United States
Environmental Protection
Agency

Environmental Criteria and
Assessment Office
Research Triangle Park NC 27711

June 1984
External Review Draft C.1

Research and Development

EPA

Air Quality Criteria for Ozone and Other Photochemical Oxidants

Review Draft

(Do Not Cite or Quote)

Volume III of V

NOTICE

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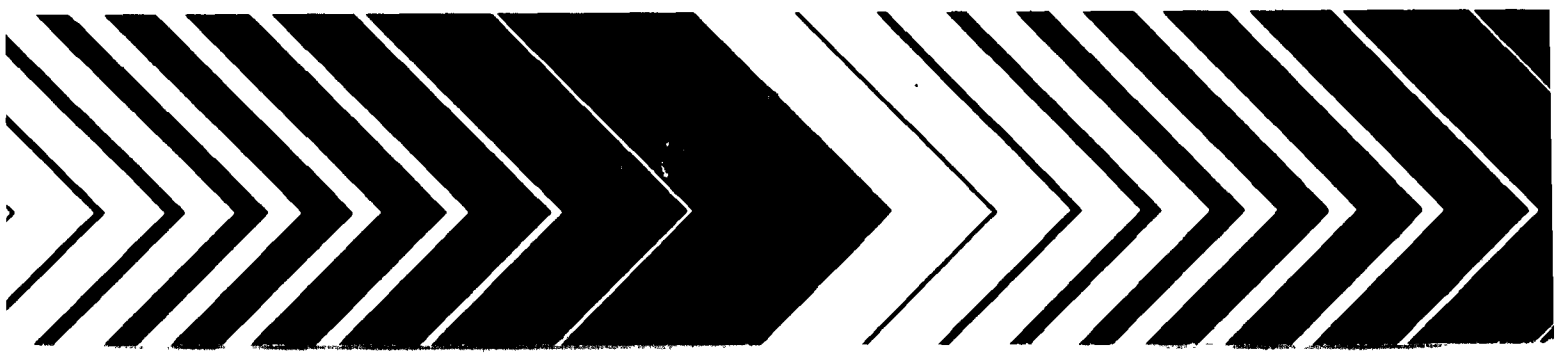

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EPA-600/8-84-020A
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Air Quality Criteria for Ozone and Other Photochemical Oxidants

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ABSTRACT

Scientific information is presented and evaluated relative to the health and welfare effects associated with exposure to ozone and other photochemical oxidants. Although it is not intended as a complete and detailed literature review, the document covers pertinent literature through 1983 and early 1984.

Data on health and welfare effects are emphasized, but additional information is provided for understanding the nature of the oxidant pollution problem and for evaluating the reliability of effects data as well as their relevance to potential exposures to ozone and other oxidants at concentrations occurring in ambient air. Separate chapters are presented on the following exposure-related topics: nature, source, measurement, and concentrations of precursors to ozone and other photochemical oxidants; the formation of ozone and other photochemical oxidants and their transport once formed; the properties, chemistry, and measurement of ozone and other photochemical oxidants; and the concentrations of ozone and other photochemical oxidants that are typically found in ambient air.

The specific areas addressed by chapters on health and welfare effects are the toxicological appraisal of effects of ozone and other oxidants; effects observed in controlled human exposures; effects observed in field and epidemiological studies; effects on vegetation seen in field and controlled exposures; effects on natural and agroecosystems; and effects on nonbiological materials observed in field and chamber studies.

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

7. EFFECTS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS ON VEGETATION

7.1 INTRODUCTION

The effects of photochemical oxidants on vegetation were first observed more than three decades ago in plants growing in localized areas of Los Angeles County, California (Middleton et al., 1950). Foliar injury on vegetation was one of the earliest and most obvious manifestations of the occurrence of photochemical oxidant air pollution. Symptoms reported by Middleton et al. (1950) included the glazing, silvering, and bronzing of lower leaf surfaces, and the development of transverse bands of injury on leaves. Subsequently, Taylor et al. (1960) showed that the injury reported by Middleton et al. (1950) was caused by an unidentified component of smog known only as "compound X" (Stephens et al., 1956). In 1960, Stephens et al. identified the compound as peroxyacetyl nitrate (PAN), a minor but potent phytotoxicant present in photochemical smog (see Chapters 5 and 6).

Injury to vegetation caused by O_3 is distinguishable from that caused by PAN. The first characteristic O_3 injury observed in the field was reported as "oxidant" stipple on grape vines (Richards et al., 1958). Similar symptoms in tobacco as the result of O_3 exposure were reported subsequently by Heggestad and Middleton (1959). Though these early reports were of vegetation injury in the oxidant-polluted urban atmosphere of Los Angeles and its environs, it is now recognized that vegetation at rural sites may be injured by O_3, as well as PAN, transported long distances from urban centers (Edinger et al., 1972; Heck et al., 1969; Heck and Heagle, 1970; Kelleher and Feder, 1978; Miller et al., 1972; Skelly et al., 1977; Skelly, 1980; see also chapters 4 and 6).

An analysis of photochemical oxidants in the ambient air has revealed several phytotoxic components including NO_2, O_3, and the peroxyacyl nitrates. The phytotoxicity of nitrogen oxides is discussed in Air Quality Criteria for Oxides of Nitrogen (U.S. Environmental Protection Agency, 1982). Ozone, the most prevalent photochemical oxidant, has been the most studied and its effects are best understood. Ozone affects vegetation throughout the United States, impairing crop production and affecting native vegetation and ecosystems more than any other air pollutant (Heck et al., 1980). On a concentration basis, however, the peroxyacyl nitrates are the most phytotoxic photochemical oxidants, but they are less widely distributed than ozone and generally occur at lower concentrations than ozone. The peroxyacyl nitrates are a homologous series of compounds, several of which have been detected in the atmosphere. The most abundant member

of this series, and often the only one detected in the atmosphere, even in urban areas, is PAN. It has also received more study than the other peroxyacyl nitrates. The data in this chapter therefore focus primarily on the effects of PAN on vegetation rather than on the effects of other peroxyacyl compounds. Other phytotoxic compounds associated with the photochemical complex may occur in the atmosphere, but the effects of such compounds on vegetation have received very limited study and are not discussed in this chapter.

The effects of O_3 and PAN on terrestrial vegetation may be envisioned as occurring at several levels, ranging from the molecular to the organismal, and then to the ecosystem level (Figure 7-1). The occurrence and magnitude of the vegetational effects depend on the concentration of the pollutant, the duration of the exposure, the length of time between exposures, and the various environmental and biological factors that influence the response. The earliest observable physiological effects include altered membrane permeability, decreased carbon dioxide fixation (photosynthesis), and altered stomatal responses. These initial physiological changes are followed by inactivation or activation, or both, of specific enzymes, changes in metabolite pools, and alterations in the translocation of photosynthate. Biochemical changes within the plants are often expressed as visible foliar injury, premature senescence, increased leaf abcission, and reduced plant growth and vigor. These changes at the individual plant level lead to altered reproduction, changes in competitive ability, or reduction of plant vigor. They subsequently are manifested by changes in plant communities and, ultimately, change in ecosystems. The sequence of topics in this chapter, which describes the effects of photochemical oxidant on plants, is based on the logical hierarchical ordering of plant responses depicted in Figure 7-1. The complexities of the entire subject are apparent in the sections on factors affecting plant response and exposure-response relationships. Effects on terrestrial ecosystems are discussed in Chapter 8.

The linkages relating altered biochemical processes, foliar injury, and plant yield are not well understood. Likewise, no clear relationship exists between foliar injury and reduced plant yield for species in which the foliage is not part of the yield. The previous criteria document (U.S. Environmental Protection Agency, 1978) focused primarily on the effects of O_3 on physiological processes, foliar injury, and plant growth and attempted to summarize the literature by presenting limiting values (i.e., those concentrations below

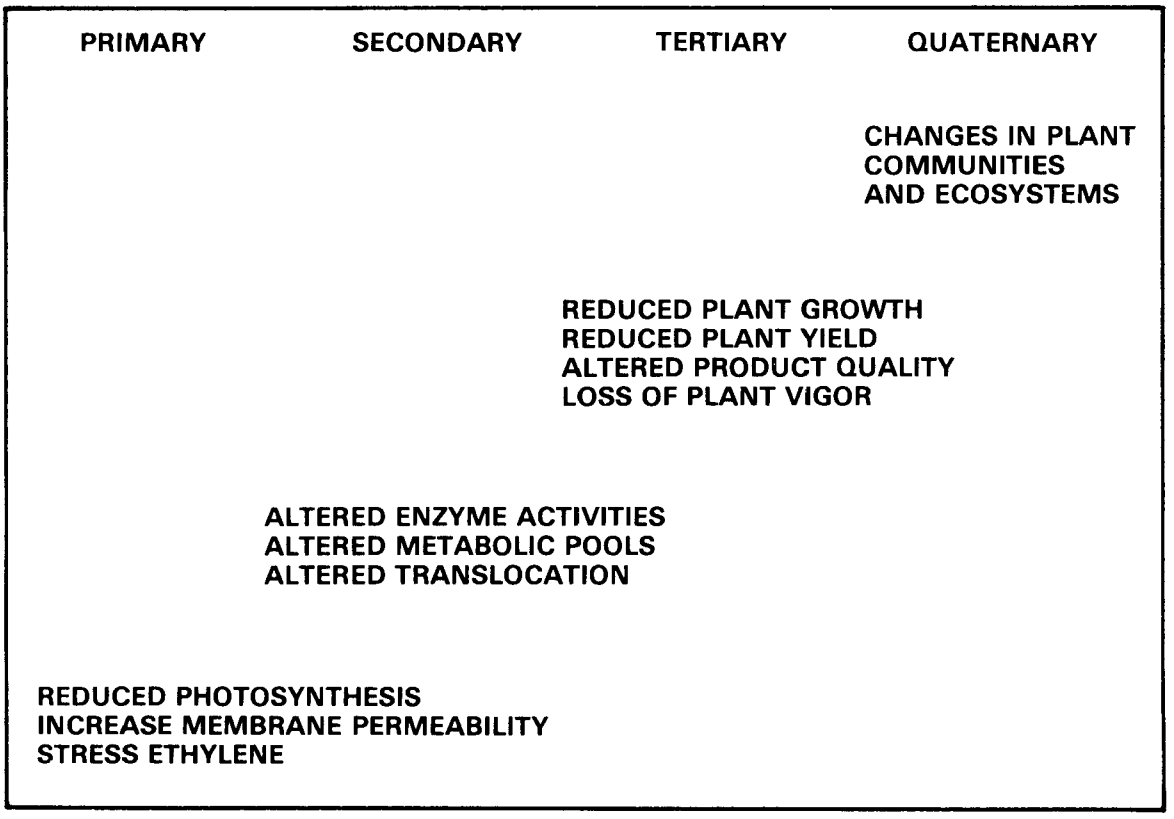

Figure 7-1. Conceptual sequence of ozone-induced responses. Source: U.S. Environmental Protection Agency (1978).

which foliar injury and, presumably, reduced growth and yield would not occur). In this document, the results of previous work on physiological processes and effects on foliar injury and growth will be briefly summarized, with major emphasis placed on the effects of photochemical oxidants on the intended use of the plant. Such effects are those that have impact on the yield, quality, and aesthetic value.

The number of scientific reports on the effects of photochemical oxidants on vegetation has increased rapidly since the early 1950's. In reviewing this extensive literature for the present revision, key references were selected for in-depth examination. For the most part, materials selected for review were publications that have appeared since the preparation of the 1978 criteria document. Earlier information considered fundamentally important is discussed and related to more recent studies. All primary references that relate exposure-response information to yield loss or crop loss were cited directly, regardless of their citation in the 1978 criteria document. In this revision, crop loss refers to economic loss and yield loss relates to reduction in the quality, quantity, aesthetic value, or intended use of the crop. Generally, the papers cited included only published material that had undergone scientific review.

Emphasis has been given to those studies that used pollutant concentrations similar to those that occur in the ambient air of the United States. On this basis, studies in which the lowest concentrations of O_3 or PAN exceeded 1.0 ppm or 200 ppb, respectively, were not included unless the paper contained unique data; e.g., documentation of a mechanism involved in a specific response. In addition, when discussing exposure-response effects of O_3 and PAN on plant yield, the primary emphasis has been given to those studies reporting effects at concentrations below 0.25 ppm for O_3 and 40 ppb for PAN. (These units have been used in the majority of the vegetational studies cited; conversion factors are: 1 ppm O_3 = 1960 $\mu g/m^3$ and 1 ppb PAN = 4947 $\mu g/m^3$.) The scientific names of the plants cited in this chapter are listed in Appendix A.

Data used in the development of this criteria document were derived from a diverse range of studies that were conducted to determine the effects of O_3 and PAN on various plant species and to characterize plant responses. The studies used a range of plant species and various experimental conditions and methodologies. Most important, these studies were generally conducted to test specific biological hypotheses or to produce specific biological data rather than to develop air quality criteria.

This review of the effects of photochemical oxidants on vegetation and the responses of vegetation to photochemical oxidants first discusses the general methodologies used in studies of air pollution effects to provide a basis for understanding the methods, approaches, and experimental designs used in the studies discussed in this chapter. Ozone and PAN are discussed separately, but the discussions of each will follow the same general outline, which includes (1) mode of action of the pollutant; (2) physical, biological, and chemical factors that alter plant response; and (3) primary emphasis on the effects of the individual pollutants on the response of plants to various concentrations and durations of exposure.

7.2 METHODOLOGIES USED IN VEGETATION EFFECTS RESEARCH

This section provides reference information that allows a better understanding of the studies discussed in the remainder of this chapter. The section contains an evaluation of exposure methods, a discussion of the strengths and limitations of various experimental designs and of the statistics used to represent pollutant exposures, and a discussion of the definitions of loss. These discussions emphasize the methodologies used in studies cited in the chapter and do not reflect a general review of scientific literature. Changes in O_3 monitoring techniques, methods of calibration, quality assurance procedures and their possible impacts on measured O_3 concentrations are discussed in Chapter 5.

7.2.1 Experimental Design and Statistical Analysis

The selection of an appropriate experimental design for specific objectives is a critical step in determining the success of a study and the application of the results. The number and kind of factors controlled, the patterns of randomization, and the number of replicates used in an experiment determine what treatment comparisons may be made, whether trends can be plotted and curves fitted, the precision of estimates, and the range of conditions over which inferences may be made. An experimental design focuses an experiment on its specific objectives, but in doing so, limits the application of the results. No experimental design has universal application.

