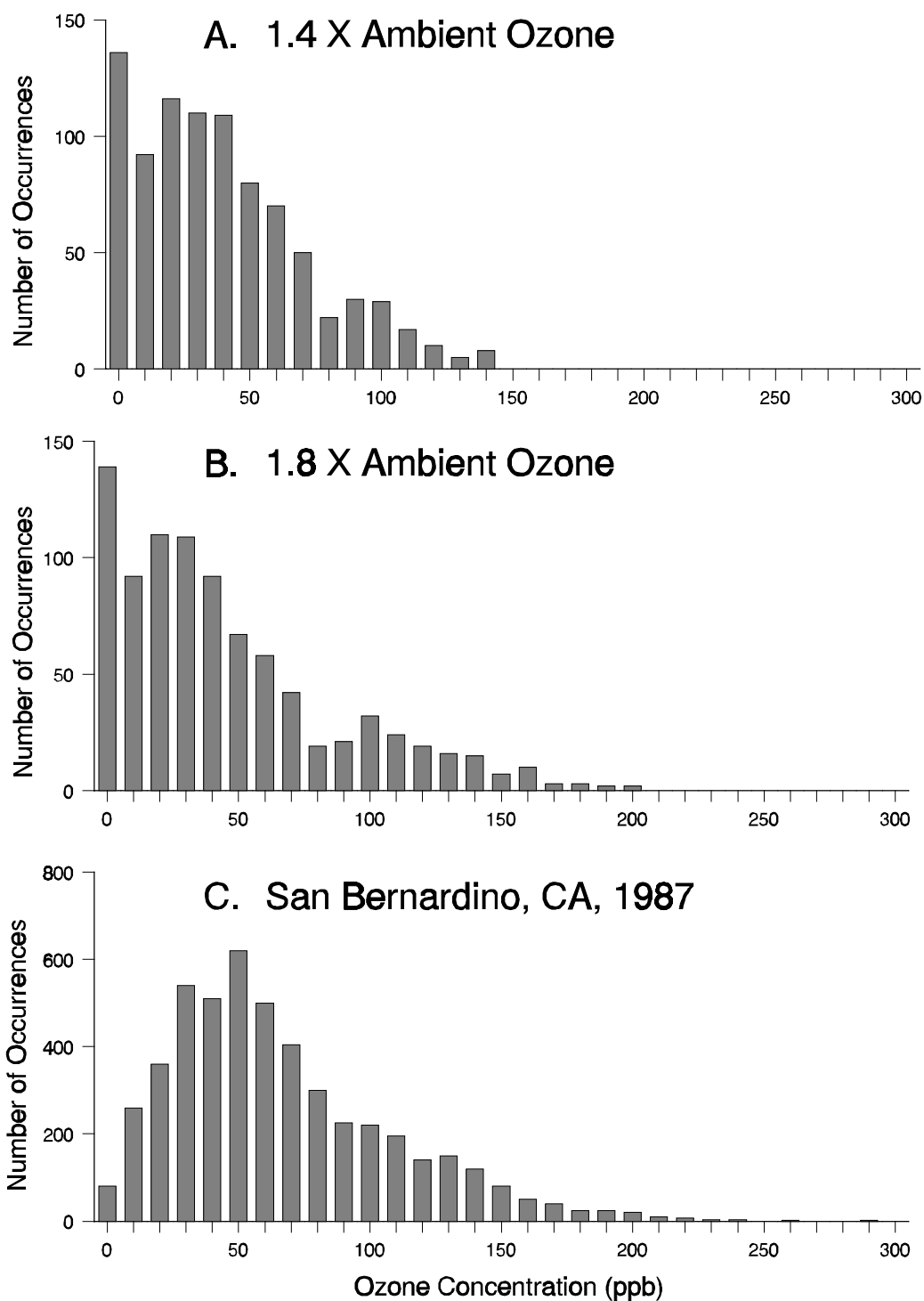
In addition to the CF concentration regimes, Lefohn et al. (1988a) have reported that the highest treatments have a tendency to display bimodal distributions that are unrealistic (Figure 5-9). At this time, there is no evidence to suggest whether or not these higher NF exposures provide realistic information on the impact of O<sub>3</sub> on plant response.

Studies that utilize exposures with peak concentrations above 0.40 ppm may not provide realistic evidence of O<sub>3</sub> impact on plant response in the United States. These studies provide limited evidence for substantiating the value of peak concentrations in influencing response. Consequently, these studies are not included in this section.

#### **5.5.2.2 Studies with Two or More Different Patterns of Exposure**

Experiments using chambers that focused on the structure of exposure have shown that plant response is differential to temporal patterns of O<sub>3</sub> exposure. For crop species, there is evidence to suggest that plant response is influenced more by higher concentrations than by lower concentrations or exposure duration. Greater response to concentration occurred when plants were predisposed to low concentrations for a few days or when peaks occurred just prior to or at maximum leaf expansion (U.S. Environmental Protection Agency, 1978, 1986). Plants exposed to two (or more) different exposure patterns of equal exposure (i.e., same SUM00 value) showed greater foliar injury response to:

- (1) the short-term, high-concentration exposure than to the longer term exposure with lower peak concentrations (Heck et al., 1966; Heck and Tingey, 1971; Bennett, 1979; Nouchi and Aoki, 1979; Amiro et al., 1984; Ashmore, 1984; Tonneijck, 1984); and
- (2) the exposure that predisposes plants to low O<sub>3</sub> concentrations for a few days prior to a high O<sub>3</sub> concentration than to exposures that have a set diurnal pattern of O<sub>3</sub> concentrations or less than 2 days of respite time between high concentrations (Heck and Dunning, 1967; Johnston and Heagle, 1982; Heagle



**Figure 5-9. Distribution pattern showing the number of ozone concentrations within specified ranges for the 1983 winter wheat proportional-addition experiment for the (A) 1.4 × ambient air and (B) 1.8 × ambient air treatments and for (C) San Bernardino, CA, in 1987.**

and Heck, 1974; Runeckles and Rosen, 1977; Mukammal, 1965; Stan and Schicker, 1982).

The studies that applied the same exposure but used different patterns of exposure have been reviewed in previous criteria documents (U.S. Environmental Protection Agency, 1978, 1986, 1992) and substantiate the role of concentration, temporal dynamics, respire time, and predisposition in influencing the magnitude of plant response to O<sub>3</sub>.

Musselman et al. (1983) and Hogsett et al. (1985b) were among the first to demonstrate that variable concentrations produced greater effect on plant growth than did fixed or set diurnal patterns of exposure of equal total exposure but with lower peak concentrations (Table 5-12). Musselman et al. (1986a), in a subsequent experiment, exposed kidney bean plants to either a variable or a uniform concentration of equal total exposure and equal peaks (at two levels of 0.30 and 0.40 ppm) and found that the effects of the two distributions were not significantly different (Table 5-12). Musselman et al. (1994), in a third experiment, exposed kidney bean plants to four different patterns of equal total exposure and, like Musselman et al. (1983), found that patterns with higher peak concentrations or longer duration of high concentrations (>0.16 ppm) produced significantly greater effect on top dry weight than the square wave pattern. Cumulative, peak-weighted exposure indices with an allometric weighting parameter between 2 and 3.5 gave the best fit for dry weight, necrosis, and number of pods. These results provide evidence that: total exposure (i.e., SUM00), being unable to differentiate among the exposure patterns, is a poor predictor of plant response; the peak concentrations or sequence of peak concentrations (>0.16 ppm) are important in determining plant response; and greater weight should be given to higher concentrations when describing exposure. Consequently, when peak concentration and total exposure are equal, the diurnal distribution of concentrations (e.g., sequence of peak concentrations >0.16 ppm) *may be* an important factor.

One recent study exposed bean plants to two consecutive exposures of 0.30 ppm for 3 h/day in the rapid vegetative growth stage and showed greater reductions in total dry weight when exposures were 3 to 6 days apart (McCool et al., 1988) (Table 5-12); this finding is consistent with earlier results on the role of predisposition in influencing response (e.g., Hogsett et al., 1988). Predisposition to a high concentration above the level that causes visible injury may increase plant sensitivity over time (Mukammal, 1965). As a result, the subsequent response to a high concentration following recovery may be greater than experienced in prior exposures. In future modeling efforts, this phenomenon may have to be taken into consideration, by the weighting of hourly concentrations, for properly characterizing plant exposure.

Sensitivity of plants to O<sub>3</sub> is a function of stomatal conductance and varies with the cultivar, time of day, and phenology. To test the role of phenology, Heagle et al. (1991b) applied 16 patterns of exposure in combinations of either CF or NF air for each quarter of the experimental period (31 days/quarter) (Table 5-12). The authors concluded that the phenological stage of development played a role in plant response, and that exposures during mid- to late-growth stages caused greater yield losses than did exposures during earlier developmental stages. For crops, foliage appears to be most sensitive to O<sub>3</sub> just prior to or during maximum leaf expansion (U.S. Environmental Protection Agency, 1978). These results are consistent with earlier studies (Lee et al., 1987) that reported better statistical fits to response using exposure indices that preferentially weighted hourly O<sub>3</sub> concentrations during the period of anthesis to seed fill.

**Table 5-12. A Summary of Studies Reporting the Effects of Ozone for Two or More Exposure Patterns on the Growth, Productivity, or Yield of Plants<sup>a</sup>**

Species	Facility <sup>b</sup> of Chambers	Total Number of Chambers	Exposure Patterns <sup>c</sup>	Exposure Duration	Concentration (ppm)/Exposure <sup>d</sup> (ppm-h)	Variable	Effect <sup>e</sup>	Reference
<i>Glycine max</i> L. Merrill cv. Davis, Forrest, Bragg, and Ransom	OTC in pots	24	16 combinations of CF or NF + over 4 quarters (31-days/quarter)	124 days	M7 (ppm): CF range from 0.016 to 0.038 over the 4 quarters, NF+range from 0.096 to 0.098 over the 4 quarters	Total seed weight	Forrest: greater effect in Q3 than in other quarters. Davis: no consistent effect Q1, significant but similar effects for Q2, Q3, and Q4. Ransom: no significant O <sub>3</sub> effects in Q1 or Q2, and equal responses in Q1, Q3, and Q4. Bragg: no significant O <sub>3</sub> effects in Q1 or Q2, significant decreases in Q3 and Q4.	Heagle et al. (1991b)
<i>Medicago sativa</i> L.	OTC in pots	8	E, DP	133 days	Equal SUM07 (ppm-h): DPH=113, DPL=63, EH=117, EL=72 Equal SUM00 (ppm-h): DPH=183, DPL=140, EH=193, EL=145 M7 (ppm): DPH=0.099, DPL=0.074, EH=0.084, EL=0.064	Shoot dry weight	91 and 67% reductions for EH and DPH. Significant difference between E and DP regimes. Treatment means are ordered CF<DPL<EL<DPH<EH.	Hogsett et al. (1985b)
<i>Phaseolus vulgaris</i> L. cv. Calif. Dark Red Kidney Bean	GC in pots	8	U, V	3 weeks (1 day/week)	Equal SUM00 (ppm-h/day): UL=VL=0.69; UH=VH=0.92 Equal Max concentration (ppm): UL=VL=0.30, UH=VH=0.40	Pod and seed dry weights	6% less yield when exposed to variable (NS). Response to O <sub>3</sub> same in reproductive and vegetative growth stages.	Musselman et al. (1986b)
<i>Phaseolus vulgaris</i> L. cv. Calif. Dark Red Kidney Bean	GC in pots	8	U, V	3 weeks (1 day/week)	Equal SUM00 (ppm-h/day): UL=VL=1.20; UH=VH=1.68 Max concentration. (ppm): UL=0.20, VL=0.50, UH=0.28, VH=0.715	Pod and seed dry weights	38% less yield when exposed to variable. No significant difference between low and high. Beans in reproductive growth stage when exposed.	Musselman et al. (1983)
<i>Phaseolus vulgaris</i> L. cv. Calif. Dark Red Kidney Bean	GC in pots	8	Square wave (SW), Triangular (T), Flattened triangular (FT), Rhomboid (R)	7 weeks (3 days/week)	Equal SUM00 (ppm-h/day): SW=T=FT=R=0.60. Max concentration (ppm): SW=0.12, T=0.36, FT=R=0.24.	Top dry weight	SW had significantly higher yield than other three patterns. Treatment means are ordered R=T<FT<SW	Musselman et al. (1994)
<i>Phaseolus vulgaris</i> L. cv. Calif. Dark Red Kidney Bean	GC in pots	10	Initial exposure of 0.3 ppm for 3-h and second exposure of 0.3 ppm at 2-6 (or 1-5) days after initial exposure	2-6 days in 1984 and 1-5 days in 1985	Equal maximum concentration of 0.30 ppm.	Total dry weight	Reductions due to the second exposure were significant when exposures were 3-6 days apart in 1984 and 5 days apart in 1985.	McCool et al. (1988)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>GC = Controlled environmental growth chamber, or CSTR; OTC = Open-top chamber.

<sup>c</sup>CA = Constant addition, PA = Proportional addition, CF = Charcoal-filtered, NF = Nonfiltered, NF+ = Nonfiltered plus ozone, E = Episodic, DP = Daily peak, U = Uniform, V = Variable, HE = High elevation.

<sup>d</sup>H = High, L = low.

<sup>e</sup>Significant at the 0.05 level, NS = not significant.

There is very limited information on the effect of O<sub>3</sub> on mature trees. Most of the information available deals with the nature of seedling response to O<sub>3</sub> (see Section 5.6.4); however, much less is known about the role of exposure-dynamic factors (e.g., concentration, duration, respite time, temporal variation) in influencing biomass response in long-lived species.

When yield is considered, a number of exposure-dynamic factors, including concentration, temporal pattern, predisposition, and respite times, as well as phenological stage of plant development, have been shown to influence the impact of O<sub>3</sub> on plant response. Evidence from studies of kidney bean (Musselman et al., 1983, 1994), alfalfa (Hogsett et al., 1985b), tobacco (Heagle et al., 1987b), soybean (Heagle et al., 1986b), ponderosa pine, and aspen suggests that concentration and temporal variation of exposure are important factors in influencing biomass production and, consequently, become considerations in measures of exposure. Because the SUM00 index weights all concentrations equally, the SUM00 is inadequate for characterizing plant exposure to O<sub>3</sub> (Lefohn et al., 1989). Other factors, including predisposition time (McCool et al., 1988) and crop development stage (Heagle et al., 1991b), contribute to variations in biological response, which suggests the need for weighting O<sub>3</sub> concentrations to account for predisposition time and phenology. However, the roles of predisposition and phenology in influencing plant response vary with species and environmental conditions and are not understood well enough to allow specification of a weighting function for use in characterizing plant exposure.

#### **5.5.2.3 Combinations of Years, Sites, or Species: Comparisons of Yield Losses with Different Exposure Durations**

Duration has not been a focus in experimental designs of studies that applied two or more exposure regimes over the growing season. Several lines of evidence suggest that the ultimate yield depends on the cumulative impact of repeated peak concentrations (U.S. Environmental Protection Agency, 1986, 1992), and that O<sub>3</sub>-induced reductions in growth are linked to reduced photosynthesis, which is impaired by the cumulative O<sub>3</sub> exposure (Reich and Amundsen, 1985; Reich, 1987; Pye, 1988). In EPA reviews of the literature (U.S. Environmental Protection Agency, 1986, 1992), EPA concluded that "When plant yield is considered, the ultimate impact of an air pollutant on yield depends on the integrated impact of the pollutant exposures during the growth of the plant." As a measure of plant exposure, the appropriate index should differentiate between exposures of the same concentration but of different duration. For example, a mean index calculated over an unspecified time cannot accomplish this (Lefohn et al., 1988a; Hogsett et al., 1988; Tingey et al., 1989, 1991; U.S. Environmental Protection Agency, 1986, 1992).

The paper by Lefohn et al. (1988a), reviewed previously in U.S. Environmental Protection Agency (1992), along with published criticisms and responses, was the first to fit a common response model to combined data from two replicate studies of unequal duration (71 and 36 days for the 1982 and 1983 wheat studies, respectively, conducted at Ithaca, NY) to test specifically for the importance of duration in influencing plant response. Greater yield losses occurred in 1982, which can be attributed partially to the longer duration. Because the mean index ignores the length of the exposure period, the year-to-year variation in plant response was minimized by the use of several cumulative indices rather than the mean. Lefohn (1988) and Lefohn et al. (1988b) concluded that duration has value in explaining variation in plant response, and that a cumulative-type index was preferred over a mean or peak index based on statistical fit.

When O<sub>3</sub> effects are the primary cause of variation in plant response, plants from replicate studies of varying duration showed greater reductions in yield or growth when exposed for the longer duration (Lee et al., 1991; Olszyk et al., 1993; Adaros et al., 1991a) (Table 5-13, Part A). Using NCLAN data for wheat, cotton, kidney bean, and potato from replicate studies with markedly different exposure durations, Lee et al. (1991) showed that year-to-year variations in the magnitude of relative yield loss were minimized by the use of exposure indices that are cumulative and weight peak concentrations more than low concentrations, indicating that O<sub>3</sub> effects are cumulative (Figure 5-10). Olszyk et al. (1993), using the two NCLAN cotton studies summarized by Temple et al. (1985) and Lee et al. (1991), in addition to cotton studies replicated at four sites in California's San Joaquin Valley over 2 years, tested and compared various exposure indices (SIGMOID, SUM06, M7, and 2HDM) based on statistical fit of a common response model. A Weibull response model with variance components was fit to the combined data and used to test for a common response (Gumpertz and Rawlings, 1991, 1992; Gumpertz and Pantula, 1992). The likelihood ratio test of parallel exposure-response curves was statistically significant for M7 and 2HDM for at least one set of cotton data, indicating significant differences in the magnitude of response across years or sites. On the other hand, the SIGMOID and SUM06 indices resulted in consistent patterns of response for both sets of cotton data, as well as between sets of cotton data (Figure 5-11). The authors concluded that the peak-weighted, cumulative indices minimized the temporal and spatial variations in crop yield and better predicted cotton yield responses than the M7 or 2HDM indices. The mean and peak indices did not differentiate between exposure seasons of differing duration and could not account for year-to-year differences in response.

The results of European studies with wheat (Adaros et al., 1991a,c), spring rape (Adaros et al., 1991b), barley (Adaros et al., 1991c), and kidney beans (Bender et al., 1990), using data from replicate studies with varying duration, are less conclusive as to the role of duration in determining plant response (Table 5-13, Part A). Exposures are reported using a mean index. Adaros et al. (1991a) showed a greater reduction in above-ground dry weight when exposed for the longer duration for the wheat cultivar Star but not for the cultivar Turbo (Figure 5-12). Adaros et al. (1991c), in another 2-year study with barley (cv. Arena and Alexis) and wheat (cv. Star and Turbo), involving mixtures of O<sub>3</sub>, SO<sub>2</sub>, and NO<sub>2</sub>, showed greater reductions in yield when exposed for the longer duration for all species and cultivars except barley cv. Alexis (Table 5-13, Part A). Ozone effects were insignificant in both years for barley cv. Alexis. The authors did not attribute the differential response in growth and yield to any single factor, but the data suggested that O<sub>3</sub> effects are cumulative. When O<sub>3</sub> exposure is the primary source of response, the mean exposure index of unspecified duration could not account for the year-to-year variation in response.

The role of duration in influencing growth or yield is unclear for the other studies because of the following limitations in the data:

- (1) Treatment levels were below the levels necessary to induce injury or damage to kidney bean plants in 2 of the 3 years. None of the years produced a significant O<sub>3</sub> effect at or below 70 ppb concentration (Bender et al., 1990). Similarly, the study with barley showed no significant O<sub>3</sub> effects.

**Table 5-13. A Summary of Studies Reporting the Effects of Ozone on the Growth, Productivity, or Yield of Plants for Two or More Replicate Studies Having Equal Total Exposures and Either Varying Durations (Part A) or Similar Durations (Part B)<sup>a</sup>**

Species	Facility <sup>b</sup>	Total No. of Plots	Duration [dates and (days)]	Concentration (ppm)/ Exposure (ppm-h) <sup>c</sup>	Variable	Effect <sup>d</sup>	Reference
<b>PART A</b>							
<i>Brassica napus</i> L. var. Napus cv. Callypso	OTC in pots	1987: 18 1988: 24 1989: 16	1987: 05-13 to 08-10 (89) 1988: 05-02 to 08-24 (113) 1989: 05-08 to 08-01 (84)	1987: M24 (M8) in ppb range from 5 (9) to 16 (43). 1988: M24 (M8) in ppb range from 3 (5) to 16 (48). 1989: M24 (M8) in ppb range from 6 (5) to 22 (62).	Seed dry weight	1987: 27% reduction at M8 = 43 ppb (***). 1988: 18% reduction at M8 = 48 ppb (***). 1989: 11% reduction at M8 = 62 ppb (***).	Adaros et al. (1991b)
<i>Gossypium hirsutum</i> L. cv. Acala SJ2	OTC	1981: 12 1982: 12	1981: 07-06 to 09-15 (72) 1982: 06-04 to 09-09 (98)	1981: M7 (SUM06) range from 18 ppb (0 ppm-h) to 138Lint (68). 1982: M7 (SUM06) range from 12 ppb (0 ppm-h) to 111 weight (71).	Lint dry weight	45 and 66% reductions at M7 = 111 ppb. 57 and 60% reductions at SUM06 = 68 ppm-h.	Lee et al. (1991), Olszyk et al. (1993)
<i>Hordeum vulgare</i> L. cf. Arena and Alexis	OTC in pots	1988: 24 1989: 16	1988: 04-29 to 08-15 (108) 1989: 05-08 to 08-15 (99)	1988: M8 (max 8-h mean) in ppb range from 5 (15) to 48 (89). 1989: M8 (max 8-h mean) in ppb range from 11 (27) to 62 (101).	Seed dry weight	Arena: 14% (*) and 6% (NS) reductions at M8 = 48 ppb. Alexis: No reductions at M8 = 48 ppb (NS).	Adaros et al. (1991c)
<i>Phaseolus vulgaris</i> L. cv. Calif. Dark Red Kidney Bean	OTC	1980: 20 1982: 20	1980: 08-20 to 09-10 (22) 1982: 08-11 to 10-06 (57)	1980: M7 (SUM06) range from 24 ppb (0 ppm-h) to 139 (19). 1982: M7 (SUM06) range from 19 ppb (0 ppm-h) to 110 weight (40).	Seed dry weight	13 and 59% reductions at M7 = 110 ppb. 28 and 8% reductions at SUM06 = 19 ppm-h.	Lee et al. (1991)
<i>Phaseolus vulgaris</i> L. cf. Rintintin	OTC in pots	1988 I: 4 1988 II: 6 1989 III: 8	1988 I: 06-15 to 08-04 (51) 1988 II: 07-24 to 08-29 (37) 1989 III: 06-04 to 07-25 (52)	I. M8 (max) in ppb range from 3 (19) to 48 (70). II. M8 (max) in ppb range from 2 (19) to 50 (105). III. M8 (max) in ppb range from 6 (26) to 109 (159).	Pod dry weight	I. 2% reduction at M8 = 48 ppb (NS). II. 0% reduction at M8 = 50 ppb (NS). III. 0% (NS) and 47% (*) reductions at M8 = 50 and 109 ppb.	Bender et al. (1990)
<i>Solanum tuberosum</i> L. cv. Norchip	OTC	1985: 15 1986: 39	1985: 06-14 to 08-22 (70) 1986: 06-20 to 08-20 (62)	1985: M7 (SUM06) range from 22 ppb (0 ppm-h) to 85 (47). 1986: M7 (SUM06) range from 24 ppb (0 ppm-h) to 88 (38).	Tuber weight	42 and 25% reductions at M7 = 85 ppb. 32 and 27% reductions at 12-h SUM06 = 38 ppm-h.	Lee et al. (1991)
<i>Triticum aestivum</i> L. cv. Vona	OTC	1982: 20 1983: 12	1982: 05-18 to 07-17 (61) 1983: 06-12 to 07-17 (36)	1982: M7 (SUM06) range from 21 ppb (0 ppm-h) to 95 (41). 1983: M7 (SUM06) range from 26 ppb (0 ppm-h) to 96 (22).	Seed dry weight	74 and 49% reductions at M7 = 95 ppb. 49 and 62% reductions at SUM08 = 21 ppm-h. 55 and 60% reductions at 7-h SUM06 = 22 ppm-h.	Lefohn et al. (1988a), Lee et al. (1991)

**Table 5-13 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth, Productivity, or Yield of Plants for Two or More Replicate Studies Having Equal Total Exposures and Either Varying Durations (Part A) or Similar Durations (Part B)<sup>a</sup>**

Species	Facility <sup>b</sup>	Total No. of Plots	Duration [dates and (days)]	Concentration (ppm)/ Exposure (ppm-h) <sup>c</sup>	Variable	Effect <sup>d</sup>	Reference
<b>PART A (cont'd)</b>							
<i>Triticum aestivum</i> L. cv. Star and Turbo	OTC in pots	1988: 6 1989: 10	1988: 04-27 to 08-23 (118) 1989: 05-09 to 08-15 (98)	1988: M8 (max,SUM06) in ppb range from 4 (58,0) to 51 (106,8.2). 1989: M8 (max,SUM06) in ppb range from 10 (34,0) to 113 (162,87).	Seed dry weight	Star: 20% (*) and 9% (NS) reductions at M8 = 51 ppb. Turbo: 25% (*) and 31% (*) reductions at M8 = 51 ppb.	Adaros et al. (1991a)
<i>Triticum aestivum</i> L., cv. Star and Turbo	OTC in pots	1988: 24 1989: 16	1988: 04-29 to 08-15 (108) 1989: 05-08 to 08-15 (99)	1988: M8 (max 8-h mean) in ppb range from 5 (15) to 48 (89). 1989: M8 (max 8-h mean) in ppb range from 11 (27) to 62 (101).	Seed dry weight	Star: 26% (*) and 12% (*) reductions at M8 = 48 ppb. Turbo: 34% (*) and 17% (*) reductions at M8 = 48 ppb.	Adaros et al. (1991c)
<b>PART B</b>							
<i>Glycine max</i> L. Merr. cv. Davis	OTC in pots	1977: 8 1978: 8	1977: 06-17 to 10-10 (116) 1978: 06-28 to 10-21 (116)	1977: M7 (max) in ppb range from 27 (78) to 154 (277). 1978: M7 (max) in ppb range from 28 (84) to 131 (241).	Seed dry weight	47 and 37% reductions at M7 = 131 ppb.	Cure et al. (1986), Heagle et al. (1983a)
<i>Glycine max</i> L. Merr. cv. Williams	OTC	1981: 31 1982: 31 1983: 31	1981: 07-20 to 09-22 (65) 1982: 07-14 to 09-22 (71) 1983: 07-23 to 09-23 (63)	1981: M7 in ppb range from 15 to 64. 1982: M7 in ppb range from 17 to 99. 1983: M7 in ppb range from 19 to 132.	Bean dry weight	28, 20, and 32% reductions at M7 = 64 ppb. 43 and 41% reductions at M7 = 99 ppb in 1982 and 1983	Heggestad and Lesser (1990), Heggestad et al. (1988)
<i>Medicago sativa</i> L. cv. WL-514	OTC	1984: 30 1985: 30	1984: 03-16 to 10-10 (209) 1985: 03-23 to 10-09 (201)	1984: M12 in ppb range from 16 to 109. 1985: M12 in ppb range from 10 to 94.	Top dry weight	29% (*) and 25% (*) reductions at M12 = 94 ppb.	Temple et al. (1988a)
<i>Pinus rigida</i> Mill.	OTC in pots	Exp. 1: 4 Exp. 2: 4	Exp. 1: 13 weeks Exp. 2: 13 weeks	1: M8 in ppb range from 0 to 200 (U). 2: M8 in ppb range from 0 to 200 (U).	Total dry weight	49 and 46% reductions at M8 = 200 ppb.	Schier et al. (1990)
<i>Pinus taeda</i> L.	GC in pots	1986: 15 1987: 15	1986: 09-15 to 12-04 (81) 1987: 07-27 to 10-15 (81)	1986: SUM00 in ppm-h range from 0 to 99 (U). 1987: SUM00 in ppm-h range from 0 to 99 (U).	Total dry weight	43 and 28% reductions at SUM00 = 99 ppm-h averaged across all families. Individual families show similar reductions (e.g., 35 and 33% reductions at SUM00 = 99 ppm-h for family 5.56, 14 and 12% reductions at SUM00 = 99 ppm-h for family 1.68).	Shafer et al. (1993)



**Table 5-13 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth, Productivity, or Yield Of Plants for Two or More Replicate Studies Having Equal Total Exposures and Either Varying Durations (Part A) or Similar Durations (Part B)<sup>a</sup>**

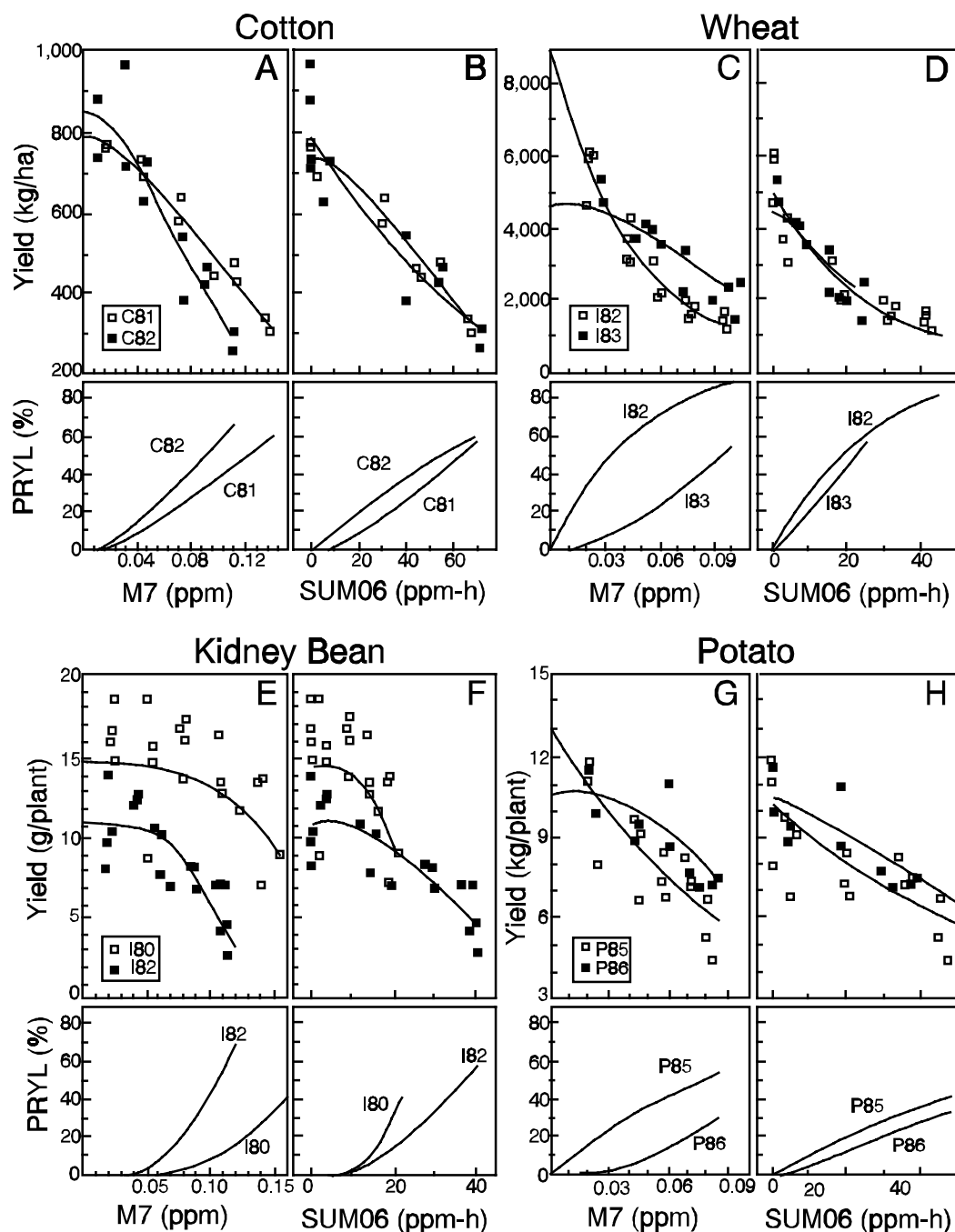
Species	Facility <sup>b</sup>	Total No. of Plots	Duration [dates and days]	Concentration (ppm)/ Exposure (ppm-h) <sup>c</sup>	Variable	Effect <sup>d</sup>	Reference
<b>PART B (cont'd)</b>							
<i>Picea rubens</i> Sarg.	OTC in pots	1987: 12 1988: 12	1987: 05-30 to 12-15 (199) 1988: 06-01 to 12-01 (184)	1987: SUM00 in ppm-h are 32, 61, 91, and 119. 1987: SUM00 in ppm-h are 36, 70, 101, and 135.	Total dry weight	0% (NS) reduction in biomass after first year, 8% (*) reduction at SUM00 = 135 ppm-h after second year of exposure.	Alscher et al. (1989) Amundson et al. (1991)
<i>Pisum sativum</i> L. cv. Puget	ZAPS	1986: 14 1987: 14	1986: last 58 days 1986: last 52 days	M12 and D25 (numbers of days with 1-h concentrations >25 ppb) used in simple linear regression.	Pea fresh weight	0% reductions at M12 = 100 ppb based on linear regression models.	Runeckles et al. (1990)
<i>Populus tremuloides</i> Michx clones	OTC in pots	1988: 18 1989: 18	1988: 07-19 to 09-27 (71) 1989: 07-20 to 09-20 (64)	1988: SUM00 in ppm-h are 5.0, 10.0, and 19.4 (U). 1989: SUM00 in ppm-h are 7.7, 15.4, and 26.4 (U).	Stem and leaf dry weights	36% (*) and 40% (*) reductions at SUM00 = 19.4 ppm-h.	Karnosky et al. (1992b)
<i>Triticum aestivum</i> L. cv. Albis	OTC	1986: 12 1987: 16 1988: 16	1986: 05-06 to 07-31 (86) 1987: 04-27 to 08-10 (92) 1988: 05-04 to 08-01 (89)	1986: M24 (max) in ppb range from 12 (61) to 47 (181). 1987: M24 (max) in ppb range from 12 (54) to 45 (175). 1988: M24 (max) in ppb range from 17 (65) to 45 (148).	Seed dry weight	1986: 61% reduction at M24 = 47 ppb. 1987: 27% reduction at M24 = 45 ppb. 1988: 65% reduction at M24 = 45 ppb.	Fuhrer et al. (1989)
<i>Triticum aestivum</i> L. cv. Albis	OTC	1989: 24 1990: 24	1989: 05-16 to 08-14 (91) 1990: 05-14 to 08-09 (88)	1989: M7 (SUM06) range from 18 ppb (0 ppm-h) to 62 (3.8). 1990: M7 (SUM06) range from 17 ppb (0 ppm-h) to 71 (5.6).	Seed dry weight	29 and 22% reduction at M7 = 62 ppb. 29 and 17% reduction at SUM06 = 3.8 ppm-h.	Fuhrer et al. (1992)
<i>Triticum aestivum</i> L. cv. Severn, Potomac, Oasis, MD5518308	OTC	1984: 20 1985: 20	1984: 05-14 to 06-22 (40) 1985: 05-06 to 06-15 (41)	1984: M4 (AOT03) in ppb (ppb-h) range from 32 (0) to 93 (10). 1985: M4 (AOT03) in ppb (ppb-h) range from 30 (0) to 86 (9).	Seed dry weight	31% (*) and 9% (NS) reductions at M4 = 86 ppb.	Slaughter et al. (1989)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>GC = Controlled environmental growth chamber, or CSTR; OTC = open-top chamber; ZAPS = zonal air pollution system.

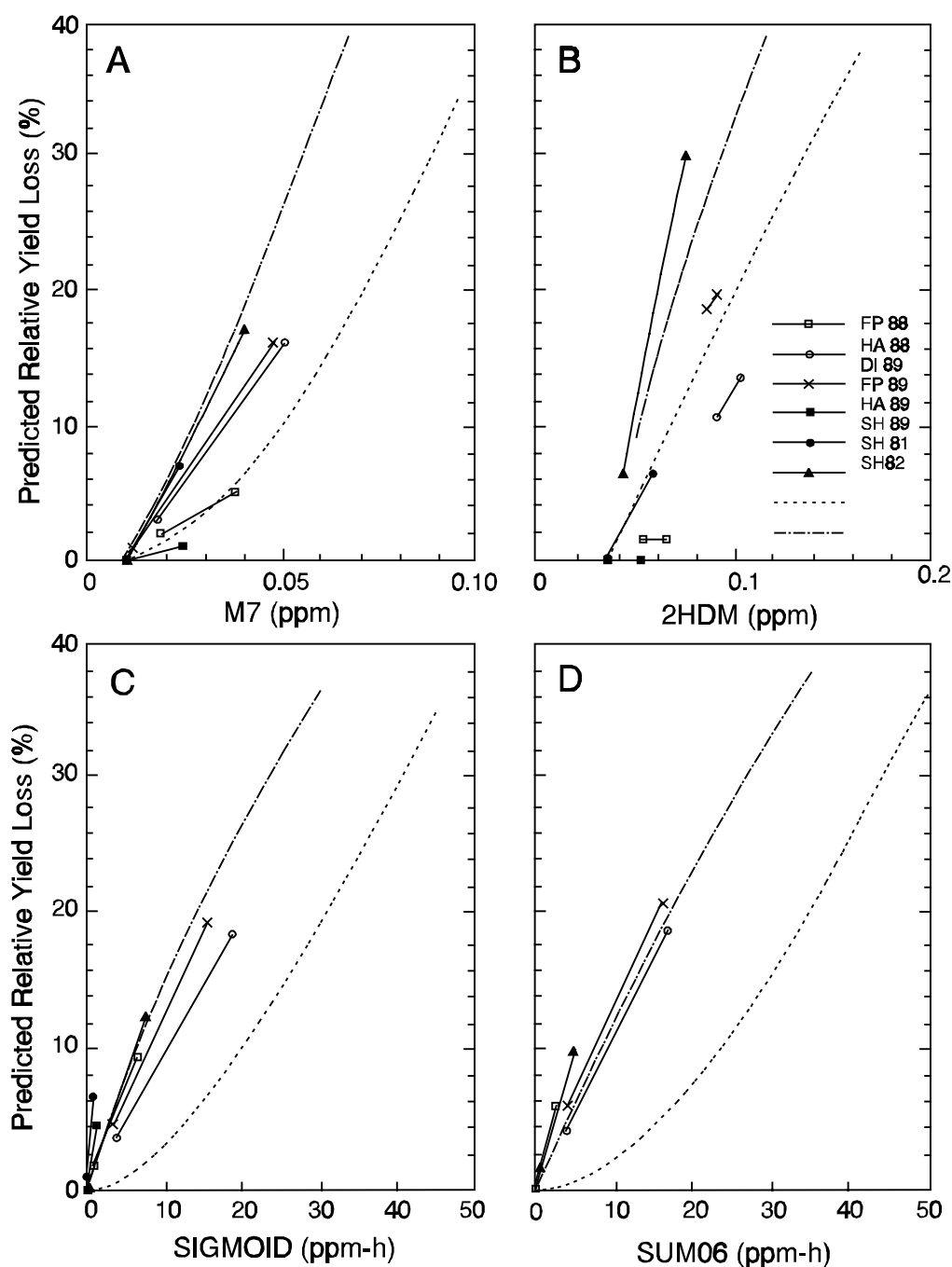
<sup>c</sup>U = Uniform.

<sup>d</sup>\* = Significant at the 0.05 level; NS = not significant.

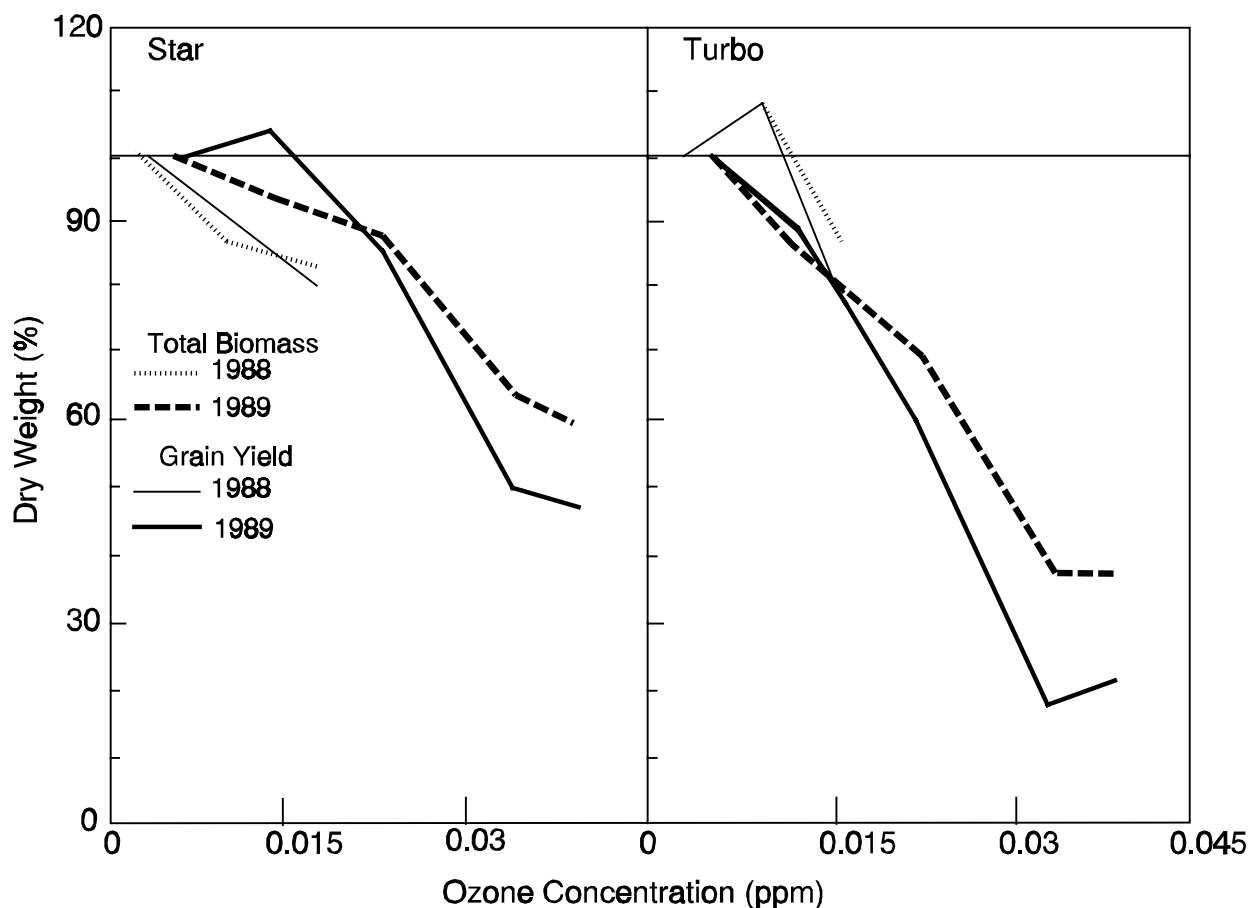


**Figure 5-10.**

***Comparison of the Weibull exposure-response functions and its predicted relative yield loss (PRYL) curves (relative to 0 ozone) using M7 and daytime SUM06 for replicate years of National Crop Loss Assessment Network Program's data for (A) and (B) cotton (var. Acala SJ-2), (C) and (D) wheat (var. Vona), (E) and (F) kidney bean (var. California light red), and (G) and (H) potato (var. Norchip), respectively. Mean dry weights and the Weibull exposure-response functions for replicate studies are given in the top portion of the graphs (Lee et al., 1991).***



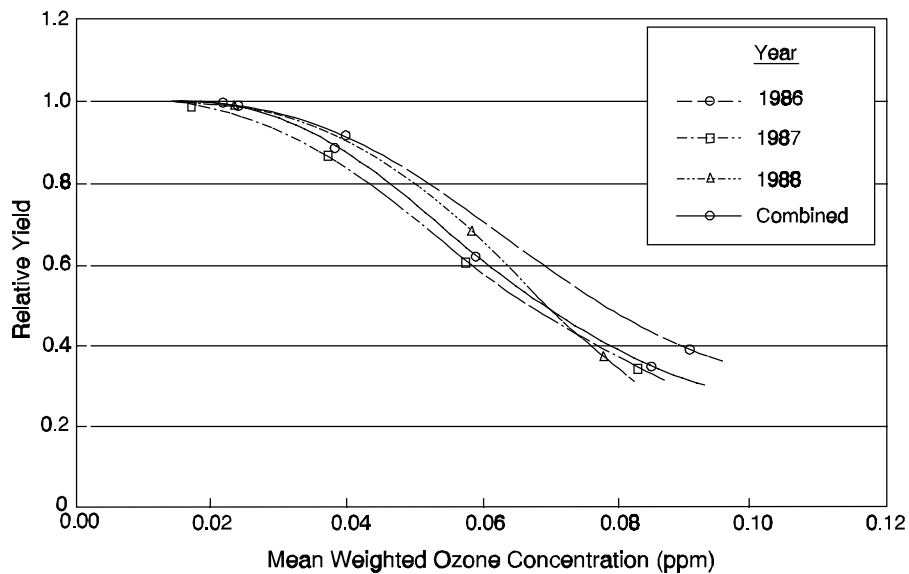
**Figure 5-11.** Predicted relative yield losses (lint weight) for Acala SJ-2 cotton for four sites and multiple years (1981, 1982, 1988, and 1989) relative to 0.01 ppm for M7, 0.035 ppm for 2HDM, 0 ppm-h for SIGMOID, and 0 ppm-h for SUM06, which correspond to typical levels in the charcoal-filtered chambers. Predicted losses are based on M7 (A), 2HDM (B), SIGMOID (C), and SUM06 (D) exposure indices. Abbreviations: DI = Dinuba, FP = Five Point, HA = Hanford, and SH = Shafter (Olszyk et al., 1993).



**Figure 5-12.** *Relative effect of ozone on growth and yield of spring wheat cultivars (var. Star and Turbo) from two growing seasons (Adaros et al., 1991a).*

- (2) Differences in growing conditions and varying kinds of interactions among  $O_3$ ,  $SO_2$ , and  $NO_2$  resulted in different sizes of control plants of spring rape over years and affected the magnitude of response to  $O_3$ . Compared to 1987, yield of control plants increased by 32% in 1988 and by 94% in 1989 (Adaros et al., 1991b). Consequently, the evidence of duration as the primary cause of differences in response over years was difficult to substantiate.

When durations were nearly equal, plant response to  $O_3$  were similar for 2- or 3-year studies with alfalfa (Temple et al., 1988a), pea (Runeckles et al., 1990), soybean (Heagle et al., 1983a; Heggstad and Lesser, 1990; Cure et al., 1986), wheat (Fuhrer et al., 1989, 1992), aspen clones (Karnosky et al., 1992b), loblolly pine (Shafer et al., 1993), and pitch pine (Schier et al., 1990) (Table 5-13, Part B). For example, year-to-year variations in wheat yield response to  $O_3$  were small for the 3 years having durations between 86 and 92 days, allowing pooling of the data to fit a common Weibull model using Rawling's solar-radiation-weighted mean index (Fuhrer et al., 1989) (Figure 5-13). Different growing conditions were reported in studies of Shafer et al. (1993), Fuhrer et al. (1989), but no



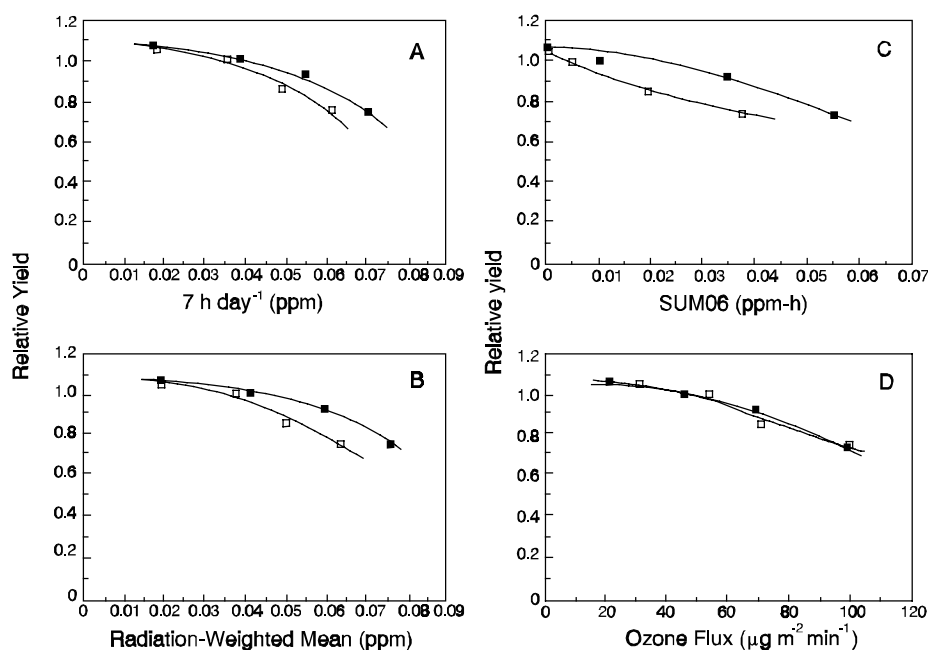
**Figure 5-13.**

***Weibull exposure-response curves for the relative effect of ozone on grain yield of spring wheat for 3 years, individually and combined (Fuhrer et al., 1989).***

interaction between  $O_3$  and climatic effects was found. On the other hand, Slaughter et al. (1989) reported reductions in wheat grain yield of 69 and 9% in a 2-year study having equal exposure durations, which the authors attribute to differences in rainfall and temperature. Environmental conditions in 1985 favored greater photosynthate partitioning for grain development rather than for vegetative growth, resulting in larger plants in 1985. Air pollution effects may not have been the primary source of variation in response, and, consequently, the data do not substantiate the role of duration in influencing response.

These studies report plant response as a function of a mean exposure index and do not evaluate or compare various exposure indices, based on statistical fit. In a series of papers that examined the response of spring wheat to  $O_3$  at higher elevations, Grandjean Grimm and Fuhrer (1992a,b) and Fuhrer et al. (1992) conducted a 2-year study in which the flux of  $O_3$  was determined in OTCs. Plants were exposed to  $O_3$  for periods lasting 44 and 50 days in 1989 and 1990, respectively, and flux measurements were taken repeatedly over the experimental period. In addition to  $O_3$  flux, exposures were characterized using M7, M24, SUM06, and the solar-radiation-weighted mean index (Rawlings et al., 1988b). The quadratic response curves relating the various indices with grain yield showed that year-to-year variations were minimized using the mean  $O_3$  flux index (Figure 5-14). The other three exposure indices showed slightly greater yield losses in 1989 than in 1990, in contrast with longer exposure in 1990 and drier conditions in 1989. The authors concluded that the  $O_3$  flux related well with yield because the mean flux incorporated environmental factors, canopy structure, and physiological processes, which affected the uptake of  $O_3$  from the air to the leaf interior. The measurements of pollutant concentrations ignored these factors and,

consequently, were unable to account for all of the year-to-year variability in wheat response. The authors suggested that O<sub>3</sub> flux was a surrogate of Fowler and Cape's



**Figure 5-14.**

***Quadratic exposure-response curves for the relative effect of ozone on grain yield of spring wheat in 1989 and 1990, using four different exposure indices (A through D).***

Source: Modified from Fuhrer et al. (1992).

(1982) "pollutant absorbed dose" and appeared to be the relevant measure for use in relating exposure and plant response.

Alscher et al. (1989) and Amundson et al. (1991) report on the impact of O<sub>3</sub> on growth, injury, and biomass response of 2-year-old red spruce seedlings after 1 and 2 years of exposure, respectively. Exposures were characterized using the M12 (or M7), M24, and SUM00 indices. No significant O<sub>3</sub> effects on biomass were detected in 1987 (Alscher et al., 1989) because stomatal conductances in red spruce are inherently low and, consequently, result in low rates of pollutant uptake (Seiler and Cazell, 1990). However, in the second year, O<sub>3</sub> reduced leaf and root starch, increased foliar antioxidant content, and reduced biomass of 1988 fixed-growth foliage. However, O<sub>3</sub> effects on biomass were slight in the second year. The authors concluded O<sub>3</sub> effects are cumulative because the onset of damage occurred in the second year rather than the first year of exposure.

Plant response is influenced by exposure duration and O<sub>3</sub> concentration. Regardless of whether concentrations are above or below levels at which injury has been observed, plant responses are determined by the cumulative effects of the number of times exposures have occurred. The results of these studies are in general agreement that O<sub>3</sub> effects are cumulative, and the ultimate impact of long-term exposures to O<sub>3</sub> on crops and seedling biomass response depends on the integration of repeated peak concentrations during the growth of the plant. Consequently, the mean or peak indices are inappropriate because the length of exposure is unspecified, and these indices cannot differentiate among exposures of

the same concentration but of various durations. These results support the conclusion that an appropriate  $O_3$  index should cumulate all hourly concentrations in some fashion to reflect the nature of  $O_3$  on plant response. Fuhrer et al. (1992) suggested that the weighting function should reflect the relationship between ambient pollutant concentration and internal  $O_3$  flux, consistent with the mode of action of  $O_3$  on plants and with earlier findings that peak-weighted, cumulative indices give better predictions of plant response than mean or peak indices.

#### **5.5.2.4 Comparisons of Measures of Exposure Based on Reanalysis of Single-Year, Single-Species Studies**

Studies cited in previous sections focused on the role of the structure of exposure in influencing plant response but do not identify specifically the weighting function for use in characterizing plant exposure to  $O_3$ . In addition to these types of studies, other studies have focused on comparison of measures of exposure based on reanalysis of single-year, single-species studies. The variety of statistical approaches used to relate exposure and plant response range from informal description of the distributions of  $O_3$  concentrations associated with response to more formal regression-based procedures.

The regression approach is designed to select those exposure indices that properly order and space the treatment means along the horizontal axis to optimize the fit of a linear or curvilinear model. However, because the experimental designs are not intended to evaluate various indices, the power of the regression approach to identify the important exposure-dynamic factors influencing plant response is less desirable (Lefohn et al., 1992a). Consequently, these retrospective studies provide less substantiating evidence of the role of exposure-dynamic factors (e.g., concentration, duration, temporal pattern, respite time) than do those studies with experimental designs and analyses that focus on specific components of exposure.

Most of the early retrospective studies reporting regression results using data from the NCLAN program or from Corvallis, OR (Lee et al., 1987, 1988; Lefohn et al., 1988a; Tingey et al., 1989), or using data collected by Oshima (U.S. Environmental Protection Agency, 1986; Musselman et al., 1988) were in general agreement and consistently favored the use of cumulative peak-weighted exposure indices. These studies have been reviewed previously by EPA (U.S. Environmental Protection Agency, 1992). Lee et al. (1987) suggested that exposure indices that included all the data (24 h) performed better than those that used only 7 h of data; this is consistent with the conclusions of Heagle et al. (1987b) that plants receiving exposures for an additional 5 h/day showed 10% greater yield loss than those exposed for 7-h/day. In a subsequent analysis using more of the NCLAN data, Lee et al. (1988) found the "best" exposure index was a general phenologically weighted, cumulative-impact index, with sigmoid weighting on concentration and a gamma weighting function as surrogate of time of increased plant sensitivity to  $O_3$ . For most cases, Lee et al. (1987) computed their exposure indices based on the daylight exposure periods used by the NCLAN investigators. The exposure indices with minimum residual sum of squares were those indices that cumulated hourly  $O_3$  concentrations over the growth of the plant, gave preferential weighting to peak concentrations, and phenologically weighted the exposures to emphasize concentrations during the plant growth stage. The paper by Tingey et al. (1989) is a summarization of the results in Lee et al. (1988) and shows the limitations of the mean index.



Lefohn and Foley (1992) characterized the NCLAN exposures that had a SUM06 level closest to those that predicted a 20% yield loss, using the exposure-response equations as reported in Lee et al. (1991) and Tingey et al. (1991). Lefohn and Foley (1992) characterized the hourly average concentrations using percentiles, HRS06, HRS10, SUM06, and W126 for each of 22 NCLAN studies. The authors noted that the frequent occurrence, in many cases, of high hourly concentrations ( $\geq 0.10$  ppm) may have been partly responsible for the 20% yield loss. The number of hourly average concentrations ranged from 0 to 515 with only one of the 22 NCLAN experiments experiencing no hourly average concentrations  $\geq 0.10$  ppm, whereas the remaining experiments experienced multiple occurrences  $\geq 0.10$  ppm. The repeated occurrences of high hourly average concentrations were a result of the NCLAN protocol (Table 5-14). As a result of their analysis, Lefohn and Foley (1992) and Lefohn et al. (1992b) stressed that, because the NCLAN experiments contained peak hourly average concentrations, it is important that any index selected to characterize those regimes responsible for growth reduction adequately capture the presence of these peak concentrations when attempting to predict biological responses using actual ambient air quality data.

For example, Tingey et al. (1991), using mostly NCLAN data, identified 24.4 ppm-h as the SUM06 value, calculated over a 3-mo period, that would protect 50% of the NCLAN crops analyzed at the 10% yield reduction level. These predicted relative yield loss (PRYL) calculations assume that the crops being protected will be grown using NCLAN protocol. There are monitoring sites in the United States that experience 3-mo cumulative SUM06 values greater than 24.4 ppm-h, but do not experience frequent occurrences of hourly average concentrations  $> 0.10$  ppm. For example, 24% (1987), 10% (1988), 30% (1989), 25% (1990), and 31% (1991) of the rural agricultural sites listed in the EPA Aerometric Information Retrieval System (AIRS) database experienced 3-mo cumulative SUM06 values greater than 24.4 ppm-h but experienced fewer than 11 hourly average concentrations equal to or greater than 0.10 ppm. Lefohn and Foley (1992) noted that agricultural crops grown at a site experiencing a 3-mo cumulative SUM06 value greater than 24.4 ppm-h, but with infrequent high hourly average concentrations (e.g.,  $\geq 0.10$  ppm), might experience less yield reduction than predicted using NCLAN experimental results. For rural forest sites, 21% (1987), 23% (1988), 54% (1989), 50% (1990), and 52% (1991) of the sites exhibited 3-mo cumulative SUM06 values greater than 24.4 ppm-h, but fewer than 11 hourly average concentrations equal to or greater than 0.10 ppm. Tables 5-15 and 5-16 illustrate that sites that experience 3-mo SUM06 values  $\geq 24.4$  ppm do not necessarily have peaks, whereas sites that experience values  $< 24.4$  ppm-h do have peaks.

Reich (1987) reviewed 44 studies on 45 species to study the effects of  $O_3$  on net photosynthesis (Pn) and growth of crops and tree species. Plants responded differently to equivalent total exposures (i.e., SUM00), when peak concentrations differed widely, with greater loss of Pn for increasing concentrations (Figure 5-15). Short-term, high concentrations above 0.40 ppm (e.g., 0.50 ppm for 8 h) caused rapid and significant reduction in Pn. Longer term exposures (for weeks) to lower concentrations had a significant effect on Pn; the observed reductions were less severe than at the higher concentrations. Based on short-term, high concentration studies, SUM00 alone was an inadequate descriptor of exposure for predicting response. However, for assessing the effects of long-term, low concentrations typical of ambient condition, SUM00 may be adequate, because the response of field-grown plants to SUM00 was roughly linear. SUM00 explained much, although not all, of the variation in Pn and the growth of conifers, hardwood trees, and agricultural crops (Figures 5-16 through 5-18). Unexplained variation can be attributed to biological variation, inherent experimental error, experimental conditions, and differences

**Table 5-14. Summary of Ozone Exposures That Are Closest to Those Predicted for  
20% Yield Reduction per SUM06 Exposure Response Models Used by  
Lee et al. (1991) in Selected National Crop Loss Assessment Network Experiments<sup>a</sup>  
(Concentrations are in parts per million.)**

Experiment <sup>b</sup>	Chamber	Min.	10	30	50	Percentiles				Max	Number of Obs.	Number of Occurrences			SUM		
						70	90	95	99			≥0.06	≥0.08	≥0.10	06 (ppm-h)	08	W126 (ppm-h)
SOYBEAN																	
A80S0 - Corsoy	NF+0.03-1	0.000	0.000	0.011	0.026	0.045	0.077	0.090	0.111	0.123	1,344	263	113	35	21.1	10.7	17.7
A83SO - Amsoy	NF+0.03-1	0.000	0.001	0.014	0.028	0.049	0.083	0.098	0.123	0.168	1,992	467	223	90	39.1	22.1	33.2
A83SO - Corsoy	NF+0.03-1	0.000	0.001	0.014	0.028	0.049	0.083	0.098	0.123	0.168	1,992	467	223	90	39.1	22.1	33.2
A85SO - Corsoy-79 D	NF×2.00-1D	0.000	0.000	0.008	0.023	0.051	0.110	0.129	0.160	0.194	2,352	657	495	319	67.5	56.2	63.0
A85SO - Corsoy-79 W	NF×2.00-1W	0.000	0.000	0.011	0.026	0.063	0.114	0.134	0.162	0.199	2,352	729	547	358	75.1	62.5	70.0
A86SO - Corsoy-79 D	NF×2.5-1D	0.000	0.002	0.016	0.035	0.085	0.137	0.161	0.207	0.279	2,040	784	654	515	92.1	83.2	88.6
A86SO - Corsoy-79 W	NF×2.0-1W	0.000	0.002	0.015	0.033	0.065	0.105	0.124	0.161	0.242	2,040	719	510	271	69.6	55.1	63.7
B83SO - Corsoy-79 D	NF-1D	0.000	0.002	0.006	0.018	0.037	0.063	0.074	0.087	0.111	1,512	184	51	5	13.5	4.4	10.6
B83SO - Corsoy-79 W	NF+0.03-1W	0.000	0.002	0.006	0.019	0.049	0.084	0.097	0.118	0.135	1,512	359	198	70	30.1	18.9	25.8
B83SO - Williams D	NF+0.03-1D	0.000	0.002	0.006	0.019	0.049	0.084	0.098	0.118	0.137	1,512	364	204	66	30.5	19.5	26.0
B83SO - Williams W	NF+0.03-1W	0.000	0.002	0.006	0.019	0.049	0.084	0.097	0.118	0.135	1,512	359	198	70	30.1	18.9	25.8
I81SO - Hodgson	NF+0.06-1	0.000	0.004	0.007	0.015	0.031	0.083	0.090	0.105	0.132	1,680	323	191	29	26.7	17.4	22.9
R81SO - Davis	NF-1	0.000	0.003	0.015	0.026	0.043	0.066	0.075	0.088	0.145	2,664	421	79	6	30.2	7.0	22.6
R82SO - Davis	NF+0.02-1	0.000	0.001	0.013	0.026	0.047	0.080	0.091	0.123	0.203	2,160	471	218	56	39.0	21.4	33.1
R83SO - Davis Dry	NF+0.02-1D	0.000	0.002	0.015	0.030	0.055	0.089	0.104	0.126	0.155	2,640	721	378	163	61.6	37.7	53.1
R83SO - Davis Wet	NF+0.02-1W	0.000	0.002	0.015	0.030	0.054	0.087	0.101	0.119	0.138	2,640	698	359	140	58.7	35.0	50.7
R84SO - Davis Dry	NF+0.015-1D	0.000	0.006	0.018	0.030	0.047	0.077	0.089	0.113	0.140	2,496	512	208	59	41.2	19.9	34.8
R84SO - Davis Wet	NF+0.015-1W	0.000	0.006	0.018	0.029	0.046	0.075	0.089	0.110	0.159	2,496	486	193	62	38.9	18.6	32.6
R86SO - Young Dry	NF×1.3-1D	0.000	0.003	0.013	0.024	0.047	0.089	0.107	0.137	0.206	2,568	597	345	175	53.7	36.2	47.7
R86SO - Young Wet	NF×1.3-1W	0.000	0.003	0.013	0.023	0.046	0.087	0.101	0.129	0.198	2,568	573	323	136	50.2	32.8	44.1
SORGHUM																	
A82SG - Dekalb	NF+0.10-1	0.000	0.001	0.010	0.023	0.055	0.145	0.160	0.185	0.223	2,040	599	557	516	79.1	76.3	78.2
WHEAT																	
A82WH - Abe	NF+0.03-1	0.000	0.002	0.015	0.027	0.047	0.079	0.094	0.113	0.149	1,344	300	130	43	24.1	12.5	19.8
A82WH - Arthur-71	NF+0.06-1	0.000	0.002	0.015	0.027	0.053	0.109	0.121	0.144	0.170	1,344	373	293	186	37.4	31.8	35.3
A83WH - Abe	NF+0.06-1	0.000	0.004	0.019	0.032	0.054	0.108	0.123	0.159	0.186	1,296	365	295	186	37.4	32.5	35.6
A83WH - Arthur-71	NF+0.06-1	0.000	0.004	0.019	0.032	0.054	0.108	0.123	0.159	0.186	1,296	365	295	186	37.4	32.5	35.6
BTI82WH - VONA	NF-1	0.000	0.011	0.025	0.034	0.042	0.057	0.064	0.072	0.098	1,464	114	2	0	7.6	0.2	6.2
BTI83WH - VONA	NF-1	0.000	0.006	0.021	0.036	0.049	0.071	0.083	0.097	0.116	864	165	51	4	12.4	4.7	9.8

**Table 5-14 (cont'd). Summary of Ozone Exposures That Are Closest to Those Predicted for 20% Yield Reduction per SUM06 Exposure Response Models Used by Lee et al. (1991) in Selected National Crop Loss Assessment Network Experiments<sup>a</sup> (Concentrations are in parts per million.)**

Experiment <sup>b</sup>	Chamber	Min.	10	30	50	Percentiles			95	99	Max	Number of Obs.	Number of Occurrences			SUM		W126 (ppm-h)
						70	90						≥0.06	≥0.08	≥0.10	06 (ppm-h)	08	
CORN																		
A81MA - PAG 397	NF+0.06-2	0.000	0.000	0.008	0.020	0.052	0.111	0.126	0.150	0.187	1,968	552	461	306	57.5	51.0	55.1	
A81MA - Pioneer	NF+0.06-2	0.000	0.000	0.008	0.020	0.052	0.111	0.126	0.150	0.187	1,968	552	461	306	57.5	51.0	55.1	
COTTON																		
R82CO - Stoneville	NF-1	0.000	0.003	0.018	0.029	0.044	0.065	0.074	0.087	0.152	2,856	390	64	7	28.2	5.8	22.7	
R85CO - McNair Dry	NF×1.99-1D	0.000	0.003	0.012	0.024	0.052	0.117	0.154	0.221	0.291	3,000	810	609	407	92.9	78.9	88.2	
R85CO - McNair Wet	NF×1.33-1W	0.000	0.003	0.012	0.024	0.041	0.073	0.091	0.129	0.166	3,000	487	226	118	41.4	23.5	35.9	
PEANUT																		
R80PN - NC-6	NF+0.015-1	0.000	0.004	0.017	0.029	0.043	0.066	0.076	0.091	0.112	2,688	369	101	5	27.2	8.8	22.0	
TOBACCO																		
R83TO - McNair 944	NF+0.020-1	0.000	0.003	0.018	0.037	0.061	0.089	0.104	0.121	0.155	1,968	611	288	117	50.7	28.4	42.6	

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Separate analyses were performed for each water stress level, dry (D) and well-watered (W).

**Table 5-15. Summary of Percentiles for Ozone Monitoring Sites in 1989  
(April through October) with a Maximum Three-Month SUM06 Value <24.4 ppm-h  
but with a Second Hourly Maximum Concentration ≥0.125 ppm**

AIRS Site	Name	Min.	10	30	50	Percentiles					Maximum Uncorrected SUM06 (ppm-h)	Number of Observ. Over 7-mo Period
						70	90	95	99	Max		
060010003	Livermore, CA	0.000	0.000	0.010	0.030	0.040	0.050	0.060	0.090	0.140	17.0	5,067
060371301	Lynwood, CA	0.000	0.000	0.010	0.020	0.030	0.050	0.070	0.100	0.140	18.1	4,793
060374002	Long Beach, CA	0.000	0.010	0.020	0.020	0.030	0.050	0.060	0.080	0.160	13.6	4,876
060375001	Hawthorne, CA	0.000	0.000	0.020	0.030	0.040	0.060	0.060	0.080	0.190	18.1	4,894
060830008	Santa Barbara, CA	0.000	0.010	0.020	0.030	0.040	0.050	0.060	0.080	0.190	17.1	4,823
060830010	Santa Barbara, CA	0.000	0.010	0.020	0.030	0.040	0.050	0.060	0.080	0.220	13.3	4,663
060833001	Santa Barbara County, CA	0.000	0.010	0.020	0.030	0.040	0.050	0.060	0.080	0.140	12.3	5,077
090010113	Bridgeport, CT	0.000	0.002	0.011	0.022	0.033	0.048	0.059	0.091	0.156	16.5	4,865
090091123	New Haven, CT	0.000	0.003	0.010	0.019	0.029	0.045	0.056	0.091	0.156	12.9	4,502
220191003	Westlake, LA	0.000	0.003	0.013	0.022	0.033	0.052	0.061	0.082	0.137	12.2	4,811
220330003	Baton Rouge, LA	0.000	0.001	0.009	0.021	0.034	0.059	0.069	0.094	0.168	17.4	4,964
220330004	Baton Rouge, LA	0.000	0.002	0.008	0.016	0.028	0.047	0.057	0.078	0.138	8.4	4,791
220331001	East Baton Rouge, LA	0.000	0.003	0.012	0.022	0.034	0.056	0.066	0.092	0.171	14.4	4,890
220470002	Iberville Parish, LA	0.000	0.005	0.014	0.023	0.034	0.057	0.068	0.093	0.149	15.9	5,040
220770001	New Roads, LA	0.000	0.001	0.011	0.021	0.033	0.052	0.062	0.083	0.141	12.0	4,964
230052003	Cape Elizabeth, ME	0.001	0.017	0.027	0.034	0.042	0.055	0.064	0.093	0.146	16.7	4,627
471630009	Kingsport, TN	0.001	0.001	0.005	0.017	0.032	0.054	0.062	0.078	0.125	13.4	4,252
481410027	El Paso, TX	0.000	0.010	0.020	0.030	0.040	0.050	0.060	0.080	0.260	14.9	4,484
481990002	Kountze, TX	0.000	0.000	0.010	0.020	0.030	0.050	0.060	0.080	0.130	10.6	4,630
482010024	Harris County, TX	0.000	0.000	0.010	0.020	0.030	0.060	0.070	0.110	0.230	19.2	4,728
482010062	Houston, TX	0.000	0.000	0.010	0.020	0.030	0.050	0.070	0.110	0.170	16.8	4,600
482011034	Houston, TX	0.000	0.000	0.010	0.010	0.030	0.050	0.060	0.100	0.220	14.0	4,595
482011037	Houston, TX	0.000	0.000	0.010	0.010	0.030	0.050	0.060	0.110	0.250	16.3	4,729
490350003	Salt Lake County, UT	0.000	0.001	0.008	0.029	0.042	0.056	0.062	0.083	0.125	17.4	4,585
490353001	Salt Lake City, UT	0.000	0.002	0.014	0.029	0.041	0.053	0.061	0.079	0.140	13.0	4,544

**Table 5-16. Summary of Percentiles for Ozone Monitoring Sites in 1989  
(April Through October) with a Maximum Three-Month SUM06 Value  $\geq$  24.4 ppm-h  
but with a Second Hourly Maximum Concentration  $<0.125$  ppm**

AIRS Site	Name	Min.	10	30	50	Percentiles				Max	Maximum Uncorrected SUM06 (ppm-h)	Number of Observ. Over 7-mo Period
						70	90	95	99			
040132004	Scottsdale, AZ	0.000	0.006	0.018	0.031	0.045	0.062	0.071	0.084	0.107	31.7	5,070
060070002	Chico, CA	0.000	0.010	0.020	0.030	0.040	0.060	0.070	0.080	0.100	33.5	4,690
060170009	South Lake Tahoe, CA	0.000	0.020	0.030	0.040	0.050	0.060	0.070	0.080	0.100	44.8	4,768
060430004	Yosemite National Park, CA	0.000	0.008	0.022	0.035	0.049	0.065	0.072	0.083	0.111	37.6	4,853
060710006	San Bernardino County, CA	0.000	0.020	0.040	0.050	0.060	0.070	0.080	0.090	0.100	70.5	4,856
061011002	Yuba City, CA	0.000	0.000	0.020	0.030	0.040	0.060	0.070	0.080	0.100	29.0	4,623
120094001	Cocoa Beach, FL	0.002	0.017	0.024	0.032	0.042	0.059	0.068	0.077	0.094	28.7	5,012
170190004	Champaign, IL	0.000	0.008	0.020	0.029	0.039	0.065	0.072	0.078	0.088	32.0	5,091
170491001	Effingham County, IL	0.000	0.009	0.023	0.036	0.046	0.063	0.070	0.081	0.104	25.3	4,600
180970042	Indianapolis, IN	0.001	0.006	0.021	0.034	0.046	0.063	0.072	0.085	0.103	25.4	4,592
240030014	Anne Arundel, MD	0.000	0.006	0.021	0.032	0.045	0.064	0.073	0.090	0.120	25.5	4,360
240053001	Essex, MD	0.000	0.002	0.010	0.024	0.038	0.059	0.069	0.089	0.121	25.2	5,028
310550032	Omaha, NE	0.002	0.021	0.030	0.037	0.047	0.062	0.067	0.075	0.098	24.9	4,160
350431001	Sandoval County, NM	0.000	0.010	0.020	0.030	0.040	0.060	0.060	0.070	0.090	25.1	5,059
360310002	Essex County, NY	0.016	0.033	0.042	0.050	0.056	0.067	0.073	0.086	0.106	45.6	4,070
370270003	Lenoir, NC	0.000	0.007	0.019	0.032	0.045	0.062	0.067	0.078	0.092	25.8	4,806
370810011	Guilford County, NC	0.004	0.010	0.023	0.034	0.046	0.063	0.070	0.083	0.113	27.7	4,853
371470099	Farmville, NC	0.000	0.010	0.023	0.034	0.044	0.062	0.070	0.083	0.100	26.4	4,833
390030002	Allen County, OH	0.000	0.007	0.022	0.032	0.043	0.060	0.068	0.086	0.107	24.5	4,854
391510016	Canton, OH	0.000	0.008	0.019	0.030	0.042	0.060	0.070	0.088	0.110	26.3	4,875
420070003	New Brighton, PA	0.000	0.008	0.021	0.032	0.043	0.062	0.070	0.087	0.102	29.4	5,055
420770004	Allentown, PA	0.000	0.003	0.016	0.028	0.039	0.060	0.070	0.087	0.102	25.1	5,040
470090101	Smoky Mountain National Park, TN	0.000	0.025	0.036	0.044	0.053	0.065	0.070	0.081	0.098	35.9	4,764
510130020	Arlington County, VA	0.000	0.001	0.010	0.023	0.037	0.059	0.071	0.088	0.116	25.7	5,029
510610002	Fauquier County, VA	0.000	0.009	0.021	0.033	0.045	0.061	0.069	0.084	0.122	24.6	5,050
511870002	Shenandoah National Park (Dickey Ridge), VA	0.004	0.027	0.037	0.045	0.054	0.065	0.071	0.082	0.100	59.0	4,454
550270001	Horicon, WI	0.002	0.019	0.029	0.037	0.047	0.062	0.070	0.088	0.111	24.6	4,142
551390007	Oshkosh, WI	0.002	0.016	0.028	0.038	0.048	0.063	0.070	0.084	0.121	27.9	4,206

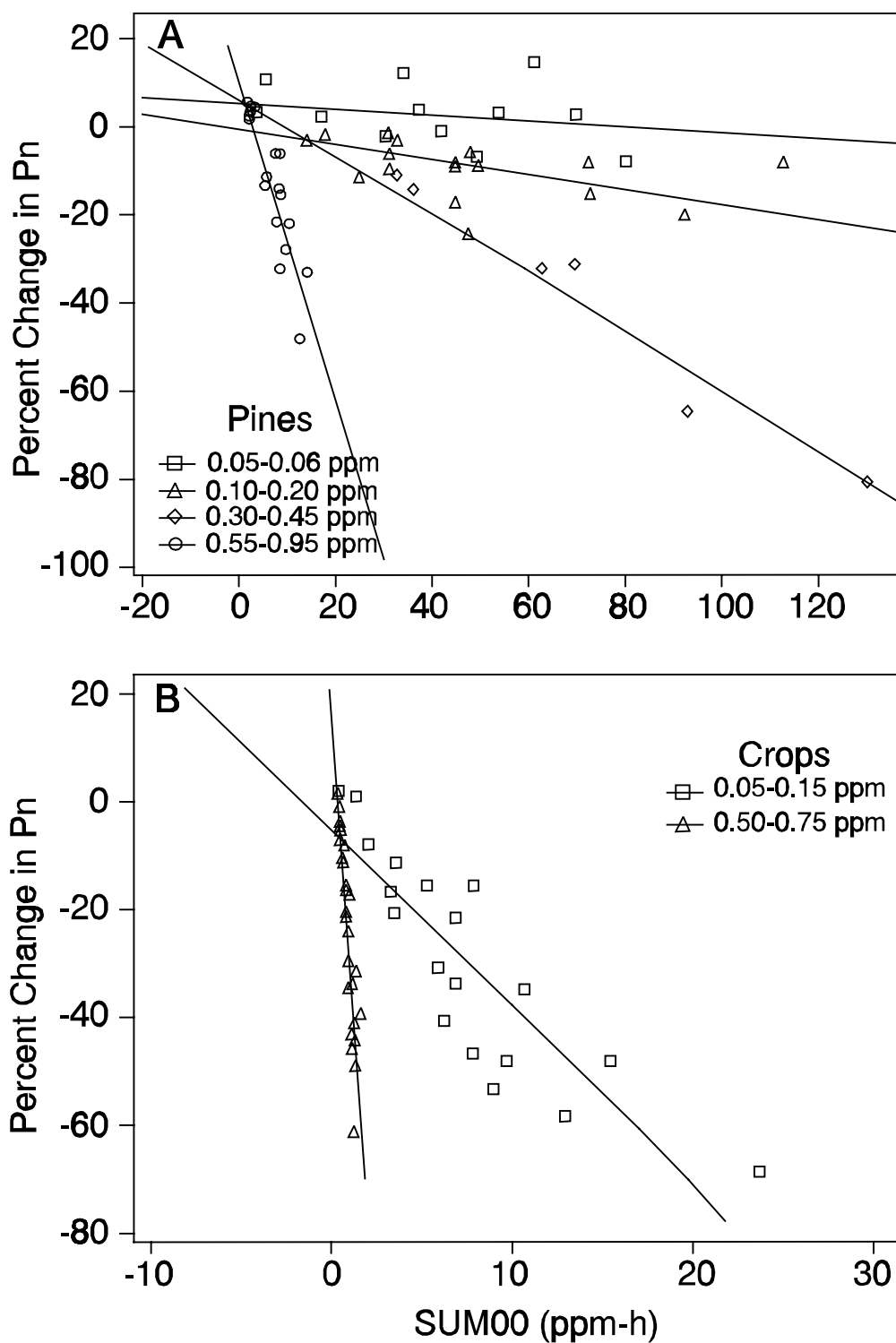
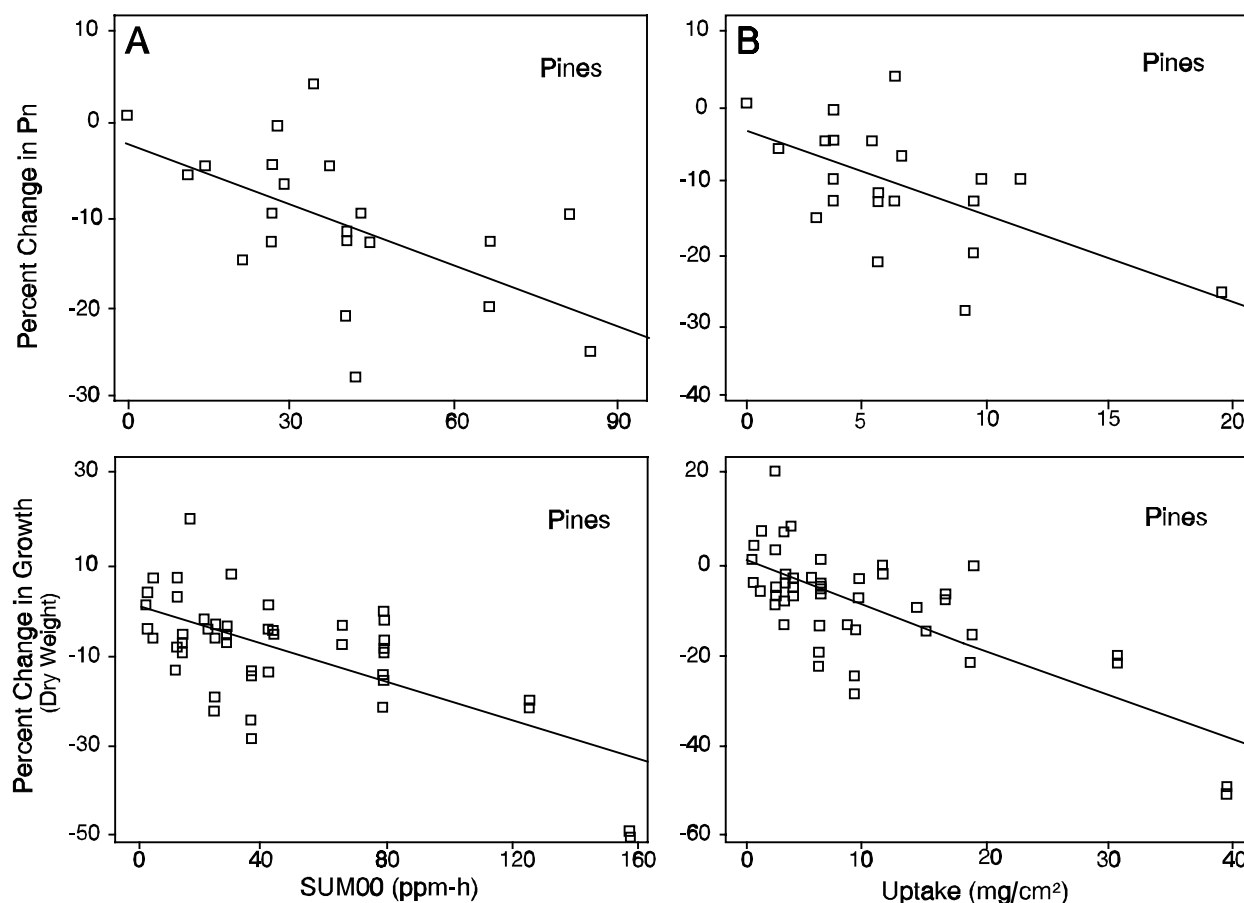


Figure 5-15. Percent reduction in net photosynthesis (Pn) of (A) pines (including one point for red spruce) and (B) agricultural crops in relation to total ozone exposure (SUM00), for several ranges of peak concentrations (Reich, 1987).

