

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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> concentrations.

#### **5.9.4.2 Environmental Factors**

Plant response to O<sub>3</sub> 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<sub>3</sub> can modify a plant's ability to integrate the effects of its environment. For example, exposure to O<sub>3</sub> 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<sub>3</sub> exposure, but there is no evidence to suggest that O<sub>3</sub> may trigger pest outbreaks in plants. Because the effects of O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> exposures.

Plant-pathogen interactions also appear to be affected by O<sub>3</sub>. The suggestion that O<sub>3</sub> 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<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.

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<sub>3</sub>. There is consistent evidence that severe drought conditions tend to reduce the direct adverse effects of O<sub>3</sub> on growth and yield, and that ready soil water availability 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. Unlike the situation with annual crops, a limited amount of evidence suggests that prolonged exposure of perennial trees to O<sub>3</sub> 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<sub>3</sub> exposure. The nature of these interactions is largely unknown. Although many studies have been conducted on the effects of O<sub>3</sub> on plants in conjunction with other gaseous air pollutants such as SO<sub>2</sub> and NO<sub>2</sub>, the data obtained in several of these studies is of academic interest only because of the unrealistic exposure scenarios used.

Because increased tropospheric O<sub>3</sub> is a component of global climate change, which is of growing concern within world communities, data on the interactions of O<sub>3</sub> with increased levels of CO<sub>2</sub> and UV-B radiation, elevated temperatures, and drought are beginning to appear. Initial data suggest that increased CO<sub>2</sub> levels may ameliorate the effects of O<sub>3</sub>, but conclusive generalizations about the outcome of this interaction are not yet possible. Studies investigating the interaction of O<sub>3</sub> with UV-B exposure reveal no significant changes in O<sub>3</sub> effect on the growth and yield of soybean due to UV-B levels, although there are significant effects of O<sub>3</sub>.

Although a number of studies have examined the interactions of O<sub>3</sub> with specific environmental factors, no quantitative database exists from which the effects of O<sub>3</sub> on species can be extrapolated across environments. The role of different growing environments in a species' O<sub>3</sub> exposure response and the effect of O<sub>3</sub> 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<sub>3</sub> exposures with the degree of plant response. The effects of O<sub>3</sub> on individual plants and the factors that modify plant response to O<sub>3</sub>, 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<sub>3</sub> 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<sub>3</sub> (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<sub>3</sub> 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<sub>3</sub> 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  $\text{SO}_2$ , and from natural damaging agents, such as sunlight, moisture, oxygen, and temperature fluctuations, tend to overshadow the role of ambient  $\text{O}_3$  in causing paint damage.

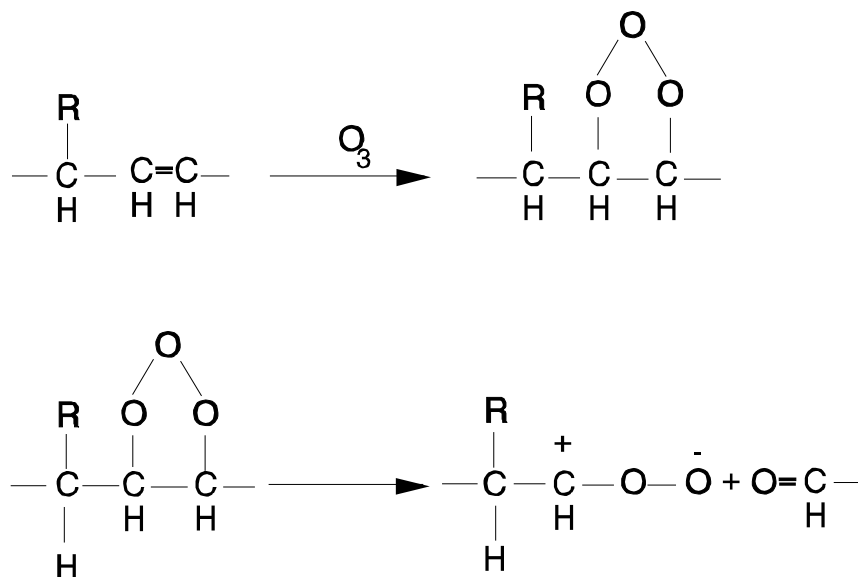
The literature selected for review in this section includes research previously reported in the 1978 and 1986 criteria documents (U.S. Environmental Protection Agency, 1978, 1986) and a limited number of other references published before and after 1986. Because little recent work has been reported on 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  $\text{O}_3$  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  $\text{O}_3$  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,  $\text{O}_3$  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  $O_3$  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  $O_3$ -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  $O_3$ ). They concluded that the "scavenger-protective film mechanism" is primarily responsible for antiozonant protection.