Most experiments use traditional experimental designs amenable to the analysis of variance, such as randomized-block and split-plot designs. When

used in conjunction with treatment mean separation techniques, these designs produce descriptive results that allow comparison of different treatments. There are many different treatment mean separation techniques available, such as Tukey's paired comparison procedure, Duncan's multiple range test, and Dunnett's test for comparing several treatments with a control. The tests all give slightly different results and have different powers. Some statisticians recommend careful inspection of the treatment averages in relation to a reference distribution in addition to or in place of formal multiple comparisons (Box et al., 1978). Few studies have attempted to partition interactions or to analyze slope and curvature trends. In factorial experiments with more than two factors, it has often been difficult to interpret the interactions fully.

Regression analyses are useful for many objectives, including the development of empirical models. Care must be taken, however, to ensure that there is no systematic deviation of the model from the observed data and to recognize that, in general, results cannot be extrapolated beyond the range of pollutant (e.g., ozone) concentrations used to construct the model. Both model validation (the testing of model fit to the experimental data) and applications validation (testing the application of the model to a new population) are appropriate precursors to model use.

In an experiment in which quantitative treatments are used and the treatments have been replicated, both analysis of variance and regression analysis may be used to analyze the data. The traditional approach is to use analysis of variance to estimate the error variance and to determine whether there are any differences among treatments; and then to break down the treatment effect into regression components to test whether there are any linear or quadratic trends as the treatment level changes (Cochran and Cox, 1957; Anderson and McLean, 1974). This is equivalent to doing analysis of variance followed by regression analysis. If a linear or quadratic equation does not fit the data well, or if there is a theorized functional relationship between treatment and response, nonlinear models may be fitted to the data at this point. Because each mathematical function can assume only a limited range of shapes, it is important to check for systematic lack of fit of the data. Ideally, confidence bands would be provided with regression curves to show the variability of the fitted curves. Confidence bands, however, are frequently omitted from research papers because their computation is complicated and because it is difficult to show more than one curve in a figure if confidence bands are

included. When confidence bands are not provided but results from similar experiments are available, the reader can obtain an idea of the variability of estimates by looking at the distribution of estimates from similar experiments. This variability encompasses sources of error beyond a single experiment.

In most of the papers cited in this document, confidence bands for dose-response curves were not provided. A 10 percent loss was considered to be a significant agricultural loss; that is, one that would be important to a grower. Therefore, a table of estimates from regression models of the O_3 concentration at which a 10 percent yield loss would occur for all the cultivars and species studied is included in the summary so that the reader can examine the range of estimates. On each graph of a fitted curve, the treatment means are also plotted. More than one model was fitted to the data in some cases. The reader may compare the results from the various models and observe whether there is a systematic lack of fit between the data and the curve. If a deviation is observed, the O_3 estimates may be biased.

The regression curves used in this document have either been calculated from the original observations or from treatment means. This distinction is noted in the figure legends whenever the method used is known. If the treatment means are used rather than the original observations in a linear regression and there are equal numbers of observations in each treatment, the results will be as follows: (1) the regression coefficients and estimated values will be the same as if individual points had been used; (2) the coefficient of variation (R^2) will be greater than or equal to the R^2 from individual points; and (3) the variance of the regression coefficients will be about the same as that computed from individual points if the variation of the means around the line is similar to the variation of individual points around the treatment means.

7.2.2 Exposure Characteristics

The occurrence of pollutants in the ambient environment is influenced by many variables (see Chapters 3 and 4). Periods of significant air pollutant episodes occur when meteorological conditions, pollutant precursors, and other environmental conditions coincide. Ozone and PAN episodes usually occur during the plant-growth season (Chapter 6). The episodes may vary in duration from one to several days and occur at varying times of the day (Chapter 6). Research has not yet clearly defined which components of an exposure are most

important in causing vegetation responses. The characterization and representation of plant exposure to air pollutants has been and continues to be a major problem. An appropriate summary statistic for one exposure duration usually cannot be easily transformed to describe a different exposure duration without access to the original aerometric data. In addition, statistics used to represent extremely short exposures cannot be readily aggregated to provide a representative summary statistic for plant responses resulting from an extended exposure (for example, a growing season).

7.2.2.1 Statistics Used to Characterize Seasonal Exposures. To define the problems associated with characterization and representation of plant exposures necessitates consideration of the temporal resolution required. When plant yield is considered, the ultimate impact of an air pollutant on yield depends on the integrated impact of the pollutant exposures during the growth of the plant. In this case, the temporal unit of interest becomes the plant growing season, which varies with the geographic location, plant species, and cultivar of interest. This period may be as short as 3 to 4 weeks for a crop such as radish or as long as years for perennial plants such as trees. Plants may be affected by exposures at several growth stages before harvest. Only a few studies have investigated the influence of plant growth stage on plant response to O_3. Studies with white beans in areas affected by photochemical oxidants indicated that crop maturity (plant growth stage) regulates the time of symptom expression and that crop vigor regulates the severity of the symptom (Haas, 1970). Petunia hybrids were less sensitive to O_3 after the flower bud differentiated (Hanson et al., 1975). Ozone reduced radish hypocotyl growth the most if the exposure occurred during the period of rapid hypocotyl growth (Tingey et al., 1973a). A single exposure to ozone produced a 37 percent reduction in hypocotyl growth in 14-day-old plants but less growth reduction in younger or in older plants.

If it is necessary to characterize the temporal distribution of exposures within a growing season to characterize a plant response adequately, it is questionable whether the current exposure statistics used by researchers are adequate. Such regimens do not characterize the effects of pollutant episodes at specific and perhaps critical periods during plant growth. Statistics used to describe cumulative seasonal exposures, such as a seasonal mean, do not characterize the temporal distribution of the exposures within the season. Lognormal (Larsen and Heck, 1976) and two-parameter Weibull (Georgopoulos and

Seinfeld, 1982) functions have been utilized to characterize seasonal exposures. These distribution functions are fitted to the frequency distribution of O_3 concentration for the season without regard to their temporal order and therefore these functions, as well, do not characterize episodes within the season. Percentiles (number of hours at a given concentration range) (McLaughlin et al., 1982) can also be used to summarize the seasonal distribution of concentrations but these likewise provide no means of characterizing when within a season these episodes occur. The use of means (Heck et al., 1982a) (averages of concentrations over specific time periods) and cumulative dose (Oshima et al., 1977 a,b) also ignores the episodic nature of seasonal exposures. Other exposure representations based on a seasonal average time suffer from similar inadequacies. The difficulty of selecting an appropriate statistic to characterize plant exposure has been summarized by Heagle and Heck (1980). Ambient and experimental O_3 exposures have been presented as (1) seasonal, monthly, weekly, or daily means; (2) peak hourly means; (3) number of hours above a selected concentration; or (4) number of hours above selected concentration intervals. None of these statistics adequately characterizes the relationships between ambient O_3 concentration, exposure duration, and plant growth stages.

Until further research defines the influence on plant responses of temporal fluctuations in ozone concentrations, which is characteristic of exposures to ambient air, the selection of a summary statistic that characterizes ozone exposures will continue to be discretionary. Unfortunately, the existing summary statistics cannot be directly compared. Each is the result of calculations from the original aerometric monitoring data and cannot be transformed to another exposure statistic without the expensive and laborious task of returning to the original data. Therefore, comparisons among studies that use different summary statistics are difficult.

7.2.2.2 Statistics Used to Characterize Short Exposures. An experiment that focuses on foliar injury or any other relatively short-term response may only require short periods of exposure, which can be characterized by a simple exposure statistic. When such results are evaluated, a problem occurs only if the results of the short-term exposure experiment are extrapolated to evaluate their significance in relation to long-term exposures. Mean and dose (concentration times time) statistics from short-term exposures usually cannot be aggregated to be representative of the temporal dynamics of long-term exposures.

Although most short-term exposures are described by a concentration and duration or dose, scientists point out that the correct exposure representation is the amount of pollutant entering the plant, not the ambient air concentration to which it is exposed (Taylor et al., 1982a; Tingey and Taylor, 1982). Plants are affected only by the O_3 or PAN that diffuses into the leaves. It is difficult, however, to measure or quantify the relationship between the concentration of pollutant in the air and the internal pollutant flux because of the interactive effects of environmental and biological variables unique to a specific set of environmental conditions. An interactive model that requires variables describing the exposure, environmental condition, and species would be necessary to relate internal pollution flux to ambient air levels.

7.2.2.3 Exposure Statistics. When pollutant concentrations exceed a given level for a specific time period, plants will be affected by O_3. Studies with beans and tobacco (Heck et al., 1966) showed that a dose over a short time period (concentration times time) induced more injury than the same dose distributed over a longer time period. Studies with tobacco showed that O_3 concentration was approximately twice as important as exposure duration in causing foliar injury (Tonneijck, 1984). In this study, plants were exposed to a range of O_3 concentrations (0.02 to 0.15 ppm) for 8 hr/day for 1 to 7 days. In beans foliar injury developed when the internal O_3 flux exceeded 5500 $\mu g/m^2$ in 1 hr (Bennett, 1979). However, a single 3-hr exposure at approximately half the concentration (0.27 compared to 0.49 ppm) required approximately a 64% greater internal O_3 flux to cause the same amount of foliar injury as the 1-hr exposure. The greater importance of concentration compared to exposure duration has been reported by many authors (e.g., Heck and Tingey, 1971; Henderson and Reinert, 1979; Reinert and Nelson, 1979).

Not only are concentration and time important but the dynamics of the O_3 exposure are also important; that is, whether the exposure is at a constant or variable concentration. Musselman et al. (1983) recently showed that fixed concentrations of O_3 cause the same pattern of responses as variable concentrations at the equivalent dose. Fixed concentrations, however, had less effect on plant growth responses than variable concentrations at similar doses. Exposures of radishes to ambient O_3 in open-top exposure chambers showed that significant yield reductions occurred when the maximum O_3 concentration exceeded 0.06 ppm at least 10% of the days when the crop was growing (Ashmore, 1984). Field studies with soybeans showed that reduced yield (weight/seed)

was most closely correlated with the number of O_3 peaks in excess of 0.10 ppm (Pratt, 1982). Similar results were previously reported for sulfur dioxide (SO_2) (McLaughlin et al., 1979; Male et al., 1983). These results suggest that the mechanisms causing the response are the same, but that exposures to fixed concentrations underestimate the magnitude of plant growth responses.

The observations that the nature of the exposure influences plant response is supported by other types of studies--for example, the study by Walmsley et al. (1980) in which they exposed radishes to O_3 continuously. During the study period, the plants acquired some O_3 tolerance. The acquired tolerance displayed two components: (1) the exposed plants developed new leaves faster than the controls and (2) there was a progressive decrease in the sensitivity of the new leaves to O_3. The newly formed leaves displayed a slower rate of senescence. The observations by Elkiey and Ormrod (1981) that the O_3 uptake decreased during a 3-day study period may provide an explanation for the results with radish. Other research has suggested that plants exposed to low levels of O_3 become more sensitive to subsequent exposures. For example, studies with soybean (Johnston and Heagle, 1982), tobacco (Heagle and Heck, 1974) and bean (Runeckles and Rosen, 1977) showed that plants exposed to low levels of O_3 for a few days became more sensitive to a subsequent O_3 exposure.

Currently, there is no consensus as to the most appropriate summary statistic for representing plant exposure to photochemical oxidants. Consequently, many different statistics are used, making direct comparisons between studies extremely difficult. Further, there is some question as to the adequacy of statistics used to characterize long exposures (season), since they do not consider exposure dynamics within the period being represented. This question cannot presently be resolved because research to date has not clearly determined whether stages of plant growth are differentially sensitive to exposures relative to ultimate yield.

7.2.3 Exposure Systems

Research methods can be organized according to the means by which exposures or environmental variables are controlled or characterized. Air pollution research often requires exposure chambers or other apparatus to maintain controlled pollutant exposures. Exposure systems may range from sophisticated, microprocessor-controlled cuvettes (Bingham and Coyne, 1977; Legge et al., 1979) to a series of tubes with calibrated orifices spatially distributed over

a field to emit gaseous pollutants (Lee et al., 1978). Each of the types of systems was designed for specific objectives and operates most efficiently under the conditions for which it was intended. Each has advantages and limitations and must be evaluated in terms of the objectives each was designed to meet.

The exposure systems discussed in this section share many common characteristics. Each uses a monitoring system that measures pollutant levels continuously during exposures or that incorporates a time-sharing system that sequentially measures concentrations in chambers or at field sites. The systems normally use inert Teflon tubing for sampling lines and continuous air flow to reduce time lags. Additionally, many systems use EPA-approved monitoring and detection systems (see chapter 5 for EPA equivalent and Federal reference methods). Recently, quality assurance programs were included in several studies to ensure that high quality, standardized air monitoring data will be available and readily comparable. The air pollutants are either generated artifically and dispensed to exposure chambers or field plots, or proportional activated-carbon filtration is used to provide different levels of ambient pollutants.

The systems described in this section represent significant advances in the methods used in air pollution research on vegetation. As systems that utilize the latest technological advances evolve, it is easy to be caught in the rapid progress of their evolution and lose sight of their limitations. Even the most sophisticated and advanced systems are only as good as the researcher who uses them. They do not insure that the research results will be of superior quality. They only provide the potential for understanding better the impact of air pollutants on vegetation.

The following discussion is limited to exposure systems used in air pollution research and is not meant to be a detailed description of the system components. These systems are described in greater detail in original publications and review articles (i.e., Heagle and Philbeck, 1979).

7.2.3.1 Laboratory Systems. Laboratory systems (Tingey et al., 1979; Winner and Mooney, 1980) typically employ artificial lighting and controlled environments. Most are designed to identify and measure effects ranging from the subcellular to the whole-plant level of biological organization. Although results from these systems are difficult to relate directly to field studies, they do contribute to an understanding of the mechanisms involved with air

pollution effects. They provide useful information in explaining or interpreting responses. The stability of the well-controlled environmental conditions characteristic of most laboratory systems allows precise measurement of an array of plant responses. By altering only one variable and holding others constant, one can define well and more easily understand responses. These systems are powerful tools for increasing the understanding of the effects of pollutants on the biological processes basic to plant growth.

The greatest drawback of laboratory systems relates to the general applicability of final results. The precise environmental conditions that make the systems valuable for defining responses also make the laboratory systems artificial. In comparison, ambient environmental conditions are complex and dynamic.