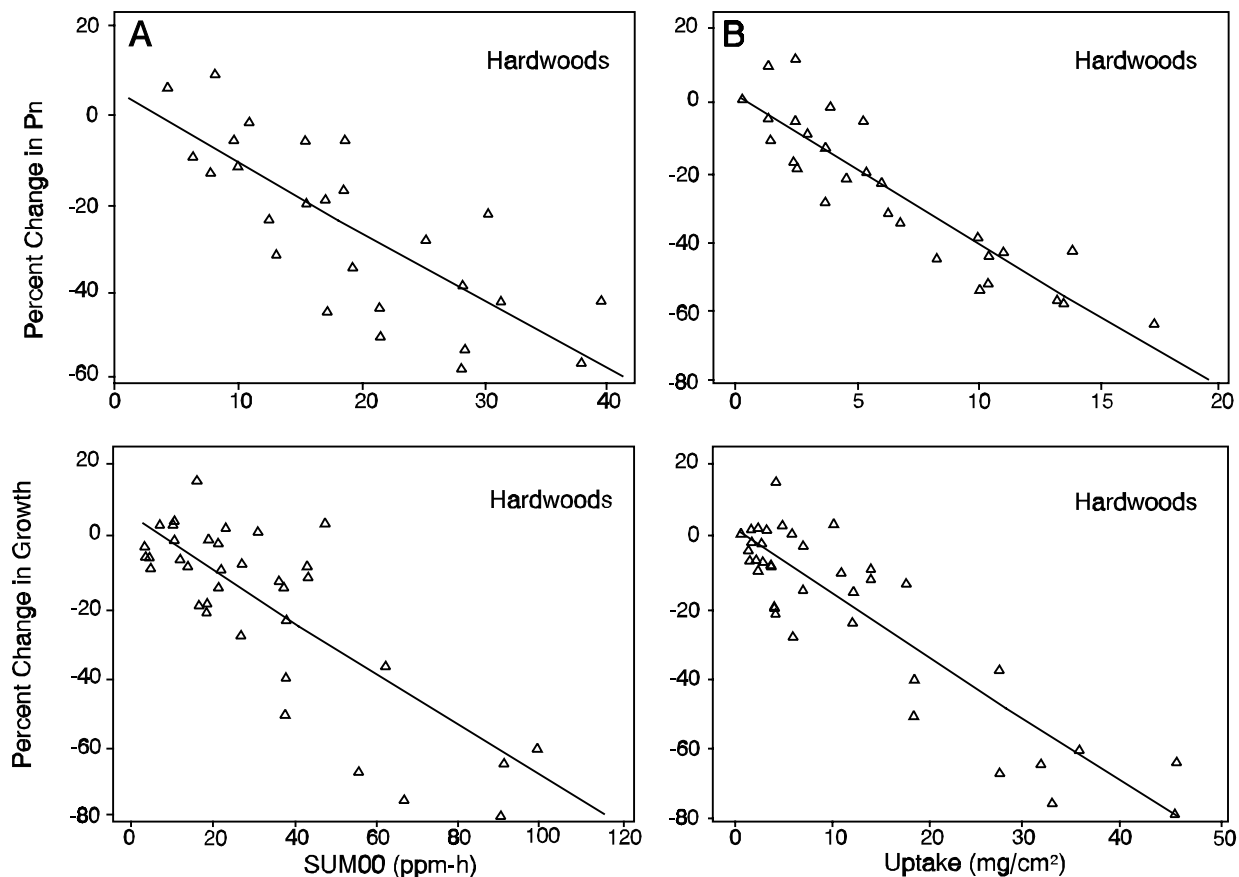


**Figure 5-16.** *Percent reduction in net photosynthesis (Pn) and biomass growth of coniferous species in relation to (A) total exposure (SUM00) and (B) estimated total ozone uptake (Reich, 1987).*

in  $O_3$  uptake. Imputed  $O_3$  uptake calculated as the product of SUM00 and mean diffusive conductance ( $k_s$ ) for each species better correlated with Pn and growth than did SUM00.

Kickert and Krupa (1991) criticized Reich's (1987) findings on the basis of insufficient reporting of statistical model parameters, possible nonnormality of Pn and growth variables, exclusion of  $k_s$  terms for imputing  $O_3$  uptake for each species, and the absence of implication for any individual plant species. However, Reich's synthesis of Pn and growth, using the SUM00 index, would not necessarily be invalidated by nonnormality of the variables. Reich's use of a mean diffusive conductance to impute  $O_3$  uptake is questionable because leaf diffusive conductance measurements vary with time of day, season, and environmental condition. In addition, the timing of an  $O_3$  exposure and stomatal conductance is of utmost importance because they determine whether a plant will respond to  $O_3$  exposure or not. Consequently, numerous measurements of conductance are required to weight hourly  $O_3$  concentrations to calculate  $O_3$  uptake over the growth of a plant.

Pye (1988) reviewed 15 studies on 26 seedling species and found reductions in biomass response increased with SUM00 (Figure 5-19). Seasonal sum of hourly



**Figure 5-17.**

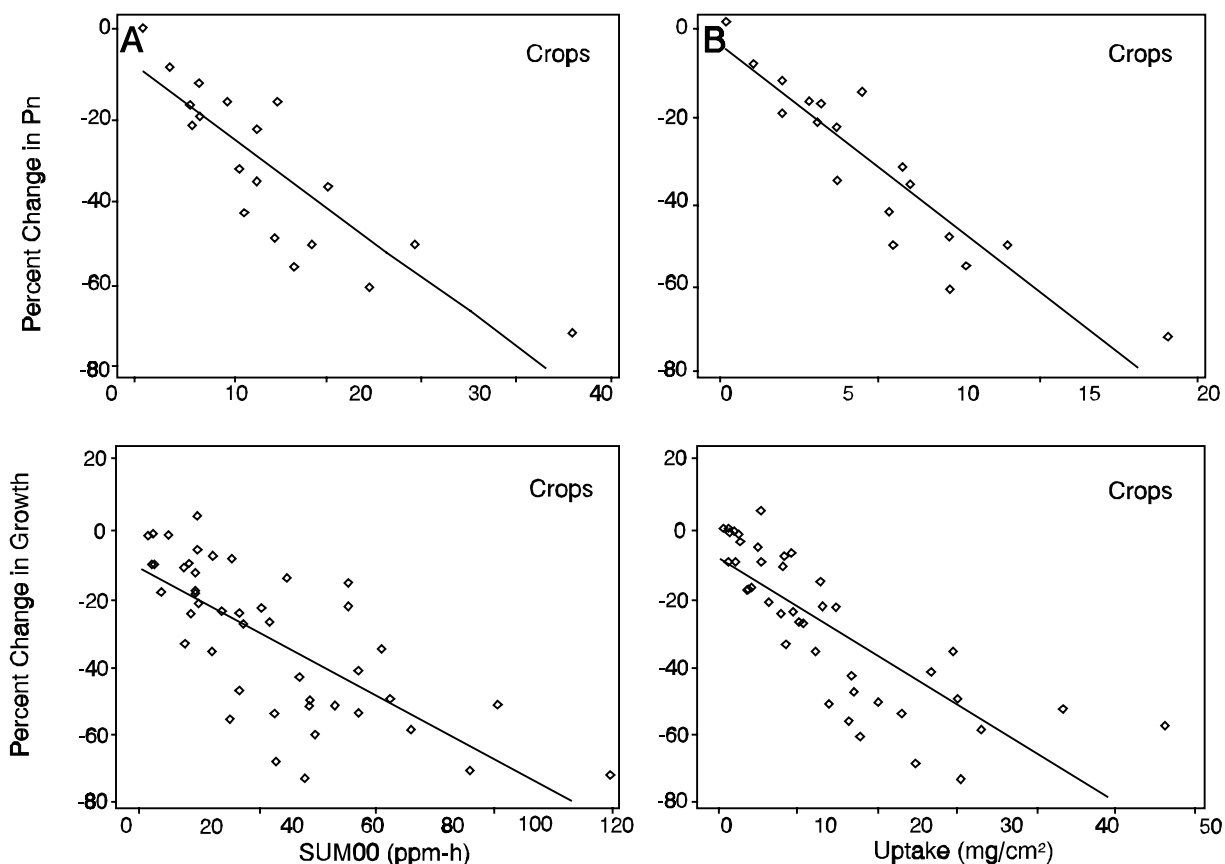
**Percent reduction in net photosynthesis (Pn) and biomass growth of hardwood species in relation to (A) total exposure (SUM00) and (B) estimated total ozone uptake (Reich, 1987).**

concentrations values ranged from 4 to 297 ppm-h. However, there was substantial variation in response. Pines, poplars, sycamore (*Platanus occidentalis*), ash, and maple (*Acer saccharum*) are all relatively sensitive. Both concentration and duration are important factors governing impact on growth and photosynthesis, but they probably are not equally important. The biomass data suggest a nonlinear response to fumigation, and the presence of convexity of response implies that for similar mean O<sub>3</sub> exposures, damage will be greater when O<sub>3</sub> concentrations are more variable.

There is limited information for assessing the relative performance of exposure indices for relating to vegetation effects. Lefohn et al. (1992a) reported that it was not possible to differentiate among the SUM00, SUM06, SUM08, and W126 exposure indices because the indices were highly correlated with one another in the experiment (Figure 5-20). However, results based on biological experiments, reported by Musselman et al. (1983, 1994) and Hogsett et al. (1985b) have shown that different exposure regimes with similar SUM00



values resulted in those exposures experiencing peak concentrations exhibiting the greater effects. The authors demonstrated that plants exposed to variable O<sub>3</sub> concentrations

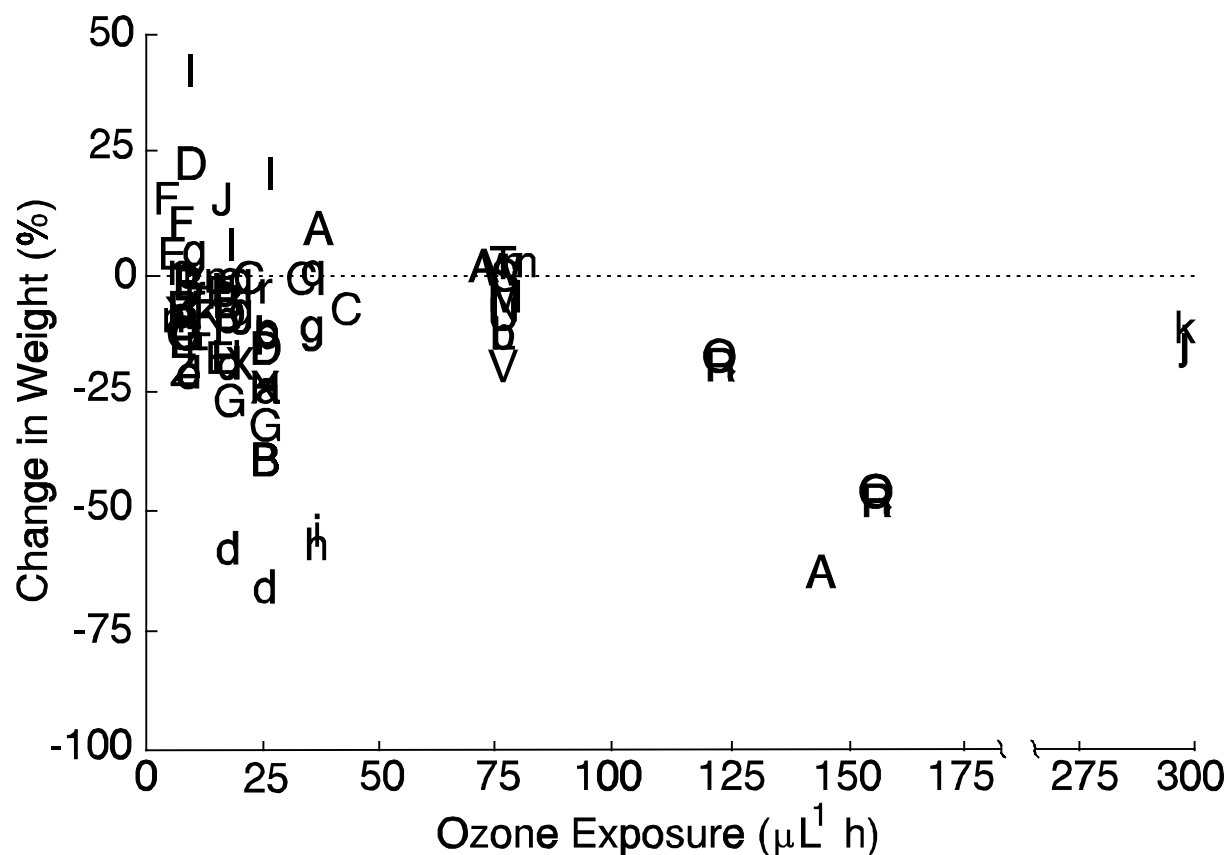


**Figure 5-18.** *Percent reduction in net photosynthesis (Pn) and biomass growth of agricultural crops in relation to (A) total exposure (SUM00) and (B) estimated total ozone uptake (Reich, 1987).*

in chambers showed greater effect on plant growth than did those exposed to a fixed or daily peak concentration of equal SUM00, but with lower peak concentrations.

Building on the above cited results of chamber studies that indicated a greater biological response to the higher hourly average concentrations, Lefohn et al. (1989) concluded that the SUM00 index did not appear to perform adequately. Using air quality data, Lefohn et al. (1989) showed that the magnitude of the SUM00 exposure index was largely determined by the lower hourly average concentrations (Figure 5-21). Figure 5-21 illustrates that the slope of the curve that described the cumulative frequency for the SUM00 index (referred to as TOTDOSE) was greater than the slope of the curve for the W126 index until approximately 0.06 ppm; thereafter, the reverse was true. This occurred because the W126 index weighted the higher concentrations more heavily than the lower ones, whereas the TOTDOSE index did not.

Supplementing the results in Lefohn et al. (1989), Lefohn et al. (1992a), using loblolly pine data exposed at Auburn, AL, to varying levels of O<sub>3</sub> over 555 days (Lefohn et al., 1992a) reported that the magnitude of the SUM00 values in the CF chamber, although



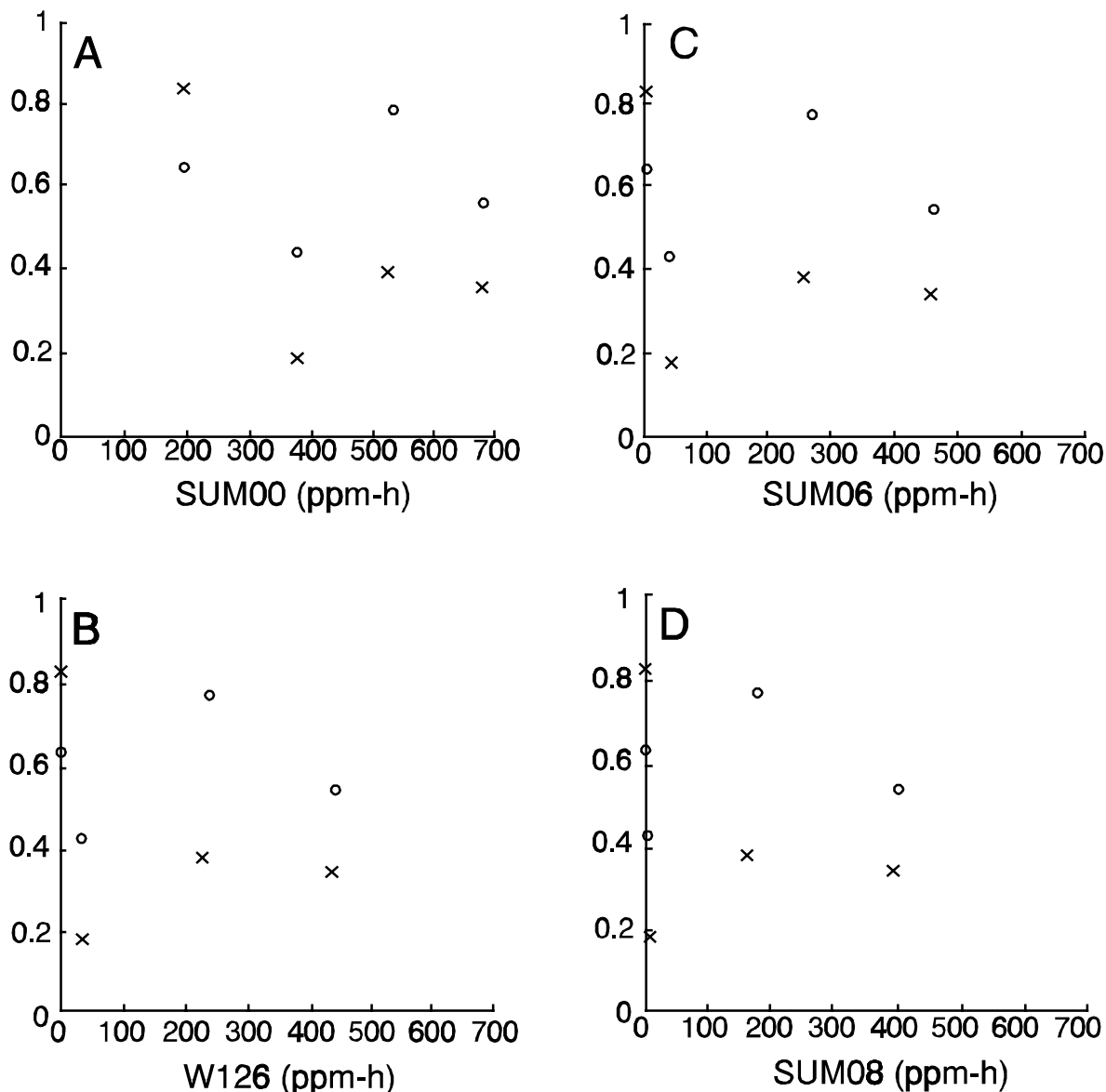
**Figure 5-19.**

***Percent reduction in biomass growth of tree seedlings in relation to total exposure (Pye, 1988).***

experiencing hourly average values greater than those at the South Pole or Pt. Barrow, AK, was about 50% less than the SUM00 values experienced at the South Pole and Pt. Barrow.

In a similar analysis using ambient data, Lefohn et al. (1992a) identified a separate set of ambient sites that experienced SUM00 values similar to those of the ambient treatments at Auburn; these ambient sites experienced fewer hourly concentrations above 0.07 ppm than did the ambient chambers. Similar to the results cited above, the authors noted that the magnitude of the SUM00 index was unable to capture the occurrence of the higher hourly average concentrations in the ambient treatments. The authors indicated that the SUM00 index was inadequate because of the observed inconsistencies of the SUM00 value between chambers and selected monitoring sites.

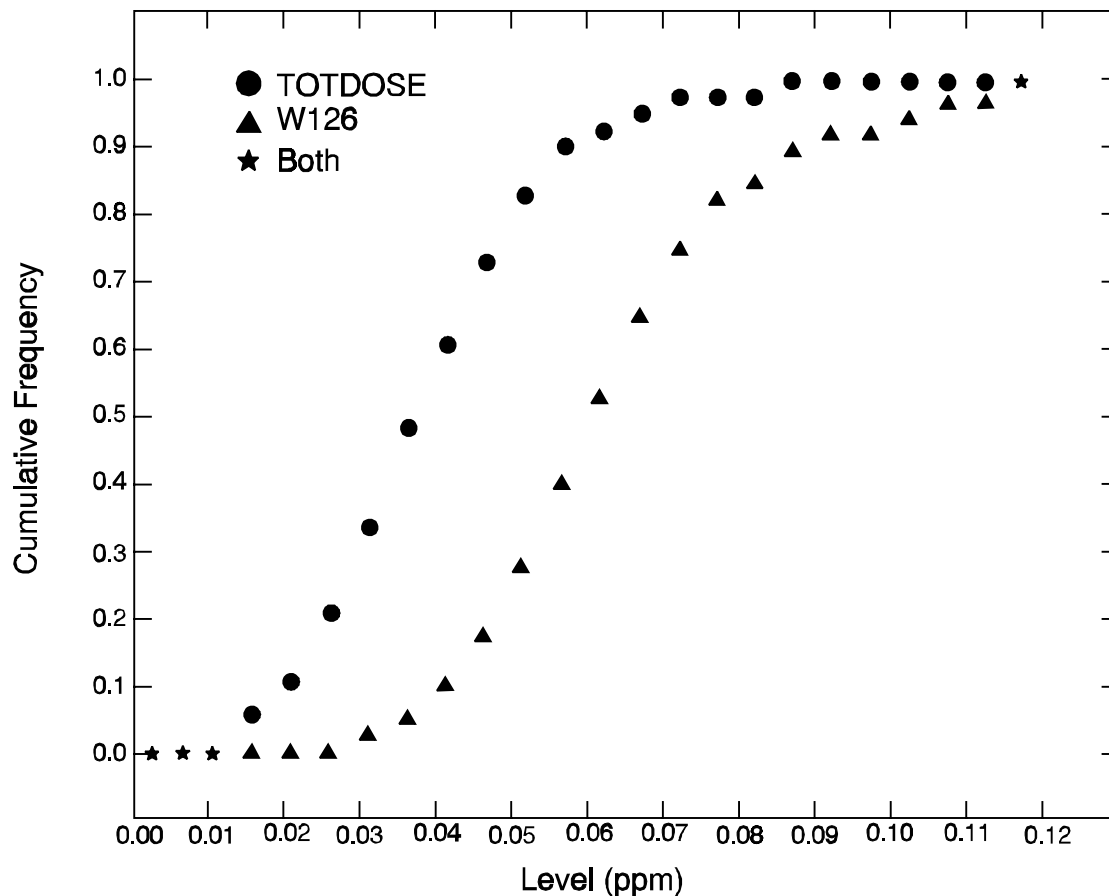
When taken by themselves, the importance of these findings may be debatable because the clean sites are not representative of loblolly growing regions, and there is no substantiating evidence of differing effects at these levels. However, the coupling of the air quality considerations, as described by Lefohn et al. (1989, 1992a), with the biological findings reported by Musselman et al. (1983, 1994) and Hogsett et al. (1985b), builds a consistent picture that the SUM00 index does not describe properly the occurrence of the higher hourly average concentrations.



**Figure 5-20.**

***Reduction in volume production of loblolly pine seedlings (family 91) in relation to four exposure indices (A through D) (Lefohn et al., 1992a).***

As noted earlier in this section (see also Section 5.4), the sensitivity of vegetation at time of exposure varies with species and is a function of several factors (e.g., soil moisture, light conditions, humidity, air turbulence). Assuming all factors are held constant (a condition not found in the ambient atmosphere), the results reported by Musselman et al. (1983, 1994), and Hogsett et al. (1985b), imply that, given any distribution of hourly average concentrations, higher hourly average concentrations should be given greater weight than lower hourly average concentrations. This statement provides only guidance concerning the potential of each hourly average concentration to affect one type of vegetation relative to



*Figure 5-21. A comparison between the resulting cumulative frequencies for the exposure parameters, sum of all hourly average concentrations (SUM00) and the sigmoidally weighted integrated exposure index, W126. The ozone data were collected in 1981 at a site located in the Mark Twain National Forest, MO, EPA AIRS site number 291230001 (Lefohn et al., 1989).*

another. This statement does not provide any insight concerning whether the magnitude of a SUM06 or a W126 value, calculated using monitoring data collected at a specific site over a specified time interval (i.e., months and hours of the day), is associated more with mid-level than high hourly average concentrations. The contribution of each range of hourly average concentrations to the magnitude of the cumulative index value is related to the distribution of the hourly average concentrations measured at the site.

#### **5.5.2.5 Comparison of Effects on Vegetation of Cumulative "Peak" Versus "Mid-Level" Ozone Exposures**

Not all studies dealing with the response of crop plants to O<sub>3</sub> exposures agree with the conclusions emphasized in the foregoing pages of this section that "higher" hourly concentrations should be given greater weight than "lower" concentrations. Based on their studies, Tonneijck (1994), Krupa et al., (1993, 1994, 1995), Grünhage et al. (1993b), and

Grünhage and Jäger (1994b) concluded that mid-level hourly average O<sub>3</sub> concentrations of 0.05 to 0.09 ppm are of greater importance than are higher hourly average concentrations in affecting vegetation.

It is clear from the studies over the years that the cumulative effects of exposure to all concentrations, peak and mid-range included, can play an important role in producing plant growth responses. The apparent difference in viewpoints is based on whether cumulative peak concentrations play a greater role in producing growth responses than do cumulative mid-range concentrations. As emphasized later, these views are based on experimental results that are not comparable. The studies that support the importance of peaks are chamber studies primarily using peak exposures, whereas the majority of the studies emphasizing that mid-range concentrations must be considered in plant response base their conclusions on both OTC and ambient field data. The key to plant response is timing because peak and mid-range concentrations do not occur at the same time. The greatest potential effect of O<sub>3</sub> on plants will occur when stomatal conductance is highest. If peaks do occur when stomatal conductance is greatest, the contribution of mid-range exposures will not be observable because they are masked. Associated with this is the importance of atmospheric conductivity (i.e., the O<sub>3</sub> concentration must reach the leaf surface if it is to be taken up by a plant).

Many studies over the years, depending on the duration of exposures and sensitivity of the plants have shown that injury to crops and other vegetation could occur when exposed to O<sub>3</sub> concentrations that ranged from 0.04 to either 0.4 or 0.5 ppm, with the higher concentration usually causing injury in the shortest period of time (Table 5-17; U.S. Environmental Protection Agency, 1978, 1986). This range encompasses both peaks and mid-range concentrations reported in the studies with the differing viewpoints cited above (Musselman et al., 1983, 1986b, 1994; Hogsett et al., 1985b; Tonneijck and Bugter, 1991; Tonneijck, 1994; Krupa et al., 1993, 1994, 1995; Grünhage et al., 1993b; Grünhage and Jäger, 1994b).

Unfortunately, the terms "high" and "low" concentrations and "peak" and "cumulative peak" concentrations are often used in publications (e.g., the majority of those cited above) without any explanation or the concentration being specified or, when specified, varying terminology has been applied with regard to what constitutes high concentrations or categories of lower values. For example, in an early paper discussing the development of vegetation effects exposure indices, Hogsett et al. (1988) termed 0.05 to 0.09 ppm as "mid-range", whereas >0.10 was considered as being "relatively high". In a recent paper, Krupa et al. (1995) term the concentrations of 0.05 to 0.09 as "moderately enhanced" and those >0.09 ppm as high. For consistency within this present review, concentrations ranging from 0.05 to 0.09 ppm are termed mid-range and those above 0.10 ppm as high or peaks.

When evaluating the results of the studies cited above, most attention has been focused on the concentrations used in the experiments (whether peaks or mid-range) by those espousing a particular viewpoint, whereas little mention has been accorded to duration of exposure, number of peaks during the exposure, whether or not there were peaks, and whether the experiments were conducted in chambers in the greenhouse, in the field, or in OTCs in the field. In the introduction to their paper, Musselman et al., (1983) describe the major problem plant scientists have encountered when attempting to relate exposures to plant responses in stating: "Pollutant dose, a quantitative description of pollutant exposure, has been defined as a product of concentration and exposure duration. The components of

**Table 5-17. Ozone Concentrations for Short-Term Exposures That Produce 5 or 20% Injury to Vegetation Grown Under Sensitive Conditions<sup>a</sup>**

Exposure time (h)	Ozone Concentrations That May Produce 5% (20%) Injury (ppm):		
	Sensitive Plants <sup>b</sup>	Intermediate Plants <sup>c</sup>	Less Sensitive Plants <sup>d</sup>
0.5	0.35 - 0.50 (0.45 - 0.60)	0.55 - 0.70 (0.65 - 0.85)	≥0.70 (0.85)
1.0	0.15 - 0.25 (0.20 - 0.35)	0.25 - 0.40 (0.35 - 0.55)	≥0.40 (0.55)
2.0	0.09 - 0.15 (0.13 - 0.25)	0.15 - 0.25 (0.25 - 0.35)	≥0.30 (0.40)
4.0	0.04 - 0.09 (0.10 - 0.15)	0.10 - 0.15 (0.15 - 0.30)	≥0.25 (0.35)
8.0	0.02 - 0.04 0.06 - 0.12	0.07 - 0.12 0.13 - 0.25	≥0.20 (0.30)

<sup>a</sup>The concentrations in parenthesis are for the 20% injury level.

<sup>b</sup>Examples of sensitive plants: oat, bean, and tobacco.

<sup>c</sup>Examples of intermediate plants: legumes, clover, and wheat.

<sup>d</sup>Examples of less sensitive plants: vegetables, woody plants, and cucumber.

Source: U.S. Environmental Protection Agency (1978, 1986).

pollutant dose are now recognized to be much more complex. Exposure concentration should consider distribution, peaks, and means, whereas exposure duration includes length of time exposed to zero concentration to indicate time intervals between exposures as well as the duration of individual exposures. Sequence and patterns of intermittent pollutant exposures also are involved when describing dose."

The papers on which the differing viewpoints are based represent attempts by the various scientists to address the problems noted in the preceding paragraph. When reading these papers, it soon becomes clear that each study is unique, some exposures were conducted in chambers in the greenhouse or in the field on plants growing in pots, and others were conducted in ambient air with plants grown in pots (See Table 5-18). None of the studies, even those in which the same scientists exposed the same plant species or cultivar, replicates a previous study. No two of the studies have exposed plants in the same manner or under similar conditions (Table 5-18). The O<sub>3</sub> concentrations, the duration, the conditions under which exposures were made, and the medium in which the plants were grown all vary. When similar exposure methods have been used, the exposures (concentration × duration [C × T]) and the plant species exposed have been different, and, when the same species or cultivar has been used, the exposure methods have been different, and plants were grown in a different medium. Therefore, the data presented in each paper were obtained under the particular set of circumstances applicable to that given study. Attempting to extrapolate the data from these studies to a broader scale causes many problems. Several of the authors of the above papers have recognized this fact (Musselman et al., 1983, 1986b, 1994; Tonneijck and Bugter, 1991; Krupa et al., 1993) and state that their studies have limited applicability,

**Table 5-18. A Summary of Studies Reporting Effects of Peaks or Mid-Range Concentrations<sup>a</sup>**

Species	Concentration (ppm)	Exposure Pattern	Exposure Duration	Methodology	Response	Reference
Kidney Bean cv. California Dark Red <i>Phaseolus</i> <i>vulgaris</i> L.	0.28 0.2 0.1-0.5 0.14-0.7	UH <sup>b</sup> UL <sup>c</sup> Simulated ambient: diurnal, variable diurnal, variable	One 6-h (0915-1515 h) exposure/week 1/3 plants: at 6 weeks; 1/3 plants: at 6 and 7 weeks; 1/3 at 6, 7, and 8 weeks plants harvested at end of exposure period	8 CSTR, in pots in soil	Greatest injury at 6 and 7 weeks; senescence at 8 weeks	Musselman et al. (1983)
Kidney Bean cv. California Dark Red <i>Phaseolus</i> <i>vulgaris</i> L.	0.3 0.4 0.06-0.3 0.08-0.4	UL "square wave" UH "square wave" Ambient, variable Ambient, variable	One 2-h (1051-1309 h) exposure/week for 6, 7, or 8 weeks One 6-h (900-1500) exposure/week 1/3 plants: at 6 weeks; 1/3 plants: at 6 and 7 weeks; 1/3 at 6, 7, and 8 weeks plants harvested at end of exposure period	8 negative pressure chambers, in pots in soil	Square wave vs. ambient: no difference in response if total dose equivalent	Musselman et al. (1986b)
Kidney Bean cv. California Dark Red <i>Phaseolus</i> <i>vulgaris</i> L.	1. 0.12 2. 0.36 peak, max 1-h avg = 0.28 3. 0.24 4. 0.24 1-h peak	Uniform Narrow-based triangle  Broad based pyramid Trapezoid	7 weeks 3 days/week 5 h daily	CSTR, 15 plants per chamber	Least injury: profiles 2 and 4 Greatest injury:  3 > 1 but less than 2 and 4	Musselman et al. (1994)
Alfalfa, <i>Medicago</i> <i>sativa</i> L.	Daily 7-h mean: 0.063, 0.064, 0.083, 0.084, peaks $\approx$ 0.2  7-h mean 0.074, 0.094, 0.099, peaks $\approx$ 0.10-0.15	Daily for 30 days: low episodic, high episodic, peaks at 1400-1500 h  30 days: low daily peak, high daily peak, peaks at 1400 h	0900-1600 h; 30 days $\times$ 5	8 OTC, in pots; alfalfa cut 3 $\times$ during exposure period	Growth reduced more for alfalfa under episodic exposures  Growth reduced less than with episodic exposures	Hogsett et al. (1985b)



**Table 5-18 (cont'd). A Summary of Studies Reporting Effects of Peaks or Mid-Range Concentrations<sup>a</sup>**

Species	Concentration (ppm)	Exposure Pattern	Exposure Duration	Methodology	Response	Reference
Tobacco cv. Bel W3 <i>Nicotiana tabacum</i> L.	Yearly mean range 1979-88: 0.025-0045	Ambient, daily not given	1 week	4 pots in soil in field: 17 locations 4 pots in soil in field: 17 locations	Foliar injury Foliar injury	Tonneijck and Bugter (1991)
	Weekly mean range 1988: 0.01-0.055	Ambient, daily not given	1 week			
Tobacco cv. Bel W3, <i>Nicotiana tabacum</i> L. Bean, <i>Phaseolus</i> <i>vulgaris</i> L. cv. Stratego cv. Groffy	Years, 1979-1983 0.005-0.15, combined in classes of 10 µg/m <sup>3</sup>	Ambient, daily not given	1 week	4 pots in soil in field: 40 locations	Foliar injury	Tonneijck (1994)
	Years 1982-1983 0.015-0.075, combined in classes of µg/m <sup>3</sup>	Ambient, daily not given	1 week	4 pots in soil in field: 10 locations	Foliar injury on Stratego	
Tobacco cv. Bel W3 Bel B <i>Nicotiana</i> <i>tabacum</i> L.	0.06-0.100	Montague weekly max	1 week	OTC (CF); OTC (NF); ambient	Foliar injury on bottommost	Krupa et al. (1993)
	0.06-0.103	Mt. Equinox weekly max	1 week	6 plants in pots in peat and Perlite 6 plants in pots in peat and Perlite	expanded leaf	

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>UH = Uniform high.

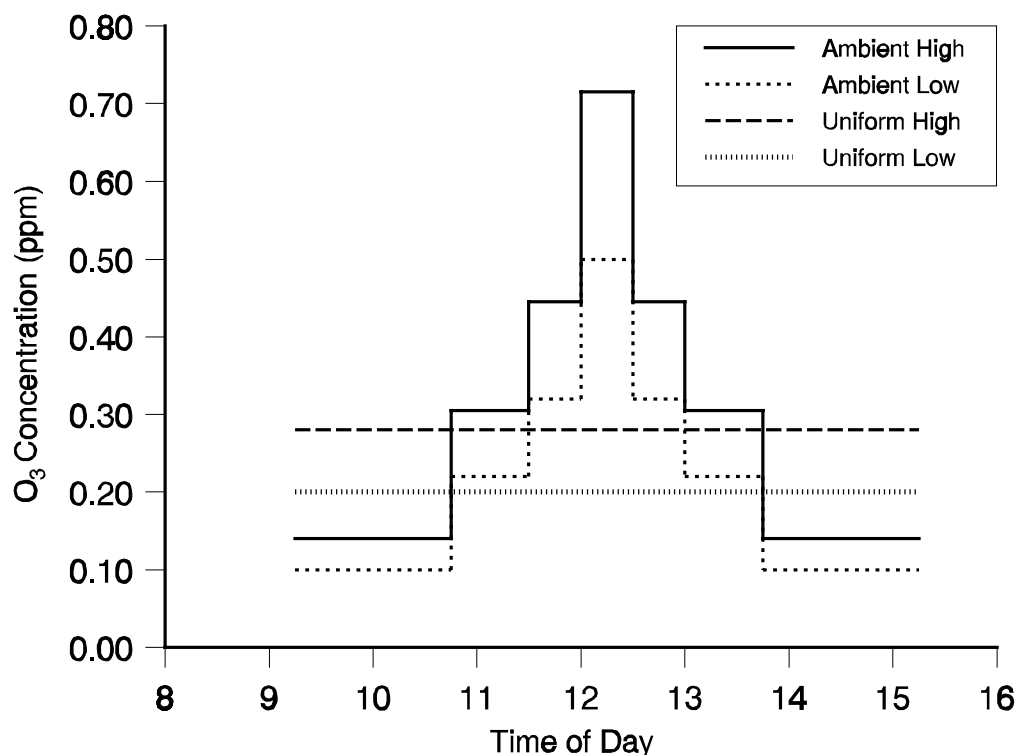
<sup>c</sup>UL = Uniform low.

and that caution should be used in applying their results on a broader scale. Had this advice been adhered to, then many apparent discrepancies in conclusions across the papers would likely not have arisen.

Musselman et al. (1983) exposed bean plants (*Phaseolus vulgaris* cv. California Red Kidney) grown in pots in soil in CSTR chambers in a greenhouse with CF air to simulated ambient O<sub>3</sub> concentration distributions specific for their region (Riverside, CA), as well as to two uniform concentration levels (Table 5-18). Plants were exposed to a 6-h O<sub>3</sub> fumigation from 0915 to 1515 Pacific Standard Time (PST) at 6, 7, and 8 weeks of age. The four exposure regimes were (1) uniform high, 0.28 ppm; (2) uniform low, 0.2 ppm; (3) variable low concentrations ranging from 0.1 to 0.5 ppm that simulated ambient exposures distributions (i.e., O<sub>3</sub> concentrations increased during the morning, peaked in the afternoon, and then decreased in the evening); and (4) variable high exposures ranging from 0.14 to 0.71 ppm that also simulated ambient concentration distributions (Table 5-18; Figure 5-22). Six days after each of the three fumigations, one-third of the plants were measured for leaflet oxidant stipple and destructively analyzed for leaf area and dry weight of plant parts. Therefore, one-third of the plants received one fumigation, the second third received two fumigations, and the remaining third received three fumigations at 6, 7, and 8 weeks of age. Simulated ambient O<sub>3</sub> distribution treatment produced significantly greater leaf injury and reduced growth and yield response than the uniform low or high exposure patterns. In addition, the simulated Riverside ambient O<sub>3</sub> concentration distribution reduced the total dry weight at both the 6- and 7-week fumigations; both pod and seed weights were reduced. The reduction in dry weights of pods resulted after the first fumigation at 6 weeks and did not change with subsequent fumigations. At 8 weeks, plants had begun to senesce. In this experiment, levels of concentration ranged from the lowest, 0.1 ppm, to the highest, 0.5 ppm. No exposure concentration, therefore, was below the "peak" level. Musselman et al. (1983) pointed out that the simulated ambient pollutant distribution used in their studies was specific for their geographic region. They also suggested that other studies determining the responses of additional species at different developmental stages to ambient O<sub>3</sub> distributions typical of other regions of the country were needed to put their findings in perspective.

Exposures in the Musselman et al. (1986b) study were designed to compare plant response to simulated ambient and uniform O<sub>3</sub> concentration distributions at two equivalent dose levels under controlled conditions (Table 5-18; Figure 5-23). Plants were fumigated in eight negative pressure chambers located within the greenhouse and received either one ambient or one uniform O<sub>3</sub> treatment during Week 6, during Weeks 6 and 7, or during Weeks 6, 7, and 8. Therefore, as in the previous study, one-third received one fumigation, the second third received two fumigations, and the other third received three fumigations. Plants were harvested 6 days after their last fumigation (Musselman et al., 1986b).

The uniform distribution in the above study was selected so that the constant concentration matched the total dose and peak concentration of the ambient distribution. Matching the peak concentration and the total dose required that plants exposed to the uniform distribution be exposed to the peak concentration (either 0.3 or 0.4 ppm) during the entire fumigation period, whereas plants in the ambient distribution were exposed to the same peak for only half an hour. The O<sub>3</sub> concentrations during the ambient exposure distribution had a fluctuating rising and falling pattern and were of longer duration overall, and the time of the peak exposure was shorter when compared with the uniform O<sub>3</sub> concentration



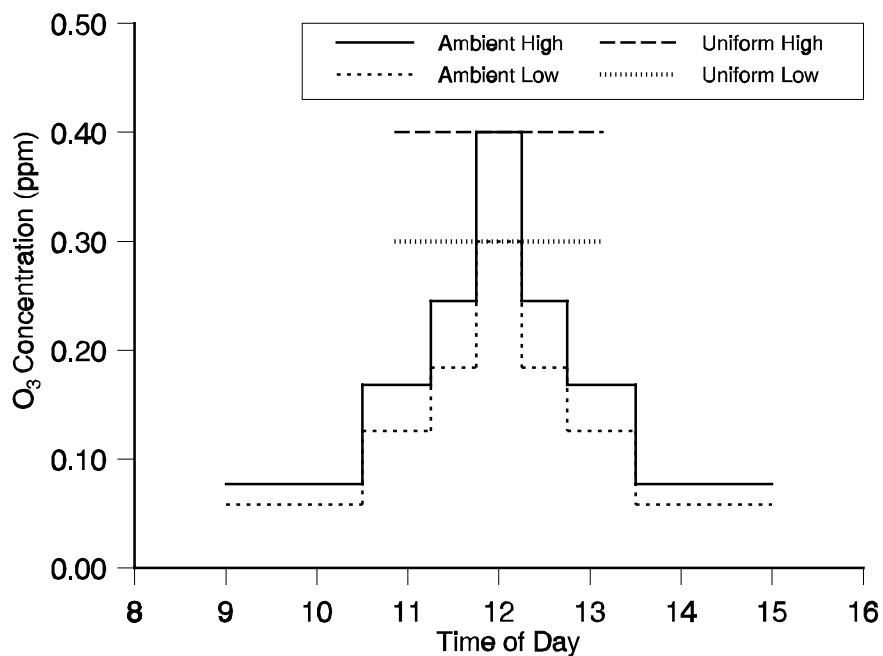
**Figure 5-22.** *Fumigation schedule of uniform and simulated ambient ozone ( $O_3$ ) concentration distributions at two equivalent dose levels.*

Source: Musselman et al. (1983).

treatment. Total exposure time for the uniform distribution was 2 h and 18 min, and, for the ambient distribution, it was 6 h (Figure 5-23). Simulated ambient  $O_3$  concentrations for the low dose ranged from 0.058 to 0.30 ppm, and for high dose, from 0.077 to 0.40 ppm.

The authors point out that ambient air quality data are generally reported as hourly average concentrations, and the dynamics of changes in  $O_3$  concentrations during the hour are not considered in the summaries of air quality data, although these have been considered important in plant response. They also state that the results of this experiment demonstrate that, when peak  $O_3$  concentrations and total dose are equivalent, the shape of the  $O_3$  distribution (normal versus square wave) had no effect on the magnitude of response. Beans responded similarly to both an ambient and a uniform  $O_3$  concentration distribution. No significant difference in injury, growth, or yield was observed. The authors conclude with the statement that "Further research is needed to examine whether peak concentration is the most important component of the concentration distribution causing plant response" (Musselman et al., 1986b).

In a further attempt to determine the response of plants to different exposure profiles but equal total exposures ( $C \times T$ ), Musselman et al. (1994) exposed the same bean cultivar, California Red Kidney, grown as in the previous studies, in CSTRs in a CF greenhouse to four different profiles having the same total cumulative exposure and the same

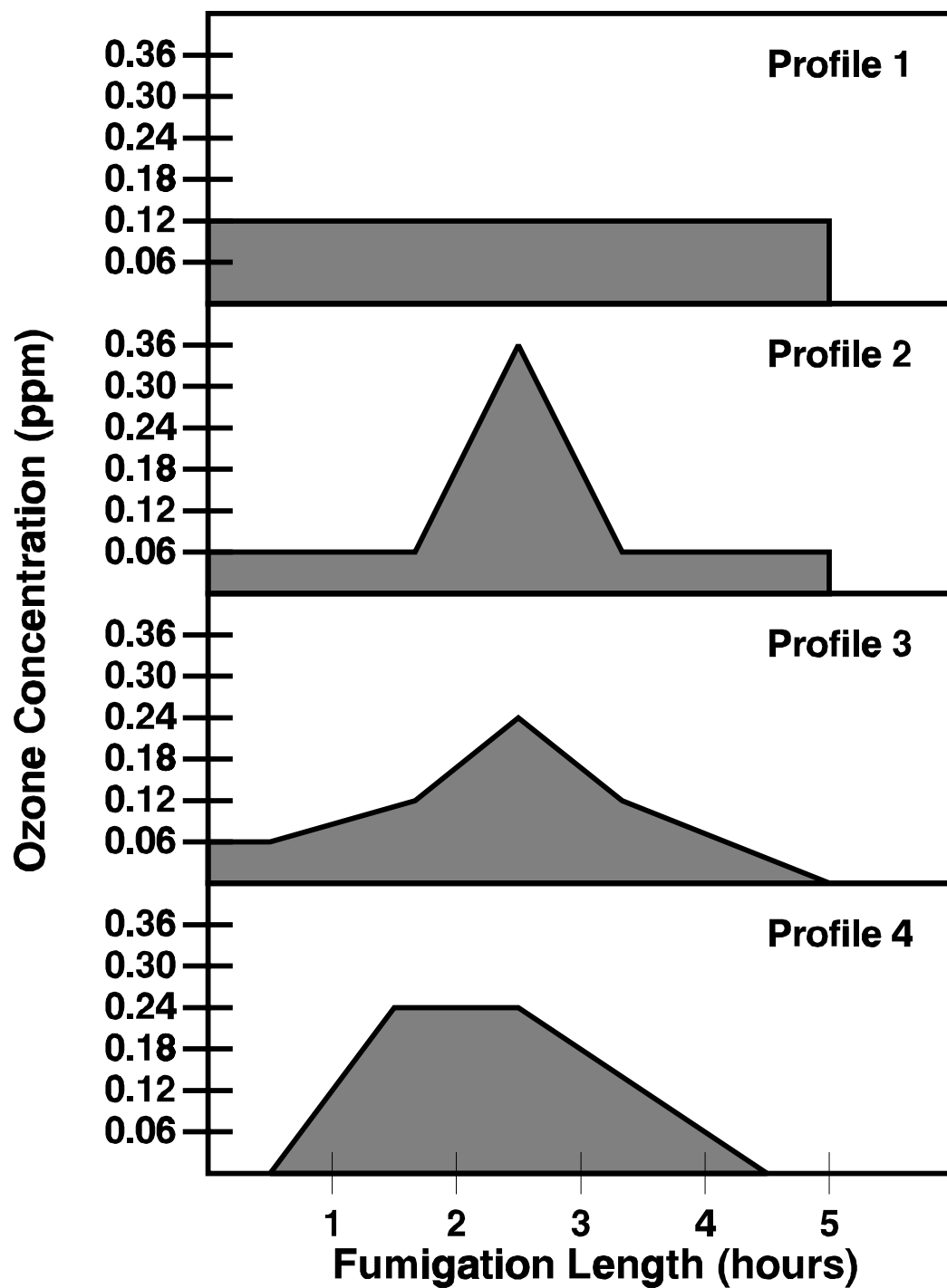


**Figure 5-23.** *Fumigation schedule of uniform and simulated ambient ozone (O<sub>3</sub>) concentration distributions at two dose levels.*

Source: Musselman et al. (1986b).

7-, 12-, and 24-h seasonal means (Table 5-18; Figure 5-24). Ozone exposures began 21 days after germination. Plants were exposed for approximately 5 h, three times a week over the seven-week growing season. The first profile used was a "square-wave" concentration of 0.12 ppm; the second exposure resembled a narrow-based triangle, during which the O<sub>3</sub> concentrations rose rapidly to a peak of 0.36 ppm with a maximum 1-h average of 0.28 ppm and then dropped off rapidly; the third profile was in the shape of a broad-based pyramid, during which the O<sub>3</sub> concentration rose slowly to a peak of 0.24 ppm and then slowly dropped off; the fourth profile rose rapidly to a plateau with a peak of 0.24 ppm that lasted for 1 h and then dropped off slowly. The maximum 1-h average concentrations of 0.22 ppm for Profiles 3 and 4 simulated the more typical summer patterns for Southern California, where hourly peaks of >0.2 ppm occurred with regularity. Each of the last three profiles had the same total O<sub>3</sub> exposure, but at least 1 h of each daily exposure had at an average peak concentration that exceeded 0.12 ppm.

Significant differences were found for all measured variables. Plants exposed using the 0.12-ppm square-wave exposure (Profile 1) exhibited the least injury. Profile 3, with the mean hourly pyramidal peak of 0.22-ppm exposure, exhibited significantly less necrosis than did Profiles 2 and 4, which also had peak exposures. Plants responded similarly to Profiles 2 and 4. There were no significant differences in plant responses for any of the measured response variables, even though the mean 1-h peak for Profile 2 (0.28 ppm) was higher than the 1-h peak mean (0.22) for Profile 4. Both of these profiles had higher peaks or a longer duration of high concentrations, those above 0.16 ppm, than did



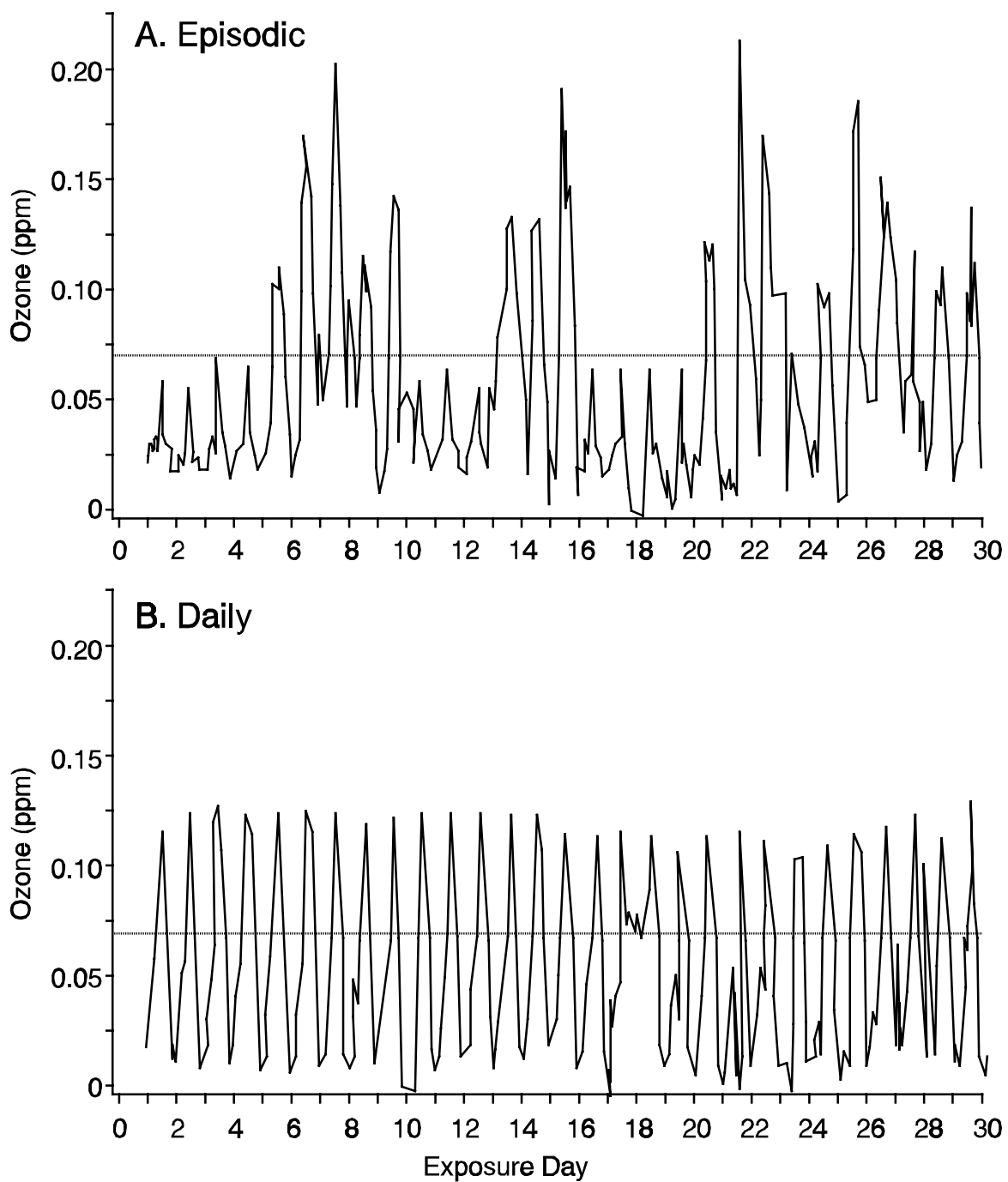
*Figure 5-24. Experimental ozone exposure profiles.*

Source: Musselman et al. (1994).

Profile 3. The three exposure profiles that incorporated peaks impacted plant response more severely than the steady-state profile, thus providing evidence of the importance of peak concentrations in defining an exposure index (Musselman et al., 1994). Total exposure, however, could not relate O<sub>3</sub> impact to plant response unless the exposure shape was held constant. The authors caution against the application of summary exposure statistics that do not give increased weight to higher concentrations for comparison of plant response in areas with differing exposure regimes. In addition, the authors state that, for Southern California, which experiences high peak O<sub>3</sub> levels, a descriptor of exposure that gives greater weight to peak concentrations is more useful when relating plant response to O<sub>3</sub> exposure. They also suggest that environmental conditions may influence stomatal conductance and O<sub>3</sub> uptake. Therefore, summary statistics might necessitate the inclusion of other parameters that relate to environmental factors. Finally, it is suggested that flattening out concentrations so that peaks remain lower than 0.10 ppm might be expected to benefit the vegetation of Southern California. Again, it should be noted that in all of the studies by Musselman et al. (1983, 1986b, 1994) peaks greatly exceed those in any of the other exposure studies.

The experiments of Hogsett et al. (1985a) were the initial studies using a newly designed modified OTC, with an automated control system in which plants were exposed to simulated ambient concentrations typical of the midwest. In the study, alfalfa and tall fescue growing in pots were exposed to generator-produced O<sub>3</sub> in OTCs using two different types of exposure profiles (Table 5-18). Concentrations used were based on a 1978 Storage and Retrieval of Aerometric Data (SAROAD) database for a selected midwestern site where a substantial acreage of hay was grown. This study used the longest exposures of any of the papers reviewed. The first exposure was a 30-day episodic profile of varying peak frequency, concentration, and duration; a profile that was repeated every 30 days throughout the growing season (Table 5-18; Figure 5-25). The second exposure was a daily peak profile of equivalent peak concentration and duration each day. Daily 7-h exposures of alfalfa were from 0900 to 1600 hours (9 a.m. to 4 p.m.) for the 133-day growing season. Episodic 7-h mean concentrations ranged from 0.064 to 0.084 ppm, with peaks of nearly 0.2 ppm occurring at 1400 to 1500 hours, whereas the profile for the mean daily peak concentrations varied from 0.074 to 0.099 ppm, with peaks ranging between 0.10 to 0.15 ppm occurring at 1400 hours. Reduction in alfalfa growth was reported under both exposure profiles; however, response to the episodic exposures was greater. Actual response data is not given in the paper. The response of tall fescue was reduced only slightly over a period of 90 days when exposed to either regime. Both alfalfa and fescue were cut three times during the exposure period. This is the only study exposing a perennial plant, alfalfa, and a grass. The growth habit of grasses differs from that of dicotyledonous plants because the growth of each leaf blade results from a meristem at the base of the leaf, not from the apical meristem. Therefore, cutting or injury to the leaf blade does not prevent its continued growth. Of the papers cited, this OTC experiment is the only long-term study in which plants were exposed to both mid-range and peak concentrations. The fluctuating episodic O<sub>3</sub> pattern in the Hogsett et al. (1985b) and the single 6-h/week exposure of the Musselman et al. (1983, 1986b) studies permit plants a brief recovery period between exposures to peak concentrations. Also, in the above studies, plant response to O<sub>3</sub> exposure resulted in a reduction in growth, whereas, in the studies discussed below, foliar injury is the plant response observed.

Tonneijck and Bugter (1991), Tonneijck (1994), and Krupa et al. (1993) were reviewed by Krupa et al. (1995) who cited these Bel W3 studies in support of the concept



**Figure 5-25.** *Ozone exposure profiles for the 1983 season.*

Source: Hogsett et al. (1985b).

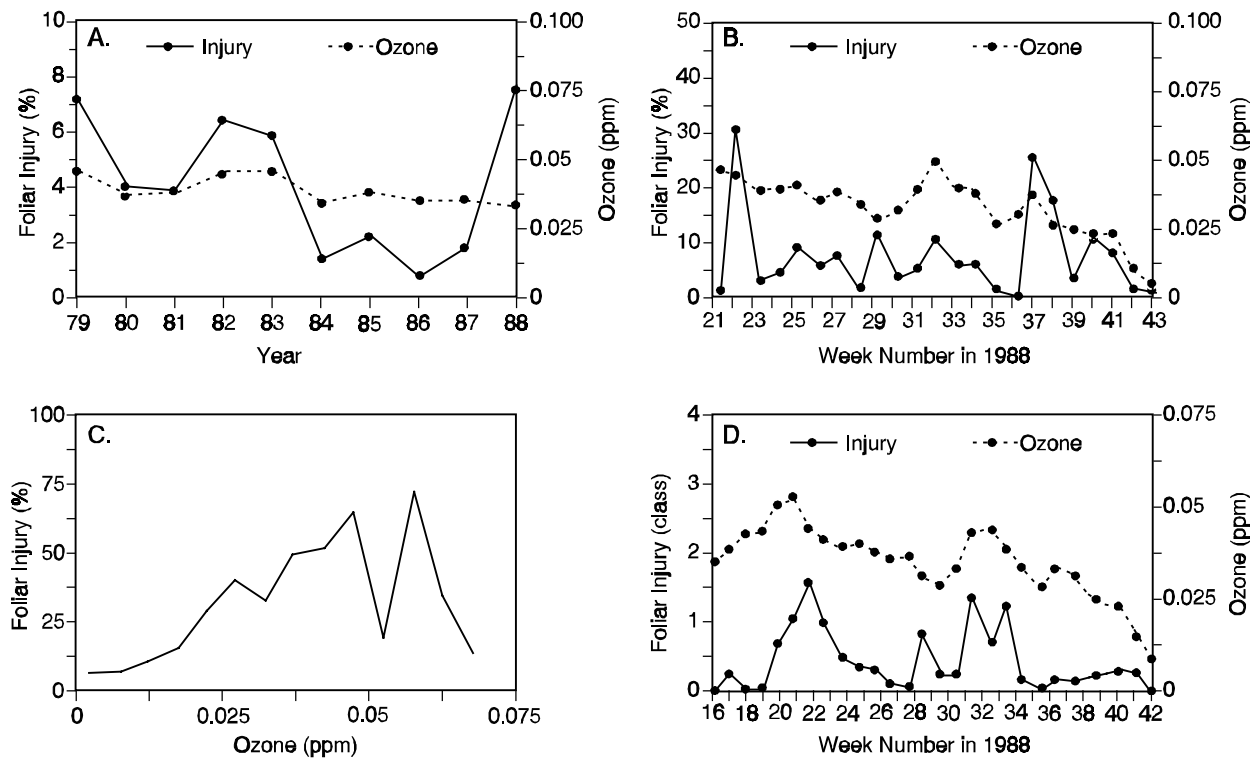
that "mid-range" concentrations (0.05 to 0.09 ppm) play a greater role than peak concentrations in causing plant response (Figures 5-5, A, B, and D, and 5-6). Bel W-3, is a variety of tobacco noted for its sensitivity to O<sub>3</sub> and has been used as a sensitive monitor for photochemical ambient air pollution for many years. Visible foliar injury is a clear and unequivocal indication of O<sub>3</sub> exposure. Heggstad and Middleton (1959) discovered Bel W3 and first reported on its sensitivity to O<sub>3</sub>. Heggstad and Menser (1962), Heck et al. (1969) and Heck and Heagle (1970) all reported its value as a sensitive monitor of photochemical ambient air pollution. Both Heck et al. (1969) and Heck and Heagle (1970) reported, however, that there was no consistent relationship between oxidant values (O<sub>3</sub> concentrations measured as total oxidants) and foliar injury. They state, however, that a monitoring system such as they describe can provide a community with estimates of the frequency of phytotoxic levels of oxidants, of the relative severity of each episode, and of regional distribution of phytotoxic air pollution (Heck and Heagle, 1970).

The papers of Tonneijck and Bugter (1991) report on observations made in the Netherlands from 1984 to 1988, during which Bel W3 was used as a part of an extensive network for monitoring the effects of ambient air pollution along with the O<sub>3</sub>-sensitive indicator plant subterranean clover cv. Geraldton (*Trifolium subterraneum*).

Indicator plants grown in the greenhouse in pots were taken to 17 field locations at weekly intervals and were exposed to ambient air for 1 week for Bel W3 tobacco and 2 weeks for clover. Foliar injury on the tobacco Bel W3 cultivar used in 1988 was greater than that on the variety used during the years 1984 through 1987 (Figure 5-5A), although mean O<sub>3</sub> concentrations to which the varieties were exposed were similar (Figure 5-26, B). The increased injury appeared to be associated with the new line of "relatively sensitive" tobacco used in 1988 when compared with the "rather tolerant" strains used from 1984 to 1987. Exposures were reported as mean weekly O<sub>3</sub> concentrations, 24-h means, daytime average concentrations, number of hours >80 µg m<sup>-3</sup> (≈0.04 ppm), and cumulative dose of hourly values >120 µg m<sup>-3</sup> (≈0.06 ppm). No peak concentrations were listed. The highest effect intensity, a mean O<sub>3</sub> concentration of 100 µg/m<sup>3</sup> (≈0.05 to 0.06 ppm), was observed during Week 22 of the exposures at the field site in 1988 (Figure 5-26, B). The mean O<sub>3</sub> concentration was the highest in Week 32.

The authors state that "foliar injury on tobacco Bel W3 was poorly related to the ambient ozone in the Netherlands" (Figure 5-26, A, B, and C), whereas foliar injury on subterranean clover correlated well with O<sub>3</sub> exposure concentrations (Figure 5-26, D). Ozone exposure indices emphasizing the importance of peak values did not correlate better with injury than those based on mean values (Figure 5-26, E). Even though no peaks, as previously defined above, were listed in their paper, foliar injury of tobacco was observed. Tobacco plants appeared to be "relatively" more sensitive to O<sub>3</sub> than did clover at the end of the season. The main reason for using Bel W3 was to demonstrate the occurrence of symptoms induced by O<sub>3</sub> and "not to examine the relationship between the level of ambient ozone and foliar injury intensity," as stated by Tonneijck and Bugter (1991). These authors further noted that care should be taken when comparing the responses of both species because of the difference in length of exposure and effect parameter. Even when both species of plants were exposed to ambient air at the same location for the same length of time (7 days), foliar injury on tobacco was not related to foliar injury on primary leaves of bean plants. Finally, the authors state, "From these results, it can be concluded that ozone injury on tobacco Bel W3 does not adequately indicate the concentration of ambient ozone nor is it a good indication of the risk of ozone to other plant species or to vegetation as a



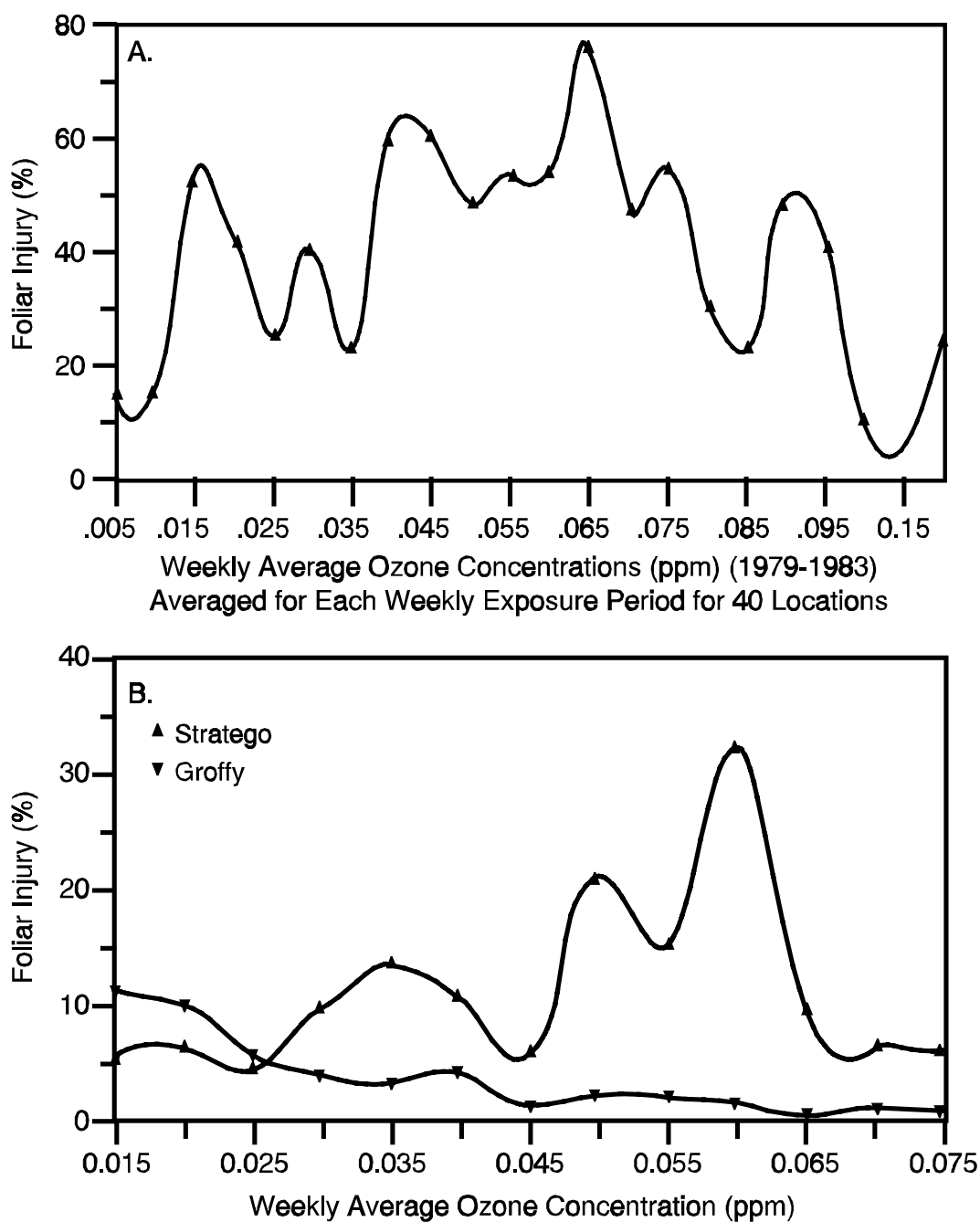


**Figure 5-26.** (A) Mean foliar injury on tobacco Bel W3 and mean ozone ( $O_3$ ) concentrations for the years 1979 to 1988, (B) mean foliar injury on tobacco Bel W3 and  $O_3$  concentrations for weekly exposures during the 1988 growing season, (C) maximal foliar injury on tobacco Bel W3 in relation to  $O_3$  concentrations for 1988, and (D) mean foliar injury on subterranean clover cv. Geraldton and mean  $O_3$  concentrations for two weekly exposures during the 1988 growing season.

Source: Tonneijck and Bugter (1991).

whole" (Tonneijck and Bugter, 1991). In other words, Tonneijck and Bugter (1991) concur with the reports of Heck et al. (1969) and Heck and Heagle (1970), who much earlier had reported similar views based on the results of their studies. Also, in their studies they observed that ratios of weekly tobacco injury indices to oxidant indices at an oxidant-monitoring site revealed no consistent relationship between weekly oxidant concentrations and weekly plant injury. In addition, they observed that, although considerable new injury was recorded each week of the season, the relationship between oxidant values and plant injury was not consistent. In other words, data from Bel W3 exposures is not a good basis from which to make extrapolations.

Tonneijck (1994) used data from the Dutch monitoring network for the years 1979 to 1983 (Figure 5-27, A) for Bel W3 and from 1982 to 1983 (Figure 5-27, B) for two bean cultivars, the  $O_3$ -sensitive "Stratego" and the  $O_3$  tolerant "Groffy", to evaluate injury-response relationships among certain indicator plants. Various  $O_3$  exposure indices were



**Figure 5-27.** (A) Maximum foliar injury (percent of leaf area affected) on tobacco *Bel W3* in relation to ozone ( $O_3$ ) concentrations expressed in classes of  $10 \mu\text{g}/\text{m}^3$  for 1979 to 1983, and (B) maximum foliar injury (percent of leaf area affected) on two bean cultivars in relation to  $O_3$  concentrations for 1982 to 1983.

Source: Tonneijck (1994).

calculated from hourly O<sub>3</sub> concentrations for all exposure periods. Data of foliar injury to Bel W3 tobacco based on 20 to 22 weekly observations for 5 years (1979 to 1983) at 40 locations (Figure 5-27, A) were regressed against several exposure indices. Results of correlation analysis indicated that the weekly sum of all hourly concentrations >40 µg/m<sup>3</sup> (0.02 ppm) has a negligibly better linear association with maximum weekly foliar injury response than does the 24-h mean. Tonneijck (1994) does not present strong evidence in favor or against the importance of mid-range concentrations in causing foliar injury response due to low correlations (<0.28). The role of mid-range concentrations is difficult to substantiate using correlation analyses because the effects of O<sub>3</sub> on maximum foliar injury response are not linear (Figures 5-27, B and C) and are confounded with environmental factors. Tonneijck stated that the results of the Dutch monitoring network generally do not support the conclusion that hourly concentrations of ambient O<sub>3</sub> above 80 to 120 µg/m<sup>3</sup> (0.05 to 0.06 ppm) may be relatively more important in causing tobacco injury. Problems with weak associations between weekly pollutant concentrations and visible foliar injury that make the ability to discriminate among exposure indices difficult, which were reported by Tonneijck (1994), also were experienced by Tonneijck and Bugter (1991) and Heck et al. (1969), and Heck and Heagle (1970).

Based on his study, Tonneijck (1994) concluded that "the greatest injury to the ozone-sensitive indicators, tobacco Bel-W3 and bean cv. Stratego, seems to occur at moderate levels of ambient ozone." At relatively high O<sub>3</sub> concentrations (>115 to 135 µg/m<sup>3</sup>; ≈0.055 to 0.065 ppm), less injury was observed than at "moderately enhanced concentrations". Results of the above study do not support the "concept that higher O<sub>3</sub> concentrations should be given more weight in terms of plant response than lower ones, since higher concentrations do not necessarily cause greater effects." In Figure 5-27, A, it can be noted that foliar injury on Bel W3 tobacco did not increase even when O<sub>3</sub> concentrations neared 0.15 ppm. However, the manner in which the data in the above study is presented makes it difficult to determine the actual concentrations to which the plants were exposed.

In neither the Tonneijck and Bugter (1991) nor Tonneijck (1994) papers are the actual O<sub>3</sub> concentrations to which the plants were exposed stated, except as mean values. Also, the terms "peak", "moderate", "moderately enhanced", and "circa" are used, but never defined. The problems associated with attempting to make extrapolations from Bel W3 have already been mentioned. In addition, Posthumus (1984) points out, in a paper describing the Dutch monitoring program, that plants grown in the greenhouse may be "more vulnerable" to ambient air pollutants than are crops grown in the field because those grown in a greenhouse have been grown under ideal circumstances.

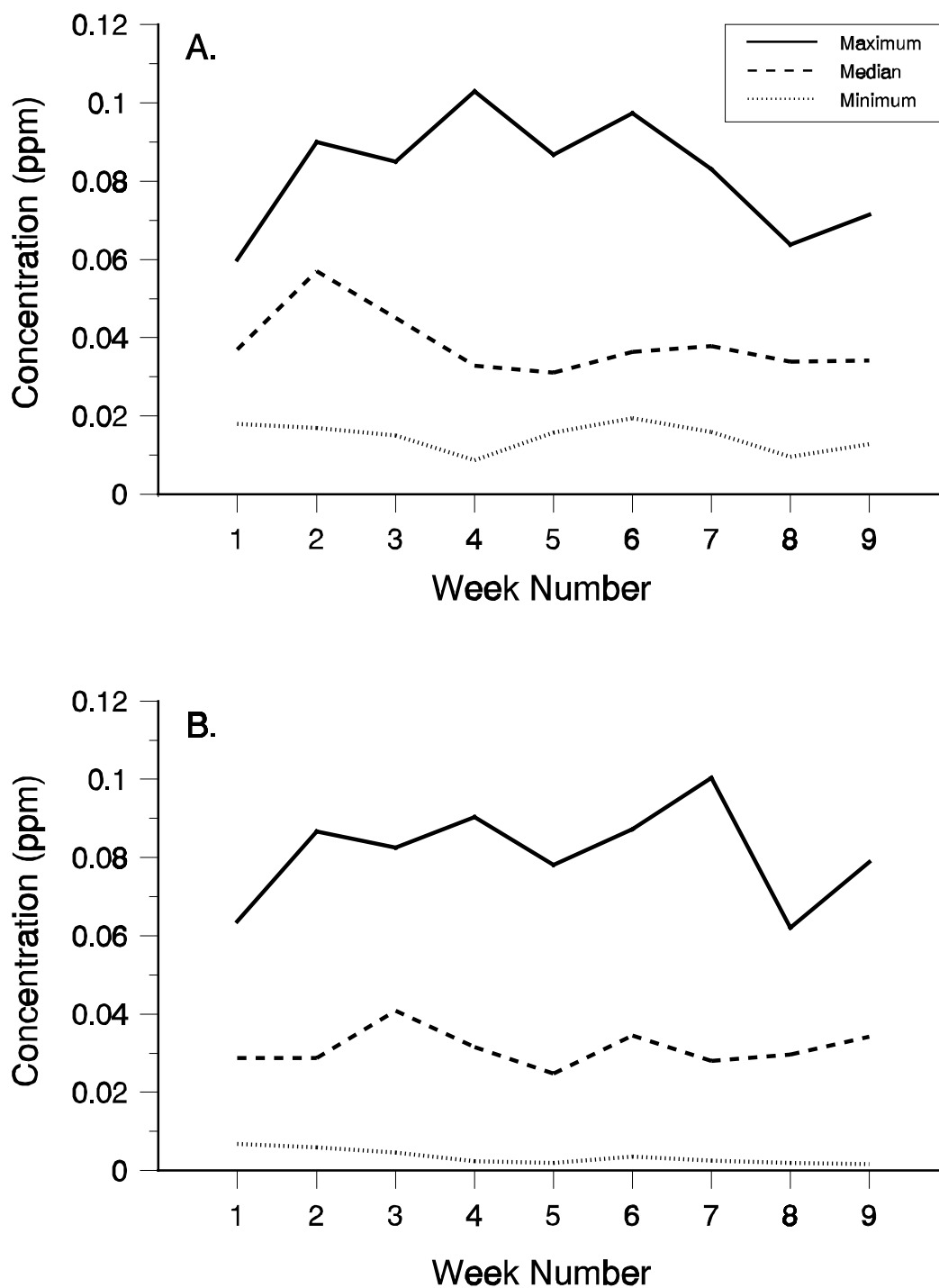
Krupa et al. (1993) used two tobacco cv. (the sensitive Bel W3 and the tolerant Bel B) as differential indicators of ambient O<sub>3</sub> pollution. When reviewing previous studies in the introduction to their paper, Krupa et al. (1993) mention that the tobacco cultivars Bel W3 and Bel B have been used for over 25 years and indicate that other studies using Bel W3 have produced conflicting results. The aim of their present study was to further examine this subject. Seedlings of the two cultivars grown in pots containing Fafard Mix No. 2 (screened peat + Perlite) in CF air and fertilized every 7 days with liquid fertilizer until the day prior to exposure were transferred to the two field sites when each set of plants reached its "true four-leaf stage" after removing the two juvenile leaves. Exposures to ambient O<sub>3</sub> concentrations were made at two different sites (near Amherst, MA, and in the Green Mountains of southern Vermont) from mid-June to August during the 9 weeks of the study (Figure 5-28, A and B). Ambient O<sub>3</sub> concentrations were measured continuously. Exposures occurred in an OTC with

CF air, an OTC with NF air, and a chamberless ambient-air field plot (Table 5-18). There were two replicates per treatment, with six plants of each cultivar in each replicate. Visual estimates of leaf area showing O<sub>3</sub> injury were made, beginning with the bottommost fully expanded leaf (leaf no. 1) at the end of each weekly exposure. Ratings were given a value from 1 to 10. A new set of plants was exposed each week. Maximum hourly average concentrations for the 9-week period ranged from 0.06 to 0.1 ppm, with the highest concentrations occurring during week seven.