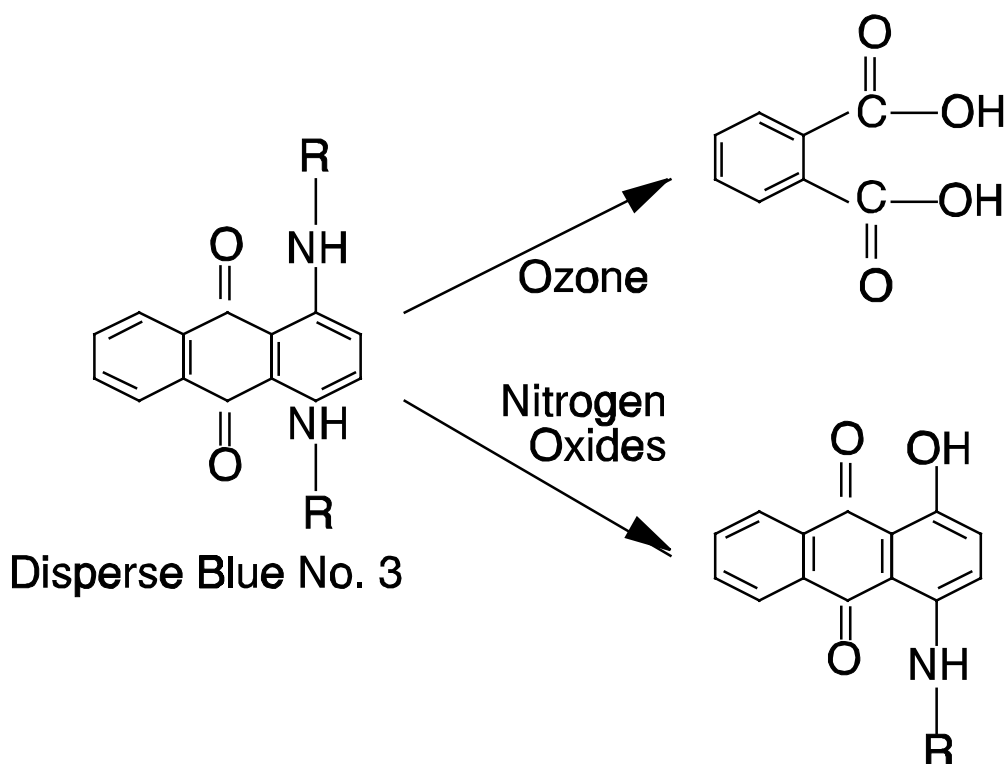
In addition to reactive antiozonants, paraffinic and microcrystalline waxes are used to protect the elastomers in rubber products such as tires. The wax migrates to the surface of the rubber and forms a barrier against  $O_3$  attack. Dimauro et al. (1979) studied the ability of 18 waxes to protect rubber against degradation from  $O_3$ . 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  $O_3$  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  $O_3$  (Zeronian et al., 1971); however, it is difficult to distinguish  $O_3$ -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  $O_3$  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  $O_3$  concentrations are usually less than outdoor  $O_3$  concentrations (Yocom et al., 1986). Accordingly, the economic significance of  $O_3$  damage to textile fibers is relatively low, and the differences in the mechanisms of attack are not important.

Many textile dyes react with  $O_3$ . Figure 5-38 illustrates the reaction of Disperse Blue No. 3 with  $O_3$  and with  $NO_x$  (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  $O_3$  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  $O_3$  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  $O_3$  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)