7.2.3.2 Greenhouse Exposure Systems. Greenhouse systems are generally used in studies to identify and quantify physiological, growth, and yield responses at the organ and whole-plant level of biological organization. Plants are usually grown in containers in greenhouses with charcoal-filtered air. Exposures are conducted under natural or artificial lighting within chambers in the greenhouse. Plants may be physically moved in and out of exposure chambers and allowed to grow on greenhouse benches during interim periods. Normally, a single plant or small groups of plants constitute the experimental unit. While the environmental conditions of greenhouse exposure systems may more closely approximate field than laboratory conditions, the plant cultural conditions are more similar to those used in laboratory studies. Although related to field studies, greenhouse studies differ sufficiently to make direct extrapolations to field conditions difficult. It must be remembered, however, that greenhouse conditions are the typical cultural environment for many floriculture and ornamental plants. In this case, the use of greenhouse conditions is appropriate and no extrapolation is necessary.

Greenhouse exposure systems usually consist of a series of chambers built with a framework of various materials and covered with a transparent film. The air exchange systems normally use a negative pressure, single directional air flow, and employ an activated-charcoal filtration device at both air entry and exhaust. Early systems were usually modifications of the system developed by Heck et al. (1968), but a variety of designs were utilized. These systems were all designed to meet common, desirable chamber characteristics (uniform pollutant concentrations with minimal environmental alteration) and succeeded

to varying degrees. The design of the continuous stirred-tank reactor (CSTR) by Rogers et al. (1977) stimulated the development of exposure systems that incorporated its desirable mixing properties and the use of FEP Teflon® film as an inert polymer film.

7.2.3.3 Field Exposure Systems. To assess economic impact or agricultural productivity, it is desirable to minimize deviations from the ambient environment and to simulate as closely as possible the conditions characteristic of agricultural systems or natural ecosystems. Field exposure systems range from adaptations of the greenhouse and laboratory chamber designs to the use of chemical protectants. In most greenhouse and field studies, the investigators have attempted to ensure that soil moisture, plant nutrients, and other cultural conditions did not limit growth.

7.2.3.3.1 Field Chamber Systems. The open-top chamber system (Heagle et al., 1973; Mandl et al., 1973) is the most popular field-exposure system presently in use. Essentially upright cylinders with a clear polymer film as a covering around the sides, these chambers have the advantage of portability, moderate cost, and ease of maintenance. The size and shape of the chambers may be modified for use with different plant types and sizes. The system uses a high-volume flow of filtered air to reduce ambient pollutant influx through the open top. Pollutants are added to the incoming air stream. Their rate of addition is adjusted to control the pollutant concentration in the chambers. Pollutants are usually measured just above canopy height. Studies of the O_3 distribution within the chambers have shown it to be quite uniform. The vertical variation of O_3 in the 2.44-m-high chambers was less than 6 percent between 0.3 and 1.2 m and less than 19 percent between 1.2 and 1.8 m. The horizontal variation over the 7.3 m^2 of the chamber was 12 percent and 14 percent at heights of 1.2 and 1.8 m, respectively (Heagle et al., 1979d). The portability of the system facilitates storage and maintenance during the winter or in periods of inactivity and allows standard agricultural practices to be carried out during field preparation, seeding, and early crop growth before chambers are set in place. Open-top chambers and well-ventilated closed-top chambers reduce temperature deviations from the ambient, allow sufficient pollutant control for either single or mixed-gas exposures, and are relatively inexpensive. They can be selectively placed in established fields to avoid unacceptable soil types or to maximize soil uniformity in treatments.

Most of the limitations of open-top chambers relate to air flow characteristics. Air flowing from the lower portion of the chamber out through the open top reduces the intrusion of outside air; this air flow pattern is different, however, from that in the open field. Because plants in the chamber experience a different air flow pattern than field-grown plants, concerns have been expressed that this might alter the influence of O_3 on plants. However, recent measurements of canopy resistance to O_3 uptake in open-top chambers by micrometeorological methods in the field yield similar results 73 and 84 s m^{-1}, respectively (Unsworth et al., 1984). This similarity led the authors to conclude that crop exposure to gaseous pollutants in open-top chambers is similar to that which would occur at the same concentrations in the field. With open-top exposure chambers some intrusion of ambient air through the chamber top is unavoidable, which can influence the concentration within the chamber (Heagle et al., 1973; Unsworth et al., 1984). The amount of intrusion increases with wind speed. Recent design innovations, however, have minimized this (Kats et al., 1976; Davis and Rodgers, 1980). For example, the addition of a frustum (a truncated cone) to the top of the open-top chambers can reduce the intrusion of ambient air by approximately 50% and also provided a more reproducible environment for a given wind speed (Unworth et al., 1984). It should be recognized that open-field environmental conditions cannot be exactly duplicated by open-top exposure chambers (Heagle et al., 1979d; Olszyk et al., 1980) or any other pollutant exposure system presently available. In summarizing studies of open-top exposure chambers, Heagle et al. (1979d) reported,

> In our 7-yr experience, the open-top chambers caused plants to grow slightly taller but rarely had significant effects on yield. Plants often grew differently in different parts of the chambers but we did not find significant interactions between chamber position and the effects of O_3. The causes for chamber-induced growth effects may be related to slower mean air velocity, slightly higher temperature, or less light at some chamber locations than in the open.... There are no reports, however, that environmental changes of the magnitude caused by open-top chambers change plant sensitivity.

Other field-exposure systems use chambers of varying design, but have the common characteristic of being fully enclosed by film (Thompson and Taylor, 1966; Oshima, 1978). These designs rely on high air-exchange rates to minimize temperature alterations. Most of these designs are adaptations or alterations of greenhouse exposure systems. Chamber shapes range from a square design

originally developed by Heck et al. (1968), to the CSTR cylinder described by Rogers et al. (1977).

7.2.3.3.2 Field Exposure Systems without Chambers. The desire to expose large field plots to increase sample size and to remove environmental alterations caused by enclosing plants in chambers led to the development of chamber-free field exposure systems. The advantage of these systems (Lee et al., 1978; deCormis et al., 1975; Reich et al., 1980; Laurence et al., 1982) is that plants are exposed to pollutants under conditions similar to the ambient. This advantage is offset to some extent by the disadvantage of losing some control over the level of pollutants and the nature of the exposure. These systems are highly influenced by wind speed direction, and are subject to ambient air levels. There have been only limited O_3 studies in these types of systems.

7.2.4 The National Crop Loss Assessment Network

The National Crop Loss Assessment Network (NCLAN) was initiated in 1980 by EPA to estimate the magnitude of national crop losses caused by air pollution. Initial emphasis was placed on O_3 (Heck et al., 1982). A research management committee is responsible for the planning, management, and execution of the program. The primary objectives of the NCLAN are:

1. To define the relationships between yields of major agricultural crops and O_3 exposure as required to support the needs of the economic assessments and the development of NAAQS;
2. To assess national economic consequences resulting from the exposure of major agricultural crops to O_3; and
3. To advance the understanding of the cause and effect relationships that determine crop responses to pollutant exposure.

NCLAN is a network of experimental field sites selected for (1) their different climatological conditions, (2) their distribution of different crop species, and (3) their proximity to established research groups with a history of research on air pollutant effects on vegetation. The test species are grown in the field under conditions approximating standard agronomic practices. Efforts are made to minimize perturbations of the plant environment from the exposure apparatus and to use realistic pollutant doses.

The pollutant concentrations around crop plants in the field are controlled and manipulated through the use of open-top chambers. Sufficient numbers of chambers permit replicated experimental designs; this also permits the development of empirical dose-response models. Models for test species and cultivars are developed from data for several sites and for several years.

Within the open-top chambers, plants are exposed to a range of ozone concentrations. Daily variation in the O_3 concentration is determined in part by changes in ambient O_3 concentrations at each site. The lowest O_3 level (control, charcoal filtered air) is 20 percent to 50 percnet of that in ambient air; the O_3 that is present enters the chamber mainly through the open top, because the inlet air to the chamber is charcoal filtered. All other chambers receive ambient air supplemented (7 hours per day) with enough O_3 to provide concentrations equal to those at field plots and three or four stepwise increments (0.02 to 0.03 ppm) above levels in ambient air. Ozone concentrations within the chambers are measured at canopy height with time-shared monitors. Plant yields are also measured for field plots of identical size exposed to ambient (non-chamber) air to obtain an estimate of potential chamber effects. Chamber fans are operational from 5:00 a.m. to 9:00 p.m. daily, and O_3 is added from 9:00 a.m. through 4:00 p.m. (local standard time) daily throughout the growing season for the crop, except on rainy days.

A quality assurance program for the collection and measurement of air quality and biological data is followed in NCLAN studies. Independent audits of the pollutant monitors are conducted at each site.

The data are analyzed by both analysis of variance and by regression analysis. The mean 7-hour daily concentration (9:00 - 4:00), averaged over the growing season, is used for a seasonal exposure statistic. This is the time period when O_3 is added to the chambers.

NCLAN has many strengths associated with a coordinated national multi-site program. Perhaps its greatest strengths are the standardization of methods for air monitoring, biological assessment, experimental design, pollutant exposure regimes, summarization of exposures, and quality assurance. Additionally, the selection of agriculturally important crops for test species and the use of close approximations of standard cultural practices ensure applicability of experimental results. The development of empirical models interfaces well with required economic inputs for a national economic assessment. Previously, very few biological models were available for economic assessments.

NCLAN has limitations that must also be considered. The potential artificiality of the O_3 exposure treatments may complicate the application of results. Further, the use of the seasonal 7-hour daily mean concentrations, a relatively new exposure summary statistic, makes comparisons with previously published studies difficult. It also does not accurately represent the temporal exposure dynamics of ambient air. The lack of validation of the model predictions is unsettling, but that is a common deficiency of all models to date and is not unique to NCLAN. These limitations may also occur with other field studies.

When viewed in perspective, NCLAN represents the state of the art for documenting yield losses resulting from ozone and for providing compatible data for economic assessments on a national scale.

7.2.5 Determination of Yield and Crop Losses

For the purposes of this chapter, yield loss is defined as reduction in quantity, quality, aesthetic value, or any impairment of the intended use of a plant. Thus, foliar injury on ornamental plants, detrimental responses in native species, and reductions in fruit or grain production by agricultural species are all considered yield loss. Crop loss, in contrast, is defined as an economic or monetary loss and is not synonymous with yield loss. Crop loss occurs at aggregative levels higher than the plant or plot. The transformation of yield loss to crop loss incorporates economic considerations such as those described in section 7.4.2.2.3.

Loss by definition implies some reduction from a reference zero-loss level. When crop yields are considered, one must first establish a reference in terms of quantitative yield units (grams, pounds, tons) and second, one must transform reductions from that level into loss units (usually a proportion, such as percentage). It is necessary to define adequately an appropriate reference level from which loss is determined. When an empirical O_3 yield-loss model is used, the zero-loss reference yield should be representative of the yield in the production area in question in the absence of O_3. The reference zero-loss level can be tested in conjunction with the model validation referred to in section 7.2.1. Zadoks (1980) cites several definitions of yield that can be used as a reference level for both biotic and abiotic crop losses.

7.3 MODE OF OZONE ACTION ON PLANTS

Plant growth and yield are the culmination of many biochemical and physiological processes. Plants absorb carbon dioxide from the atmosphere through portals called stomata. Within the chloroplasts located in the mesophyll cells of the leaf (Figure 7-2), the carbon dioxide is converted into carbohydrates in the presence of light (photosynthesis). Plants absorb the necessary water and mineral nutrients for growth from the soil. Growth and yield depend not only on the rate of photosynthesis and the uptake of water and nutrients, but also on subsequent metabolic processes and the allocation of the photosynthetic products to the rest of the plant. The uptake of carbon dioxide and its subsequent metabolism and allocation within the plant is influenced by various environmental conditions. The impairment of any of these processes may affect plant growth and yield.

The responses of vascular plants to O_3 may be viewed as the culmination of a sequence of physical, biochemical, and physiological events. Ozone in the ambient air is not directly phytotoxic, only the O_3 that diffuses into the plant. A phytotoxic effect will occur only if a sufficient amount of O_3 reaches the sensitive cellular sites within the leaf. The O_3 diffuses from the ambient air into the leaf through the stomata, which can exert some control on O_3 uptake to the active sites within the leaf. Ozone injury will not occur if 1) the rate of O_3 uptake is sufficiently small so that the plant is able to detoxify or metabolize O_3 or its metabolites or 2) the plant is able to repair or compensate for the O_3 impacts (Tingey and Taylor, 1982). The uptake and movement of O_3 to the sensitive cellular sites are subject to various physiological and biochemical controls.