Observations, based on foliar injury scores, indicated that injury to leaves no. 1 and 2 on Bel W3 was much greater than corresponding leaves on Bel B. Foliar injury on Bel W3 was much higher in the NF OTCs and chamberless ambient-air exposures than in the filtered-air OTC exposures. Injury scores indicated that leaf no. 1 on Bel W3 was more sensitive than leaf no. 2. Also, injury scores on leaf no. 1 were very similar in the NF OTC and the chamberless ambient field plot. Study results indicated that, in all cases, of the several O<sub>3</sub> descriptors tested, the number of hours with O<sub>3</sub> concentrations >40 ppb (N40) and >60 ppb (N60) or the number of hours with O<sub>3</sub> concentrations >40 ppb (SUM40) and >60 ppb (SUM60) were best predictors of O<sub>3</sub> injury. Neither the N40 or N60 nor the SUM40 or SUM60 performed well independently of the corresponding variable in the best regression.

The authors state that the results of the present study support the conclusions of Menser et al. (1963), who pointed out that mature leaves were more sensitive than over-mature and rapidly expanding younger leaves. Consequently, all subsequent analyses were based on the responses of leaf no. 1. The authors also point out that their analysis had two limitations: (1) the number of foliar injury observations was low (nine) on a per-site basis, and, hence, results had to be pooled; and (2) foliar injury observations each week involved new groups of plants, and the results on consecutive weeks were thus independent of each other. This is the only study, of those being discussed, in which plants were grown in an artificial medium.

Krupa et al. (1994) suggested that mid-level hourly average concentrations of O<sub>3</sub> (0.05 to 0.087 ppm) are more important than higher hourly average concentrations in affecting vegetation. The key result of Krupa et al. (1994) is questioned because the CF-NF and AA-NF (i.e., comparisons between CF and NF OTC plots and between ambient air nonchambered and NF chambered plots) differences, as reported by the authors, were inconsistent with earlier publications of the same NCLAN studies, which found few cases with significant CF-NF differences (e.g., Heagle et al., 1988a; Rawlings et al., 1988a; Kress et al., 1985; Kohut and Laurence, 1983). For three of the eight harvests, which Krupa et al. (1994) reported as having significant CF-NF difference, Kohut and Laurence (1983) reported a 2% yield reduction at NF for kidney bean plants at the Ithaca site in 1980; Heagle et al. (1987a) reported 0 and 34% yield reductions at NF for well-watered and water-stressed soybean plants, respectively, at the Raleigh, NC, site in 1983; and Kohut et al. (1987) reported an 11% yield reduction at NF for wheat plants at the Ithaca site in 1983, which was not significant at the 5% level. Another two harvests of clover in the 1985 Raleigh experiment should not have been used by Krupa et al. (1994) because Heagle et al. (1989b) reported significant chamber effects on total biomass, based on a 33% yield reduction at NF relative to AA. Two other inconsistencies were found in Krupa et al. (1994). First, the two clover studies conducted at Raleigh in 1984 and 1985 had six and seven harvests during each year of the studies (Heagle et al., 1989b), not 12 and 14 as reported by Krupa et al. (1994).



**Figure 5-28.** (A) Summary hourly ambient ozone ( $O_3$ ) concentrations during 9 weeks of experimentation (1990) at Montague-Amherst, MA, and (B) summary hourly ambient  $O_3$  concentrations during 9 weeks of experimentation (1990) at Mount Equinox.

Source: Krupa et al. (1993).

Second, the two clover studies conducted at Ithaca in 1984 and 1985 had three harvests during each year of the studies (Kohut et al., 1988a), not six as reported by the authors.

Krupa et al. (1995) attempted in another paper to present "a cohesive view of the dynamics of ambient O<sub>3</sub> exposure and adverse crop response relationships, coupling the properties of photochemical O<sub>3</sub> production, flux of O<sub>3</sub> from the atmosphere into crop canopies and the crop response per se." The results from two independent approaches, (1) statistical and (2) micrometeorological, were analyzed for understanding cause and effect relationships of foliar injury responses of tobacco Bel W3 to the exposure dynamics of ambient O<sub>3</sub> concentrations. Additionally, other results from two independent approaches were analyzed to (1) establish a micrometeorological relationship between hourly ambient O<sub>3</sub> concentrations and their vertical flux from the atmosphere into a grassland canopy and (2) establish a statistical approach relationship between hourly O<sub>3</sub> concentrations in long-term, chronic exposures and crop yield reductions. Based on the above approaches, Krupa et al. (1995) noted that atmospheric conditions appeared to be most conducive and crop response appeared to be explained best statistically by the cumulative frequency of hourly ambient O<sub>3</sub> concentrations between 0.05 and 0.09 ppm. The diurnal occurrence of this concentration range, frequently between the hours 9:00 a.m. and 4:00 p.m. in a polluted agricultural environment, coincided with the optimal CO<sub>2</sub> flux from the atmosphere into the crop canopy, thus facilitating high uptake. The frequency of hourly concentration >0.90 ppm appeared to be of little importance. The higher concentrations, generally appeared to occur when atmospheric conditions did not facilitate optimal vertical flux into the crop canopy, therefore uptake was low.

Krupa et al. (1995) concluded, based on their overall results, that, if the cumulative frequency of hourly ambient O<sub>3</sub> concentrations between 0.05 and 0.062 ppm (100 and 124 µg m<sup>-3</sup>) occurred during 53% of the growing season, and the corresponding cumulative frequency of hourly concentrations between 0.05 and 0.074 ppm occurred during 71% of the growing season, a potential yield reduction in sensitive crops could be expected, if other factors supporting growth, such as adequate soil moisture, are not limiting. In summary, they concluded that these results need further verification.

High correlations can be obtained from chamber experiments because exchange properties inside chambers are more or less constant in time (Grünhage and Jäger, 1994b). Under ambient conditions, however, exposure indices obtained from the chamber studies frequently yield unsatisfactory results (Grünhage and Jäger, 1994a). Grünhage and Jäger (1994a,b) support this view by presenting the results of O<sub>3</sub> flux density measurements above a permanent grassland in Germany. Two years of observations demonstrate the influence of atmospheric conditions on O<sub>3</sub> exposure potential (i.e., how vertical flux and stomatal conductance change during the day). Diurnal flux densities of O<sub>3</sub> varied during the growing seasons of 1990 and 1991 (Grünhage et al., 1994). Vertical flux densities have to be calculated using micrometeorological approaches. Though similar in pattern, the higher flux densities in 1991 coincided with lower O<sub>3</sub> concentrations. Therefore, under ambient conditions, exposures cannot be expressed as a simple function of the concentration in the air. Flux densities and deposition velocities of O<sub>3</sub>, as well as the biological activity of the canopy, need to be considered when determining the effects of ambient air exposures on vegetation. Grünhage and Jäger (1994a,b) and Grünhage et al. (1994), using the information obtained from the micrometeorological measurements of vertical flux densities of CO<sub>2</sub> and O<sub>3</sub> above the native grassland, developed a mathematical model. Grünhage and Jäger (1994b) fit this mathematical model to Bel W3 tobacco data to describe a dose-response relationship for leaf

injury. They concluded that it is possible with this model to attribute the DLA on Bel W3 tobacco to  $O_3$  flux densities. Correlations between  $O_3$  fluxes and leaf injury to tobacco are significantly higher than those using exposure indices based on chamber studies. Grünhage and Jäger (1994b) emphasize the need for taking ambient conditions into account when developing exposure indices to determine critical levels that will prevent injury to vegetation.

Finally, it is not possible at this time, based on a comparison of data from the above mixed studies, to conclude whether the cumulative effects of mid-range concentrations are of greater importance than those of peak hourly average concentrations in determining plant response. The data are not comparable; exposure methods, concentrations and durations used, age of plants at exposure, length of exposure, the plants exposed, and the media in which they were grown all differ across experiments. Some exposures were in chambers in the greenhouse, others in OTCs and others in the ambient air. Many of the exposures in the studies supporting the importance of mid-level  $O_3$  concentrations were only 1 week in duration. It is doubtful that an exposure duration of only 1 week and foliar response data from a sensitive plant species like Bel W3 or from any other plant species are sufficient to ascertain whether cumulative peaks or mid-range concentrations play a greater role in plant growth response. It should be noted, however, that plants are not exposed just to peak  $O_3$  concentrations, therefore, response to  $O_3$  involves the cumulative effect of all concentrations that enter the plants. The short-term exposures indicate that foliar injury can occur even in the absence of peaks. The timing is the key to plant response. Peak and mid-range concentrations do not occur at the same time. A plant effect is determined by which concentrations occur when stomatal conductance is highest. Peaks are important in plant response only where and when plants are exposed to them.

Most important of all is that the response parameters measured in the studies of Musselman et al. (1983, 1986b, 1994) and Hogsett et al. (1985b) differ from those of Tonneijck and Bugter (1991), Tonneijck (1994), and Krupa et al. (1993, 1994). The former measured both foliar injury and growth reductions; all but one of the latter based their conclusions on foliar injury alone. Although foliar injury in tobacco can result in important economic loss to the grower, for the majority of crops, reduction in growth and yield is the measure of importance. As stated in the previous criteria document (U.S. Environmental Protection Agency, 1986), foliar injury in crops does not necessarily signify growth or yield loss. Many studies can be cited to illustrate the inconsistency of relationship between foliar injury and yield loss when foliage is not the yield component.

The studies of Musselman et al. (1983, 1986b) and Hogsett et al. (1985b) have been cited previously (U.S. Environmental Protection Agency, 1986, 1992) as a basis for emphasizing the importance of episodic peak exposures. In addition, the conclusions discussed in previous sections that favored the concept that cumulative effects of hourly  $O_3$  ( $>0.10$  ppm) concentrations are of greater importance than seasonal mean exposures in causing vegetation injury are based on subsequent reanalyses of the NCLAN data. The information presented above in Section 5.5.2.5 does not alter the conclusions reached in the retrospective statistical analyses of NCLAN (Lee et al., 1987, 1991; Tingy et al., 1989; Lefohn and Foley, 1992) that episodic peaks are of importance in causing growth effects, nor does it rule out the possibility that mid-range exposures also could have had an effect.

### 5.5.3 Summary

The effects of O<sub>3</sub> on individual plants and the factors that modify plant response to O<sub>3</sub> are complex and vary with species and environmental soil and nutrient conditions. Because the effects of O<sub>3</sub> and its interactions with physical and genetic factors that influence response are complex, it is difficult to develop a measure of exposure that relates well with plant response based on experimental data. At best, experimental evidence of the impact of O<sub>3</sub> on biomass production can suggest the important factors of O<sub>3</sub> exposure that modify plant response, which should be considered when developing an exposure index.

Considerable evidence of the primary mode of action of O<sub>3</sub> on plants (injury to proteins and membranes, reduction in photosynthesis, changes in allocation of carbohydrate, and early senescence), which ultimately lead to reductions in biomass production, identifies O<sub>3</sub> uptake as an important factor (see Section 5.2). Ozone uptake is controlled by canopy conductance, stomatal conductance, O<sub>3</sub> concentration outside the leaf and gases emitted from the leaf (see Figure 5-2). Any factor that will affect stomatal conductance (e.g., light, temperature, humidity, soil and atmospheric chemistry and nutrients, time of day, phenology, biological agents) will affect O<sub>3</sub> uptake and, consequently, plant response.

The factors such as respite time, temporal variation, phenology, canopy structure, physiological processes, environmental conditions, and soil and nutrient conditions are important in determining the impact of O<sub>3</sub> on crops and trees but are not well understood and interact with concentration and duration in different fashions depending on species. Ozone uptake integrates these factors with atmospheric conditions and relates well with plant response, but is difficult to measure. Empirical functions to predict stomatal conductance have been developed for particular species (e.g., Lösch and Tenhunen, 1981) but have not been used to estimate O<sub>3</sub> uptake or used in development of exposure indices. Based on atmospheric measurement of deposition and diurnal patterns of O<sub>3</sub> and gas exchange in a natural grassland ecosystem, Grünhage and Jäger (1994a,b) and Grünhage et al. (1993a) proposed an ambient O<sub>3</sub> exposure potential for characterizing O<sub>3</sub> uptake and related it to the DLA of Bel W3 tobacco. Grünhage and Jäger (1994a,b) proposed a weighting scheme that preferentially weights the hourly O<sub>3</sub> concentrations occurring during periods of optimal vertical flux into the canopy. For the diurnal pattern of distribution at the natural grassland site in Germany, there was a greater frequency of concentrations in the 0.05- to 0.09-ppm range during the 0900 to 1559 period that matched the DLA of Bel W3 when atmospheric and canopy resistance was minimal.

Further, the biochemical mechanisms, discussed in Section 5.2, describe the mode of action of O<sub>3</sub> on plants as the culmination of a series of physical, biochemical, and physiological events leading to alterations in plant metabolism. Ozone-induced injury is cumulative, resulting in net reductions in photosynthesis, changes in allocation of carbohydrate, and early senescence, which lead to reductions in biomass production (Section 5.2). Increasing O<sub>3</sub> uptake will result in increasing reductions in biomass production.

The optimum exposure index that relates well with plant response should incorporate the factors (directly or indirectly) described above; unfortunately, such an index has not yet been identified. At this time, exposure indices that weight the hourly O<sub>3</sub> concentrations differentially appear to be the best candidates for relating exposure with predicted plant response. Peak concentrations in ambient air occur primarily during daylight, thus, these indices, by providing preferential weight to the peak concentrations, give greater



weight to the daylight concentrations than to the nighttime concentrations (when stomatal conductance is minimal). The timing of peak concentrations and maximum plant uptake is critical in determining their impact on plants.

Some studies reported in the literature show that, when  $O_3$  is the primary source of variation in response, year-to-year variations in plant response are minimized by the peak-weighted, cumulative exposure indices. However, the study of Fuhrer et al. (1992) illustrates some of the limitations in applying exposure indices. The study is significant for its use of the mean  $O_3$  flux in minimizing the year-to-year variation in response when combining replicate studies, indicating the importance of environmental conditions in quantifying the relationship between  $O_3$  exposure and plant response.

## **5.6 Exposure-Response of Plant Species**

### **5.6.1 Introduction**

Determining the response of plants to  $O_3$  exposures continues to be a major challenge. The effects of exposure usually are evaluated by exposing various plant species under controlled experimental conditions, such as those discussed in Section 5.2, to known concentrations and exposure periods. Plant responses are influenced not only by the biochemical and physiological changes that may occur within the plant after  $O_3$  entry (Section 5.3, Mode of Action, see also Figure 5-5) but also by the many factors (both internal and external) that modify plant response (Section 5.4). Of the internal factors discussed in Section 5.4, those that are most likely to apply under controlled experimental conditions are the genetic makeup and age of the plant at the time of exposure. Compensatory responses (Section 5.3.4.2) also will influence plant response. This section analyzes, summarizes, and evaluates what is known about the response of various plant species or cultivars, either as individuals or in populations, to  $O_3$  exposure. Species as populations will be considered only in the case of pasture grasses, or forage mixes, which commonly occur as mixed stands. The response of forest and trees in their natural habitats is discussed in the next section. Emphasis will be placed on those studies conducted since the publication of the previous criteria document 1986 (U.S. Environmental Protection Agency, 1986). Much of the discussion of vegetation response to  $O_3$  exposure in the current document is based on the conclusions of both the 1978 and 1986 criteria documents (U.S. Environmental Protection Agency, 1978, 1986); therefore, to provide a basis for understanding the effects presented below, the conclusions of the two documents are summarized.

Finally, the results of  $O_3$  exposure-response presented in this section must be related to one or more assessment endpoints. Historically, the dollar value of lost production was the endpoint of interest; however, other endpoints (e.g., biodiversity, habitat, aesthetics, recreation) must be considered now, particularly as the impacts of  $O_3$  on long-lived species of ecological importance are evaluated (Tingey et al., 1990).

### **5.6.2 Summary of Conclusions from the Previous Criteria Documents**

The experimental data presented in the 1978 and 1986 criteria documents dealt with the effects of  $O_3$  primarily on agricultural crops species (U.S. Environmental Protection Agency, 1978, 1986). The chapter on vegetation effects in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) emphasized visible injury and growth effects;

however, the growth effects were not those that affected yield. This emphasis was dictated by the kind of data available at the time. The document also presented data dealing with the response of the San Bernardino forest ecosystem to O<sub>3</sub>. This information also was discussed in the 1986 document (U.S. Environmental Protection Agency, 1986). It remains the best and most comprehensive study of forest ecosystem responses to O<sub>3</sub> stresses (see Section 5.7).

The 1986 document emphasized the fact that although foliar injury on vegetation is one of the earliest and most obvious manifestations of O<sub>3</sub> exposure, the effects of exposure are not limited to visible injury. Foliage is the primary site of plant response to O<sub>3</sub> exposures. Significant secondary effects include reduced growth, both in foliage and roots. Impacts range from reduced plant growth and decreased yield to changes in crop quality and alterations in plant susceptibility to biotic and abiotic stresses. Also, the 1986 document noted that O<sub>3</sub> exerts a phytotoxic effect only if a sufficient amount reaches sensitive sites within the leaf (see Section 5.3). Ozone injury will not occur if the rate of uptake is low enough that the plant can detoxify or metabolize O<sub>3</sub> or its metabolites or if the plant is able to repair or compensate for the effects (Tingey and Taylor, 1982; U.S. Environmental Protection Agency, 1986). Cellular disturbances that are not repaired or compensated are ultimately expressed as visible injury to the leaf or as secondary effects that can be expressed as reduced root growth or as reduced yield of fruits or seeds, or both. Ozone would be expected to reduce plant growth or yield if it directly impacts the plant process (e.g., photosynthesis) that limits plant growth or if it impacts another step to the extent that it becomes the step limiting plant growth (U.S. Environmental Protection Agency, 1986; Tingey, 1977). Conversely, if the process impacted is not or does not become rate-limiting, O<sub>3</sub> will not limit plant growth. These conditions also suggest that there are combinations of O<sub>3</sub> concentration and exposure duration that a plant can experience that will not result in visible injury or reduced plant growth and yield. Indeed, numerous studies have demonstrated this fact. This information is still pertinent today (Section 5.3)

Ozone can induce a diverse range of effects beginning with individual plants and then proceeding to plant populations and, ultimately, communities. The effects may be classified as either injury or damage. Injury encompasses all plant reactions, such as reversible changes in plant metabolism (e.g., altered photosynthesis), leaf necrosis, altered plant quality, or reduced growth that does not impair yield or the intended use or value of the plant (Guderian, 1977). In contrast, damage or yield loss includes all effects that reduce or impair the intended use or value of the plant. Thus, for example, visible foliar injury to ornamental plants, detrimental responses in native species, and reductions in fruit and grain production by agricultural species all are considered damage or yield loss. Although foliar injury can not always be classified as damage, its occurrence indicates that phytotoxic concentrations of O<sub>3</sub> are present, and, therefore, studies should be conducted to assess the risk to vegetation.

The concept of limiting values used to summarize visible foliar injury in the 1978 document also was considered valid in the 1986 document (U.S. Environmental Protection Agency, 1978, 1986). Jacobson (1977) developed limiting values by reviewing the scientific literature and identifying the lowest concentration and exposure duration reported to cause visible injury to a variety of plant species. Expressed in another way, limiting values were concentrations and durations of exposure below which visible injury did not occur. A graphical analysis presented in both of the previous documents indicated the limit for reduced plant performance was an exposure to 0.05 ppm for several hours per day for more than 16 days. Decreasing the exposure period to 10 days increased the concentration required

to cause injury to 0.1 ppm, and a short, 6-day exposure further increased the concentration to cause injury to 0.3 ppm.

By 1986, a great deal of new information concerning the effects of O<sub>3</sub> on the yield of crops plants had become available, both through EPA's NCLAN and the results of research funded by other agencies. The NCLAN project was initiated by EPA in 1980, primarily to improve estimates of yield loss in the field and of the magnitude of crop losses caused by O<sub>3</sub> (Heck et al., 1982, 1991). The primary objectives were:

- (1) to define the relationships between yields of major agricultural crops and O<sub>3</sub> exposure as required to provide data necessary for economic assessments and the development of National Ambient Air Quality Standards;
- (2) to assess the national economic consequences resulting from the exposure of major agricultural crops to O<sub>3</sub>; and
- (3) to advance understanding of the cause and effect relationships that determine crop responses to pollutant exposures.

The cultural conditions used in the NCLAN studies approximated typical agronomic practices. The methodology used in these studies is described in Section 5.2.

Yield loss in the 1986 document was defined as "damage", an impairment in the intended use of the plant. This concept included reductions in aesthetic values, the occurrence of foliar injury (changes in plant appearance), and losses in terms of weight, number, or size of the plant part that is harvested. Yield loss also may include changes in physical appearance, chemical composition, or the ability to withstand quality storage (collectively termed crop quality). Losses in aesthetic values are difficult to quantify. Foliar injury symptoms can substantially reduce the marketability of ornamental plants or crops in which the foliage is the plant part (e.g., spinach, lettuce, cabbage) and constitute yield loss with or without concomitant growth reductions. At that time (1986), most studies of the relationship between yield loss and O<sub>3</sub> concentration focused on yields as measured by weight of the marketable organ of the plant.

The OTC studies conducted to estimate the impact of O<sub>3</sub> on the yield of various crop species (e.g., the NCLAN program) were grouped into two types, depending on the experimental design and statistical methods used to analyze the data: (1) studies that developed predictive equations relating O<sub>3</sub> exposure to plant response and (2) studies that compared discrete treatment level to a control. The advantage of the regression approach is that exposure-response models can be used to interpolate results between treatment levels (see Section 5.2.2).

Using NCLAN data as an example of plant response, the O<sub>3</sub> concentrations that could be predicted to cause 10 or 30% yield loss were estimated using the Weibull function (Table 5-19). The data in Table 5-19 are based on yield-response functions for 38 species or cultivars developed from studies using OTCs. Review of that data indicated that 10% yield reductions could be predicted for 58% of the species or cultivars, when 7-h seasonal mean concentrations were below 0.05 ppm, and for 34%, when seasonal mean concentrations were between 0.04 and 0.05 ppm, but only 18% required 7-h seasonal mean concentrations in excess of 0.08 ppm to suffer a 10% loss in yield. Furthermore, approximately 11% of the 38 species or cultivars would be expected to have a yield reduction of 10% loss at 7-h seasonal mean concentrations below 0.035 ppm, suggesting that these plants are very sensitive to O<sub>3</sub>.

Grain crops were apparently less sensitive than the other crops. The data also demonstrate that the sensitivity within species may be as great as differences between

**Table 5-19. Estimates of the Parameters for Fitting the Weibull Model Using the 7-Hour Seasonal Mean Ozone Concentrations<sup>a,b</sup>**

Crop	Parameters for Weibull Model				Concentration for Predicted Yield Losses of:	
	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\gamma}$	CF <sup>c</sup>	10% <sup>d</sup>	30% <sup>d</sup>
<b>LEGUME CROPS</b>						
Soybean, Corsoy	2,785.00	0.133	1.952	0.022	0.048	0.082
Soybean, Davis (81)	5,593.00	0.128	0.872	0.025	0.038	0.071
Soybean, Davis (CA-82) <sup>e</sup>	4,931.00	0.12/	2.144	0.019	0.048	0.081
Soybean, Davis (PA-82) <sub>e</sub>	4,805.00	0.103	4.077	0.019	0.059	0.081
Soybean, Essex (81)	4,562.00	0.187	1.543	0.014	0.048	0.099
Soybean, Forrest (82-I)	4,333.00	0.171	2.752	0.017	0.076	0.118
Soybean, Williams (81)	4,992.00	0.211	1.100	0.014	0.039	0.093
Soybean, Williams (82-I)	5,884.00	0.162	1.577	0.017	0.045	0.088
Soybean, Hodgson	2,590.00	0.138	1.000	0.017	0.032	0.066
Bean, Kidney (FP) <sup>f</sup>	2,878.00	0.120	1.171	0.019	0.033	0.063
Peanut, NC-6	7,485.00	0.111	2.249	0.025	0.046	0.073
<b>GRAIN CROPS</b>						
Wheat, Abe (82)	5,363.00	0.143	2.423	0.023	0.059	0.095
Wheat, Arthur 71 (82)	4,684.00	0.148	2.154	0.023	0.056	0.094
Wheat, Roland	5,479.00	0.113	1.633	0.023	0.039	0.067
Wheat, Vona	7,857.00	0.053	1.000	0.022	0.028	0.041
Wheat, Blueboy II (T)	5.88	0.175	3.220	0.030	0.088	0.127
Wheat, Coker 47-27 (T)	5.19	0.171	2.060	0.030	0.064	0.107
Wheat, Holly (T)	4.95	0.156	4.950	0.030	0.099	0.127
Wheat, Oasis (T)	4.48	0.186	3.200	0.030	0.093	0.135
Corn, PAG 397	13,968.00	0.160	4.280	0.015	0.095	0.126
Corn, Pioneer 3780	12,533.00	0.155	3.091	0.015	0.075	0.111
Corn, Coker 16 (T)	240.00	0.221	4.460	0.020	0.133	0.175
Sorghum, DeKalb-28	8,137.00	0.296	2.217	0.016	0.108	0.186
Barley, Poco	1.99	0.205	4.278	0.020	0.121	0.161
<b>FIBER CROPS</b>						
Cotton, Acala SJ-2 (81-I)	5,546.00	0.199	1.228	0.018	0.044	0.096
Cotton, Acala SJ-2 (82-I)	5,872.00	0.088	2.100	0.012	0.032	0.055
Cotton, Stoneville	3,686.00	0.112	2.577	0.026	0.047	0.075
<b>HORTICULTURAL CROPS</b>						
Tomato, Murrieta (81)	32.90	0.142	3.807	0.012	0.079	0.108
Tomato, Murrieta (82)	32.30	0.082	3.050	0.012	0.040	0.059
Lettuce, Empire (T)	1,245.00	0.098	1.220	0.043	0.053	0.075
Spinach, America (T)	21.20	0.142	1.650	0.024	0.046	0.082
Spinach, Hybrid (T)	36.60	0.139	2.680	0.024	0.043	0.082
Spinach, Viroflay (T)	41.10	0.129	1.990	0.024	0.048	0.080
Spinach, Winter Bloom (T)	20.80	0.127	2.070	0.024	0.049	0.080

**Table 5-19 (cont'd). Estimates of the Parameters for Fitting the Weibull Model Using the 7-Hour Seasonal Mean Ozone Concentrations<sup>a,b</sup>**

Crop	Parameters for Weibull Model				Concentration for Predicted Yield Losses of:	
	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\gamma}$	CF <sup>c</sup>	10% <sup>d</sup>	30% <sup>d</sup>
HORTICULTURAL CROPS (cont'd)						
Turnip, Just Right (T)	10.89	0.090	3.050	0.014	0.043	0.064
Turnip, Pur Top W.G. (T)	6.22	0.095	2.510	0.014	0.040	0.064
Turnip, Shogoin (T)	4.68	0.096	2.120	0.014	0.036	0.060
Turnip, Tokyo Cross (T)	15.25	0.094	3.940	0.014	0.053	0.072

<sup>a</sup>Data are from Heck et al. (1984) and are based on individual plot means unless the crop name is followed by "(T)". The "(T)" indicates that the parameters were based on treatment means and the data are from Heck et al. (1983). The parameters given in Heck et al. (1983, 1984) also contain the standard errors of the parameters.

<sup>b</sup>All estimates of  $\hat{\alpha}$  are in ppm. The yield is expressed as kilograms per hectare for all crops except barley—see weight (grams per head); tomato (both years)—fresh weight (kilograms per plot); cotton—lint + seed weight (kilograms per hectare); peanut—pod weight (kilograms per hectare). In cases where the estimated  $\hat{\gamma}$  parameter is exactly 1.0, it has been bounded from below to obtain convergence in the nonlinear model fitting routine. Parameters were estimated from data not showing the expected Weibull form. Caution should be used in interpreting these Weibull models. Other models might better describe the behavior observed in these experiments. For those crops whose name is followed by "(T)", the yield is expressed as grams per plant.

<sup>c</sup>The ozone (O<sub>3</sub>) concentration in the charcoal-filtered (CF) chambers expressed as a 7-h seasonal mean concentration.

<sup>d</sup>The 7-h seasonal mean O<sub>3</sub> concentration (parts per million) that was predicted to cause a 10 or 30% yield loss (compared to CF air).

<sup>e</sup>CA and PA refer to constant and proportional O<sub>3</sub> addition.

<sup>f</sup>Only the bean data from the full plots are shown. The partial plot data are given Heck et al. (1984).

Source: U.S. Environmental Protection Agency (1986).

species. For example, at 0.04 ppm O<sub>3</sub>, estimated yield losses ranged from 2 to 15% in soybean and from 0 to 28% in wheat. Year-to-year variations in plant response also were observed during the studies.

Discrete treatments were used to determine yield loss in some studies. These experiments were designed to test whether specific O<sub>3</sub> treatments were different from the control rather than to develop exposure-response equations, and the data were analyzed using analyses of variance. When summarizing these studies using discrete treatment levels, as opposed to the variable concentrations used in NCLAN, the lowest O<sub>3</sub> concentration that significantly reduced yield was determined from analyses done by the authors. Frequently, the lowest concentration used in the study was the lowest concentration reported to reduce yield; hence, it was not always possible to estimate a no-effect exposure concentration. In general, the data indicated that O<sub>3</sub> concentrations of 0.10 ppm (frequently the lowest concentration used in the studies) for a few hours per day for several days to several weeks generally caused significant yield reductions. The concentrations derived from the regression

studies were based on a 10% yield loss, whereas, in the studies using the analysis of variance, the 0.10-ppm concentration frequently induced mean yield losses of 10 to 50%.

A chemical protectant, EDU was used to provide estimates of yield loss. The impact of O<sub>3</sub> on yield was determined by comparing the yield data from plots treated with EDU with those that were not. Studies indicated that yields were reduced by 18 to 41% when ambient O<sub>3</sub> concentrations exceeded 0.08 ppm during the day for 5 to 18 days over the growing season.

In summary, the 1986 criteria document (U.S. Environmental Protection Agency, 1986) states that several general conclusions can be drawn from the various approaches used to estimate crop loss yield.

- (1) Based on the comparison of crop yield in CF and unfiltered (ambient) exposures, data clearly indicate that O<sub>3</sub> at ambient levels is elevated sufficiently in several parts of the country to impair the growth and yield of plants. Data from the chemical protectant studies support the conclusion and extend it to other plant species.
- (2) Both of the above-mentioned approaches indicate that effects occur with only a few O<sub>3</sub> occurrences above 0.08 ppm.
- (3) The growth and yield data cited in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) indicate that several plant species exhibited growth and yield effects when the mean O<sub>3</sub> concentration exceeded 0.05 ppm for 4 to 6 h/day for at least 2 weeks.
- (4) The data obtained from regression studies conducted to develop exposure-response functions for estimating yield loss indicated that at least 50% of the species and cultivars tested were predicted to exhibit a 10% yield loss at 7-h season mean O<sub>3</sub> concentrations of 0.05 ppm or less.

Though most of the data from the discrete treatment studies (non-NCLAN studies) did not use concentrations low enough to support the values cited above, the magnitude of yield losses reported at 0.10 ppm under a variety of exposure regimes indicate that, to prevent O<sub>3</sub> effects, a substantially lower concentration is required (U.S. Environmental Protection Agency, 1986).

The limiting values established in 1978 were still deemed appropriate in the 1986 criteria document for ornamentals and certain vegetable crops where visible injury was still considered the response of interest because appearance is of importance (e.g., spinach, lettuce, cabbage) (U.S. Environmental Protection Agency, 1986). This remains the case today.

### **5.6.3 Information in the Published Literature Since 1986**

The major question to be addressed in this section is whether the conclusions of the 1986 criteria document summarized in the previous section, remain valid, given the results of research published since 1988. In particular, whether the response of plants to experimental treatments at or near concentrations of 0.05 ppm (7-h seasonal mean), which are characteristic of ambient concentrations in many areas, can be compared to a control or to reduced O<sub>3</sub> treatment to establish a potential adverse effect.

The 1986 criteria document (U.S. Environmental Protection Agency, 1986) made the following statement: "The characterization and representation of plant exposures to O<sub>3</sub> has been and continues to be a major problem because research has not yet clearly identified which components of the pollutant exposure cause plant response." This is still true

today, although some insight into the importance of peak concentrations versus long-term means has been gained (See Section 5.5). The importance of the timing of exposure during the growing season, the duration of peaks, the rate of increase of concentration, and the respite periods is unresolved.

The aim of most air pollution research experiments have been designed to quantify the relationship between pollutant exposure and agricultural crop yield. The problem is the incorporation of the concentration, duration, frequency, age, genetic composition, and respite time into an exposure statistic or index that may be used to predict yield loss. The correct exposure representation is the amount of pollutant entering the plant, not the ambient concentration to which the plant is exposed (Taylor et al., 1982; Tingey and Taylor, 1982). Unfortunately, it is rarely possible to know the amount of pollutant taken up by the plant, so therefore, an appropriate index of exposure must be chosen. Most indices were not developed from a biological basis, nor were they developed using an experimental approach specifically designed to address all key factors (Lee et al., 1991). A number of exposure indices have been developed in an attempt for depicting plant response to O<sub>3</sub> exposure (see Section 5.5). Much of the data in this section is evaluated using these indices. For this reason, several different exposure statistics are used to determine the effect of an exposure on plant response. It should be remembered that the SUM06, which is used more than any of the other indices, is the seasonal sum of hourly concentrations at or above 0.06 ppm (see Section 5.5).

Exposure indices calculated for each of 10 years (1982 to 1991) and two exposure periods, June through August (3 mo) and May through September (5 mo), are presented in Table 5-20 (modified from Tingey et al., 1991). The monitoring data, collected at nonurban sites, show that ambient O<sub>3</sub> is frequently at, or near, the 7-h seasonal mean that would be expected to cause a yield loss in crops, based on the conclusions of the 1986 criteria document. This table may be used for comparison of ambient-O<sub>3</sub> concentrations to those used in experiments. Although the examples here are based on 10% loss figures, losses below that level may occur and be important. Thirty-four percent of the 38 species or cultivars under consideration would be predicted to have a 10% yield loss at a 7-h mean concentration of between 0.04 and 0.05 ppm, but only 19% required a 7-h mean concentration of greater than 0.08 ppm to suffer a predicted 10% loss in yield. Furthermore, 11% of the 38 species or cultivars would be expected to have a yield reduction of 10% at a 7-h mean, or less than 0.028 to 0.035 ppm (Tables 6-17 and 6-19; U.S. Environmental Protection Agency, 1986). It also was concluded that grain crops (with the exception of a few very sensitive cultivars) were generally less sensitive than others, but that within-species variability in sensitivity may be as great or greater than between species. The preceeding results are similar to those previously obtained from Table 6-19 in the 1986 document. Lee et al. (1994a,b) have revised Table 6-19 in U.S. Environmental Protection Agency (1986) (see Table 5-19) using recalculated peak-weighted exposure indices (shown to be more appropriate than long-term means for relating effects to ambient concentrations) for the 54 studies (listed in Tables 5-21 and 5-22).

In 1992, the Supplement to the Air Quality Criteria Document for Ozone and Other Photochemical Oxidants (1986) reviewed effects of oxidant exposure on vegetation. Considerable emphasis was placed on the appropriate exposure index for relating biological effects of O<sub>3</sub> on plants (U.S. Environmental Protection Agency, 1992). An analysis of the data at that time indicated that a seasonal mean concentration (e.g., 7 or 24 h) might not be the best expression of the exposure because it did not weight high concentrations differently from low concentrations, and it did not account for the variable length of growing seasons or

exposure durations. Unfortunately, it is often impossible to calculate the different possible exposure indices (means, cumulative peak- or threshold-weighted, or continuously weighted [sigmoid] cumulative) from information given in published papers. Thus, difficulties remain when comparing exposure-response studies that utilize different exposure indices. However, reported responses and concentrations of O<sub>3</sub> can be compared to those that occur at ambient concentrations and then to other exposure indices (Table 5-20).

#### **5.6.3.1 Effects of Ozone on Short-Lived (Less Than One Year) Species**

Plant species can be characterized by their life span. They are either short-lived annual species or longer lived perennials and trees. Physiological processes may be related to life span (for instance, leaf gas exchange tends to be lower in longer-lived trees than in crop species), so the response to O<sub>3</sub> may be different (Reich, 1987). In addition, multiple-year exposures and carry-over effects may be of importance in long-lived species, but of no concern in annuals. Accordingly, annuals and perennials will be discussed separately. The response of plants to O<sub>3</sub> also is affected by interactions with other physical, chemical, and biological factors. Those interactions are discussed elsewhere in this document (Section 5.3). In most cases, the research analyzed here was conducted under near-optimal conditions of water and nutrient availability. Although deviations from these conditions may affect the magnitude of response, it is important to understand the potential of O<sub>3</sub> exposure and its consequences.

Several papers (Lee et al., 1988, 1991, 1994a,b; Lefohn et al., 1988a; Lesser et al., 1990; Tingey et al., 1991) present a reanalysis of NCLAN data and data from field studies conducted on potato that were not part of the NCLAN project. Lee et al. (1988, 1991) examined a number of measures of O<sub>3</sub> exposure in relation to response data collected in the experiments. The investigators were particularly interested in examining the ability of a seasonal mean, a cumulative exposure index, and the second-highest daily maximum concentration (2HDM) to predict the biological response of the plant. They found that no particular index of O<sub>3</sub> concentration dominated as best in all studies, but that cumulative indices that weighted high concentrations at the "grain-filling" stage of the life cycle were better than a seasonal mean. Seasonal means did work well within a given experiment where treatments were highly correlated. The 2HDM was consistently a poor predictor of plant response.

In a reanalysis of NCLAN data, Lesser et al. (1990) presented composite exposure-response functions for a number of crop species, or groups of species. Predicted yield losses (compared to yield at an assumed background concentration of 0.025 ppm) of up to 20% occurred at a 12-h seasonal mean of 0.06 ppm, with a loss of 10% at a 12-h mean concentration of about 0.045 ppm.

Tingey et al. (1991) and Lee et al. (1991) went on to reanalyze the crop response data using three measures of exposure: (1) the SUM06, (2) the 7-h seasonal mean, and (3) the 2HDM. Their analysis included crops that account for 70% of all crop land in the United States and 73% of the agricultural receipts. The analysis included 31 field experiments with 12 crop species, conducted in OTCs and resulted in composite exposure-response functions. The results of their studies and additional reanalyses done since then are summarized in Tables 5-23 and 5-24. They concluded that to limit yield loss to 10% or less in 50% of the cases (all experiments and crops), a SUM06 of 24.4 ppm·h (or 26.4 ppm·h,



**Table 5-20. Summary of Ozone Exposure Indices Calculated for 3- or 5-Month Growing Seasons from 1982 to 1991<sup>a</sup>**

3 mo (June-August)											
Year	No. of Sites <sup>b</sup>	HDM2 <sup>c</sup> ppm		M7 ppm		SUM00 ppm·h		SUM06 ppm·h		SIGMOID ppm·h	
		Mean	CV <sup>d</sup>	Mean	CV	Mean	CV	Mean	CV	Mean	CV
1982	99	0.114	23.7%	0.052	18.7%	82.9	19.1%	26.8	68.8%	26.3	56.7%
1983	102	0.125	24.9%	0.056	21.9%	86.1	22.1%	34.5	58.1%	33.0	52.3%
1984	104	0.117	24.6%	0.052	18.2%	84.1	19.9%	27.7	58.4%	27.4	47.9%
1985	117	0.117	24.6%	0.052	17.1%	84.6	18.0%	27.4	59.6%	27.4	47.6%
1986	123	0.115	21.8%	0.052	19.1%	85.3	18.0%	27.7	65.0%	27.7	51.8%
1987	121	0.119	22.9%	0.055	17.6%	86.9	17.3%	31.2	56.4%	30.4	46.8%
1988	139	0.129	21.3%	0.060	17.8%	97.6	19.6%	45.2	46.8%	42.9	42.4%
1989	171	0.105	23.1%	0.051	17.5%	86.4	19.9%	24.8	78.7%	25.8	59.4%
1990	188	0.105	21.6%	0.053	18.3%	85.7	21.0%	25.8	76.2%	26.6	59.2%
1991	199	0.106	22.0%	0.054	18.4%	87.7	21.3%	28.3	74.2%	28.9	59.5%
Among Years		0.113	11.1%	0.054	10.0%	87.0	9.9%	29.5	42.1%	29.4	31.0%

5 mo (May-September)									
Year	No. of Sites	M7 ppm		SUM00 ppm·h		SUM06 ppm·h		SIGMOID ppm·h	
		Mean	CV	Mean	CV	Mean	CV	Mean	CV
1982	88	0.048	20.6%	122.9	22.3%	37.3	70.9%	37.1	57.8%
1983	87	0.051	22.1%	129.6	24.4%	44.4	61.9%	43.8	52.7%
1984	95	0.048	18.0%	126.2	19.1%	36.7	60.8%	37.6	46.9%
1985	114	0.048	18.4%	124.5	19.4%	36.2	63.8%	37.0	50.3%
1986	118	0.048	20.3%	123.3	21.4%	34.9	70.7%	35.6	55.7%
1987	116	0.050	20.3%	128.7	20.4%	42.2	62.0%	41.8	50.3%
1988	134	0.054	18.7%	141.7	22.0%	58.0	50.5%	55.6	45.0%
1989	158	0.047	18.6%	127.8	22.5%	32.7	87.8%	35.2	64.1%
1990	172	0.049	19.8%	129.4	22.7%	34.6	82.7%	37.0	62.1%
1991	190	0.050	19.8%	130.6	23.6%	36.8	80.7%	38.8	62.9%
Among Years		0.049	9.8%	129.0	9.9%	38.7	42.5%	39.6	29.8%

<sup>a</sup>Updated and additional years from data given in Table III of Tingey et al. (1991), where the spatial and temporal variation in ambient O<sub>3</sub> exposures is expressed in terms of several exposure indices.

<sup>b</sup>Indicates the number of separate monitoring sites included in the analysis; fewer sites had 5 mo of available data than had 3 mo of available data.

<sup>c</sup>The 2HDM index is calculated for sites with at least 3 mo of available data. SUM00, SUM06, M7, SIGMOID, and 2HDM are the cumulative sum above 0.0 ppm, the cumulative sum above 0.06 ppm, the 7-h seasonal mean, the sigmoid weighted summed concentration, and the second highest daily maximum 1-h concentration, respectively.

<sup>d</sup>CV = coefficient of variation.

Source: Tingey et al. (1991).

**Table 5-21. Comparison of Exposure-Response Curves Calculated  
Using the 3-Month, 24-Hour SUM06 Values for  
54 National Crop Loss Assessment Network Cases<sup>a</sup>**

Species	Cultivar	Moisture <sup>b</sup>	Wiebull/Linwear Model Parameters <sup>c</sup>			RMSE <sup>d</sup>	R <sup>2e</sup>	3 mo 24-h SUM06 <sup>f</sup> Values for Yield Losses of	
			A	B	C			10%	30%
Barley (Linear)	CM-72	Dry	7,741.1	-4.412		1,215	0.12	175.5	526.4
Barley (Linear)	CM-72	Wet	8,776.6	15.485		1,175	NA	250.0	250.0
Corn (L)	Pio		9,627.4	92.61	2.823	680	0.93	41.7	64.3
Corn (L)	Pag		10,730.1	94.36	4.316	1,248	0.80	56.0	74.3
Cotton (L)	Acala	Dry	6,465.0	92.59	2.361	1,097	0.45	35.7	59.8
Cotton (L)	Acala	Wet	9,808.0	71.17	1.997	521	0.96	23.1	42.5
Cotton (L)	Acala	Dry	7,009.8	83.78	1.849	949	0.80	24.8	48.0
Cotton (L)	Acala	Wet	7,858.8	78.01	1.311	937	0.85	14.0	35.5
Cotton (L, Linear)	Acala	Dry	5.693	-0.0011		104	0.06	94.9	321.3
Cotton (L, Linear)	Acala	Wet	5.,883	-0.0017		90	0.20	60.3	204.0
Cotton	Stoneville		3,576.1	94.6	2.012	226	0.91	30.9	56.7
Cotton	McNair	Dry	3,698.8	165.81	2.778	342	0.46	73.8	114.4
Cotton	McNair	Wet	4,811.0	117.02	1.534	366	0.89	27.0	59.7
Kidney Bean	California Light Red		2,488.2	27.41	3.885	333	0.72	15.4	21.0
Kidney Bean (L)	California Light Red		2,484.3	44.24	2.691	397	0.71	19.2	30.2
Lettuce (T)	Empire		7,196.6	54.87	5.512	613	0.74	36.5	45.5
Peanut (L)	NC-6		6,402.5	100.12	2.226	351	0.97	36.4	63.0
Potato	Norchip		5,900.7	93.84	1.000	742	0.63	9.9	33.5
Potato	Norchip		5,755.6	79.26	1.654	675	0.49	20.3	42.5
Sorghum	Dekalb		8,046.2	178.05	2.338	441	0.48	68.0	114.6
Soybean	Corsoy		2,652.6	57.1	1.726	166	0.91	15.5	31.4
Soybean	Corsoy		1,891.7	65.21	5.160	282	0.63	42.2	53.4
Soybean	Amsoy		1,907.2	75.91	2.739	390	0.41	33.4	52.1
Soybean	Pella		2,619.9	174.13	1.000	311	0.51	18.3	62.1

**Table 5-21 (cont'd). Comparison of Exposure-Response Curves  
Calculated Using the 3-Month, 24-Hour SUM06 Values for  
54 National Crop Loss Assessment Network Cases<sup>a</sup>**

Species	Cultivar	Moisture <sup>b</sup>	Weibull/Linwear Model Parameters <sup>c</sup>			RMSE <sup>d</sup>	R <sup>2e</sup>	3 mo 24-h SUM06 <sup>f</sup> Values for Yield Losses of	
			A	B	C			10%	30%
Soybean	Williams		2,368.4	146.37	1.000	527	0.27	15.4	52.2
Soybean	Corsoy	Dry	2,229.8	92.0	9.593	193	0.16	72.8	82.6
Soybean	Corsoy	Wet	2,913.8	311.04	1.527	330	0.38	71.3	158.4
Soybean	Corsoy	Dry	3,528.1	103.83	15.709	400	0.55	90.0	97.2
Soybean	Corsoy	Wet	4,905.0	117.98	3.590	401	0.80	63.0	88.5
Soybean	Corsoy	Dry	5,676.1	97.46	1.000	508	0.81	10.3	34.8
Soybean	Corsoy	Wet	5,873.9	65.73	1.319	512	0.89	11.9	30.1
Soybean	Williams	Dry	6,305.2	99.18	1.456	389	0.87	21.1	48.8
Soybean	Williams	Wet	7,338.4	78.71	1.344	377	0.94	14.8	36.5
Soybean	Hodgson		2,052.4	79.97	1.000	361	0.78	8.4	28.5
Soybean	Davis		3,929.7	131.57	1.000	524	0.64	13.9	46.9
Soybean	Davis		4,815.5	85.71	1.734	346	0.87	23.4	47.3
Soybean	Davis	Dry	2,007.1	542.36	1.000	556	0.04	57.1	193.4
Soybean	Davis	Wet	4,568.0	158.57	1.539	495	0.61	36.8	81.2
Soybean	Davis	Dry	5,775.6	90.18	3.348	920	0.55	46.0	66.3
Soybean	Davis	Wet	8,082.7	113.89	1.442	927	0.71	23.9	55.7
Soybean	Young	Dry	5,978.8	183.63	1.448	244	0.93	38.8	90.1
Soybean	Young	Wet	7,045.0	145.63	1.277	424	0.93	25.0	65.0
Tobacco (L)	McNair		5,177.4	172.55	1.186	306	0.81	25.9	72.3
Turnip (T)	Just Right		12.7	25.68	1.806	0.810	0.96	7.4	14.5
Turnip (T)	Purple Top		5.7	29.26	1.437	0.590	0.92	6.1	14.3
Turnip (T)	Shogon		4.4	29.18	1.548	0.660	0.81	6.8	15.0
Turnip (T)	Tokyo Cross		11.7	27.83	2.142	3.250	0.78	9.7	17.2
Wheat	Abe		5,149.8	52.89	3.077	399	0.90	25.5	37.8
Wheat	Arthur		4,455.8	60.87	2.176	264	0.92	21.6	37.9

**Table 5-21 (cont'd). Comparison of Exposure-Response Curves  
Calculated Using the 3-Month, 24-Hour SUM06 Values for  
54 National Crop Loss Assessment Network Cases<sup>a</sup>**

Species	Cultivar	Moisture <sup>b</sup>	Weibull/Linear Model Parameters <sup>c</sup>			RMSE <sup>d</sup>	R <sup>2e</sup>	3 mo 24-h SUM06 <sup>f</sup> Values for Yield Losses of	
			A	B	C			10%	30%
Wheat	Roland		5,028.9	52.32	1.173	405	0.91	7.7	21.7
Wheat	Abe		6,043.1	47.39	7.711	226	0.74	35.4	41.5
Wheat	Arthur		5,446.9	72.34	2.462	349	0.57	29.0	47.6
Wheat	Vona		5,384.0	27.74	1.000	608	0.88	2.9	9.9
Wheat	Vona		4,451.0	33.5	1.818	654	0.64	9.7	19.0

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Wet refers to experiments conducted under well-watered conditions, whereas dry refers to experiment conducted under some controlled level of drought stress.

<sup>c</sup>For those studies whose species name is followed by "Linear", a linear model was fit. A Weibull model was fit to all other studies, and estimates of "B" parameter are in parts per million per hour. The yield is expressed in kilograms per hectare for all crops except turnip (grams per meter per plant) and lettuce (grams per meter). In cases where the estimated "C" parameter is exactly 1.0, the shape parameter has been bounded from below to obtain convergence in the nonlinear-model-fitting routine. For those studies whose species name is followed by "L", a log transformation was used to stabilize the variance. For those crops whose name is followed by "T", the yield is expressed as either grams per plant or grams per meter.

<sup>d</sup>The root mean square error, based on individual plot means.

<sup>e</sup>Multiple correlation coefficient (R<sup>2</sup>) measures the proportion of total variation about the mean response explained by the regression on individual plot means.

<sup>f</sup>The 24-h SUM06 value (ppm-h) that was predicted to cause a 10 or 30% yield loss (compared to zero SUM06).

Source: Based on analyses by Lee et al. (1991, 1994a,b).

based on 24 h), a 7-h seasonal mean of 0.049 ppm, or a 2HDM of 0.094 ppm would be required. A SUM06 of about 37 ppm·h should limit yield losses to 20% in 50% of the cases. If one standard error were added to or subtracted to account for the variability, the metrics would be reduced to 21 ppm·h, 0.046 ppm, and 0.088 ppm or increased to 27.8 ppm·h, 0.049 ppm, and 0.10 ppm, respectively. To limit the loss to 10% or less in 75% of the cases would require 14.2 ppm·h, 0.040 ppm, and 0.051 ppm, respectively (Table 5-23). These values are based on studies of both well-watered and drought stressed plants.

Further analyses by Lee et al. (1991, 1994a,b) provides composite exposure-response functions for all NCLAN studies, as well as for soybean and wheat experiments (Table 5-22). In the analysis, they calculated the SUM06 based on 24-h/day O<sub>3</sub> concentrations, and the resulting exposure to prevent crops from yield loss is slightly higher than they previously calculated (26.4 ppm·h versus 24.4 ppm·h; Table 5-23).

**Table 5-22. Comparison of Exposure-Response Curves Calculated Using the 24-Hour W126 Values for 54 National Crop Loss Assessment Network Cases<sup>a</sup>**

Species	Cultivar	Moisture <sup>b</sup>	Weibull <sup>c</sup>			RMSE <sup>d</sup>	R <sup>2</sup> <sup>e</sup>	24-h W126 <sup>f</sup> Values for Yield Losses of	
			A	B	C			10%	30%
Barley	CM-72	Dry	8,133.2	1,109.6	1.000	1,214	0.13	116.9	395.8
Barley	CM-72	Wet	8,927.2	57,439.6	1.000	1,175	NA	6,051.9	20,487.3
Corn (L)	Pio		9,605.0	92.9	2.594	650	0.93	39.0	62.4
Corn (L)	Pag		10,686.7	94.5	4.190	1,253	0.80	55.2	73.9
Cotton (L)	Acala	Dry	6,482.8	89.9	1.949	1,075	0.47	28.3	53.0
Cotton (L)	Acala	Wet	9,817.3	66.6	1.603	514	0.96	16.4	35.0
Cotton (L)	Acala	Dry	7,022.7	81.3	1.540	948	0.80	18.8	41.6
Cotton (L)	Acala	Wet	7,927.1	74.7	1.070	943	0.85	9.1	28.5
Cotton (L)	Acala	Dry	310.1	174.1	2.189	104	0.06	62.3	108.7
Cotton (L)	Acala	Wet	393.2	582.6	1.000	90	0.20	61.4	207.8
Cotton	Stoneville		3,592.1	94.1	1.582	223	0.91	22.7	49.1
Cotton	McNair	Dry	3,700.9	174.1	2.430	344	0.45	68.9	113.9
Cotton	McNair	Wet	4,817.6	113.5	1.410	360	0.89	23.0	54.6
Kidney bean	California Light Red		2,484.7	28.0	3.706	332	0.72	15.3	21.2
Kidney bean (L)	California Light Red		2,475.2	44.2	2.353	401	0.70	17.0	28.5
Lettuce (T)	Empire		7,197.4	54.6	4.921	614	0.74	34.6	44.3
Peanut (L)	NC-6		6,386.0	97.4	1.905	370	0.96	29.9	56.7
Potato	Norchip		5,867.2	96.3	1.000	754	0.62	10.1	34.3
Potato	Norchip		5,777.9	113.9	1.299	675	0.48	20.1	51.5
Sorghum	Dekalb		8,049.7	205.9	1.963	439	0.48	65.4	121.8
Soybean	Corsoy		2,660.3	58.8	1.455	169	0.91	12.5	28.9
Soybean	Corsoy		1,895.6	63.3	4.032	280	0.63	36.2	49.0
Soybean	Amsoy		1,926.1	79.0	1.977	390	0.41	25.3	46.9
Soybean	Pella		2,602.4	161.5	1.000	314	0.50	17.0	57.6
Soybean	Williams		2,341.8	138.6	1.000	533	0.25	14.6	49.4
Soybean	Corsoy	Dry	2,229.3	88.2	8.632	192	0.16	67.9	78.2

**Table 5-22 (cont'd). Comparison of Exposure-Response Curves  
Calculated Using the 24-Hour W126 Values for 54 National  
Crop Loss Assessment Network Cases<sup>a</sup>**

Species	Cultivar	Moisture <sup>b</sup>	Weibull <sup>c</sup>			RMSE <sup>d</sup>	R <sup>2e</sup>	24-h W126 <sup>f</sup> Values for Yield Losses of	
			A	B	C			10%	30%
Soybean	Corsoy	Wet	2,929.7	470.2	1.128	329	0.39	64.0	188.6
Soybean	Corsoy	Dry	3,533.5	113.2	11.095	403	0.54	92.4	103.1
Soybean	Corsoy	Wet	4,909.5	126.5	2.803	405	0.80	56.7	87.6
Soybean	Corsoy	Dry	5,597.1	95.7	1.000	526	0.80	10.1	34.1
Soybean	Corsoy	Wet	5,884.8	65.6	1.139	515	0.88	9.1	26.6
Soybean	Williams	Dry	6,314.1	106.3	1.243	391	0.87	17.4	46.4
Soybean	Williams	Wet	7,352.3	80.7	1.162	368	0.95	11.6	33.2
Soybean	Hodgson		2,044.6	76.2	1.000	361	0.78	8.0	27.2
Soybean	Davis		3,837.6	130.3	1.000	530	0.63	13.7	46.5
Soybean	Davis		4,810.8	87.5	1.494	352	0.86	19.4	43.9
Soybean	Davis	Dry	1,992.3	537.6	1.000	558	0.03	56.6	191.7
Soybean	Davis	Wet	4,595.4	170.9	1.253	496	0.61	28.4	75.1
Soybean	Davis	Dry	5,770.1	90.6	2.796	928	0.54	40.5	62.7
Soybean	Davis	Wet	8,101.3	118.2	1.220	939	0.70	18.7	50.8
Soybean	Young	Dry	5,994.2	199.8	1.251	244	0.93	33.1	87.7
Soybean	Young	Wet	7,075.0	149.7	1.133	418	0.93	20.5	60.2
Tobacco (L)	McNair		5,223.9	179.8	1.018	291	0.83	19.7	65.3
Turnip (T)	Just Right		12.7	24.1	1.473	1.0	0.96	5.2	12.0
Turnip (T)	Purple Top		5.8	28.2	1.155	1	0.92	4.0	11.6
Turnip (T)	Shogon		4.4	28.2	1.174	1	0.82	4.1	11.7
Turnip (T)	Tokyo Cross		11.7	26.8	1.710	3	0.78	7.2	14.7
Wheat	Abe		5,138.1	53.3	2.602	407	0.89	22.4	35.8
Wheat	Arthur		4,467.4	63.8	1.747	264	0.92	17.6	35.4
Wheat	Rol		5,074.4	51.2	1.000	397	0.91	5.4	18.3
Wheat	Abe		6,042.8	48.5	5.843	225	0.75	33.0	40.6

**Table 5-22 (cont'd). Comparison of Exposure-Response Curves  
Calculated Using the 24-Hour W126 Values for 54 National  
Crop Loss Assessment Network Cases<sup>a</sup>**

Species	Cultivar	Moisture <sup>b</sup>	Weibull <sup>c</sup>			RMSE <sup>d</sup>	R <sup>2</sup> <sup>e</sup>	24-h W126 <sup>f</sup> Values for Yield Losses of	
			A	B	C			10%	30%
Wheat	Arthur		5,440.0	76.1	2.100	349	0.57	26.1	46.6
Wheat	Vona		5,300.8	25.0	1.000	679	0.85	2.6	8.9
Wheat	Vona		4,462.7	32.3	1.517	665	0.63	7.3	16.4

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Wet refers to experiments conducted under well-watered conditions, whereas dry refers to experiments conducted under some controlled level of drought.

<sup>c</sup>All estimates of "B" parameter are in parts per million per hour. The yield is expressed in kilograms per hectare for all crops except turnip (grams per plant) and lettuce (grams per meter). In cases where the estimated "C" parameter is exactly 1.0, the shape parameter has been bounded from below to obtain convergence in the nonlinear-model-fitting routine. For those studies whose species name is followed by "L", a log transformation was used to stabilize the variance. For those crops whose name is followed by "T", the yield is expressed as either grams per plant or grams per meter.

<sup>d</sup>The root mean square error, based on individual plot means.

<sup>e</sup>Multiple correlation coefficient (R<sup>2</sup>) measures the proportion of total variation about the mean response explained by the regression on individual plot means.

<sup>f</sup>The 24-h W126 value (parts per million per hour) that was predicted to cause a 10 or 30% yield loss (compared to zero W126).

Source: Based on analyses by Lee et al. (1991, 1994a,b).

Research since 1986 has focused largely on understanding the response of trees and other perennials to O<sub>3</sub> (covered in the next section) and of five crop species: (1) cotton, (2) wheat, (3) spring rape, (4) bean, and (5) soybean. A number of the studies were conducted as part of NCLAN, but many also were the result of research activity in Europe. Results of these studies, as well as those species studied less intensively, are summarized in Table 5-25. A composite exposure-response function is illustrated in Figure 5-29.

Yield losses in cotton of 13 to 19% have been reported at 12-h mean concentrations of 0.050 or 0.044 ppm by Heagle et al. (1988a) and Temple et al. (1988b) (Table 5-25). These are typical ambient concentrations, as listed under M7 (Table 5-20). The same experiments showed that drought stress reduced the predicted yield loss due to O<sub>3</sub>, but did not eliminate it.

Wheat yields have been reduced by 0 to 29%, depending on the cultivar and exposure conditions (Adaros et al., 1991a; Fuhrer et al., 1989; Grandjean and Fuhrer, 1989; Kohut et al., 1987; Pleijel et al., 1991) (Table 5-25). In no case was a 7-h average of greater than 0.062 ppm required to cause the reported loss, but Slaughter et al. (1989) suggest that hourly concentrations above 0.06 ppm during the period following anthesis may be particularly effective in reducing yield.

**Table 5-23. The Exposure Levels (Using Various Indices)  
Estimated To Cause at Least 10% Crop Loss in  
50 and 75% of Experimental Cases<sup>a</sup>**

50th PERCENTILE <sup>b</sup>	SUM06	SE <sup>c</sup>	SIGMOID	SE	M7	SE	2HDM	SE
NCLAN Data (N = 49; wet and dry) <sup>d</sup>	24.4	3.4	21.5	2.0	0.049	0.003	0.094	0.006
NCLAN Data (N = 39; wet only)	22.3	1.0	19.4	2.3	0.046	0.003	0.090	0.010
NCLAN Data (N = 54; wet and dry) <sup>e</sup>	26.4	3.2	23.5	2.4	NA	NA	0.099	0.011
NCLAN Data (N = 42; wet only) <sup>e</sup>	23.4	3.1	22.9	4.7	NA	NA	0.089	0.008
NCLAN Data (N = 10; wet)	25.9	4.5	23.4	3.2	0.041	0.001	0.110	0.042
NCLAN Data (N = 10; dry)	45.7	23.3	40.6	0.1	0.059	0.014	0.119	0.017
Cotton Data (N = 5)	23.6	2.3	19.3	2.3	0.041	0.001	0.066	0.032
Soybean Data (N = 13)	26.2	5.4	22.6	3.6	0.044	0.005	0.085	0.013
Wheat Data (N = 6)	21.3	15.2	19.3	12.7	0.061	0.018	0.098	0.059
Cotton Data (N = 5) <sup>e</sup>	30.0	12.7	27.2	12.8	NA	NA	0.075	0.012
Soybean Data (N = 15) <sup>e</sup>	23.9	6.5	22.0	8.0	NA	NA	0.088	0.008
Wheat Data (N = 7) <sup>e</sup>	25.9	10.5	21.4	9.4	NA	NA	0.097	0.028
75th PERCENTILE <sup>b</sup>								
NCLAN Data (N = 49; wet and dry)	14.2	4.2	11.9	5.6	0.040	0.007	0.051	0.010
NCLAN Data (N = 39; wet only)	14.3	2.7	12.6	2.3	0.039	0.005	0.056	0.006
NCLAN Data (N = 54; wet and dry) <sup>e</sup>	16.5	4.3	14.5	3.2	NA	NA	0.073	0.006
NCLAN Data (N = 42; wet only) <sup>e</sup>	17.2	3.0	14.7	2.4	NA	NA	0.070	0.006
NCLAN Data (N = 10; wet)	16.4	3.7	13.7	3.2	0.040	0.001	0.080	0.032
NCLAN Data (N = 10; dry)	24.0	0.8	22.3	0.1	0.053	0.022	0.093	0.003
Cotton Data (N = 5)	21.8	5.0	17.5	2.8	0.041	0.001	0.065	0.014
Soybean Data (N = 13)	14.2	0.1	12.4	0.1	0.041	0.006	0.069	0.004
Wheat Data (N = 6)	11.7	2.5	10.9	2.4	0.054	0.032	0.062	0.035
Cotton Data (N = 5) <sup>e</sup>	21.1	6.0	16.7	5.7	NA	NA	0.070	0.034
Soybean Data (N = 15) <sup>e</sup>	15.3	4.1	13.4	4.1	NA	NA	0.078	0.007
Wheat Data (N = 7) <sup>e</sup>	5.1	2.6	8.5	3.4	NA	NA	0.054	0.027

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>The numbers in parentheses are the number of cases used in deriving the various exposure levels.

<sup>c</sup>Standard error (SE).

<sup>d</sup>NCLAN data refers to studies conducted as part of the NCLAN project. Wet and dry refer to watery regimes used in the studies, wet being well-watered, and dry meaning some level of drought stress was imposed.

<sup>e</sup>24-h exposure statistics reported in Lee et al. (1994b). Relative yield loss for 2HDM is relative to yield at 0.04 ppm rather than 0.00 ppm as was used in Tingey et al. (1991).

Source: Modified from Tingey et al. (1991).

Studies with spring rape in Europe have documented yield losses of 9.5 to 26.9% at 8-h growing season average concentrations ranging from 0.03 to 0.06 ppm (Adaros et al., 1991b,c) (Table 5-26).

The yield of beans (fresh pods) was reduced by 17% at a 7-h average of 0.045 ppm (Schenone et al., 1992) or 20% at an 8-h growing season average of 0.080 ppm (Bender et al., 1990). In a similar study, Heck et al. (1988) found that the predicted yield of sensitive cultivars was reduced an average of 17.3% by exposure to a 7-h growing season



**Table 5-24. SUM06 Levels Associated with 10 and 20% Yield Loss for 50 and 75% of the National Crop Loss Assessment Network (NCLAN) Crop Studies<sup>a</sup>**

Weibull Equations (all 54 NCLAN studies):

50th Percentile<sup>b</sup> PRYL =  $1 - \exp(-[\text{SUM06}/89.497]**1.84461)$

75th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/60.901]**1.72020)$

Weibull Equations (all 22 NCLAN soybean studies; 15 well-watered, 7 water-stress):

50th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/117.68]**1.46509)$

75th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/88.99]**1.47115)$

Weibull Equations (15 NCLAN well-watered soybean studies):

50th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/112.75]**1.46150)$

75th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/79.62]**1.36037)$

Weibull Equations (7 NCLAN wheat studies):

50th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/49.02]**3.52788)$

75th Percentile PRYL =  $1 - \exp(-[\text{SUM06}/29.56]**1.29923)$

SUM06 Levels Associated with 10 and 20% Yield Loss for 50 and 75% of the Crops:

All 54 NCLAN Cases

		Percent of Crops	
		50%	75%
Relative	10%	26.4	16.5
Yield Loss	20%	39.7	25.5

All 22 NCLAN Soybean Cases

		Percent of Crops	
		50%	75%
Relative	10%	25.3	19.3
Yield Loss	20%	42.3	32.1

15 Well-Watered Soybean Cases

		Percent of Crops	
		50%	75%
Relative	10%	24.2	15.2
Yield Loss	20%	40.4	26.4

All Seven NCLAN Wheat Cases

		Percent of Crops	
		50%	75%
Relative	10%	25.9	5.2
Yield Loss	20%	32.0	9.3

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>50th and 75th percentiles refer to the percentage of studies analyzed in which loss of the stated magnitude would have been prevented.

Source: Based on analyses by Lee et al. (1994b).

**Table 5-25. A Summary of Studies Reporting the Effects of Ozone  
on the Growth, Productivity, or Yield of Annual Plants Published Since  
U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Soybean	18 or 24 ppb vs. 59 or 72 ppb 9-h mean	13 weeks, two growing seasons	OTC	Seed yield	12.5% reduction over filtered air averaged over cultivars. Between-cultivar differences as great as ozone effect.	Mulchi et al. (1988)
Soybean	23, 40, and 66 ppb 7-h mean	84 days	OTC	Seed yield	15.8 and 29% reduction over 23 ppb.	Mulchi et al. (1992)
Soybean	97 ppb vs. 38, 23, 16, and 23 ppb 7-h mean	Four 31-day periods, one growing season	OTC in pots	Seed yield	30 to 56% reduction over control, most loss in mid- to late-growth stage.	Heagle et al. (1991b)
Soybean	17 to 122 ppb 7-h mean	69 days	OTC	Seed yield	8% at 35 ppb to 41% at 122 ppb.	Kohut et al. (1986)
Soybean	25 and 50 ppb 7-h mean	About 90 days	OTC	Seed yield	Predicted loss of 10%.	Heagle et al. (1986b)
Soybean	20 and 50 ppb 12-h mean	107 days	OTC	Seed yield	Predicted loss of 13%.	Miller et al. (1989b)
Soybean	25 and 55 ppb 7-h mean	64, 70, and 62 days, three growing seasons	OTC	Seed yield	Predicted loss of 15%.	Heggestad and Lesser (1990)
Soybean	27 and 54 ppb 7-h means	About 109 and 103 days, two growing seasons	OTC	Seed yield	Predicted loss of 12 and 14%.	Heagle et al. (1987a)
Soybean	Filtered and nonfiltered air-concentration not reported	About 125 days, two growing seasons	OTC	Seed yield	No difference.	Johnston and Shriner (1986)
Soybean	10 to 130 ppb	8 weeks, 6.8 h/day	GC	Biomass	Predicted reduction of 16 or 33% at 60 and 100 ppb vs. 25 ppb.	Amundson et al. (1986)
Soybean	200 ppb	12 h, up to four times	GC	Shoot and root weight	No effect at maturity.	Smith et al. (1990)

**Table 5-25 (cont'd). A Summary of Studies Reporting the Effects of  
Ozone on the Growth, Productivity, or Yield of Annual Plants  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Cotton	15 to 111 ppb 12-h mean	123 days	OTC	Leaf, stem, and root weight	Up to 42% reduction in leaf and stem and 61% reduction in root weights.	Temple et al. (1988c)
Cotton	10 to 90 ppb 12-h mean	102 days	OTC	Lint weight	40 to 71% reduction at highest concentration determinant cultivars more susceptible.	Temple (1990b)
Cotton	25 to 74 ppb 12-h mean	123 days	OTC	Lint weight	Predicted loss of 26.2% at 74 ppb.	Temple et al. (1988b)
Cotton	22 to 44 ppb 12-h mean	124 days	OTC	Lint weight	Predicted loss of 19% at 44 ppb.	Heagle et al. (1988a)
Cotton	26 to 104 ppb 7-h mean	119 days	OTC	Lint weight	Predicted loss of 11% at 53 ppb.	Heagle et al. (1986a)
Bean, fresh	35 to 132 ppb 7-h mean	42 days	OTC in pots	Green pod weight	Significant yield reductions of >10% in eight lines at 63 ppb 7-h mean.	Eason and Reinert (1991)
Bean, fresh	11 to 40 ppb 12-h mean, 7 to 42 ppm·h	69 days	OTC	Pod weight	15.5% reduction at 45 ppb (39 ppm·h).	Schenone et al. (1992)
Bean, fresh	26 to 126 ppb 7-h mean	26 days and 44 days, early and late in season	OTC in pots	Pod weight	3.5 to 26% reduction in resistant and sensitive cultivars at 55 to 60 ppb.	Heck et al. (1988)
Bean, fresh	24 to 109 ppb 8-h mean	43 days 34 days, two growing seasons	OTC	Pod weight	20% reduction at 80 ppb.	Bender et al. (1990)
Bean, dry	15 to 116 ppb 12-h mean, 339 ppb highest hour	54 days	OTC	Seed yield	55 to 75% reduction at 72 ppb 12-h mean, 198 highest hour.	Temple (1991)

**Table 5-25 (cont'd). A Summary of Studies Reporting the Effects of  
Ozone on the Growth, Productivity, or Yield of Annual Plants  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Bean, dry	10 to 50 ppb 7-h mean	86 days	OTC	Seed weight	26 to 42% reduction at 38 to 50 ppb.	Sanders et al. (1992)
Bean, dry	300 ppb	3 h, two exposures	GC	Dry weight	Growth response detected if exposure separated by 3 to 5 days.	McCool et al. (1988)
Wheat, spring	14 to 46 ppb 24-h mean	79, 92, and 79 days in three growing seasons	OTC	Seed weight	13% reduction at 40 ppb.	Fuhrer et al. (1989)
Wheat, spring	21.6 to 80 and 24.6 to 93.5 ppm·h	82 and 88 days in two growing seasons	OTC	Seed weight	48 to 54% reduction at 80 and 93.5 ppm·h.	Grandjean and Fuhrer (1989)
Wheat, spring	3 to 56 ppb 7-h mean	61 and 55 days in two growing seasons	OTC	Seed weight	7% reduction at 15 and 22 ppb.	Pleijel et al. (1991)
Wheat, spring	8 to 101 and 20 to 221 ppb 8-h mean	118 and 98 days in two growing seasons	OTC	Seed weight	10% reduction at 17 to 23 ppb.	Adaros et al. (1991a)
Wheat, spring	0 to 38 ppb 8-h mean	Entire growing season	OTC	Seed weight	5% reduction at 38 ppb.	De Temmerman et al. (1992)
Wheat, spring	17 to 77 ppb 7-h mean	90 and 87 days in two growing seasons	OTC	Seed weight	9.5 to 11.6 reduction at 37 and 45 ppb.	Fuhrer et al. (1992)
Wheat, spring	25 to 75 ppb 8-h mean	40 days	OTC	Total weight	Reductions at 75 ppb.	Johnsen et al. (1988)
Wheat, spring	6 to 10 ppb, 6 h/day	21 days	GC	Shoot dry weight	Decreased 35 to 60% at 101 ppb in low and high light.	Mortensen (1990b)
Wheat, spring	10 to 125 ppb, 6 h/day	21 and 17 days	GC	Top dry weight	Reduced by up to 35%.	Mortensen (1990c)

**Table 5-25 (cont'd). A Summary of Studies Reporting the Effects of  
Ozone on the Growth, Productivity, or Yield of Annual Plants  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Wheat, winter	11 to 42 ppb 14-week mean	109 days	OTC	Seed weight	No effect.	Olszyk et al. (1986b)
Wheat, winter	30 to 93 ppb 4-h mean	39 and 40 days in two growing seasons 5 days/week 4 h/day	OTC	Seed weight	Exposures >60 ppb during anthesis reduce yield.	Slaughter et al. (1989)
Wheat, winter	27 to 96 ppb 7-h mean	36 days	OTC	Seed weight/ head	50% reduction at 96 ppb.	Amundson et al. (1987)
Wheat, winter	22 to 96 ppb 7-h mean	65 days and 36 days in two growing seasons	OTC	Seed weight	33 and 22% reductions at 42 and 54 ppb, respectively.	Kohut et al. (1987)
Wheat, winter	23 to 123 ppb 4 h/day	5 days at anthesis	OTC	Seed weight	Up to 28% reduction.	Mulchi et al. (1986)
Barley, spring	6 to 45 ppb 7-h mean	96 days	OTC	Seed weight	No effect.	Pleijel et al. (1992)
Barley, spring	0.6 to 27 ppb monthly mean	Growing season	OTC	Seed weight	No effect.	Weigel et al. (1987)
Barley, spring	0.8 to 83 ppb 8-h mean	97, 108, and 98 days in three growing seasons	OTC in pots	Seed weight	0 to 13% reduction at highest.	Adaros et al. (1991b)
Rape, spring	25 to 75 ppb 8-h mean	31 days	OTC	Premature senescence	Increased at 75 ppb.	Johnsen et al. (1988)
Rape, spring	0.8 to 83 ppb 8-h mean	89, 113, and 84 days in three growing seasons	OTC in pots	Seed weight	9.4 to 16% reduction at 30 or 51 ppb.	Adaros et al. (1991b)

**Table 5-25 (cont'd). A Summary of Studies Reporting the Effects of  
Ozone on the Growth, Productivity, or Yield of Annual Plants  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Rape, spring	43 to 60 ppb 8-h mean	89, 113, and 84 days in three growing seasons	OTC in pots	Seed weight	12 to 27% reduction.	Adaros et al. (1991c)
Tomato	13 to 0.109 ppm 12-h mean, 79.5 ppm-h	75 days	OTC	Fresh weight	17 to 54% reduction at 0.109 ppm; no reduction at ambient.	Temple (1990a)
Tomato	10 to 85 ppb, 6 h/day	12 to 21 days	GC	Shoot dry weight	35 to 62% reduction.	Mortensen (1992b)
Tomato	18 to 66 ppb 12-h mean	11 weeks	OTC	Fresh fruit weight	No effect.	Takemoto et al. (1988c)
Moss campion	5 to 80 ppb, 8 h/day	Up to 90 days	GC	Dry weight	25% reduction at 80 ppb.	Mortensen and Nilsen (1992)
Buckhorn	5 to 80 ppb, 8 h/day	Up to 90 days	GC	Dry weight	14% reduction at 50 ppb.	Mortensen and Nilsen (1992)
16 Other species	5 to 80 ppb, 8 h/day	Up to 90 days	GC	Dry weight	No effect.	Mortensen and Nilsen (1992)
Radish	20 or 70 ppb 24-h mean	27 days	GC	Shoot and root growth	36 and 45% reduction at 70 ppb.	Barnes and Pfirman (1992)
Lettuce	21 to 128 ppb 7-h mean	52 days	OTC	Head weight	Significant reduction at 83 ppb, 35% at 128 ppb.	Temple et al. (1986)
Lettuce	10 to 34 ppb 7-week mean	64 days	OTC	Fresh weight	No effect.	Olszyk et al. (1986b)
Faba bean	6 or 15 ppb 24-h mean	134 days	OTC	Seed weight	No effect.	Sanders et al. (1990)
Fenugreek	120 ppb, 7 h/day	4 weeks	CC	Dry weight	No significant effect.	Kasana (1991)

**Table 5-25 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth, Productivity, or Yield of Annual Plants Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Chickpea	120 ppb, 7 h/day	4 weeks	CC	Dry weight	No significant effect.	Kasana (1991)
Gram, black	120 ppb, 7 h/day	4 weeks	CC	Dry weight	No significant effect.	Kasana (1991)
Rice	0 to 200 ppb, 5 h/day	5 days/week 15 weeks	OTC	Seed weight	12 to 21% reduction at 200 ppb.	Kats et al. (1985)
Rice	50 ppb 24-h mean	8 weeks	GC	Dry weight	No effect at 50 ppb.	Nouchi et al. (1991)
Watermelon	15 to 27 ppb 7-h mean	81 days	OTC	Fresh weight and number (marketable)	20.8 and 21.5% reduction at 27 ppb.	Snyder et al. (1991)
Pea	10 to 35 ppb 12-h mean	58 and 52 days in two growing seasons	OF	Fresh weight	Linear decrease in yield with increasing O <sub>3</sub> .	Runeckles et al. (1990)
Green pepper	19 to 66 ppb 12-h mean	77 days	OTC	Fresh fruit weight	12% reduction at 66 ppb.	Takemoto et al. (1988c)
Green pepper	18 to 66 ppb 12-h mean	11 weeks	OTC	Fresh fruit weight	13% reduction in fruit weight at 66 ppb.	Takemoto et al. (1988c)
Celery	18 to 66 ppb 12-h mean	11 weeks	OTC	Shoot dry weight	12% reduction at 66 ppb.	Takemoto et al. (1988c)

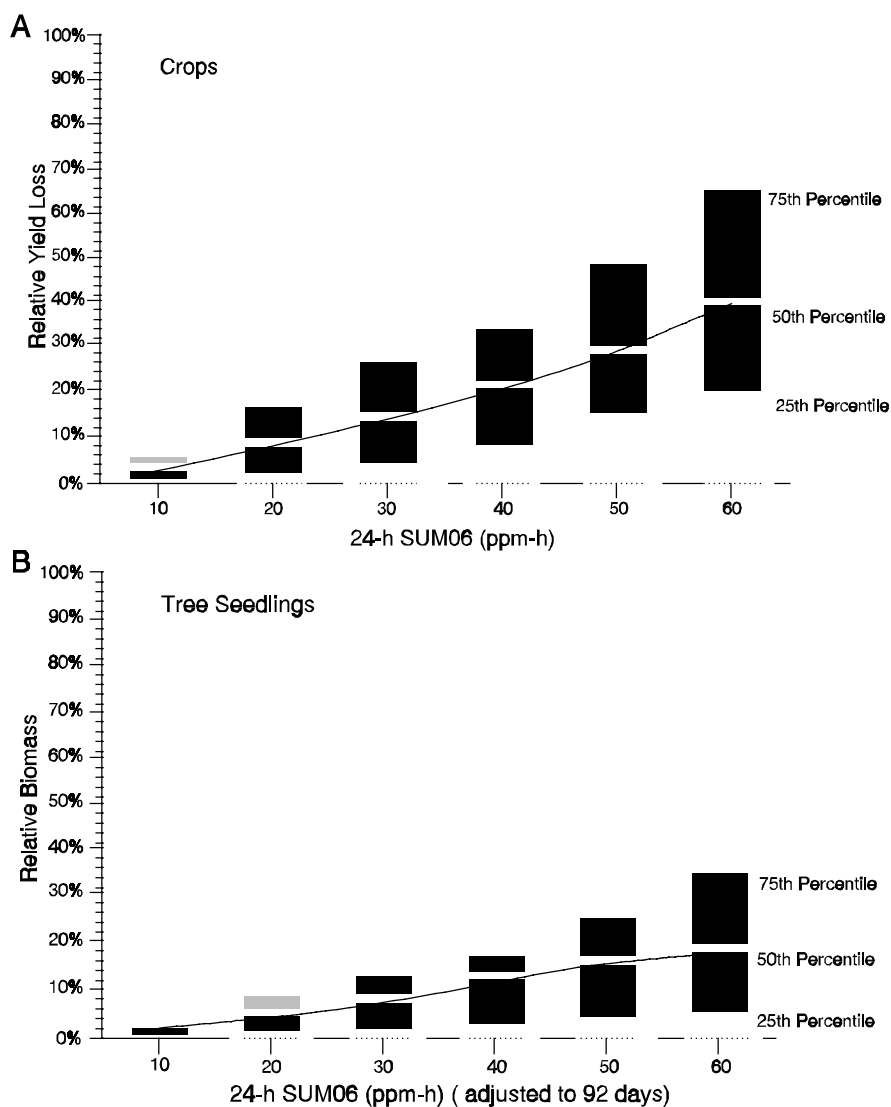
<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Means are seasonal means unless specified. Maximums are 1-h seasonal maxima unless otherwise specified. Cumulative exposures are SUM00 unless otherwise specified; accumulation based on 24 h/day unless otherwise noted.