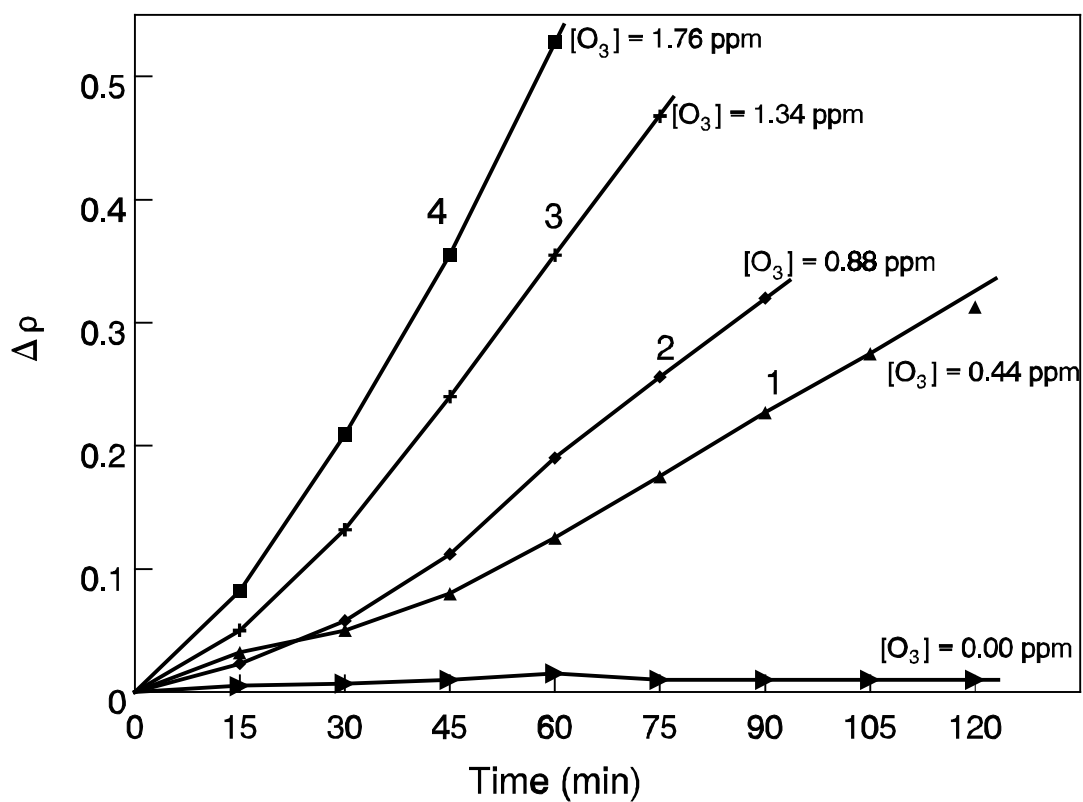
<sup>a</sup>See Appendix A for abbreviations and acronyms.

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 °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 °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.*