Ozone may diffuse into the leaf through stomata; and it should again be noted that only the O_3 diffusing into the leaf can affect plant growth and yield. Once ozone enters the leaf through stomata it quickly dissolves in the aqueous layer on the cells lining the air spaces. Ozone then diffuses through the cell wall and membrane into the cell, where it may affect cellular or organellar processes. Ozone flux (J) into the leaf may be represented by the following equation (Tingey and Taylor, 1982);

$$J = \Delta C/(R_a + R_s + R_r). \qquad (7\text{-}1)$$

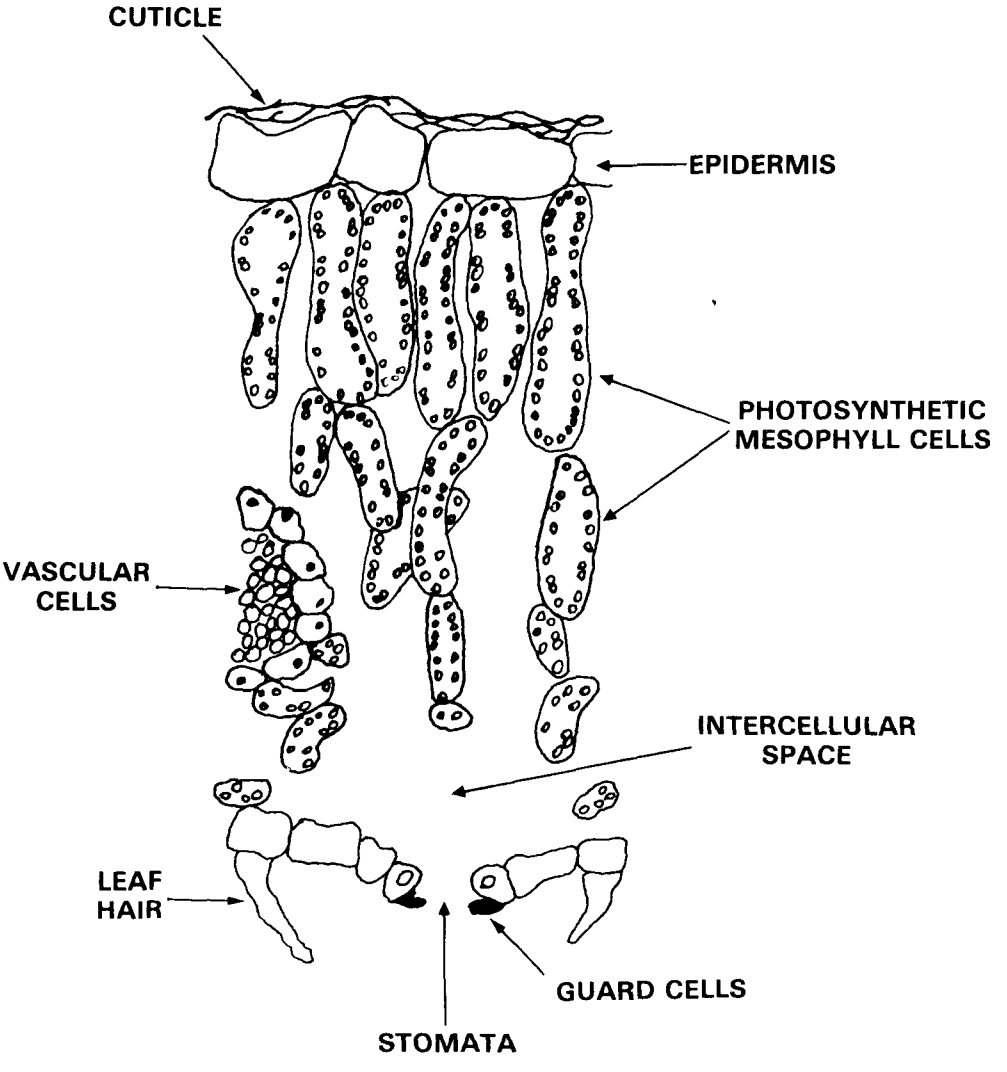

Figure 7-2. Schematic cross section of a typical dicot leaf.

Flux is directly proportional to the change in O_3 concentration (ΔC) between the ambient air and the leaf interior (gas-to-liquid transfer) and is inversely proportional to resistance to the mass transfer of gas. Resistance to O_3 movement can be divided into components, including boundary layer (R_a), stomatal and intercellular space (R_s), and liquid-phase (R_r) resistances.

At any point along this pathway, O_3 or its decomposition products may react with cellular components. Altered cell structure and function may result in changes in membrane permeability, carbon dioxide fixation, and many secondary metabolic processes (Tingey and Taylor, 1982). The magnitude of O_3-induced effects will depend upon the physical environment of the plant, including macro- and microclimate considerations; the chemical environment of the plant, including other gaseous air pollutants and a variety of chemicals; and biological factors, including genetic potential and developmental age of the plant and interaction with plant pests. Cellular injury manifests itself in a number of ways, including foliar injury, premature senescence, reduced yield or growth, or both, reduced plant vigor, and sometimes death. Depending upon the intended use of a plant species (viz., for food, forage, fiber, shelter, or amenity), any of the effects discussed above could impact society adversely.

In the following sections, selected references will be cited to describe how O_3 induces some of its effects. Some of the physiological studies have been conducted with O_3 exposures that would rarely, if ever, be encountered in ambient air. This literature can, however, serve as a tool for identifying the potential sequence of the physiological and biochemical responses of plant species, and for identifying potential metabolic sites of action that may or may not be visibly expressed.

7.3.1 Biochemical and Physiological Responses to Ozone

Phytotoxic effects of air pollution on plant tissue will occur only when sufficient concentrations of a gas diffuse into the leaf interior and pass into the liquid phase of the cells. Once a gas is deposited on a wet cell surface, it may move by diffusion or bulk flow to sites of action, such as the interior of the cell membrane, the cytoplasm, or cellular organelles (Heath, 1980; Tingey and Taylor, 1982).

7.3.1.1 Gas Phase Movement into the Leaf. Ozone, as well as other gases, diffuses from the atmosphere into the leaf through stomata. The stomata

control the rate of O_3 uptake into the leaf and are influenced by various plant and environmental stimuli. A variety of factors, including O_3, have been shown to induce stomatal closure. The previous criteria document (U.S. Environmental Protection Agency, 1978) cited a number of studies that directly correlated O_3 concentration and stomatal closure. Engle and Gabelman (1966) reported that in the presence of O_3 (0.3 ppm for 0.5 hours), stomata closed more quickly in tolerant than in sensitive onion cultivars. Rich and Turner (1972) found that when tobacco plants were exposed to 0.20 to 0.25 ppm O_3 for 2 hours, leaf conductance (a measure of stomatal closure) decreased 32 percent in a resistant cultivar and only 9 percent in a sensitive cultivar (no statistics provided), suggesting possible differences in O_3 uptake between cultivars. More recently, Krause and Weidensaul (1978b) observed that geranium guard cells, which control stomatal opening, ruptured after a 10-day exposure to O_3 at concentrations of 0.15 ppm for 6 hours per day. In contrast, when four cultivars of peas were exposed to an O_3 concentration of 0.15 ppm for 6 hours per day and stomatal conductance was measured, the two more sensitive cultivars had greater decreases in leaf conductance (85 percent and 86 percent) than did the two more tolerant cultivars (62 percent and 69 percent) (Dijak and Ormrod, 1982). Clearly, decreased conductance could not explain differential cultivar tolerance in this case. When they reviewed the O_3 uptake literature, Tingey and Taylor (1982) found examples of species for which the O_3 response was apparently limited by leaf conductance (i.e., O_3 uptake) and species for which O_3 response was not controlled by O_3 uptake but rather by metabolic processes within the mesophyll cells.

Ozone flux into the leaf may also be regulated by stomatal density. Butler and Tibbitts (1979a) correlated stomatal density directly with O_3-induced visible injury in bean plants, but Gesalman and Davis (1978) found no such relationship for azalea cultivars. There was no apparent relationship between stomatal frequency or guard-cell length and differential O_3 sensitivity of two corn cultivars (Harris and Heath, 1981). They found that the leaf water potential was poised near the point at which only a slight water loss in the tolerant cultivar would induce stomatal closure. Hence, they suggested a rapid stomatal closure in response to an O_3-induced water loss. In the 1978 criteria document (U.S. Environmental Protection Agency, 1978), equally disparate results were offered for several plant species. Dean (1972) reported that tobacco cultivars that exhibited tolerance to oxidant-induced weather

fleck in the field had lower stomatal density than did sensitive cultivars. Evans and Ting (1974) found that the maximum O_3 sensitivity of primary leaves of bean could not be accounted for by stomatal density.

In summary, different plant responses to O_3 are the result of the diffusion of O_3 into the leaf interior. A knowledge of the O_3 uptake rate or amount, however, is not sufficient for predicting subsequent responses for all species. In some species, injury is apparently not directly related to O_3 uptake; while in others, there is a relationship between the quantity of O_3 entering the plant and the degree of subsequent injury. The physical and chemical environment and biological potential of the plant influence stomatal behavior and O_3 uptake, as will be documented in later sections. Once O_3 enters the plant, there are potential reactions with many cellular constituents.

7.3.1.2 Transition between Gas-Phase and Liquid Phase Movement into the Cell. Once it enters the intercellular spaces, ozone passes into the liquid phase at the gas-liquid interface of the cell wall surface. The diffusive process is dependent on physical, chemical, and biological factors that govern this diffusive step (Tingey and Taylor, 1982). The solubility of O_3 is critical to further reaction and depends on microclimatic factors, including temperature.

The rate at which gas diffusion occurs may also depend upon the internal cell surface area exposed (Evans and Ting, 1974; Pell and Weissberger, 1976; Uhring, 1978). Taylor et al. (1982b) reported that in soybean foliage, pollutant flux was not regulated solely by the number of sites of O_3 deposition. When plants were exposed to O_3 concentrations ranging between 0.25 and 0.58 ppm for 1 to 4 hours, uptake rates were higher and the ratio of internal/external leaf area was lower for "Hood," a relatively resistant soybean cultivar, than for "Dare," which was more susceptible. Athanassious (1980) did not identify surface-volume ratio as a determinant of relative response of radish mesophyll cells to O_3 but suggested that differential suberization of cell walls may explain relative sensitivity of parenchymal tissue. This idea was offered previously by Glater et al. (1962).

7.3.1.3 Chemical and Biochemical Response. When O_3 passes into the liquid phase, it is likely that the molecule will rapidly undergo transformations that yield a variety of free radicals, including superoxide and hydroxyl radicals (Pryor et al., 1981; Hoigne and Bader, 1975; Tingey and Taylor, 1982). Whether these chemical species result from decomposition of O_3 or reactions between O_3 and biochemicals in the extracellular fluid has not been determined.

Ozone or its decomposition products, or both, will then react with cellular components, resulting in structural or functional effects, or both.

The potential for O_3, directly or indirectly, to oxidize biochemicals *in vitro* has been demonstrated. Ozone can oxidize a number of biological molecules, including reduced nicotinamide adenine dinucleotide (NADH), DNA, RNA, purine, pyrimidines, indole acetic acid, some amino acids (including tryptophan and methionine), many proteins (including glyceraldehyde-3-phosphate dehydrogenase, catalase, peroxidase, papain, ribonuclease, and urease), and a variety of lipids (Christensen and Geise, 1954; Todd, 1958; Ordin and Propst, 1962; Heath, 1975; Mudd, 1982). In these studies, and in similar ones, the concentrations of O_3 bubbled into the biochemical solutions were all very high. It is difficult to compare the exposure to ozone in solution to the ambient air exposure that plants experience. Coulson and Heath (1974) have suggested, however, that solution and atmospheric exposures are not highly dissimilar. They showed that most of the O_3 bubbled into solutions exited unreacted and that the O_3 dose required to injure cells in solution was of a magnitude similar to that required to injure intact plants exposed to atmospheric O_3. Todd (1958) predicted sensitivity within the plant by relating concentrations of protein used *in vitro* to levels in the plant and extrapolated to lower concentrations of O_3. Similar comparisons could be made for other biochemicals studied *in vitro*. Because biochemicals are compartmentalized within the plant, such calculations of potential sensitivity may deviate from actual responses observed. Data acquired from *in vitro* studies are best utilized to demonstrate that many cellular constituents are susceptible to oxidation by O_3. Different approaches will have to be used to determine which, in fact, are important *in vivo*.

The potential for biochemicals to be affected within the plant has been explored by a number of researchers. Increases and decreases have been observed in the status of proteins, sulfhydryl residues, fatty acids, and sterols (Pell, 1979; Trevathan et al., 1979; Swanson et al., 1973). Results vary among laboratories. For example, Trevathan et al. (1979) observed a decrease in fatty acids 3 days after tobacco plants were exposed to 0.24 ppm O_3 for 6 hours, whereas Swanson et al. (1973) detected no change in fatty acid content in the same species 2 hours after plants received 0.30 ppm O_3 for 2 hours. It is likely that Trevathan et al. (1979) were observing a late plant response associated with injury and cell death while Swanson et al. (1973) provided

evidence that lipids were not particularly sensitive to O_3. Similarly, Fong and Heath (1981) were unable to detect any changes in either phospholipid content or fatty acid composition of total polar lipids in bean leaves that sustained mild visible injury after exposure to an O_3 concentration of 0.30 ppm for 1 hour. Changes in mono- and digalactolipids were observed after severe injury was induced by a concentration of 0.50 ppm for 1 hour.

The examples above serve to underscore the importance of recognizing the limitations of studies in which biochemical effects are determined for whole leaf tissue rather than for organelles, or are determined in terms of cell function. Such data neither describe the dynamics of injury development nor identify the cellular site at which biochemical changes are occurring. This kind of biochemical information is useful in characterizing the nature of a response to O_3 as it relates to altered metabolism, in general, and to visible foliar injury.

7.3.1.4 Physiological Responses. Physiological measurements have been more useful than biochemical quantifications in characterizing cell responses to oxidants. Many consider membranes to be the primary site of action of O_3 (Heath, 1980; Tingey and Taylor, 1982). The alteration in plasma membrane function is an early event in the sequence of O_3-induced effects that eventually leads to leaf injury and subsequent yield loss. Changes in the semipermeability of the membrane are evidenced by changes in fluxes of carbohydrates, amino acids, inorganic ions, and water (Heath, 1975, 1980; Tingey and Taylor, 1982). Whether the plasma membrane or some organelle membrane is the primary site of O_3 action is open to speculation (Tingey and Taylor, 1982). Mudd (1982) suggested that O_3 may penetrate the plasma membrane and injure organelles. A number of membrane-dependent functions of organelles can be altered by O_3. MacDowall (1965) reported that oxidative phosphorylation was inhibited when tobacco plants were exposed to O_3 at concentrations from 0.6 to 0.7 ppm for 1 hour. Photophosphorylation was inhibited in isolated spinach chloroplasts exposed to O_3 at a concentration of 400 ppm for 15 minutes (Coulson and Heath, 1974). Using the Bensen coefficient for O_3 and the partial pressure of the gas above the aqueous solution, Coulson and Heath (1974) calculated the latter dose to be equivalent to a concentration of 0.20 ppm in ambient air surrounding a terrestrial plant.

Ozone can also affect biochemical functions not associated with membranes. The activity of 1,5-ribulose bisphosphate (RuBP) carboxylase, an enzyme that

catalyzes CO_2 fixation during photosynthesis, can be inhibited by O_3. For example, 0.12 ppm for 2 hours inhibited the activity of RuBP carboxylase in rice (Nakamura and Saka, 1978). Inhibition of RuBP carboxylase activity is a relatively early event occurring several hours after conclusion of the O_3 exposure. Pell and Pearson (1983) observed 36, 68, and 80 percent decreases in the concentration of 1,5-RuBP carboxylase in foliage of three alfalfa cultivars that had been exposed to an O_3 concentration of 0.25 ppm for 2 hours. Observations were made 48 hours after exposure on leaves that did not exhibit macroscopic injury symptoms. Crystals observed in the chloroplast stroma of beans and hybrid poplars exposed to O_3 were thought to be 1,5-RuBP carboxylase (Thomson, 1975; Noble et al., 1980).