<sup>c</sup>OTC = open-top chamber with plants in ground unless specified in pots; CC = closed chamber, outside; GC = controlled environment growth chamber or CSTR; OF = open-field fumigation.

<sup>d</sup>The effect reported in the study that is a measure of growth, yield, or productivity.

<sup>e</sup>Effect measured at specified ozone concentration, over the range specified under concentration, or predicted (if specified) to occur based on relationships developed in the experiment.



**Figure 5-29.** *Box-plot distribution of biomass loss predictions from Weibull and linear exposure-response models that relate biomass and ozone exposure as characterized by the 24-h SUM06 statistic using data from (A) 31 crop studies from National Crop Loss Assessment Network (NCLAN) and (B) 26 tree seedling studies conducted at U.S. Environmental Protection Agency's Environmental Research Laboratory in Corvallis, OR; Smoky Mountains National Park, TN; Michigan; Ohio; and Alabama. Separate regressions were calculated for studies with multiple harvests or cultivars, resulting in a total of 54 individual equations from the 31 NCLAN studies and 56 equations from the 26 seedling studies. Each equation was used to calculate the predicted relative yield or biomass loss at 10, 20, 30, 40, 50, and 60 ppm h, and the distributions of the resulting loss were plotted. The solid line is the calculated Weibull fit at the 50th percentile (from Hogsett et al., 1995).*



**Table 5-26. A Summary of Studies Reporting the Effects of  
Ozone on the Growth, Productivity, or Yield of Perennial Crop Plants  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Strawberry	18 to 66 ppb 12-h mean	11 weeks	OTC	Fresh fruit weight	20% increase in fruit weight at 66 ppb.	Takemoto et al. (1988c)
Timothy	10 to 55 ppb 7-h mean	5 weeks	GC	Shoot dry weight	45% reduction at 55 ppb.	Mortensen (1992a)
Orchard grass	10 to 55 ppb 7-h mean	5 weeks	GC	Shoot dry weight	28% reduction at 55 ppb.	Mortensen (1992a)
Kentucky blue grass	10 to 55 ppb 7-h mean	5 weeks	GC	Shoot dry weight	28% reduction at 55 ppb.	Mortensen (1992a)
Red grass	10 to 55 ppb 7-h mean	5 weeks	GC	Shoot dry weight	23% reduction at 55 ppb.	Mortensen (1992a)
Tall fescue	10 to 55 ppb 7-h mean	5 weeks	GC	Shoot dry weight	16% reduction at 55 ppb.	Mortensen (1992a)
Colonial bent grass	10 to 55 ppb 7-h mean	5 weeks	GC	Shoot dry weight	No effect.	Mortensen (1992a)
Rye grass	62 ppb 7-h mean	5 weeks	GC	Shoot dry weight	No effect.	Mortensen (1992a)
Red clover	6 to 59 ppb 7-h mean	5 weeks	GC	Shoot dry weight	30% reduction at 59 ppb.	Mortensen (1992a)
Common plantain	70 ppb 7-h mean	8 weeks	GC	Total dry weight	Reduced up to 36% depending on growth stage.	Reiling and Davison (1992c)
Red clover	19 to 62 ppb 12-h mean	83 and 91 days in two growing seasons	OTC	Dry weight	11% reduction at 62 ppb.	Kohut et al. (1988a)
Timothy	19 to 62 ppb 12-h mean	83 and 91 days in two growing seasons	OTC	Dry weight	No effect.	Kohut et al. (1988a)

**Table 5-26 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth, Productivity, or Yield of Perennial Crop Plants Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Ladino clover-tall fescue pasture	22 to 114 ppb 12-h mean	Five 3- to 4-week exposure periods. Six 3- to 4-week exposures in 2 years	OTC	Shoot dry weight, root dry weight	18 to 50% reduction in shoot dry weight (SDW) at 40 to 47 ppb clover; 25% reduction root dry weight at 40 to 47 ppb. SDW increased by up to 50% in fescue.	Rebbeck et al. (1988)
Ladino clover	28 to 46 ppb 12-h mean	180 and 191 days in two growing seasons	OTC	Dry weight	Predicted yield of mix reduced 10%, with 19% decrease in clover and 19% increase in fescue at 46 ppb.	Heagle et al. (1989b)
Alfalfa	14 to 98 ppb 12-h mean	32 days	OTC	Dry weight	2.4% reduction at 40 ppb, 18.3% reduction at 66 ppb.	Temple et al. (1987)
Alfalfa	20 to 53 ppb 12-h mean	11 weeks	OTC	Dry weight	22% reduction at 53 ppb.	Takemoto et al. (1988a)
Alfalfa	18 to 66 ppb 12-h mean	11 weeks	OTC	Shoot dry weight	22% reduction at 36 ppb.	Takemoto et al. (1988c)
Alfalfa	10 to 109 ppb 12-h mean	208 and 200 days in two growing seasons	OTC	Dry weight	0 to 25% reduction at levels of 38 ppb and above.	Temple et al. (1988a)
Alfalfa	60 to 80 ppb 6-h day	5 days/week for 8 weeks	GH	Relative growth rate	Reduced up to 40% in Saranac.	Cooley and Manning (1988)
Grape	Not reported	Two growing seasons	OTC	Yield	No effects of ambient air vs. filtration.	Musselman et al. (1985)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Means are seasonal means unless specified. Maximums are 1-h seasonal maxima unless otherwise specified. Cumulative exposures are SUM00 unless otherwise specified; accumulation based on 24 h/day unless otherwise noted.

<sup>c</sup>OTC = open-top chamber with plants in ground unless specified in pots; GC = controlled environment growth chamber or CSTR; GH = greenhouse.

<sup>d</sup>The effect reported in the study that is a measure of growth, yield, or productivity.

<sup>e</sup>Effect measured at specified ozone concentration, over the range specified under concentration, or predicted (if specified) to occur based on relationships developed in the experiment.

mean of 0.05 ppm, but resistant cultivars suffered only a 1.6% loss. Temple (1991) reported reductions in dry bean yield of 44 to 73% in three cultivars grown in California and exposed to a 12-h seasonal mean of 0.072 ppm. One other cultivar increased in yield in NF chambers but was severely affected in higher concentration O<sub>3</sub> treatments. Sanders et al. (1992) also observed yield stimulation at a 7-h growing season mean of 0.025 ppm; however, significant yield reductions were measured as O<sub>3</sub> concentrations increased to 50 ppb (7-h seasonal mean).

Several studies have shown soybean yields to be reduced by 10 to 15% at 7- or 12-h seasonal mean concentrations of 0.05 to 0.055 ppm (Table 5-26; Heagle et al., 1986b, 1987a; Heggestad and Lesser, 1990; Miller et al., 1989b).

A number of the studies cited above and some of those in Table 5-26 were conducted as part of NCLAN and are considered in the discussions of Tingey et al. (1991), Lee et al. (1993), and Lesser et al. (1990), but many of the experiments (primarily those not part of NCLAN) were not included in their analyses. Although the range of variability in species response to O<sub>3</sub> is apparent, these studies support, for the most part, the conclusions of U.S. Environmental Protection Agency (1986), Tingey et al. (1991), and Lesser et al. (1990). Table 5-24 summarizes the studies reporting the response of annual plants, particularly crops, as growth, dry weight, or yield to O<sub>3</sub> exposures (C × T) under experimental conditions since the previous criteria document (U.S. Environmental Protection Agency, 1986). Based on the results of the studies reviewed in this section, including the reanalysis of NCLAN, exposures for a 3-mo period to O<sub>3</sub> concentrations currently occurring in the ambient air (0.048 to 0.06 ppm, 7-h seasonal mean; see M7, Table 5-20) have been shown to cause losses of 10% or more in the yield of the majority of major crop plants grown in the country. A number of crop species are more sensitive, and greater losses could be expected (Tables 5-21 through 5-25). It should be noted that a variety of methodologies has been used to generate these data. Generally speaking, data obtained through growth chamber experiments and experiments conducted using potted plants, in fact, are more scientifically reliable but less relevant to ambient conditions when assessing the effects of O<sub>3</sub> than are results from field growth plants.

#### **5.6.4 Effects of Ozone on Long-Lived Plants**

Quantifying exposure-response in the case of perennial plants (agricultural crops such as pastures, alfalfa, and shrubs and trees) is complicated by the fact that they can receive multi-year exposures and because the results of exposures in a previous year, or over a number of years, may be cumulative. Reduction in growth and productivity, a result of altered carbon allocation, may appear only after a number of years or when carbohydrate reserves are depleted (U.S. Environmental Protection Agency, 1986; Laurence et al., 1993; Garner, 1991; Garner et al., 1989). A further complication is that, in the case of evergreen plants, the life span of a leaf exceeds 1 year and usually persists for several years. In such cases, loss of a leaf or a reduction in photosynthetic performance may have a large effect on a plant's ability to survive and grow. Physiological differences among species (rates of gas exchange, for instance) may have a tendency to equalize exposure over a number of years, however, as shown in Reich's (1987) analysis of crops, hardwoods, and conifers and in Pye's analysis of tree species (1988). Unfortunately, there is little experimental data regarding the effects of long-term O<sub>3</sub> exposure on perennial plants, because only a few experimental studies have extended exposures beyond a single growing season. Most of what is known regarding the effects of O<sub>3</sub> on mature trees is from field observations. There have been some studies that have extended observation of growth alterations into the season following exposures and,

thus, observed "carry-over effects" in several species. Hogsett et al. (1989) reported altered bud elongation in ponderosa pine, lodgepole pine (*Pinus contorta*), and western hemlock (*Tsuga heterophylla*), following a season of O<sub>3</sub> exposure. Altered root regrowth in ponderosa pine in the season following exposure that was correlated with root storage carbohydrate was observed by Andersen et al. (1991). Most studies have used seedlings because of the difficulty of exposing large trees. The extrapolation from seedlings to large trees and to forest stands is not straight-forward and, most likely, will depend on the use of models (Hogsett et al., 1995; Laurence et al., 1993; Taylor and Hanson, 1992). Correlative studies, such as those conducted in the San Bernardino Mountains of California, indicate potentially large impacts on ecosystems (U.S. Environmental Protection Agency, 1986). Cregg et al. (1989), however, point out that notable differences between trees and seedlings are their carbon allocation and use patterns. There is a significantly higher ratio of respiring to photosynthetic tissue in mature trees. This section will address three distinct types of long-lived plants: (1) multiple-year agricultural crops, (2) deciduous shrubs and trees, and (3) evergreen coniferous trees.

#### 5.6.4.1 Perennial Agricultural Crops

Cooley and Manning (1988) conducted a greenhouse study of the response of alfalfa to O<sub>3</sub> applied at 0.06 to 0.08 ppm for 6 h/day, 5 days/week for 8 weeks during 2 different years (to different plants). Ozone treatment reduced the growth and relative growth rate (by about 15 to 20% for tops and 20 to 40% for roots) of plants before cutting, when compared to a filtered-air control. The growth of roots was affected more than the growth of tops, with a shift in the allocation pattern. In the second year of the study, O<sub>3</sub> exposure was continued after the plants were harvested and the impact of exposure on regrowth was determined. In this case, they found that the relative growth rate in O<sub>3</sub> exposed plants was higher, perhaps because of an increased demand for carbon by the root systems of the O<sub>3</sub>-stressed plants. It is unclear whether these plants would sustain their increased growth, and, in fact, the authors speculate that the increased growth, in lieu of partitioning carbon to other compounds, might alter the cold hardiness of the plants.

Ozone has been demonstrated to affect the growth of field grown alfalfa. Temple et al. (1988a) reported a 2-year study of alfalfa in which O<sub>3</sub> at ambient concentrations (0.049 in 1984 and 0.042 ppm in 1985 for the seasonal 12-h means, April to October) did not affect the growth and yield of the plants, but at 12-h seasonal means of 0.063 and 0.078 ppm, yield was reduced by about 15 and 19%, respectively. The exposure-response functions for the 2 years were homogeneous; there was no indication of cumulative effect of O<sub>3</sub> exposure; however, crown weight (an indicator of health and vigor) of exposed plants was reduced significantly.

In a different field experiment conducted to determine the interactive effects of O<sub>3</sub> and simulated acid fog on stomatal conductance, photosynthesis, foliar injury, and yield of an established stand of alfalfa, plants were exposed 12 h daily for 4 weeks (Temple et al., 1987). Ozone was added in proportion to its concentration in the ambient air. Ambient O<sub>3</sub> concentrations during the experiment were 0.043 ppm. Ozone injury symptoms appeared on the alfalfa exposed to 0.098 ppm (NF × 2.0), 1 week after the start of the regrowth period. When exposures were at 0.081 and 0.066 ppm (NF × 1.7 and NF × 1.3), more than a week was required for injury to appear. A 1-mo exposure of the plants at the end of the growing season resulted in a reduction of about 2.5% in aboveground yield at a 12-h seasonal mean concentration of 0.04 ppm. At a concentration of 0.066 ppm, the exposure resulted in a

reduction in yield of approximately 18%. It should be noted that the whole plant was exposed to ambient O<sub>3</sub> for the growing season, only new leaves that had developed after harvest received the 1-mo exposure. Ozone exposures could shorten the productive life of alfalfa stands, in addition to its affecting yield.

Kohut et al. (1988a) and Heagle et al. (1989b) experimented with forage mixtures characteristic of the northeast and southeast, respectively. In both cases, exposure to O<sub>3</sub> resulted in a reduction in total forage yield of about 10 to 20% at 12-h seasonal mean O<sub>3</sub> concentrations of 0.045 to 0.05 ppm. In both cases, the clover component of the mix was more sensitive than the grass and was reduced in prevalence in the stand. The relevance of these studies to competition and species composition is discussed in the section on ecosystem response (Section 5.7).

Results of studies on perennial plants conducted since 1986 are summarized in Table 5-26. As with single-season agricultural crops, yields of multiple-year forage crops are reduced at concentrations at or near ambient (0.05 to 0.06 ppm for 5 weeks) in many parts of the country.

#### **5.6.4.2 Effects of Ozone on Deciduous Shrubs and Trees**

Most of the information concerning the response of deciduous shrubs and trees to episodes or season-long or multiple-year exposures to O<sub>3</sub> is based on field observations. The longevity of perennial plants and their size, in the case of trees, makes their study under experimental conditions difficult. For this reason, there is little experimental data concerning the response of deciduous shrubs and trees.

Trees, because of their size, are difficult to study under controlled conditions, therefore, most experiments have used seedlings in pots or in OTCs. Most of the hardwood experiments included in Reich's analysis (1987), for example, were exposed under laboratory or greenhouse conditions to relatively high concentrations for short periods of time. Although exposure durations of weeks were used, square-wave exposure regimes that do not capture important characteristics of ambient exposure were used. In addition, in Pye (1988), the majority of the studies were conducted in a laboratory or greenhouse. The results of a few OTC studies are cited; however, the majority of these studies used O<sub>3</sub> concentrations of 0.10 ppm or higher, a condition found only during peak exposures in the ambient air. Although the studies reported in the previous criteria document (U.S. Environmental Protection Agency, 1986) (see Section 5.6.2) support the sensitivity of the seedlings of some species grown in chambers, little information of value with regard to tree growth or biomass production in the long-term can be extrapolated from the experiments. Since 1986, a number of studies have been conducted documenting the sensitivity of hardwoods to O<sub>3</sub> (Table 5-27). Some species, such as black cherry, are very sensitive, although great variability in foliar injury was observed among individual trees, indicating that sensitivity varies greatly within species (Davis and Skelly, 1992a,b; Simini et al., 1992). No significant reductions in basal diameter and height growth were observed during the 3 years of the study, although growth was reduced during 1988 at two sites where O<sub>3</sub> concentrations exceeded 0.12 ppm (Simini et al., 1992), with SUM06 exposures as low as 12.9 ppm·h over 92 days (concentrations not given) predicted to cause a 10% yield loss (Hogsett et al., 1995; Table 5-28).

Based on studies previously reviewed, the growth of some hardwood species, particularly those of the genus *Populus*, may be affected by ambient concentrations of

**Table 5-27. A Summary of Studies Reporting the Effects of  
Ozone on the Growth or Productivity of Deciduous Shrubs and Trees  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Almond	38 to 112 ppb 12-h mean	153 days	OTC	Total dry weight	Linear reduction in two cultivars, no effect in three.	Retzlaff et al. (1992a)
Almond	30 to 117 ppb 12-h mean	3.5 mo	OTC	Cross-sectional area	6% reduction at 51 ppb.	Retzlaff et al. (1991)
Almond	250 ppb, 4 h/week	16 weeks in each of two growing seasons	CC	Net growth	28 and 36% reduction in years 1 and 2.	McCool and Musselman (1990)
Plum	44 to 111 ppb 12-h mean	191 and 213 days	OTC	Number of fruit per tree	29% fewer fruit at ambient and above.	Retzlaff et al. (1992b)
Plum	30 to 117 ppb 12-h mean	3.5 mo	OTC	Cross-sectional area	19% reduction at 51 ppb.	Retzlaff et al. (1991)
Pear	30 to 117 ppb 12-h mean	3.5 mo	OTC	Cross-sectional area	8% reduction at 51 ppb.	Retzlaff et al. (1991)
Apricot	30 to 117 ppb 12-h mean	3.5 mo	OTC	Cross-sectional area	53% reduction at 117 ppb.	Retzlaff et al. (1991)
Skunk bush	10 to 75 ppb 12-h mean	3 mo	OTC in pots	Growth	Increase in leaf weight in ambient air; no other effect.	Temple (1989)
Black cherry	16 to 67 ppb 12-h mean	Three growing seasons	OTC	Growth and leaf dynamics	Leaf abscission increased with increasing ozone.	Simini et al. (1992)
Black cherry	40 or 80 ppb, 7 h/day, 5 days/week	8 or 12 weeks	GC	Growth	Reduced leaf, stem, and root dry weight, and height at 80 ppb.	Davis and Skelly (1992b)
Red oak	18 to 87 ppm-h 15 to 69 ppb 7-h mean	177 days	OTC	Tree canopy	Reduced 41% at 82 ppm-h or 69 ppb 7-h mean.	Samuelson and Edwards (1993)
Red oak	16 to 67 ppb 12-h mean	Three growing seasons	OTC	Growth and leaf dynamics	No effect.	Simini et al. (1992)

**Table 5-27 (cont'd). A Summary of Studies Reporting the Effects of  
Ozone on the Growth or Productivity of Deciduous Shrubs and Trees  
Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Red oak	40 or 80 ppb, 7 h/day, 5 days/week	8 or 12 weeks	GC	Growth	Reduced root dry weight at 80 ppb.	Davis and Skelly (1992b)
Red maple	16 to 67 ppb 12-h mean	Three growing seasons	OTC	Growth and leaf dynamics	No effect.	Simini et al. (1992)
Red maple	40 or 80 ppb, 7 h/day, 5 days/week	8 or 12 weeks	GC	Growth	Reduced stem diameter and dry weight at 80 ppb.	Davis and Skelly (1992b)
Tulip poplar	16 to 67 ppb 12-h mean	Three growing seasons	OTC	Growth and leaf dynamics	Leaf abscission increased with increasing ozone.	Simini et al. (1992)
Yellow poplar	40 or 80 ppb, 7 h/day, 5 days/week	8 or 12 weeks	GC	Growth	Reduced leaf dry weight and stem diameter at 80 ppb.	Davis and Skelly (1992b)
European beech	10 to 90 ppb weekly mean	5 years	OTC	Growth	Reduced shoot growth and leaf area.	Billen et al. (1990)
Aspen	80 ppb, 6 h/day, 3 days/week	70 and 92 days in two growing seasons	OTC	Stem weight	No effect on tolerant clones; 46% reduction for sensitive clones in 1 year 5% (tolerant), and 74% (sensitive) reductions in the second year.	Karnosky et al. (1992b)
Aspen	Filtered air or 80 ppb, 6 h/day, 3 days/week	93 days at two sites in Michigan	OTC	Growth	18 to 26% reduction in diameter growth.	Karnosky et al. (1992a)
Aspen	Ambient + 27, 51, or 102-ppb exposure period mean	105 days	CC	Dry weight	40% reduction; 44% reduction in early growth the following year.	Keller (1988)

**Table 5-27 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth or Productivity of Deciduous Shrubs and Trees Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Yellow poplar	0 to 200 ppb, 8 h/day, 3 days/week	4.5 mo	GC	Growth	Up to a 24% reduction at 200 ppb but moderated by pH treatment.	Jensen and Patton (1990)
Paper birch	60 to 80 ppb, 7 h/day, 5 days/week	12 weeks	GH	Dry weight	Decreased shoot and root weight and leaf area.	Keane and Manning (1988)
Downy birch	25 to 82 ppb, 7 h/day	50 days	GC	Dry weight	Shoot and root dry weight decreased linearly with ozone.	Mortensen and Skre (1990)
Downy birch	25 to 82 ppb, 7 h/day	50 days	GC	Dry weight	Shoot and root dry weight decreased linearly with ozone.	Mortensen and Skre (1990)
Red alder	25 to 82 ppb, 7 h/day	50 days	GC	Dry weight	Shoot and root dry weight decreased linearly with ozone.	Mortensen and Skre (1990)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Means are seasonal means unless specified. Maximums are 1-h seasonal maxima unless otherwise specified. Cumulative exposures are SUM00 unless otherwise specified, accumulation based on 24 h/day unless otherwise noted.

<sup>c</sup>OTC = open-top chamber with plants in ground unless specified in pots; CC = closed chamber, outside; GC = controlled environment growth chamber or CSTR; GH = greenhouse.

<sup>d</sup>The effect reported in the study that is a measure of growth, yield, or productivity.

<sup>e</sup>Effect measured at specified ozone concentration, over the range specified under concentration, or predicted (if specified) to occur based on relationships developed in the experiment.



**Table 5-28. Exposure-Response Equations That Relate Total Biomass (Foliage, Stem, and Root) to 24-Hour SUM06 Exposures (C) Adjusted to 92 Days (ppm-h/year)<sup>a</sup>**

Rate of Growth	Habit	Study	Species	Location (State)	Exposure <sup>b</sup>		Harvests <sup>c</sup>	Weibull Parameters			SUM06 for Loss of <sup>d</sup>	
					Days	Year		A	B	C	10%	30%
Fast	D	1	Aspen, wild	OR	84	1989	1	9.9	96.3	1.316	19.09	48.21
Fast	D	1	Aspen, wild	OR	84	1989	2	17.7	165.2	1.000	19.06	64.54
Fast	D	2	Aspen, wild	OR	118	1991	1	31.0	130.0	3.062	48.62	72.41
Fast	D	2	Aspen, wild	OR	118	1991	2	75.6	124.9	5.529	64.80	80.79
Fast	D	3	Aspen, wild	OR	112	1990	1	67.8	111.0	6.532	64.60	77.86
Fast	D	3	Aspen, wild	OR	112	1990	2	96.9	142.1	1.257	19.48	51.40
Fast	D	4	Aspen 216	MI	82	1990	1	54.5	121.1	1.609	33.56	71.60
Fast	D	4	Aspen 253	MI	82	1990	1	73.1	265.5	1.000	31.38	106.23
Fast	D	4	Aspen 259	MI	82	1990	1	79.1	92.7	1.000	10.96	37.10
Fast	D	4	Aspen 271	MI	82	1990	1	91.3	44.9	8.964	39.20	44.91
Fast	D	5	Aspen 216	MI	98	1991	1	37.4	128.6	1.000	12.72	43.06
Fast	D	5	Aspen 259	MI	98	1991	1	35.2	95.9	1.000	9.49	32.11
Fast	D	5	Aspen 271	MI	98	1991	1	35.7	73.1	4.012	39.16	53.07
Fast	D	6	Aspen, wild	MI	98	1991	1	19.0	263.1	1.000	26.02	88.08
Slow	E	7	Douglas fir	OR	113	1989-90	1	16.8	462.7	1.844	111.17	215.37
Slow	E	7	Douglas fir	OR	113	1989-90	2	27.9	3.8E+17	1.000	250.00	250.00
Slow	E	7	Douglas fir	OR	234	1989-90	3	33.3	438.9	5.383	113.61	142.49
Slow	E	7	Douglas fir	OR	234	1989-90	4	83.5	2,887.0	1.000	119.61	404.91
Slow	E	8	Douglas fir	OR	118	1991-92	1	26.7	109.5	57.655	82.13	83.88
Slow	E	8	Douglas fir	OR	118	1991-92	2	85.9	-0.0058	(lin)	250.00	250.00
Slow	E	8	Douglas fir	OR	230	1991-92	3	119.1	218.7	12.254	72.80	80.42
Slow	E	9	Ponderosa pine	OR	111	1989	1	12.8	246.9	1.000	21.56	73.00
Slow	E	9	Ponderosa pine	OR	111	1989	2	25.8	365.2	1.000	31.89	107.95
Slow	E	10	Ponderosa pine	OR	113	1989-90	1	12.9	233.7	1.000	20.05	67.87
Slow	E	10	Ponderosa pine	OR	113	1989-90	2	25.7	358.8	1.000	30.77	104.18
Slow	E	10	Ponderosa pine	OR	234	1989-90	3	32.1	327.8	1.000	13.58	45.97
Slow	E	10	Ponderosa pine	OR	234	1989-90	4	90.1	634.3	1.000	26.27	88.94
Slow	E	11	Ponderosa pine	OR	118	1991-92	1	20.2	266.4	1.000	21.88	74.09
Slow	E	11	Ponderosa pine	OR	118	1991-92	2	47.1	206.5	1.000	16.96	57.42
Slow	E	11	Ponderosa pine	OR	230	1991-92	3	44.5	458.5	1.257	30.61	80.77
Slow	E	12	Ponderosa pine	OR	140	1992	1	134.6	235.8	2.570	64.56	103.76
Slow	E	13	Ponderosa pine	OR	84	1991	1	136.0	442.8	1.000	51.10	172.98
Fast	D	14	Red alder	OR	121	1990	1	42.4	217.0	1.427	34.08	80.10
Fast	D	15	Red alder	OR	113	1989	1	84.4	253.0	1.000	21.70	73.46
Fast	D	15	Red alder	OR	113	1989	2	206.8	179.9	5.294	95.76	120.57
Fast	D	16	Red alder	OR	118	1991	1	63.5	501.7	1.000	41.21	139.51
Fast	D	16	Red alder	OR	118	1991	2	248.8	2.0E+13	1.000	250.00	250.00
Fast	D	17	Red alder	OR	112	1992	1	54.1	274.4	1.107	29.50	88.79
Fast	D	18	Black cherry	TN	76	1989	1	53.7	79.1	1.123	12.91	38.23
Fast	D	19	Black cherry	TN	140	1992	1	37.1	176.6	1.168	16.90	48.00
Slow	D	20	Red maple	TN	55	1988	1	28.5	387.1	1.537	149.75	331.07
Fast	D	21	Tulip poplar	TN	75	1990-91	1	45.8	46.4	4.518	34.56	45.27
Fast	D	21	Tulip poplar	TN	184	1990-91	3	334.1	623.5	1.000	32.85	111.19
Fast	D	22	Tulip poplar	TN	81	1992	1	150.1	50.8	1.852	17.12	33.07

**Table 5-28 (cont'd). Exposure-Response Equations That Relate Total Biomass (Foliage, Stem, and Root) to 24-Hour SUM06 exposures (C) Adjusted to 92 days (ppm-h/year)<sup>a</sup>**

Rate of Growth	Habit	Study	Species	Location (State)	Exposure <sup>b</sup>			Weibull Parameters			SUM06 for Loss of <sup>d</sup>	
					Days	Year	Harvests <sup>c</sup>	A	B	C	10%	30%
Fast	E	23	Loblolly GAKR 15-91	AL	555	1988-89	3	22.7	4,402.5	1.000	76.89	260.30
Fast	E	23	Loblolly GAKR 15-23	AL	555	1988-89	3	20.4	13,125.4	1.000	229.24	250.00
Slow	D	24	Sugar maple	MI	83	1990-91	1	4.12	100.0	40.069	104.79	108.03
Slow	D	24	Sugar maple	MI	180	1990-91	3	24.63	110.2	5.987	38.68	47.42
Slow	E	25	Eastern white pine	MI	83	1990-91	1	0.35	63.1	4.191	40.90	54.72
Slow	E	25	Eastern white pine	MI	180	1990-91	3	1.21	719.5	1.000	38.74	131.16
Slow	E	26	Virginia pine	MI	98	1992	1	78.3	3,045.1	1.000	250.00	250.00

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Duration corresponds to the length in days of the first year of exposure for Harvests 1 and 2 and to the total length of the first and second years of exposure for Harvests 3 and 4.

<sup>c</sup>Harvest 1 occurs immediately following the end of the first year of exposure. Harvest 2 occurs in the spring following the first year of exposure. Harvest 3 occurs immediately following the end of the second year of exposure. Harvest 4 occurs in the spring following the second year of exposure.

<sup>d</sup>To compare the results from seedling studies of varying exposure duration, the SUM06 value is calculated for an exposure of fixed period of 92 days per year. For example, Study 1 Harvest 1 has an exposure duration of 84 days and a SUM06 value of 19.09 ppm-h over 92, days which corresponds to a SUM06 value of  $19.09 \times 84/92 = 17.43$  ppm-h over 84 days, at which biomass loss is 10%. The calculation assumes that exposures can be scaled up or down in uniform fashion.

<sup>e</sup>Based on GIS, TREGRO, and ZELIG models projections. No data given in paper.

Source: Hogsett et al. (1995).

O<sub>3</sub> (U.S. Environmental Protection Agency, 1978, 1986). In studies of the response of aspen clones to O<sub>3</sub> at two field sites in Michigan, Karnosky et al. (1992a,b) documented reductions in stem weight of up to 46% in sensitive aspen clones after 70 days of exposure in OTCs to 0.08 ppm for 6 h/day, 3 days/week.

Tjoelker and Luxmoore (1991) found leaf abscission on tulip poplar (*Liriodendron tulipifera*) seedlings to be increased by exposure to a 7-h seasonal mean concentration of 0.108 ppm, resulting in a doubling of the leaf turnover rate, but this was not translated into an effect on growth, perhaps due to the indeterminate growth habit of the plant. In such plants, leaf production continues throughout the growing season, which may permit the tree to maintain an optimal leaf area; however, continued leaf growth could deplete carbon or nitrogen reserves.

Samuelson and Edwards (1993), in a study to determine if seedlings and trees responded similarly to O<sub>3</sub>, found canopy weight of 30-year-old northern red oak, exposed in large OTCs, to be reduced by 41% after exposure for 177 days at a 7-h seasonal mean of 0.069 ppm (87 ppm-h SUM08), compared to a subambient treatment at a 7-h seasonal mean of 0.015 ppm (18 ppm-h SUM00). Two-year-old seedlings were not affected by similar exposures. Trees produced only one flush of leaves, seedlings produced as many as three.

Hogsett et al. (1995) developed exposure-response functions for aspen, red alder (*Alnus rubra*), black cherry (*Prunus serotina*), red maple (*Acer rubrum*), and tulip poplar (Table 5-28), as well as composite functions for deciduous tree seedlings (Table 5-29). Their results suggest that, for 28 deciduous seedling cases, a SUM06 exposure of 31.5 ppm-h over 92 days with a mean concentration of approximately 0.055 ppm could result in less than a

**Table 5-29. SUM06 Levels Associated with 10 and 20% Total Biomass Loss for 50 and 75% of the Seedling Studies  
(The SUM06 value is adjusted to an exposure length of 92 days per year.)<sup>a</sup>**

Weibull Equations (all 51 seedling studies):

$$50\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/176.342]**1.34962)$$

$$75\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/104.281]**1.46719)$$

Weibull Equations (27 fast-growing seedling studies):

$$50\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/150.636]**1.43220)$$

$$75\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/89.983]**1.49261)$$

Weibull Equations (24 slow to moderate growing seedling studies):

$$50\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/190.900]**1.49986)$$

$$75\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/172.443]**1.14634)$$

Weibull Equations (28 deciduous seedling studies):

$$50\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/142.709]**1.48845)$$

$$75\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/87.724]**1.53324)$$

Weibull Equations (23 evergreen seedling studies):

$$50\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/262.911]**1.23673)$$

$$75\text{th Percentile PRYL} = 1 - \exp(-[\text{SUM06}/201.372]**1.01470)$$

Levels Associated with Prevention of a 10 and 20% Total Biomass Loss for 50 and 75% of the Seedlings:

All 51 Seedling Cases

		Percent of Seedlings	
		50%	75%
Relative	10%	33.3	22.5
Biomass Loss	20%	58.0	37.5

27 Fast-Growing Seedling Cases

		Percent of Seedlings	
		50%	75%
Relative	10%	31.3	19.4
Biomass Loss	20%	52.9	32.4

24 Slow-to-Moderate-Growth Seedling Cases

		Percent of Seedlings	
		50%	75%
Relative	10%	42.6	24.2
Biomass Loss	20%	70.2	46.6

28 Deciduous Seedling Cases

		Percent of Seedlings	
		50%	75%
Relative	10%	31.5	20.2
Biomass Loss	20%	52.1	33.0

**Table 5-29 (cont'd). SUM06 Levels Associated with 10 and 20% Total Biomass Loss for 50 and 75% of the Seedling Studies**  
**(The SUM06 value is adjusted to an exposure length of 92 days per year.)<sup>a</sup>**

23 Evergreen Seedling Cases		Percent of Seedlings	
		50%	75%
Relative	10%	42.6	21.9
Biomass Loss	20%	78.2	45.9

<sup>a</sup>See Appendix A for abbreviations and acronyms.

Hogsett et al. (1995).

10% growth (biomass) reduction in 50% of the cases. A 20% reduction in growth should result from a SUM06 exposure of greater than 52.1 ppm·h. Comparison with Table 5-20 shows a SUM06 for 3 mo of 29.5 ppm·h at ambient concentrations, a value near that (33.3 ppm·h) expected to prevent a 10% growth reduction in 50% of the cases (Table 5-27). An individual year, such as 1988, might be significantly above the no-injury exposure value (Table 5-20). By further grouping the seedlings by rate of growth (fast or slow), the investigators were able to refine estimates of the SUM06 exposure that would protect seedlings, based on growth strategy. Deciduous seedlings, and fast-growing species are more sensitive than evergreen and slow-growing seedlings (Table 5-27). Seedlings utilize more of the carbon compounds formed during photosynthesis for growth, whereas mature trees use more for maintenance; therefore, extrapolation of exposure response from seedlings to mature trees may lead to inaccurate assumptions.

The response of a number of fruit and nut trees to O<sub>3</sub> has been reported (McCool and Musselman, 1990; Retzlaff et al., 1991, 1992a,b). Almond (*Prunus amygdalis* Batsch) has been identified as the most sensitive, but peach (*Prunus persica*), apricot, pear, and plum (*Prunus domestica*) also have been affected. Net growth of almond, the stem diameter of peach, and the stem diameter and number of shoots produced on apricot were reduced by 4 mo (the exposure duration specified by the authors) of once-weekly exposure to 0.25 ppm for 4 h (an exposure found only in California), a relatively small exposure cumulatively (16 ppm·h as a SUM00 or as a SUM06) (McCool and Musselman, 1990), but one with a high peak value. Cross-sectional area of almond, plum, apricot, and pear stems decreased linearly with increasing O<sub>3</sub>, with a significant reduction at a 12-h seasonal mean of 0.051; dry weight of roots, trunk, and foliage also was reduced in one variety of almond (Retzlaff et al., 1992a).

Finally, two studies report the response of citrus and avocado to O<sub>3</sub> (Eissenstat et al., 1991a; Olszyk et al., 1990b). These species retain their leaves for more than 1 year, but fit best in the deciduous category because, although evergreen, leaves are replaced more frequently than in most evergreen species. Valencia orange trees (*Citrus sinensis*), exposed during a production year to a seasonal 12-h mean of 0.04 or 0.075 ppm, had 11 and 31% lower yields than trees grown in filtered air at 0.012 ppm and atypical concentration. During an off-production year, yield was not affected. Growth of Ruby Red grapefruit (*Citrus paradisi*) was not affected by concentrations of three times that of the ambient concentration

(Eissenstat et al., 1991b). Avocado growth was reduced by 20 or 61% by exposure during two growing seasons at 12-h seasonal mean concentrations of 0.068 and 0.096 ppm.

In summary, deciduous trees appear to be less sensitive to O<sub>3</sub> than are most crop plants, but there are species that are as sensitive or more so because of their genetic composition than are crops (e.g., *Populus* species and perhaps black cherry; see discussion in Section 5.4.2). Analysis of the shrub and tree data presented in Table 5-25 and discussed above suggests that a 7-h seasonal mean exposure of approximately 0.055 ppm over a 3-mo period would not result in injury to tree seedlings. However, the absence of multiple-year studies, or studies using older, more mature trees, leaves unanswered the question of long-term and cumulative effects.

#### **5.6.4.3 Effects of Ozone on Evergreen Trees**

As with hardwoods, little long-term data from controlled studies of evergreen trees were available at the time the literature was reviewed for the previous criteria document (U.S. Environmental Protection Agency, 1986). The 1986 document did point out, however, that studies conducted on eastern white pine on the Cumberland Plateau in Tennessee indicated that ambient O<sub>3</sub> may have reduced the radial growth of sensitive individuals by as much as 30 to 50% annually over a period of 15 to 20 years (Mann et al., 1980). Also, field studies in the San Bernardino National Forest indicated that, over a period of 30 years, O<sub>3</sub> may have reduced the growth in height of ponderosa pine by as much as 25%, radial growth by 37%, and total volume of wood produced by 84% (Miller et al., 1982). Calculations of biomass in these studies were based on apparent reductions in radial growth without standardization of the radial growth data with respect to tree age. Since 1986, studies on the effects of O<sub>3</sub> on evergreen trees have focused primarily on three species or groups: (1) red spruce in the eastern United States, (2) southern pines (loblolly and slash), and (3) western conifers (primarily ponderosa pine). For the most part, the research has been conducted with tree seedlings or saplings and has involved exposures lasting one to four growing seasons. In many cases, the research has concentrated on defining the mode of action of O<sub>3</sub> in conifers and is discussed elsewhere in this document (Section 5.3). Results of studies with evergreen trees are summarized in Table 5-30.

Studies of the response of red spruce to O<sub>3</sub> exposures, regardless of whether they have been conducted in growth chambers (Lee et al., 1990a,b; Patton et al., 1991; Taylor et al., 1986) or in the field (Kohut et al., 1990; Laurence et al., 1993; Thornton et al., 1992) have failed to detect effects on growth of seedlings or saplings, even after exposure to 12-h seasonal means of up to approximately 0.09 ppm (concentrations that are considerably greater than those expected in ambient air) each year for up to 4 years. There was an indication that total nonstructural carbohydrate content was reduced by O<sub>3</sub>, which might be an indicator of cumulative stress (Woodbury et al., 1992). However, results of these studies indicate red spruce is tolerant of O<sub>3</sub>, at least for exposures of a few years.

Growth of seedlings of loblolly pine (a much faster growing species than red spruce) has been reduced by O<sub>3</sub> under some conditions. In growth chamber experiments, height growth was reduced after exposure to 0.10 ppm for 4 h/day, 3 days/week for 10 weeks, but only in combination with a "control" rain treatment. The effect was not observed in trees that received significant inputs of potential nutrients in simulated rain. Conversely, Tjoelker and Luxmoore (1991) reported a significant reduction in the weight of current year needles following an OTC exposure to O<sub>3</sub> at a 7-h seasonal mean of 0.056 or 0.108 ppm, only in a high-nitrogen treatment.

**Table 5-30. A Summary of Studies Reporting the Effects of Ozone on the Growth or Productivity of Evergreen Trees Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Avocado	0.010 to 0.108 ppm 12-h mean	4 and 8 mo in two growing seasons	OTC in pots	Leaf mass	20 and 61% reduction in leaf mass at 86 and 108 ppb.	Eissenstat et al. (1991a)
Orange	0.010 to 0.108 ppm 12-h mean	4 and 8 mo in two growing seasons	OTC in pots	Leaf mass	No effect.	Eissenstat et al. (1991a)
Orange	0.012 to 0.075 ppm 12-h mean	7 mo/season for 5 years	OTC	Fruit weight	"On" production year: 11 and 31% reduction at 40 and 75 ppb; "off" year: no effect.	Olszyk et al. (1990b)
Ponderosa pine	0.036 to 0.051 ppm 24-h mean	June to August	F	Radial growth rate	No change in growth rate on symptomatic trees.	Peterson and Arbaugh (1988)
Ponderosa pine	0.013 to 0.095 ppm 12-h mean, 0.047 to 0.0350 ppm·h over 3 years	Three growing seasons	OTC	Growth	19.5% reduction at 95 ppb.	Beyers et al. (1992)
Ponderosa pine	0.011 to 0.087 ppm 12-h mean	Three growing seasons	OTC	Leaf weight	70 and 48% loss of 1- and 2-year-old needles at 87 ppb.	Temple et al. (1993)
Ponderosa pine	5, 122, or 169 ppm·h	112 days	OTC in pots	Root growth	43% reduction in coarse and fine nongrowing roots; 50, 65, and 62% reduction in coarse, fine, and new growing roots, respectively.	Andersen et al. (1991)
Ponderosa pine	0.067 to 0.071 ppm 7-h mean	134 days	OTC in pots	Leaf, stem, and root dry weight	20 to 33% reduction from filtered air at 67 ppb.	Hogsett et al. (1989)
Lodgepole pine	0.067 to 0.071 ppm 7-h mean	134 days	OTC in pots	Leaf, stem, and root dry weight	No effect.	Hogsett et al. (1989)
Jeffrey pine	0 to 0.0200 ppm, 4 h/day, 3 days/week	44 and 58 days in two growing seasons	GC	Root, stem, and needles dry weight	Reduced 10 to 20% ppb in 1 year.	Temple (1988)

**Table 5-30 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth or Productivity of Evergreen Trees Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Jeffrey pine	>0.10 ppm	On 34 days of 1985	F	Radial growth	11% reduction in symptomatic trees.	Peterson et al. (1987)
Western hemlock	0.067 to 0.071 ppm 7-h mean	134 days	OTC in pots	Leaf, stem, and root dry weight	11 to 30% reduction at 71 ppb.	Hogsett et al. (1989)
Western red cedar	0.067 to 0.071 ppm 7-h mean	134 days	OTC in pots	Leaf, stem, and root dry weight	No effect.	Hogsett et al. (1989)
Douglas fir	0.067 to 0.071 ppm 7-h mean	134 days	OTC in pots	Leaf, stem, and root dry weight	No effect.	Hogsett et al. (1988)
Giant sequoia	0-0.0200 ppm, 4 h/day, 3 days/week	44 and 58 days in two growing seasons	GC	Root, stem, and needles dry weight	No effect.	Temple (1988)
Red spruce	0.08 to 0.0166 ppm 8-h mean, 8 to 156 ppm·h	135 days	OTC	Scion growth	No effect on juvenile or mature scion growth.	Rebbeck et al. (1992)
Red spruce	0.023 to 0.087 ppm 12-h mean	Two growing seasons	OTC in pots	Dry weight	No effect.	Kohut et al. (1990)
Red spruce	0.120 ppm, 4 h/day, twice per week	4 mo	GC	Growth	No effect.	Taylor et al. (1986)
Red spruce	0, 0.150 ppm, 6 h/day or 150 ppb, 6 h, plus 70 ppb 18 h/day	195 days	GC	Dry weight	No effect.	Patton et al. (1991)
Red spruce	0.025 or 0.100 ppm, 4 h/day, 3 day/week	10 weeks	GC	Growth	No effect.	Lee et al. (1990b)

**Table 5-30 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth or Productivity of Evergreen Trees Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Red spruce	0.027 to 0.054 ppm 12-h mean	Three growing seasons	OTC in pots	Dry weight, diameter, and height	No effect.	Thornton et al. (1992)
Norway spruce	0.080 to 0.100 ppm, 7 to 8 h/day	100 days	GC	Dry weight	0 to 14% reduction vs. filtered air, five provenances.	Mortensen (1990a)
Norway spruce	0.014 to 0.070 ppm 8-h mean	5 to 6 mo in two growing seasons	OTC in pots	Growth	No effect.	Nast et al. (1993)
Norway spruce	0.010- to 0.090-ppm weekly mean	5 years	OTC	Growth	Reduced lateral shoot growth in last year.	Billen et al. (1990)
Sitka spruce	0.05 to 0.170 ppm, 7 h/day, 5 days/week	65 days	GH	Growth and winter hardiness	No effect on growth, reduced winter hardiness.	Lucas et al. (1988)
Silver fir	0.010- to 0.090-ppm weekly mean	5 years	OTC	Growth	Increased dry matter production.	Billen et al. (1990)
Fraser fir	0.020 to 0.100 ppm, 4 h/day, 3/week	10 weeks	GC	Biomass	No effect.	Tseng et al. (1988)
White pine	0.020 to 0.140 ppm, 7 h/day, 3 day/week	3.5 mo	GC	Dry weight	No effect.	Reich et al. (1987)
Loblolly pine	0.021 to 0.086 ppm 7-h mean	96 days	OTC in pots	Dry weight	18% reduction at 86 ppb; 20% reduction in foliage at 40 or 86 ppb.	Adams et al. (1988)
Loblolly pine	0.021 to 0.117 ppm 7-h mean	Three growing seasons	OTC in pots	Growth	No effect on five families.	Adams et al. (1990b)
Loblolly pine	0.022 to 0.094 ppm 7-h mean	Three growing seasons	OTC in pots	Dry weight	4% reduction at 30 to 38 ppm; 8% reduction at 51 to 65 ppm.	Edwards et al. (1992a)
Loblolly pine	0.032 to 0.108 ppm 7-h mean	18 weeks	OTC in pots	Dry weight	20% reduction in needles at 108 ppm.	Tjoelker and Luxmoore (1991)
Loblolly pine	0.023 to 0.090 ppm 12-h mean, 46 to 0.209 max 12-h	150 days	OTC in pots	Growth	10% reduction at 46 ppm.	Shafer et al. (1987)



**Table 5-30 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth or Productivity of Evergreen Trees Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Loblolly pine	0.022 to 0.092 ppm 12-h mean, 37 to 0.143 ppm 1-h max	Three growing seasons	OTC in pots	Dry weight	0 to 13% reduction after 3 years at about 45 to 50 ppm 12-h seasonal mean, depending on family.	Shafer and Heagle (1989)
Loblolly pine	0.007 to 0.166 ppm 12-h mean, 12-h max 248 ppm	245 days	OTC in pots	Foliar weight	35% reduction at 166 ppm.	Qiu et al. (1992)
Loblolly pine	0.007 to 0.132 ppm 12-h mean 17 to 382 ppm·h	Three growing seasons	OTC	Foliage abscission	Initiated above 130 to 220 ppm·h in trees exposed to ambient or above.	Stow et al. (1992)
Loblolly pine	0.021 to 0.137 ppm 12-h mean 60 to 397 ppm·h	241 days	OTC	Shoot growth	Shoot length reduced 30% at 137 ppm.	Mudano et al. (1992)
Loblolly pine	0.020 to 0.137 ppm 12-h mean 0.050 to 0.286 ppm max 12-h mean	Two growing seasons	OTC	Needle retention and fascicle length	Needle retention decreased in elevated ozone—fascicle length reduced by ozone in early flushes, increased in later flushes.	Kress et al. (1992)
Loblolly pine	0 to 0.150 ppm, 5 h/day, 5 days/week	6 to 12 weeks	GC	Dry weight	8% reduction at 150 ppm.	Meier et al. (1990)
Loblolly pine	0 to 0.320 ppm, 6 h/day, 4 days/week	8 weeks	GC	Height and diameter growth	20% reduction in height growth; 36% reduction in diameter growth in three open-pollinated families.	Horton et al. (1990)
Loblolly pine	0 to 0.120 ppm, 7 h/day, 5 days/week	12 weeks	GC	Dry weight	Top dry weight increased up to 60%; root dry weight reduced 6%.	Spence et al. (1990)
Loblolly pine	0 to 0.320 ppm, 8 h/day, 4 days/week	9 weeks	GC	Relative growth rate (RGR)	36% reduction in height RGR; 10% reduction in diameter RGR.	Wiselogle et al. (1991)

**Table 5-30 (cont'd). A Summary of Studies Reporting the Effects of Ozone on the Growth or Productivity of Evergreen Trees Published Since U.S. Environmental Protection Agency (1986)<sup>a</sup>**

Species	Concentration <sup>b</sup>	Duration	Facility <sup>c</sup>	Variable <sup>d</sup>	Effect <sup>e</sup>	Reference
Loblolly pine	0.020 to 0.100 ppm, 4 h/day, 3 days/week	10 weeks	GC	Dry weight	No effect.	Lee et al. (1990a)
Slash pine	0.076 to 0.104 ppm 7-h mean 0.126 ppm 1-h max 122 and 155 ppm·h	112 days	GC	Top and root dry weight	18% reduction in top dry weight and 39% reduction in root dry weight at 122 ppm·h.	Hogsett et al. (1985a)
Slash pine	200 to 1,000 ppm·h	28 mo	OTC	Litterfall	Twice as much litterfall at ozone above 220 ppm·h.	Byres et al. (1992)
Slash pine	179 to 443 ppm·h 24-h SUM00 multiples of ambient	28 mo	OTC	Leaf area	Reduced up to 33% by 443 ppm·h.	Dean and Johnson (1992)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Means are seasonal means unless specified. Maximums are 1-h seasonal maxima unless otherwise specified. Cumulative exposures are SUM00 unless otherwise specified, accumulation based on 24 h/day unless otherwise noted.

<sup>c</sup>OTC = open-top chamber with plants in ground unless specified in pots; GC = controlled-environment growth chamber or CSTR; GH = greenhouse; F = field.

<sup>d</sup>The effect reported in the study that is a measure of growth, yield, or productivity.

<sup>e</sup>Effect measured at specified ozone concentration, over the range specified under concentration, or predicted (if specified) to occur based on relationships developed in the experiment.

Multiple-year OTC exposures of loblolly pine have resulted in decreased foliar weight, partly through accelerated abscission, and decreased root surface area in the first year following exposure to a 2.5-times-ambient O<sub>3</sub> treatment (0.10 ppm 12-h seasonal average, 318 ppm·h) (Qiu et al., 1992). In a 2-year study, Kress et al. (1992) found that fascicle length and number of early season needle flushes decreased linearly with increasing O<sub>3</sub>, but the reverse was true in flushes produced later in the season. This may occur only in seedlings that produce more than two leaf flushes per year. Foliage retention decreased with O<sub>3</sub>, and fewer fascicles were retained on trees exposed to ambient concentrations of O<sub>3</sub> (12-h seasonal mean of 0.045 ppm averaged over 2 years). Shafer and Heagle (1989) exposed seedlings of four families of loblolly pine to O<sub>3</sub> over three growing seasons and, based on their data, predicted growth suppressions of above ground plant parts of 0 to 19% (depending on the sensitivity of the family) at a 12-h seasonal mean of 0.05 ppm, after 2 years; after 3 years, suppressions of 13% were predicted in the most sensitive family. Cumulative effects of multiple-year exposures were not apparent from the above study, but no measures of root growth, which has been reported to be affected in other species (Andersen et al., 1991; Edwards et al., 1992a; Temple et al., 1993), were reported. Edwards et al. (1992a) also conducted a 3-year exposure and found a 4% reduction in whole plant biomass after exposure to a 7-h seasonal concentration of about 0.050 ppm. An 8% reduction was associated with a 7-h concentration of about 0.10 ppm. Growth reductions occurred in both above- and belowground plant parts.

Many studies with loblolly pine have used multiple families with a range of reported tolerance to O<sub>3</sub> (Adams et al., 1988, 1990b; Kress et al., 1992; Qiu et al., 1992; Shafer and Heagle, 1989; Wiselogle et al., 1991). These studies have demonstrated the range of response, from tolerant to sensitive, in the species. Adams et al. (1990b) suggest that resistance to natural stresses, such as drought, may be linked to tolerance to O<sub>3</sub>, thereby affecting the response of the species to multiple stresses.

The response of slash pine to O<sub>3</sub> also has been characterized. Dean and Johnson (1992) found leaf area to be reduced by O<sub>3</sub> in all three growing seasons studied, with an intensification of the effect each year at an O<sub>3</sub> exposure of about 0.03 to 0.04 ppm (12-h seasonal means) or 77 to 216 ppm·h (SUM00). Leaf litterfall also was increased by O<sub>3</sub> (Byres et al., 1992a,b). Volume increment of the trees was affected, with an increased sensitivity to simulated acid rain in trees exposed to twice the ambient concentration. Hogsett et al. (1985a) found reduced height (22%), diameter (25%), top (18%), and root growth (39%) in slash pine exposed to a 7-h seasonal mean of 0.076 ppm, with a maximum concentration of 0.094 ppm. From these studies, it is clear that slash pine is relatively sensitive to O<sub>3</sub> on an annual basis.

Hogsett et al. (1989) report the results of exposing five western conifers to O<sub>3</sub> at a seasonal 7-h mean concentration of 0.067 or 0.071 ppm (SUM06 for 134 days was 49.5 and 63 ppm·h, respectively; SUM00 was 140 and 153 ppm·h, respectively). Ponderosa pine and western hemlock had reduced needle, stem, and root dry weight after 134 days of exposure. Douglas fir (*Pseudotsuga menziesii*) and western red cedar (*Thuja plicata* D. Don) were not different from the CF air control, but Douglas fir showed consistent decreases in weight of plant components. Lodgepole pine was not affected by either O<sub>3</sub> treatment. Carry-over effects were observed in bud elongation in the following spring in lodgepole pine, ponderosa pine, and hemlock. Andersen et al. (1991) also observed reduced root dry weight in ponderosa pine after exposure to SUM00 of 122 or 169 ppm·h during a 120-day growing

season. In addition, they observed a reduction in the weight of newly formed roots the following spring, possibly due to reduced levels of root starch.

In a 3-year field study, Temple et al. (1993) and Beyers et al. (1992) found that ponderosa pine trees exposed to a 24-h seasonal mean of 0.087 ppm had a 48 and 70% loss of 2- and 3-year-old needles, respectively. Radial stem growth and coarse root growth also were reduced but not as severely as needle weight (due to abscission). After three seasons of exposure, current-year needles in elevated O<sub>3</sub> treatments had a higher photosynthetic performance than those in filtered air. The compensation was apparently due to higher foliar nitrogen in O<sub>3</sub>-exposed needles, a product of redistribution of nitrogen before abscission of needles. Cumulative responses would suggest that, eventually, reductions in growth of the trees would occur at lower concentrations of O<sub>3</sub>.

A number of field studies have been conducted in North America in which an attempt was made to relate air quality to growth or injury of forest trees. Two field studies have correlated radial growth with visible injury in ponderosa and Jeffrey pine in California (Peterson and Arbaugh, 1988; Peterson et al., 1987). An 11% reduction in radial growth was measured in symptomatic Jeffrey pine, compared to trees that did not show symptoms of O<sub>3</sub> injury, but no reduction could be demonstrated in ponderosa pine; however, the authors point out that the trees they measured were not under competitive stress, which might alter their response.

The response of evergreen trees varies widely, depending on species and genotype within species. It is clear, however, that major forest species, such as ponderosa, loblolly, and slash pine are sensitive to O<sub>3</sub> (depending on length of exposure, based on seedling studies) at or slightly above the concentrations of O<sub>3</sub> (0.04 to 0.05 ppm) that occur over wide areas of the United States. Furthermore, because of the long life span of these trees, including those that have not been reported sensitive to O<sub>3</sub>, there is ample opportunity for a long-term, cumulative effect on growth of the trees. Most of the experiments are conducted over only 2% or less of the life expectancy of the tree; an equivalent exposure in field crop plants would be 2 to 3 days. Consideration also must be given to the fact that most of these trees grow as part of mixed forests, in competition with many other species. Small changes in growth might be translated into large changes in stand dynamics, with concomitant effects on the structure and function of the ecosystem.

### **5.6.5 Assessments Using Ethylene Diurea as a Protectant**

A chemical protectant, EDU (*N*-[2-(2-oxo-1-imidagolidinyl)ethyl]-*N'*-phenylurea), has been used to study the response of plants to O<sub>3</sub> without attempting to control the concentration of the pollutant during the exposure (Table 5-31) (U.S. Environmental Protection Agency, 1986).

Disadvantages of the use of OTCs for assessing the effects of O<sub>3</sub> on the growth of plants include relatively high cost, the need for electrical power, and potential effects of the chambers themselves on the growth of the plants. In many cases, no chamber effects can be detected, and because most studies compare against a control, chamber effects would have a minimal effect on interpretation of results. Although, the number of experiments conducted with OTCs has led to a firm understanding of plant response to a chamber environment, the possibility of interactions with treatment cannot be ruled out. The use of EDU is attractive due to low cost and ease of application; however, it is essential to establish the correct dosage for protection from O<sub>3</sub>, without direct effects of EDU on the plant, and an estimate of

**Table 5-31. Effects of Ethylene Diurea (EDU) on Ozone Responses<sup>a</sup>**

Crop/Species	EDU Application	O <sub>3</sub> Exposure	Effects of EDU	Reference
White bean	Spray to runoff, 2,000 ppm	Field; 34 h > 0.08 ppm	Reduced O <sub>3</sub> injury, 38%; delayed defoliation; increased yield, 24%.	Temple and Bisessar (1979)
	Spray to runoff, 2,000 ppm	Field; hours > 0.08 ppm = 518 ppm·h	Reduced O <sub>3</sub> injury, 20 to 80%; increased yield up to 35%.	Toivonen et al. (1982)
	Soil drench, 500 ppm, 0.5 L/pot	Greenhouse (charcoal-filtered)	No effect on growth.	Brennan et al. (1990)
	Soil drench, 500 ppm, 4 L/6 m row	Field; 78 h > 0.12 ppm (0.2 ppm max)	Reduced O <sub>3</sub> injury up to 50%; retarded maturation.	Brennan et al. (1990)
Corn	Spray to runoff, 500 ppm	Field (no details)	19% yield reduction.	Heggestad (1988)
Cotton	Spray to runoff, 500 ppm	Greenhouse (no details)	Increased yield in nonfiltered air; reduced yield in filtered air.	Heggestad (1988)
Potato	Spray to runoff, 1.1 kg/ha, five applications	Field; > 0.08 ppm on 18 days (0.138 ppm max)	Reduced O <sub>3</sub> injury, 50%; increased tuber weight, 35%.	Bisessar (1982)
	Soil drench, 6.7 kg/ha, four applications	Field; 282 h > 0.08 ppm	Reduced O <sub>3</sub> injury; increased tuber weight, 20 to 30%.	Clarke et al. (1990)
Radish	Soil drench, 100 mg/L, 2 L/m of row	Field; 0 h > 0.1 ppm, hours > 0.05 ppm = 0.76 ppm·h	No response to O <sub>3</sub> . Reduced growth rates at low O <sub>3</sub> exposures.	Kostka-Rick and Manning (1992a)
	Soil drench, up to 800 mg/L, 100 mL/pot	Greenhouse, < 0.025 ppm	Increased shoot growth at <300 mg/L; reduced shoot growth at >300 mg/L. Reduced hypocotyl growth at all EDU levels.	Kostka-Rick and Manning (1993)
	Soil drench, up to 400 mg/L, 100 mL/pot	Greenhouse, 0.075 ppm/7 h, 6 days/week, with one weekly peak to 0.14 ppm	Complete protection against O <sub>3</sub> injury at 100 mg/L.	Kostka-Rick and Manning (1993)

**Table 5-31 (cont'd). Effects of Ethylene Diurea (EDU) on Ozone Responses<sup>a</sup>**

Crop/Species	EDU Application	O <sub>3</sub> Exposure	Effects of EDU	Reference
Radish (cont'd)	Soil drench, 150 mg/L, 60 mL/pot	Greenhouse, 0.07 ppm/7 h, 5 days/week, with two weekly peaks to 0.12 ppm	Reduced O <sub>3</sub> injury, 90 to 100%; less reduction in hypocotyl weight.	Kostka-Rick and Manning (1992b)
Soybean	Soil drench, 500 ppm, 0.5 L/pot	Greenhouse; 0.2 ppm, 6 h/day, 2 days	Reduced O <sub>3</sub> injury, 80 to 90%.	Brennan et al. (1987)
	Soil drench, 500 ppm, 4 L/6 m row	Field; 78 h > 0.12 ppm (0.2 ppm max)	No effect on loss of chlorophyll; no effect on seed weight.	Smith et al. (1987) and Brennan et al. (1990)
Tobacco	Spray to runoff, 1 kg/ha, seven applications	Field; > 0.08 ppm on 2 days	Increased growth, 22%.	Bisessar and Palmer (1984)
Beech	Stem injection 1 g/L; 0.25 mL	OTC; ambient and ambient +0.08 ppm, 8 h/day	No consistent effect.	Ainsworth and Ashmore (1992)
Black cherry	Spray to runoff, 1,000 ppm, seven applications per year	Field; 75 h > 0.08 ppm (over 4 years)	Twofold increase in growth.	Long and Davis (1991)
Other woody species:				
Red maple	Spray to runoff, 500 ppm or soil drench, 500 or 2,000 ppm, 250 mL/pot	Up to 0.95 ppm, 3 h	Reduced O <sub>3</sub> injury.	Cathey and Heggstad (1982)
Paper birch			Reduced O <sub>3</sub> injury.	
White ash			Reduced O <sub>3</sub> injury.	
Honey locust			Reduced O <sub>3</sub> injury.	
Golden-rain			Reduced O <sub>3</sub> injury.	
London plane			Reduced O <sub>3</sub> injury.	
Lilac			Reduced O <sub>3</sub> injury.	
Basswood			Reduced O <sub>3</sub> injury.	

<sup>a</sup>See Appendix A for abbreviations and acronyms.

the level of protection from O<sub>3</sub> achieved (Kostka-Rick and Manning, 1992a,b, 1993). Ethylene diurea is known to be phytotoxic, so studies under controlled O<sub>3</sub> conditions to establish an effective level of protection without phytotoxicity are essential before EDU can be used as an assessment tool.

Previous studies with EDU led to the conclusion, as did experiments with OTCs, that ambient concentrations of O<sub>3</sub> were sufficient to reduce crop yields (U.S. Environmental Protection Agency, 1986). If hourly O<sub>3</sub> concentrations exceeded 0.08 ppm for 5 to 18 days during the growing season, yields of crops might be reduced 18 to 41% (U.S. Environmental Protection Agency, 1986).

Inspection of Table 5-31 shows that in many cases there were clear-cut reductions in O<sub>3</sub>-induced injury and increases in yield resulting from the application of EDU. However, the conflicting results for field-grown soybean indicated that, at the rate of EDU application used, no beneficial effects could be demonstrated. Similarly, experiments with corn and cotton suggest that any possible effects of O<sub>3</sub> may have been confounded by direct effects of EDU on growth.

A few studies using EDU have been conducted since 1986. Kostka-Rick and Manning (1992a,b, 1993) conducted studies to determine the direct effects of EDU on growth and to develop an understanding of dose-response to EDU itself. Their studies used EDU and radish (*Raphanus sativus*) in the presence or absence of a controlled O<sub>3</sub> fumigation in a greenhouse and found that the chemical did suppress O<sub>3</sub>-induced reductions in belowground plant organs; it also protected the plants from foliar injury. The EDU itself did not cause effects on growth at a concentration of 150 mg L<sup>-1</sup> applied as a 60-mL drench to each plant, a dosage much lower than often has been used (e.g., Long and Davis, 1991; Smith et al., 1987; discussed below). Kostka-Rick and Manning emphasize that it is essential to establish the appropriate dose for the species under consideration. Armed with this background, the investigators used EDU in a field study and found an O<sub>3</sub>-induced decrease in the relative growth rates of sink organs of field-grown radish plants above a threshold level of about 0.052 to 0.058 ppm (7-h daily mean), an exposure that is near ambient O<sub>3</sub> concentrations.

Ethylene diurea also has been used to estimate the effect of O<sub>3</sub> on field-grown soybean in New Jersey (Smith et al., 1987; Brennan et al., 1990). In this case, the researchers did not establish the appropriate dose level for O<sub>3</sub> protection, as was done by Kostka-Rick and Manning. No differences in yield were found, and the authors concluded that O<sub>3</sub> does not impact soybean yield of the tested cultivars in New Jersey. However, they did not demonstrate that EDU was an effective protectant at the concentrations used and on the cultivars grown.

In a similar study, potato yields were measured and related to foliar injury in EDU-treated and nontreated plots over a 4-year period (Clarke et al., 1990). The cumulative O<sub>3</sub> dose ranged from 45 to 110 ppm·h, depending on the year, producing a range of foliar injury from 1 to 75%. The authors found that significant differences in yield between EDU-treated and control plants occurred only when foliar injury on untreated plants was 75% of leaf area. No level of protection, other than from foliar injury, could be assessed.

In a 3-year study of potted green ash, no significant effects on growth were measured using EDU (2 years) or by comparison of filtered and NF air in OTCs (1 year) (Elliot et al., 1987). Foliar injury was observed only late in the season of the first year in the NF chambers.

An effort by Ensing et al. (1986) to assess the impact of O<sub>3</sub> on yield of peanut in Ontario found that year-to-year variation was greater than that they could account for either by correlation of O<sub>3</sub> concentration with yield of test plots or by EDU treatment. They conclude that a correlative approach to assessing losses due to O<sub>3</sub> will not work.

Finally, a 4-year study of black cherry using EDU as a protectant was conducted by Long and Davis (1991). They found significant effects with a 47% reduction in aboveground biomass compared to EDU-treated trees. The authors do not believe the difference was due to a stimulation in growth due to nitrogen in the EDU, but they did not conduct studies, as recommended by Kostka-Rick and Manning, to characterize the EDU system for black cherry.

In summary, the EDU method for assessing the impact of O<sub>3</sub> is promising, particularly for remote areas or as a validation tool for existing crop-loss models. The system must be carefully characterized, however, as pointed out by many of its users.

It should be noted that, in spite of the promise shown by EDU as a field protectant over many years, it has not been developed commercially and, until recently, was unavailable for further experimentation.

### 5.6.6 Summary

Several conclusions were drawn from the various approaches used to estimate crop yield loss. In 1986, U.S. Environmental Protection Agency (1986) established that 7-h/day growing season mean exposures to O<sub>3</sub> concentrations above 0.05 ppm were likely to cause measurable yield loss in agricultural crops. At that time, few conclusions could be drawn about the response of deciduous or evergreen trees or shrubs because of the lack of information about the response of such plants to season-long exposures to O<sub>3</sub> concentrations of 0.04 to 0.06 ppm and above. However, the 1978 and 1986 criteria documents (U.S. Environmental Protection Agency, 1986) indicate that the limiting values for foliar injury to trees and shrubs was 0.06 to 0.10 ppm for 4 h. Since 1986, considerable research has been conducted, and the sensitivity of many tree species has been established.

Based on research published since U.S. Environmental Protection Agency (1986), a number of conclusions can be drawn.

- (1) An analysis of 10 years of monitoring data from more than 80 to almost 200 nonurban sites in the United States established ambient 7-h growing season average concentrations of O<sub>3</sub> for 3 or 5 mo of 0.051 to 0.060 ppm and 0.047 to 0.054 ppm, respectively. The SUM06 exposures ranged from 24.8 to 45.2 ppm-h for 3 mo, and 32.7 to 58.0 ppm-h for 5 mo (Tingey et al., 1991).
- (2) The results of OTC studies that compare yields at ambient O<sub>3</sub> exposures with those in filtered air and retrospective analyses of crop data summarized in this section establish that the current ambient (0.04 to 0.05 ppm) concentrations of O<sub>3</sub> at some sites are sufficient to reduce the yield of major crops in the United States. The results of research since 1978 do not invalidate the conclusions of the U.S. Environmental Protection Agency (1978, 1986) that visible injury due to O<sub>3</sub> exposures reduces the market value of certain crops and ornamentals where leaves are the product (spinach [*Spinacea oleracea*], petunia, geranium [*Pelargonium hotortorum*], and poinsettia [*Euphorbia pulcherrima*] for



instance), and that such injury occurs at O<sub>3</sub> concentrations (0.04 to 0.10 ppm) that presently occur in the United States.

- (3) A growing season SUM06 exposure of 26.4 ppm·h, corresponding to a 7-h growing season mean of 0.049 ppm and a 2HDM of 0.094 ppm may prevent a 10% loss in 50% of the 54 experimental cases analyzed by Tingey et al. (1991) and Lee et al. (1994a,b). A 12-h growing season mean of 0.045 should restrict yield losses to 10% in major crop species (Lesser et al., 1990).
- (4) Concentrations of O<sub>3</sub> and SUM06 exposures, depending on duration, that occur at present in the United States are sufficient to affect the growth of a number of trees species. Given the fact that multiple-year exposures may cause a cumulative effect on the growth of some trees (Simini et al., 1992; Temple et al., 1992), it is likely that a number of species currently are being impacted, even at ambient exposures (0.04 to 0.05 ppm).
- (5) Exposure-response functions for 51 cases of seedling response to O<sub>3</sub> (Hogsett et al., 1995), including 11 species representing deciduous and evergreen growth habits, suggest that a SUM06 exposure for 5 mo of 31.5 ppm·h would protect hardwoods from a 10% growth loss in 50% of the cases studied. A SUM06 exposure of 42.6 ppm·h should provide the same level of protection for evergreen seedlings. It should be noted that these conclusions do not take into the account the possibility of effects on growth in subsequent years, an important consideration in the case of long-lived species.
- (6) Studies of the response of trees to O<sub>3</sub> have established that, in some cases poplars (*Populus*) and black cherry, for instance, trees are as sensitive to O<sub>3</sub> as are annual plants, in spite of the fact that trees are longer lived and have lower rates of gas exchange, and, therefore, a lower uptake of O<sub>3</sub>.
- (7) The use of the chemical protectant, EDU is of value to establish O<sub>3</sub>-related losses in crop yield and tree growth, providing care is exercised in establishing the appropriate dosage of the compound to protect the plants without affecting growth. Ethylene diurea cannot be used to predict the response of plants at concentrations greater than those that exist in ambient air.

## 5.7 Effects of Ozone on Natural Ecosystems

### 5.7.1 Introduction

Ozone is a regionally distributed phytotoxic air pollutant capable of changing the chemical environment of forests. It is the only gaseous air pollutant capable of exposing a large region without a leaving a permanent trace of its presence. Ozone molecules are ephemeral. They decompose rapidly to oxygen and free radicals and leave no residuals; therefore, O<sub>3</sub>-caused stresses are frequently difficult to determine (Taylor and Norby, 1985; Garner, 1991).

Ozone stresses can be acute, chronic, or both. Trees may experience O<sub>3</sub> exposures for minutes, hours, a few days, or weeks. In addition, exposures usually occur more than once during a growing season. During an episode, O<sub>3</sub> trajectories may cover very large areas. Concentrations can increase as the air trajectories move across the country and pass over new sources of O<sub>3</sub> (Wolff et al., 1977a,b,c, 1980; Wolff and Liroy, 1980). Acute episodic exposures (short-term high concentrations) may be experienced several times in a year.

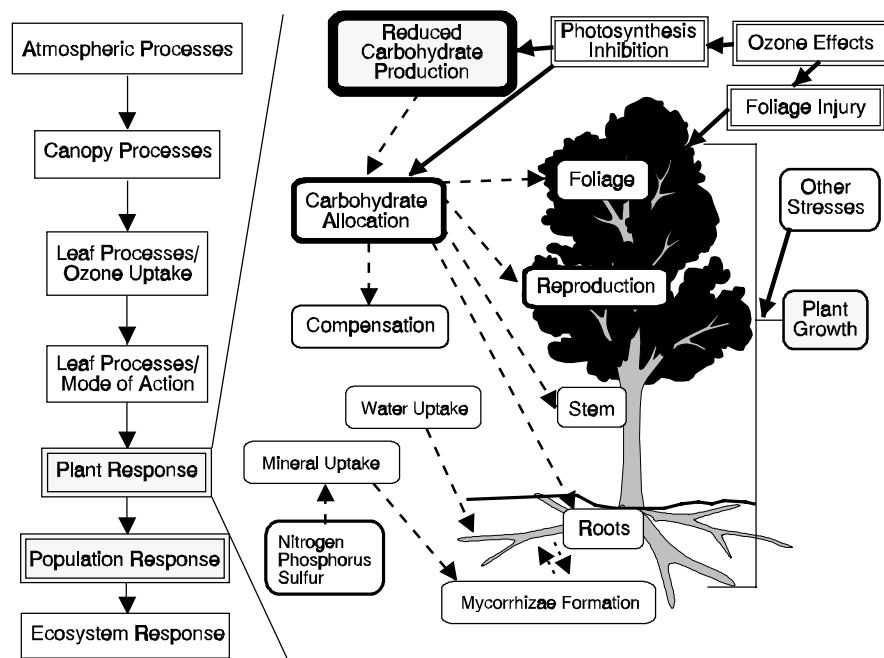
During chronic exposures, low concentrations may be experienced continuously for a major portion of the life of a plant. Forest trees, shrubs, and other perennial plants must cope with the cumulative effects of several acute episodes; chronic, long-term exposures; or both. Trees may respond rapidly; for example, the needles of sensitive eastern white pine exhibit visible injury symptoms within days after exposure to high O<sub>3</sub> concentrations (Garner, 1991). In most instances, however, responses are subtle and not observable for many years because trees adapt and respond to cumulative stresses by differential growth, which is the result of altered carbon allocation (Waring and Schlesinger, 1985). Trees usually can recover when the stresses are removed, depending on the length of exposure.

Ozone concentrations and the effects, past and present, of exposure to O<sub>3</sub> on ecosystems in the San Bernardino Mountains and the Sierra Nevada Mountains of California and in the Appalachians Mountains of the eastern United States are presented in the pages that follow. The final section relates known ecosystem responses to stress and presents possible reasons why the effects on the ecosystem components in the two regions resulted in different responses. How plants respond to O<sub>3</sub> exposures and may compensate for stresses has been pointed out in the section on mode of action (Section 5.3). The importance of genetic variability in plant response and plant competition, as well as the multiple biological and physical factors that may modify plant response and, in some cases, cause stress, have been discussed in factors that modify plant response (Section 5.4). The discussion regarding modifying factors is of particular importance in understanding ecosystem response to stresses because they are much more likely to be encountered by plants growing in their natural habitats. Figure 5-30 outlines how plant response can lead to ecosystem response.