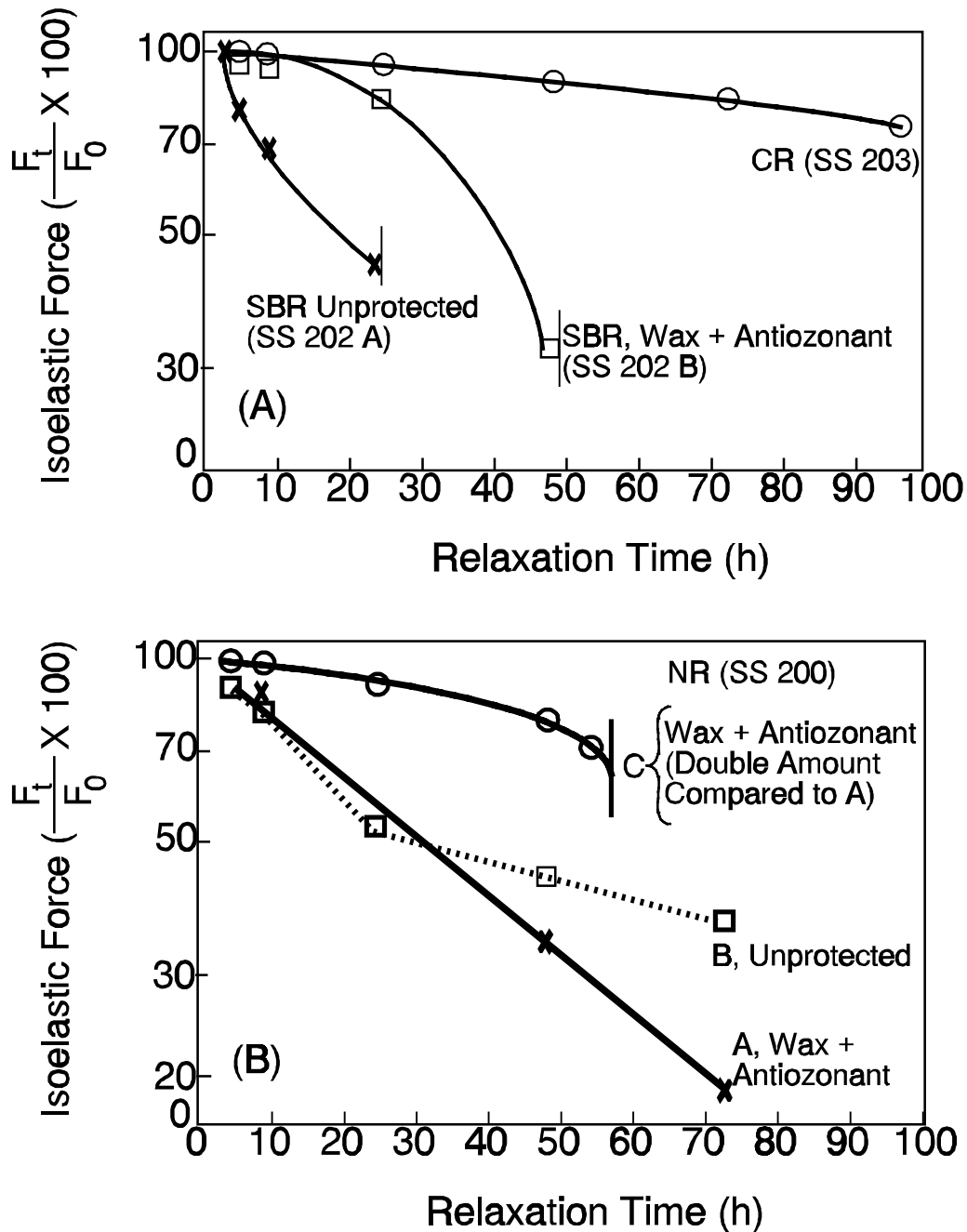
Source: Razumovskii et al. (1988).

**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  $O_3$  on adhesion of tire cords dipped in resorcinal-formaldehyde latex (RFL). Many fibers and dip formulations were studied to determine their sensitivity to  $O_3$ , humidity,  $NO_2$ , UV light, and heat. Wenghoefer exposed these materials at a constant temperature of 100 °F (37.8 °C) to  $O_3$  levels that varied between 0 and 1.5 ppm (0 and 2,940  $\mu g/m^3$ ) 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  $O_3$ , humidity, UV light, and heat. The adhesion losses from  $O_3$  and the combined effects of  $O_3$  and humidity were most notable in the first 6 h of exposure. The detrimental effects of heat,  $NO_2$ , and the synergistic interaction of  $NO_2$  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  $O_3$ . Although  $NO_2$  was originally identified as the pollutant most important to color fading, the effects of  $O_3$  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  $O_3$  on dyes. By using a combination of laboratory chamber studies and outdoor exposures, Salvin and Walker (1955) demonstrated that  $O_3$  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  $O_3$ . 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  $O_3$  fading, thus providing additional evidence of the effects of  $O_3$  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  $O_3$  concentrations.

Ajax et al. (1967) also exposed the fabrics to irradiated and nonirradiated auto exhaust, with and without  $SO_2$ , 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  $SO_2$ , 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  $O_3$  itself are easily substantiated in the research literature, the  $O_3$  levels measured in their test chamber are questionable. The daily 9-h average  $O_3$  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  $O_3$  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  $O_3$  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  $O_3$  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  $O_3$ . After exposure for 7 days, Zeronian and co-workers found that  $O_3$  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  $O_3$  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  $O_3$  and other pollutants ( $NO_x$ ,  $SO_2$ , 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  $O_3$  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  $O_3$ . It was not possible to statistically isolate the effects of  $O_3$  exposure from other pollutant exposures for the samples in these tests; thus other factors besides  $O_3$  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  $O_3$  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  $O_3$  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  $O_3$  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  $O_3$  on synthetic fibers. Thus, it appears that  $O_3$  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  $O_3$  exposure,  $O_3$  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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>; the threshold O<sub>3</sub> 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<sub>3</sub> exposure.

An additional complication is that repair, replacement, and substitution are frequently dominated by factors unrelated to O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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."