In some of the studies cited above, researchers examined the specific effects of O_3 on key steps in photosynthesis. The effect of O_3 on apparent photosynthesis, a measure of CO_2 uptake or fixation or both, was measured for many more plant species (Table 7-1). Reductions in apparent photosynthesis may reflect the direct impairment of chloroplast function or reduced CO_2 uptake, or both, resulting from O_3-induced stomatal closure. Regardless of the mechanism, a sustained reduction in photosynthesis will ultimately affect growth, yield, and vigor of the plant.

When considering dose-response effects of O_3 on plant yield in this document, emphasis has been placed on studies in which O_3 concentrations of 0.25 ppm or below were utilized (Table 7-1). Examples of O_3-induced reduction in apparent photosynthesis at concentrations exceeding 0.25 ppm are also presented (Table 7-1). These data highlight the potential of O_3 to reduce primary productivity. Several of the studies provide data more pertinent to the ambient atmosphere. Barnes (1972a) examined the impact of O_3 on seedlings of three species of pine at concentrations of 0.05 or 0.15 ppm continuously for 19 days to 18 weeks. In younger seedlings of eastern white pine, which bore only primary needles, O_3 had little influence on photosynthetic rate. In older seedlings with secondary needles, photosynthesis was slightly depressed. With seedlings of slash, eastern white, and loblolly pines, exposure at 0.15 ppm O_3 had a relatively consistent depressing influence on photosynthesis of all species. At 0.05 ppm, however, O_3 appeared to stimulate photosynthesis in older secondary needles and depress photosynthesis in younger secondary needles. Barnes (1972a,b) used a Mast meter to measure O_3, which can underestimate the O_3 concentration unless it is calibrated against a reference standard (chapter 5).

TABLE 7-1. EFFECT OF OZONE ON PHOTOSYNTHESIS

Species	O_3 Concentration ppm[a]	Exposure duration	% inhibition	Reference
Loblolly pine	0.05	18 weeks continuously	15[b]	Barnes, 1972a
Slash pine	0.05	18 weeks continuously	9[b]	Barnes, 1972a
Bean	0.072	4 hr/day for 18 days	18[b]	Coyne and Bingham, 1978
Alfalfa	0.10	1 hr	4[b]	Bennett and Hill, 1974
	0.20	1 hr	10[b]	
Ponderosa pine	0.15	9 hr daily/ 60 days	25[c]	Miller et al., 1969
	0.30	9 hr daily/ 30 days	67[c]	
Eastern white pine	0.15	19 days	10[c]	Barnes, 1972a
Eastern white pine	0.10	4 hr/day for 50 days	24[b]	Yang et al., 1983
Sensitive	0.20	4 hr/day for 50 days	42[b]	
	0.30	4 hr/day for 50 days	51[b]	
Tolerant	0.10	4 hr/day for 50 days	Not sig. different	
	0.20	4 hr daily/50 days	14[b]	
	0.30	4 hr daily/50 days	20[b]	
Bean	0.30	3 hr	22[c]	Pell and Brennan, 1973
Black Oak	0.50	4 hr daily/2 days	30 ± 10[d]	Carlson, 1979
Sugar maple	0.50	4 hr daily/2 days	21 ± 10[d]	Carlson, 1979
White pine				
Sensitive	0.7 or 0.9	3.0 or 10	100[b]	Botkin et al., 1972
Tolerant	0.70 to 0.95	10/30 days	0[b]	
Poplar hybrid	0.90	1.5 h	60[e]	Furukawa and Kadota, 1975
Ponderosa pine	450, 700 800 ppm-hr	Cumulative dose over 1,2,3 yr.	90[b]	Coyne and Bingham, 1981

[a] 1 ppm = 1960 µg/m.

[b] $P < 0.05$.

[c] $P < 0.01$.

[d] Standard deviation.

[e] No statistical information.

Also, the sample size used in these experiments was very small, four to nine seedlings. It is possible that variation among samples may have masked potential effects in some of the experiments (Barnes, 1972a). More recently, Coyne and Bingham (1978) exposed field-grown snap beans to an O_3 concentration of 0.072 ppm (the O_3 monitor was calibrated by UV photometry; see chapter 5) for 4 hours per day for 18 days. Apparent photosynthesis was reduced 18 percent in plants treated with O_3. Bennett and Hill (1974) reported that apparent photosynthesis of alfalfa plants was depressed 4 percent and 10 percent when O_3 concentrations were 0.1 and 0.2 ppm for 1 hour, respectively. Methods of O_3 monitoring and calibration were not given by the authors.

Black et al. (1982) found a significant ($p < 0.001$) relationship ($r = -0.8$) between net photosynthetic rate of broad bean and 4-hour exposures to concentrations of O_3 from 0.05 to 0.30 ppm. Exposure to O_3 concentrations of less than 0.10 ppm resulted in a reversible depression of photosynthesis. Twenty hours after exposure to O_3 concentrations of 0.10, 0.20, and 0.30 ppm, photosynthetic rate was depressed 0.037, 0.59 and 1.14 g CO_2/m^2 per hour, respectively, when compared with an initial rate of approximately 2.1 g CO_2/m^2 per hour (based on values presented for one example in the study). Miller et al. (1969) found that 3-year-old ponderosa pine seedlings sustained a 25 percent reduction in apparent photosynthesis after a 60-day exposure to an O_3 concentration of 0.15 ppm for 9 hours per day. Yang et al. (1983) exposed three clones of white pine, classified by foliar response to O_3 as sensitive, intermediate, and insensitive, to O_3 concentrations of 0.10, 0.20, or 0.30 4 hours per day for 50 days in CSTR chambers. Net photosynthesis was reduced in the foliage of sensitive and intermediate clones by 14 to 51 percent in direct relation to O_3 dose and relative clonal sensitivity (Table 7-1). In another study, Coyne and Bingham (1981) measured changes in gross photosynthesis in needles of ponderosa pine trees of various sensitivities to O_3. Needles sustaining slight, moderate, and severe injury exhibited a 90 percent reduction in gross photosynthesis after exposure to 800, 700, and 450 ppm-hours O_3, respectively, in a 3-year time period (2 years for the most sensitive class of trees). The percentage inhibition in gross photosynthesis was based on photosynthetic rates of newly emerged needles; no true controls were used in the experiment. The authors emphasized that the decline in photosynthesis reflected the superimposition of O_3 effects on normal aging.

7.3.1.5 Tissue and Organ Responses. In addition to depressing photosynthesis in the foliage of many plant species, O_3 inhibits the translocation of photosynthate (e.g., sucrose) from the shoots to the roots (Tingey, 1974; Jacobson, 1982). Tingey et al. (1971a) found that when radish plants were exposed to O_3 (0.05 ppm for 8 hours, 5 days per week for 5 weeks), hypocotyl growth was inhibited 50 percent, while foliage growth was inhibited only 10 percent (both significant at $p < 0.01$). Walmsley et al. (1980) confirmed that radish plants exposed to O_3 (0.17 ppm continuously for 36 days) exhibited an altered pattern of assimilation such that below-ground biomass was more severely affected than foliage. Ponderosa pine exposed to 0.10 ppm O_3 for 6 hours per day for 20 weeks stored significantly less sugar and starch in their roots than did control plants (Tingey et al., 1976). Such an effect on translocation could reduce root weight and directly affect the yield of a crop like radish or carrot.

Snap beans exposed to O_3 (0.30 ppm or 0.60 ppm for 1.5 hours) exhibited a greater reduction in root than shoot growth (Blum and Heck, 1980). The root-to-shoot ratio of crimson clover was suppressed 17 percent and 23 percent, respectively, ($p < 0.05$) when plants were exposed to O_3 at 0.03 and 0.09 ppm for 8 hours per day for 6 weeks (Bennett and Runneckles, 1977). The root-to-shoot ratio of rye grass was reduced 22 percent ($p < 0.05$) when plants were exposed to 0.09 ppm with the same exposure regime. In other experiments, the effects of O_3 were measured on the partitioning of photosynthate in carrot, parsley, sweet corn, cotton, and pepper (Oshima, 1973; Bennett and Oshima, 1976; Oshima et al., 1978; Oshima et al., 1979; Bennett et al. 1979). In each of these experiments, plants were exposed to O_3 concentrations of 0.12 to 0.25 ppm for 3 to 6 hours for 0.2 percent to 7 percent of the total growth period of the plants. In all species but pepper, root dry weight was depressed much more than leaf dry weight. For example, root dry weight of cotton was reduced 60 percent, whereas leaf dry weight was depressed only 17 percent by O_3 (Oshima et al., 1979). Ozone had virtually no effect on the dry weight of parsley leaves, but it reduced root dry weight 43 percent (Oshima et al., 1978). The photosynthetic rate of tomato plants exposed to O_3 (0.3 ppm for 3 hr) was reduced 35% and the translocation of photosynthate from the leaves was reduced 29% (McCool and Menge, 1983). This combined reduction in photosynthate available for root growth can significantly affect plant growth. The reduction in photosynthate translocation to roots and the resulting decrease in root size

indicates that the plant had fewer stored reserves, rendering it more sensitive to injury from cold, heat, or water stress.

When less carbohydrate is present in roots, less energy will be available for root-related functions. In the 1978 criteria document (U.S. Environmental Protection Agency, 1978), evidence was presented for O_3-induced reduction in nodulation and nitrogen fixation in soybean and ladino clover. Blum and Tingey (1977) reported that when 2-week old soybean plants were exposed to an O_3 concentration of 0.50 ppm for 4 hr, nodulation was inhibited 60% ($p < 0.05$). Ensing and Hofstra (1982) measured nitrogenase activity in the roots of red clover 1 and 6 days after the plants were exposed to O_3 (0.20 ppm 16 hr/day for 4 days) in non-filtered open top chambers and found nitrogenase activity was reduced 50 and 24% ($p = 0.05$), respectively, when compared to the activity in plants growing in charcoal filtered open-top chambers. By 16 days post- exposure, enzyme activity was comparable to other treatments. An ozone-induced suppression of atmospheric nitrogen fixation by root nodules could affect total biomass and agricultural yield, especially in areas where soil nitrogen is low.

7.3.1.6 Secondary Metabolic Responses. In addition to the physiological effects more directly related to productivity, there are many secondary metabolic responses in a plant exposed to O_3. While these responses do not explain the initial reaction to O_3, they may contribute to the manifestation of foliar injury. Ethylene is an important stress metabolite produced by many plants exposed to O_3 (Tingey, 1980). Ozone at 0.15 ppm for 8 hours increased ethylene evolution in beans (Stan et al., 1981). Ethylene evolution ceased prior to necrosis (visible injury). It has been proposed that ethylene may initiate the observed stimulation of oxidizing enzymes such as phenylalanine lyase, polyphenoloxidase, and peroxidase (Tingey et al., 1975). The accumulation of phenols has been observed in many plant species in response to O_3 (Howell and Kremer, 1973; Hurwitz et al., 1979; Keen and Taylor, 1975; Koukol and Dugger, 1967). There appears to be a direct relationship between the concentration of phenols detected in foliage and the extent of necrosis (visible injury) induced by O_3 (Hurwitz et al., 1979). The pigmented lesions that are visible in the leaf following O_3 exposure are thought to occur when phenols are oxidized and polymerized (Howell and Kremer, 1973).

Ozone enters the cell and initiates biochemical and physiological responses. Critical effects, including reduction in photosynthesis and a shift

in the assimilation of photosynthate, will lead to reduced biomass, growth, and yield. Visible injury, which results from O_3-induced cell injury and death, reflects the occurrence of both primary and secondary metabolic events. Visible injury serves as an indicator of the presence of O_3 and reflects potentially harmful effects on plant vigor.

7.3.2 Factors that Modify Plant Response

There is a great deal of variation in the magnitude of plant response to O_3. Biological, physical, and chemical variables influence plant response. For example, trees in a stand of ponderosa pine will not respond equally to exposure to O_3 because of genetic diversity in the sensitivity of individual trees and because of environmental heterogeneity in the habitat. Plants at different ages or at different temperatures, humidities, light intensities, or soil moisture regimes will respond differently to an equivalent O_3 exposure. The presence of several pollutants, chemical sprays, and biological pests all will contribute to determining the magnitude of plant response to O_3. In developing an understanding of O_3 effects, it is important to consider the O_3 sensitivity of the plant and the environmental conditions it is likely to experience during exposure. It is equally important to recognize that plants at certain stages of development or under a given set of environmental conditions may be differentially sensitive to O_3. The factors that modify plant response are grouped into three categories: biological, physical, and chemical factors.

7.3.2.1 Biological Factors

7.3.2.1.1 Genetic Factors. The genetic complement of a plant determines its potential response to O_3. Genetically controlled variation in response to O_3 has been observed among species, cultivars, and individuals within a population. Inherited variation in plant response to O_3 can be measured by using many plant response variables. Most researchers have investigated relative O_3 sensitivity by measuring foliar injury. Genetically controlled differences in response to O_3, however, are also reflected in differential yield and physiological effects, as well. A list of the plant species studied that exhibited differential ozone sensitivity within a species is presented in Appendix B.

The relative O_3 sensitivity of cultivars can vary with dose and the nature of the response measured (Tingey et al., 1972; Heagle, 1979b). There is also some disparity between the relative sensitivity ranking of cultivars

from controlled O_3 exposures in a laboratory and exposure of the same cultivars to ambient air oxidants in the field (Engle and Gabelman, 1966; Taylor, 1974; Huang et al., 1975; Meiners and Heggestad, 1979; Hucl and Beyersdorf, 1982; DeVos et al., 1983). The inconsistent results may be explained in part by the nature of the inheritance of the O_3 susceptibility. In the case of onion and bean, one or a few gene pairs were associated with O_3 susceptibility (Engle and Gabelman, 1966; Butler et al., 1979); while for corn (Cameron, 1975), tobacco (Povilaitis, 1967; Sung et al., 1971; Aycock, 1972; Huang et al., 1975), potato (DeVos et al., 1982) and petunia (Hanson et al., 1976), several genes determine plant responses to O_3. The apparent genetic complexity explains the potential variability in plant response as gene expression changes during plant development and with variations in the environment.

In agricultural ecosystems, tolerant germplasm is selected deliberately, or inadvertently, in order to reduce the effects of O_3. In natural ecosystems in areas receiving long-term O_3 stress, it is predictable that susceptible individuals within a population may decline and be replaced by those more tolerant to the pollutant (see chapter 8). Many stresses, including SO_2, elicit this kind of response in populations in natural ecosystems (Taylor and Murdy, 1975; Roose et al., 1982). Narrowing of the gene pool creates the potential for increased vulnerability of a plant population to various assaults, including those of biotic pests.