The responses to a variety of O<sub>3</sub> concentrations and exposure durations of various species of deciduous trees and shrubs (Table 5-27) and evergreen trees (Table 5-30) under experimental conditions have been presented in the previous section. The studies cited in the tables in the previous section, whether conducted in chambers, greenhouses, or OTCs, suggest that all sensitive plants will respond within hours to O<sub>3</sub> concentrations above 0.06 ppm. In general, depending on the length of exposure, the number and height of peaks, and the sensitivity of the vegetation, data from the field supports this contention. This section places the response of the individual trees, shrubs, and other perennial plants in the ecosystem context. The responses of forest ecosystems to pollutant exposure have received more study than unmanaged ecosystems of other biomes (grasslands, shrublands, or deserts), therefore, the following discussion relies mainly on forest ecosystems for examples.

### **5.7.2 Ecosystem Characteristics**

Ecosystems are composed of populations of "self-supporting" and "self-maintaining" living plants, animals, and microorganisms (producers, consumers, and decomposers) interacting with one another and with the nonliving chemical and physical environment within which they exist (Odum, 1989; U.S. Environmental Protection Agency, 1993). Ecosystems respond to stresses through their constituent organisms. The response of plant species and populations to environmental perturbations depends on their genetic constitution (genotype), their life cycles, and the microhabitats in which they are growing. Stresses such as the changes in the physical and chemical environment of plant populations apply new and additional selection pressures on individual organisms (Treshow, 1980). The



**Figure 5-30. Effects of ozone ( $O_3$ ) on plant function and growth. Reduced carbohydrate production decreases allocation and resources needed for plant growth processes. Individual plant responses must be propagated hierarchically through the more integrative levels of population and community to produce an ecosystem response. Solid black arrows indicate the effects of  $O_3$  absorption; stippled arrows indicate affects on plant functions. Double border indicates site of response; darkened border indicates site of impact.**

changes that occur within plant communities reflect these new and different pressures. A common response in a community under stress is the elimination of the more sensitive populations and an increase in abundance of species that tolerate or are favored by the stress (Woodwell, 1970; Guderian et al., 1985).

Ecosystems usually have definable limits within which the integrated functions of energy flow, nutrient cycling, and water flux are maintained (Odum, 1993). Their boundaries, and the organisms that live within them, are determined by the environmental conditions of that particular habitat, area, or region. Structurally complex communities, they are held in an oscillating steady state by the operation of a particular combination of biotic and abiotic factors. They may be large or small (e.g., fallen logs, forests, grasslands, meadows, old uncultivated fields, ponds, lakes or rivers, estuaries, oceans, the earth) (Odum, 1971). Together, the environment, the organisms, and the physiological processes resulting from their interactions form the life-support systems that are essential for the existence of any species on earth, including man (Odum, 1993).

Human existence on this planet is dependent on ecological systems and processes. Natural ecosystems traditionally are spoken of in terms of their structure and functions. Ecosystem structure includes the species (richness and abundance) and their mass and arrangement in an ecosystem. This is termed an ecosystem's standing stock—nature's free

"goods" (Westman, 1977; U.S. Environmental Protection Agency, 1978, 1986, 1993). Society reaps two kinds of benefits from the structural aspects of an ecosystem: (1) products with market value such as fish, minerals, forest products and pharmaceuticals, and genetic resources of valuable species (e.g., plants for crops and timber and animals for domestication); and (2) the use and appreciation of ecosystems for recreation, aesthetic enjoyment, and study (Westman, 1977; U.S. Environmental Protection Agency, 1978, 1986, 1993).

More difficult to comprehend, but of equal or greater importance are the functional aspects of an ecosystem. Ecosystem functions are characterized by the way in which components interact. They are the dynamics of ecosystems—nature's free "services". The benefits imparted to society include absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance, climate, and the fixation of solar energy. These, in short, are the functions that maintain clean air pure water, a green earth, and a balance of creatures, the functions that enable humans to obtain the food, fiber, energy, and other materials for survival (Westman, 1977). The majority of the free services are performed by the microorganisms that constitute as many as half of all living creatures on the earth but are seldom recognized.

The term "ecological risk" highlights the importance of ecosystems to human existence. Ecosystems change dramatically throughout time, have no optimal condition, and are only healthy when compared to some desired state specified by humans (Lackey, 1994). The importance of ecosystems to human existence is presented in more detail in the nitrogen oxides (NO<sub>x</sub>) criteria document (U.S. Environmental Protection Agency, 1993).

### **5.7.3 Effects of Exposure to Ozone on Natural Ecosystems**

#### **5.7.3.1 The San Bernardino Forest Ecosystem—Before 1986**

The mixed-conifer forest ecosystem in the San Bernardino Mountains of Southern California is one of the most thoroughly studied ecosystems in the United States. Chronic O<sub>3</sub> exposures over a period of 50 or more years has resulted in major changes in the San Bernardino National Forest ecosystem. The primary effect was on the more susceptible members of the forest community, individuals of ponderosa and Jeffrey pine, such that they were no longer able to compete effectively for essential nutrients, water, light, and space. As a consequence of altered competitive conditions in the community, there was a decline in the sensitive species, permitting the enhanced growth of more tolerant species (Miller et al., 1982; U.S. Environmental Protection Agency, 1978, 1986). The results of the studies of the San Bernardino Forest ecosystem were reported in both the 1978 and 1986 criteria documents (U.S. Environmental Protection Agency, 1978, 1986). The information summarized below is from these two documents.

An inventory of the forest was begun in 1968 and conducted through 1972 to determine the results of more than 30 years of exposure to O<sub>3</sub>. Based on that inventory and accompanying studies, the conclusions reached are presented in Table 5-32. Data from the inventory indicated that, during 5 mo/year from 1968 through 1972, trees were exposed to O<sub>3</sub> concentrations greater than 0.08 ppm for more than 1,300 h. Concentrations rarely fell below 0.05 ppm at night near the crest of the mountain slope (elevation approximately 5,500 ft [Miller, 1973]). The importance of altitude in plant response was discussed in the

**Table 5-32. San Bernardino Forest—Status 1972**

1. Ponderosa and Jeffrey pine suffered the most injury. Mortality of one population of ponderosa pine ( $n = 160$ ) was 8% between 1969 and 1971 ( $p = 0.01$ ); in a second population ( $n = 40$ ), mortality was 10% between 1968 and 1972. White fir populations suffered slight damage, with scattered individual trees showing severe symptoms. Sugar pine, incense cedar, and black oak exhibited only slight foliar injury from oxidant exposure.
2. A substantial shift occurred in ponderosa pines from the "slight injury" category in 1969 to the "moderate injury" category in 1971, indicating that there was continuing oxidant stress and that the selective death of ponderosa pines was occurring.
3. Suppression of photosynthesis in seedlings was observed (Miller et al., 1969). In ponderosa pine saplings, needles shortened by exposure to oxidants returned to normal length when the seedlings were moved to  $O_3$ -free air from 1968 to 1973 (Miller and Elderman, 1977).
4. Bark beetles were judged to be responsible for the death of weakened trees in the majority of cases. Elimination of ponderosa pine from the mixed-conifer forest was postulated to occur in the future if the rate of bark beetle attack were to continue unabated (Cobb and Stark, 1970).
5. Aerial portions of  $O_3$ -injured pine trees showed a decrease in vigor that was associated with deterioration of the feeder root system (Parmeter et al., 1962).
6. Seed production was decreased in injured pines. Ordinarily, trees 25 to 50 in. diameter at breast height produce the most cones, but they were also the most sensitive to oxidants (Luck, 1980).
7. Under-story plant species sensitive to oxidant pollution may already have been removed by air pollution stress at the time of these early studies (Miller and Elderman, 1977).

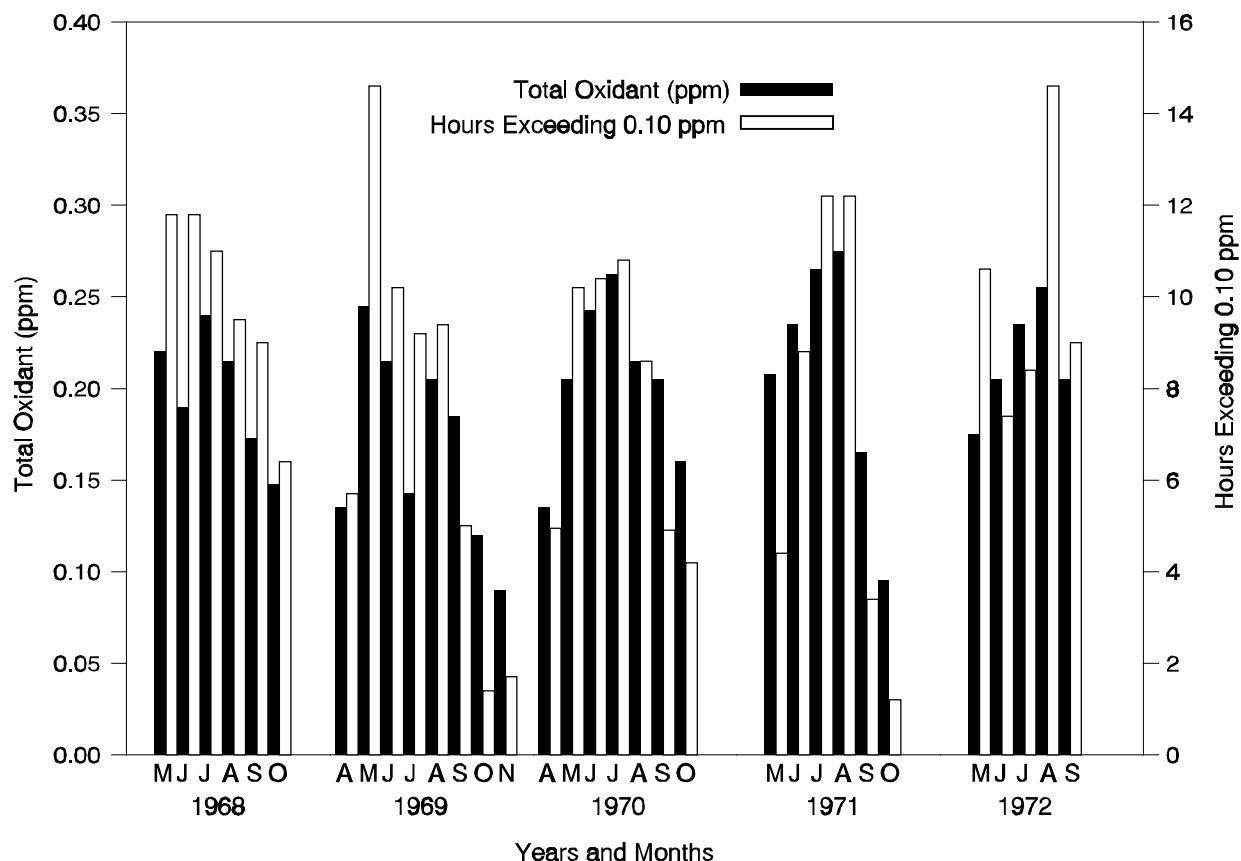
Source: U.S. Environmental Protection Agency (1986).

1986 criteria document (U.S. Environmental Protection Agency, 1986) and also is discussed in Chapter 4 of this document. The monthly averages of the daily maxima of total oxidant concentrations for the 5 years of the study are given in Figure 5-31. The highest single daily maximum oxidant concentration of 0.58 ppm occurred in June 1970 between 4:00 and 9:00 p.m., PST (Miller, 1973).

The survey cited above indicated the need for further information. To more accurately determine the effects of the 30 years of exposure to  $O_3$  of the San Bernardino Forest ecosystem, an interdisciplinary research team designed a study to answer the following questions: how do organisms and biological processes of the conifer forest respond to different levels of chronic oxidant exposure? and how can these responses be interpreted within an ecosystem context?

Included in the study plan were the following ecosystem processes: carbon (energy) flow (the movement of  $CO_2$  into the plants, its incorporation into carbohydrates, and then its partitioning among consumers, decomposers, litter, and soil); the movement of water in the soil-plant-atmosphere continuum; mineral nutrient flow through the green plant, litter, and soil-water compartments; and the shift in diversity patterns in time and space, as represented by changes in age, structure, and density in the composition of tree species in communities.

The major abiotic components studied were water (precipitation), temperature, light, mineral nutrients (soil substrate), and oxidant pollution. The biotic components studied



**Figure 5-31. Total oxidant concentrations at Rim Forest (5,640 ft) in Southern California during May through September, 1968 through 1972. Values of total oxidant are averages of daily maxima for a month. The number of hours in which total oxidant exceeded 0.10 ppm also was recorded for the 5-year period.**

Source: Miller (1973).

included producers (an assortment of tree species and lichens), consumers (wildlife, insects, and disease organisms), and decomposers, (populations of saprophytic fungi responsible for the decay of leaf and woody litter) (U.S. Environmental Protection Agency, 1978, 1986).

During the period of the study, 1973 to 1978, average 24-h  $O_3$  concentrations ranged from a background of 0.03 to 0.04 ppm in the eastern part of the San Bernardino Mountains to a maximum of 0.10 to 0.12 ppm in the western part during May through September. Hourly average concentrations for 1975 (measured by ultraviolet [UV]) indicated that  $O_3$  buildup began around 10 a.m. and reached a maximum at all six monitoring stations in all months (May through September) at around 4 p.m. For example, at the Rim Forest-Sky station, where the highest concentrations usually were recorded, the 1-mo average of hourly values ranged from 0.07 to 0.10 ppm at 10 a.m. and from 0.15 to 0.22 at 4 p.m. The highest concentrations occurred in June, July, and August, and the lowest were observed in September. The total number of hours with concentrations of 0.08 ppm or more during June through September was never less than 1,300 h per season during the first 7 years (1968

through 1974) of the study (Miller and Elderman, 1977). In addition to total oxidant, PAN and NO<sub>2</sub> concentrations were measured. Peroxyacetyl nitrate injury symptoms could not be distinguished from O<sub>3</sub> symptoms on herb-layer plant species while NO<sub>2</sub> remained at nontoxic concentrations (Miller et al., 1982; U.S. Environmental Protection Agency, 1978, 1986).

The study indicated that the major changes in the ecosystem began with injury to ponderosa and Jeffrey pine. Ponderosa pine was the most sensitive of the trees to O<sub>3</sub>, with Jeffrey pine, white fir, California black oak (*Quercus kelloggii*), incense cedar (*Calocedrus decurrens*), and sugar pine (*Pinus lambertiana*) following in decreasing order of sensitivity. Foliar injury on sensitive ponderosa and Jeffrey pine was observed when the 24-h average O<sub>3</sub> concentrations were 0.05 to 0.06 ppm (Miller et al., 1982). Foliar injury, premature senescence, and needle fall decreased the photosynthetic performance of stressed pines and reduced the production of carbohydrates needed for use in growth and reproduction by the trees. Nutrient availability to the trees also was reduced by the trees retention of smaller amounts of green foliage (Miller et al., 1982). Decreased carbohydrate resulted in a decrease in radial growth and height of stressed trees (McBride et al., 1975; Miller and Elderman, 1977).

A reduction in available carbohydrate also influenced tree reproduction. Injured ponderosa and Jeffrey pines older than 130 years produced significantly fewer cones per tree than uninjured trees of the same age (Luck, 1980). Tree-ring analysis indicated declines in ring-width indices for many trees. Stand thinning, however, reversed the trend (Miller et al., 1982).

Summarized, the responses of individual conifers sensitive to O<sub>3</sub> include visible foliar injury; premature needle senescence; reduced photosynthesis; reduced carbohydrate production and allocation; reduced plant vigor; and reduced growth or reproduction, or both (Miller et al., 1982).

The ecosystem components most directly affected by O<sub>3</sub> exposure were tree species, the fungal microflora of conifer needles, and the foliose lichens growing on tree bark. Injury to or changes in the functioning of other living ecosystem components affected, either directly or indirectly, the processes of carbon (energy) flow, mineral nutrient cycling, water movement, and changed vegetational community patterns (Miller et al., 1982). Early senescence and abscission resulted in accumulation of pine needles into a thick layer under the stands of O<sub>3</sub> injured trees and changed decomposition patterns, which changed successional patterns of the fungal microflora as well. Altering the taxonomic diversity and population density of the microflora that normally develop on needles while they are on the tree influenced the relationship of the microflora with the decomposer community. Change in the type of fungi on needles weakened the decomposer community and slowed the rate of decomposition (Bruhn, 1980). Nutrient availability was influenced by the carbon and mineral nutrients accumulated in the heavy litter and thick needle layer under stands with the most severe needle injury and defoliation.

A comparison of species of lichens found on conifers during the years 1976 to 1979 with collections from the early 1900s indicated a 50% reduction in species in the more recent period. Marked morphological deterioration of the common species *Hypogymnia enteromorpha* was documented in areas of high oxidant concentrations (Sigal and Nash, 1983).

Biotic interactions associated with predators, pathogens, and symbionts were influenced by changes in the energy available to the trees. The decrease in vigor and lack of ability to recover from O<sub>3</sub> injury associated with reduced carbohydrates made the ponderosa

pinus more susceptible to attack by predators and pathogens (Stark and Cobb, 1969). Dahlsten and Rowney (1980) have pointed out that oxidant-weakened pinus can be killed by fewer western pine beetles than are required to kill healthier trees. In stands with a high proportion of O<sub>3</sub>-injured trees, a given population of western pine beetles therefore could kill more trees. James et al. (1980a,b) observed that the root rot fungus, *Heterobasidium annosum*, increased more rapidly because freshly cut stumps and roots of weakened trees were more vulnerable to attack (U.S. Environmental Protection Agency, 1986).

Changes in the plant populations that alter communities and forest stands also can affect the animal populations. Production of fewer cones, seeds, and fruits reduces the food available to small vertebrates living in the ecosystem (U.S. Environmental Protection Agency, 1978). The continuum of ecosystem responses associated with increasing pollutant stress (presented in Table 5-33) are reflected in the response of the San Bernardino mixed forest ecosystem (Garner et al., 1989; U.S. Environmental Protection Agency, 1986). The influence of pollutants on the processes of carbon production and allocation are presented in continuum Stage II, Table 5-33.

**Table 5-33. Ecosystem Response to Pollutant Stress**

	Continuum of Vegetation Responses	Continuum of Ecosystem Responses
0	Anthropogenic pollutants insignificant.	Unaffected; systems pristine.
I	Pollutant concentrations low; no measurable physiological response.	Ecosystem functions unaffected; pollutants transferred from atmosphere to organic or available nutrient compartments.
II	Pollutant concentrations injurious to sensitive species: (1) Reduced photosynthesis, altered carbon allocation, and reduced growth and vigor; (2) Reduced reproduction; (3) Predisposition to entomological or microbiological stress.	Altered species composition; populations of sensitive species decline; some individuals are lost. Their effectiveness as functional ecosystem members diminishes; they could be lost from the system. Ecosystem reverts to an earlier stage.
III	Severe pollution stress. Large plants of sensitive species die. Forest layers are peeled off; first trees and tall shrubs, then, under the most severe conditions, short shrubs and herbs.	(1) Simplification, basic ecosystem structure changes, becomes dominated by weedy species not previously present.  (2) Reduced stability and productivity; loss of capability for repairing itself. Runoff increases and nutrient loss and erosion accelerates; a barren zone results. Ecosystem collapses.

Source: Garner et al. (1989); adapted from Bormann (1985); Kozlowski (1985); Smith (1974).

### 5.7.3.2 The San Bernardino Forest Ecosystem—Since 1986



Monitoring of O<sub>3</sub> trends in the South Coast Air Basin of Southern California, the source of pollutants transported to the mixed-conifer forests of the San Bernardino Mountains, resulted in the conclusion that the air quality had improved substantially between 1976 and 1984.

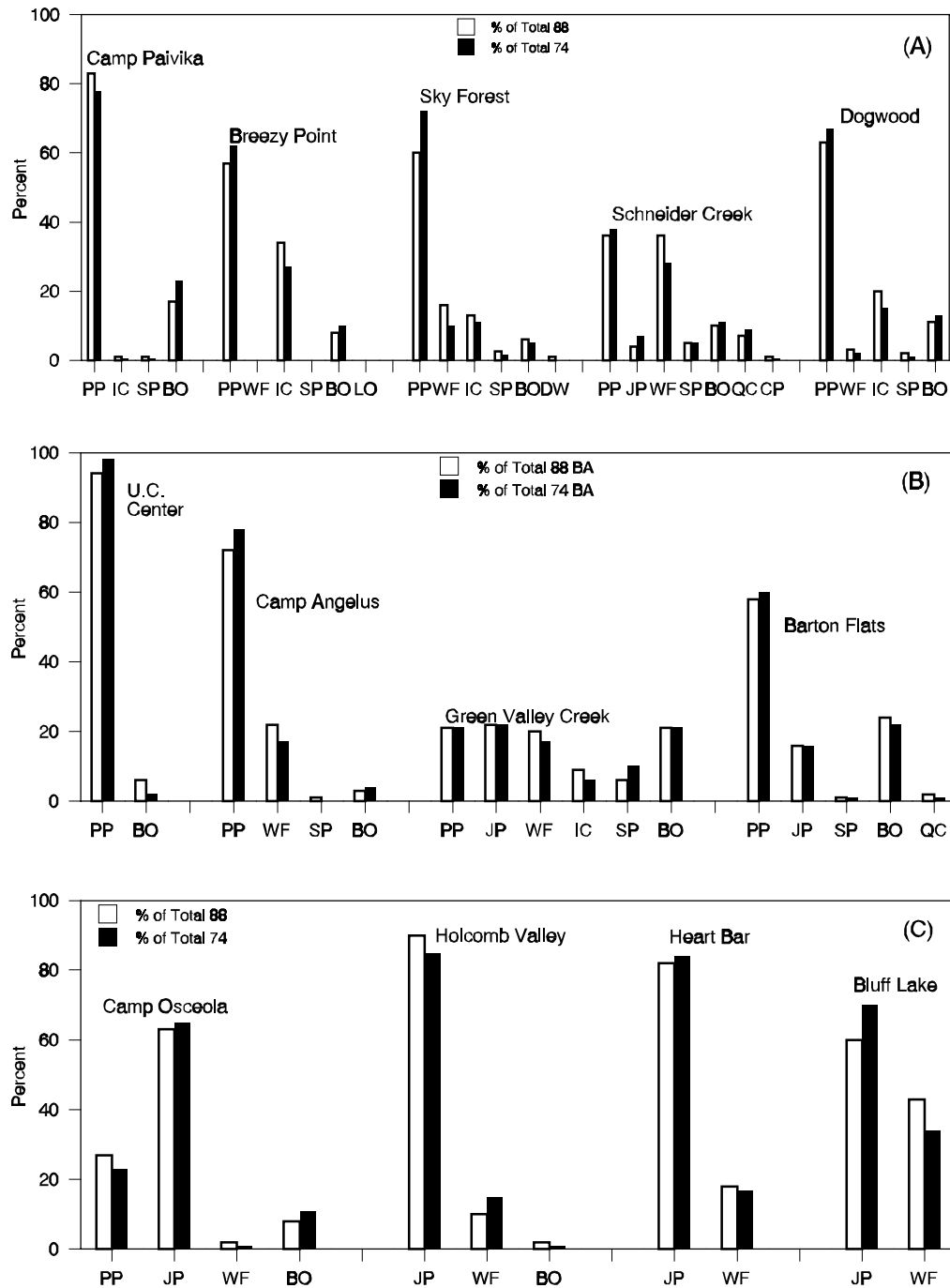
Between 1976 and 1991 the weather-adjusted O<sub>3</sub> data for the May through October "smog season" indicates that the number of Basin days exceeding 0.12 ppm, 1-h average, have declined at an average annual rate of 2.27 days/year, whereas the number of days with episodes greater than 0.2 ppm, 1-h average, have declined at an average annual rate of 4.70 days/year over the same period. The total days per year with concentrations greater than 0.12 ppm was as high as 159 in 1978, with the lowest number being 105 days in 1990 (Davidson, 1993). The 1974 to 1988 trends of the May through October hourly average and the average of monthly maximum O<sub>3</sub> concentrations for Lake Gregory, a forested area in the western section of the San Bernardino Mountains, also have shown a gradual decline (Miller et al., 1989a). Similarly, for the same period, there was an improvement shown in the injury index used to describe chronic injury to the crowns of ponderosa and Jeffrey pines in 13 of 15 plots located on the gradient of decreasing O<sub>3</sub> exposure in the San Bernardino Mountains (Miller et al., 1989a). The two exceptions were plots located at the highest exposure end of the gradient. The basal area increase of ponderosa pines was generally less than competing species at 12 of the 13 plots evaluated. The total basal area for each species as a percent of the total basal area for all species indicates that ponderosa and Jeffrey pines in plots with slight to severe crown injury lost basal area in relation to competing species that are more tolerant to O<sub>3</sub>, namely, white fir, incense cedar, sugar pine, and California black oak (Figure 5-32).

In effect, stand development had been reversed (i.e., the development of the normal fire climax mixture dominated by fire-tolerant ponderosa and Jeffrey pines was altered). The accumulation in the understory of a greater number of stems of more O<sub>3</sub>-tolerant species resulted in the formation of a fuel ladder that jeopardized the remaining overstory trees in the event of a catastrophic fire. The O<sub>3</sub>-tolerant species, because of thinner bark and branches growing close to the ground, are inherently more susceptible to fire injury. The important question for the future at that time was whether the declining O<sub>3</sub> exposure eventually would allow ponderosa and Jeffrey pine to resume dominance in basal area.

The possible interactive effects of nitrogen and O<sub>3</sub> on the forests of the San Bernardino Mountains has come under consideration more recently. For some time, there has been a concern that O<sub>3</sub> is not the only pollutant in the photochemical mixture that may be causing lasting changes in the mixed-conifer forest ecosystem. A multidisciplinary study to investigate the possibility of the combined impacts on ecosystem processes from chronic O<sub>3</sub> injury and both wet and dry deposition of acidic nitrogen compounds has been under way since 1991 at Barton Flats in the San Bernardino Mountains. The database includes frequent measurements of stomatal conductance in relation to weather and O<sub>3</sub> exposure.

The NO<sub>x</sub> criteria document (U.S. Environmental Protection Agency, 1993) explored the possible effects of increased nitrogen on litter content and decomposition. That discussion is presented here.

Increases in the nitrogen litter content and in litter decomposition rates and an alteration in nitrogen cycling have been observed in the more highly polluted areas when compared with moderately polluted and low-polluted areas of the San Bernardino Mountains



**Figure 5-32.** Total basal area for each species as a percent of the total basal area for all species in 1974 and 1988 on (A) plots with severe to moderate damage, (B) plots with slight damage, and (C) plots with very slight damage or no visible symptoms. PP = Ponderosa pine, IC = Incense cedar, SP = Sugar pine, BO = Black oak, WF = White fir, LD = Libocedrus decurrens, DW = Dogwood, QC = Quercus chrysolepis, CP = Coulter pine, and JP = Jeffrey pine.

Source: Miller et al. (1991).

(Fenn and Dunn, 1989). A pollutant concentration gradient was observed to exist, with 24-h  $O_3$  concentrations at the high sites in the west averaging 0.1 ppm or more, moderate sites ranging from 0.06 to 0.08 ppm, and low sites in the east averaging 0.05 ppm or less (Fenn, 1991). Nitrogen and sulfur compounds also occur in the pollutant mixture to which the mountains downwind of the Los Angeles Basin are exposed (Bytnerowicz et al., 1987a,b; Solomon et al., 1992). A nitrogen deposition gradient from west to east parallels the decreasing  $O_3$  gradient. Deposition of nitrogen exceeds that of sulfur (Fenn and Bytnerowicz, 1993). Annual average  $HNO_3$  concentrations in 1986 ranged from 1.2 ppb near the Southern California coast to 2.7 ppb in the San Gabriel Mountains (Solomon et al., 1992).

The litter layers under trees severely injured by  $O_3$  are deeper than those under trees less severely injured (Fenn and Dunn, 1989). A comparison study of decomposition rates of the undecomposed surface layer of needle litter indicates that litter in the more polluted areas in the west decomposed at a significantly ( $p = 0.01$ ) faster rate than did litter from moderate to low pollution levels (Fenn and Dunn, 1989; Fenn, 1991). Nitrogen content of litter was greatest at the high pollution sites and was positively correlated with the litter decomposition rate. The higher nitrogen and lower calcium contents of the litter suggest that litter in the western plots originated from younger needles than those at the less polluted sites, possibly due to  $O_3$ -induced needle abscission. Fungal diversity was also greater in the litter from the western San Bernardino Mountains (Fenn and Dunn, 1989).

When the factors associated with enhanced litter decomposition were investigated, it was found that nitrogen concentrations of soil, foliage, and litter of ponderosa and Jeffrey pine were greater in the plots where pollution concentrations were high than in moderately polluted or low-pollution sites. This was also true for sugar pine and for incense cedar, two  $O_3$ -tolerant species. The rate of litter decomposition for sugar pine, incense cedar, and Ponderosa pine species was greatest at the high-pollution sites. Therefore, the increased rate of litter decomposition in the high-pollution plots does not appear to be related to  $O_3$  sensitivity or premature needle abscission, but, instead, it is associated with higher levels of nitrogen in the soils (Fenn, 1991). Foliage and litter nitrogen is higher in high-pollution sites when compared with moderate- or low-pollution sites.

At the present time, data dealing with the response of trees or other vegetation to the combined stresses of  $O_3$  exposure above ground and nitrate deposition through the soil are sparse. Tjoelker and Luxmoore (1991), however, have assessed the effects of soil nitrogen availability and chronic  $O_3$  stress on carbon and nutrient economy in 1-year-old seedlings of loblolly pine and yellow poplar. Elevated  $O_3$  concentrations altered biomass partitioning to needles of the current year. Ozone concentrations of 0.108 ppm reduced the biomass of current-year needles in loblolly pine seedlings grown at the highest (172  $\mu\text{g/g}$ ) nitrogen supply by 20%, but not those grown with a low (59  $\mu\text{g/g}$ ) supply of nitrogen. The interaction between  $O_3$  and nitrogen suggests that plants grown with a high nitrogen supply are more sensitive to chronic  $O_3$  stress in terms of biomass reduction (Tjoelker and Luxmoore, 1991). Similar results in the growth of domestic radish were obtained by Pell et al. (1990). Brewer et al. (1961) and Harkov and Brennan (1980) observed increased foliar injury when plants were grown with an adequate nitrogen supply (U.S. Environmental Protection Agency, 1986).

### 5.7.3.3 The Sierra Nevada Mountains

The continued presence over the years of O<sub>3</sub> concentrations injurious to trees in the San Bernardino Mountain forests and the knowledge that O<sub>3</sub> is a regionally dispersed gaseous air pollutant led to concern that other forests in California, and possibly other western states as well, were being exposed to injurious concentrations. Summary statistics for the 1980 to 1988 growing season (May through October), using data from O<sub>3</sub>-monitoring sites in or near Western forests, substantiated the concern. Growing season (May through October) means, percentiles and percent occurrence of hourly O<sub>3</sub> concentrations above 0.06, 0.08, 0.10, and 0.120 ppm for all O<sub>3</sub> sites near Western forests are presented in Table 5-34 (Böhm, 1992). The lowest O<sub>3</sub> concentrations with little hourly variation were experienced at sites far from urban or point sources. Sites on the fringe of urbanized centers or valleys, on the other hand, experienced patterns with some variation in hourly concentrations; the higher concentrations usually occurred during the late afternoon. Forests located on the rims of valleys with large urban areas experienced O<sub>3</sub> concentrations >0.10 ppm. Yosemite and Sequoia National Parks, which receive pollutants transported from highly urbanized areas, had 24-h means ranging from 0.036 to 0.085 ppm on 75% of summer days, whereas Lake Gregory had a growing season mean of 0.073 ppm. During 49% of the summer days, means of diurnal patterns ranged from 0.085 to 0.100 ppm, decreasing with altitude and distance from the source (Böhm, 1992). The San Bernardino National Forest was exposed to O<sub>3</sub> levels >0.10 ppm during all seasons. Ozone concentrations tended to decrease with altitude and distance from the source.

There is little evidence of O<sub>3</sub> injury in forests in the western United States outside of California, even near urban sites. Growing season means near forests ranged between 0.012 and 0.022 ppm in Washington, between 0.028 and 0.037 ppm in Utah, and between 0.032 and 0.058 ppm in Colorado (Table 5-34; Böhm, 1992; Böhm et al., 1995).

The Sierra Nevada, the largest forested area in the world documented to have visible injury from high O<sub>3</sub> exposures, is an area approximately 300 miles long (Peterson and Arbaugh, 1992). Since 1991, there has been an annual survey of the amount of crown injury by O<sub>3</sub> to the same trees in approximately 33 sample plots located in the Sierra Nevada. These include Tahoe, Eldorado, Stanislaus, Yosemite, Sierra, Sequoia, and San Bernardino National Forests and Yosemite and Sequoia-Kings Canyon National Parks.

Dominant tree species in the area are ponderosa and Jeffrey pine, white fir, sugar pine, incense cedar, Douglas fir, and California black oak, and the giant sequoia (*Sequoiadendron giganteum*) is locally common (Peterson and Arbaugh, 1992).

Foliar O<sub>3</sub> injury to ponderosa and Jeffrey pine was first documented in the Sierra Nevada Mountains of California in the early 1970s (Miller and Millecan, 1971). Monitoring of visible injury to ponderosa pine on national forest land in the western Sierra Nevada, however, was not begun until 1975 (Duriscoe and Stolte, 1989). Results of the monitoring in the Sierra and Sequoia National Forests showed that there was an increase in chlorotic mottle of pines in the plots from approximately 20% in 1977 to approximately 55% in 1988, and an increase in severity of injury was observed as well.

In general, the results of this study document the regional nature of the O<sub>3</sub> pollution problem originating primarily from the San Joaquin Valley Air Basin, as well as from the San Francisco Bay Air Basin further to the west. Oxidant air pollution is transported southward in the San Joaquin Valley Air Basin until it reaches the southern boundary of the air basin, the Tehachapi Mountains. Because of this barrier, polluted air

**Table 5-34. Growing Season (May Through October) Summary Statistics for Ozone Monitoring  
Sites in or Near Forests for the Period 1980 through 1988  
(Percentiles and means were generated using the entire data set [1980 through 1988; May through October].)**

Site <sup>b</sup>	Elevation (m)	Percent Data Capture	Percentiles (ppb)								Percent Hours <sup>a</sup>			
			5	10	25	50	Mean $\pm$ SD <sup>c</sup>	75	90	95	$\geq 60$	$\geq 80$	$\geq 100$	$\geq 120$
Aptos, CA	78	100	0	10	10	20	25.1 $\pm$ 15	30	40	50	3	0	0	0
Ash Mountain, CA (AIRS)	526	50	20	30	50	60	64.1 $\pm$ 26	80	100	110	64	36	12	2
Ash Mountain, CA (NPS)	610	57	20	30	47	61	62.9 $\pm$ 24	80	93	100	59	29	8	1
Azusa, CA	185	93	0	0	0	20	43.3 $\pm$ 56	70	130	160	28	22	17	12
Banning, CA	722	98	10	10	20	40	49.6 $\pm$ 35	70	100	120	35	19	11	6
Bishop, CA	1,260	84	0	10	20	30	31.5 $\pm$ 16	40	50	60	7	0	0	0
Burbank, CA	170	95	0	0	0	20	36.3 $\pm$ 45	50	100	130	25	18	12	8
Camp Mather, CA	1,432	33	22	26	36	46	47.5 $\pm$ 16	59	70	76	24	3	0	0
Carmel Valley, CA	131	86	10	10	20	30	28.4 $\pm$ 14	40	50	50	4	1	0	0
Fresno County, CA	1,723	85	20	20	30	40	44.9 $\pm$ 17	60	70	80	26	5	0	0
Lake Gregory, CA	1,397	93	10	20	40	60	72.5 $\pm$ 49	100	140	170	55	37	26	18
Lassen NP, CA	1,788	36	17	21	28	36	37.8 $\pm$ 14	46	58	64	9	0	0	0
Kaweah, CA (AIRS)	1,901	35	10	20	40	60	59.7 $\pm$ 26	80	90	100	57	32	8	1
Kaweah, CA (NPS)	1,890	58	21	30	41	56	56.3 $\pm$ 21	71	83	90	44	15	2	0
Mammoth Lakes, CA	2,395	92	20	30	40	50	46.6 $\pm$ 16	60	70	70	30	5	0	0
Monterey, CA	23	86	10	10	20	30	27.3 $\pm$ 12	30	40	50	1	0	0	0
Ojao, CA	233	87	10	10	20	40	42.3 $\pm$ 26	60	80	90	30	12	3	1
Pasadena, CA	255	89	0	0	10	20	47.8 $\pm$ 58	70	130	170	30	24	18	14
Pinnacles NM, CA	355	66	10	16	26	41	42.8 $\pm$ 22	58	72	80	22	5	1	0
Redwood NP, CA	233	49	8	10	15	22	22.0 $\pm$ 0.09	28	34	39	0	0	0	0
San Bernardino, CA	320	80	0	0	0	30	50.2 $\pm$ 57	80	140	170	35	28	21	15
Santa Barbara, CA	25	96	0	10	20	30	32.2 $\pm$ 19	40	60	60	11	2	0	0
Santa Barbara County, CA	12	96	0	10	20	30	31.5 $\pm$ 20	40	60	70	13	2	1	0
Santa Monica Mountains, CA	191	55	0	2	10	30	39.6 $\pm$ 35	59	86	110	25	13	7	4
Scotts Valley, CA	171	79	0	0	10	20	22.4 $\pm$ 18	30	50	50	5	1	0	0
South Lake Tahoe, CA	1,907	88	10	20	20	40	37.8 $\pm$ 17	50	60	60	18	1	0	0
Ventura County, CA	1,600	83	0	10	20	40	36.2 $\pm$ 22	50	60	70	18	5	1	0
Wawona Valley, CA	1,280	66	9	15	27	42	44.0 $\pm$ 23	61	76	83	26	7	1	0

**Table 5-34 (cont'd). Growing Season (May Through October) Summary Statistics for Ozone Monitoring  
Sites in or Near Forests for the Period 1980 through 1988  
(Percentiles and means were generated using the entire data set [1980 through 1988; May through October].)**

Site <sup>b</sup>	Elevation (m)	Percent Data Capture	Percentiles (ppb)								Percent Hours <sup>a</sup>			
			5	10	25	50	Mean ± SD <sup>c</sup>	75	90	95	≥60	≥80	≥100	≥120
Yreka, CA	809	80	0	0	10	20	25.9 ± 18	40	50	60	6	0	0	0
Clackamas County, OR	174	94	4	8	14	23	25.3 ± 16	33	45	55	4	1	0	0
Columbia County, OR	6	88	1	4	11	20	21.3 ± 14	29	39	46	2	0	0	0
Crook County, OR	1,372	90	20	25	30	35	36.5 ± 0.09	40	50	55	2	0	0	0
Eugene, OR	187	77	1	3	9	18	21.4 ± 17	30	42	52	3	1	0	0
Marion County, OR	102	94	1	1	7	18	20.3 ± 16	30	41	50	3	1	0	0
Medford, OR	503	93	1	3	9	22	24.8 ± 18	37	50	59	5	1	0	0
Cedar River, WA	210	82	11	14	19	28	31.4 ± 17	39	53	64	7	2	0	0
King County, WA	22	90	0	0	0	10	14.9 ± 17	20	40	50	3	1	0	0
Olympic NP, WA (DOE)	100	85	0	0	10	20	16.3 ± 11	20	30	40	0	0	0	0
Olympic NP, WA (NPS)	125	26	0	1	1	2	4.8 ± 0.07	3	17	23	0	0	0	0
Pack Forest, WA	24	80	10	10	20	30	30.0 ± 18	40	50	70	8	3	1	0
Pierce County, WA	14	85	0	0	0	10	15.1 ± 16	20	40	40	2	0	0	0
Port Angeles, WA	30	71	0	0	1	2	8.4 ± 10	10	20	30	0	0	0	0
Snohomish County, WA	120	83	0	0	0	10	17.0 ± 15	30	40	40	2	0	0	0
Spokane, WA	584	74	0	0	10	20	20.9 ± 16	30	40	50	20	0	0	0
Stampede Pass, WA	1,217	80	20	20	30	30	35.2 ± 14	40	50	60	7	0	0	0
Apache-Sitgreaves, AZ	2,462	94	25	30	35	40	42.3 ± 12	50	60	65	12	1	0	0
Cochise County, AZ	1,401	56	13	17	26	37	37.4 ± 15	49	58	63	8	0	0	0
Flagstaff, AZ	2,117	77	17	24	34	44	43.7 ± 15	53	62	67	13	1	0	0
Grand Canyon NP, AZ	2,073	56	17	20	23	27	29.4 ± 0.09	33	43	46	0	0	0	0
Pima County, AZ	695	86	1	2	10	28	29.8 ± 22	46	60	68	10	1	0	0
Prescott, AZ	1,673	69	5	9	16	30	29.9 ± 16	43	52	55	2	0	0	0
Saguaro NM, AZ	933	66	19	22	30	38	38.8 ± 14	47	57	63	8	1	0	0
Douglas County, NV	1,951	60	6	11	20	35	35.5 ± 19	49	62	69	12	1	0	0
Reno, NV	1,280	92	0	0	10	30	28.4 ± 20	40	50	60	10	1	0	0
Boulder County, CO	1,635	95	8	14	24	35	36.0 ± 18	47	60	69	11	2	0	0
Colorado Springs, CO	1,842	88	0	2	10	25	26.3 ± 18	40	51	57	4	0	0	0

**Table 5-34 (cont'd). Growing Season (May Through October) Summary Statistics for Ozone Monitoring Sites in or Near Forests for the Period 1980 through 1988**  
**(Percentiles and means were generated using the entire data set [1980 through 1988; May through October].)**

Site <sup>b</sup>	Elevation (m)	Percent Data Capture	Percentiles (ppb)								Percent Hours <sup>a</sup>			
			5	10	25	50	Mean ± SD <sup>c</sup>	75	90	95	≥60	≥80	≥100	≥120
Colordao NM, CO	1,750	30	30	32	37	42	44.1 ± 14	48	54	57	2	0	0	0
Denver, CO	1,591	96	0	2	7	19	21.9 ± 18	33	47	55	3	1	0	0
Great Sand Dunes, CO	2,487	54	24	27	33	39	38.4 ± 0.09	44	49	52	1	0	0	0
Larimer Country, CO	1,522	90	1	4	14	27	27.9 ± 18	40	52	59	5	0	0	0
Rocky Mountains NP, CO	2,743	49	25	31	38	46	46.0 ± 12	54	60	65	10	1	0	0
Arches NP, UT	1,567	32	28	31	36	43	42.8 ± 0.09	49	54	58	4	0	0	0
Bountiful, UT	1,335	87	8	14	25	38	38.3 ± 20	49	62	72	12	3	1	0
Logan, UT	1,382	45	8	12	20	32	32.5 ± 15	45	52	58	4	0	0	0
Ogden, UT	1,314	97	0	1	9	30	29.8 ± 22	46	58	65	8	1	0	0
Provo, UT	1,402	72	2	5	14	29	32.1 ± 22	49	62	68	12	2	0	0
Salt Lake, UT	1,305	87	2	4	11	28	30.4 ± 22	45	59	70	10	3	1	0
Albuquerque, NM	1,585	89	1	5	15	29	29.8 ± 19	43	55	61	6	1	0	0
Yellowstone NP, WY	2,484	58	15	19	27	36	35.4 ± 12	44	51	55	2	0	0	0

<sup>a</sup>Percent hours are normalized to represent the average occurrence of ozone levels during May through October. Percent data capture = number of valid hours/4,416 × 100, where 4,416 is the total number of hours during the period May through October.

<sup>b</sup>Site abbreviations: NPS = National Park Service, NM = National Monument, DOE = Department of Energy.

<sup>c</sup>SD = Standard deviation.

Source: Modified from Böhm (1992).

masses circulate back northward. This circulation cell causes higher O<sub>3</sub> levels to be advected to the southernmost sites, the Sequoia National Forest and the Sequoia-Kings Canyon National Park. Mean hourly average concentrations in the Sierra Nevada during 1987 ranged from 0.018 to 0.076 ppm, with annual hourly maxima of 0.11 to 0.17 ppm. An O<sub>3</sub> exposure gradient with highest concentrations in the south and lowest in the north was observed. Associated with the gradient, injury is most severe at the southern end of the range and least severe in the north (Peterson et al., 1991).

The studies cited above reported visible O<sub>3</sub> injury only to the trees in the Sierra Nevada forests. To evaluate growth changes in O<sub>3</sub>-stressed ponderosa and Jeffrey pine, Peterson and his coworkers, beginning in 1985, conducted the largest investigation of regional tree growth in the western United States (Peterson et al., 1987; Peterson and Arbaugh, 1988, 1992; Peterson et al., 1991). Using cores to determine whether growth reductions had occurred, they randomly sampled both trees with visible O<sub>3</sub> injury symptoms and asymptomatic trees. Major decreases in growth occurred for both symptomatic and asymptomatic trees during the 1950s and 1960s. The percentage of trees exhibiting growth decreases at any given site never exceeded 25% in a given decade (Peterson et al., 1991). The mean annual radial increment of trees with symptoms of O<sub>3</sub> injury was 11% less than trees at sites without O<sub>3</sub> injury. Trees larger than 40 cm in diameter and trees older than 100 years showed greater decreases in growth than did smaller and younger trees. Differences in growth between injured and uninjured trees were prominent after 1965 (Peterson et al., 1987).

The region-wide survey (Peterson et al., 1991) of ponderosa pine provides a useful backdrop for reporting a number of other studies or surveys in the Sierra Nevada that were more narrowly focused. Another tree ring analysis and crown injury study concentrated on Jeffrey pines in Sequoia-Kings Canyon National Park (Peterson et al., 1989). This study suggested that decreases of radial growth of large, dominant Jeffrey pines growing on thin soils with low moisture holding capacity and direct exposure to upslope transport of O<sub>3</sub> amounted to as much as 11% in recent years when compared with similar trees without symptoms.

Both a network of permanent plots established in 1980 and cruise surveys have been employed in Sequoia-Kings Canyon and Yosemite National Parks to determine the spatial distribution and temporal changes of injury to ponderosa and Jeffrey pine within the parks (Duriscoe and Stolte, 1989). In Sequoia-Kings Canyon, O<sub>3</sub> injury to individual trees and the mean number of trees injured in each plot increased from 47% for 1980 to 1982 to 79% for 1984 to 1985. Foliar injury was the most common response among the 28 plots studied. Ozone injury tends to decrease with the increasing elevation of plots. The O<sub>3</sub> concentrations associated with the highest levels of tree injury in the Marble Fork drainage of the Kaweah River, at approximately 1,800 m elevation, are hourly averages peaking frequently at 80 to 100 ppb but seldom exceeding 120 ppb.

During a cruise survey in 1986 (Duriscoe and Stolte, 1989) to identify the partial distribution of injury, there were 3,120 ponderosa or Jeffrey pines evaluated for O<sub>3</sub> injury in Sequoia-Kings Canyon and Yosemite National Parks. Approximately one-third of this number were found to have some level of chlorotic mottle. At Sequoia-Kings Canyon, symptomatic trees comprised 39% of the sample (574 of 1,470), and, at Yosemite, they comprised 29% (479 of 1,650). Ponderosa pines generally were injured more severely than Jeffrey pines.



In Sequoia-Kings Canyon, observations at field plots showed that giant sequoia seedlings developed O<sub>3</sub> injury symptoms at both ambient O<sub>3</sub> concentrations and 1.5 × ambient O<sub>3</sub> (0.08- to 0.1-ppm hourly peaks) in OTCs during the 8 to 10 weeks following germination (Miller et al., 1994). Field-plot observations of seedling health and mortality in natural giant sequoia groves over a 4-year period showed that seedling numbers were reduced drastically from drought and other abiotic factors. Any variable, such as O<sub>3</sub>, that could stress seedlings sufficiently to reduce root growth immediately after germination could increase vulnerability to late summer drought. Significant differences in light-compensation point, net assimilation at light saturation, and dark respiration were found between seedlings in CF air treatments and 1.5 × ambient O<sub>3</sub> treatments (0.08- to 0.1-ppm hourly peaks) (Grulke et al., 1989). One interpretation of these results is that O<sub>3</sub> could be a new selection pressure during the regeneration phase of giant sequoia, possibly reducing genetic diversity.

The Lake Tahoe Basin is located at the northern end of the Sierra Nevada (near Eldorado National Forest) (Peterson et al., 1991). Because it is an air basin unto itself, the air quality situation is distinct from other Sierra Nevada sites. Ozone injury was first reported for the area in the late 1970s. In 1987, a survey of 24 randomly selected plots in the basin included a total of 360 trees, of which 105 (29.2%) had some level of foliar injury (Pedersen, 1989).

The radial growth response of big cone Douglas firs (*Pseudotsuga macrocarpa*) to long-term O<sub>3</sub> exposure was studied throughout the range of these firs in the San Bernardino Mountains of Southern California. Big cone Douglas fir is found in the mountain ranges of Southern California and northern Baja California, Mexico. In the San Bernardino Mountains, the species grows in canyons and on dry slopes at elevations from 700 to 2,200 m and, in association with canyon live oak (*Quercus chrysolepis*), throughout the chaparral and lower elevation mixed-forest communities. Big cone Douglas fir is usually rated as less sensitive than ponderosa or Jeffrey pine; however, injury symptoms resulting from elevated O<sub>3</sub> exposures have been seen (Peterson et al., 1995).

Dendroecological analyses indicate that growth rates have decreased considerably since 1950 (Peterson et al., 1995). Differences in basal area indices for 1913 to 1950 were compared with those for 1951 to 1988 to determine whether there were growth changes associated with increased air pollution during the latter period. More than 80% of all trees had reduced growth. Trees growing in regions of high O<sub>3</sub> exposure had the largest growth decreases, with approximately 30% of those growing under these conditions having reductions greater than 50%, and 60% having reductions greater than 20%. Fewer than 10% of the trees in any O<sub>3</sub> exposure area had growth increases greater than 25%. Based on their study, the authors conclude that, although O<sub>3</sub> does not have the same level of impact on these trees as it does on ponderosa and Jeffrey pine, reduced needle retention and lower recent growth rates could indicate increased O<sub>3</sub> stress (or O<sub>3</sub> stress mediated by climate) in big cone Douglas fir. Long-term monitoring of this species could provide an early warning of additional injury caused by air pollution in forest ecosystems of Southern California (Peterson et al., 1995).

### ***Site Variables Affecting Ozone Response in the California Ecosystems***

Structural changes in forest stands are highly related to their position or site on the landscape. Site variables can be defined at regional and local levels. For example, the regional level is defined in California by the location of forested mountain slopes and summits in relation to polluted urban air basins. In both the Sierra Nevada and the San Bernardino Mountains in California the greatest tree injury is found on ridges that

overlook the polluted air basins. The polluted air masses are transported up-slope or up-canyon in terrain that is usually sunlit in the afternoon and early evening, thus the thermal convection on warm slopes is a major means by which O<sub>3</sub> and associated pollutants are delivered to the first forested ridges. Both vertical mixing and horizontal diffusion into cleaner air results in a distinct gradient of decreasing O<sub>3</sub> concentration in more distant forest stands. Two such gradients have been described in the San Bernardino Mountains (Miller et al., 1986). Along the longer, west-to-east orientation axis of the mountain range, 24-h average O<sub>3</sub> concentrations for the highest summer months ranged from 0.09 to 0.140 ppm nearest the polluted South Coast Air Basin to 0.04 to 0.05 ppm at a downwind distance of 35 to 40 km. In the more narrow, south-to-north direction, the same concentration gradient is seen over a much shorter distance of 5 to 8 km because of a more rapid transition to the warm desert influence, which causes mixing and dilution (Miller et al., 1972). Accordingly, O<sub>3</sub> injury to sensitive vegetation ranges from severe to none over these distances.

In the Sierra Nevada Mountains, a gradient of decreasing injury is observed from west to east and south to north (Peterson and Arbaugh, 1992). But the worst level of chronic injury is generally much less than observed in the San Bernardino Mountains.

With respect to localized site variables, there is evidence from repeated surveys in Sequoia-Kings Canyon National Parks that the percent of trees injured and the severity of foliar injury both increased with decreasing elevation in the 1,500- to 2,500-m zone on generally west-facing slopes adjacent to the polluted San Joaquin Valley Air Basin (Stolte et al., 1992). In Sequoia-Kings Canyon National Parks, radial growth reductions in Jeffrey pine with foliar injury by O<sub>3</sub> were documented only for large, dominant trees growing on shallow soils (Peterson et al., 1987). Soil moisture availability is generally lower on such sites. One hypothesis for explaining radial growth decline on these sites and not on more favorable sites with greater moisture-holding capacity is that O<sub>3</sub> defoliation in favorable moisture years and water stress in dry years integrate sequentially to suppress growth.

In the San Bernardino Mountains, radial growth of ponderosa and Jeffrey pines in plots along the decreasing O<sub>3</sub> gradient was not well correlated with level of chronic injury but was better correlated with soil-moisture-holding capacity. Within a single plot with relatively uniform moisture availability there was a good correlation between increased radial growth and a decreasing level of chronic O<sub>3</sub> visible injury to crowns.

#### **5.7.3.4 The Appalachian Mountains—Before 1986**

Oxidant-induced injury on vegetation in the Appalachian Mountains has been observed for many years but has not produced the same ecosystem responses as vegetational injury in the San Bernardino Mountains. Results of studies in the eastern United States were reported in the 1986 criteria document and are summarized in the following passages (U.S. Environmental Protection Agency, 1986). Needle blight of eastern white pine was first reported in the early 1900s, but it was not known until 1963 that the needle blight was the result of acute and chronic O<sub>3</sub> exposure (Berry and Ripperton, 1963). In the 1950s, the U.S. Forest Service studied the decline of eastern white pine in an area covering several hundred square miles on the Cumberland Plateau in Tennessee and concluded that atmospheric constituents were the causes of this decline (Berry and Hepting, 1964; Garner et al., 1989; Garner, 1991).

Growth reductions in trees growing on the Cumberland Plateau of eastern Tennessee were studied by Mann et al. (1980) and McLaughlin et al. (1982). A steady growth decline in annual-ring increment was observed during the years 1962 through 1979.

Reductions of 70% in average annual growth and of 90% in average bole growth were observed in sensitive trees, when compared to the growth of tolerant and intermediate trees. Tolerant trees, when compared to trees of intermediate sensitivity, consistently showed a higher growth rate (from 5 to 15%) than did intermediate trees for the 1960 to 1968 interval, similar growth rate from 1969 through 1975, and a reduction in growth (5 to 15%) for the period 1976 through 1979. The decline was attributed to chronic O<sub>3</sub>, which frequently exceeded 1-h average concentrations of 0.08 ppm. Maximum 1-h concentrations ranged from 0.12 to 0.30 ppm for the years 1975 to 1979 (U.S. Environmental Protection Agency, 1986).

McLaughlin et al. (1982) observed that the decline in vigor and the reduction in growth in trees and the production of carbohydrates (carbon flow) were associated with the following sequence of events and conditions: premature senescence of mature needles at the end of the growing season; reduced carbohydrate storage capacity in the fall and reduced resupply capacity in the spring to support new needle growth; increased reliance of new needles on self-support during growth; shorter new needles, resulting in lower gross photosynthetic productivity; and higher retention of current photosynthate (carbohydrate) by foliage, resulting in reduced availability for transport for external use, including repair of chronically stressed tissues of older needles (U.S. Environmental Protection Agency, 1986).

Despite the early field observations of Berry (1961) and Berry and Ripperton (1963), no concerted effort was made to determine the effects of O<sub>3</sub> on vegetation in the Appalachian Mountains until the 1970s, when, between April 1975 and March 1976, Skelly and his coworkers began monitoring total oxidant concentrations and recording associated injury to eastern white pine in three rural Virginia sites. Injury was observed in the Jefferson and George Washington National Forests and throughout the Blue Ridge Mountains, including areas in the Shenandoah National Park and along the Blue Ridge Parkway in Virginia and North Carolina (Hayes and Skelly, 1977; Skelly et al., 1984). Taylor and Norby (1985), in their analysis of the 4-year monitoring data of Skelly et al. (1984), point out that there were an average of five episodes (any day with a 1-h mean O<sub>3</sub> concentration >0.08 ppm) during the growing season in this area. Episodes lasted from 1 to 3 days.

In studies conducted in the Blue Ridge Mountains of Virginia, Benoit et al. (1982) used annual-ring increments to evaluate the possible effects of oxidant air pollution on the long-term growth on eastern white pine of reproducing age. Reductions in overall growth of eastern white pine trees classified as tolerant, intermediate, and sensitive to O<sub>3</sub> exposure were observed. Comparison of growth from 1974 to 1978 with that for 1955 to 1959 indicated decreases of 26, 37, and 51% for tolerant, intermediate, and sensitive trees, respectively. No significant changes in seasonal precipitation had occurred during the 1955 to 1963 period or the 1963 to 1978 period; therefore, the significant reduction in radial growth was assumed by the authors to be the result of cumulative O<sub>3</sub> stress and reduced photosynthetic performance due to oxidant injury. Monitoring of O<sub>3</sub> indicated monthly average concentrations of 0.05 to 0.07 ppm on a recurring basis, with episodic 1-h peaks frequently in excess of 0.12 ppm for the latter time period (Benoit et al., 1982; U.S. Environmental Protection Agency, 1986). Duchelle et al. (1982), monitoring in the same area, reported peak hourly averages >0.08 ppm for the months of April through September in 1979 and 1980. As early as 1979, Skelly (1980) concluded that the most sensitive eastern white pines were injured so severely by oxidant exposure that they probably were being removed from the population. It was estimated that, of the population, 22% were tolerant, 67% were intermediate, and 11% were sensitive.

In the previous O<sub>3</sub> document (U.S. Environmental Protection Agency, 1986), Duchelle et al. (1982, 1983) reported that exposing native tree seedlings and herbaceous vegetation in the Big Meadows area of the Shenandoah National Park in the Blue Ridge Mountains of Virginia to ambient O<sub>3</sub> reduced both the growth of the native trees other than eastern white pine and the productivity of the native herbaceous vegetation found growing in forested areas. Comparison of growth of seedlings in open plots or OTCs with CF air revealed that growth was suppressed in wild-type seedlings of tulip poplar, green ash, sweet gum (*Liquidambar styraciflua*), black locust (*Robinia pseudoacacia*), eastern hemlock (*Tsuga canadensis*), Table Mountain pine (*Pinus pungens*), Virginia pine (*Pinus virginiana*), and pitch pine, usually without visible foliar injury symptoms. Open-top chambers were operated continuously from May 9 until October 9 during 1979 and from April 24 until September 15 in 1980 (U.S. Environmental Protection Agency, 1986). Common milkweed and common blackberry (*Rubus allegheniensis*) were two species of native vegetation that exhibited visible injury symptoms (Duchelle and Skelly, 1981). Monthly 8-h average O<sub>3</sub> concentrations ranged from 0.035 to 0.065 ppm, and peak hourly concentrations from 0.08 to 0.13 ppm (Skelly et al., 1984; U.S. Environmental Protection Agency, 1986). Common milkweed and common blackberry represented natural vegetation sensitive to O<sub>3</sub> exposure (Duchelle and Skelly, 1981; U.S. Environmental Protection Agency, 1986).

Forest ecosystems at high altitudes experience higher total exposures because of the prolonged duration of elevated O<sub>3</sub> at high altitudes (see Section 5.4; Wolff et al., 1987; Winner et al., 1989; U.S. Environmental Protection Agency, 1986). Although daily maximum and mid-day O<sub>3</sub> concentrations are similar at different altitudes, the dosage increases with height. Ozone is depleted rapidly at night near the earth's surface below the nocturnal inversion layer; however, mountainous sites above the nocturnal inversion layer do not experience this depletion. Therefore, the total exposure to O<sub>3</sub> in mountainous areas can be much higher than that in nearby valleys (Berry, 1964; Garner et al., 1989). Maximum O<sub>3</sub> concentrations observed at elevated mountain sites often occur at night; in addition, higher elevations are often exposed to sustained or multiple peak concentrations of O<sub>3</sub> within a given 24-h period. High morning concentrations occur at a time when stomatal conductance is high and photosynthetic activity is greatest. The cumulative effects of O<sub>3</sub> uptake, therefore, could be severe. These considerations need to be taken into account when assessing the exposure-response relationships of forest ecosystems at high altitudes (Wolff et al., 1987; Garner et al., 1989; Garner, 1991).

The field observations cited above indicate that oxidant-induced injury to vegetation has been occurring in the Appalachian Mountains for many years. By the time intensive studies were begun in Pocahontas County, WV, in 1957, to determine the cause of "emergence tipburn", many people living in the area had been reporting casual observations of the phenomenon for over 20 years. Emergence tipburn, also known as needle blight, of eastern white pine was observed first in the early 1900s, however it was not shown to be the result of acute or chronic O<sub>3</sub> exposure until 1963 (Berry and Ripperton, 1963).

Although vegetation injury resulting from O<sub>3</sub> exposure had been observed in New Jersey in the 1940s, its cause was not recognized until 1960 (Daines et al., 1960). Ozone was first recognized as a causal factor of foliar injury when Heggestad and Middleton (1959) reported that weatherfleck of tobacco was the result of O<sub>3</sub> exposures. Concentrations of 0.38, 0.43, and 0.5 ppm were measured at Beltsville by newly developed Mast meters during 1958. (The concentrations cited are approximately 0.1 ppm higher than those measured more recently. Calibration of the then new Mast meters was sometimes a problem [Garner, 1991]).

Regular oxidant monitoring stations were first established east of the Mississippi River in 1962. Valid oxidant data, however, was not available until 1964, and then only for the cities of Chicago, Cincinnati, St. Louis, Philadelphia, Washington, DC, and Denver (National Air Pollution Control Administration, 1968). Maximum oxidant concentrations recorded between 1964 and 1967 indicated that Cincinnati had 10 days  $>0.15$  ppm; Philadelphia, 60 days  $>0.06$  and 13 days  $>0.15$  ppm; and Washington, DC, 65 days  $>0.10$  ppm and 7 days  $>0.15$  ppm (U.S. Environmental Protection Agency, 1986). Berry and Ripperton (1963) reported the presence of oxidant concentrations above 0.10 ppm during 1961 and 1962 in West Virginia and in North Carolina as far east as Raleigh. These data indicate that  $O_3$  concentrations sufficient to injure vegetation regularly were present from the Midwest to the east coast (Garner et al., 1989; Garner, 1991).

In retrospect, it is apparent that  $O_3$  episodes in the eastern United States have not been unusual. Taylor and Norby (1985) analyzed the 4-year monitoring data of Skelly et al. (1984) and concluded that episodes in which the 1-h  $O_3$  concentration was  $>0.08$  ppm were experienced, on average, five times during the growing season. Episodes when peak  $O_3$  concentrations exceeded 0.10 ppm in the southern Appalachian Mountains were recorded during 1975 (Hayes and Skelly, 1977) and 1979 through 1982 (Skelly, 1980). Injury to eastern white pine at three rural sites in Virginia from July 1 to 5, 1975, was associated with a high pressure over the Great Lakes and a low, Hurricane Amy, off the Atlantic coast. Air parcels bearing  $O_3$  moved in from the Northeast and Midwest into Virginia. The episode dissipated when the cold from the Midwest moved across Virginia into the Atlantic Ocean (Hayes and Skelly, 1977). More recent  $O_3$  episodes in the same area have been associated with meteorological phenomena similar to the one mentioned above (Skelly et al., 1984; Garner et al., 1989).

Ozone episodes for the eastern United States also were recorded during 1976 and 1977. Typical episodes were associated with high-pressure systems that originated in Canada, moved southeastward into the Midwest, and then eastward to the Atlantic coast. For example, an episode covering most of a 20-state area occurred April 12 to 23, 1976. During this episode,  $O_3$  concentrations in excess of 0.08 ppm occurred simultaneously from the Midwest to the Atlantic coast and into the northeastern United States. Ozone trajectories extended from Ohio to New Jersey (Wolff et al., 1977a,b,c; Garner, 1991). Additional studies indicated that two other episodes exhibiting trajectories similar to the one described above took place in August 1976. These episodes included an area extending from West Virginia across Virginia in the south and north to Maine. Maximum concentrations measured in the trajectories during the two August episodes were 0.20 ppm (Wolff et al., 1980; Garner, 1991).

In 1977, there were three episodes: (1) July 12 to 21, (2) July 21 to 24, and (3) July 26 to 30 (Wolff et al., 1980). The first episode, unlike the ones the previous year, originated in the Texas-Louisiana area. Air parcels traveled northeastward to the lower Midwest and then to the Atlantic coast, extending an "ozone river" from the gulf coast of Texas to Louisiana to the northeast Atlantic coast, exposing the entire area to concentrations averaging 0.12 to 0.13 ppm. The second and third episodes, like the 1976 episodes, originated in Canada. Because the southern part of the first episode persisted at the time the second and third episodes began,  $O_3$  from the south was pulled into the Midwest, and the region from the Texas gulf coast eastward to the Atlantic coast continued to be exposed to the high concentrations. These episodes simultaneously exposed nearly two-thirds of the United States (Wolff and Liroy, 1980; Garner, 1991).

Long-range transport of O<sub>3</sub> need not begin in Canada, the Midwest or Texas. Fankhauser (1976) reported the transport of O<sub>3</sub> in a giant loop stretching from New York City, Philadelphia, Baltimore, and Washington, DC, west through Virginia and Ohio and back to Wheeling, WV, to the Pittsburgh, PA, area. This path continued for 4 to 5 days in September, 1972. Earlier, in May 1972, a stagnant high and a slow-moving low transported air parcels from the Chicago and Pittsburgh areas to Miami, FL (Garner et al., 1989; Garner, 1991).

The foregoing discussion not only depicts the episodic nature of O<sub>3</sub> exposures, but also points out the fact that the major portion of the United States east of the Mississippi River has been exposed frequently to phytotoxic O<sub>3</sub> concentrations. Taylor and Norby (1985) estimate the probability is 80% that any given O<sub>3</sub> episode in the Shenandoah forest will persist for at least 3 days. This information concerning the effects of O<sub>3</sub> exposure is summarized from the 1986 criteria document (U.S. Environmental Protection Agency, 1986).

#### **5.7.3.5 The Appalachian Mountains and the Eastern United States—Since 1986**

Changes in growth, decline, and mortality of certain tree species have been reported for high-elevation forest ecosystems from Maine, New Hampshire, Vermont, and New York, south to North Carolina and Tennessee. Studies indicate that the decrease in growth of forest trees began during the late 1950s or early 1960s (Adams et al., 1985; Benoit et al., 1982; Johnson et al., 1984; Phipps and Whiton, 1988; Garner et al., 1989; Garner, 1991). The extent of decrease in growth and of dieback and mortality, and the factors that precipitated them, are subject to controversy (Garner, 1991; Garner et al., 1989; Taylor and Norby, 1985). Many hypotheses, including O<sub>3</sub> exposure, have been advanced as possible causes. The problem, as pointed out by Woodman and Cowling (1987), is establishing causation. Rigorous proof is needed, but only circumstantial evidence is available. Because the growth reductions began so many years ago, long-term historical data regarding forest structure and composition is lacking (Garner, 1991; Garner et al., 1989). An additional factor that makes causation difficult to determine is that mature ecosystems are not completely stable, but maintain themselves in an oscillating steady state (Kozlowski, 1985). No long-term studies of the effects of tree decline and mortality on ecosystems similar to those dealing with the exposure and response of the San Bernardino mixed-forest ecosystem in California have been made in the East.

Surveys made in 1982, but mentioned only briefly in the previous criteria document (U.S. Environmental Protection Agency, 1986) give quantitative evidence of a marked dieback and large reductions in basal area and in density of red spruce in the high-elevation forests of New York, Vermont, and New Hampshire (Johnson and Siccama, 1983). Red spruce is the most characteristic species of subalpine forests that occupy the higher peaks and ridges of the Appalachian Mountains from Maine to North Carolina and Tennessee. A co-dominant species in the North is balsam fir (*Abies balsamea*), whereas Fraser fir, a closely related species, is co-dominant in the South (Adams et al., 1985). A detailed description of the red spruce decline in the eastern United States and possible causes and studies conducted to determine the causes can be found in Eager and Adams (1992). In the summary chapter of that text, Johnson et al. (1992) write that they "are in a position to state and support with field and laboratory data that regional scale air pollution has played a significant role in the decline of red spruce in the eastern United States." Ozone usually is considered the only regional air pollutant. In this instance, however, the authors are referring to NO<sub>x</sub> and SO<sub>x</sub>, the precursors of acidic deposition. Studies evaluating the

direct effects of O<sub>3</sub> on red spruce have found little evidence for a significant effect (McLaughlin and Kohut, 1992). Recent studies evaluating the responses of red spruce and loblolly pine to acidic precipitation and O<sub>3</sub> indicate that high-elevation red spruce forests could be impacted by acidic deposition enhancing soil acidification, mobilization of aluminum ions (Al<sup>3+</sup>), and reducing the availability of important base cations (Edwards et al., 1995).

In the Southeast, the decline and mortality of Fraser fir in the Great Smoky Mountains National Park, and, in North Carolina, the Plott Balsam Mountains and the Black Mountains, which include Mt. Mitchell, have been attributed to infestation by the balsam wooly adelgid (Hain and Arthur, 1985). The west-facing slope of Mt. Mitchell showed the greatest injury. During a 20-year experimental study of Fraser fir growing in the Smoky Mountains National Park, balsam wooly adelgids killed almost all of the canopy trees and reduced the basal area in two plots established in the 1960s. Red spruce basal area in these plots remained about the same for the same period. The report does not mention whether atmospheric pollutants were monitored, nor does it discuss possible pollutant-pathogen interaction or possible predisposition (Busing et al., 1988).

Other studies on Mt. Mitchell, however, do not attribute the death of Fraser fir solely to the balsam wooly adelgid, but suggest that atmospheric deposition and multiple pollutant stresses also had a role in tree mortality. These studies cite exposure to gaseous air pollutants, particularly O<sub>3</sub>, and cloud-water deposition of acidic substances among possible stresses that have increased host susceptibility to attack by the balsam wooly adelgid (Hain and Arthur, 1985; Aneja et al., 1992). Ozone levels for the area have ranged from 0.01 to 0.150 ppm, with the highest concentrations occurring early in the summer (Aneja et al., 1992).

Other than the studies of tree death in the specific regions cited above, the studies in the Appalachian Mountains have been field surveys made to identify possible O<sub>3</sub>-related foliar injury symptoms on native vegetation and experimental exposures to verify the symptoms and to determine O<sub>3</sub> response of individual forest tree species and other native vegetation, usually using OTCs. Unfortunately, some of the studies exposing individual forest tree species cannot be used because the concentrations at which exposure occurred are given as ambient plus 1, plus 1.5, or plus 2, etc. The actual ambient concentration at the time of exposure is never mentioned in the paper. A few studies use an index, again without stating the O<sub>3</sub> concentration and duration of exposure from which the index was derived. These papers are of little scientific value in this discussion because the actual concentrations and duration of exposures at which vegetational injury occurred cannot be determined.

Data from the Forest Inventory Analysis timber inventory taken between 1972 and 1982, revealed that the annual growth rate of most southern yellow pines (loblolly, pitch, shortleaf, and slash) under 16 in. in diameter had declined by 30 to 50% throughout the Piedmont and mountain areas of the Southeast since measurements were made during the survey of 1957 to 1966 (Sheffield et al., 1985). Ozone has been suggested as a possible cause; however, verification of growth effects on mature trees has been lacking (McLaughlin and Downing, 1995).

Additional studies of the forest condition were conducted by the United States Forest Service. Millers et al. (1989) reviewed the information on tree mortality that has occurred in the eastern hardwood forest during the last century to determine whether a relationship exists between the patterns of mortality and the patterns of atmospheric pollution. The authors suggest "that the apparent increase in the decline and mortality of many hardwood species during the last few decades may be due to intensification of reporting and

to the maturation of the forest itself." Most of the mortality observed was attributed to abiotic and biotic stress factors such as weather, silviculture, and injury by insects and diseases. Although there is evidence of injury to hardwoods from point-source pollutants such as smelters and to eastern white pine from  $O_3$ , there is no conclusive evidence of an association between patterns of hardwood mortality and regional atmospheric pollution (Millers et al., 1989). Millers et al. (1989) point out, however, that historical data on atmospheric deposition are not readily available to compare with historical data on mortality.

Twardus et al. (1993) describe forest conditions in twenty states within the Northeastern United States. Information on forest health in this report was obtained from the Cooperative Forest Health Program, from the Forest Inventory and Analysis Surveys conducted by the U.S. Department of Agriculture Forest Service between 1971 and 1993, and from the Northern Forest Health Monitoring Program. They state that "there continues to be no evidence of large, regional-scale declines in forest ecosystem health as determined by observation of visible crown indicators on trees, e.g., crown dieback, crown density, and foliage transparency." Symptoms of exposure to  $O_3$  were noted on sensitive plants on 10 of 98 plots where bioindicator plants were located.

Recently, McLaughlin and Downing (1995) completed a 5-year study of the interactive effects of ambient  $O_3$  and climate on the growth of mature loblolly pines. Ozone, temperature, and moisture stress often correlate well with each other in the southeastern United States because hot, dry years often are associated with air stagnation systems that result in regional  $O_3$  episodes. Tree growth rates, as measured by annual circumference increase per tree for two drier upland sites (16 trees) and a wetter more fertile stand near a stream bottom (18 trees), were compared. Short-term changes in stem circumference of 24 to 34 mature trees were measured at 138 intervals during five growing seasons (May through October) using a sensitive dendrometer band system. During the period of the study, widely variable temperature, rainfall, and  $O_3$ -exposure conditions and growth rates that varied by 75% across the years were observed. Growth rates were consistently influenced by 3-day average  $O_3$  exposures  $\geq 40$  ppm during the period from 0900 to 2000 hours (9:00 a.m. to 8:00 p.m.). McLaughlin and Downing (1995) stated that their model, which combined 5 years of growth data, suggested that the high-frequency effects of the 0.30 ppm-h increase in mean daily  $O_3$  exposure in the most polluted year (1988), when compared to the cleanest year (1989), would reduce stem growth by approximately 7% in a relatively moist year and by almost 30% in a moderately dry year. They conclude that both episodic and chronic alterations of stem growth in mature trees are associated with ambient levels of  $O_3$ . Episodic reductions are related directly to  $O_3$  exposure, whereas chronic alterations reflect the interaction of  $O_3$  exposures and climatic stresses.

The surveys described below, specifically those made in the Shenandoah National Park, indicate that the injury to native vegetation reported by Hayes and Skelly (1977), Skelly (1980), Benoit et al. (1982), and Duchelle et al. (1982) continues to occur. This is cause for concern because the 48 national parks, including the Great Smoky Mountain and Shenandoah National Parks, are designated as Class I areas under the amended Clean Air Act (U.S. Code, 1991). Air pollution effects on resources in Class I areas constitute an unacceptable adverse impact if such effects diminish the national significance of the area, impair the quality of the visitor experience, or impair the structure and functioning of the ecosystem (Fox et al., 1989; Chappelka et al., 1992). Factors considered in determining if an effect is unacceptable include the frequency, magnitude, duration, location, and reversibility of the impact.



In a survey of eastern white pine stands in the southern Appalachians, 50 white pines were examined for foliar symptoms (chlorotic mottle) believed to be caused by O<sub>3</sub> at each of 201 sites distributed on a 24 × 24-km grid across the natural range of the species in South Carolina, Tennessee, Virginia, North Carolina, Kentucky, and Georgia (Anderson et al., 1988). The survey was conducted from September through November 1985. The percentage of stands with at least one symptomatic tree was highest in Kentucky (77%), followed by Tennessee (31%), and lowest in Georgia (10%). The mean percentage of symptomatic trees per plot for all six states was 27%. The mean volume difference of 48 pairs of symptomatic and nonsymptomatic trees was 49% less for symptomatic trees. Elevation and percent slope were not correlated with occurrence of symptomatic trees, but most symptomatic trees were found on southwest-facing slopes. Plantations had a higher percentage of symptomatic trees than did natural stands. Ozone exposure concentrations were not reported, but it may be possible to make estimates of exposure using data from the nearest O<sub>3</sub> monitoring sites.

Shenandoah and Great Smoky Mountains National Parks are contained within the survey area investigated by Anderson et al. (1988). Winner et al. (1989) surveyed 7 to 10 individuals of five native species at 24 sites in Shenandoah National Park. These species included tulip poplar, wild grape (*Vitis sp.*), black locust, virgin's bower (*Clematis virginiana*), and milkweed. Visible foliar injury due to O<sub>3</sub> was most prevalent on milkweed species (up to 70%), whereas the remaining species had injury approaching 20%. In each case, the level of foliar injury increased with the elevation of the sites. The summer monthly 24-h mean O<sub>3</sub> concentrations at Blacksburg, Rocky Knob, Salt Pond, and Big Meadows did not exceed 0.06 ppm, and foliar injury still was observed.

Another survey made during August to September, 1991, in the Shenandoah National Park included black cherry, yellow poplar, and white ash; and, in the Great Smoky Mountains National Park, black cherry, sassafras (*Sassafras albidum*), and yellow poplar (Chappelka et al., 1992). Black cherry exhibited symptoms in both parks. In the former, the percentage of leaves injured ranged from 18 to 40, whereas, in the latter, the range was 8 to 29% in 1991. Black cherry at Cove Mountain in the Great Smoky Mountains National Park exhibited the highest percentage of symptomatic trees (97%). This site also had the highest number of hours exceeding 0.08 ppm. The majority of occurrences of concentrations exceeding 0.08 ppm occurred during evening hours. Chappelka et al. (1992) suggest that some of the variability in foliar injury response of hardwood species to O<sub>3</sub> in the Shenandoah and Great Smoky Mountains National Parks is due to elevation and microsite conditions, including proximity to streams.

During surveys made in the summers of 1987 through 1990, a total of 95 different plant species, approximately 6% of those growing in Smoky Mountain National Park, exhibited possible foliar injury symptoms attributable to O<sub>3</sub> exposures (Neufeld et al., 1992). Plant species exhibiting foliar injury varied from herbaceous herbs, a grass and a fern, to woody deciduous angiosperms and nine species of evergreens, of which six were conifers. Species exhibiting field symptoms included the native trees (black cherry; sycamore; tulip poplar; black locust; sweet gum; eastern hemlock; and Virginia, Table Mountain, and pitch pines) and herbaceous plants, such as virgin's bower, wild grape, and tall milkweed, all plants previously reported by Duchelle and Skelly (1981) and listed in the previous criteria document (U.S. Environmental Protection Agency, 1986) as being sensitive to O<sub>3</sub> exposures. Ozone concentrations during the period of the surveys did not exceed 0.12 ppm. The observation was made that plants growing at the highest elevations experienced higher maximum and higher minimum concentrations and were exposed to 50% more O<sub>3</sub>.

To verify the foliar injury observed in the field as being due to O<sub>3</sub>, 39 species, 28 of them with field injury symptoms, had been fumigated experimentally in OTCs at the time of publication. Exposures resulted in injury symptoms on 25 of the 28 species that exhibited injury in the field (Neufeld et al., 1992).