It appears that as wide a range of susceptibility to O_3 exists among plant species as within them. Ozone is prevalent in most agricultural regions in the United States. Sensitive plant species are found throughout the country and the environmental conditions that favor injury occur in many geographic locations.

7.3.2.1.2 Developmental Factors. Plant foliage appears to be most sensitive to O_3 just prior to or at maximum leaf expansion (U.S. Environmental Protection Agency, 1978). At this stage, stomata are functional, intercellular spaces are expanded, and barriers to gas exchange such as internal cutin and secondary thickening of cell walls are minimal (U.S. Environmental Protection Agency, 1978). Blum and Heck (1980) analyzed the response of bean plants to O_3 concentrations of 0.30 and 0.60 ppm for 1.5 hours at various stages during growth. The plants were most sensitive to O_3 early in development and just before senescence. Virginia pine and petunia seem to be most sensitive to O_3 early in development as described in the 1978 criteria document (U.S. Environmental Protection Agency,

1978). Tolerance of foliage to O_3 increased at or just before appearance of flower buds in plants from six F_1 hybrid multiflora petunia lines, at eight physiological ages, that were exposed to O_3 (0.20 ppm for 8 hours) (Hanson et al., 1975). The effect of O_3 on root dry weight of radish was related to timing of the exposure (Tingey et al., 1973a). Plants exposed to an O_3 concentration of 0.40 ppm for 1.5 hours at 7, 14, or 21 days from seeding, sustained 25, 37, amd 15 percent ($p < 0.05$) inhibition of hypocotyl root dry weight, respectively. Radish plants may be particularly sensitive to O_3 at 14 days because maximum root enlargement begins at that time.

One of the first observations of the effects of photochemical oxidants on plants in the field was the development of leaf chlorosis followed by premature leaf aging (senescence) and early leaf drop (abscission) (e.g., Richards et al., 1958; Menser and Street, 1962). Ozone (0.05 or 0.10 ppm 6 hours per day for 133 days) induced premature leaf drop in soybeans (Heagle et al., 1974). The premature senescence and leaf drop increased throughout the study period. Ozone-induced premature leaf senescence has been observed in both greenhouse and field-grown potatoes (Heggestad, 1973; Pell et al., 1980). Field studies with white beans (Hofstra et al., 1978) confirmed that O_3 induced premature leaf drop; the premature leaf drop was associated, in part, with the O_3-induced yield reductions. The photosynthetic rate of hybrid poplars exposed to O_3 (0.085 or 0.125 ppm for 5.5 hours/day for 65 days) decreased more rapidly with age than unexposed plants, indicating that O_3 induced a premature senescence (Reich, 1983). Another study with hybrid poplar showed that O_3 (0.04 ppm 12 hour/day for 5 months) significantly increased leaf drop (Mooi, 1980). The effects of O_3 on the senescence process, regardless of time of initiation, may be responsible for many of the documented reductions in yield.

7.3.2.1.3 Pollutant-Plant-Pest Interactions. Plant pests (pathogens and insects) are normal components of both agro- and natural ecosystems. Crop losses from pests can be significant and have been estimated at 20 to 30 billion dollars per year in the United States alone (James, 1980). When considering the effects of O_3 on crop plants or forests, it is important to realize that the pollutant does not occur alone, but rather in conjunction with other stresses that are modifying the productivity of the system. The purpose of this section is to indicate what is known about interactions between O_3, plants, and pests, and how these interactions might modify the effects of O_3 on the quality, quantity, or the intended use of the plant.

Disease is the result of a complex interaction between host plant, environment, and pathogen. In the context of this general discussion of biotic stress, problems caused by pathogens and insects will both be termed disease. To understand the ways in which O_3, as a part of the environment, may modify pest dynamics, it will be helpful to consider a generalized disease cycle.

The cycle begins with the arrival of the inoculum or pest at the plant (host). Following deposition of the pest on the plant surface, in the presence of favorable conditions (temperature, moisture), penetration of the plant (or insect feeding, or oviposition) may begin.

Host penetration may occur quickly or, in some cases, the pathogen may live as a resident on the plant surface for a period of time. Once penetration occurs, and favorable conditions are present, infection may occur that results in an intimate relationship between plant and pathogen. Growth and development or colonization by the pathogen or plant pest proceeds until the pest reaches a reproductive stage. Propagules of the pest are formed and dispersed either passively or actively.

At each stage of this cycle, O_3 may modify the success of the pest, either directly through effects on the invading organisms, or indirectly, through modification of the host plant. Similarly, the complex interaction between plant and pest may alter the sensitivity of the plant to O_3.

7.3.2.1.3.1 Pollutant-plant-pathogen interactions. Most pollutant-plant-pathogen interaction studies have been conducted under controlled laboratory conditions, but a few field studies have been performed. This topic has been reviewed recently (Heagle, 1973, 1982; Laurence, 1981; Manning, 1975; Treshow, 1980a; U.S. Environmental Protection Agency, 1978). The results of published studies are summarized in Table 7-2.

Infection of plants by pathogens may be inhibited or stimulated by O_3. Manning et al. (1969; 1970a,b) found that potato and geranium leaves injured by O_3 (0.07 to 0.25 ppm, 6 to 10 hours) had a larger number of lesions caused by Botrytis. Wukasch and Hofstra (1977a) found that field-grown O_3-injured onion plants developed twice as many Botrytis squamosa lesions as did uninjured plants growing in charcoal-filtered air. The same authors (1977b) found fewer natural B. squamosa lesions on plants treated with an antioxidant chemical. Ambient air O_3 concentrations exceeded 0.15 ppm for 4 hours and 0.08 ppm on several occasions during the growing season. Bisessar (1982) found similar results with the interaction of O_3, potato, and Alternaria solani. The fungus

TABLE 7-2. PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS DOSES OF OZONE UNDER LABORATORY AND FIELD CONDITIONS (MODIFIED FROM LAURENCE, 1981)

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b,c]	Reference
AGRONOMIC CROP/FUNGI					
Pinto bean/root fungi	0.10 ppm O_3, 8 hr daily, 10 wk	L	Increased number fungal colonies	NR	Manning et al. (1971b)
Barley/Erysiphe graminis	0.15 ppm O_3, 6 hr daily for 4, 6, or 8 exposures after inoculation	L	Increased colony size	NR	Heagle and Strickland (1972)
Wheat/Puccinia graminis	0.06 to 0.18 ppm O_3, 6 hr daily, 17 days after inoculation	L	Decreased hyphal growth, numbers of spores, infection	Decreased	Heagle and Key (1973a)
Wheat/Puccinia graminis	0.1 ppm O_3, 6 hr daily, 12 days after inoculation	L	Reduced sporulation	NR	Heagle (1975)
Corn/Helminthosporium maydis	0.06 to 0.18 ppm O_3 6 hr variable days before and after inoculation	L	Increased lesion size, increased number of spores produced at highest concentration	NR	Heagle (1977)
Oats/Puccinia coronata	0.10 ppm O_3, 6 hr/day 10 days after inoculation 0.20 ppm O_3/3 hr, 1 to 5 days after inoculation	L	No effect on disease development	NR	Heagle (1970)
Potato/Botrytis cinerea	0.15 to 0.25 ppm O_3, 6 to 8 hr	L	Increased disease development	NR	Manning et al. (1969)
Cabbage/Fusarium oxysporium	0.10 ppm O_3, 8 hr daily, 10 wk	L	Decreased disease development	NR	Manning et al. (1971b)
Onion/Botrytis cinerea, B. squamosa	0.15 ppm O_3, 4 hr	FC	Increased disease development	NR	Wukasch and Hofstra (1977a,b)
Potato/Alternaria solani	0.03 to 0.04 ppm O_3 monthly	F	Increased disease development	NR	Bisessar (1982)

TABLE 7-2. (cont'd). PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS OZONE DOSES UNDER LABORATORY AND FIELD CONDITIONS (MODIFIED FROM LAURENCE, 1981)

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury	Reference
TREES AND ORNAMENTALS/FUNGI					
White pine/*Lophodermium pinastri*	0.07 ppm O_3, 4.5 hr	L	Slight increased disease occurrence	NR	Costonis and Sinclair (1972)
Ponderosa, Jeffrey Pine/ *Heterobasidion annosum*	0.18 ppm O_3/12 hr seasonal	F	Increased disease development Increased colonization of stumps	NR NR	James et al. (1980a) James et al. (1980b)
Eastern white pine/ *Verticicladiella procera*	0.045 ppm O_3 monthly average 0.128 ppm monthly peak hourly	F	Increased disease incidence	NR	Skelly (1980)
Lilac/*Microsphaera alni*	0.25 ppm O_3, 72 hr	L	No influence on germination, early fungal development	NR	Hibben and Taylor (1975)
Poinsettia/*Botrytis cinerea*	0.15 to 0.45 ppm O_3, 4 hr	L	No effect	NR	Manning et al. (1972)
Geranium/*Botrytis cinerea*	0.15 ppm O_3, 6 hr, 2x at 24-hr intervals after inoculation	L	Reduced sporulation; reduced infection by exposed spores Flocculent material produced	NR	Krause and Weidensaul (1978a)
Geranium/*Botrytis cinerea*	0.07 to 0.10 ppm O_3 10 hr daily for 15 to 30 days	L	Increased disease development when visible O_3 injury evident	NR	Manning et al. (1970b)
Citrus/*Glomus faciculatus*	0.45 ppm 3 hr/day, 2 days/wk for 19 wks	L	Decreased infection	NR	McCool et al. (1979)
Tomato/*Glomus faciculatus*	0.30 or 0.60 ppm, 3 hr/wk for 8 wks	L	Retarded infection	NR	McCool et al. (1982)

TABLE 7-2. (cont'd). PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS OZONE DOSES UNDER LABORATORY AND FIELD CONDITIONS (MODIFIED FROM LAURENCE, 1981)

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b]	Reference
AGRONOMIC CROPS/VIRUS					
Tobacco/tobacco mosaic	0.30 ppm O_3, 6 hr	L	NR	< O_3 injury	Brennan and Leone (1969)
	Seasonal maximum hour, 0.236 ppm O_3	F		< O_3 injury	Bisessar and Temple (1977)
Tobacco/tobacco etch	0.25 ppm O_3, 4 hr, once 9 days after inoculation	L	NR	< O_3 injury	Moyer and Smith (1975)
Tobacco/tobacco streak	0.30 ppm O_3, 3 hr for 1 or 2 days	L	NR	> O_3 injury	Reinert and Gooding (1978)
Tobacco-pinto bean/tobacco mosaic	0.35 ppm O_3, 4 hr; 0.25 ppm O_3, 3 hr, respectively	L	NR	< O_3 injury	Brennan (1975)
Pinto bean/bean common mosaic	0.25 ppm O_3, 4 hr, 5 days after inoculation	L	NR	< O_3 injury	Davis and Smith (1975)
Pinto bean/alfalfa mosaic tobacco ringspot, tobacco mosaic, tobacco ringspot	0.25 ppm O_3 4 hr, 5 days after inoculation		NR	< O_3 injury	Davis and Smith (1976)
Tomato/tobacco mosaic, cucumber mosaic	0.0 to 0.45 ppm or 0 to 0.90 ppm 3 hr; 7 to 21 days after inoculation	L	NR	> O_3 injury at 7 or 14 days < O_3 injury at 21 days	Ormrod and Kemp (1979)
Soybean/tobacco ringspot	0.35 to 0.40 ppm O_3, 4 hr, once 6, 8, or 10 days before inoculation	L	NR	< O_3 injury	Vargo et al. (1978)

TABLE 7-2. (cont'd). PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS OZONE DOSES UNDER LABORATORY AND FIELD CONDITIONS (MODIFIED FROM LAURENCE, 1981)

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b]	Reference
AGRONOMIC CROP/BACTERIA					
Alfalfa/*Xanthomonas alfalfae*	0.20 ppm O_3, 4 hr at 24 hr before or after O_3 exposure	L	Reduced disease development	< O_3 injury	Howell and Graham (1977)
White bean/*Xanthomonas phaseoli*	0.08 ppm O_3, 11 hr average, seasonal	F	No effect	< O_3 injury	Temple and Bisessar (1979)
Soybean/*Pseudomonas glycinea*	0.08, 0.25 ppm O_3, 4 hr	L	Reduced disease incidence	No effect	Laurence and Wood (1978a)
Ladino clover/*Rhizobium* sp.	0.30 to 0.60 ppm O_3, 2 times to 2 hr	L	Reduced nodule number		Letchworth and Blum (1977)
Soybean/*Rhizobium japonicum*	0.75 ppm O_3, 1 hr	L	Reduced growth and nodulation	No effect	Tingey and Blum (1973)
Wild strawberry/*Xanthomonas fragariae*	0.20 ppm O_3, 3 hr before or after inoculation		Reduced disease incidence	No effect	Laurence and Wood (1978b)
	0.08 ppm (as above)		Inconsistent results		
NEMATODES					
Soybean/cyst, stubby root	0.25 ppm O_3, 4 hr/4 days before inoculation. 3 days/wk for 4 hr/day after inoculation until harvest	L	Reduced reproduction of nematode		Weber et al. (1979)
Begonia/foliar	0.25 ppm O_3, 4 hr at 3 days before or after inoculation	L	Reduced reproduction of nematode		Weber et al. (1979)

[a] L = Laboratory, greenhouse, growth, or fumigation chamber studies; F = field studies; FC = chambers used in field studies.

[b] > = Increased; < = decreased.

[c] NR = Not reported.

colonized O_3-injured sites on potato leaves, and fewer lesions were present on plants protected from O_3 with ethylene diurea (EDU), a compound developed to reduce O_3 injury (see Section 5.3.2.3.2). Ambient air O_3 concentrations exceeded 0.08 ppm during 68 hours, and the highest measured concentration was about 0.14 ppm. Similar results were obtained by James et al. (1980a) in a field study of Heterobasidion annosum (syn. Fomes annosus) infection of oxidant-injured ponderosa and Jeffrey pines in the San Bernardino Mountains. They found increased infection of the roots of severely affected trees. The results of the field study were confirmed under controlled laboratory conditions. They also found that the colonization of roots and freshly cut stumps of ponderosa and Jeffrey pine was positively correlated with the severity of the oxidant injury observed on needles. In laboratory studies, colonization of both species was directly related to O_3 exposure over the range of 0 to 0.45 ppm for 58 to 92 days (additional discussion in Chapter 8). Skelly (1980) reported increased incidence of root disease caused by Verticicladiella procera in oxidant-injured eastern white pines in Virginia.

Ozone can inhibit infection of plants by pathogens. In general, infection by obligate parasites is inhibited in plants that have been exposed to elevated concentrations of O_3 (Heagle 1970, 1973, 1975, 1982; Heagle and Strickland, 1972; Heagle and Key, 1973a,b).

McCool et al. (1979) reported that infection of citrus by Glomus fasciculatus, an endomycorrhizal fungus, was decreased by exposure to O_3 (0.45 ppm, 3 hours per day, 2 days per week for 19 weeks). Exposure of tomato to 0.30 ppm O_3 for 3 hours once per week for 8 weeks retarded infection by the same fungus (McCool et al., 1982). These exposures did not affect root growth of the plants or sporulation by the fungus, but did reduce the number of successful infections. Ozone reduced mycorrhizal infections of tomato roots 46 and 63% when the plants were 0.15 (3 h/exposure, twice weekly for 9 weeks) or 0.30 ppm (3 h, once weekly for 9 weeks), respectively. Rhizobium, a nitrogen-fixing bacterium of legumes, induced fewer nodules in soybean plants exposed to 0.75 ppm O_3 for 1 hour (Tingey and Blum, 1973) and in ladino clover exposed to 0.3 or 0.6 ppm O_3 twice for 2 hours each (Letchworth and Blum, 1977).

Infection of soybean by Pseudomonas glycinea was decreased when plants were exposed to 0.08 or 0.25 ppm O_3 for 4 hours at times ranging from 8 days to 1 hour before inoculation. When exposures occurred more than one day after inoculation, however, inhibition was not observed (Laurence and Wood, 1978a).

Similar results were found with Xanthomonas fragariae and wild strawberry (Fragaria virginiana) (Laurence and Wood, 1978b). Temple and Bisessar (1979), however, did not find fewer Xanthomonas phaseoli lesions on O_3-injured white beans in the field.

In most cases, colonization of plant tissue by pathogens is assessed by measuring lesion size. Lesions of obligate parasites are usually smaller on plants exposed to O_3 when compared to controls (Laurence, 1981). Heagle and Strickland (1972), however, found larger colonies of Erysiphe graminis f. sp. hordei on barley plants that were exposed repeatedly to low levels of O_3 (up to 0.15 ppm, 6 hours per day for 8 days).

Little is known about colonization of ozone-affected plants by facultative parasites. Heagle (1977) inoculated corn plants with Helminthosporium maydis race T and exposed them to O_3 (0.06, 0.12, or 0.18 ppm) for 6 hours per day for up to 7 days before inoculation, 9 days after inoculation, or combinations of before and after. He found that lesion length was significantly increased by O_3 exposure (0.18 ppm) before and after inoculation, but was not affected at other concentrations or time regimes.

Based on these few reports on the relationship of O_3 to plant colonization by pathogens, it is impossible to generalize and predict effects in particular disease situations. It is apparent that the outcome of a pollutant-plant-pathogen interaction depends on the particular plant and pathogen involved. It also is affected by the environmental conditions and O_3 concentrations before and after inoculation.

Rist and Lorbeer (1981) recently reviewed the effects of O_3 on sporulation of fungi. In axenic culture, sporulation and growth of fungi were almost always inhibited or unchanged by exposure to O_3. In a few studies, significant inhibition of growth, sporulation, or germination has been observed following exposures to concentrations as low as 0.10 ppm for 4 hours, but fungi often are resistant to 1.0 ppm O_3 for several hours. Germination of spores produced during O_3 exposure (0.15 or 0.30 ppm, 6 hours per day for 2 days) may also be lower than that of controls (Krause and Weidensaul, 1978a,b). These spores may subsequently be less successful in colonizing the leaf surface (Krause and Weidensaul, 1978a,b). Both decreases and increases in sporulation have resulted from O_3 exposure of infected plants (Laurence, 1981), and the particular result seems to depend on the plant-pathogen combination and the specific O_3 exposure regime.

In the case of bacterial diseases, reproduction of the pathogen is generally reflected in the size of lesions on the plant. Bacteria are generally resistant to ambient concentrations of O_3, but may be much more sensitive to changes in plant metabolism induced by O_3 (Hughes and Laurence, 1984).

Reproduction of the soybean cyst nematode and the stubby root nematode was reduced by exposure of infested soybean plants to 0.25 ppm O_3 applied on three alternate days a week for about 2 months (Weber et al., 1979). Similar O_3 treatments also reduced the reproduction of a foliar nematode on begonia plants. This reduction was related to the amount of O_3-induced leaf injury (Weber et al., 1979).

Only a few studies have been reported that relate the effects of O_3 in combination with another pollutant (SO_2) to disease development. Weidensaul and Darling (1979) found that Scotch pines inoculated with Scirrhia acicola and exposed to O_3 (0.20 ppm for 6 hours) or O_3 combined with SO_2 (0.20 ppm for 6 hours) had fewer lesions than controls, but did not differ from each other. More lesions formed when inoculation preceded fumigation by 5 days than when inoculation followed exposure by 30 minutes.

7.3.2.1.3.2 Effects of ozone on plant-insect interactions. The effects of air pollutants on insect populations were reviewed recently (Alstad et al., 1982). Very little is known about O_3-insect interactions. Ozone-induced injury in ponderosa pine has been shown to predispose trees to subsequent invasion by several species of pine bark beetles (Stark et al., 1968). Elden et al. (1978) found that O_3 injury induced by exposures of 0.20 ppm for 4 hours had little or no effect on the development of pea aphids on alfalfa. They did note that two of three varieties having higher levels of O_3 resistance also had greater resistance to pea aphid.

7.3.2.1.3.3 Effects of pathogen infection on plant sensitivity to O_3. Fungal, bacterial, or viral infections have been reported to provide some protection to plants from the visible effects of O_3. Although of interest mechanistically, most of the studies have been conducted under controlled conditions, and it is questionable whether they are relevant in field situations.

Yarwood and Middleton (1954) noted that pinto bean leaves infected by Uromyces phaseoli were less sensitive to photochemical oxidants than were uninfected leaves. Similar results have been observed with many pathogen-plant combinations. The protection afforded by fungal and bacterial pathogens is

usually localized at the margins of lesions, while virus infections can provide more generalized effects (Heagle, 1982).

Although bacterial pathogens often provide protection against O_3 injury near lesions, they did not in the case of bacterial blight of soybean or angular leafspot of strawberry (Laurence and Wood, 1978a,b). Pratt and Krupa (1979), however, reported that in chlorotic soybean leaves Pseudomonas glycinea infection did inhibit expression of O_3 symptoms. Temple and Bisessar (1979) found less visible O_3 injury on Xanthomonas phaseoli-infected white beans in the field in Ontario, Canada. Using the same species of bacterium, Olson and Saettler (1979) observed no protection from O_3 injury in controlled laboratory experiments. Pell et al. (1977) investigated the interaction between O_3 and a species of Pseudomonas that caused a hypersensitive reaction in soybean. They found that inoculation with the pathogen provided some protection from O_3 when plants were inoculated 1 day before exposures to a relatively high concentration of the pollutant (0.35 ppm for 2 hours). The effect was not observed when inoculation took place 4 hours before exposure.

Many reports have appeared on the effects of virus infection on plant response to O_3, beginning with those of Brennan and Leone (1969) and Brennan (1975). Davis and Smith (1975, 1976) reported protection of pinto bean leaves following inoculation with common mosaic, tobacco ringspot, tomato ringspot, alfalfa mosaic, and tobacco mosaic viruses. The protection depended upon an establishment time of 4 to 5 days between inoculation and exposure, which is apparently linked to the time required to attain sufficient virus titer to afford protection. The protection was localized except in the case of tobacco ringspot, in which a more general effect was observed. Tobacco etch virus infection also protected tobacco plants from O_3 injury (Moyer and Smith, 1975). All experiments were under controlled conditions with exposures of 0.25 ppm O_3 for 4 hours.

Virus infection in one part of a plant has also been shown to provide protection against O_3 injury in other parts. Davis and Smith (1976) found that inoculation of one primary leaf of a pinto bean plant resulted in some degree of protection in the uninoculated leaf exposed to O_3 (0.20 ppm for 4 hours), but was not effective at O_3 concentrations greater than 0.20 ppm. Vargo et al. (1978) found that sensitivity to O_3 (0.35 to 0.4 ppm for 4 hours) of the primary leaf opposite the leaf inoculated with tobacco ringspot virus was decreased with increasing time after inoculation. They also found that as virus-induced apical necrosis increased, less O_3 injury occurred.

Two recent reports show that O_3 injury may be increased following virus infection. Reinert and Gooding (1978) found that tobacco plants systemically infected with tobacco streak virus and exposed to O_3 (0.3 ppm for 3 hours on 1 or 2 days) 3 weeks after inoculation displayed more injury than the combined injury of plants exposed to O_3 or virus. Ormrod and Kemp (1979) found both increases and decreases in O_3 sensitivity of tomato plants infected with cucumber mosaic virus or tobacco mosaic virus or both, depending on the tomato cultivar, O_3 concentration, the virus, and the virus incubation period. Ozone injury was observed more frequently on tobacco mosaic virus-infected plants than on those inoculated with cucumber mosaic virus. They also observed that increases in O_3 injury usually occurred when O_3 exposures (0.15 to 0.90 ppm for 3 hours) occurred within 14 days of inoculation; 21 days after inoculation, most of the differences observed were decreases in injury.

In the only field study reported, Bisessar and Temple (1977) found 60 percent less oxidant injury on tobacco plants infected with tobacco mosaic virus than on uninfected plants. The ozone concentration exceeded 0.10 ppm for 16 percent of the daylight hours during the study period.

The effects described in the above sections are not of commercial importance but the observations may provide some information as to the mode of action of O_3 in plants.

Ozone affects the development of disease in plant populations. Most laboratory evidence indicates that O_3 (at ambient concentrations or higher for 4 hours or more) inhibits infections by pathogens and subsequent disease development; however, increases in disease development have been noted in certain cases. Most often these increases occur with "stress pathogens" that incite diseases such as Botrytis blight of potatoes or onions or Heterobasidion annosum root rot of ponderosa and Jeffrey pine. Increases in disease development have been observed in these host-parasite relationships under both laboratory and field conditions (plants exposed to ambient air levels of O_3).

That ozone can also modify plant-insect relationships is best illustrated by studies conducted in the San Bernardino Mountains that showed increased invasion of O_3-stressed pine trees by bark beetles.

The mode of action of O_3-plant-pest interaction probably involves indirect effects on the pathogen or insect that are the result of the direct interaction of O_3 and the plant. Effects on disease development have been documented at concentrations of O_3 and durations of exposure that are considered to be low

(i.e., < 0.10 ppm for a few hours). Thus, it would appear that O_3 is affecting plant metabolism at these low concentrations and short exposure durations.

7.3.2.2 Physical Factors. The environment of the plant is composed of various biological, chemical, and physical factors that change throughout the plant growth period. The physical factors (e.g., light, temperature, relative humidity, soil moisture, and soil fertility) interact to provide the conditions for and also govern plant growth. Short-term variations in one or several of these environmental factors, if they coincide with a pollution episode, may render the plant more or less sensitive to pollutant exposure.

Environmental conditions before and during plant exposure are critical to the plant response, while postexposure conditions are less important. Although the influence of physical factors on plant response to O_3 has been studied primarily under laboratory and greenhouse conditions, field observations have often substantiated these results. Most studies have evaluated the effects of a single environmental factor and have usually used foliar injury as the measure of plant response. Information sufficient to make some generalizations about the influence of these factors on plant response to O_3 is available, but for most factors, substantial uncertainty exists because of the small number of species studied and the lack of information on the interactions of the environmental factors. In this section, the various environmental factors will be discussed individually for organizational convenience, even though these factors interact to influence plant growth and sensitivity to O_3.

7.3.2.2.1 Light. It was concluded in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) that a short photoperiod and a relatively low light intensity during growth maximize O_3-induced foliar injury. These results were consistent across contrasting light regimes. For example, bean and tobacco plants were more sensitive to O_3 at 0.4 ppm for 1 hour if grown at 420 $\mu E\ s^{-1}\ m^{-2}$ than if grown at 840 $\mu E\ s^{-1}\ m^{-2}$ (Dunning and Heck, 1973). Cotton grown at 276 $\mu E\ s^{-1}\ m^{-2}$ was less sensitive to O_3 concentrations of 0.9 ppm for 1 hour than similar plants grown with 27.6 $\mu E\ s^{-1}\ m^{-2}$ (Ting and Dugger, 1968). Subsequently, Dunning and Heck (1977) demonstrated the complex nature of environmental interactions. They reported that tobacco showed increased sensitivity to an O_3 concentration of 0.40 ppm for 1 hour when grown under high light intensity (840 $\mu E\ s^{-1}\ m^{-2}$) and subsequently exposed at an intermediate light intensity (420 $\mu E\ s^{-1}\ m^{-2}$). In contrast, pinto bean leaves were most sensitive when plants were grown at a lower light intensity (209 $\mu E\ s^{-1}\ m^{-2}$) and subsequently exposed at the high intensities cited above.

The responsiveness of photosynthetic processes and stomatal function to O_3 has already been noted. The importance of light to these physiological functions may in part explain the influence of light on the O_3 response in plants.

In the field, vegetation will not often be exposed to O_3 at the low light intensities and the short photoperiods (8 hours) used in simulations described above. Therefore, special consideration of light may not be as relevant as other environmental factors. There are, however, some cultural practices for which light intensity and photoperiod are controlled. Shade-grown tobacco and bedding plants (in the commercial floriculture industry) represent two examples of production settings in which low light intensity is used and where losses attributable to oxidants have been documented.

7.3.2.2.2 Temperature. The 1978 criteria document (U.S. Environmental Protection Agency, 1978) reported that there was no consistent pattern relating temperature to plant response to O_3. Radish was more sensitive to O_3 if grown under cool conditions, whereas snap bean, soybean, Bel W-3 tobacco, Virginia pine, and white ash were sensitive if grown under warm conditions (U.S Environmental Protection Agency, 1978). Miller and Davis (1981a) found that pinto bean plants exposed to O_3 at a concentration of 0.10 ppm for 3 hours at 15° or 32°C sustained more severe foliar injury than when the exposure temperature was 24°C. Dunning and Heck (1977) also found that bean plants were more sensitive to O_3 when exposed at 16° or 32°C rather than at 21° or 27°C. Tobacco behaved differently from bean, exhibiting less sensitivity to 0.40 ppm O_3 for 1 hour when the exposure temperature was 32°C as opposed to 16°, 21°, or 27°C.