Surveys also were made in a Class I areas in New Hampshire and Vermont during the years 1988 to 1990 (Manning et al. 1991; Lefohn and Manning, 1995). Ozone injury was extensive on vegetation growing in open-top and ambient air experimental plots in both states in 1988, when O<sub>3</sub> concentrations were unusually high. The incidence and intensity of O<sub>3</sub> injury symptoms were considerably less in 1989, whereas, in 1990, injury symptoms were evident on all plants. Based on the studies, it was determined that black cherry, milkweed, white ash, white pine, and two species of blackberry were all reliable biological indicators of ambient O<sub>3</sub> exposure (Manning et al., 1991).

The above surveys indicated that although there has been evidence of widespread injury to native trees and other vegetation from exposure to O<sub>3</sub>, the amount of injury has not been great enough for it to be transferred from the tree level to the stand level. Undoubtedly, there has been selection for and removal of the most sensitive tree species of eastern white pine, for example. However, the numbers of sensitive individuals in a stand have not been great enough to make a visible impact on the forest. Simulations suggest that, in forests with mixed species of uneven-aged stands, long-term responses are likely to be shifts in species composition rather than widespread degradation (Taylor and Norby, 1985; U.S. Environmental Protection Agency, 1986).

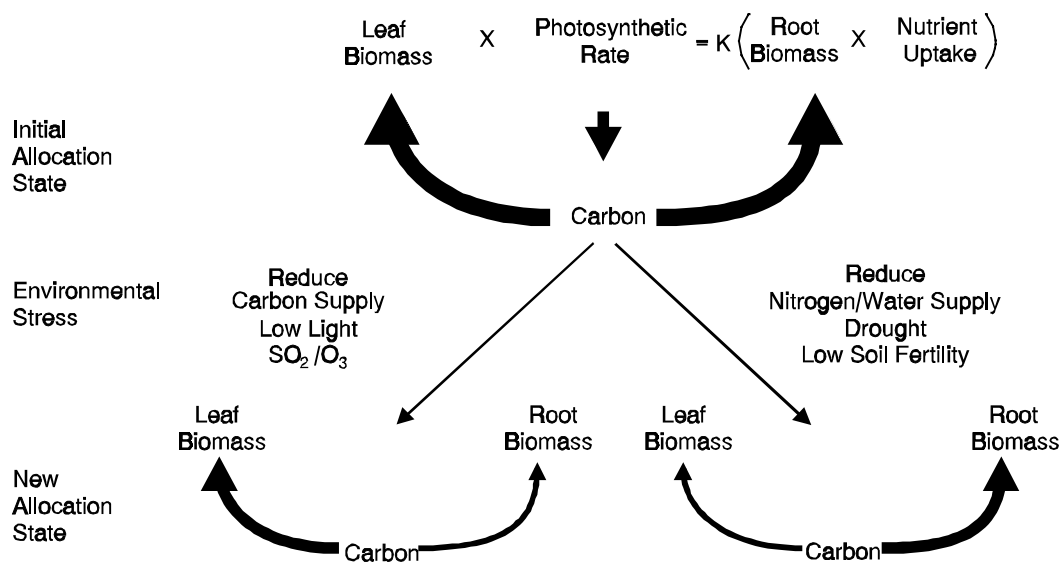
#### **5.7.3.6 Rhizosphere and Mycorrhizal-Plant Interactions**

The importance of the below-ground ecosystem largely has been overlooked when evaluating ecological responses to oxidant exposure. Although the soil system is part of the larger terrestrial ecosystem, it is a system that operates independently and, therefore, is itself an ecosystem (Richards, 1987). Although above-ground components of the terrestrial ecosystem are dominated by producers, the below-ground system is composed primarily of consumers. Thus, the below-ground system is dependent on the above-ground system for inputs of energy-containing substrates. Bacteria, fungi, protozoa, nematodes, microarthropods, earthworms, and enchytraeids all serve various functions in maintaining biological, physical and chemical characteristics of soil, and all are dependent on plant residues for their maintenance. Although the uniqueness of the below-ground ecosystem needs to be recognized, the interdependence between the above- and below-ground systems cannot be over emphasized.

Mycorrhizal fungi are an integral part of the below-ground ecosystem of terrestrial plant communities and are of great importance for vegetational growth. The 1986 criteria document (U.S. Environmental Protection Agency, 1986) discussed mycorrhizae-plant interactions and their importance in some detail. Mycorrhizae are formed on the roots of the vast majority of terrestrial plants and contribute substantially to ecosystem function (Allen, 1991; Harley and Smith, 1983). Fungi invade the roots of terrestrial plants and transform them into mycorrhizae or "fungus roots". The fungus and the host plant live together in an association beneficial to both organisms. Most terrestrial plants cannot adequately take up soil nutrients and water and achieve optimum growth and reproduction without mycorrhizae (HacsKaylo, 1973; Ho and Trappe, 1984; Allen, 1991). Mycorrhizal fungi increase the solubility of minerals, improve the uptake of nutrients for host plants, protect their roots against pathogens, produce plant growth hormones, and transport carbohydrate from one plant

to another (HacsKaylo, 1973). In exchange, the roots of the host plant provide the fungi with simple sugars (HacsKaylo, 1973; Krupa and Fries, 1971). The fungus-plant root relationship is particularly beneficial to plants growing on nutrient-poor soils.

Ozone stress reduces photosynthesis and growth, and roots often are more affected than shoots (Figure 5-33; Winner and Atkinson, 1986; McCool and Menge, 1984; Blum and Tingey, 1977; Manning et al., 1971b; Tingey and Blum, 1973; Hogsett et al., 1985a; Tingey et al., 1976b; Spence et al., 1990; McLaughlin et al., 1982). It has been shown to affect both leaf senescence and root production in plants, thereby disrupting carbon availability for maintenance of the below-ground system (Gorissen et al., 1991b; Andersen and Rygielwicz, 1991), and to alter mycorrhizal colonization and compatibility (Stroo et al., 1988; Reich et al., 1986a; Simmons and Kelly, 1989).



**Figure 5-33.** *Impact of a reduced supply of carbon to the shoot, or water and nitrogen to the roots, on subsequent allocation of carbon.*

Source: Winner and Atkinson (1986).

Mycorrhizae are sensitive to the capacity of the plant to translocate carbohydrate compounds to the roots. Studies have shown that simple sugars provided by plant roots are utilized readily by mycorrhizae and enhance fungal inoculation (McCool and Menge, 1984; HacsKaylo, 1973). Ozone has the capability of disrupting the association between the mycorrhizal fungi and host plants by inhibiting photosynthesis and reducing the amount of sugars available for transfer from the shoot to the roots (see Figure 5-3). Reduction in the roots of available sugars can reduce mycorrhizal formation and root growth as well (Andersen et al., 1991). Berry (1961) examined the roots of eastern white pine injured by  $\text{O}_3$  and observed that healthy trees had almost twice the percentage of living feeder roots as trees with  $\text{O}_3$  injury. In the San Bernardino Forest in California, Parmeter et al. (1962) observed

that the feeder roots system of ponderosa pine exposed to O<sub>3</sub> showed marked deterioration (U.S. Environmental Protection Agency, 1986).

Some studies of the effects of O<sub>3</sub> on tree species that include the investigation of the effects on ectomycorrhizal associations and have been discussed in a series of articles (Shafer and Schoeneberger, 1991). Selected studies are summarized in Table 5-35. The understanding of oxidant effects on root symbioses has not changed substantially since 1986 (U.S. Environmental Protection Agency, 1986); however, the understanding of the importance of symbiotic organisms in ecosystem function has improved. The basic hypothesis on mechanisms remains the same (i.e., effects are mediated through host carbohydrate metabolism) because oxidants do not penetrate the soil more than a few centimeters. Most of the research has been conducted on individual plant species, usually as seedlings, in controlled environments. Although the role of mycorrhizae in community structure has been recognized, it has not specifically been addressed experimentally.

Other studies have refined the understanding of oxidant stress effects on roots. In Douglas fir, root/soil respiration was reduced significantly during the first 1 to 2 weeks after exposure to O<sub>3</sub> or SO<sub>2</sub>, followed by a recovery period that resulted in similar total respiratory release between treatments and controls (Gorissen and van Veen, 1988; Gorissen et al., 1991a). Total allocation to roots did not appear to be reduced, but O<sub>3</sub> apparently reduced translocation to roots in that respiration of <sup>14</sup>C was suppressed. Edwards (1991) found that root and soil respiration were reduced in loblolly pine seedlings exposed to O<sub>3</sub> levels ranging from 0.07 to 0.11 ppm (7-h mean) compared to seedlings exposed to levels below ambient (0.02 to 0.04 ppm). Nouchi et al. (1991) found that O<sub>3</sub> at 0.1 ppm reduced root respiration by 16% in domestic rice (*Oryza. sativa*) after 1 week of exposure. However, exposure to 3 to 7 weeks of 0.1 ppm O<sub>3</sub> resulted in elevated levels of root respiration.

The effects of O<sub>3</sub> on carbohydrate allocation to roots and subsequent shifts in biomass allocation have been examined (Cooley and Manning, 1987; Kostka-Rick and Manning, 1992a; Karnosky et al., 1992b; De Temmerman et al., 1992; Qui et al., 1992; Sharpe et al., 1989; Gorissen and van Veen, 1988; Gorissen et al., 1991a; Spence et al., 1990). Gorissen et al. (1991b) also studied the effects of O<sub>3</sub> exposure on Douglas fir inoculated with the fungi *Rhizopogon vinicolor* and *Lactarius rufus* and watered with ammonium sulfate. The investigators found greater needle retention of <sup>14</sup>C-labeled compounds in the new needles of O<sub>3</sub>-treated plants, and a trend towards fewer <sup>14</sup>C-labeled substrates recovered in roots and root/soil fractions. Short-term transport of <sup>11</sup>C-labeled substrates were followed throughout loblolly pine (Spence et al., 1990). A 45% reduction in transport of photosynthates to roots occurred in O<sub>3</sub>-treated plants compared to controls. Collectively, the studies have shown a general trend of diversion of carbohydrate from roots and retention in the photosynthetically active portions of plants. A reduction in allocation to roots can be associated with a change in the availability of carbohydrate for maintenance of root symbioses.

**Table 5-35. Interactions of Ozone and Forest Tree Ectomycorrhizae<sup>a</sup>**

Host Plant	Mycorrhizae	Exposure Conditions	Effect of O <sub>3</sub> on Mycorrhiza	Reference
Loblolly pine	<i>Pisolithus tinctorius</i>	OTC, field	Reduced root infection	Adams and O'Neill (1991)
	Not stated	OTC, field, 3 years	Reduced root infection	Edwards and Kelly (1992)
	Not stated	CEC	No effect	Mahoney et al. (1985)
	Not stated	CSTR	Reduced root infection	Meier et al. (1990)
Scots pine	Ten species	Open air, field, 3 years	No significant effects	Shaw et al. (1992)
White pine	<i>Pisolithus tinctorius</i>	CEC	Reduced root infection	Stroo et al. (1988)
Norway spruce	Six species	Open air, field, 3 years	No significant effects	Shaw et al. (1992)
	Four species	CEC	No consistent effects	Blaschke and Weiss (1990)
Paper birch	<i>Pisolithus tinctorius</i>	CEC	No effects	Keane and Manning (1988)
Red oak	Not stated	CEC and OTC	Significant increase	Reich et al. (1985)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

The effects of O<sub>3</sub> on mycorrhizal colonization have varied depending on the experimental conditions and the species used. Stroo et al. (1988) studied the effects of O<sub>3</sub> on mycorrhizal infection in eastern white pine seedlings grown for 4 mo in several soils. Results varied by soil type and nitrogen availability; however, in several soils, the number of mycorrhizal short roots increased slightly at low O<sub>3</sub> levels and decreased significantly at higher O<sub>3</sub> concentrations. Reich et al. (1986a) found similar results in eastern white pine and red oak and concluded that O<sub>3</sub> may stimulate mycorrhizal infection at low O<sub>3</sub> concentrations. Simmons and Kelly (1989) observed a trend of greater mycorrhizal short roots in loblolly pine seedlings exposed to subambient O<sub>3</sub> treatment than those exposed to ambient or twice ambient O<sub>3</sub> levels, but the results were not statistically significant. In another study with two families of loblolly pine, Adams and O'Neill (1991) found that mycorrhizal colonization tended to increase with O<sub>3</sub> during the first 6 weeks of exposure and decrease with O<sub>3</sub> after 12 weeks of exposure. Meier et al. (1990) found a decrease in ectomycorrhizal root tips and percentage of feeder roots in loblolly pine seedlings. Keane and Manning (1988) found significant interactions among O<sub>3</sub>, soil type, and pH; however, the direct effects of O<sub>3</sub> were difficult to elucidate. Collectively, these results suggest that O<sub>3</sub> does impact colonization of roots by mycorrhizal fungi; however, the results illustrate the variability in response due to such factors as soil condition, duration of experiment, and timing of measurements.

Altered root carbohydrate allocation resulting from O<sub>3</sub> exposure can affect host-fungus compatibility (Edwards and Kelly, 1992; Simmons and Kelly, 1989). Combined effects of O<sub>3</sub>, rainfall acidity, and soil magnesium status on growth and ectomycorrhizal colonization of loblolly pine has been studied (Simmons and Kelly, 1989). Although variation was high, there was a trend towards altered species composition and reduced mycorrhizal infection in O<sub>3</sub>-treated seedlings. Edwards and Kelly (1992) found high variability in morphotype (morphologically different) frequency in response to O<sub>3</sub> treatments in loblolly pine and noted changes in morphotype frequency over the 3-year study that suggested fungal succession had occurred. Fungal succession and the effects of oxidant stress on normal successional patterns are poorly understood. Shaw et al. (1992), using an open-field exposure system, found no differences in morphotype frequency or fruit-body succession in response to O<sub>3</sub> treatments.

The availability of current photosynthate for root growth is reduced under O<sub>3</sub> stress, and maintenance of below-ground processes dependent on roots for their carbon substrates may be affected. Mycorrhizae alter the size, quality, and retention time of carbon-pools below ground. As noted in the previous section, a 45% reduction in transport of photosynthates to roots occurred in O<sub>3</sub>-treated loblolly pine (Spence et al., 1990). Ozone reduces concentrations of root carbohydrates (Jensen, 1981; Tingey et al., 1976b; Meier et al., 1990; Andersen et al., 1991). Starch in roots was reduced significantly in ponderosa pine by the end of one growing season of O<sub>3</sub> exposure (Tingey et al., 1976b). Reductions in coarse and fine root starch concentrations persisted over the winter in O<sub>3</sub>-treated ponderosa pine and were lower during shoot flush in subsequent years (Andersen et al., 1991). In this study, lower starch concentrations in O<sub>3</sub>-treated seedlings were associated with suppressed growth of new roots. The consequences of a reduction in carbon allocation below ground include reduced substrate availability for soil flora and fauna; altered soil physical characteristics, such as total organic matter and aggregation; and altered soil chemical characteristics including cation exchange capacity.

Premature leaf senescence has been observed in plants exposed to O<sub>3</sub> stress (U.S. Environmental Protection Agency, 1986). Premature senescence affects the

belowground ecosystem by reducing canopy photosynthesis and carbon availability for transport to the belowground system and by increasing leaf litter inputs to the forest floor (Miller, 1984; Fenn and Dunn, 1989). The result is increased flux of nutrients, especially nitrogen, below ground, due to oxidant exposure.

The increased flux of nitrogen due to premature needle senescence in oxidant-exposed plants may act to disrupt the nutrient flow of the ecosystem. Allocation of carbon resources throughout a plant is based on a priority scheme that is driven by carbon and nutrient availability (Waring and Schlesinger, 1985). When soil nutrient levels are high, allocation to the shoot is favored over the roots (Figure 5-32). By shifting carbon allocation to organs in this fashion, plants can adjust to shifts in resource availability in their environment. Oxidant stress alters typical allocation schemes and, in the process, may impair the plant's ability to cope with drought or other stresses. In addition, reductions in allocation to roots can alter root-system size, architecture, and spatial arrangement, which, in turn, can influence populations of soil organisms.

Bacteria and fungi are particularly important in nutrient cycles and act to immobilize nitrogen, carbon, phosphorus, and other nutrients in the biomass. The turnover of these nutrient pools is relatively short because bacterial and fungal predators act to release these nutrients. The majority of plant-available nitrogen during the growing season comes from these predatory interactions in the soil (Kuikman et al., 1990; Ingham et al., 1985), emphasizing their importance in the maintenance of terrestrial ecosystems. Currently, there are no data available on the effect of O<sub>3</sub> on soil fauna.

In summary, mycorrhizal fungi are essential for optimal plant growth. Mycorrhizal fungi increase the solubility of minerals, improve the uptake of nutrients for the host plants, and protect plant roots against pathogens. In turn, the plant roots furnish the fungi with simple sugars that readily are utilized by the fungi and enhance their ability to form mycorrhizae. Mycorrhizae are sensitive to the capacity of the plant to translocate these carbohydrates to the roots. Ozone, by inhibiting photosynthesis, reduces the production of sugars available for transport to the roots. Reduction of sugars in the roots can reduce formation of mycorrhizae and root and tree growth as well.

## **5.7.4 Ecosystem Response to Stress**

### **5.7.4.1 Introduction**

Mature forest ecosystems are seldom stable. They are complex, dynamic communities of living and dead trees interacting among themselves; with populations of native forest floor plants; and with an array of microorganisms, insect pests, and environmental, human, and other factors to continuously shape and reshape the community over time (Manion and Lachance, 1992). Forest communities are held in steady state by the operation of a particular combination of biotic and abiotic factors. Stresses that alter or remove any of the factors can alter the community and change the ecosystem (Kozlowski, 1980; Garner et al., 1989).

Growth of new trees and other vegetation requires the expenditure of energy in the form of carbon compounds. Plants accumulate, store, and use carbon compounds to build their structure and to maintain their physiological processes. Carbon dioxide absorbed from the atmosphere is combined in plant leaves with water from the soil to produce the carbon compounds (sugars) that provide the energy utilized by trees for growth and maintenance (Figure 5-34; Waring and Schlesinger, 1985). Patterns of carbon allocation to roots, stems,

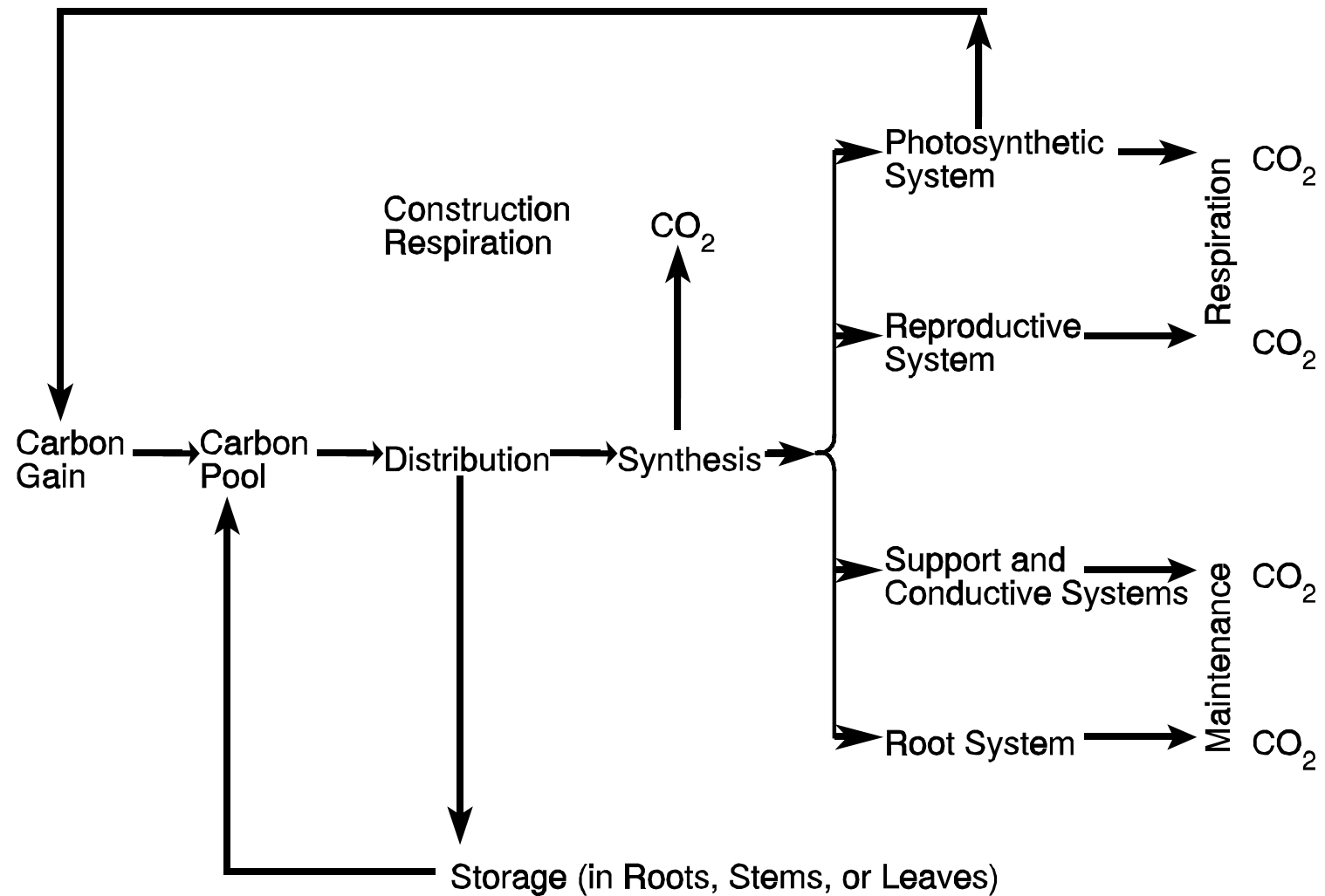
and leaves directly influence growth rate. The strategy for carbon allocation changes during the life of a plant, as well as with different environmental conditions (Figure 5-33; Winner and Atkinson, 1986). Mature trees have a higher ratio of respiration to photosynthetic tissue (Cregg et al., 1989). Even small changes in photosynthesis or carbon allocation can profoundly alter the structure of a forest (Waring and Schlesinger, 1985). Impairment of the process of photosynthesis shifts carbon allocation from growth and maintenance to repair and increased respiration and can result in resource imbalances. The significant changes observed in the San Bernardino Forest ecosystem were possible outcomes of the combined influences of O<sub>3</sub> on carbon, water, and nutrient allocation (McLaughlin, 1994).

Intense competition among plants for light, water, nutrients, and space, along with recurrent natural climatic (temperature) and biological (herbivory, disease, or pathogen) stresses, can alter the species composition of communities by eliminating those individuals sensitive to specific stresses, a common response in communities under stress (Woodwell, 1970; Guderian, 1985). Individual organisms within a population vary in their ability to withstand the stress of environmental changes. The range of variability within which these organisms can exist and function determines the ability of the population to survive. Those organisms able to cope with stresses survive and reproduce. Competition among different species results in succession (community change over time) and ultimately produces ecosystems composed of populations of plant species that have a capacity to tolerate the stresses (Kozlowski, 1980). Pollutant stresses, such as those caused by exposure to O<sub>3</sub>, are superimposed on the naturally occurring competition stresses mentioned above (see also Section 5.4). Communities, due to the interaction of their populations, respond to pollutant stresses differently from individuals (U.S. Environmental Protection Agency, 1993). Air pollutants are known to alter the diversity and structure of plant communities (Guderian et al., 1985). The extent of change that may occur in a community depends on the condition and type of community, as well as on the pollutant exposure.

The plant processes of photosynthesis, nutrient uptake, respiration, translocation, carbon allocation, and growth are directly related to the two essential ecosystem functions of energy flow and nutrient cycling. Altering the above processes can alter energy flow and nutrient cycling and impact ecosystems (Smith, 1992). Response of forest ecosystems to stress are growth-related processes that begin within individual trees and progress to increasing levels of integration and complexity (Figure 5-35; McLaughlin, 1994). Cytological and biochemical changes within a tree can impact physiological functions and alter the tree's growth and productivity. Plants acclimate to changing environmental stresses through both short- and long-term physiological responses, as well as through structural and morphological modifications (Dickson and Isebrands, 1991). When there are many sensitive individuals, the forest structure is changed. As indicated above, response begins with the interaction of the individual and its environment, progresses to the population and its environment, and then to the biological community and its environment (Billings, 1978).

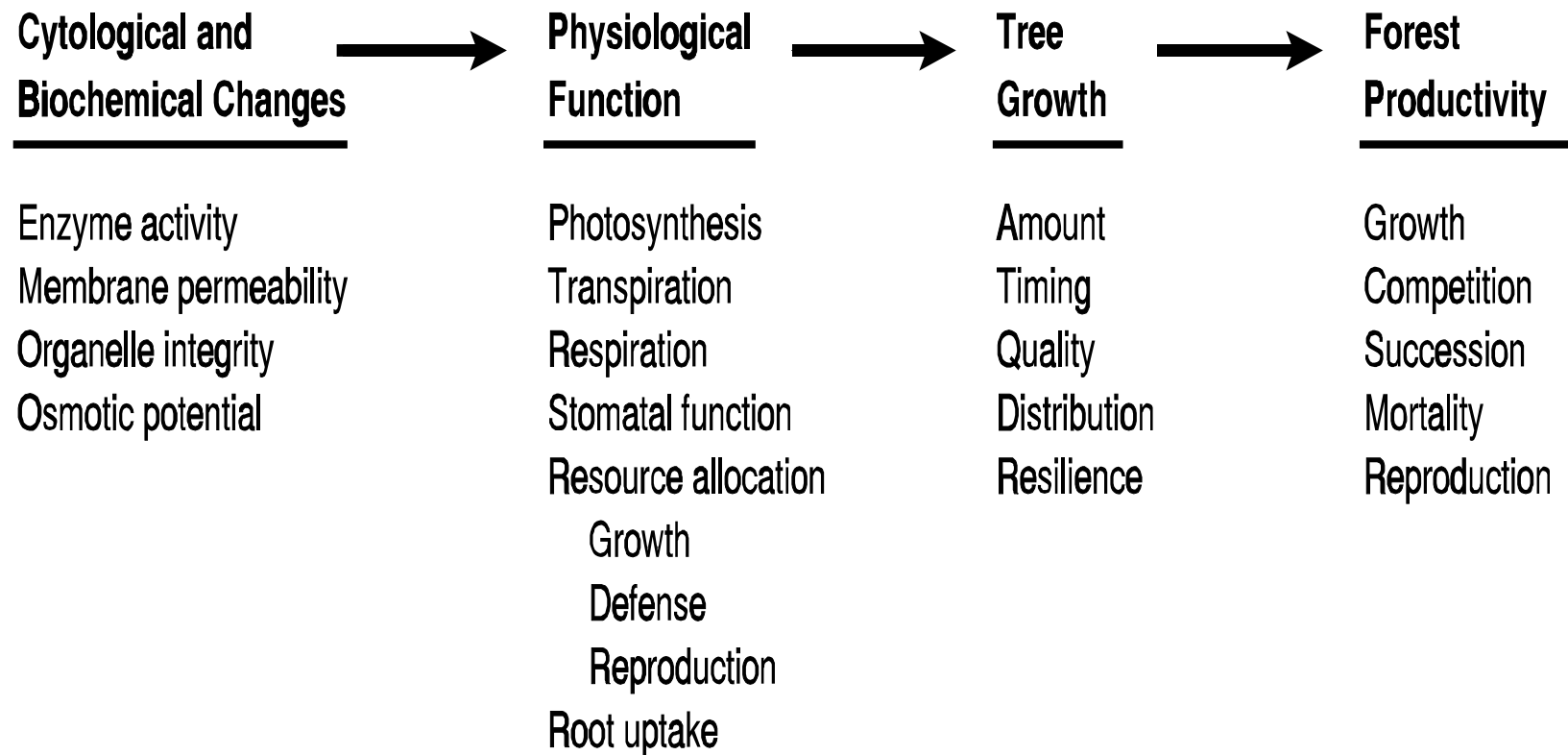
In unpolluted atmospheres, the number of species in an ecosystem usually increases during succession. Productivity, biomass, community height, and structural complexity increase in the early stages of development. Severe stresses, on the other hand, divert energy from growth and reproduction to maintenance and repair and alter succession (Waring and Schlesinger, 1985). In addition, biomass accumulation and production decrease,





**Figure 5-34.** Carbon uptake through photosynthesis is made available to a general pool of carbohydrates used in construction and maintenance of various tissues. Carbohydrates may be shifted from one category to another, depending on environmental conditions.

Source: Waring and Schlesinger (1985).



*Figure 5-35. Organizational levels at which air pollutants have been shown to affect the growth-related process of forest trees.*

Source: McLaughlin (1994).

**Table 5-36. Interaction of Air Pollution and Temperate Forest Ecosystems Under Conditions of Intermediate Air Contaminant Load**

Forest Soil and Vegetation: Activity and Response	Ecosystem Consequence and Impact
1. Forest tree reproduction, alteration, or inhibition	1. Altered species composition
2. Forest nutrient cycling, alteration <ul style="list-style-type: none"> <li>a. Reduced litter decomposition</li> <li>b. Increased plant and soil leaching and soil weathering</li> <li>c. Disturbance of microbial symbioses</li> </ul>	2. Reduced growth, less biomass
3. Forest metabolism <ul style="list-style-type: none"> <li>a. Decreased photosynthesis</li> <li>b. Increased respiration</li> <li>c. Altered carbon allocation</li> </ul>	3. Reduced growth, less biomass
4. Forest stress, alteration <ul style="list-style-type: none"> <li>a. Phytophagous insects, increased or decreased activity</li> <li>b. Microbial pathogens, increased or decreased activity</li> <li>c. Foliar damage increased by direct air pollution influence</li> </ul>	4. Altered ecosystem stress: increased or decreased insect infestations; increased or decreased disease epidemics; reduced growth, less biomass, altered species composition

Source: Smith (1990).

and structural complexity, biodiversity, environmental modification, and nutrient control are reduced (Bormann, 1985). With maturity, energy utilization in ecosystems shifts from production to maintenance (Odum, 1993) (see Figure 5-34). When catastrophic disturbances or injury, whether from natural (e.g., fire, flood, windstorm) or anthropogenic stresses (e.g., O<sub>3</sub>), alter the species composition (biodiversity) of a forest sufficiently to disrupt food chains and to modify rates of energy flow and nutrient cycling, succession reverts to an earlier, less complex stage. The effects of stresses on ecosystems, unless the effects are catastrophic disturbances, are frequently difficult to determine (Kozlowski, 1985; Garner et al., 1989). In a mature forest, a mild disturbance becomes part of the oscillating steady state of the forest community or ecosystem. Responses to catastrophic disturbances, however, as a rule, are readily observable and measurable (Garner, 1994). How changes in plant processes attributed to O<sub>3</sub> exposure affect forest ecosystems is discussed in the following text.

#### **5.7.4.2 Forest Ecosystems**

The primary responses of a forest ecosystem to sustained exposure of O<sub>3</sub> are reduced growth and biomass production (Table 5-36; Smith, 1990). Exposure to O<sub>3</sub> inhibits photosynthesis and decreases carbohydrate production and allocation, and, as has been

discussed previously, decreased allocation to the roots interferes with mycorrhizae formation and nutrient uptake (Figure 5-33). The resulting loss in vigor affects the ability of trees to compete for resources and makes them more susceptible to a variety of stresses (Table 5-36; see also Sections 5.3, 5.6.4.2, 5.6.4.3, and 5.7.3.1). Responses of seedlings under experimental conditions indicate that reductions in growth occur at  $O_3$  concentrations of 0.06 ppm or greater (Table 5-30). Cregg et al. (1989) state that information on seedling response must be used with caution. The environments in which seedlings and trees grow are substantially different due to differences in rooting depth and canopy structure. Trees have the potential to significantly alter their environments through shading, whereas seedlings do not. In the San Bernardino Forest, mortality of canopy trees leads to replacement by trees (white fir, incense cedar, sugar pine, and black oak) more tolerant to  $O_3$  and reduced ecosystem structure. Reduction in structure altered nutrient cycling and energy flow and affected the functioning of other ecosystem components (see Section 5.7.3.1). Ozone concentrations capable of causing injury to forest trees and affecting forest processes continue to occur both in the West and the East. Although reports have described the presence of sensitive species in other U.S. forests; only the San Bernardino Forest has been severely impacted by exposure to  $O_3$ . Why this is the case is impossible to answer definitively because of the absence of data. Evidence obtained from many studies of a variety of ecosystems over the years indicates that ecosystems, in response to pollution or other disturbances, follow definite patterns that are similar even in different ecosystems (Woodwell, 1970). It is possible, therefore, to predict broadly the basic biotic responses to the disturbance of an ecosystem. These responses are reduction in standing crop (trees), inhibition of growth or reduction in productivity, differential kill (removal of sensitive organisms at the species and subspecies level), food chain disruption, successional setback, and changes in nutrient cycling (U.S. Environmental Protection Agency, 1978).

The effects of the stresses associated with  $O_3$  exposure that have developed over the years in the San Bernardino Forest ecosystem are similar to those listed in the previous paragraph.

The extent of injury that an ecosystem will experience from  $O_3$  exposure is determined by the severity and extent of individual response. Leaf injury, as has been stated previously, is usually the first visible indication of  $O_3$  exposure. Structural effects develop when physiological processes within individual plants are disrupted severely (see Table 5-37 and Figure 5-35). With ecosystem responses such as those seen in the San Bernardino Forest, four levels of biological organization beginning with the individual organism are altered (see Table 5-37; Sigal and Suter, 1987). Taylor and Norby (1985) discuss the possible effects on ecosystems at the individual population and community levels. Alteration of functional properties (ecosystems functions) results in structural dysfunction. Stresses, whose primary effects occur at the molecular or cellular physiology level in the individual, must be scaled progressively up through more integrative levels of organ physiology (e.g., leaf, branch, root) to whole plant physiology, stand dynamics, and then to the landscape level to produce ecosystem effects (Figure 5-36; Table 5-37). Particularly, this is true if the stress is of low-level because only a small fraction of stresses at the molecular and cellular level become disturbances at the tree, stand, or landscape level. The processes of energy flow and nutrient cycling must be altered if ecosystems are to be affected. Insect defoliation, for example, may reduce severely the growth of one or several branches, whereas the growth of the tree appears not to be affected (Hinckley et al., 1992).

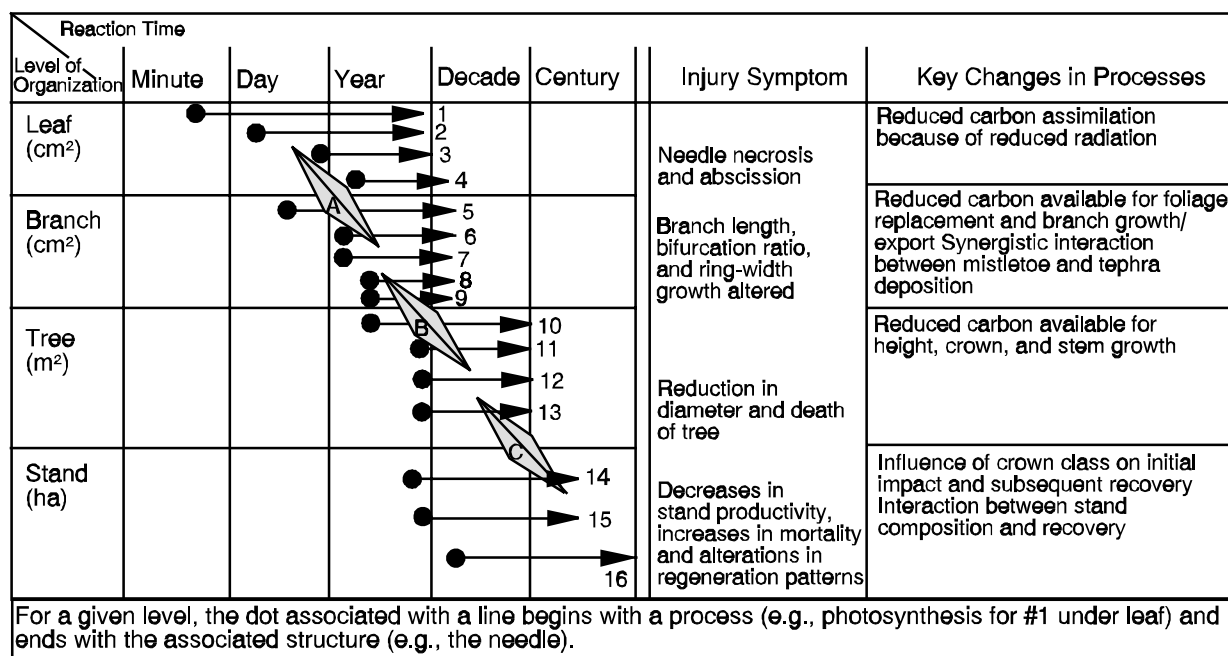
**Table 5-37. Properties of Ecological Systems Susceptible to Ozone at Four Levels of Biological Organization**

Level of Organization Properties	Structural Properties	Functional Properties
Organism	Leaf area and distribution Biomass and allometry	Photosynthesis, respiration Nutrient uptake and release Carbon allocation
Population	Age and size structure Population density Genetic composition Spatial distribution Dispersion (spatial pattern)	Natality (reproduction, mortality) Competition Productivity
Community	Species composition (diversity) Trophic levels and food webs Physical structure (leaf-area index)	Redundancy and resilience Succession (the integration of all species processes such as competition and predation)
Ecosystem	Biomass Element pools Soil properties	Ecosystem productivity Nutrient cycling Hydrologic cycling Energy flow

Source: Adapted from Sigal and Suter (1987).

Variability and compensation are two properties important in determining the effect a stress at one hierarchical level will have on a higher level of organization (see Sections 5.3 and 5.4). Variability in individual response to stress can be the result of each individual being genetically different (See Section 5.4). Individual trees do not respond equally to O<sub>3</sub> exposure. Ponderosa, Jeffrey, and eastern white pine all have been observed to have sensitive, intermediate, and tolerant varieties based on the degree of response. Variability in exposure-response also can be influenced by the movement of O<sub>3</sub> from the leaf surface through the stomata to the metabolic site of action in the leaf interior (Taylor and Hanson, 1992). The stomatal conductance also influences this action.


Variation in age and stage of growth of the organism also can determine response to O<sub>3</sub> exposure (see Section 5.3). Variability in response between seedlings, saplings, and canopy black cherry trees at a site in north-central Pennsylvania was observed by Frederickson et al. (1994). Physiological, phenological, and morphological differences among seedlings, saplings, and canopy trees were associated with altered O<sub>3</sub> uptake and differential response. Leaves at different crown positions of larger trees exhibited differences in leaf physiology and O<sub>3</sub> uptake. Seedling uptake of O<sub>3</sub> and apparent sensitivity per unit leaf area was greater, based on foliar injury symptoms; however, the relative



#### Evaluating Impacts Within a Level of Organization

<b>Leaf Level</b>	Carbon exchange-1 Carbon pools-2 Needle number and size-3 Needle retention/abscission-4	<b>Tree Level</b>	Height and diameter growth-10 Crown shape and size-11 Tree vigor-12 Mortality-13
<b>Branch Level</b>	Carbon allocation-5 Branch growth-6 Branch morphology-7 Branch vigor-8 Branch retention-9	<b>Stand Level</b>	Productivity-14 Mortality-15 Species composition-16

#### Evaluating Interactions Between Different Levels of Organization

	<p>The diagonal arrow indicates the interaction between any two levels of organization. The types of interaction are due to the properties of variability and compensation.</p> <p><b>A</b> - Refers to the interaction between the leaf and branch levels, where, for example, variability at the branch level determines leaf quantity, and compensation at the leaf level in photosynthesis may compensate for the reduction in foliage amount.</p> <p><b>B</b> - Refers to the interaction between the branch and the tree, where variability in branches determines initial interception, branch vigor, and branch location in the crown; compensation may be related to increased radiation reaching lower branches.</p> <p><b>C</b> - Refers to the interaction between the tree and the stand. Both genetic and environmental variability, inter- and intraspecific compensations, and tree historical and competitive synergisms are involved.</p>
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**Figure 5-36.** Effects of environmental stress on forest trees are presented on a hierarchical scale for the leaf, branch, tree, and stand levels of organization. The evaluation of impacts within a level of organization are indicated by horizontal arrows. The evaluation of interactions between different levels of organization are indicated by diagonal arrows.

Source: Hinckley et al. (1992).

exposure of seedlings to O<sub>3</sub> was reduced by an indeterminate growth habit because the majority of their leaves were produced after shoot growth had ceased for sapling and canopy trees. Therefore, their relative uptake was reduced on a whole-crown basis over the growing season and cumulative exposure. Lower crown leaves of saplings and canopy trees appear to be more sensitive to O<sub>3</sub> than upper crown leaves, despite lower uptake, which possibly is due to low availability of photosynthate for anti-oxidant defense and repair of injured leaf cell membranes. Shade leaf morphological characteristics also may play a significant role. The above study describes the interaction of multiple factors that determine O<sub>3</sub> uptake and potential response and illustrates the complexity involved in scaling responses from controlled studies of open-grown seedlings to larger forest trees (Fredericksen et al., 1994).

Compensation in response to stress involves the capacity of the individual to adapt to the stress. Some plants compensate physiologically by detoxifying the O<sub>3</sub> entering the leaves. Other plants compensate by altering the root-shoot ratio. They reallocate carbohydrates to the source of injury in the leaves instead of to the roots, as do uninjured trees (see Figure 5-33 and Section 5.1.3). At the stand level, the slower growth of some trees may be compensated for by the relatively faster growth of others that are experiencing reduced competition so that the overall growth of the stand is not affected (Hinckley et al., 1992). These properties, when taken together, will determine the extent and the rate at which stress at one hierarchical level will impact the next highest level. A framework of hierarchical scales (Figure 5-36) was developed by Hinckley et al. (1992) to provide a means by which the effects of the eruption of Mount St. Helens on forest trees could be followed and understood. This framework is also applicable for use when considering O<sub>3</sub> effects and can be used to explain the difference between the response of the San Bernardino Forest ecosystem and the forests in the eastern United States. As pointed out above, variability and compensation determine the severity of the response of the individual.

Variability and compensation also occur at the population level, all populations do not respond equally (Taylor and Pitelka, 1992). Plant populations can respond in four different ways: (1) no response, the individuals are resistant to the stress; (2) mortality of all individuals and local extinction of the extremely sensitive population (the most severe response); (3) physiological accommodation, growth, and reproductive success of individuals are unaffected because the stress is accommodated physiologically; and (4) differential response, members of the population respond differentially, with some individuals exhibiting better growth and reproductive success due to genetically determined traits (Taylor and Pitelka, 1992). Differential response results in the progressive elimination over several generations of the sensitive individuals and a shift in the genetic structure of the population toward greater resistance (microevolution). Physiological accommodation or microevolution, with only the latter affecting biodiversity, are the most likely responses for exposure to chronic stress (i.e., stresses that are of intermediate-to-low intensity and of prolonged duration). The primary effect of O<sub>3</sub> on the more susceptible members of the plant community is that the plants can no longer compete effectively for essential nutrients, water, light, and space, hence are eliminated. The extent of change that can occur in a community depends on the condition and type of community, as well as the exposure (Garner, 1994). Forest stands differ greatly in age, species composition, stability, and capacity to recover from disturbance. For this reason, data dealing with the responses of one forest type may not be applicable to another forest type (Kozlowski, 1980).

In the eastern United States, ecosystem reduction in structure and diversity has never reached the proportions seen in the San Bernardino Mountains. Visible tree decline has

been observed only in the southern Appalachian Mountains, particularly Mt. Mitchell, and on Camel's Hump, VT. The actual cause of decline and mortality of trees in these areas is a matter of question.

Among the hypotheses suggested for the absence of major changes in the eastern forests is a difference in the O<sub>3</sub> exposures experienced by the eastern forests when compared with the San Bernardino Forest, a region noted for high O<sub>3</sub> levels. Lefohn et al. (1994) characterized and compared O<sub>3</sub> concentrations measured from 1988 to 1992 at Bearden Knob and Parsons, located in a remote forested region of north-central West Virginia, with other sites in the region. It was observed that 1988, when compared with 1992, was a year with very high O<sub>3</sub> exposures. At almost all sites in 1992, few hourly concentrations were  $\geq 0.10$  ppm, whereas in 1988, several sites had 100 or more average concentrations  $\geq 0.10$  ppm. These concentrations were found at both high- and low-elevation sites. In 1992, Bearden Knob, a high-elevation site, experienced a flat diurnal pattern, whereas Parsons, the nearby low-elevation site, experienced a varying diurnal pattern, an indication that O<sub>3</sub> was being scavenged. Horton Station, a high-elevation site in southwestern Virginia, in 1992, experienced 25 episodes with hourly average concentrations near 0.05 ppm for 8 h or longer, 18 episodes with hourly average concentrations near 0.06 ppm, and three episodes with concentrations at or near 0.07 ppm. For the same period, Bearden Knob experienced 31 episodes of 8 h or longer for average hourly concentrations near 0.05 ppm, 13 episodes at or near 0.06 ppm, and 3 episodes at or near 0.07 ppm.

Maximum hourly average concentrations from April to October during 1988 were 0.145 ppm at or near Horton Station, compared with the 0.29 ppm received by the San Bernardino National Forest. Horton Station was exposed to 2,758 hourly concentrations between 0.05 ppm and 0.087 ppm, whereas the San Bernardino site received 2,027 h. The latter site had more concentrations above 0.10 ppm; therefore, it received fewer exposures between 0.05 and 0.087 ppm. It was suggested that the extreme growth reduction and injury that has been observed in the San Bernardino area over the years, when compared with the absence of such injury in the Horton Station area, could be attributed solely to the higher number of hourly average concentrations exceeding 0.10 ppm at the former site (Lefohn et al., 1994). Factors not considered were differences in sensitivity, stand composition, and the ability to compensate for the stress, as well as site variables.

These factors definitely apply in the Appalachian Mountains and, to a degree, in the Sierra Nevada, where the sensitive individuals and composition of the forests vary from the San Bernardino Mountains. The forests of the Appalachian Mountains are known to be more biologically diverse than western forests. Only in the San Bernardino Forest did the removal of sensitive trees reach the population level. Population dynamics impact the ecosystem functions of energy flow and nutrient cycling.

Eastern white pine responses to O<sub>3</sub> exposures were classified into three sensitivity levels ([1] sensitive, [2] intermediate, and [3] tolerant) by both McLaughlin et al. (1982) and Benoit et al. (1982). Black cherry also has been observed to have three sensitivity levels. None of these trees can be termed canopy dominants. In addition to conifers, the forest canopy includes varieties of oaks that are not as sensitive to O<sub>3</sub> exposures. Species removal, therefore, has not affected the eastern forests as did removal of ponderosa and Jeffrey pine from the San Bernardino Forest. Taylor and Norby (1985) have pointed out that the nature of community dynamics, particularly in mixed species, and stands with trees of uneven age play important roles in forest response. Shifts in species composition are more likely responses to stresses such as O<sub>3</sub> than to community degradation. The removal of the codominant



American chestnut (*Castanea dentata*) in the first half of this century caused no major change in the tree species relationships in the Appalachian forests. The effects of O<sub>3</sub> exposure also will probably not cause major change.

The previous O<sub>3</sub> document (U.S. Environmental Protection Agency, 1986) concluded that none of the tree species shown to be injured by O<sub>3</sub> play a dominant role in the Blue Ridge Mountain ecosystem. Therefore, the removal of any of these species probably would not have the impact that the decline and death of ponderosa and Jeffrey pine have had on the San Bernardino Forest ecosystem. This same conclusion applies today.

### 5.7.5 Summary

Ecosystems are composed of populations of "self-supporting" and "self-maintaining" living plants, animals, and microorganisms (producers, consumers, and decomposers) interacting with one another and with the nonliving chemical and physical environment within which they exist (Odum, 1989; U.S. Environmental Protection Agency, 1993). Mature ecosystems are seldom stable. Structurally complex communities, they are held in an oscillating steady state by the operation of a particular combination of biotic and abiotic factors, and they must respond and adapt continually to changing environments (Kozlowski, 1985).

Ecosystem response to stress begins with individuals (Figures 5-34, 5-35, and 5-36). Growth of trees and other vegetation requires the expenditure of energy in the form of carbon compounds. Carbon compounds are accumulated, stored, and used by plants to build their structure and maintain their physiological processes (Figure 5-34). Carbon dioxide absorbed from the atmosphere, combined with water from the soil in plant leaves during photosynthesis, provides the energy in the form of carbon compounds (sugars) utilized by trees for growth and maintenance (Figure 5-34; Waring and Schlesinger, 1985). Patterns of carbon allocation to roots, stems, and leaves directly influence growth rate. The strategy for carbon allocation may change during the life of a plant, as well as with different environmental conditions (Figure 5-33; Winner and Atkinson, 1986). Trees acclimate to changing environmental stresses through both short-term and long-term physiological responses and structural and morphological modifications (Dickson and Isebrands, 1991). Even small changes in photosynthesis or carbon allocation can alter profoundly the structure of a forest (Waring and Schlesinger, 1985). Impairment of the processes of photosynthesis shifts carbon allocation from growth and maintenance to repair, increases respiration, and can result in resource imbalances. The significant changes observed in the San Bernardino Forest ecosystem were a possible outcome of the combined influences of O<sub>3</sub> on carbon, water, and nutrient allocation (McLaughlin, 1994).

Mycorrhizae are an extremely important, but unheralded, component of all ecosystems. The majority of plants depend on them for the uptake of mineral nutrients from the soil. Their absence from the roots of plants has been shown to have a detrimental impact on plant growth. Decreased carbohydrate production and reduced allocation to the roots due to O<sub>3</sub> exposure affect the formation of mycorrhizae and impact plant growth. Exposure to O<sub>3</sub>, therefore, affects plant growth both above and below ground.

Intense competition among plants for light, water, nutrients, and space, along with recurrent natural climatic (temperature) and biological (herbivory, disease, pathogens) stresses, can alter the species composition of communities by eliminating those individuals sensitive to specific stresses, which is a common response in communities under stress (Woodwell, 1970;

Guderian, 1985). Those organisms able to cope with stresses survive and reproduce. The effects of stresses on ecosystems, unless the effects are catastrophic disturbances, are frequently difficult to determine (Kozlowski, 1985; Garner et al., 1989). In a mature forest, a mild disturbance becomes part of the oscillating steady state of the forest community or ecosystem. Responses to catastrophic disturbances, however, as a rule, are readily observable and measurable and return ecosystems to a less complex stage (Garner, 1994).

Ecosystem responses are hierarchical. The extent of injury that an ecosystem can experience from exposure to O<sub>3</sub> will be determined by the severity of the effect on individual members of a population. Stresses, whose primary effects occur at the molecular or cellular physiology level of an individual, must be propagated progressively through the more integrative levels, from the leaf, branch, or root, to whole plant physiology, to stand dynamics, and, ultimately, to the ecosystem (see Figures 5-35 and 5-36). Only a small fraction of the stresses at the molecular, cellular, or leaf level leads to disturbances at the tree, stand, or ecosystem level. Variability in response to stress at both the individual and the population level and the ability to compensate for the stress determine the hierarchical extent of the response.

The mixed-conifer forest ecosystem in the San Bernardino Mountains of Southern California is one of the most thoroughly studied ecosystems in the United States. The changes observed in the mixed-conifer forest ecosystem exemplify those expected in a severely disturbed ecosystem. Chronic O<sub>3</sub> exposures over a period of 50 or more years resulted in major changes in the San Bernardino National Forest ecosystem by influencing forest processes. The primary effect was on the more susceptible members of the forest community, individuals of ponderosa and Jeffrey pine, in that they were no longer able to produce the energy required to compete effectively for essential nutrients, water, light, and space. As a consequence of altered competitive conditions in the community, there was a decline in the sensitive species, permitting the enhanced growth of more tolerant species (Miller et al., 1982; U.S. Environmental Protection Agency, 1978, 1986). Changes in the function of other ecosystem components directly or indirectly affected the processes of carbon (energy) flow, mineral-nutrient cycling, and water movement and changed community patterns. Biotic interactions associated with predators, pathogens, and symbionts were influenced by changes in available energy. The results of the studies of the San Bernardino Forest ecosystem were reported in both the 1978 and 1986 criteria documents (U.S. Environmental Protection Agency, 1978, 1986). The more recent data from the San Bernardino Forest and from other ecosystems in California indicate that O<sub>3</sub> concentrations capable of injuring forest vegetation continue to occur, but at lower concentrations and with shorter durations. Therefore, vegetational injury has not been as great.

There is some indication from new data that O<sub>3</sub> may not have been the only stress encountered by the San Bernardino Forest ecosystem. Nitrate deposition gradients similar to those measured for O<sub>3</sub> suggest that possible soil-mediated exposures to nitrate could have been and continue to be combined with the foliage-mediated O<sub>3</sub> exposures as an additional stress. Research in this area is continuing.

Ozone concentrations capable of causing injury to trees in the Sierra Nevada Mountains have been occurring for many years. Injury to sensitive trees, however, has never reached the same proportions as in the San Bernardino Forest. Differences in forest stand composition (fewer conifers, more hardwoods), ability to compensate for stress, and site dynamics undoubtedly play roles in the forest response.

The forests of the Appalachian Mountains have been episodically exposed to O<sub>3</sub> concentrations capable of causing vegetational injury for many years. Visible injury to foliage of eastern white pine and reduction in growth have been associated with the exposures to concentrations >0.06 ppm lasting for several days. Black cherry also has been shown to be sensitive to O<sub>3</sub> exposures. Surveys of various regions, including the Smoky Mountain and Shenandoah National Parks, indicate that visible injury to a variety of different types of vegetation is continuing to occur. Neither eastern white pine nor black cherry are dominant canopy trees. Removal of sensitive individuals and the absence of changes in the population of these species have not resulted in any visible change in the forest ecosystems along the Appalachian Mountains, possibly because no changes in the ecosystem functions of energy flow or nutrient cycling have occurred. Decline and dieback of trees on Mt. Mitchell and Camel's Hump cannot be related solely to O<sub>3</sub> injury. Ongoing research is attempting to better understand the effects of O<sub>3</sub> exposure on individual plants and the effect, if any, on the ecosystems to which the plants belong.

## **5.8 Effects of Ozone on Agriculture, Forestry, and Ecosystems: Economics**

### **5.8.1 Introduction**

Evidence from the plant science literature cited in the 1986 O<sub>3</sub> Criteria Document (U.S. Environmental Protection Agency, 1986) and in the present document is unambiguous with respect to the adverse effects of tropospheric O<sub>3</sub> on some types of vegetation. For example, findings from EPA's multiyear NCLAN program provide rigorous corroboration of at least a decade of previous research that showed that O<sub>3</sub> at ambient levels caused physical damage to important species. Specifically, NCLAN established that ambient O<sub>3</sub> levels resulted in statistically significant reductions in yields for these crops. Literature reviewed in Section 5.6 of this document assesses the state of natural science findings regarding O<sub>3</sub> effects on crops, forests, and other types of vegetation in more detail.

Information on the benefits and costs of alternative policy options or states of the world (such as changes in air pollution) is of use to decision makers in a variety of settings. For example, economic information provides one means by which to choose from alternative policies or public investments. The role of cost-benefit analysis in federal rule making or standard setting was enhanced by President Reagan's Executive Order 12291 (February 19, 1981), which required that such calculations be performed on any rule or regulation promulgated by the federal government. President Clinton's Executive Order 12886 (October 4, 1993) reconfirmed the importance of economic information in the federal regulatory process. These executive orders provided the stimulus for a large increase in the use of economic analysis in evaluating federal actions, including environmental policies. Although the Clean Air Act and its amendments do not allow the use of cost-benefit analysis in the standard-setting process for primary (human health) effects, economic information has been introduced into the discussion of secondary or welfare effects. A number of economic studies addressing vegetation and other welfare effects have been performed in the last decade.

Assessments of the economic consequences of O<sub>3</sub> on vegetation reflect the state of natural science information on each vegetation category. The natural science evidence concerning effects of O<sub>3</sub> on individual tree species or plant communities is less secure than for agricultural crops (see Section 5.6). As a result, most economic assessments focus on

agricultural crops. The economics literature on effects of O<sub>3</sub> and other air pollutants on forest productivity is very sparse; the few assessments are confined to evaluations of assumed or hypothetical changes in output (e.g., board feet of lumber). The economic effects of O<sub>3</sub> on plant communities or ecosystems have not been measured in any systematic fashion.

This section reviews economic assessments across these vegetation categories. The discussion of economic valuation of ecosystem effects is limited to conceptual and methodological issues in performing such assessments, given the absence of empirical analyses in this category.

## **5.8.2 Agriculture**

In view of the importance of U.S. agriculture to both domestic and world consumption of food and fiber, reductions in crop yields could adversely affect human welfare. The plausibility of this premise resulted in numerous attempts to assess, in monetary terms, the losses from ambient O<sub>3</sub> or the benefits of O<sub>3</sub> control to agriculture. Fourteen assessments of the economic effects of O<sub>3</sub> on agriculture were reviewed in the 1986 document (U.S. Environmental Protection Agency, 1986). Since the preparation of the 1986 document, there have been at least nine other studies published in the peer review literature that provide estimates of the economic consequences of O<sub>3</sub> on agriculture.

The 1986 document highlighted key issues in judging the validity of economic assessments that are applicable to post-1986 studies (i.e., how well the biological, aerometric, and economic inputs used in the assessment conform to specific criteria). First, the evidence on crop response to O<sub>3</sub> should reflect how crop yields will respond under actual field conditions. Second, the air quality data used to frame current or hypothetical effects of O<sub>3</sub> on crops should represent actual exposures sustained by crops at individual sites or production areas. Finally, the assessment methodology into which such data are entered should capture the economic behavior of producers and consumers as they adjust to changes in crop yields and prices that may accompany changes in O<sub>3</sub> air quality; should reflect accurately institutional considerations, such as regulatory programs and income support policies (e.g., provisions of federal "Farm Bill" legislation), that may result in market distortions; and use measures of well-being that are consistent with principles of welfare economics.

### **5.8.2.1 Review of Key Studies from the 1986 Document**

Assessments of O<sub>3</sub> damages to agricultural crops reported in the 1986 document displayed a range of procedures for calculating economic losses, from simple monetary calculation procedures to more complex assessment methodologies that conform to some or all of the economic criteria above. As noted in the 1986 document, the simple procedures calculate monetary effects by multiplying predicted changes in yield or production resulting from exposure to O<sub>3</sub> by an assumed constant crop price. By failing to recognize possible crop price changes arising from yield changes and not accounting for potential producer responses, such assessments are flawed, except for highly restricted situations such as localized pollutant events. Conversely, some assessments provide estimates of the economic consequences of O<sub>3</sub> and other air pollutants that reflect producer-consumer decision-making processes, associated market adjustments, and some measure of distributional consequences between affected parties. The distinctions between studies based on naive or simple models and those based on correct procedures is important at the regional and national levels, because the simple procedures may be biased and lead to potentially incorrect policy decisions.

Most (9 of 14) of the economic assessments reviewed in the 1986 document focused on O<sub>3</sub> effects in specific regions, primarily California and the Corn Belt (Illinois, Indiana, Iowa, Ohio, and Missouri). There have been a number of additional regional assessments since the 1986 document; most are non-peer-reviewed reports arising from consulting or contract research. This regional emphasis in the earlier literature may be attributed to the relative abundance of data on crop response and air quality for selected regions, as well as the importance of some agricultural regions, such as California, in the national agricultural economy. Most of the recent state or regional assessments are commissioned by state public utility commissioners or similar regulatory agencies and use variants of the simple "price times yield" approach, where yields are calculated from response functions arising from the NCLAN data. Although perhaps of use to public utility commissioners concerned with effects from single power plants or other localized sources, these studies generally contribute little to the assessment of pollution effects at the national level. (Most local or regional studies abstract from physical and economic interdependencies between regions, which limits their utility in evaluating secondary National Ambient Air Quality Standards [NAAQS].)

National studies that account for economic linkages between groups and regions can overcome some limitations of regional analyses. A proper accounting of these linkages, however, requires additional data and more complex models and frequently poses more difficult analytical problems. Thus, detailed national assessments tend to be more costly to perform. As a result, there are fewer assessments of pollution effects at the national level than at the regional level.

Two national studies reported in the 1986 document were judged to be "adequate" in terms of the three critical areas of data inputs. Together, they provided a reasonably comprehensive estimate of the economic consequences of changes in ambient air O<sub>3</sub> levels on agriculture. Because of their central role in the 1986 document, these two studies are reported in Table 5-38 and are reviewed briefly below.

In the first of these studies, Kopp et al. (1985 [cited as 1984 in the earlier document but subsequently published as a journal article in 1985]) measured the national economic effects of changes in ambient O<sub>3</sub> levels on the production of corn, soybeans, cotton, wheat, and peanuts. In addition to accounting for price effects on producers and consumers, the assessment methodology used is notable in that it placed emphasis on developing producer-level responses to O<sub>3</sub>-induced yield changes (from NCLAN data available at the time) in 200 production regions. The results of the Kopp et al. study indicated that a reduction in O<sub>3</sub> from 1978 regional ambient levels to a seasonal 7-h average of approximately 0.04 ppm would result in a \$1.2 billion net benefit in 1978 dollars. Conversely, an increase in O<sub>3</sub> to an assumed ambient concentration of 0.08 ppm (seasonal 7-h average) across all regions produced a net loss of approximately \$3.0 billion.

The second study, by Adams et al. (1986a), was a component of the NCLAN program. The results were derived from an economic model of the U.S. agricultural sector that includes individual farm models for 63 production regions integrated with national supply and demand relationships for a range of crop and livestock activities. Using NCLAN data, the analysis examined yield changes for six major crops (corn, soybeans, wheat, cotton,

**Table 5-38. Recent Studies of the Economic Effects of Ozone and Other Pollutants on Agriculture<sup>a</sup>**

Study	Region	Pollutant and Concentration	Model Features				Results (Annual 1980 U.S. Dollars)			
			Price Changes	Output Substitutions	Input Substitutions	Quality Changes	Crops	Consumer Benefits	Producer Benefits	Total Benefits (Costs)
Garcia et al. (1986)	Illinois	Ozone, 10% increase from 46.5 ppb <sup>b</sup>	No	Yes	Yes	No	Corn, soybeans	None	$226 \times 10^6$	$226 \times 10^6$
Adams et al. (1986a) <sup>d</sup>	U.S.	Ozone, 25% reduction from 1980 level for each state <sup>a</sup>	Yes	Yes	Yes	No	Corn, soybeans, cotton, wheat, sorghum, barley	$1,160 \times 10^6$	$550 \times 10^6$	$1,700 \times 10^6$
Kopp et al. (1985) <sup>d</sup>	U.S.	Ozone, universal reduction from 53 to 40 ppb <sup>b</sup>	Yes	Yes	Yes	No	Corn, soybean, wheat, cotton, peanuts	Not reported	Not reported	$1,300 \times 10^6$
Shortle et al. (1988)	U.S.	Ozone, universal reduction from 53 to 49 ppb <sup>a</sup>	Yes	No	No	Yes	Soybeans	$880 \times 10^6$	$90 \times 10^6$	$790 \times 10^6$
Adams et al. (1986b)	U.S.	Acid deposition, 50% reduction in wet acidic deposition	Yes	Yes	Yes	No	Soybeans	$172 \times 10^6$	$30 \times 10^6$	$142 \times 10^6$
Kopp and Krupnick (1987)	U.S.	Ozone, 10% reduction from annual levels (1986 to 1990) for rural areas. Includes adjustments for 1985 Farm Bill.	Yes	Yes	Yes	No	Corn, cotton, soybeans, wheat	NA	NA	$2,500 \times 10^6$ (sum of discounted values at 5%, 1986 to 1990)
Adams et al. (1989)	U.S.	Ozone, seasonal standard of 50 ppb with 95% compliance <sup>c</sup> ; includes adjustments for 1985 Farm Bill.	Yes	Yes	Yes	No	Corn, soybeans, cotton, wheat, sorghum, rice, hay, barley	$905 \times 10^6$	$769 \times 10^6$	$1,674 \times 10^6$
Adams and Rowe (1990)	U.S.	Increased UV-B radiation and associated increase of tropospheric O <sub>3</sub> (of 16%)	Yes	Yes	Yes	No	Soybeans (for UV-B) and all crops in Adams et al. (1989) for tropospheric O <sub>3</sub>	NA	NA	$-830 \times 10^6$ (for the increase in tropospheric O <sub>3</sub> only)

<sup>a</sup>All studies except Garcia et al. (1986) use NCLAN data to generate yield changes due to ozone; see Appendix A for abbreviations and acronyms.

<sup>b</sup>Seven-hour growing season geometric mean. Given a log-normal distribution of air pollution events, a 7-h seasonal ozone level of 40 ppb is approximately equal to an hourly standard of 80 ppb, not to be exceeded more than once a year Heck et al. (1982).

<sup>c</sup>Seven and 12-h growing season geometric mean. Analysis includes both fixed roll-backs (e.g., 25%) and seasonal standards (with variable compliance rates).

<sup>d</sup>Reported in the previous criteria document (U.S. Environmental Protection Agency, 1986).

sorghum, and barley) that together account for over 75% of U.S. crop acreage. The estimated annual benefits (in 1980 dollars) from O<sub>3</sub> adjustments are substantial, but make up a relatively small percentage of total agricultural output (about 4%). Specifically, in this analysis, a 25% reduction in O<sub>3</sub> from 1980 ambient levels resulted in benefits of \$1.7 billion. A 25% increase in O<sub>3</sub> resulted in an annual loss (negative benefit) of \$2.4 billion. When adjusted for differences in years and crop coverages, these estimates are close to the Kopp and Krupnick (1987) benefit estimates.

The Kopp et al. (1985) and Adams et al. (1986a) studies indicated that ambient levels of O<sub>3</sub> were imposing substantial economic costs on agriculture. However, both Kopp et al. (1985) and Adams et al. (1986a) were judged to suffer from several sources of uncertainty. These include the issue of exposure dynamics (7-h/day exposures from the NCLAN experiments versus longer exposure periods, such as 12-h exposures) and the lack of environmental interactions, particularly O<sub>3</sub>-moisture stress interactions, in many of the response experiments. Also, the O<sub>3</sub> data in both studies are based on a limited set of the monitoring sites in the AIRS system, mainly sites in urban and suburban areas. Although the spatial interpolation process used for obtaining O<sub>3</sub> concentration data (Kriging) resulted in a fairly close correspondence between predicted and actual O<sub>3</sub> levels at selected validation points, validation for rural sites was limited (Lefohn et al., 1987a). The economic models, with their large number of variables and parameters and the underlying data used to derive these values, also were noted as potential sources of uncertainty, including the effects on economic estimates of market-distorting factors such as the federal farm programs. Concern over farm programs stems from the evidence that reductions in O<sub>3</sub> will increase yields and hence total production of some crops. If the crop is covered (eligible for deficiency payments) under the provisions of the farm program, then the total costs to the government (of the farm program) may *increase* as a result of reduced O<sub>3</sub> (McGartland, 1987). Thus, the benefits of the O<sub>3</sub> reduction may not be as great as estimated.

The 1986 criteria document concluded that these possible improvements in future assessments were not likely to alter greatly the range of agricultural benefit estimates for several reasons. First, the studies covered about 75 to 80% of U.S. agricultural crops (by value). For inclusion of the other 20% to change the estimates significantly would require that their sensitivities to O<sub>3</sub> be much greater than for the crops included to date. Second, model sensitivity analyses reported in past studies indicate that changes in plant exposure-response relationships must be substantial to translate into major changes in economic estimates. For example, it was believed unlikely that use of different exposure measures or inclusion of interaction effects would alter greatly the magnitude of the economic estimates. Third, it was believed that there were likely to be countervailing effects that would mitigate against large swings in the estimates (e.g., longer exposure periods may predict greater yield losses), but O<sub>3</sub>-water stress tends to dampen or reduce the yield estimates. Finally, the document noted that potential improvements in economic estimates are policy-relevant only to the extent that they alter the relationship between total benefits and total costs of that policy. The possible exception to this generally optimistic assessment of the robustness of the estimates was inclusion of market-distorting factors (i.e., farm programs), an issue that is addressed in some of the post-1986 assessments reviewed below.

#### **5.8.2.2 A Review of Post-1986 Assessments**

The previous criteria document (U.S. Environmental Protection Agency, 1986) concluded that the O<sub>3</sub> assessments of economic benefits to agriculture by Kopp et al. (1985)

and Adams et al. (1986a) provided the most defensible evidence in the literature at that time of the general magnitude of such effects. These two studies, in combination with the underlying NCLAN data on yield effects, were judged to be the most comprehensive information available on which to evaluate the economic impact of O<sub>3</sub> on crops.

Seven national assessments performed since the last criteria document are reported in Table 5-38. Of these, all use defensible economic approaches to quantify dollar effects, where "defensible" is measured in terms of conforming to the criteria cited earlier. An evaluation of these studies in terms of the adequacy of critical plant science, aerometric, and economic data is presented in the table, along with estimates of benefits or damages associated with changes in O<sub>3</sub>.

The concluding statements in the 1986 document are a benchmark against which to judge these seven national studies published since the last document. Most of the contemporary studies build on either Kopp et al. (1985) or Adams et al. (1986a); indeed, the motivation of some of the more recent studies is to test whether the problems noted above (such as exclusion of farm programs) are sufficient to alter the original estimates in a meaningful manner. A relevant question is whether these new studies provided any "surprises" in terms of magnitude of economic effects. These studies are summarized in Table 5-38.

In discussing these latest evaluations, there are several points that relate to the comparability of the evaluations with those of Kopp et al. (1985) and Adams et al. (1986a). First, all studies use NCLAN response data to generate yield effects (for inclusion in the respective economic models). In most cases, data used in the post-1986 assessments reflect improvements of earlier NCLAN data. Second, these studies may be characterized as second generation assessments. They build on the first generation of studies reported in the 1986 document by refining selected aspects of those earlier studies, including interactions with other stresses; use of aerometric data and assumptions that, in some cases, more closely follow the seasonal and regional characteristics of O<sub>3</sub> exposure (Adams et al., 1989); and effects of O<sub>3</sub> on quality of commodities (Shortle et al., 1988). Several of the studies use updated versions of the economic models in Adams et al. (1986a) and Kopp et al. (1985). In addition, some of the studies model the effects of government programs to judge the potential consequences of such distortions on economic estimates (Kopp and Krupnick, 1987; Adams et al., 1989). Third, there are differences in underlying aerometric assumptions; some studies include both O<sub>3</sub> and other environmental stresses (e.g., acid deposition, ultraviolet-B [UV-B], radiation); others reflect O<sub>3</sub> data for more recent time periods. Because ambient O<sub>3</sub> levels vary across years, the choice of year will influence the yield estimates and ultimately the economic estimates.

Common themes or findings from these (and earlier) O<sub>3</sub> and other air pollution studies have been summarized in two recent synthesis papers (Adams and Crocker, 1989; Segerson, 1991). The results of the post-1986 assessments in Table 5-38 and the recent synthesis papers corroborate the general findings of the 1986 document. Specifically, the agricultural effects of tropospheric O<sub>3</sub> at ambient levels impose economic costs to society (or conversely, that reductions in ambient O<sub>3</sub> result in societal benefits). The magnitude of the economic costs reported in the more recent studies is similar to the estimates in Kopp et al. (1985) and Adams et al. (1986a). Such a similarity is not surprising, given the points noted above concerning use of similar data and economic models.

One important recent finding pertains to farm programs. In each case, the inclusion of farm programs in the economic models resulted in modest changes (reductions)



in the economic benefits of O<sub>3</sub> control (due to increased farm program costs). As Segerson notes, however, it is not clear that these increased costs should be charged against the potential benefits of an O<sub>3</sub> regulatory standard but rather as an additional cost associated with the inefficiencies of the federal farm program. Even with the inclusion of farm programs and other elements, the general magnitude of further effects reported in the 1986 criteria document are reduced only by approximately 20%.

In addition to including farm programs, there are a couple of other notable additions to the assessment literature. One study (Adams et al., 1989) attempts to analyze economic benefits under a regulatory alternative involving a seasonal (crop growing season) O<sub>3</sub> exposure index measured as a 12-h mean, instead of hourly levels or percent changes from ambient reported in earlier studies. Specifically, a seasonal average of 50 ppb O<sub>3</sub> (measured as a 12-h seasonal average), with a 95% compliance level, is reported in Adams et al. (1989). The result (of a \$1.7-billion benefit) is similar to the assumed 25% reduction across all regions reported by Adams et al. (1986a). At least one study also has combined environmental stresses (e.g., O<sub>3</sub>, UV-B, radiation) in performing economic assessments. Adams and Rowe (1990), using the same model as Adams et al. (1986a, 1989), report that a 15% depletion of stratospheric O<sub>3</sub> (which results in a 13% increase in tropospheric O<sub>3</sub>) caused an economic loss of approximately \$0.8 billion attributed to the tropospheric O<sub>3</sub> increase.

### **5.8.2.3 Limitations and Future Research Issues**

The recent literature (post-1986) on economic effects of O<sub>3</sub> on agriculture supports the general conclusions drawn in the 1986 document. That is, ambient levels of O<sub>3</sub> are imposing economic costs on producers and consumers. As in earlier economic assessments, the validity of this finding is conditional on the quality of the supporting agronomic and aerometric data. In addition, there are at least three issues that are not addressed in the extant literature on the topic. First, the existing assessments do not consider the external costs of changes in agricultural production arising from changes in O<sub>3</sub> exposures (Segerson, 1991). These costs are important if changes in O<sub>3</sub> result in changes in crop mixes or production practices, which in turn result in changes in soil erosion, fertilizer and pesticide runoff, or other agricultural externalities. For example, if reductions in O<sub>3</sub> increase the relative profitability of a crop that uses higher levels of chemical inputs, then some increase in chemical effluent may result. Given that some assessments suggest that such changes in crop mixes and production practices are likely to accompany O<sub>3</sub> changes, these costs/benefits need to be addressed.

A second issue not directly assessed in the current literature is the relationship between climate change and tropospheric O<sub>3</sub> effects. This relationship is important if global warming is expected to increase tropospheric O<sub>3</sub> levels. In addition, research indicates that global climate change will lead to a relocation of crops (Adams et al., 1990d). This relocation may change the vulnerability of crop species to O<sub>3</sub>, given the spatial distribution of O<sub>3</sub> across the United States (i.e., increased crop production in areas of relatively low ambient O<sub>3</sub>, such as the Pacific Northwest, implies lower O<sub>3</sub> damage).

A third issue involves the institutional setting in which agricultural production occurs. Several recent studies have assessed O<sub>3</sub> effects in the presence of federal farm programs. However, the United States and most industrialized economies are moving away from price supports, production quotas, and import restrictions, the traditional form of government intervention in agriculture. At the same time that these market distortions are

being removed, there is increasing government regulation of agricultural production practices to reduce agricultural externalities. Future assessments of O<sub>3</sub> effects may need to pay less attention to farm program effects and instead include other institutional features of U.S. agriculture.

### **5.8.3 Forests (Tree Species)**

The plant science literature on O<sub>3</sub> and other air pollutant effects on tree species is evolving rapidly as a result of recent research initiatives by EPA and other agencies. The long-term nature of air pollution effects on perennial species creates challenges to plant scientists in sorting out the specific effects of individual stresses from among the many potential explanatory factors, such as O<sub>3</sub> (Skelly, 1989), and in measuring impacts of direct economic value, such as reductions in board-feet of lumber produced per unit of time.

To date, most natural science literature on forest species reports O<sub>3</sub> effects in terms of foliar injury or similar measures (Taylor and Hanson, 1992; Davis and Skelly, 1992b; Simini et al., 1992; Freer-Smith and Taylor, 1992). This emphasis on foliar effects (rather than on marketable yield) is similar to the state of science for agricultural crops prior to 1975. Such visible foliar effects information is of limited use in economic assessments. The exception is in measuring the economic value of aesthetic changes in a forest stock (see Crocker, 1985).

The lack of usable data concerning changes in marketed output, such as board-feet of lumber (or even changes in growth rates), has limited the number of economic assessments of O<sub>3</sub> effects on forests. The few studies that attempt to measure economic losses arising from O<sub>3</sub> or other pollutants circumvent the lack of plant science data by assuming various arbitrary reductions in forest species growth or harvest rates (Callaway et al., 1985; Haynes and Adams, 1992; Adams, 1986; Crocker and Forster, 1985). These studies are summarized in Table 5-39.

Although the economic estimates reported in Table 5-39 are comparable to those reported for agricultural crops (e.g., \$1.5 billion for eastern Canada, \$1.7 billion for eastern U.S. forests), the lack of defensible natural science data makes these studies suggestive, at best, of possible economic consequences of forest (tree species) effects of O<sub>3</sub> or other environmental stresses. In addition, the economic methodology used in the assessments varies, from simple price-times-quantity calculations (e.g., Crocker, 1980) to the use of large, econometric-based representations of the U.S. timber market (Haynes and Adams, 1992). With appropriate data, the Timber Assessment Market Model methodology laid out by Haynes and Adams holds promise for assessing the economic consequences of O<sub>3</sub> when requisite natural science data become available.

In summary, the plant science literature shows that O<sub>3</sub> adversely influences the physiological performance of tree species; the limited economic literature also demonstrates that changes in growth have economic consequences. However, the natural science and economic literature on the topic is not yet mature enough to conclude unambiguously that ambient O<sub>3</sub> is imposing economic costs. The output from ongoing natural science research on this topic will be important to the understanding of this potentially important class of effects.

**Table 5-39. Studies of the Economic Effects of Ozone and Other Pollutants on Forests**

Study	Pollutant/Coverage	Response and Air Quality Data	Economic Model	Annual Damages or Benefits of Control (billions of dollars)
Callaway et al. (1985)	All pollutants. Forest products (hardwood and softwood) in the eastern United States.	Assumes three arbitrary growth reductions (10, 15, and 20%) for hardwood and softwood tree species.	Spatial equilibrium models of softwood and hardwood stumpage and forest products industries in the United States.	–270 to 563 damage in 1984 dollars for assumed reductions in growth levels
Crocker (1980)	Acid deposition. Forest products and forest ecosystem service flows for eastern United States.	Assumes a 5% reduction in products due to acid deposition: assumes a pristine background pH of approximately 5.2	Naive; assumed changes in output multiplied by average value of those goods or services.	–1,750 damage in 1978 dollars from current levels of acid deposition
Crocker and Forster (1985)	Acid deposition. Forest products and forest ecosystem services for eastern Canada.	Assumes 5% reduction in forest productivity for all eastern Canadian forests receiving $\geq 10$ kg/ha/year sulphate deposition.	Naive; assumed changes in output multiplied by average value of goods or services.	–1,500 damage in 1981 Canadian dollars from current levels of acid deposition
Haynes and Adams (1992)	Air pollutants, including acid precipitation. Losses estimated for eastern U.S softwoods.	None; paper demonstrates a methodology for assessing economic effects of yield (growth and inventory) reductions due to any course. Assumes losses from 6 to 21% for softwoods.	Econometric model of U.S. timber sector (Timber Assessment Market Model).	–1,500 to –7,200 in 1986 dollars

## 5.8.4 Valuing Ecosystem Service Flows

### 5.8.4.1 Background

Over the last 30 years, economists have developed a variety of techniques for assessing the value of nonmarket goods and services (recently surveyed by Braden and Kolstad [1991] and Smith [1993]). "Nonmarket" refers to those goods and services not priced and traded in markets. Although most applications are to natural resources and environmental assets, the concepts extend to a range of goods not usually traded in markets. Early applications focused primarily on commodities used directly by the consumer, such as outdoor recreation. Within the last decade, attention has shifted to estimating nonuse (or passive) values, such as what individuals are willing to pay to insure the existence of

species or unique natural settings. The values elicited with these techniques are being used in an increasing array of settings; however, their use is not without controversy.

Valuing complex ecological functions and the associated range of ecosystem service flows is relatively uncharted territory and raises a number of conceptual and practical issues. Some difficulties in valuing ecosystem services lie in the inability of ecologists to unambiguously define and measure ecosystem performance and endpoints (see Section 5.7). Other problems arise from the inability of economic science to measure adequately the consequences of long-term and complex phenomenon. A related problem is the difference in disciplinary perspectives between ecologists and economists. As a result, the current state-of-the-art for valuing ecosystem service flows is inadequate for benefit-cost assessments used in environmental regulatory processes. Improvement in valuation of ecosystem service flows will require increased interdisciplinary cooperation and research between ecologists and economists.

#### **5.8.4.2 Nonmarket Valuation: Implications for Ecosystem Service Flows**

Nonmarket valuation techniques consist of two basic types: (1) indirect approaches rely on observed behavior to infer values, and (2) direct approaches use a variety of survey-based techniques to directly elicit preferences for nonmarket goods and services. Both sets of techniques share a common foundation in welfare economics, where measures of willingness-to-pay (WTP) and willingness-to-accept (WTA) compensation are taken as the basic data for individual benefits and costs.

Indirect approaches, sometimes referred to as revealed preference approaches, rely on observed behavior to infer values. Examples include the travel-cost method, where the relationship between visits to a recreational site and travel expenditures to reach the site (the "price" of the site) is used to infer the value of the site, and the hedonic pricing method, which attempts to infer the value of environmental attributes (e.g., clean air) by comparing the value of a market good (such as residential housing) across neighborhoods with varying levels of air quality. Travel-cost methods encompass a variety of models ranging from the simple, single-site, travel-cost model, to regional and generalized models that incorporate quality indices and account for substitution across sites. Hedonic pricing methods encompass both land price (real estate) and wage models, which account for variations in prices or wages due to environmental attributes (e.g., air and water quality, noise, aesthetics, environmental hazards). The indirect approaches can measure only use values. Recent summaries of the indirect approaches can be found in Braden and Kolstad (1991), Mendelsohn and Markstrom (1988), Peterson et al. (1992), and Smith (1989, 1993).

Direct approaches to nonmarket valuation are survey-based techniques to directly elicit preferences. The hypothetical nature of these experiments requires that markets (private goods or political) be "constructed" to convey a set of changes to be valued. Although there are a number of variants on these constructed markets, the most common is the contingent valuation method (CVM).

Contingent valuation method can be viewed as a highly structured conversation (Smith, 1993) that provides respondents with background information concerning the available choices and specific increments or decrements in one or more environmental goods. Values are elicited directly in the form of statements of maximum WTP or minimum WTA compensation for the hypothetical changes in environmental goods. This method can be applied to both use and nonuse values. The flexibility of constructing hypothetical markets

accounts for much of the popularity of the technique. However, measurement of nonuse value has been the subject of considerable debate (Federal Register, 1993; McFadden, 1994).

There are numerous methodological issues associated with application of CVM, including the specification of the hypothetical environmental change, the elicitation format for asking valuation questions, the appropriate welfare measure to be elicited (i.e., WTP or WTA), and various types of response biases. Randall (1991) argues that, because of the importance of nonuse values, CVM is likely to be the primary tool for measuring the environmental benefits of biodiversity. Recent summaries of CVM can be found in Mitchell and Carson (1989) and Carson (1991).

#### **5.8.4.3 Challenges in Linking Valuation Techniques to Ecosystem Service Flows**

The need for and interest in values of nonmarket goods and services have arisen independently of concerns regarding ecosystem management and sustainability. As environmental planning and management change to accommodate new issues, the need for de novo valuation studies may increase (e.g., standard Resources Planning Act [1974] values may be poor indicators of the economic benefits and costs produced by forest quality changes under alternative air pollution regimes). The process of developing a tractable framework for ecosystem management may require that valuation studies also co-evolve to aid critical management decisions. For example, explicitly linking valuation techniques to physical resource functions through bioeconomic models, remains an important research area (Adams et al., 1990c). Linking valuation measures, from both market and nonmarket studies, to indices of biological diversity is a fundamental challenge.

Ecologists have a traditional skepticism of attempts to assign monetary values to ecosystem functioning, due both to the inherent limitations of benefit-cost analysis and to the inadequacy of quantitative information about ecological and social factors (Westman, 1977; Higgs, 1987). Attempts to monetize environmental benefits also are seen as having an inherent "quantitative bias"; poorly understood ecological functions are neglected, whereas traditional commodities (e.g., outdoor recreation) receive full attention (Foy, 1990).

A further question is whether total economic value really captures total value. Economists make no claim that all values are being considered, only total economic value. A related question is whether complex ecological functions can be accurately expressed in monetary terms? Although the CVM has been applied to an impressive array of nonmarket goods, precise valuation of ecosystem services with CVM will require a precisely defined commodity. As researchers move from valuing single environmental endpoints or services to addressing more complex "bundles" of endpoints and services, it will become more difficult to define the commodity in a CVM survey. This may prevent unambiguous estimation of such values.

#### **5.8.4.4 Valuing Ecosystem Service Flows: Summary**

Economists have a variety of valuation techniques to help guide policy choices concerning the effects of air pollution or other environmental change on environmental assets. Applying these techniques to ecosystem management issues and valuing the full range of ecosystem service flows is a new and, as yet, unresolved challenge. Many scholars, in both ecology and economics, are inherently skeptical of any economic valuation of the full complex of ecosystem services and, hence, turn toward other value indicators. The identified research agenda for valuing ecosystem service flows crosses traditional disciplinary boundaries (Russell, 1993). Interdisciplinary dialogue, cooperation, and the development of a

shared language are necessary for successfully designing future valuation experiments concerning ecosystem service flows and for determining the proper role for such valuation.

### **5.8.5 Summary**

The 1986 criteria document (U.S. Environmental Protection Agency, 1986) contained a review of assessments of the economic consequences of O<sub>3</sub> on U.S. agriculture. This section has evaluated selected post-1986 literature on the same topic. In addition, the review has been expanded to include potential economic effects on forests and ecosystems.

Based on economic assessments and physical science data available at the time, the previous criteria document concluded that O<sub>3</sub> at ambient levels was imposing economic costs on society. The review of more recent (post-1986) literature on agriculture corroborates that earlier conclusion. Specifically, the recent literature, using the full set of NCLAN data and addressing some deficiencies in the pre-1986 assessments, confirms the findings of substantial economic losses from ambient O<sub>3</sub> concentrations.

The exact level of these economic effects is a function of cropping patterns, O<sub>3</sub> concentrations (both ambient and episodic), and the spatial and temporal characteristics of projected or observed O<sub>3</sub> levels. The current economic assessments represent improvements in the scientific understanding of O<sub>3</sub> effects on agriculture. However, the assessments of economic effects initially incident on the agricultural sector remain incomplete.

Only a few assessments consider the economic effects of O<sub>3</sub> on forest trees and on urban trees, shrubs, and ornamentals. These studies assess the economic effects of hypothetical changes resulting from O<sub>3</sub> or other stressors on forest productivity and aesthetics and are best viewed as measures of the potential effect of O<sub>3</sub> on these receptors. Improvements linking O<sub>3</sub> effects data to productivity and aesthetic effects will improve the utility of such economic analyses.

The economic effects of O<sub>3</sub> on ecosystems have not been addressed in the published literature. There is, however, an emerging interest in applying economic concepts and methods to the management of ecosystems. Economic techniques for valuing nonmarket goods and services hold the potential to value some ecosystem goods and services. Ecological research also is addressing the challenging conceptual and practical issues in understanding and managing ecosystem functions. Increased dialogue between the disciplines is needed before empirical analyses of the economic consequences of ecosystem management are feasible.

In summary, the state of science concerning O<sub>3</sub> economic effects on agricultural crops is sufficient to conclude that O<sub>3</sub> imposes costs on society. Conclusions regarding effects on forests and ecosystems must await the acquisition of additional data and possible refinements in ecological and economic methods.

## **5.9 Summary and Conclusions for Vegetation and Ecosystem Effects**

### **5.9.1 Introduction**

Review of the post-1986 literature has not altered the conclusions of the 1986 O<sub>3</sub> criteria document (U.S. Environmental Protection Agency, 1986) or its supplement (U.S. Environmental Protection Agency, 1992). In the 1986 criteria document, several general

conclusions were drawn from various experimental approaches: (1) current ambient O<sub>3</sub> concentrations (>0.04 ppm) in many areas of the country were sufficient to impair growth and yield of plants, (2) effects occur with only a few hourly occurrences above 0.08 ppm, (3) data cited in the 1978 O<sub>3</sub> criteria document (U.S. Environmental Protection Agency, 1978) indicate growth and yield effects for some species when the mean O<sub>3</sub> concentration exceeded 0.05 ppm for 4 to 6 h/day for at least 2 weeks, and (4) regression analyses of NCLAN data to develop exposure-response functions for yield loss indicate that at least 50% of the crops studied will exhibit a 10% yield loss at 7-h seasonal mean O<sub>3</sub> concentrations of 0.05 ppm or less. These conclusions remain valid today. The 1992 supplement reviewed the literature on the appropriate exposure index for expressing O<sub>3</sub> effects on vegetation, including evaluation of the roles of exposure duration and peak concentrations and the 7- and 12-h mean concentrations, and compared many possible exposure indices to summarize seasonal exposures related to yield loss. It was concluded that, in light of research that indicated the influential roles of episodic, peak concentrations and the duration of the exposure, the 7- or 12-h seasonal mean is not an appropriate index because it treats equally all concentrations and fails to consider exposure duration. Instead, the supplement (U.S. Environmental Protection Agency, 1992) recommended use of indices that cumulate all hourly concentrations during the growing season and preferentially weight the higher concentrations. Since 1988, a few experimental studies have addressed directly the roles of individual exposure components in order to develop a more appropriate exposure index. Also, however, results from several retrospective statistical analyses of NCLAN data have increased scientific confidence in the use of the peak-weighted, cumulative indices.

The post-1986 literature includes additional analyses of the NCLAN database and of several European crop-yield-loss studies that substantiate the O<sub>3</sub> effects observed in this country. Although there has been little increase in the information about the response of mature trees individually or in stands, new studies of forest tree seedlings have substantiated pre-1986 reports concerning the sensitivity of a number of species as seedlings. Seedling growth response of several species is altered at the O<sub>3</sub> concentrations (>0.08 ppm) experienced for hours to days in many areas of the United States. Studies of the effects of O<sub>3</sub> on mature trees in their natural habitats are limited. Literature on the roles played by various biotic and abiotic environmental factors in plant response to O<sub>3</sub> indicates the need for more research concerning the response of plants in natural ecosystems, where the interaction of species of various genotypes with a multitude of environmental influences dictates the eventual response of the species or community in question.

The species is the level of biological complexity for which the understanding of O<sub>3</sub> response is greatest. The focus of research for developing quantitative relationships between O<sub>3</sub> exposure and biological effects has emphasized the response of individual species for three reasons. First, single species studies are achievable experimentally, including ease of developing adequate experimental design and exposure technology. Second, in many instances, the plants are grown in monoculture (e.g., most crop plants, ornamentals, fruit and nut species, plantation forests), and the interspecific competition and plant diversity, which typify natural communities, are not issues. The environmental influences of a plant's growing environment (e.g., drought) that modify the exposure-response relationship can be observed more readily. Third, in systems that are comprised of a multitude of species (e.g., mixed forest stands, pastures, grasslands), it is important to understand the response of the individual components so that behavior of the system may be analyzed systematically. The underlying assumption is that understanding how a forest stand responds to O<sub>3</sub> requires knowledge of the

response of sensitive individuals of each species within that stand as a starting point. The interactions that typify the population and the community are subject to O<sub>3</sub> effects as well and may manifest themselves as a measurable effect some time later as a result of these interactions.

The potential for using individual plant (species) responses to an environmental stress (such as O<sub>3</sub> exposure) to predict population and community response may be limited (Woodward, 1992). Propagation of stress responses from a tissue or organ to the whole plant, the population, the community, or the ecosystem level can be influenced by interactions between plants and by feedback mechanisms at the different levels. Important components of such feedback are the mechanisms of homeostasis that involve injury repair (at the metabolic level) or various types of compensation (Tingey and Taylor, 1982). Compensation, which may occur at all levels of organization, from the subcellular to the ecosystem, invokes processes that counteract the detrimental effects of the stress. At the ecosystem level, an effect on the growth rate of a sensitive species may not be translated into a comparable effect on the growth rate of a population of the species, because of changes in the intensity of competition within a community (Woodward, 1992).

Currently, most of the knowledge of O<sub>3</sub> concerns effects on individual plants or their parts. Although some information exists on effects at the population level with some agricultural crops, little is known about how, and to what extent, effects may be propagated through the different hierarchical levels within natural and forest ecosystems.

## 5.9.2 Methodologies

Most of the currently available information dealing with the effects of O<sub>3</sub> exposure on crops and tree seedlings is the result of experimental fumigation studies. The type of fumigation study determines the applicability of the data. Ozone-fumigation, plant-response studies require fumigation of well-characterized vegetation to varying regimes. Variation in regimes may be achieved by controlled fumigation, chemical/mechanical fumigation exclusion, or natural O<sub>3</sub> gradients. Controlled fumigation systems are designed to maintain a modified gaseous atmosphere around a plant for a specified period of exposure in order to monitor plant responses to that modified atmosphere. All fumigation systems share some features in common, namely, general plant growth conditions (light, temperature, humidity, CO<sub>2</sub>, and soil moisture) must be met, and differential concentrations of O<sub>3</sub> generated either artificially or naturally must be supplied to the vegetation and maintained during the exposure period. Exposure systems have been established in controlled environments, greenhouses, and the field. Controlled fumigation systems may range from cuvettes that enclose leaves or branches to a series of tubes with calibrated orifices spatially distributed over a field to emit gaseous pollutants to a plant canopy. Systems that exclude O<sub>3</sub> by mechanical or chemical means have been used, as have natural gradients.

Open-top chambers represent the best technology for determination of crop yield to O<sub>3</sub> at the present time. Concentration and duration of the gaseous exposures are well controlled and plants are grown under near-field-culture conditions; however, plot size is small when compared with a field, microclimate may influence plant sensitivity to O<sub>3</sub>, and air quality after passage through the charcoal filter has not been widely characterized. Caution should be used when extrapolating results to field conditions. Exclusion methods, particularly those using chemicals such as EDU, are the least disruptive of ambient culture conditions in



the field; therefore, these approaches most closely estimate "real" crop losses to O<sub>3</sub>. However, the mechanism by which EDU protects plants is unknown.

### 5.9.3 Species Response/Mode of Action

The mode of action of O<sub>3</sub> on plant species described in the 1986 criteria document (U.S. Environmental Protection Agency, 1986) still holds true. The plant leaf is the site of O<sub>3</sub> action, and the critical effect is on the plant's carbon budget (the amount of carbohydrate produced). Inhibition of photosynthesis limits carbohydrate production and allocation resulting in reduced biomass, growth, and yield and increases susceptibility to abiotic and biotic stresses.

Ozone exerts a phytotoxic effect only if a sufficient amount reaches the sensitive cellular sites within the leaf. To do this, it must diffuse from the atmosphere into the leaf through the stomata, which exert control on O<sub>3</sub> uptake. Ozone effects will not occur if the rate of O<sub>3</sub> uptake is low enough that the plant can detoxify or metabolize O<sub>3</sub> or its metabolites, or if the plant is able to repair or compensate for the effects. Cellular disturbances that are not repaired or compensated are expressed ultimately as visible injury to the leaf or effects on growth, yield, or both (Tingey and Taylor, 1982; U.S. Environmental Protection Agency, 1986). The effects of O<sub>3</sub> exposures on plants are cumulative. The level of O<sub>3</sub> concentration and length and number of exposures determine the extent of plant effects. Annual plant responses are determined by the number of exposures during a single growing season. For trees and other perennial plants the effects are determined by multiple exposures over a number of years.

Ozone is expected to reduce growth or yield only if it directly impacts the plant process that is limiting to plant growth (e.g., carbon produced), or it impacts another step sufficiently so that it becomes the step limiting plant growth (e.g., allocation of carbohydrates to roots and nutrient uptake becomes limiting to plant growth) (Tingey, 1977). Conversely, O<sub>3</sub> will not limit plant growth if the process impacted by O<sub>3</sub> is not growth limiting. This implies that not all effects of O<sub>3</sub> exposures on plants are reflected in growth or yield reductions. These conditions also suggest that there are combinations of O<sub>3</sub> concentration and exposure duration that the plant can experience that may not result in visible injury or reduced plant growth and yield (U.S. Environmental Protection Agency, 1986). However, subtle physiological effects that may not result in immediate growth reductions may result in increased plant susceptibility to other environmental factors (e.g., drought, fungal pathogens, insects, at these concentrations) and competition.

Studies since 1986 corroborate this understanding, adding information on the effect of O<sub>3</sub> on photosynthetic capacity, respiration, leaf dynamics, and the detoxification and compensatory processes. In particular, exposure to O<sub>3</sub> concentrations at or near current ambient levels (0.04 to 0.06 ppm) (see Section 5.6; Table 5-18), depending on their duration, can affect photosynthesis, but exposures of longer duration are necessary to produce growth responses, taking days to weeks, rather than hours, as in earlier studies with high concentrations (0.25 ppm or greater). The loss of leaves prematurely as a result of O<sub>3</sub> exposure has been observed in several species and is particularly important in coniferous trees. However, the mechanism of premature senescence is not understood. Both reduced photosynthetic capacity and reduced leaf area due to O<sub>3</sub>-induced leaf loss contribute to the reduction in carbohydrate production by plants. In addition to leaf loss, reports of stimulation of production of new leaves and higher photosynthetic capacity of new leaves represent

compensation processes that operate in some species of trees. More information is needed to understand  $O_3$  uptake at the canopy level and how plants integrate the effects of  $O_3$ . Some quantitative understanding of these processes is needed to be able to predict long-term effects of  $O_3$  on tree species. Unfortunately, there is little experimental evidence to date regarding effects of long-term  $O_3$  exposure on perennial plants. Few experimental studies of tree seedlings have extended exposures beyond one season, and only in a limited number of studies have observations of growth effects been extended into the following year, thus observing "carry-over" effects. These carry-over effects are significant to long-lived species such as trees because they affect the elongation of new spring shoots or root growth in the year following exposure to  $O_3$ . In at least one instance, this has been correlated with reduced storage carbohydrate in roots. Reduction in growth and productivity, a result of altered carbohydrate production and allocation, may appear only after a number of years or when carbohydrate reserves in the tree are severely depleted. To enable prediction of long-term effects of  $O_3$  exposure in ecosystems, species response as a function of interactions with other species and the effects of abiotic and biotic environmental factors on these interactions both must be known.

#### **5.9.3.1 Exposure Dynamics**

The uptake of  $O_3$  from the atmosphere is a complex process involving absorption of  $O_3$  primarily through the leaves. Plant uptake is influenced by temporal and seasonal variation of exposures. Plant response is influenced by canopy structure, stomatal conductance, respite time between exposures, phenology, and environmental conditions (e.g., soil moisture and nutrient content). Studies both prior to and after the 1996 criteria document, indicate that the components of exposure (i.e., peak concentrations  $>0.10$  ppm, frequency of occurrence, duration, temporal distribution of hourly  $O_3$  concentrations during a growing season) play influential roles in plant response. Greater yield reductions in both annual and perennial crop species (e.g., bush beans and alfalfa) and greater biomass reductions in tree seedlings (e.g., ponderosa pine and aspen) have resulted from experimental episodic peak exposures than from equivalent exposures with either daily peak occurrences or nondiurnal, continuously elevated exposures. In addition to the temporal distribution of concentration, the distribution of  $O_3$  exposure during the growing season, as related to plant phenology, is also important. Some phenotypic stages of growth (e.g., the time of pod-fill in beans and the period of starch storage in perennial species) are more sensitive to  $O_3$  than are others. Thus, effects of early-season versus late-season exposure will vary depending both on the phenology of the plant species and the growth response measured. Another key to plant response is the timing of the exposure. Ozone uptake is greatest when stomatal conductance is highest; therefore, the greatest potential effect for  $O_3$  exposures to produce an effect on plants occurs at that time. Neither peak nor mid-range concentrations occur at the same time. Plant effects are determined by which concentrations occur when stomatal conductance is highest. Associated with stomatal conductance is atmospheric turbulence;  $O_3$  concentrations must reach leaf surfaces if they are to be taken up by a plant.

In most crop-exposure studies, in particular, those included in the NCLAN database, the exposure treatments used in developing response functions have been based on  $O_3$  concentrations at the experimental site. Few studies have been designed specifically to study the effect of varying the types of exposure regimes on crop and tree seedling responses. Research results enable only the prioritization of components of the exposure in terms of their degree of influence on growth alterations. For example, peak or higher concentrations are

more effective than lower concentrations in altering growth when those peaks occur in the daytime when stomatal conductance is high. Episodic occurrences of high concentrations during daylight hours are more injurious according to experimental chamber studies by Musselman et al. (1983, 1986b, 1994) than are either the daily occurrences of the same peak value with the regime having the same total exposure value as the episodic regime, or regimes having no episodic occurrence of peaks and no rise and fall diurnal pattern to daily concentrations (i.e., "flat", but relatively moderate to high concentrations) and having the same total exposure value over a growing season as the episodic regime. The concentrations used in these chamber studies were all >0.10 ppm, exposures seldom experienced outside of California. Because of the variation in species' growth/yield response as a function of exposure dynamics (i.e., concentration, distribution, duration), it is important to have an exposure index that is biologically based (i.e., a measure of ambient O<sub>3</sub> concentration that is related to the measured biological effects).

#### **5.9.3.2 Age and Size**

The role of age and size in modifying tree response to O<sub>3</sub> is the single largest uncertainty in quantifying O<sub>3</sub> effects on tree species. To date, most of the biological effects data and all of the exposure-response functions for trees have been developed with seedlings and saplings. The implicit assumption is that seedling response is a good indicator of large-tree response. However, gas-exchange and water-use differences with tree size and age presumably would affect O<sub>3</sub> uptake and thus O<sub>3</sub> exposure response. Indeed, published reports indicate that O<sub>3</sub> sensitivity is related to the gas-exchange characteristics of the current life stage. Recent data indicate that, for some species (e.g., giant sequoia), seedling growth is affected more by O<sub>3</sub> than is growth in large trees, whereas, for other species (e.g., red oak), seedling growth is less affected than is growth in large trees. These observations of differences in O<sub>3</sub> growth response between seedlings and large trees follow the differences in leaf conductance with age for each of these two species.

Another factor related to tree and size is the occurrence of "carry-over effects" (i.e., the impact of O<sub>3</sub> on growth responses in the season following exposure). For example, reductions in root growth and starch concentration and in shoot elongation in the year following exposure have been reported for ponderosa pine and aspen. Carry-over effects are significant in determining long-term growth response in long-lived species exposed year after year to both O<sub>3</sub> and changing environments.

#### **5.9.4 Factors That Modify Plant Response to Ozone**

Plant response to O<sub>3</sub> exposure is modified by factors within and external to the plant species; cultivars and individuals within populations display variable response to O<sub>3</sub>. The plant's response and the variation of that response is dictated by genetics and the plant's present and past environmental milieu. The environment includes biotic and abiotic factors of the species' growing environment, the temporal pattern of exposure concentrations, and the plant's phenotypic stage during exposure.

##### **5.9.4.1 Genetics**

The response of an individual plant within a species and at any age is affected both by its genetic makeup and the environment in which it is growing. The specific genes controlling O<sub>3</sub> response and involved in mechanisms of O<sub>3</sub> tolerance are largely unknown;

however, control of stomatal conductance and internal biochemical defense systems are among the most commonly postulated tolerance mechanisms. Ozone tolerance is generally thought to be controlled by multiple genes. The implications of genetic variation for managed and natural ecosystems are several-fold. First, the potential for natural selection for  $O_3$  tolerance and associated loss of sensitive genotypes is regional in nature, unlike point-source pollution impacts that occur mainly on plant populations in the vicinity of the source. However, the intensity of  $O_3$  selection is generally thought to be quite low, 0.3 or less (Taylor and Pitelka, 1992), across most U.S. areas. Second, although it is known that individual plants within a species vary in their  $O_3$  tolerance, the physiological costs to tolerant plants in terms of carbohydrate assimilation (energy production) and allocation are not known. Tolerance mechanisms based on reduced stomatal conductivity in the presence of  $O_3$  presumably would reduce the growth of tolerant plants. Similarly, tolerance mechanisms based on the productivity of antioxidant compounds would shunt plant resources away from growth to the production of the defense compounds. Third, exposure-response equations and yield-loss equations developed for a single or small number of cultivars, genotypes, families or populations may not represent adequately the response of the species as a whole. As a corollary to this, the sensitivity of responder genotypes can not be determined by measuring effects just in relation to mean  $O_3$  concentrations.

#### **5.9.4.2 Environmental Factors**

Plant response to  $O_3$  exposure can be modified by a number of biotic and abiotic factors in the plants' past and present growing environment. Understanding and, if possible, quantifying these modifications will reduce uncertainty in the estimates of species' exposure responses. Also important is an understanding of how exposure to  $O_3$  can modify a plant's ability to integrate the effects of its environment. For example, exposure to  $O_3$  has been shown to reduce a tree's ability to withstand winter injury due to freezing temperatures and also to increase the success of pest infestations.

Biotic factors in a plant's environment include pests, pathogens, and plants of the same or competing species. Although only a limited number of plant-insect systems have been studied, some insect pests appear to have a preference for and to grow better when feeding on plants that have been affected by  $O_3$  exposure, but there is no evidence to suggest that  $O_3$  may trigger pest outbreaks in plants. Because the effects of  $O_3$  on the vast majority of plant-insect systems are unknown, quantitative assessment of such interactions on crops and natural vegetation is impossible. At best, it reasonably may be concluded that some insect pest problems will increase as a result of increased ambient  $O_3$  levels. Indeed, this phenomenon was observed in the San Bernardino Forest study where injured ponderosa pines experienced an increase in bark beetle infestations at higher  $O_3$  exposures.

Plant-pathogen interactions also appear to be affected by  $O_3$ . The suggestion that  $O_3$  exposure tends to diminish diseases caused by obligate pathogens and to favor those diseases caused by facultative pathogens (Dowding, 1988) generally is supported by the limited evidence currently available. This suggests that continued exposure to  $O_3$  may lead to a change in the overall pattern of the incidence and severity of specific plant diseases affecting crops and forest trees.

Abiotic environmental factors include, among other physical and chemical elements, solar radiation, wind/atmospheric turbulence, and air and soil moisture and temperature. Collectively, abiotic factors greatly affect plant growth because of their influence on the processes of photosynthesis, respiration, and transpiration. For agricultural

crops, water availability may be the most important of these interactions with  $O_3$ . There is consistent evidence that severe drought conditions tend to reduce the direct adverse effects of  $O_3$  on growth and yield, and that ready soil water availability tends to increase the susceptibility of plants to  $O_3$  injury. However, a lack of water should not be viewed as a potentially protective condition, because of the adverse effects of drought per se. Unlike the situation with annual crops, a limited amount of evidence suggests that prolonged exposure of perennial trees to  $O_3$  may lead to greater water-use efficiency, which, in turn, would better enable the exposed trees to survive drought conditions.

The numerous chemical components in a plant's environment, including soil nutrients, agricultural chemicals, and other air pollutants, also potentially influence the plant's response to  $O_3$  exposure. The nature of these interactions is largely unknown. Although many studies have been conducted on the effects of  $O_3$  on plants in conjunction with other gaseous air pollutants such as  $SO_2$  and  $NO_2$ , the data obtained in several of these studies is of academic interest only because of the unrealistic exposure scenarios used.

Because increased tropospheric  $O_3$  is a component of global climate change, which is of growing concern within world communities, data on the interactions of  $O_3$  with increased levels of  $CO_2$  and UV-B radiation, elevated temperatures, and drought are beginning to appear. Initial data suggest that increased  $CO_2$  levels may ameliorate the effects of  $O_3$ , but conclusive generalizations about the outcome of this interaction are not yet possible. Studies investigating the interaction of  $O_3$  with UV-B exposure reveal no significant changes in  $O_3$  effect on the growth and yield of soybean due to UV-B levels, although there are significant effects of  $O_3$ .

Although a number of studies have examined the interactions of  $O_3$  with specific environmental factors, no quantitative database exists from which the effects of  $O_3$  on species can be extrapolated across environments. The role of different growing environments in a species'  $O_3$  exposure response and the effect of  $O_3$  exposure on a species' ability to integrate its' environment remain uncertain.

### **5.9.5 Effects-Based Air Quality Exposure Indices**

A measurement is needed that relates ambient  $O_3$  exposures with the degree of plant response. The effects of  $O_3$  on individual plants and the factors that modify plant response to  $O_3$ , however, as indicated in the previous sections, are complex and vary with species, environmental conditions, and soil and nutrient conditions. Due to the complexities of the processes associated with uptake and  $O_3$  interactions with external physical and internal genetic factors that influence plant response, the development of exposure indices that characterize plant exposure and response in a quantifiable manner has been and continues to be a major problem.

Plant uptake of  $O_3$  (either rate of uptake or cumulative seasonal uptake) is a critical factor in determining plant response. Ozone uptake is controlled by canopy conductance, stomatal conductance,  $O_3$  concentration external to the leaf and gases emitted from the leaf through the stomata. Any factor that affects stomatal conductance (e.g., light, temperature, humidity, atmospheric chemistry, soil and nutrients, time of day, phenology, biological agents) will affect  $O_3$  uptake and, consequently, plant response. Empirical functions for predicting stomatal conductance have been developed for particular species (Losch and Tenhunen, 1981) but have not been used in development of exposure indices.

The mode of action of O<sub>3</sub> on plants, as presented in Section 5.2, is a culmination of a series of biochemical and physiological processes that lead to alterations in plant metabolism. Ozone-induced injury is cumulative, the result of net reduction in photosynthesis, changes in carbohydrate allocation, and early leaf senescence, which lead to reduction in biomass formation and reduction in yield. Increasing O<sub>3</sub> uptake results in increasing reduction in biomass production and yield.

The optimum exposure index that relates well with plant response should incorporate, directly or indirectly, the factors described above; unfortunately, such an index has not yet been identified. Exposure indices that weight the hourly O<sub>3</sub> concentration differentially appear to be the best candidates for relating exposure with predicted plant response. Peak concentrations occur primarily during daylight hours, thus indices that provide differential weight to the peak concentrations give greater weight to daylight concentrations, when stomatal conductance is usually greatest, than to nighttime concentrations, when conductance is minimal. Peak concentrations do not occur throughout the day; therefore, the timing of the exposure is important in determining plant response.

Evidence from the Musselman et al. (1983, 1986b, 1994) and Hogsett et al. (1985b) experimental chamber studies that applied two or more different exposure regimes support the view that daytime peak concentrations and respite time are important in eliciting plant responses. Ozone effects on plants exposed to two (or more) regimes having equal total exposure were greater for exposures experiencing the higher peak concentrations, respite time of 2 to 6 days, or peak concentrations during period of maximum leaf expansion. This conclusion is consistent with the mode of action of O<sub>3</sub> on plants and with the conclusions in the previous EPA criteria document (U.S. Environmental Protection Agency, 1986) and its supplement (U.S. Environmental Protection Agency, 1992).

No studies have been designed specifically to evaluate the adequacy of the peak-weighted, cumulative indices. Consequently, it is not possible to discriminate among the various peak-weighted, cumulative indices based on experimental data. Functional weighting approaches, including allometric, sigmoid, or threshold weighting, have been suggested and, in earlier retrospective studies, compared, but there is no evidence to favor one approach over the other on the basis of statistical fits to the data. Generally, the peak-weighted, cumulative indices relate well with plant response and order the treatment means in monotonically decreasing fashion with increasing exposure, based on studies that apply two or more types of exposure regimes and when combining data from replicate studies of the same species.

Peak-weighted, cumulative indices appear to have major advantages over the mean (e.g., 7-h seasonal mean), peak indices (e.g., 2HDM), and the index that cumulates all hourly average concentrations (i.e., SUM00). Crop yield loss and biomass reduction are estimated better using the peak-weighted, cumulative indices than the 2HDM index; when duration of exposure is taken into consideration, peak-weighted, cumulative indices perform better than the seasonal mean indices. In addition, results have been published to indicate that the SUM00 index does not relate adequately exposure with biological effects because the index focuses on the lower hourly average concentrations.

The greater importance of cumulative peak concentrations (>0.10 ppm) when compared with cumulative mid-range concentrations (0.50 to 0.09 ppm) in eliciting plant response has been questioned. The data supporting the two viewpoints are not comparable because the response parameters used in these studies were different. Musselman et al. (1983, 1986b) and Hogsett et al. (1985b), whose studies have been cited as a basis for emphasizing the importance of cumulative peaks, measured both foliar injury and growth

reductions and were based on exposures in open-top or greenhouse chambers to concentrations higher than those usually encountered in the ambient air outside of California. The biological evidence for supporting the importance of mid-range concentrations is based on ambient air field exposures using plants sensitive to O<sub>3</sub> in which exposures, seldom if ever, exceeded 100 ppb. The conclusions of Krupa et al. (1993, 1994, 1995), Tonneijck and Bugter (1991), and Tonneijck (1994) must be interpreted with caution because they are based on data from Bel W3 tobacco and other O<sub>3</sub>-sensitive indicator plants. Tonneijck and Bugter (1991) concluded that O<sub>3</sub> effects varied with species and climatic condition; therefore, O<sub>3</sub> injury on Bel W3 tobacco was not an adequate indication of ambient condition, nor was it an adequate indicator to determine the risk of O<sub>3</sub> to other plant species or to vegetation as a whole. It should be obvious that plants take up all O<sub>3</sub> concentrations present in the atmosphere, not just O<sub>3</sub> peaks. Cumulative effects result from all O<sub>3</sub> concentrations that enter the plant. Plants can not respond to peaks if there are none in the ambient air. When peaks occur at the time of greatest stomatal conductance, the effect of mid-range concentrations will not be observable.

When predicting the effects of O<sub>3</sub> on vegetation under ambient conditions using experimental exposure-response models, the types of exposure regimes used in the experiments should be taken into consideration. For example, NCLAN experiments contained peak hourly average concentrations in their regimes. Any exposure index based on the NCLAN experiments should take into consideration the presence of these peak concentrations. By doing so, the situation may be avoided where two sites that experience two distinct distributions of high hourly average concentrations but have the same value of cumulation (e.g., same SUM06 or W126 value) exhibit differing biological effects.

The concentration level for a cumulative, peak-weighted index was determined from the best available biological response data (i.e., the crop yield responses from NCLAN). The concentration level selected to prevent a particular yield loss will have associated with it any uncertainty inherent in the methodology employed in NCLAN studies, in particular, the modified ambient exposures of NCLAN protocol typified by a relatively large number of episodic occurrences of high concentrations. The episodic occurrence of high concentrations is typical of many, but not all, agricultural areas in the United States. Some regions of the country may have different exposure regimes, typified by the lack of a large number of high concentration occurrences but still having a high cumulative, weighted exposure index value. The particular concentration level determined to protect 50% of the crops studied from a 10% yield loss based on NCLAN data may over- or underestimate the yield loss from a different regime type. Lefohn and Foley (1992) and Musselman et al. (1994) have suggested that a multi-component index, combining a cumulative, weighted index and the number of occurrences of concentrations  $\geq 0.10$  ppm would capture more adequately both the plant exposure response and the air quality at the site, thus overcoming some of the uncertainty associated with selection of a concentration level from the NCLAN crop response data.

Other experimental approaches have been employed to demonstrate effects of ambient O<sub>3</sub> exposure (e.g., chemical protectants [EDU]) but are of limited value in determining an exposure index. The ambient exposure approach addresses one of the shortcomings of the NCLAN methodology, but the experimental designs can not provide a range of O<sub>3</sub> treatments necessary for statistical robustness, quantifying the effect of ozone on yields, and the results cannot be extrapolated beyond the site and year of the exposure study.

## 5.9.6 Exposure Response of Plant Species

### 5.9.6.1 Introduction

The Clean Air Act seeks to protect public welfare resources, including plants and natural ecosystems, from adverse effects of criteria pollutants, including tropospheric O<sub>3</sub>. "Adverse effect" has been interpreted in the 1986 criteria document (U.S. Environmental Protection Agency, 1986) and its supplement (U.S. Environmental Protection Agency, 1992) to be equated with yield loss and impairment in the intended use of the plant. In the instance of crop species, for example, an adverse effect of O<sub>3</sub> is agronomic yield loss. Foliar injury also can be an adverse effect, especially when decreasing marketability of foliar crops (e.g., spinach, lettuce, cabbage) or reduced aesthetic value of ornamentals. These effects constitute yield loss with or without concomitant growth reductions. With tree species grown for timber, paper, or pulp, biomass loss (and therefore loss of forest productivity) can be quantified as being an adverse effect.

Diverse experimental procedures, ranging from field exposures without chambers to field exposures with OTCs to exposures in chambers under highly controlled laboratory conditions, have been used to study O<sub>3</sub> effects on crops and trees seedlings. In general, the highly controlled laboratory experiments are most useful for investigating specific responses and for providing a scientific basis for interpreting and extrapolating results. Such experiments are very important in increasing the understanding of the biological effects of air pollutants. To accurately assess the economic impacts of O<sub>3</sub> on crop yield or ecological impact of altered carbon partitioning in tree species, however, requires exposure methodology that provides a range of O<sub>3</sub> treatments sufficient for quantifying effects (i.e., exposure-response functions) and also provides growing conditions that closely match those in the plants' natural growing environment. Because the OTC methodology provides control over O<sub>3</sub> exposure treatments and still allows some replication of field conditions, as well as permits replication of studies from year to year, this has been the primary methodology used for developing the empirical database of O<sub>3</sub> effects on crop and seedling tree species during the last 15 years. Many of the studies reviewed in this document, as well as those in the 1986 O<sub>3</sub> criteria document (U.S. Environmental Protection Agency, 1986) utilized the OTC methodology, including the NCLAN studies (see Section 5.6.2) that were initiated by EPA in 1980 primarily to improve estimates of yield loss in the field and the magnitude of crop losses resulting from O<sub>3</sub> exposure. The NCLAN studies used numbers of treatments sufficient to permit robust statistical designs and the development of exposure-response functions. It is the largest database available for establishing a quantitative relationship between O<sub>3</sub> exposure and crop yield. Studies of tree seedlings also have been conducted utilizing OTCs as a means of exposing seedlings to a range of treatments, replicate treatments, and approximate field conditions. The exposure-response function for each species permits estimations and generalizations of biological response to O<sub>3</sub>, unlike the multiple comparison approach.

There has been debate concerning the experimental designs, particularly the number, types of regimes, and exposure concentrations used in the NCLAN studies. The O<sub>3</sub> exposures utilized by the NCLAN program have been described as artificial regimes that do not mimic actual conditions. The exposure treatments were "modified ambient" (i.e., treatments were achieved by addition of some amount of O<sub>3</sub> above the ambient concentration). Another criticism of NCLAN studies was the alteration of the environment by the OTCs to the degree that exposure-response functions obtained using this methodology can not be extrapolated to ambient environments. A study by Heagle and co-workers (1989a) of



OTCs suggests that, although departures from field conditions can occur, "they allow control of pollutant concentrations with dynamics that compare closely to exposure dynamics in ambient air." For NCLAN studies, although it was noted that OTCs decreased mean wind velocity, altered light profiles, and eliminated the vertical gradient in O<sub>3</sub> concentration (less near the ground) that usually occurs in the canopy of plants grown in the ambient air, chamber effects were found not to enhance consistently the treatment differences or plant responses to O<sub>3</sub>. Despite the criticisms of the NCLAN studies, there is no other database that matches it. Approximately, 90% of the available O<sub>3</sub> dose-yield response data comes from these studies (Heagle et al., 1989a).

#### **5.9.6.2 Predicted Crop Yield Losses**

The NCLAN studied the major agronomic crop species, including corn, soybean, wheat, cotton, bean, and alfalfa, as well as several other regionally important species; collectively, the species studied account for 70% of all cropland in the United States and for 73% of the nation's agricultural receipts. To predict crop yield loss due to O<sub>3</sub> exposure, two approaches to developing a composite exposure-response function for all crops from the NCLAN database were taken. The first approach predicted crop yield losses of up to 20% at a 12-h seasonal mean of 0.06 ppm and a 10% loss at a 12-h seasonal mean of 0.045 ppm. The second approach calculated separate regressions for studies with multiple harvests or cultivars, resulting in a total of 54 individual equations from the 31 NCLAN studies (average study duration of 74 days) and 12 crop species using three different exposure indices, and concluded that 50% of the crops would experience 10% yield loss at a 3-mo SUM06 concentration of 26.4 ppm-h (Table 5-22), a 7-h seasonal mean of 0.049 ppm, or a 2HDM of 0.094 ppm. (These are averaged yield losses for all species; losses for many of the crops would be higher at these concentrations.) The box-plot distribution of yield loss for the compiled studies, expressed as a SUM06, is shown in Figure 5-23A.

Results reported for European crop studies support the NCLAN analyses results. For example, in the European studies, wheat yields were reduced by up to 29%, depending on the O<sub>3</sub> exposure level and cultivars used, but in no instance did the exposure level exceed a 0.062 ppm 7-h seasonal mean. Spring rape yields were reduced by 9 to 26% at 8-h seasonal means of 0.03 to 0.06 ppm. Seasonal 7-h means of 0.045 ppm reduced bean yield by 17%.

Perennial crop exposure response, unlike annual crops, is complicated by the fact that such crops receive multiple-year exposures, and the effects of such exposures may be cumulative. Yields of multiple-year forage crops (e.g., alfalfa and forage mixtures), as with yields of single-season crops, are reduced at O<sub>3</sub> concentrations at or near ambient (0.04 to 0.06 ppm, 7- and 12-h mean) in many parts of the growing areas for these crops. The question of cumulative effects in perennial crops has been addressed only in one instance (a 2-year alfalfa study in Southern California), and, in this study, there was no indication of carryover effects from year to year.

#### **5.9.6.3 Predicted Biomass Changes in Trees**

Trees, depending on species and genotype, exhibit a wide range of responses to O<sub>3</sub> exposure. Ozone exposures alter gas exchange, early senescence and needle retention on conifers, carbohydrate allocation, root growth, total biomass production, and reproduction. The alteration by O<sub>3</sub> of photosynthetic performance and needle retention shifts carbon allocation priorities and changes growth. In particular, root growth in tree seedlings is often reduced, whereas shoot growth is maintained. Root growth reductions can decrease

mycorrhizal formation and water and nutrient uptake in seedlings and impede seedling establishment. Changes in carbon budgets due to O<sub>3</sub> exposures also can affect long-term changes in tree growth. Small changes (even less than 1 to 2% biomass loss per year) that may not be detectable statistically may be translated into large changes during the life span of the tree and may result in changes in stand dynamics when sufficient trees are affected, with concomitant effects on the structure and function of the ecosystem. The implication of these effects on long-lived species is significant. However, most of the experiments have been conducted on seedlings for 1 to 3 seasons, only 2% or less of the life span of the tree. Seedlings and mature trees have different carbon allocation use patterns. Mature trees have a significantly higher ratio of respiring to photosynthetic tissue. Carbohydrate reserves also differ between trees and seedlings. Extrapolation of information from seedlings to mature trees must be done with caution because the environments in which trees and seedlings grow differ substantially due to differences in rooting depth and canopy structures.

### **5.9.7 Effects of Ozone on Natural Ecosystems**

Ozone is the only regionally distributed phytotoxic pollutant capable of changing the chemical environment of forests without leaving a permanent trace of its presence. Ozone molecules are ephemeral, decompose rapidly to oxygen and free radicals, and leave no residuals; therefore, stresses resulting from exposure to O<sub>3</sub> are frequently difficult to determine (Taylor and Norby, 1985).

Ozone exposures are episodic. Ozone may be transported for long distances and may cover very large areas during an episode. Concentrations can increase as O<sub>3</sub> trajectories move across the country and pass over new sources (Wolff et al., 1977a,b,c, 1980; Wolff and Lioy, 1980). Forest trees, shrubs, and other perennial plants often must cope with the cumulative effects of several acute or chronic episodes. Exposures may last for minutes, hours, days, or weeks. Trees may respond rapidly as, for example, when needles of eastern white pine exhibit visible injury symptoms within days after exposure to high (>0.08 ppm) O<sub>3</sub> concentrations (Garner, 1991). In most instances, however, responses are more subtle and not observable for many years because trees compensate, adapt, and respond to cumulative stress by differential growth, the result of altered carbon allocation (Waring and Schlesinger, 1985).

Ecosystems are complex, dynamic communities composed of populations of living plants, animals, and microorganisms (producers, consumers, and decomposers). Because they must continually respond and adapt to changing environments, mature ecosystems are seldom stable (Kozlowski, 1985). They are held in an oscillating steady state by the operation of a particular combination of biotic and abiotic factors. Ecosystems can change dramatically throughout time, have no optimal condition, and are only healthy when compared to some desired state specified by humans (Lackey, 1994). Ecosystem functions maintain clean air, pure water, a green earth, and a balance of organisms. These functions enable humans to obtain food, fiber, energy, and other material needs for survival (Westman, 1977).

Ozone concentrations capable of causing injury to forest ecosystems (0.06 ppm or higher of varying durations; see Section 5.7.3) continue to occur in the San Bernardino and the Sierra Nevada Mountains and in the Appalachian Mountains from Georgia to Maine. Visible injury to forest trees and other sensitive vegetation in these areas has been observed.

The impact that an ecosystem can experience from exposure to O<sub>3</sub> will be determined by the severity of the effect on individual members of a population. Stresses,

whose primary effects occur at the molecular or cellular physiology level of an individual, must be propagated progressively through the more integrative levels, from the leaf, branch, or root, to whole plant physiology and stand dynamics, and, ultimately, to the ecosystem (see Section 5.7.4; Hinckley et al., 1992; Figure 5-36). Variability and compensation in response to stress at both the individual and the population levels determine the hierarchical extent of the response. Other factors, in addition to compensation and variability in response to stress, that affect response in individuals and populations include the location of a site and environmental factors, such as air and soil moisture and temperature and genetic composition of the individuals of a population. Responses at the population level must alter the ecosystem functions of energy flow, water movement, and nutrient cycling to produce an ecosystem impact.

The primary responses of a forest ecosystem to sustained O<sub>3</sub> exposure are reduced growth and biomass production (Section 5.7.4; Figure 5-34; Table 5-36; Smith, 1990). In mature trees, most of the carbohydrate produced is utilized in maintenance (Figure 5-34). Exposure to O<sub>3</sub> inhibits photosynthesis and decreases carbohydrate production and allocation, and, as has been stated previously, decreases allocation to the roots and interferes with mycorrhizal formation and nutrient uptake. The resulting loss in vigor affects the ability of trees to compete for resources and makes them more susceptible to a variety of stresses (Section 5.7.4; Table 5-36; see also Sections 5.3 and 5.7.3.1). In the San Bernardino Forest, the only available study dealing with the effects of O<sub>3</sub> exposure on forest ecosystems, the sensitive canopy trees, ponderosa and Jeffrey pine, no longer were able to compete effectively for essential nutrients, water, light, and space. Altered competitive conditions in the plant community, resulting from a decrease in the most sensitive species, permitted the enhanced growth of more tolerant species, white fir, incense cedar, sugar pine, and black oak (Miller et al., 1982; U.S. Environmental Protection Agency, 1978, 1986). Although the primary effect was on the more susceptible members of the forest community, changes in the function of other ecosystem components directly or indirectly affected the processes of carbon (energy) flow, mineral-nutrient cycling, and water movement, leading to changes in community patterns. Changes in available energy influenced biotic interactions associated with predators, pathogens, and symbionts (mycorrhizae).

The forests of the Appalachian Mountains have been episodically exposed to O<sub>3</sub> concentrations capable of vegetational injury for many years. Visible injury to foliage and reduction in growth of sensitive eastern white pine has been associated with peak hourly concentrations ranging from 0.08 to 0.13 ppm. Black cherry, also has been shown to be sensitive to O<sub>3</sub> exposures. Surveys of various regions of the Appalachian Mountains, including the Smoky Mountain and Shenandoah National Parks, indicate that visible injury to a variety of different types of vegetation continues to occur. Neither eastern white pine nor black cherry are canopy trees. Removal of sensitive individuals and the absence of population changes of these species have not resulted in any visible change in the forest ecosystems along the Appalachian Mountains, possibly because, as stated earlier (Section 5.7.4; Figure 5-36), "only a small fraction of the stresses at the molecular, cellular, or leaf level become disturbances at the stand or ecosystem level" (Hinckley et al., 1992). Decline and dieback of trees on Mt. Mitchell and Camel's Hump cannot be related solely to O<sub>3</sub> injury. Ongoing research is attempting to understand better the effects of O<sub>3</sub> exposure on vegetation in these areas and the effect, if any, on the ecosystems to which they belong.

Injury to sensitive trees in the Sierra Nevada also appear to be in the same category as stated above. Injury to individuals has not been propagated to the population

level and has not altered ecosystem functions; therefore, no changes have taken place in the ecosystems in those mountains.

The previous O<sub>3</sub> document (U.S. Environmental Protection Agency, 1986) concluded that "none of the plant species shown to be injured by O<sub>3</sub> plays a dominant role in the Blue Ridge Mountain ecosystem. Therefore, the removal of any of these species would probably not have an impact that the decline and death of ponderosa and Jeffrey pine have had on the San Bernardino Forest ecosystem." This same conclusion applies today.

### **5.9.8 Economic Assessments**

Based on economic assessments and scientific data available at the time, the previous criteria document (U.S. Environmental Protection Agency, 1986) concluded that O<sub>3</sub> at ambient levels was imposing economic costs on society. The review of more recent (post-1986) literature on agriculture corroborates that earlier conclusion. Specifically, the recent literature, using the full set of NCLAN data and addressing some deficiencies in the pre-1986 assessments, confirms the finding of economic losses from ambient O<sub>3</sub> concentrations.

The exact level of these economic effects is a function of cropping patterns, O<sub>3</sub> concentrations (both ambient and episodic), and the spatial and temporal characteristics of projected or observed O<sub>3</sub> levels. The current economic assessments represent improvements in the scientific understanding of O<sub>3</sub> effects on agriculture. However, the assessments of economic effects initially incident on the agricultural sector remain incomplete.

Only a few assessments consider the economic effects of O<sub>3</sub> on forest trees and on urban trees, shrubs, and ornamentals. These studies assess the economic effects of hypothetical changes resulting from O<sub>3</sub> or other stressors on forest productivity and aesthetics and are best viewed as measures of the potential effect of O<sub>3</sub> on these receptors. Improvements linking O<sub>3</sub> effects data to productivity and aesthetic effects will improve the utility of such economic analyses.

The effects of O<sub>3</sub> on ecosystems have not been addressed in the published literature. There is, however, an emerging interest in applying economic concepts and methods to the management of ecosystems. Ecological research also is addressing the challenging conceptual and practical issues in understanding and managing ecosystem functions. Economic research continues to develop, refine, and apply techniques for valuing market and nonmarket products and services that will be of help in estimating the economic effects of O<sub>3</sub> on ecosystems. Increased dialogue between the disciplines is needed before empirical analyses of the economic consequences of ecosystem management are feasible.

In summary, the state of science concerning O<sub>3</sub> economic effects on agricultural crops is sufficient to conclude that O<sub>3</sub> imposes costs on society.

## **5.10 Effects of Ozone on Materials**

### **5.10.1 Introduction**

Photochemical oxidants are capable of reacting with a number of man-made and natural materials. Nearly all materials-damage research on photochemical oxidants has focused on economically important or abundant materials that are susceptible to oxidant damage. These include elastomers (natural rubber and certain synthetic polymers), textile fibers and dyes, and, to a lesser extent, paints. Recent research has been conducted on culturally important materials, such as artists' paints and pigments. It has been shown that oxidants harden and embrittle elastomers, causing cracking and loss in physical integrity. Oxidant exposure weakens certain textile fibers (i.e., reduces the breaking strength and increases the rate of wear) and changes the color of some dyes. The effects of oxidants on paints are not defined well, but they may be similar to some of the effects on elastomers; damage from other gaseous pollutants, such as SO<sub>2</sub>, and from natural damaging agents, such as sunlight, moisture, oxygen, and temperature fluctuations, tend to overshadow the role of ambient O<sub>3</sub> in causing paint damage.

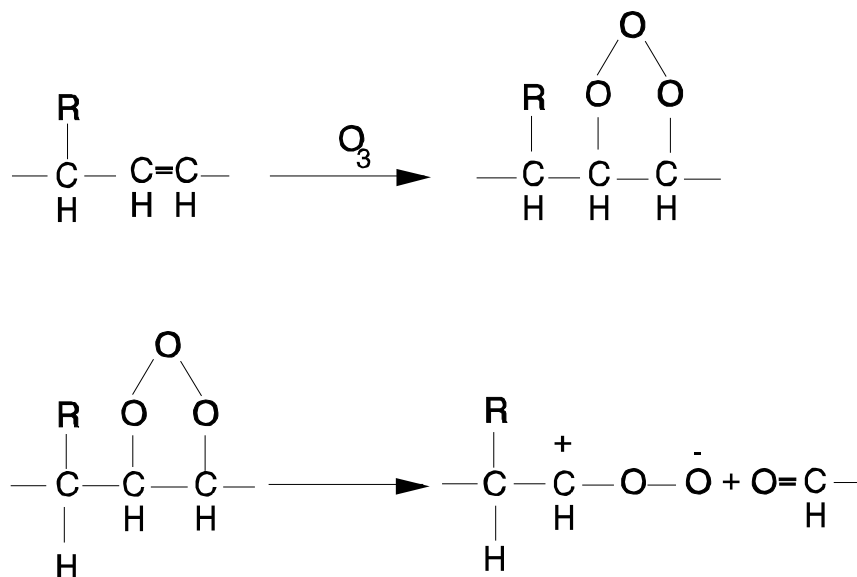
The literature selected for review in this section includes research previously reported in the 1978 and 1986 criteria documents (U.S. Environmental Protection Agency, 1978, 1986) and a limited number of other references published before and after 1986. Because little recent work has been reported on the effects of ozone on materials, reference to older studies is necessary for completeness. This assessment of the effects on materials includes a review of the mechanisms of damage and protection; it also presents dose-response information from laboratory and field studies and evaluates previously reported economic assessments.

### **5.10.2 Mechanisms of Ozone Attack and Antiozonant Protection**

#### **5.10.2.1 Elastomers**

Most elastomeric materials found in the marketplace are composed of unsaturated, long-chain organic molecules (i.e., the molecules contain carbon-carbon double bonds). Natural rubber and synthetic polymers and copolymers of butadiene, isoprene, and styrene account for the bulk of elastomer production for products such as automobile tires (Mueller and Stickney, 1970). These types of compounds are particularly susceptible to O<sub>3</sub> attack. In contrast, synthetic elastomers with saturated chemical structures, such as butyl rubber, polymers of silicones, ethylene, propylene, hypalon, and polyurethanes, have an inherent resistance to O<sub>3</sub> damage, but higher cost and limiting physical and chemical properties have constrained their use in outdoor environments.

Ozone is thought to attack elastomers by adding a chain of three oxygen atoms directly across the double bond, forming a five-membered ring structure (Mueller and Stickney, 1970). This structure quickly rearranges (via Criegee ozonolysis) to form a zwitterion and an aldehyde (see Figure 5-37). The aldehyde-zwitterion pair can be formed on either side of the point of chain scission. Subsequent reactions of the zwitterion lead to a permanently oxidized elastomer. Ozone damage in the form of cracking is a surface phenomenon. It is greatly accelerated by mechanical stress, which produces fresh surface area at crack boundaries. At very high concentrations and high mechanical stress, O<sub>3</sub> damage can result in a large number of surface microcracks that produce a frosted appearance and mechanical weakening (Crabtree and Malm, 1956). At pollutant



**Figure 5-37. Postulated mechanism for damage to elastomers by ozone.**

Source: Mueller and Stickney (1970).

concentrations normally encountered outdoors (and in many indoor environments), the elastomer hardens or becomes brittle and cracked, which results in loss of physical integrity.

According to Fisher (1957), work at the Rock Island Arsenal by R. F. Shaw, Z. T. Ossefa, and W. J. Tonkey in 1954 led to the development of effective antioxidant additives to protect elastomers from  $\text{O}_3$  degradation. Subsequently, antiozonants generally were incorporated into elastomeric formulations during mixing, and their protection was effective, even when elastomers were stretched or flexed (Fisher, 1957; Mueller and Stickney, 1970).

Several theories (Andries and Diem, 1974) have been advanced to explain the mechanism of antiozonant protection. The two best supported theories are (1) the scavenger theory and (2) the protective film theory. The scavenger theory suggests that the antiozonant diffuses to the surface, where it reacts with the  $\text{O}_3$  at a faster rate than with the carbon-carbon double bonds of the rubber, thereby protecting the rubber sacrificially. The protective film theory also includes diffusion to the surface, but assumes that the resulting layer is less reactive with  $\text{O}_3$  than is the rubber and, thus, constitutes a protective layer.

The work of Razumovskii and Batashova (1970) on the mechanism of protective action by the antiozonant *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (PIPP) is most consistent with the scavenger mechanism. These investigators showed that  $\text{O}_3$  reacts preferentially with PIPP at a ratio of three  $\text{O}_3$  molecules to one PIPP molecule.

Andries et al. (1979), using carbon-black-loaded natural rubber compounds, with and without antiozonants, attempted to distinguish among possible mechanisms with attenuated total reflectance spectroscopy and scanning electron microscopy. Their

experiments indicated that a combination of the scavenger and protective film mechanisms best explains antiozonant protection. Examination of the surface of the rubber samples with antiozonant showed that only ozonized antioxidant, not ozonized rubber, was present. This layer of ozonized antioxidant functioned as a relatively nonreactive film over the surface, preventing the O<sub>3</sub> from reaching and reacting with the rubber below.

Lattimer et al. (1984) conducted a series of experiments on cross-linked rubber (*cis*-polyisoprene and *cis*-polybutadiene) containing *N,N'*-di-(1-methylheptyl)-*p*-phenylenediamine antiozonant. They concluded that, although a number of O<sub>3</sub>-rubber reactions and mechanisms are possible, these reactions do not become significant until the antiozonant is nearly completely consumed (i.e., the antiozonant preferentially reacts with the O<sub>3</sub>). They concluded that the "scavenger-protective film mechanism" is primarily responsible for antiozonant protection.

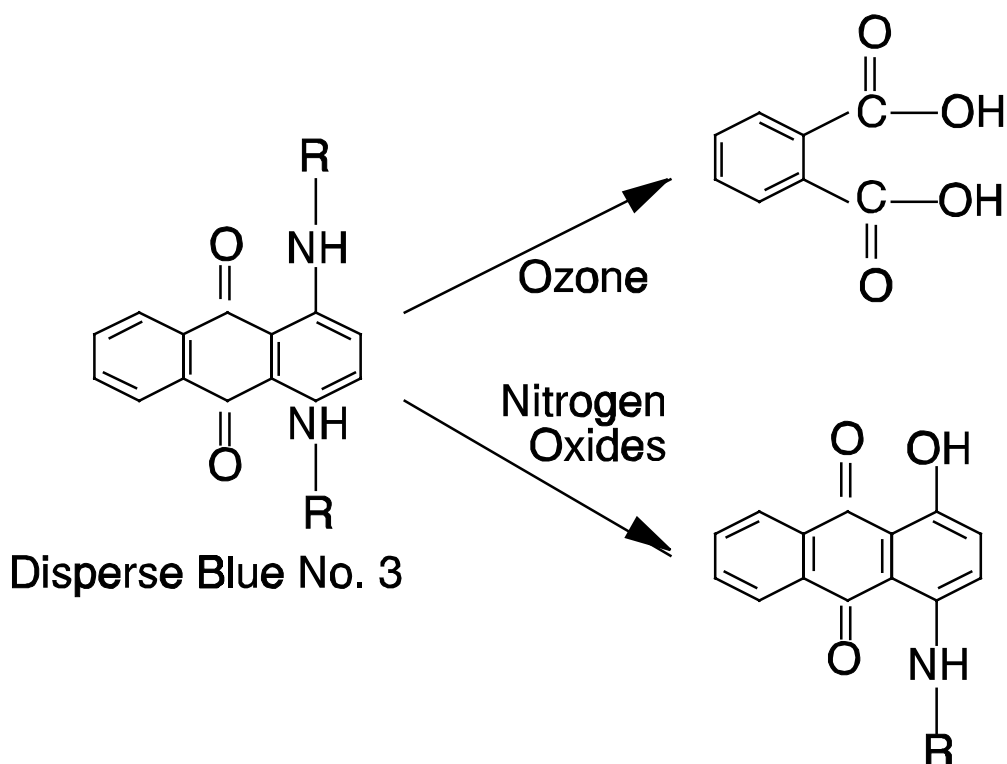
In addition to reactive antiozonants, paraffinic and microcrystalline waxes are used to protect the elastomers in rubber products such as tires. The wax migrates to the surface of the rubber and forms a barrier against O<sub>3</sub> attack. Dimauro et al. (1979) studied the ability of 18 waxes to protect rubber against degradation from O<sub>3</sub>. Dimauro found that no wax by itself provided an optimal level of protection; blending with a reactive antiozonant was required. The paraffinic waxes protected best at lower exposure temperatures, and the microcrystalline waxes were more effective at higher temperatures. Wax blends, which combine the best effects of each type of wax, offered the best protection over a wide range of temperature (Lake and Mente, 1992). It was found, however, that wax alone can be detrimental to dynamic O<sub>3</sub> resistance. Wax can induce localized stresses in the rubber that can lead to premature rubber failure under dynamic testing conditions.

#### 5.10.2.2 Textile Fibers and Dyes

Cellulose-based, acrylic, and nylon fibers are affected by O<sub>3</sub> (Zeronian et al., 1971); however, it is difficult to distinguish O<sub>3</sub>-induced damage from oxidation by molecular oxygen. Reduction in breaking strength and an increased rate of wear are the types of damage most commonly observed. As stated by Bogaty et al. (1952), however, for most uses of textile fibers, the action of O<sub>3</sub> is less important in affecting product lifetime than are physical abrasion, biological degradation, soiling, fashion, and other factors. Furthermore, most textiles are used and spend most of their life indoors, where O<sub>3</sub> concentrations are usually less than outdoor O<sub>3</sub> concentrations (Yocom et al., 1986). Accordingly, the economic significance of O<sub>3</sub> damage to textile fibers is relatively low, and the differences in the mechanisms of attack are not important.

Many textile dyes react with O<sub>3</sub>. Figure 5-38 illustrates the reaction of Disperse Blue No. 3 with O<sub>3</sub> and with NO<sub>x</sub> (Haylock and Rush, 1976). Ozone attacked the quinoid portion of the molecule, completely rupturing the ring system chromophore and oxidizing the dye to phthalic acid, which is colorless. Matsui et al. (1988) investigated the reactions of O<sub>3</sub> with aromatic azo compounds. Ozone was found to attack both the aromatic rings and the more electron-rich nitrogen atoms. Both the direct attack on the azo dye structure and the production of daughter products alter the original dye color.

The reactions between various dyestuffs and O<sub>3</sub> are influenced by the chemical nature of the fiber to which the dye is applied and the manner in which the dye is applied. Additional factors include the presence of protective agents; effects of temperature, air moisture, and other pollutants; and even the degree of strain of the base fiber caused by folding or creasing. In a study of O<sub>3</sub> fading of anthraquinone dyes on nylon, Haylock and



**Figure 5-38.** *Reaction of anthraquinone dyes with ozone and with nitrogen oxides.*

Source: Haylock and Rush (1976).

Rush (1976, 1978) found that fiber properties such as cross-section shape, draw ratio, and the degree of steam heat setting had significant effects on the rate and severity of  $O_3$  damage, even for chemically identical systems. Moore et al. (1984) found that the rate of  $O_3$  fading of acid and disperse dyes on polyamide fibers appeared to be a function of the rate of dye migration to the surface of the fibers. Thus, using dyes that diffuse slowly (high-molecular-weight dyes) improved resistance to  $O_3$  fading. Given this complexity and sensitivity for both dye and fiber type, it is not possible to relate a specific mechanism of damage to a broad class of damage situations.

#### 5.10.2.3 Paint

The mechanisms of architectural paint and coil coating damage caused by  $O_3$  have not been well defined. Damage is probably related to oxidation of the organic binders that hold the pigment and form the protective seal over the surface. Damage is likely to be similar to that of elastomers; that is, embrittlement and cracking as the result of chain scission and cross-linking. The data available on  $O_3$  damage to architectural paints, however, come primarily from studies of surface erosion caused by gaseous pollutants, and the suspected  $O_3$  damage patterns (embrittlement and cracking) are not quantified. Because the polymeric structure of dried paint film is significantly different from that of an elastomer under elongation stress, direct comparisons should be made with great caution.



In a series of experiments (Shaver et al., 1983; Grosjean et al., 1987, 1988a,b, 1989) the direct attack of O<sub>3</sub> on artists' pigments and paints was investigated. Ozone was found to react with alizarin pigments, indigos, curcumin, and triphenylmethane colorants. The exact mechanism and site of the attack (e.g., carbon-carbon unsaturated bonds, aromatic rings, or carbon-nitrogen bonds) and subsequent reactions with the daughter products depended on the initial structure of the pigment. Often the products of these reactions were colorless or of a noticeably different color than the original pigments, resulting in fading or color changes.

### **5.10.3 Exposure-Response Data**

Laboratory exposure-response studies are criticized for their reliance on artificial environments that do not contain all the critical variables encountered under ambient conditions. Scientists realize the limitations of laboratory tests; no model could simulate conditions identical to an ambient environment. Nevertheless, many laboratory tests have represented the outdoor environment to some extent, and the findings from these tests have been used in conjunction with field tests to estimate the nature and amount of damage to materials. Controlled field tests have the advantage of being carried out under real exposure conditions, but, because of the highly variable nature of real exposure conditions, data interpretation is difficult.

#### **5.10.3.1 Elastomer Cracking**

Table 5-40 presents an overview of the available laboratory and field studies of the effects of O<sub>3</sub> on elastomers. Hofmann and Miller (1969) demonstrated correlations between laboratory tests and the actual service use of passenger vehicle tires in the Los Angeles area. Basically, three laboratory test methods were used: (1) indoor and outdoor belt flex, (2) indoor and outdoor wheel, and (3) stress relaxation. The investigators found that the behavior of rubber exposed to O<sub>3</sub> under laboratory conditions correlated well with the service behavior of tires in localities where atmospheric O<sub>3</sub> concentrations were high.

Bradley and Haagen-Smit (1951) evaluated a natural rubber (NR) formulation for susceptibility to O<sub>3</sub> cracking. Strips were strained approximately 100% by bending and then exposed in a small chamber to 20,000 ppm of O<sub>3</sub>; these specimens cracked almost instantaneously and broke completely within 1 s. When these NR formulations were exposed to lower concentrations of O<sub>3</sub> (approximately 0.02 to 0.46 ppm), time periods of about 5 min to over an hour were required for cracks to develop.

Meyer and Sommer (1957) exposed thin polybutadiene specimens to constant load, ambient room air, and O<sub>3</sub>. Specimens exposed in the summer to average O<sub>3</sub> concentrations of about 0.048 ppm broke after 150 to 250 h. In the fall, at average O<sub>3</sub> concentrations of 0.042 ppm, specimens failed after exposures of 400 to 500 h. In the winter, at average O<sub>3</sub> concentrations of 0.024 ppm, failures occurred between 500 and 700 h. These data show the strong dependence of breakage on O<sub>3</sub> dose over the average time of exposure at which failure occurred (average C × T).

Edwards and Storey (1959) presented data demonstrating the O<sub>3</sub> resistance of two styrene-butadiene rubber (SBR) compounds (Polysar S and Polysar Krylene). Both compounds were exposed with and without different levels of antiozonant protection to 0.25 ± 0.05 ppm of O<sub>3</sub> at 120 °F (49 °C) under 100% strain (twice the original sample length). Without antiozonants, a linear relationship was found between O<sub>3</sub> dose (ppm·h) and

**Table 5-40. Laboratory and Field Studies on Effects of Ozone on Elastomers<sup>a</sup>**

Conditions	Material/ Product	Pollutant	Concentration, (ppm)	Exposure	Environmental Variables	Dose, (ppm-h)	Effects	Comment	Reference
Laboratory/ field	Automotive tires	Ozone	0.25 to 0.5	NA	Tires under stress	—	Cracking of white side wall.	Purpose was to correlate lab and field tests. Exposure time, detailed pollutant measurements, and statistical analyses were not reported.	Hofmann and Miller (1969)
		Ambient air	0.04 (annual average)	>1 year	Los Angeles environment; actual service use	>350	Positive correlation between laboratory and ambient air tests.		
Laboratory	Vulcanized rubber strips	Ozone	0.02 to 0.46, 20,000	3 to 65 min	Physical stress	~0.02 to 0.03	Surface cracking.	Test was designed to establish dose/response curves on O <sub>3</sub> -sensitive rubber for use as an analytical method.	Bradley and Haagen-Smit (1951)
Field	Rubber tires and various polymers	Ambient air	0.023 to 0.048	150 to 700 h	Physical stress and ambient environment	9 to 20	Time of cracking.	Cracking occurred over a broad range of values and was related to stress.	Meyer and Sommer (1957)
Laboratory	SBR: Plysar S and Plysar Krylene, with and without antiozonants	Ozone	0.25	19 to 51 h	120 °F, 100% strain	4.75 to 12.75	Percent antiozonant was related to cracking depth rate.	Demonstrated dose/response linear relationship for O <sub>3</sub> on unprotected rubber.	Edwards and Storey (1959)
Laboratory	White sidewall tire specimens	Ozone	0.05 to 0.5	250 to 1,000 h	10 and 20% strain	20 to 500	Mean cracking rates were determined for different stress and O <sub>3</sub> levels.	Detailed data not available to verify author's statement that 2 to 5 years of ambient conditions were required for O <sub>3</sub> cracks to penetrate cord depth.	Haynie et al. (1976)
Laboratory	Polyisoprene	Ozone	0 to 1.8	2 h	22 °C	Up to 3.6	Cracking and stress relaxation.	Rate of attack rapid and proportional to O <sub>3</sub> concentration.	Razumovskii et al. (1988)

**Table 5-40 (cont'd). Laboratory and Field Studies on Effects of Ozone on Elastomers<sup>a</sup>**

Conditions	Material/ Product	Pollutant	Concentration (ppm)	Exposure	Environmental Variables	Dose (ppm-h)	Effects	Comment	Reference
Laboratory	Ten different NR, SBR, and CR formulations with and without protection	Ozone	0.5	Up to 300 h	30 °C	Up to 50	Time to 10 to 20% relaxation.	Both formulation and protection affected relaxation.	Ganslandt and Svensson (1980)
Laboratory	Natural rubber, epoxidised rubber, and copolymers	Ozone	0.05 to 1,000	To 16 h	-20 to 70 °C, 10 to 100% strain	0 to 240	Time to first cracking.	Temperature dependence of antiozonant protection.	Lake and Mente (1992)
Laboratory	Several NR/SBR blends, with and without protection	Ozone	0.05 to 0.15	~3 to 16 h	Sunlight, humidity	~0.15 to 2.4	Interply adhesion affected at 0.05 ppm and above.	Both waxes and antiozonants needed for protection against sunlight plus O <sub>3</sub> .	Davies (1979)
Laboratory	Tire cords (66 nylon; Dacron polyester; Kevlar aramid)	Ozone	0 to 1.5	0 to 48 h	UV light; heat (100 °C); RH (20 to 90%); NO <sub>2</sub>	Up to 72	RFL adhesion loss occurred primarily during 6-h exposure to high RH and 0.2 ppm O <sub>3</sub> .	Synergism between O <sub>3</sub> and RH; RFL deterioration occurred at surface.	Wenghoefer (1974)

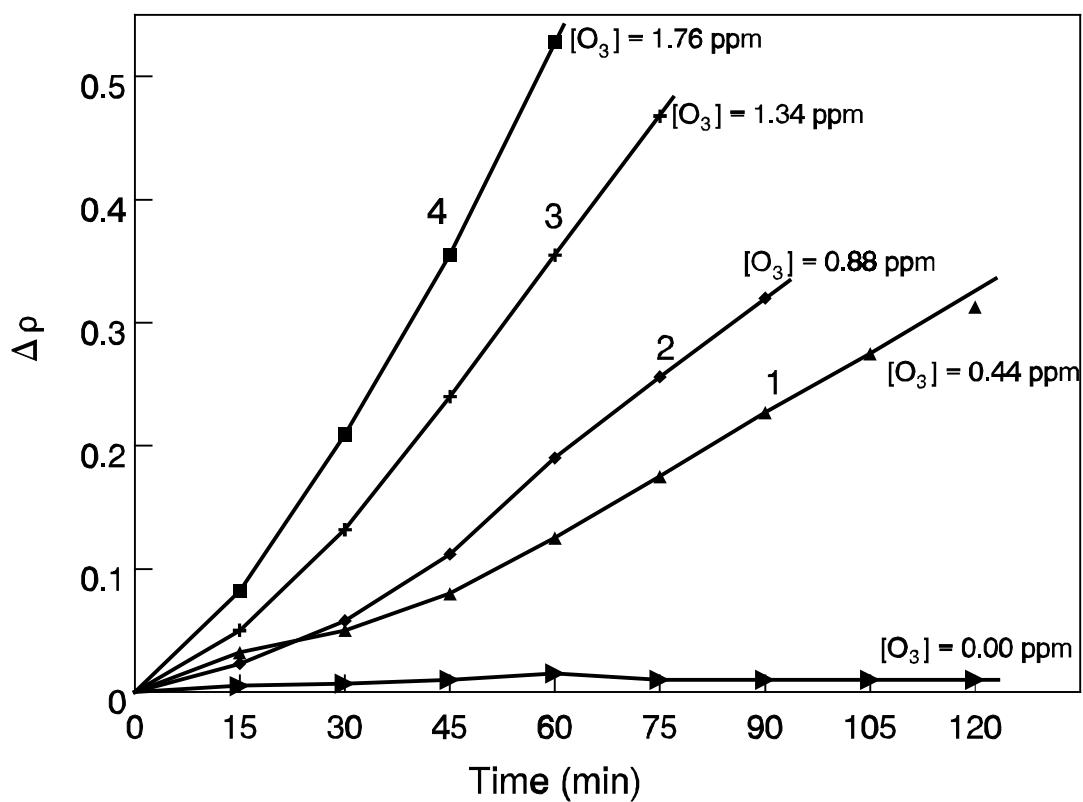
<sup>a</sup>See Appendix A for abbreviations and acronyms.

cracking depth. Increasing the amount of antiozonants significantly reduced the rate of cracking for both rubber compounds in a dose-related manner.

Haynie et al. (1976) conducted a chamber study to evaluate the effects of various pollutants, including  $O_3$ , on several materials. In one part of the study, white sidewall specimens from a top-quality, steel-belted radial tire were exposed (strained at 10 and 20%) for 250, 500, and 1,000 h to  $O_3$  concentrations of 0.082 ppm ( $160 \mu\text{g}/\text{m}^3$ ) and 0.5 ppm ( $1,000 \mu\text{g}/\text{m}^3$ ). The  $O_3$  level was found to be statistically significant in the rate of cracking of this rubber; however, cracking rates were not directly proportional to  $O_3$  concentrations for these two levels. Using the mean cracking rate calculated after long-term (1,000-h) exposure to conditions representative of the primary air quality standard for  $O_3$  and the annual average standard for  $\text{NO}_2$ , Haynie et al. (1976) concluded that it would take a minimum of 2.5 years for a crack to penetrate to the cord depth. For this particular premium tire, therefore, sidewall failure from  $O_3$  damage does not appear to be the cause of reduced tire life. Tread wear, rather than sidewall failure, probably determines the life of a typical rubber tire.

Razumovskii et al. (1988) studied the decrease in stress (stress relaxation) of polyisoprene vulcanizates in an exposure chamber at  $22^\circ\text{C}$  at five  $O_3$  concentrations ranging from  $O_3$ -free to  $3,450 \mu\text{g}/\text{m}^3$  (1.76 ppm). Stress relaxation resulting from the growth of surface cracks caused irreversible changes in the dimension of the elastomer and decreased tensile strength. Figure 5-39 presents the rate of change of stress as a function of time for various  $O_3$  concentrations. The rate of stress reduction was proportional to  $O_3$  concentration, with virtually no change for the  $O_3$ -free samples and progressively more rapid relaxation as  $O_3$  levels increased. Razumovskii et al. (1988) concluded that  $O_3$  absorption, attack of the C=C bonds, cracking, and the resulting stress relaxation were fast processes for unprotected elastomers.

Ganslandt and Svensson (1980) tested 10 different mixtures of three rubber compounds, NR, SBR, and CR, with the isoelastic force method. The  $O_3$  protection afforded each rubber formulation is summarized in Table 5-41. The samples at 50% elongation were exposed to  $O_3$  concentrations of 0.5 ppm at  $30^\circ\text{C}$ . The time to 10 and 20% relaxation of the isoelastic force in the rubber test samples was used to gauge the  $O_3$  resistance of the formulation. Compounds GL 2073 B, SS 202, and SS 200 C showed greatest resistance to the effects of  $O_3$ , and those formulations that were unprotected (GL 2073 D, SS 200 B, SS 202 A, SS 203) and the formulations protected only by paraffin wax (GL 2073 G) demonstrated the least resistance to  $O_3$  attack. The testing showed great variety in the kinds of visible cracking effects as a result of the exposure. The compounds with no protection often showed a large number of small cracks over the entire surface of the material, but those compounds protected by a combination of wax and antiozonant or by wax alone sometimes showed only a single crack, which grew rapidly. These effects are demonstrated in Figure 5-40. Compounds SS 202 B (Figure 5-40A) and SS 200 C (Figure 5-40B), both protected with wax and antiozonant, showed fairly good resistance when gauged by the 10 and 20% stress relaxation tests but failed after approximately 50 and 58 h of exposure, respectively. On the other hand, compounds SS 203 and SS 200 B, both unprotected, exhibited small surface cracking and outlasted some of the protected compounds. Moreover, protection with wax and antiozonant may afford long-term protection, but when one crack appears, it can grow rapidly and cut off the test piece, as shown in Figure 5-40b.



**Figure 5-39.** *Relative decrease in stress ( $\Delta\rho$ ) with time as a function of ozone concentration for polyisoprene vulcanizate.*

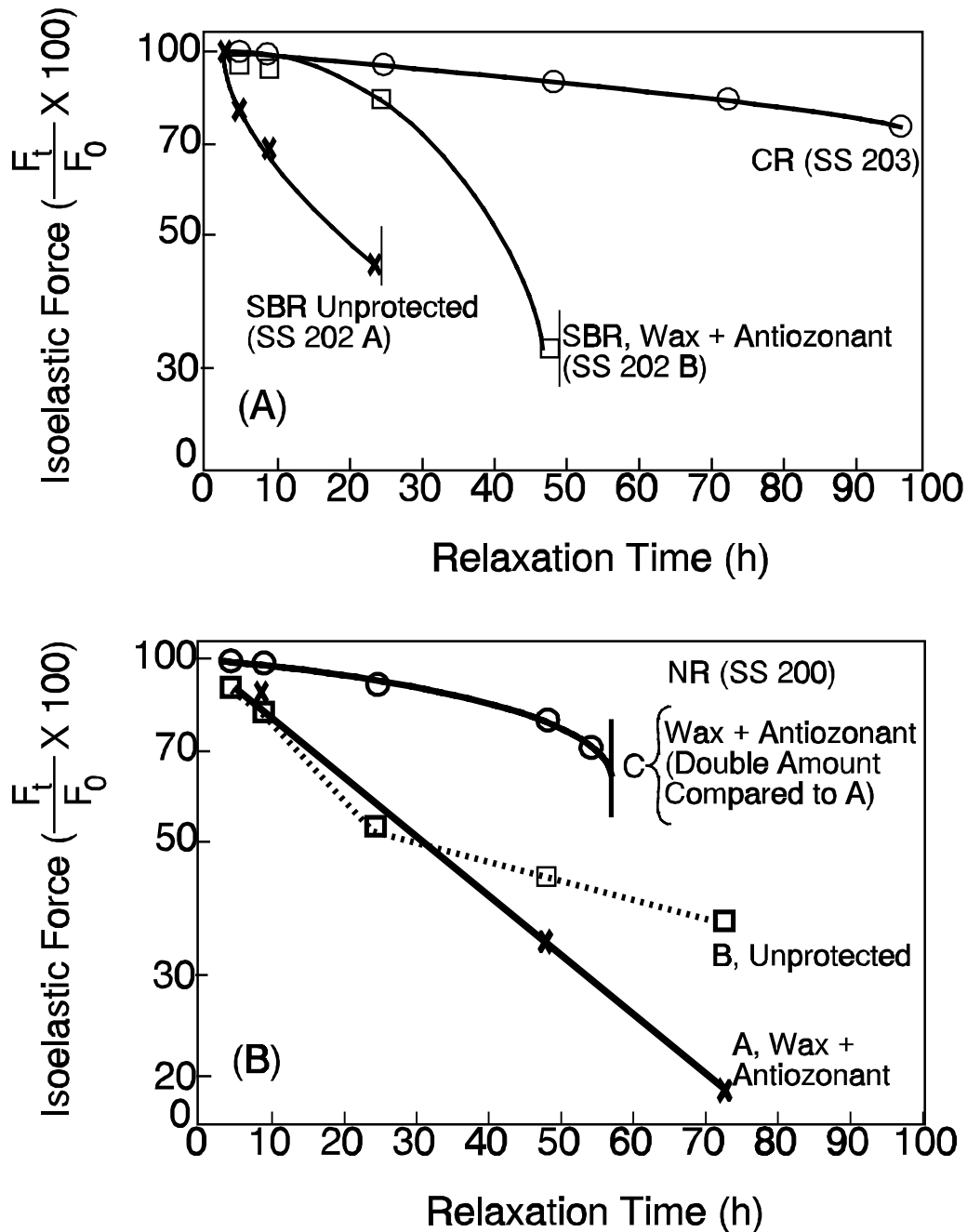
Source: Razumovskii et al. (1988).

**Table 5-41. Protection of Tested Rubber Materials<sup>a</sup>**

Rubber Formulation	Mixtures	Unprotected	Protected	
			Wax	Antiozonant
GL 2073 (NR)	B, C		X	X
	D	X		
	G		X	
SS 200 (NR)	A, C		X	X
	B	X		
SS 202 (SBR)	A	X		
	B		X	X
SS 203 (CR)		X		

<sup>a</sup>See Appendix A for abbreviations and acronyms.

Source: Ganslandt and Svensson (1980).



**Figure 5-40.** Relaxation of rubber compounds in ozone ( $O_3$ ) is affected by the combination of rubber formulation and type of  $O_3$  protection. Compounds SS 202B (A) and SS 200C (B) were tested at an  $O_3$  concentration of 0.5 ppm, a temperature of 30 °C, and elongation of 50%. The vertical lines at the end of curves mean total failure, and vertical axes represents relaxation, where  $F_0$  is the initial force, and  $F_t$  is the force after time  $t$ .

Source: Ganslandt and Svensson (1980).

Lake and Mente (1992) exposed natural rubber, epoxidised rubber, and two acrylonitrile-butadiene copolymers with chemical antioxidants, waxes, or a combination of antioxidants and waxes to a variety of O<sub>3</sub> concentrations and temperatures in environmental testing enclosures. Ozone concentrations ranged from 0.05 ppm to 1,000 ppm with temperatures from –20 to 70 °C. Samples were kept under constant strain between 10 and 100%. Antiozonant chemicals in the concentration range from 2 to 20 p.h.r. (parts per hundred of rubber by weight) were tested, and wax/antiozonant combinations at 6 p.h.r. wax and 3 p.h.r. antiozonant also were tested. Lake and Mente found that O<sub>3</sub> protection was most effective at higher temperatures, when diffusion of the antiozonant and wax to the surface of the elastomers was most rapid. This relationship is fortunate because ambient O<sub>3</sub> concentrations correlate well with higher temperatures. Antiozonants became generally less effective as temperatures dropped; however, dialkyl paraphenylenediamine provided reasonable protection for natural rubber to –17 °C.

Davies (1979) reported on the effects of O<sub>3</sub> and other environmental factors on interply adhesion of natural and synthetic rubber compounds. Excellent adhesion of plies is essential to the proper manufacturing of tires. The rubber strips must make interlocking contact at the joint boundary, or the strength of the tire will be inadequate. Ozone attack on synthetic poly isoprene and polybutadiene produces a surface layer of ozonides. With NR, the film consists of ozonides and carbonyl groups (Andries and Diem, 1974; Andries et al., 1979). The results of the Davies (1979) tests indicated that, before curing, the adhesion of SBR compounds is unaffected by exposure to O<sub>3</sub> concentrations of 0.15 ppm, but the adhesion of the NR/SBR blend decreases by approximately 30%. Large reductions (on the order of 70%) in adhesion between plies were noted with the NR compounds; even exposure for a few hours at 0.05 ppm reduced adhesion considerably. The adhesion tests on cured NR, SBR, and isoprene rubber (IR) compounds after exposure to various levels of O<sub>3</sub> and humidity are summarized in Table 5-42. The adhesion of the SBR compound is superior to that of the other two compounds, which were affected greatly by increased RH.

**Table 5-42. Effect of Ozone and Humidity on Interply Adhesion<sup>a,b</sup>**

Compound	Initial Adhesion	Final Adhesion <sup>c</sup>		
		0.15 ppm O <sub>3</sub> (294 µg/m <sup>3</sup> ), 30% RH	0.25 ppm O <sub>3</sub> (490 µg/m <sup>3</sup> ), 30% RH	0.15 ppm O <sub>3</sub> (294 µg/m <sup>3</sup> ), 60% RH
NR	5	2 to 3	1	1
IR	5	4 to 5	2 to 1	1
SBR	5	4 to 5	3 to 4	3 to 4

<sup>a</sup>Adhesion is rated from 1 (bad) to 5 (excellent), based on visual scale standardized by the authors.

<sup>b</sup>See Appendix A for abbreviations and acronyms.

<sup>c</sup>All exposures were 16 h in duration.

Source: Adapted from Davies (1979).

Wenghoefer (1974) studied the effects of O<sub>3</sub> on adhesion of tire cords dipped in resorcinal-formaldehyde latex (RFL). Many fibers and dip formulations were studied to determine their sensitivity to O<sub>3</sub>, humidity, NO<sub>2</sub>, UV light, and heat. Wenghoefer exposed these materials at a constant temperature of 100 °F (37.8 °C) to O<sub>3</sub> levels that varied between 0 and 1.5 ppm (0 and 2,940 µg/m<sup>3</sup>) and to RH levels ranging from 20 to 90%. Adhesion deteriorated from changes in surface properties of the RFL-dipped cords as a result of exposure to O<sub>3</sub>, humidity, UV light, and heat. The adhesion losses from O<sub>3</sub> and the combined effects of O<sub>3</sub> and humidity were most notable in the first 6 h of exposure. The detrimental effects of heat, NO<sub>2</sub>, and the synergistic interaction of NO<sub>2</sub> and humidity were much less pronounced.

#### **5.10.3.2 Dye Fading**

Color fading of certain textile dyes has been attributed to the effects of ambient O<sub>3</sub>. Although NO<sub>2</sub> was originally identified as the pollutant most important to color fading, the effects of O<sub>3</sub> were noted by Salvin and Walker (1955). The primary products affected were permanent-press garments (polyester and cotton) and nylon carpeting. Table 5-43 summarizes studies on the effects of O<sub>3</sub> on dyes. By using a combination of laboratory chamber studies and outdoor exposures, Salvin and Walker (1955) demonstrated that O<sub>3</sub> was responsible for dye fading observed on drapery fabrics. Blue anthraquinone dyes and certain red anthraquinone dyes were markedly bleached after exposure to just 0.1 ppm of O<sub>3</sub>. Azo red and yellow dyestuffs and diphenylamine yellow dyes were shown to be resistant to fading at these concentrations, also confirming the results of the field study. The use of known antiozonants, such as diphenyl-ethylenediamine and diallyl phthalate, in combination with disperse blue dyes, was effective against O<sub>3</sub> fading, thus providing additional evidence of the effects of O<sub>3</sub> on dyed fabrics.

Ajax et al. (1967) summarized the results of a study of 69 dye-fabric combinations that were exposed outdoors in light-free cabinets at 11 sites. These sites were Sarasota, FL; Phoenix, AZ; Cincinnati, OH; and four urban-rural combinations: (1) Chicago and Argonne, IL; (2) Washington, DC, and Poolesville, MD; (3) Los Angeles and Santa Paula, CA; and (4) Tacoma and Purdy, WA. Among those fabrics exhibiting a high degree of fading at both urban and rural sites in the first 6 mo, fading was much greater at the urban sites than at the rural sites. The samples exposed in Phoenix, Sarasota, and Purdy showed the lowest amount of fading, which indicated that humidity and temperature are not, by themselves, the primary factors in fading. The highest fading rates occurred in samples exposed in Los Angeles, Chicago, and Washington, DC. In addition, there was a marked seasonal variation in the test results, with greater fading during the spring and summer seasons. Generally, the results correspond with seasonal peaks in O<sub>3</sub> concentrations.

Ajax et al. (1967) also exposed the fabrics to irradiated and nonirradiated auto exhaust, with and without SO<sub>2</sub>, for 9 h/day for 6 consecutive days. From the results of this chamber study, the investigators noted that "photochemically produced by-products of automobile exhaust are a prime cause of fading compared to fading caused by nonirradiated auto exhaust or by clean air with sulfur dioxide added." In the presence of SO<sub>2</sub>, however, a more than additive effect was seen in the dye-fading tests for both chamber and field studies. Although the conclusions of Ajax and co-workers concerning O<sub>3</sub> itself are easily substantiated in the research literature, the O<sub>3</sub> levels measured in their test chamber are questionable. The daily 9-h average O<sub>3</sub> concentrations (measured by neutral-potassium



**Table 5-43. Laboratory and Field Studies of the Effects of Ozone on Dye Fading<sup>a</sup>**

Dye	Fabric	Concentration (ppm)	Exposure	Environmental Variables	Effects	Comments	Reference
Blue and red	Drapery	0.1	—	—	Both dyes were markedly bleached. No fading occurred when antioxidants were added.	Insufficient data for dose-response determinations. This study followed a field study showing that oxidants other than NO <sub>x</sub> caused fading.	Salvin and Walker (1955)
Disperse Direct, fiber reactive vat, sulfur, azo Disperse Disperse, basic Disperse, acid Direct Premetolized, acid	Cellulose acetate Cotton  Polyester Orlon Nylon taffeta Viscose Wool	Laboratory 0.02 to 0.55; field exposure concentrations not reported	54 h 3 mo	Light-proof cabinets, 11 rural and urban sites	Photochemical agents caused more fading than nonradiated samples. Urban locations produced more fading, and temperature and humidity are not the primary causes of fading.	Both laboratory and field measurements. Reported laboratory O <sub>3</sub> concentrations questionable. SO <sub>2</sub> was also present in laboratory exposures.	Ajax et al. (1967)
Direct red 1 Reactive red 2 Sulfur green 2 Azoic <sup>b</sup> red Direct red 1 Acid red 151 Acid yellow 65 Acid violet 1 Basic red 14 Basic yellow 11 Acid orange 45 Disperse blue 3 Disperse blue 3 Disperse blue 3 Disperse blue 27 Disperse blue 27 AATCC O <sub>3</sub> ribbon	Cotton Cotton Cotton Cotton Rayon Wool Wool Wool Acrylic Acrylic Nylon Nylon Cellulose Acetate Acetate Polyester Acetate	0.05 0.5	12 weeks	Temperature = 55 °F, 90 °F RH = 50%, 90%	Induced fading at both levels, but at a nonlinear rate. Both temperature and humidity increased fading rate, and RH was more important. Eight of the tested fabric-dye combinations faded measurably in response to O <sub>3</sub> . Only trace amounts of fading occurred in the remaining fabrics.	Insufficient data to show detailed dose-response relationships. Although samples were measured throughout the exposure, only the 12-week data were presented.	Beloin (1973)

**Table 5-43 (cont'd). Laboratory and Field Studies of the Effects of Ozone on Dye Fading<sup>a</sup>**

Dye	Fabric	Concentration (ppm)	Exposure	Environmental Variables	Effects	Comments	Reference
Olive I and II Disperse blue 3 and 7	Nylon fibers Nylon fibers	0.2 0.9	1 to >6 h	RH = 70 to 90% Temperature = 40 °C	Visible fading in Olive I after 16 h at 70% RH; same effect after 4 h at 90% RH. Linear increase in fading at 0.9 ppm O <sub>3</sub> .	Both RH and O <sub>3</sub> concentration affected fading and in a nearly linear fashion. Sleeve form was more susceptible than skein form. Haylock and Rush (1976) found that: (1) increased fiber draw ratio reduced fading; (2) increased heat-setting temperature increased fading; and increased fiber surface area increased fading.	Haylock and Rush (1976)
Disperse blue dye in an avocado green mixture	Nylon 6 yarn	0.5	—	RH = 85% Temperature = 40 °C	Fading was closely correlated with fiber surface area (diameter).	Insufficient data for dose-response relationship determinations.	Huevel et al. (1978)
2 Disperse dyes and 2 acid dyes	Nylon 6 and Nylon 66 carpet		3 mo to 3 years	28 homes in different parts of the country	Geographic and seasonal variation in fading.	Field study.	Nipe (1981)
Disperse blue 3	Nylon 6 yarn	0.2	2 to 120 h	RH = 65%, 85%, and 90% Temperature = 40 °C	Nearly linear increase in fading with time. RH had a major influence on fading rate.	This study focused more on mechanisms of O <sub>3</sub> fading than on dose-response relationships.	Kamath et al. (1983)
Disperse, basic Disperse Direct vat, sulfur, fiber reactive Disperse Disperse, acid Direct Acid, mordant	Acrylic Cellulose acetate Cotton Polyester Nylon Viscose rayon Wool	—	2 years in 3-mo blocks	Light-proof cabinets, eight rural and urban sites	Two-thirds of samples exhibited substantial fading, O <sub>3</sub> was significant for eight fabric/dye combinations.	Field study.	Beloin (1972)

**Table 5-43 (cont'd). Laboratory and Field Studies of the Effects of Ozone on Dye Fading<sup>a</sup>**

Dye	Fabric	Concentration (ppm)	Exposure	Environmental Variables	Effects	Comments	Reference
Disperse blue 3 Acid blue 25 Acid blue 40 Acid blue 45 Acid blue 80 Acid blue 127	Nylon 6 yarn Nylon 66 yarn	0.2	0 to 96 h	RH = 85% Temperature = 40 °C	Fading proceeded consistent with diffusion of dye to fiber surface.	Study of mechanisms of O <sub>3</sub> fading, follow-on the Kamath et al. (1983).	Moore et al. (1984)
Royal blue Red Plum	Drapery fabric Rayon acetate Rayon acetate Cotton duck	0.5 and 1.0	250 to 1,000 h	50 and 90% RH, NO <sub>2</sub> and SO <sub>2</sub> .	O <sub>3</sub> was not a statistically significant cause of fading.	Laboratory study.	Haynie et al. (1976)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Coupling component 2, azoic diazo component 32.

iodide and a Mast instrument) were identical for UV-irradiated and nonirradiated exhaust (0.02 ppm); irradiated exhaust plus SO<sub>2</sub> produced 0.55 ppm of O<sub>3</sub>.

Beloin (1972, 1973) investigated the effects of air pollution on various dyed textiles by conducting field and controlled-environment laboratory studies. For the field study, a wide range of dyed fabric was exposed in light-tight cabinets at the same four urban-rural combined sites used in the Ajax studies. The study was carried out over a 2-year period, in eight consecutive 3-mo, seasonal exposure periods. Color-change data and air pollution and weather measurements were analyzed to identify the factors that caused fading. About two-thirds of the fabrics studied showed appreciable fading. Most of these fabrics faded significantly more at urban sites than at rural sites. The small amount of fading evidenced by the samples exposed at extreme temperatures or humidity indicated that these factors, by themselves, have no effect on fading. The samples also showed some seasonal variations in fading. In areas of high oxidant concentration, maximum fading occurred primarily in summer and fall. Fabrics exposed in Chicago, where SO<sub>2</sub> concentrations are higher in the winter, showed greater fading during this season.

The results of the outdoor fading study were used in a multiple regression analysis. The analysis focused on 25 fabric dye samples, 23 of which showed SO<sub>2</sub> to be a significant variable. Ozone was also a significant contributor to the fading of eight dyed fabrics, as was NO<sub>2</sub> to the fading of seven dyed fabrics. The dominance of SO<sub>2</sub> as a factor in fading may have been complicated by soiling.

Beloin's laboratory study was designed to assess the effects of air pollutants, temperature, and RH on the colorfastness of 30 samples selected from those exposed during the field study. Fabric samples were exposed to two concentrations of O<sub>3</sub>: 0.05 and 0.50 ppm. The laboratory studies demonstrated that high O<sub>3</sub> levels produced more significant fading in more fabric samples than did low levels. Visible fading did occur in about one-third of the sensitive fabrics (cellulose acetate, viscose, and cotton muslin with red and blue dyes) exposed to O<sub>3</sub> concentrations of 0.05 ppm. These levels are similar to those frequently found in metropolitan areas. The laboratory study also demonstrated that high RH (90%) is a significant factor in promoting and accelerating O<sub>3</sub>-induced fading.

Haynie et al. (1976) and Upham et al. (1976) reported on the degree of fading of three different drapery fabrics exposed in a laboratory chamber to combinations of high and low O<sub>3</sub> concentrations (0.5 and 0.1 ppm, respectively), high and low RH (90 and 50%, respectively), and high and low concentrations of NO<sub>2</sub> and SO<sub>2</sub>. The three commercially obtained fabrics selected for this study were royal blue and red rayon-acetates and a plum cotton duck. The samples were exposed in the chamber for periods of 250, 500, and 1,000 h; the degree of fading was measured with a color difference meter. The fading of the plum-colored material was related statistically to RH and the NO<sub>2</sub> concentration. For the red and blue fabrics, only RH appeared to be a significant factor. The effects of concentrations of O<sub>3</sub> on the amount of fading of these dyes were not statistically significant, even after exposure for 1,000 h to 0.5 ppm, levels much higher than typical ambient exposures.

Haylock and Rush (1976, 1978) studied the fading of anthraquinone dyes on nylon fibers. In the first test, nylon carpet yarn dyed with Olive I (0.081% Celliton Pink RF, 0.465% Celliton Yellow GR, 0.069% Celliton Blue FFRN) and Olive II (0.082% Latyl Cerise Y, 0.444% Celliton Yellow GA, 0.143% Cellanthrene Blue CR) was exposed to varying levels of temperature, RH, and O<sub>3</sub>. Material dyed with Olive I and exposed at 70% RH, 40 °C (104 °F), and 0.2 ppm of O<sub>3</sub> showed visible fading after 16 h of exposure. At 90% RH, similar fading occurred in less than 4 h. Under the same RH and temperature conditions,

increasing the O<sub>3</sub> concentration from 0.2 to 0.9 ppm resulted in a corresponding increase in fading. Samples in knitted sleeve form demonstrated much greater susceptibility to O<sub>3</sub> attack than samples in skein form.

Using Disperse Blue 3 and 7 dyes exposed to constant conditions of 40 °C (104 °F), 90% RH, and 0.2 ppm of O<sub>3</sub>, Haylock and Rush (1976) investigated the effect on fading of changing the fiber cross section, the fiber-draw ratio, and the method of setting the nylon fibers with steam heat. They found that increasing the surface area of the fibers resulted in an increased fading rate. Increasing the fiber draw ratio reduced dye fading, and increasing the heat-setting temperature decreased resistance to fading in disperse dyes.

The effect of high temperature and high humidity for induction of O<sub>3</sub> fading in nylon was confirmed further by the additional work of Haylock and Rush (1978). Their studies showed a good correlation between accelerated O<sub>3</sub> fading in the laboratory and in outdoor, in-service exposure, during which temperature and humidity extremes were common. Control samples exposed indoors, however, where temperatures and humidities were lower, did not exhibit nearly the same magnitude of fading as the laboratory samples.

Huevel et al. (1978) investigated the importance of the physical nature of Nylon 6 yarns on the O<sub>3</sub> fading behavior of a disperse blue dye. Samples of Nylon 6 yarns dyed avocado green with a dye mixture including Disperse Blue 3 were exposed in a laboratory cabinet to 0.5 ppm of O<sub>3</sub> at 40 °C and an RH of 85%. Huevel et al. found that the microfibril diameter and specific surface area of the fiber were the fiber characteristics most closely related to O<sub>3</sub> fading, thus confirming suspicions expressed earlier by Salvin (1969).

Nipe (1981) summarized the results of a 3-year study to establish the relationship between in-service fading of carpets in a home versus O<sub>3</sub> fading as determined by the American Association of Textile Chemists and Colorists (AATCC) Standard Test Method 129, "Colorfastness to Ozone in the Atmosphere Under High Humidities." (Measurements also were taken to compare the fading caused by NO<sub>x</sub>.) The test carpets were made of Nylon 6 and 66 dyed with two disperse and two acid dye formulas. Test samples from the homes of 28 participants were returned every 3 mo for the 3-year period. The exposure sites selected for this long-term study represented variations in home heating and cooling, utilities, climate, and geographical locations. The carpet samples were placed in areas as close as possible to the kitchen but away from exposure to sunlight or any traffic. No measurements of O<sub>3</sub> concentrations were collected; however, an O<sub>3</sub>-sensitive sample strip was included with each carpet sample. Analysis of the sample strip enabled the researchers to determine the relative O<sub>3</sub> exposure of each carpet sample.

Geographical location appeared to have a significant effect on fading. Test samples from sites in the Southeast and Northeast showed far more O<sub>3</sub> fading than did those in the West and Far West. Test samples in homes with air conditioning exhibited less fading during the summer than those without air conditioning. In all samples, much greater fading was caused by O<sub>3</sub> during July, August, and September than in January, February, and March. Typically, O<sub>3</sub> levels indoors are higher during the summer, when doors and windows are more likely to be open, thus allowing a greater exchange between inside and outside air. The results of the study of in-service interior carpet exposures were compared with the results of AATCC Test 129. In a sample that performs satisfactorily through 1.08 cycles of O<sub>3</sub> exposure in AATCC Test 129, there is a 98% probability against in-service fading over a 1-year period. A sample that performs satisfactorily through only 0.6 cycles of O<sub>3</sub> testing has only a 90% probability of satisfactory performance after 1 year of in-service exposure.

Kamath et al. (1983) studied the effect of atmospheric  $O_3$  dye fading on nylon fibers. Prior studies had postulated that  $O_3$  does not penetrate into the fiber to destroy the dye, but instead attacks the dye at the surface of the fiber. Dye then diffuses outward from the fiber interior because of the concentration gradient set up as the surface dye is destroyed. Using microspectrophotometry to test this postulated mechanism, Kamath et al. (1983) studied the diffusion and destruction of C.I. Disperse Blue Dye 3 on Nylon 6 continuous filament yarn measuring about 45  $\mu m$  in diameter. With this method, the investigators were able to generate a dye distribution profile across the cross section of the fiber and to determine the diffusion coefficient of a dye in the fiber. The fibers were exposed in a controlled environment to  $O_3$  concentrations of 0.2 ppm for 2 to 120 h at a temperature of 40 °C and RH levels of 90, 85, and 65%. The results of these laboratory studies indicated that RH has a significant positive effect on fading, that destruction of the dye begins near the surface of the fiber in the early stages of exposure, and that  $O_3$  penetration into the fiber may be an important mechanism in  $O_3$  fading. The dependence of fading rates on humidity was substantial. Even slight rises in humidity from 85 to 90% caused a significant increase in the extent of fading. At 65% RH, the fading rate drops dramatically. This effect was attributed to the breakage of hydrogen bonds in the presence of water, which leads to a more open structure with high segmented mobility; this condition is more favorable to diffusion of  $O_3$  and disperse dyes.

A follow-on study by Moore et al. (1984) used the Kamath et al. (1983) approach with a variety of dyes, yarns, and treatments. Moore and coworkers used untreated, phenol-treated, and steam-treated Nylon 6 and Nylon 66 continuous filament yarns, with six disperse blue and acid blue dyes. Molecular weights of the dyes ranged from MW = 296 (Disperse Blue 3) to MW = 872 (Acid Blue 127). Dyed filaments were exposed to 0.2 ppm  $O_3$  at 40 °C and 90% RH for various periods up to 96 h. For Nylon 6, steam-treated fibers faded more quickly than untreated fibers, whereas phenol-treated fibers faded less quickly. In Nylon 66, both treatments increased the rate of dye loss. The authors attributed this effect, at least in part, to the change in morphology of the treated fibers. Faster fading was attributed to higher diffusion rates of the dye in the fiber. They also observed that low-molecular-weight dyes faded faster than high-molecular-weight dyes, again suggesting the dye mobility within the fiber (rate of diffusion of the dye molecules to the surface of fiber) played a significant role in the fading process. Cross-sectional analysis of the exposed fibers showed that most of the dye loss appeared to occur due to reactions at the fiber surface, and that penetration of  $O_3$  into the fiber did not seem to be significant.

Salvin (1969) reported that  $O_3$  and, to a lesser extent,  $NO_2$  caused dye fading of cotton-polyester/permanent-press fabrics. As summarized by Dorset (1972),  $O_3$  was found to be the major fading agent, with  $NO_x$  also capable of causing fading, although to a lesser extent. Remedial measures to avoid this problem include selecting dyes more resistant to reaction with  $O_3$  and  $NO_2$ , avoiding the use of magnesium chloride ( $MgCl_2$ ) catalyst in the permanent-press process, and using different surfactants and softeners. The use of  $MgCl_2$  as a catalyst makes  $O_3$ -sensitive dyes more sensitive to  $O_3$  (Dorset, 1972). When the catalyst is zinc nitrate, dyes are more washfast and resistant to  $O_3$  fading. The use of a zinc nitrate catalyst appears generally to have eliminated the problem of the prefading of dyes in permanent-press fabrics from  $O_3$  exposure.

Much of the research reported on dye fading is qualitative in nature. Earlier studies relied on comparisons among various geographical locations and seasonal variations, with little attention given to actual concentration and exposure characterizations. For several

of the initial field investigations reported here, neither O<sub>3</sub> nor oxidant concentrations were given; rather, notations such as high versus low or urban versus rural were the only description of oxidant levels. The few laboratory studies employed, at most, only two concentrations of O<sub>3</sub>, making it nearly impossible to derive meaningful exposure-response relationships. Comparisons among studies are difficult owing to the various dye and fabric combinations tested. Also, the importance of RH on O<sub>3</sub> fading rate confounds comparisons among many of the studies that did not use the same RH percentages. Despite these shortcomings, the current body of research clearly demonstrates a strong relationship between dye fading and O<sub>3</sub> exposure. A definitive study to develop exposure-response functions that covers a broad spectrum of fabric/dye combinations, O<sub>3</sub> exposures, humidities, and temperatures has not been undertaken, although the available literature establishes the likely significant variables for such a study.

### 5.10.3.3 Fiber Damage

Sunlight, heat, alternate wetting and drying, and microorganisms are causative factors in the weathering and deterioration of fabrics exposed outdoors. The influence of O<sub>3</sub> at normal ambient levels is generally small by comparison. Table 5-44 summarizes the experiments of the effects of O<sub>3</sub> on textile fibers.

Bogaty et al. (1952), as part of a program aimed at segregating some of the elements that cause weathering, carried out experiments to study the possible role of O<sub>3</sub> in the deterioration of cotton textiles. These investigators exposed samples of duck and print cloth to air containing 0.02 and 0.06 ppm of O<sub>3</sub>. Samples were exposed both dry and wet and tested for 50 days. The wet samples were water-saturated once per week, and moisture was added regularly so that the moisture content of the cloth was never less than 50%. Similar fabric samples were exposed to similar O<sub>3</sub> concentrations with no moisture added, and another control group was wetted similarly but exposed to clean (O<sub>3</sub>-free) air. After exposure to O<sub>3</sub>, the wetted samples showed a loss in breaking strength of approximately 20%. The wet print control cloth showed a loss in breaking strength of only half this amount. The study showed that low levels of O<sub>3</sub> degrade cotton fabrics if they are sufficiently moist. Bogaty and co-workers surmised that an estimated 500 to 600 days of natural exposure might be required to reach a stage of degradation similar to that caused by a 50-day exposure to O<sub>3</sub> alone. Because unprotected fabrics typically reach a much more advanced state of decay after such long exposures to weathering, Bogaty and co-workers concluded that the effect of O<sub>3</sub> is slighter than that of other agents. Although not noted by Bogaty and co-workers, the O<sub>3</sub> and increased moisture may have caused the formation of H<sub>2</sub>O<sub>2</sub>, which could account for the loss in breaking strength.

Morris (1966) also studied the effects of O<sub>3</sub> on cotton. Samples were exposed in the absence of light to 0.5 ppm of O<sub>3</sub> (more than four times the NAAQS of 0.12 ppm) for 50 days in a chamber maintained at 70 °F (21 °C) and 72% RH. No appreciable effect on breaking strength was found. Apparently, the moisture content of the cotton was not high enough to produce the degradation that Bogaty et al. (1952) measured in wet cotton samples, even though the concentration of O<sub>3</sub> was considerably higher.

The laboratory study of Kerr et al. (1969) examined the effects of the periodic washing of dyed cotton fabrics exposed to O<sub>3</sub> and the amount of fading and degradation of moist, dyed fabrics exposed to O<sub>3</sub>. They exposed samples of print cloth, dyed with C.I. Vat Blue 29, in a chamber to a continuous supply of purified air containing O<sub>3</sub> concentration levels of 1 ± 0.1 ppm. The samples were exposed at room temperature (25 °C) in the

**Table 5-44. Laboratory and Field Studies of the Effects of Ozone on Fibers<sup>a</sup>**

Fiber	Concentration (ppm)	Exposure	Environmental Variables	Effects	References
Cotton	0.02 and 0.06	50 days	Cloth, both wet and dry	O <sub>3</sub> -exposed wetted samples had 20% loss of breaking strength.	Bogaty et al. (1952)
Cotton	0.5	50 days	21 °C, 72% RH	No loss of breaking strength.	Morris (1966)
Cotton	1.0	60 days	25 °C, periodic washing or wetting	Washed O <sub>3</sub> -exposed fabrics had 18% loss of breaking strength.	Kerr et al. (1969)
Modacrylic, Acrylic, Nylon 66, Polyester	0.2	7 days	48 °C, 39% RH, artificial sunlight, wetting	No effect on modacrylic and polyester. Slightly reduced breaking strength in acrylic and nylon.	Zeronian et al. (1971)
Nylon	0.03	Up to 445 days	Exposed in industrial warehouse	Loss of dyeability.	Makansi (1986)

<sup>a</sup>See Appendix A for abbreviations and acronyms.



absence of light, and a shallow container of water was kept on the chamber floor to increase the humidity. Samples were withdrawn from the chamber after 12, 24, 36, 48, and 60 days. After an exposure period of 60 days, which included either 20 washing or 20 soaking treatments, the change in strength of control fabrics was not significant. By comparison, the fabrics exposed to O<sub>3</sub> changed significantly; the loss in strength of the washed fabrics was 18%, and that of the soaked fabrics, 9%. Fading was also evident in the fabrics exposed to O<sub>3</sub> but not in the control samples. Differences in the amount of fading between the washed and soaked samples were evident, but the reason for the differences was not. Kerr et al. concluded that washing in hot, soapy water may have affected properties of the dye.

In laboratory studies, Zeronian et al. (1971) simultaneously exposed modacrylic (dynel), acrylic (orlon), Nylon 66, and polyester (dacron) fabrics to artificial sunlight (xenon arc) and CF air contaminated with 0.2 ppm of O<sub>3</sub> at 48 °C (118 °F) and 39% RH. During exposure, the fabric samples were sprayed with water for 18 min every 2 h. Ozone damage was measured by comparing these samples with fabrics exposed to the same environmental conditions without O<sub>3</sub>. After exposure for 7 days, Zeronian and co-workers found that O<sub>3</sub> did not affect the modacrylic and polyester fibers. The exposure did seem to affect the acrylic and nylon fibers slightly by reducing breaking strength. The degree of difference, however, in the change of fabric properties between those exposed to light and air and those exposed to light and air containing 0.2 ppm of O<sub>3</sub> was not significant.

Ageing of nylon yarns causes a reduction in the dyeability of the yarn. Ageing is caused by the reaction of amine end groups in the filament skin with O<sub>3</sub> and other pollutants (NO<sub>x</sub>, SO<sub>2</sub>, etc.). This phenomenon is well known within the textile trade, and procedures such as minimizing time from yarn production to yarn dyeing are in place to reduce problems of ageing. Makansi (1986) investigated the relationship between yarn ageing, as defined by reduction in dyeability, and pollutant levels in yarn storage warehouses. Makansi assessed the yarn dyeability with Acid Blue 45 and Acid Blue 122 dyes of exposed test fiber versus unexposed control samples. Gaseous pollutant concentrations in the warehouse were estimated either using nearby air quality station data or measured twice weekly during the tests with commercial sampling tubes (Draeger<sup>TM</sup> Tubes). Yarn samples were exposed for up to 1 year of ageing. Makansi found that dyeability decreased proportionally with the O<sub>3</sub> exposure during storage. Dyeability, as weight of dye absorbed for Acid Blue 45, decreased over 75% for Nylon 66 stored in the warehouse at an average concentration of 0.03 ppm O<sub>3</sub>. It was not possible to statistically isolate the effects of O<sub>3</sub> exposure from other pollutant exposures for the samples in these tests; thus other factors besides O<sub>3</sub> may have contributed to the loss in dyeability. Makansi suggested that yarns should be dyed as quickly as possible after manufacture or should be stored in airtight wrappings to prevent ageing.

In general, the contribution of O<sub>3</sub> to degradation of fabrics has not been quantified well. Bogaty et al. (1952) concluded that the effects of other factors (sunlight, heat, wetting and drying, and microorganisms) far outweighed the effects of O<sub>3</sub> on cotton duck and print cloth. The work by Morris (1966) and Kerr et al. (1969) does point to the synergistic effect of moisture and O<sub>3</sub> as an important ingredient in material degradation, possibly caused by the formation of a more potent oxidizing agent. Finally, the work of Zeronian et al. (1971) also indicates little if any effect of O<sub>3</sub> on synthetic fibers. Thus, it appears that O<sub>3</sub> has little if any effect on textiles, fibers, and synthetic cloth exposed outdoors. Because most fabrics are used primarily indoors, where they are partially shielded from O<sub>3</sub> exposure, O<sub>3</sub> damage to textile fibers is considered an insignificant problem. This was a finding of Murray et al. (1986) in a

study of material damage and costs in the Los Angeles area, an area with relatively high ambient O<sub>3</sub> concentrations.

#### 5.10.3.4 Paint Damage

A paint surface may suffer several types of damage (including cracking, peeling, erosion, and discoloration) that affect its usefulness. Of these, erosion (i.e., wearing away of the paint surface) is the type of damage most often studied with respect to the impact of gaseous pollutants on architectural and coil-coating finishes. (Coil coatings are industrial, continuous-dip process finishes typically applied to sheet metal.) Studies of paint cracking and peeling have focused on the effects of moisture and have not dealt with the possible influence of ambient pollutants on these types of finishes.

Several damage functions for O<sub>3</sub>-induced erosion of paint have been reported in the literature. Such reports are based either on accelerated chamber studies or on long-term outdoor exposure studies. Unfortunately, all studies to date have shortcomings that render their results questionable in regard to actual exposures. Damage to a paint surface is the cumulative effect of the conditions to which the surface is exposed, including various combinations of temperature, moisture, sunlight, and pollution level. No exposure study to date has been able to match all factors exactly to separate the impact of O<sub>3</sub> from the other factors. Table 5-45 summarizes the studies of the effect of O<sub>3</sub> on architectural and industrial paint and coating systems.

In a laboratory chamber exposure study, Haynie et al. (1976) exposed oil-based house paint, latex house paint, vinyl coil coating, and acrylic coil coating to 0.5- and 0.05-ppm concentrations of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> in various combinations. Statistically significant effects of O<sub>3</sub>-caused damage were observed on the vinyl and the acrylic coil coatings: a positive interaction between O<sub>3</sub> and RH on the vinyl coil coating and a positive direct O<sub>3</sub> effect on the erosion rate of the acrylic coil coating. The rate of erosion was low, however, and both vinyl and acrylic coil coatings were shown to be very durable. A linear regression for the acrylic coil coating data gives

$$\text{Erosion rate} = 0.159 + 0.000714 \text{ O}_3, \quad (5-2)$$

where erosion rate is in micrometers per year and O<sub>3</sub> is in micrograms per cubic meter.

Although the O<sub>3</sub> effect on this coating was found to be statistically significant, it has no practical significance because the erosion rate is so slow; at 0.12 ppm of O<sub>3</sub>, the erosion rate is 0.33 µm/year. At an average annual O<sub>3</sub> level of 0.05 ppm, this regression predicts that a 20-µm-thick coating would last over 80 years.

In a comprehensive study by Campbell et al. (1974), panels painted with different exterior paints (automotive refinish, latex coating, coil coating, industrial maintenance coating, and oil-based house paint) were exposed to air pollutants in an environmental chamber under accelerated weathering conditions. The panels were exposed to low (0.1 ppm) and high (1.0 ppm) concentrations of O<sub>3</sub> and SO<sub>2</sub>. After exposure, the panels were examined by measuring erosion, gloss, surface roughness, tensile strength, attenuated total reflectance (ATR), and the surface effects that were revealed by scanning electron microscopy and infrared examination. The panels were examined after 0, 400, 700, and 1,000 h of chamber exposure (considered as equivalent to 0, 200, 350, and 500 days of exposure, respectively).

**Table 5-45. Laboratory and Field Studies of the Effects of Ozone on Architectural/Industrial Paints and Coatings<sup>a</sup>**

Paint/Coating Type	Substrate	Concentration (ppm)	Exposure	Environmental Variables	Effects	Comments	Reference
Latex house paint Oil house paint Vinyl coil coating Acrylic coil coating	Aluminum panels	0.05 and 0.5	To 1,000 h	Chamber exposures with SO <sub>2</sub> , NO <sub>2</sub> , and O <sub>3</sub> ; 50 and 90% RH; 13 and 35 °C; and artificial dew and sunlight cycles.	Very slow erosion of coil coatings.		Haynie et al. (1976)
Automotive refinish Latex Coil coating Industrial maintenance coating Oil house paint	Stainless steel panels	0.1 and 1.0	To 1,000 h	Chamber study with SO <sub>2</sub> , 70 to 100% RH, 50 to 65 °C, and artificial dew and sunlight cycles.	Although 1 ppm O <sub>3</sub> produced significant changes in finishes, 0.1 ppm O <sub>3</sub> did not produce statistically increased erosion.		Campbell et al. (1974)
			To 24 mo	Field studies in four sites, rural to industrial.	Erosion greater in urban areas.	No environmental measurements conducted.	
Latex house paint Oil house paint	Stainless steel	0.006 to 0.055	3 to 30 mo	Field study.	Effects of O <sub>3</sub> not independently statistically significant.	Nine sites around St. Louis.	Mansfeld (1980)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

In general, exposures to 1 ppm of O<sub>3</sub> produced greater increases in erosion rates than did clean air. Concentrations of this magnitude, however, do not represent typical ambient exposure levels of O<sub>3</sub>. At the more representative level of 0.1 ppm, O<sub>3</sub> did not produce statistically significant increases in erosion rates. The various finishes produced a variety of changes for the other measures. Some finishes lost gloss or showed changes in ATR, but O<sub>3</sub> exposure did not produce consistent changes over the suite of finishes examined.

In conjunction with Campbell's chamber studies, field measurements were made of the erosion of paint from test panels exposed to outdoor environments consisting of a clean, rural atmosphere (Leeds, ND); a moderately polluted atmosphere (Valparaiso, IN); a heavily polluted (SO<sub>2</sub>) atmosphere (Chicago); and a high-oxidant, moderately polluted atmosphere (Los Angeles). The results of this study showed that paint erosion was much greater in the polluted areas than in relatively clean, rural areas. The highest erosion rates were observed for the coil coating and oil-based house paints at the Chicago and Los Angeles exposure sites. Because meteorology and air quality were not measured at the exposure sites, correlation of film damage with the environmental parameters was not possible. The study does suggest that SO<sub>2</sub> exerts an adverse effect on exterior paints with calcium carbonate as an extender pigment. The coil coating and oil house paints were formulated with calcium carbonate. Oxidants were probably reacting with the organic binder of the coil coating and oil house paints, although no mechanism for this reaction was developed from this exposure study.

In an outdoor exposure test of the effects of air pollutants on materials, Mansfeld (1980) exposed latex and oil-based house paints, as well as galvanized steel, weathering steel, stressed aluminum, silver, marble, and nylon, at nine test sites in St. Louis. In conjunction with the material exposures, measurements of meteorological parameters, O<sub>3</sub>, NO<sub>x</sub>, total hydrocarbons, total sulfur, SO<sub>2</sub>, and hydrogen sulfide were made.

Haynie and Spence (1984) analyzed Mansfeld's (1980) St. Louis data, accounting for covariances among the pollutant and meteorological variables. They analyzed the paint damage data and found significant correlations of O<sub>3</sub> flux with time, temperature, and NO<sub>2</sub> flux for the experimental period. Although Haynie and Spence expected O<sub>3</sub> to attack the binder in latex paint, multiple regression analysis showed little dependence of paint erosion on O<sub>3</sub> flux. They speculate that the effects of O<sub>3</sub> are masked by the covariance of O<sub>3</sub> with temperature and NO<sub>x</sub>.

#### **5.10.3.5 Cultural Properties Damage**

Ozone-induced degradation of cultural properties (e.g., fine arts paintings) contributes to the deterioration and, ultimately, to the loss of these unique objects. Many cultural properties are expected to last indefinitely, and irreversible damage, even at a slow rate, is considered unacceptable by curators and the art community.

A significant series of tests of the effects of O<sub>3</sub> on a variety of artist's pigments and dyes was reported by Shaver et al. (1983), Grosjean et al. (1987), Whitmore et al. (1987), Grosjean et al. (1988a,b), Whitmore and Cass (1988), Grosjean et al. (1989), Cass et al. (1991), and Grosjean et al. (1993). The experiments are summarized in Table 5-46. The doses of O<sub>3</sub> applied during these tests were the equivalent of less than 10 years exposure in a typical air conditioned indoor environment. Many pigments, notably traditional organic pigments such as indigo, were found to be very sensitive to O<sub>3</sub> exposure. Many of the affected pigments underwent significant color changes on exposure to O<sub>3</sub>, and some were

**Table 5-46. Laboratory Studies of the Effects of Ozone on Artists' Pigments and Dyes<sup>a</sup>**

Pigment Types	Substrate	Concentration	Exposure	Environmental Variables	Effects	Comments	Reference
17 Artists' watercolor pigments	Paper	0.4 ppm	95 days	23 °C 47% RH	Alizarin-based watercolors were very sensitive; other pigments showed lesser degrees of fading.	Also investigated fading on Japanese wood-block print.	Shaver et al. (1983)
Alizarin, Alizarin crimson, anthraquinone	Silica gel	0.4 ppm	95 days	22 °C	Each pigment tested faded on all substrates.	Presented possible reaction mechanisms and products.	Grosjean et al. (1987)
	cellulose	0.4 ppm	95 days	50% RH			
	—	—	—	—			
	Teflon	10 ppm	18-80 h	24 °C ≤40% RH			
16 Traditional organic colorants	Paper	0.4 ppm	12 weeks	23 °C 50% RH	Eleven colorants were reactive with O <sub>3</sub> , three were possibly reactive.		Whitmore et al. (1987)
Indigo, dibromoindigo, thioindigo, tetrachlorothioindigo	Teflon	10 ppm	4 days	24 °C 5% RH	All indigo, dibromoindigo consumed. Thioindigo and tetrachlorothioindigo were much less reactive and still retained much color.	Presented possible reaction mechanisms.	Grosjean et al. (1988a)
Curcumin	Cellulose, watercolor	0.4 ppm	95 days	25 °C	Faded rapidly on all substrates, producing colorless products.	Somewhat slower fading on watercolor paper.	Grosjean et al. (1988b)
	Paper, silica gel	0.4 ppm	95 days	50% RH			
	—	—	—	—			
	Teflon	10 ppm	4 days	24 °C ≤20% RH			

**Table 5-46 (cont'd). Laboratory Studies of the Effects of Ozone on Artists' Pigments and Dyes<sup>a</sup>**

Pigment Types	Substrate	Concentration	Exposure	Environmental Variables	Effects	Comments	Reference
Traditional Japanese colorants and dyes	Paper, silk cloth	0.4 ppm	12 weeks	22 °C 50% RH	Several organic and one inorganic pigment faded significantly.	Also investigated fading on ca. 1810 Japanese woodblock print.	Whitmore and Cass (1988)
Triphenylmethane colorants	Teflon	10 ppm	4 days	24 °C ≤20% RH	Found that, although some are not affected, those colorants with unsaturated C-C bonds may fade.	Presented possible reaction mechanisms.	Grosjean et al. (1989)
Alizarin crimson	Watercolor paper	0.4 ppm	7 days	22 °C 50% RH	Severe fading.	Framed sample behind glass exhibited virtually no fading.	Cass et al. (1991)
Various artists' colorants	Watercolor paper Cellulose	Mixture 0.2 ppm O <sub>3</sub> 0.01 ppm PAN 0.08 ppm NO <sub>2</sub>	12 weeks	16 to 26 °C 46 to 83% RH	11 colorants, negligible changes; 12 colorants, small changes; 3 colorants, modest changes; 9 colorants, substantial changes.		Grosjean et al. (1993)

<sup>a</sup>See Appendix A for abbreviations and acronyms.

virtually completely consumed, producing colorless reaction products. Cass et al. (1991) noted that O<sub>3</sub> damage to artwork is proportional to the O<sub>3</sub> exposure (C × T). Because artworks are intended to have long service lives and their appearance is important, fading is generally considered to be unacceptable, and even low concentrations for long periods of time can lead to noticeable fading. Grosjean et al. (1987) suggest that formulations of substitute pigments be developed with O<sub>3</sub> sensitivity in mind.

Druzik et al. (1990) investigated the indoor/outdoor O<sub>3</sub> concentration ratios at 11 museums, art galleries, and historical houses in the Los Angeles area. They found that the indoor/outdoor ratio of 8-h average O<sub>3</sub> concentrations ranged from 0.10 to 0.87. The ratio was strongly dependent on the type of building ventilation. Buildings with high air-exchange rates (about two to three air changes per hour) had the highest indoor/outdoor ratios. Low exchange rate buildings (ca. less than one air change per hour) and buildings with air conditioning systems had significantly lower indoor/outdoor O<sub>3</sub> concentration ratios.

De Santis et al. (1992) investigated concentrations of SO<sub>2</sub>, HNO<sub>3</sub>, HNO<sub>2</sub>, and O<sub>3</sub> as well as particulate sulfate, nitrate, and ammonium in the Galleria degli Uffizi in Florence for a 5-day period. Although the museum was equipped with an air conditioning system, O<sub>3</sub> concentrations in the galleries correlated strongly with outdoor O<sub>3</sub> concentrations. Indoor hourly average O<sub>3</sub> concentrations ranged from 0.019 to 0.030 ppm. To reduce concentrations in the galleries, they suggested that the Uffizi's air handling system be upgraded to include filtration and modified to include less make-up air. Cass et al. (1991) and Grosjean et al. (1993) suggest that museums design and maintain air conditioning and air filtration systems to control the concentrations of oxidants in order to protect their collections. Cass et al. (1991) note that framing behind glass is an effective means of protecting oxidant sensitive pigments. Grosjean and Parmar (1991) found that activated carbon and Purafil (4% potassium permanganate on neutral activated alumina) could be used to reduce O<sub>3</sub> and oxidant concentrations in museum display cases.

## **5.10.4 Economics**

### **5.10.4.1 Introduction**

Damage to materials from O<sub>3</sub> usually is expressed in terms of one or both of the following two general classes of costs to producers and consumers: (1) O<sub>3</sub>-accelerated replacement and repair costs, as when the service life or aesthetics of a material are impaired, and (2) increased avoidance costs, as when certain industries (e.g., tires, plastics, paints, dyes, and fabrics) are obligated to incur expenditures for antiozonant research and development, substitute processes and materials, additives and formulations, product packaging, advertising, etc., in order to offset sales losses that otherwise would occur.

In theory, the approach selected should depend on the observed behavior of the producers and consumers of the materials in question, and the type of damage to which they are reacting. In practice, the empirical estimates of O<sub>3</sub> damage to materials are far from reliable.

### **5.10.4.2 Methods of Cost Classification and Estimation**

Computation of accelerated replacement is probably the most widely applied method of estimating the costs of materials damage to air pollutants. In this approach, a materials damage function is developed to show the increase in physical damage for an increase in the dose of the pollutant. Then a cost schedule is constructed to show how

maintenance or replacement schedules are influenced by the pollutant level. Hershaft et al. (1978) note, however, that this method usually assumes existing inventories and does not take into account substitutions of materials with more (or less) resistance to pollution. As a result, this method tends to overestimate the cost of damage from pollutant increases and to underestimate the net savings realized from pollutant reductions.

A second approach considers avoidance costs. This refers to practices such as adopting alternative production processes and materials. Some industries add antiozonants to their products or change the chemical formulation of their output. All of these measures mitigate the impact of  $O_3$  on the service life or aesthetics of the products in question. Moreover, these measures also require research, development, and implementation expenditures. As such, estimation of these costs is conceptually and empirically difficult, since the opportunity to use different materials changes in response to the level of  $O_3$  concentration.

A number of factors complicate the use of both the replacement and the avoidance methodologies. Data on key variables generally are missing or merely assumed. Lessening the reliability of the final cost estimates are deficiencies in knowledge of the physical damage functions; the quantities and types of materials exposed to  $O_3$  indoors, outdoors, and in respective regions of the country; the actual expenditures incurred for increased replacement, maintenance, and avoidance that can be directly attributed to  $O_3$ ; the threshold  $O_3$  damage levels that prompt mitigating action; and the range of substitution strategies that can be used to ameliorate degradation. On the last point, few attempts have been made to identify current technology practices and potential innovations. The variety of rubber compounds, paint mixtures, and fabric dyes reflects the number of proprietary formulations, and each formulation presumably has a different response to  $O_3$  exposure.

An additional complication is that repair, replacement, and substitution are frequently dominated by factors unrelated to  $O_3$  concentrations. This can lead to spurious correlations if studies are accepted uncritically. For example, tire replacement may be high in a given region of the country because of high  $O_3$  levels associated with automotive exhaust. Alternatively, tire replacement may be high simply because the total miles of automotive use per year are higher in that region than in the nation as a whole.

#### **5.10.4.3 Aggregate Cost Estimates**

The important caveats identified in the preceding discussion qualify the empirical data presented in this and following sections. Table 5-47 summarizes reports of highly aggregated estimates of oxidant damage of all materials. Unfortunately, there are no known recognized studies that are more recent than those reported in the table. For purposes of gross comparison only, where possible, the figures are expressed in 1984 currency equivalents along with 1970 currency equivalents, the base data for most of the reference studies. The figures do *not*, however, represent 1984 supply-demand relationships, production technologies, or  $O_3$  concentrations. It must be emphasized that the costs cited in 1984 currency equivalents therefore cannot be considered true 1984 costs. Because the data in Table 5-47 are reported to four significant figures, the accuracy of this information is exaggerated.

Salmon (1970) was among the first to attempt to estimate the annual cost of air pollution damage to materials. His computation included the dollar value of annual materials production, a weighted average economic life of each material included in his study, a weighted average factor for the percentage of the material exposed to air pollution, and a



**Table 5-47. Summary of Damage Costs to Materials by Oxidants  
(in millions of 1970 and 1984 dollars)<sup>a</sup>**

Study	Materials Costs		
	Elastomers/Plastics	Fabric/Dye	All
Barrett and Waddell (1973)	ND	(260)	(3,878)
Mueller and Stickney (1970)	500.0 (1,500)	ND	ND
Salmon (1970)	295.2 (915)	358.4 (1,111)	653.6 (2,026)
Salvin (1970)	ND	83.5 (259)	ND
Waddell (1974)	ND	ND	900.0 (2,790)
Yocom and Grappone (1976)	ND	ND	572.0 (1,773)
Freeman (1979)	ND	ND	505.0 (1,566)

<sup>a</sup>ND = No data; investigator(s) did not develop estimates in this category. 1984 dollars are listed parenthetically.

factor for increased labor to treat damaged materials. Cost was defined as the value of the material multiplied by the difference between the rate of material deterioration in a polluted urban versus an unpolluted rural environment. All data, except for annual production levels of materials, were assumed.

If it is assumed that O<sub>3</sub> affected all of the fibers, plastics, and rubber in the study by Salmon, then annual damage costs attributed to O<sub>3</sub> would have been \$2.026 billion (1984\$). Salmon did not consider O<sub>3</sub>-related damage to paint, since the dominant paint-damaging mechanisms are soiling and gaseous SO<sub>2</sub>. His costs refer to maintenance and replacement only, and do not allow for materials protection, substitution, etc.

In discussing other limitations of his study, Salmon cautioned that his estimates were of potential loss, not of actual observed loss. Despite this and other qualifications that lessen the usefulness of the figures derived, the Salmon study has been cited extensively and used quantitatively in a number of the subsequent studies cited here.

For example, the materials estimate by Barrett and Waddell (1973) is based primarily on the work of Salmon (1970). Barrett and Waddell supplemented this by drawing on Mueller and Stickney (1970) for damage costs on elastomers and on Salvin (1970) for damage costs related to dye fading. Combining some of these numbers, Barrett and Waddell stated that materials damage costs attributable to oxidants alone were \$3.878 billion (1984\$).

Freeman (1979) reviewed earlier studies that categorized the cost of damage to materials. Using the work of Waddell (1974) and Salvin (1970), Freeman calculated that the materials damage costs attributable to oxidants and  $\text{NO}_x$  were \$2.031 billion (1984\$). Of this total, roughly 46% was damage to textiles and dyes (from Salvin, 1970), whereas the remaining 54% was damage to elastomers (from Mueller and Stickney, 1970). Freeman then assumed a 20% reduction in oxidant levels since 1970 and concluded that the monetary benefits of controlling oxidants, oxidant precursors, and  $\text{NO}_x$  were between \$170 and \$510 million (1984\$). Freeman computed that the savings attributable to oxidant controls alone were \$128 to \$383 million (1984\$).

Waddell (1974) likewise depended primarily on existing studies to calculate the national cost of air pollution in 1970. Waddell used Salmon (1970), Salvin (1970), Mueller and Stickney (1970), and Spence and Haynie (1972) to derive an estimate of \$6.820 billion (1984\$) as the total gross annual damage for materials losses in 1970 resulting from air pollution. The component attributable to  $\text{O}_3$  and oxidants alone was \$2.790 billion (1984\$), within a wide range of \$1.550 to \$4.030 billion (1984\$).

Yocom and Grappone (1976), in work for the Electric Power Research Institute, estimated that the cost of air pollution damage to materials was about \$6.820 billion (1984\$) in 1970. Of this total,  $\text{O}_3$  was estimated to be responsible for \$1.773 billion (1984\$), or some 26% of the total.

Because of the reliance of the later studies on the questionable data and unverified assumptions contained in the earlier ones, the results compared here are of extremely limited usefulness for cost-benefit purposes. Updated research, using current economic evaluation approaches, should be undertaken to determine the costs of  $\text{O}_3$ -induced damage.

### **5.10.5 Summary and Conclusions**

More than four decades of research show that  $\text{O}_3$  damages certain materials. The materials most studied in  $\text{O}_3$  research are elastomers and textile fibers and dyes. The amount of damage to actual in-use materials and the economic consequences of that damage are poorly characterized.

Natural rubber and synthetic polymers of butadiene, isoprene, and styrene, used in products like automobile tires and protective outdoor electrical coverings, account for most of the elastomer production in the United States. The action of  $\text{O}_3$  on these compounds is well known, and dose-response relationships have been established and corroborated by several studies. These relationships, however, must be correlated with adequate exposure information based on product use. For these and other economically important materials, protective measures have been formulated to reduce the rate of oxidative damage. When antioxidants and other protective measures are incorporated in elastomer production, the dose rate for cracking is reduced considerably, although the extent of reduction differs widely according to the material and the type and number of protective measures used.

The effects of  $\text{O}_3$  on dyes have been known for nearly four decades. In 1955, Salvin and Walker exposed certain red and blue anthraquinone dyes to a 0.1-ppm concentration of  $\text{O}_3$  and noted fading, which until that time was thought to be caused by  $\text{NO}_2$ . Subsequent work confirmed the fading action of  $\text{O}_3$  and the importance of RH in the absorption and reaction of  $\text{O}_3$  in vulnerable dyes. Both the type of dye and the material in which it is incorporated are important factors in resistance of a fabric to  $\text{O}_3$ . Researchers found no effects from  $\text{O}_3$  on royal blue rayon-acetate, red rayon-acetate, or plum cotton.

On the other hand, anthraquinone dyes on nylon fibers were sensitive to fading from O<sub>3</sub>. Field studies and laboratory work showed a positive association between O<sub>3</sub> levels and dye fading of nylon materials. At present, the available research is insufficient to quantify the amount of damaged material attributable to O<sub>3</sub> alone.

The degradation of fibers from exposure to O<sub>3</sub> is poorly characterized. In general, most synthetic fibers like modacrylic and polyester are relatively resistant, whereas cotton, nylon, and acrylic fibers have greater but varying sensitivities to the gas. Ozone reduces the breaking strength of these fibers, and the degree of reduction depends on the amount of moisture present. The limited research in this area indicates that O<sub>3</sub> in ambient air may have a minimal effect on textile fibers, but additional research is needed to verify this conclusion.

The effects of O<sub>3</sub> on paint are small in comparison with those of other factors. Past studies have shown that, of various architectural and commercial paints, only vinyl and acrylic coil coatings are affected, and that this impact has a negligible effect on the useful life of the material coated. Preliminary results of current studies have indicated a statistically significant effect of O<sub>3</sub> and RH on latex house paint, but the final results of those studies are needed before conclusions can be drawn.

A number of artists' pigments and dyes have been found to be sensitive to O<sub>3</sub> and other oxidants. Many organic pigments in particular are subject to fading or other color changes when exposed to O<sub>3</sub>. Although most, but not all, modern fine arts paints are O<sub>3</sub> resistant, many older works of art are at risk of permanent damage because of O<sub>3</sub>-induced fading. Museums and private collectors should take steps to ensure that susceptible artwork is protected from O<sub>3</sub> exposure.

For a number of important reasons, the estimates of economic damage to materials are problematic. Most of the available studies are outdated in that the O<sub>3</sub> concentrations, technologies, and supply-demand relationships that prevailed when the studies were conducted are no longer relevant. Additionally, little was (and is) known about the physical damage functions, and cost estimates were simplified to the point of not properly recognizing many of the scientific complexities of the impact of O<sub>3</sub>. Assumptions about exposure to O<sub>3</sub> generally ignored the difference between outdoor and indoor concentrations. Also, analysts have had difficulty separating O<sub>3</sub> damage from other factors affecting materials maintenance and replacement schedules. For the most part, the studies of economic cost have not had the resources to marshal factual observations on how materials manufacturers have altered their technologies, materials, and methods in response to O<sub>3</sub>. Rather, the analysts have had to rely on assumptions in this regard, most of which remain unverified.

It is apparent that a great deal of work remains to be done in developing quantitative estimates of materials damage from photochemical oxidant exposures. This is not meant to deprecate the years of research reported in this document, for much has been gained in refining the initial methodologies used for assessing damage. The current state of knowledge still can be summarized by the following from Yocom et al. (1985):

"We have learned that some costs may be difficult to quantify either because they are minimal or because they are overshadowed by other factors, such as wear or obsolescence. We have learned that damage functions are complex and are influenced by the presence of other pollutants and by weather. We have learned that more accurate estimates of materials in place may be obtained using selective

sampling and extrapolation. And we have learned that a mere cost-accounting of damage does not present a true estimate of economic cost if it does not account for the welfare effects induced by shifts in the supply-demand relationship."

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# Appendix A

## *Abbreviations and Acronyms*

ADOM	Acid Deposition and Oxidant Model
AGL	Above ground level
AIRS	Aerometric Information Retrieval System
AM	Alveolar macrophage
AQCD	Air Quality Criteria Document
AQCR	Air Quality Control Region
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
C	Carbon
C	Concentration
CA	Chromotropic acid
CAA	Clean Air Act
CAAA	Clean Air Act Amendments of 1990
CAL-RAMS	Coast and Lake Regional Atmospheric Modeling System
CAR	Centriacinar region
CASAC	Clean Air Scientific Advisory Committee
CBM	Carbon-bond mechanism
CCM	Community Climate Model
CFC	Chlorofluorocarbon
CH <sub>3</sub> OH	Methanol
CH <sub>4</sub>	Methane
CI	Chemical ionization
CIT	California Institute of Technology
CL	Chemiluminescence
CMB	Chemical mass balance
CNG	Compressed natural gas
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CTWM	Complex Terrain Wind Model
DIAL	Differential absorption lidar

DNPH	2,4-Dinitrophenylhydrazine
DOAS	Differential optical absorption spectrometry
DWM	Diagnostic Wind Model
ECD	Electron capture detection
EKMA	Empirical Kinetic Modeling Approach
EMS	Emissions Modeling System
EPA	U.S. Environmental Protection Agency
EPEM	Event Probability Exposure Model
EPRI	Electric Power Research Institute
EPS	Emissions Preprocessor System
ERAQS	Eastern Regional Air Quality Study
ETBE	Ethyl-tertiary-butyl ether
EtOH	Ethanol
FDDA	Four-dimensional data assimilation
FeSO <sub>4</sub>	Ferrous sulfate
FEV <sub>1</sub>	Forced expiratory volume in 1 s
FVC	Forced vital capacity
FID	Flame ionization detection
FTIR	Fourier transform infrared absorption spectroscopy
GC	Gas chromatography
GMEP	Geocoded Model of Emissions and Projections
GPT	Gas-phase titration
H <sup>+</sup>	Hydrogen ion
HC	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HCHO	Formaldehyde
HNO <sub>2</sub>	Nitrous acid
HNO <sub>3</sub>	Nitric acid
HO <sub>2</sub>	Hydroperoxyl
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
HPLC	High-performance liquid chromatography
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
IC	Ion chromatography
ID	Identification (number)
I/O	Indoor/outdoor

IR	Infrared radiation
<i>IR</i>	Incremental reactivity
LMOS	Lake Michigan Oxidant Study
LPG	Liquified petroleum gas
MBTH	3-Methyl-2-benzothiazolone hydrazone
MCCP	Mountain Cloud Chemistry Program
MM4/MM5	Mesoscale Model, versions 4 and 5
MOBILE	U.S. Environmental Protection Agency emissions model for mobile sources
MODELS 3	Modeling framework that consolidates all of the U.S. Environmental Protection Agency's three-dimensional photochemical air quality models
MPAN	Peroxy methacryloyl nitrate
MSA	Metropolitan Statistical Area
MSCET	Month and state current emissions trends
MTBE	Methyl-tertiary-butyl ether
NA	Not available
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NAMS	National Air Monitoring Station
NAPAP	National Acid Precipitation Assessment Program
NAPBN	Western National Air Pollution Background Network
NAS	National Academy of Sciences
NBKI	Neutral buffered potassium iodide
NBS	National Bureau of Standards; now National Institute of Standards and Technology
NCAR	National Center for Atmospheric Research
NCLAN	National Crop Loss Assessment Network
NDDN	National Dry Deposition Network
NEM	National Air Quality Standards Exposure Model
NF	National forest
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> HSO <sub>4</sub>	Ammonium bisulfate
NH <sub>4</sub> OH	Ammonium hydroxide
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Ammonium sulfate



NIST	National Institute of Standards and Technology
NM	National monument
NMHC	Nonmethane hydrocarbon
NMOC	Nonmethane organic compound
NO	Nitric oxide
NO <sub>2</sub>	Nitrogen dioxide
N <sub>2</sub> O	Nitrous oxide
NO <sub>3</sub> <sup>-</sup>	Nitrate
NO <sub>x</sub>	Nitrogen oxides
NP	National park
NPN	<i>n</i> -propyl nitrate
NTP	National Toxicology Program
O <sub>3</sub>	Ozone
OAQPS	Office of Air Quality Planning and Standards
Obs.	Observations
OH	Hydroxyl
OHBA	Hydroxybenzoic acid
PAMS	Photochemical Aerometric Monitoring System
PAN	Peroxyacetyl nitrate
PANs	Peroxyacyl nitrates
PAR	Proximal alveolar region
PBL	Planetary boundary layer
PBzN	Peroxybenzoyl nitrate
PDFID	Cryogenic preconcentration-direct flame ionization detection
PF/TPLIF	Photofragmentation two-photon laser-induced fluorescence
pH	Hydrogen ion concentration
PL	Liquid-phase vapor pressure
PLANR	Practice for Low-cost Application in Nonattainment Regions
PMN	Polymorphonuclear leukocyte (also called neutrophil)
ppmC	Parts per million carbon
PPN	Peroxypropionyl nitrate
PSD	Passive sampling device
PVOC	Polar volatile organic compound
Q <sub>E</sub>	Latent heat flux
Q <sub>H</sub>	Heat flux
r	Linear regression correlation coefficient

R <sup>2</sup>	Multiple correlation coefficient
RADM	Regional Acid Deposition Model
RAPS	Regional Air Pollution Study
REHEX	Regional Human Exposure Model
RMSD	Root-mean-square difference
ROG	Reactive organic gas
ROM	Regional Oxidant Model
ROMNET	Regional Ozone Modeling for Northeast Transport program
RT	Respiratory tract
SAB	Science Advisory Board
SAI	Systems Applications International
SAPRC	Statewide Air Pollution Research Center, University of California, Riverside
SARMAP	San Joaquin Valley Air Quality Study (SJVAQS)/Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) Regional Model Adaptation Project
SAROAD	Storage and Retrieval of Aerometric Data (U.S. Environmental Protection Agency centralized database; superseded by Aerometric Information Retrieval System [AIRS])
SCAQS	South Coast Air Quality Study (California)
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Station
SJVAQS	San Joaquin Valley Air Quality Study
SO <sub>2</sub>	Sulfur dioxide
SO <sub>4</sub> <sup>2-</sup>	Sulfate
SOS	Southern Oxidant Study
SRM	Standard reference material
SRP	Standard reference photometer
STEM-II	Sulfur Transport Eulerian Model (version II)
SUM06	Seasonal sum of all hourly average concentrations □0.06 ppm
SUM07	Seasonal sum of all hourly average concentrations □0.07 ppm
SUM08	Seasonal sum of all hourly average concentrations □0.08 ppm
SURE	Sulfate Regional Experiment Program
T	Temperature
TAMS	Toxic Air Monitoring Study (U.S. Environmental Protection Agency)
TDLAS	Tunable-diode laser absorption spectroscopy

TEA	Triethanolamine
Tg	Teragram
TGTP	The Global Thinking Project
TNMHC	Total nonmethane hydrocarbons
TPLIF	Two-photon laser-induced fluorescence
TTFMS	Two-tone frequency-modulated spectroscopy
UAM	Urban Airshed Model
UV	Ultraviolet
UV-B	Ultraviolet radiation of wavelengths 280 to 320 nm
VMT	Vehicle miles traveled
VOC	Volatile organic compound
$\dot{V}_E$	Minute ventilation; expired volume per minute
WFM	White Face Mountain
WMO/UNEP	World Meteorological Organization/United Nations Environment Program
W126	Cumulative integrated exposure index with a sigmoidal weighting function

# Appendix B

## *Colloquial and Latin Names*

Alder	<i>Alnus serrulata</i> (Aiton) Willdenow
Alder, red	<i>Alnus rubra</i> Bong.
Alder, speckled	<i>Alnus incana</i> (L.) Moench.
Alfalfa	<i>Medicago sativa</i> L.
Almond	<i>Prunus amygdalus</i> Batsch cv. Nonpareil
Apple	<i>Malus</i> spp.
Apricot	<i>Prunus armeniaca</i> L.
Ash, green	<i>Fraxinus pennsylvanica</i> Marsh.
Ash, white	<i>Fraxinus americana</i> L.
Aspen, trembling	<i>Populus tremuloides</i> L.
Avocado	<i>Persea americana</i> Mill.
Azalea	<i>Rhododendron</i> spp.
Barley, spring	<i>Hordeum vulgare</i> L.
Basswood (linden)	<i>Tilia americana</i> L.
Bean, broad	<i>Vicia faba</i> L.
Bean, bush	<i>Phaseolus vulgaris</i> L. var. <i>humulis</i> Alef.
Bean, kidney, pinto, snap, white	<i>Phaseolus vulgaris</i> L.
Beech, European	<i>Fagus sylvatica</i> L.
Beet, sugar	<i>Beta vulgaris</i> L.
Begonia	<i>Begonia</i> sp.
Begonia, bedding	<i>Begonia semperflorens</i> Link & Otto
Bentgrass	<i>Agrostis capillaris</i> L.
Birch, European white	<i>Betula pendula</i> Roth.
Birch, downy	<i>Betula pubescens</i> Ehrh.
Birch, paper	<i>Betula papyrifera</i> Marsh.
Blackberry, common	<i>Rubus allegheniensis</i> Porter
Black-gram	<i>Vigna mungo</i> L.
Bluegrass, Kentucky	

Buckhorn	<i>Poa praetensis</i> L.
Cabbage	<i>Plantago lanceolata</i> L.
Campion, bladder	<i>Brassica oleracea capitata</i> L.
Campion, moss	<i>Silene cucubalus</i> Wibel.
Carnation	<i>Silene acaulis</i> L.
Cedar, incense	<i>Dianthus caryophyllus</i> L.
	<i>Libocedrus decurrens</i> Torr. =
	<i>Calocedrus decurrens</i> [Torr.] Florin.
Cedar, western red	<i>Thuja plicata</i> Donn ex D. Don
Celery	<i>Apium graveolens</i> L. var. <i>dulce</i> Pers.
Chestnut, American	<i>Castanea dentata</i> (Marsh.) Borkh.
Cherry, black	<i>Prunus serotina</i> Ehrh.
Chickpea	<i>Cicer arietinum</i> L.
Clover, ladino, white	<i>Trifolium repens</i> L.
Clover, red	<i>Trifolium pratense</i> L.
Corn	<i>Zea mays</i> L.
Cotton	<i>Gossypium hirsutum</i> L.
Cottonwood (poplar)	<i>Populus deltoides</i> Marsh
Cress, garden	<i>Lepidium sativum</i> L.
Cucumber	<i>Cucumis sativus</i> L.
Dock	<i>Rumex obtusifolius</i> L.
Fenugreek	<i>Trigonella foenum-graecum</i> L.
Fescue, tall	<i>Festuca elatior</i> L. = <i>Festuca praetensis</i> Huds.
Fir, balsam	<i>Abies balsamea</i> (L.) Mill.
Fir, Douglas	<i>Pseudotsuga menziesii</i> (Mirb.) Franco.
Fir, Douglas, big-cone	<i>Pseudotsuga macrocarpa</i> (Vasey) Mayr
Fir, Fraser	<i>Abies balsamea</i> (L.) <i>fraseri</i> (Pursh) Poir.
Fir, silver	<i>Abies alba</i> Mill.
Fir, white	<i>Abies concolor</i> Lindl.
Geranium	<i>Pelargonium x hortorum</i> Bailey
Golden-rain	<i>Koeleria paniculata</i> Laxm.
Grape	<i>Vitis labruscana</i> Bailey
Grape, wild	<i>Vitis</i> spp.

Grapefruit, Ruby Red  
Grass, colonial bent  
Grass, orchard  
Grass, red  
Grass, rye  
Gum, sweet  
Hemlock, eastern

*Citrus paradisi* L.  
*Agrostis tenuis* Sibthorp.  
*Dactylis glomerata* L.  
*Festuca rubra* Gaud.  
*Lolium perenne* L.  
*Liquidambar styraciflua* L.

Hemlock, western  
Ivy  
Kenaf  
Juniper, shore  
Lemon, Volkamer  
Lettuce  
Lichen  
Lichen, parmelia  
Lichen, umbilical  
Lilac  
Locust, black  
Locust, honey  
Lupine  
Mangel  
Maple, red  
Maple, sugar  
Milkweed  
Milkweed  
Mint  
Oak, California black  
Oak, Canyon live  
Oak, red  
Oak, white  
Oats

*Tsuga canadensis* (L.) Carr.  
*Tsuga heterophylla* (Raf.) Sarg.  
*Hedera helix* L.  
*Hibiscus cannabinus* L.  
*Juniperus conferta* Parl.  
*Citrus volkameriana* Ten. & Pasq  
*Lactuca sativa* L.  
*Lobaria* spp.  
*Flavoparmelia caperata*  
*Umbilicaria mammulata*  
*Syringa vulgaris* L.  
*Robinia pseudoacacia* L.  
*Gleditsia triacanthos* L.  
*Lupinus bicolor* Lindl.  
*Beta vulgaris* L.  
*Acer rubrum* L.  
*Acer saccharum* Marsh  
*Asclepias syriaca* L.  
*Asclepias* sp.  
*Mentha piperita* L.  
*Quercus kelloggii* Newb.  
*Quercus chrysolepis* Liebm.  
*Quercus rubra* L.  
*Quercus alba* L.  
*Avena sativa* L.

Onion	<i>Allium cepa</i> L.
Orange	<i>Citrus sinensis</i> (L.) Osbeck
Pea	<i>Pisum sativum</i> L.
Peach	<i>Prunus persica</i> (L.) Batsch cv. Halford
Pepper	<i>Capsicum annuum</i> L.
Pear	<i>Pyrus pyrifolia</i> Rhd. cv. 20th Century
Petunia	<i>Petunia hybrida</i> Vilm.
Pine, eastern white	<i>Pinus strobus</i> L.
Pine, Coulter	<i>Pinus coulteri</i> D. Don
Pine, Jeffrey	<i>Pinus jeffreyi</i> Grev. & Balf.
Pine, loblolly	<i>Pinus taeda</i> L.
Pine, pitch	<i>Pinus rigida</i> Mill.
Pine, ponderosa	<i>Pinus ponderosa</i> Laws.
Pine, Scots	<i>Pinus sylvestris</i> L.
Pine, shortleaf	<i>Pinus echinata</i> Mill.
Pine, Sierra lodgepole	<i>Pinus contorta</i> var. <i>murrayana</i> (Grev. & Balf.) Engelm.
Pine, slash	<i>Pinus elliotti</i> Englem. ex Vasey
Pine, sugar	<i>Pinus lambertiana</i> Dougl.
Pine, Table Mountain	<i>Pinus pungens</i> Lamb.
Pine, Virginia	<i>Pinus virginiana</i> Mill.
Plane, London	<i>Platanus x acerifolia</i> (Ait.) Willd.
Plantain, (plantago) common	<i>Plantago major</i> L.
Plum	<i>Prunus domestica</i> L.
Poinsettia	<i>Euphorbia pulcherrima</i> Willd.
Poplar, hybrid	<i>Populus maximowiczii</i> x <i>P. trichocarpa</i>
Poplar, yellow or tulip	<i>Liriodendron tulipifera</i> L.
Potato	<i>Solanum tuberosum</i> L.
Radish	<i>Raphanus sativus</i> L.
Radish	<i>Raphanus sativus</i> L. cv. Cherry Bell
Rape, spring	<i>Brassica napus</i> L. var. <i>napus</i>
Rhododendron, azalea	<i>Rhododendron obtusum</i> (Lindl.) Planch.
Rice, domestic	<i>Oryza sativa</i> L.
Sassafras	<i>Sassafras albidum</i> [Nutt.] Nees
Sequoia, giant	<i>Sequoiadendron giganteum</i> Buchholz

Sorghum, hybrid

*Sorghum bicolor* (L.) Moench x *Sorghum* x

Soybean

*drummondii* (Steudel) Millsp. & Chase

Spinach

*Glycine max* (L.) Merr.

Spruce, Norway

*Spinacea oleracea* L.

Spruce, red

*Picea abies* (L.) Karst.

Spruce, sitka

*Picea rubens* Sarg.

Strawberry, cultivated

*Picea sitchensis* (Bong.) Carr.

Strawberry, wild

*Fragaria* x *ananassa* Duch.

Sunflower

*Fragaria virginiana* Duch.

Skunk bush

*Helianthus annuus* L.

Sycamore

*Rhus trilobata* Nutt.

Timothy

*Platanus occidentalis* L.

Tobacco

*Phleum pratense* L.

Tomato

*Nicotiana tabacum* L.

Virgin's Bower

*Lycopericon esculentum* Mill.

Watermelon

*Clematis virginiana* L.

Wheat

*Citrullus lanatus* (Thunb.) Mastsum & Nakai

*Triticum aestivum* L.