The effects of temperature on plant response to O_3 are probably both physical and biological. Temperature affects solubility of gases, enzymatic reactivity, membrane conformation, and stomatal movement; the disparate O_3 responses of various plant species at different temperature regimes may also reflect morphological or biochemical differences or both.

7.3.2.2.3 Relative Humidity. It was concluded in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) that in general, plants seem to be more sensitive to O_3 when growth or exposure, or both, occur under conditions of high relative humidity (RH). Table 7-3 is a modification of a summary table in the 1978 criteria document (U.S. Environmental Protection Agency, 1978). Dunning and Heck (1977) reported that the sensitivity of tobacco to O_3

TABLE 7-3. RESPONSE OF PLANTS TO OZONE AS CONDITIONED BY HUMIDITY DURING GROWTH AND EXPOSURE[a]

Plant species	Ozone Concentration ppm	Exposure Duration hr	Notes[b]	Growth or exposure[c]	Response % injury[d]			
					60% RH	85% RH		
Pine, Virginia	0.25	4	3-yr seedlings	Exposure	4	25		
	0.25	4	Juvenile	Growth	50	58		
	0.25	4	Juvenile	Exposure	1	35		
					60% RH	80% RH		
Bean, cultivar Pinto	0.40	1	8 hr PP; 420 $\mu E\ s^{-1}\ m^{-2}$ control conditions; 8 hr PP	Growth	66	78		
				Exposure	52	67		
					60% RH	80% RH		
Tobacco, cultivar Bel W_3	0.40	1	8 hr PP; 420 $\mu E^{-1}\ m^{-2}$ control conditions, 8 hr PP	Growth	42	36		
				Exposure	33	36		
					60% RH	80% RH		
Ash, white	0.25	4	1-yr seedlings	Growth	33	46		
				Exposure	38	41		
				Post-exposure	36	41		
					26% RH	51% RH	95% RH	
Tobacco, cultivar Bel W_3	0.30	1.5	31°C	Exposure	9	39	50	
Bean, cultivar Pinto	0.20	1.5	31°C	Exposure	0	0	55	
					45% RH	60% RH	75% RH	90% RH
Bean cultivar Pinto and Tobacco, cultivar Bel W_3, averaged	0.40	1	8 hr PP	Growth				
				45% EH	36	39	41	31
				90% EH	73	67	81	80
			8 hr PP	Exposure 75% GH	41	53	70	81

[a]Modified from 1978 criteria document (U.S. Environmental Protection Agency, 1978); all the studies were conducted in controlled environment facilities

[b]PP = photoperiod, GH = relative humidity during growth, EH = relative humidity during exposure

[c]Time when humidity treatment was applied

[d]Relative humidity levels during growth or exposure as indicated

(0.40 ppm for 1 hr) was not affected by the relative humidity during growth until the level reached 90 percent RH, at which point plants became more tolerant to O_3. McLaughlin and Taylor (1980) have demonstrated that in pinto bean plants exposed to O_3 concentrations of 0.079 ppm for 2 hours, uptake of the pollutant increased fourfold when the exposure RH was increased from 35 percent to 73 percent. At the low RH (35 percent), O_3 uptake decreased when the pollutant concentration exceeded 0.079 ppm, while at the higher RH (73 percent), O_3 uptake increased with increasing O_3 concentration.

The influence of RH on stomatal function may help to explain the influence of RH and plant responses to O_3. As RH decreases, a water deficit can develop in the guard cells, and stomatal closure occurs to minimize internal foliar water deficit (Ludlow, 1980). Stomatal closure would reduce O_3 flux into the leaf. The influence of RH on plant sensitivity may explain important variations in plant response under field conditions. It is generally accepted that plants in the eastern United States respond to lower concentrations of O_3 than their counterparts in California (U.S. Environmental Protection Agency, 1978). The low RH in the western United States compared to the high RH often found in the eastern United States during the growing season could, at least in part, explain differential plant responses.

7.3.2.2.4 Soil Moisture. Plant response to oxidants is modified by soil moisture, probably through an influence on stomatal function. As soil moisture decreases, water stress increases and there is a reduction in plant sensitivity to O_3. In the previous criteria document (U.S. Environmental Protection Agency, 1978), the major studies on effects of soil moisture prior to 1978 were reviewed and examples are shown in Table 7-4. More recently, Harkov and Brennan (1980) demonstrated that potted hybrid poplar plants were more tolerant of O_3 concentrations of 0.10 ppm after 6 to 9 days without water. Olszyk and Tibbitts (1981) found that pea plants exposed to O_3 concentrations of 0.23 ppm for 2 hours exhibited less foliar injury when the plant water potential was -388 kPa than when it was -323 kPa (reflecting relatively low and high soil moisture levels, respectively).

It appears that the stomata of plants grown under soil moisture stress close more rapidly in the presence of O_3 than stomata of plants under optimal water availability (Tingey et al., 1982; Olszyk and Tibbitts, 1981; U.S. Environmental Protection Agency, 1978). Such a plant response would reduce O_3 ingress and confer some resistance to O_3 injury.

TABLE 7-4. EFFECTS OF SOIL MOISTURE ON RESPONSE OF SELECTED PLANTS TO OXIDANT[a]

Plant species	Ozone exposure: Concentration, ppm	Ozone exposure: Duration	Type of Response	Response, %reduction from control[b]: Moisture conditions: High	to	low
Tomato, cultivar				90% turgid[c]	80% turgid[c]	
Fireball	1.00	1.5 hr	Reduction in chlorophyll	54	10	
	1.00	1.0 hr	Reduction in chlorophyll	67	24	
	0.50	1.0 hr	Reduction in chlorophyll	36	(3)[d]	
	1.00	1.0 hr	Reduction leaf dry wt	48	(40)[d]	
Beet, garden	0.00	3 hr (daily for 38		-40 kPa	-440 kPa	-840 kPa
	0.20	days)	Reduction in dry wt of storage root from nonsaline control	0	24	68
				40	52	69
Bean, cultivar				-40 kPa	-200 kPa	-400 kPa
Pinto	0.00		Reduction in shoot dry wt from nonsaline control	0	18	78
	0.15	2 hr/day (63 days)		27	42	87
	0.25	2 hr/day (63 days)		93	91	88
	0.00		Reduction in root dry wt from nonsaline control	0	25	65
	0.15	2 hr/day (63 days)		25	28	78
	0.25	2 hr/day (63 days)		91	89	79

[a]Modified from Table 11-9 in 1978 criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978).

[b]Special soil moisture conditions are underlined; kPa = kilopascals.

[c]Percent turgid is a measure of the amount of water in the plant leaf.

[d]A stimulation rather than a reduction.

Tingey et al. (1982) found that when bean plants were water stressed, their leaf conductance as compared with nonstressed plants, decreased, 24 hours after the stress was applied. A coincident reduction in plant response to O_3 (1 ppm for 1 hour) occurred. If plants were water stressed for 7 days and then the water stress was relieved, leaf conductance and plant response to O_3 both increased.

Plants subject to long-term soil moisture stress may also exhibit morphological or functional changes, or both, that could modify the O_3 response. Drought or salt stress, which can confer long-term moisture stress, are more limiting to plant health than the air pollution stress that they may modify; hence, any of their protective effects are offset (U.S. Environmental Protection Agency, 1978).

It is important to recognize that plants grown under optimal soil moisture, as in irrigated field or greenhouses, generally are particularly vulnerable to O_3 injury. On this basis, vegetation in natural ecosystems would be expected to be more sensitive to O_3 in years of normal rainfall than in years of drought.

7.3.2.2.5 Soil Fertility. Nutrient balance is fundamental to plant growth; any imbalance could lead to variations in the O_3 response. Plant nutrients, including nitrogen, phosphorus, potassium, and sulfur may all influence plant response to O_3 (U.S. Environmental Protection Agency, 1978). Results of studies cited in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) were inconsistent for a variety of reasons, including species differences and differences in experimental protocols and designs. Since then, additional data have appeared, but the relationship between soil fertility and O_3 sensitivity has not been clarified. Harkov and Brennan (1980) grew hybrid poplar seedlings in varied amounts of slow-release fertilizer, 18:16:12 (N:P:K), that yielded plants with foliar contents of 1.53, 2.69, 3.12, or 3.47 percent nitrogen. Visible injury was greatest in leaves containing 2.69 percent nitrogen when plants were exposed to an O_3 concentration of 0.10 ppm for 6 hours. Using a different N:P:K ratio (6:25:15), Heagle (1979a) found that potted soybean plants exposed to an O_3 concentration of 0.60 ppm for 1.5 hours were more sensitive when fertilized with 100 ml of N:P:K (6:25:15) solution at a rate of 0 or 7.5 g fertilizer/3.8 liters of water than when 15 or 22.5 g/3.8 liter of water was used. Optimum soybean growth was observed at fertilizer rates of 15.0 and 22.5 g/3.8 liters of water. Noland and Kozlowski (1979) reported that silver maple became more sensitive to O_3 (0.30 ppm for 6

hours for 2 successive days) when grown with 117 ppm potassium as compared to 0 to 2 ppm potassium for 6.5 weeks. The authors suggested that potassium may stimulate the guard cells to open, thereby increasing the uptake of O_3 by this species. Dunning et al. (1974) found that pinto bean and soybean foliage were injured more severely by O_3 when plants were grown with low potassium levels (105 meq/liter) rather than normal levels (710 meq/liter). Greenhouse studies of tobacco showed a negative correlation between the calcium content of the leaf tissue and O_3-induced (0.25 ppm for 4 hours) foliar injury (Trevathan and Moore, 1976). This result was observed at eight combinations of O_3 concentration and exposure duration. Additional explanations for the variable response of plants to O_3 when grown with different fertility regimes have not been formulated.

7.3.2.3 Chemical Factors. The chemical environment of plants (e.g., air pollutants, herbicides, fungicides, insecticides, nematocides, antioxidants, and chemical protectants) influences plant responses to O_3. These factors may be grouped into the subject areas of pollutant interactions and chemical sprays.

7.3.2.3.1 Pollutant Interactions. Components of ambient atmospheres such as SO_2, NO_2, and other pollutants may change, modify, or alter plant sensitivity to O_3. These substances all contribute to intensifying or reducing the effects of O_3 on the quality, quantity, or intended use of the plant and must be considered along with the discussion of biological (Section 7.3.2.1) and physical (Section 7.3.2.2) factors that modify plant responses to O_3. The magnitude of these modifications depends on the plant species, cultivar, pollutant concentration, duration and frequency of exposure, and the environmental and edaphic conditions in which plants are grown.

The study of the effects of pollutant combinations on plants has evolved from the basic premise that pollutants co-occur, and that together, therefore, they may induce more plant damage than that induced by the individual pollutants. Researchers have tried to develop terminology that is meaningful in evaluating the effects of pollutant mixtures on plants (Reinert et al., 1975; Ormrod, 1982; Ormrod et al., 1984). Two categories of plant response are possible when the effects of two pollutants (A and B) are evaluated. When one pollutant has no effect on plant response but the second one does, it is termed "no joint action." Thus, the term "joint action" implies that both pollutants have some effect on plant response. The concept of joint action can be further

divided into subcategories that can be used to describe the response of plants to pollutants, A and B:

1. Additive response: $Effect_{AB} = Effect\ A + Effect\ B$
2. Interactive response: $Effect_{AB} \neq Effect_A + Effect_B$

The interactive response may be of two possible types:

1. Synergism: $Effect_{AB} > Effect_A + Effect_B$

2. Antagonism: $Effect_{AB} < Effect_A + Effect_B$

It is important to quantify interactive effects. It is equally important to identify and quantify additive effects. It is the intent of this section to discuss the effects of the joint action of $SO_2 + O_3$, $NO_2 + O_3$, and $NO_2 + SO_2 + O_3$; and to identify the concentrations of O_3, alone or in combination with other pollutants, that cause yield loss.

7.3.2.3.1.1 Ozone and sulfur dioxide. The joint action of O_3 and SO_2 has been extensively studied. The previous criteria document (U.S. Environmental Protection Agency, 1978) stated that mixtures of O_3 plus SO_2 were of special interest because of the Menser and Heggestad (1966) study. In that study, a sensitive 'Bel W_3' cigar wrapper tobacco exposed to mixtures of O_3 (0.03 ppm) and SO_2 (0.25 ppm) for 2 or 4 hours sustained 23 percent and 48 percent foliar injury, respectively; but no visible injury was produced by the same concentrations of the individual pollutants. The additive and frequently synergistic foliar-injury response of tobacco has been reported to occur in numerous tobacco cultivars and types. Menser and Hodges (1970), Grosso et al. (1971), and Hodges et al. (1971) determined the response of several Nicotiana species and various N. tabacum cultivars to SO_2 and O_3 mixtures. They found that O_3 and SO_2 acted synergistically and produced O_3-type symptoms on all cultivars of burly and Havana tobacco. When plants were fumigated for 4 hours with 0.03 ppm O_3 alone or with 0.45 ppm SO_2 alone, no injury was observed. When the gases were combined and the plants were exposed for the same length of time, foliar injury, ranging from 5 percent to 15 percent was produced. Tingey et al. (1973c) exposed 11 species of plants to different combinations of O_3 and SO_2: either 0.05 or 0.1 ppm O_3 and 0.1, 0.25, or 0.5 ppm SO_2 for 4

hours. They observed additive and synergistic foliar-injury responses as summarized for six of the species in Table 7-5.

TABLE 7-5. SUMMARY OF EFFECTS OF SULFUR DIOXIDE AND OZONE MIXTURES ON FOLIAR INJURY

Plant species	Response at stated ppm SO_2/O_3 concentrations[a]			
	0.50/0.05	0.50/0.10	0.10/0.10	0.25/0.10
Alfalfa	-	+	+	+
Broccoli	+	0	+	0
Cabbage	0	+	0	0
Radish	0	+	+	+
Tomato	0	0	-	0
Tobacco, Bel W_3	+	+	0	+

Source: Tingey et al. (1973c)

[a] + = greater than additive; 0 = additive; - = less than additive

Foliar injury symptoms decrease the aesthetic value of various types of woody ornamental and floriculture crop species (7.4.3). When foliage is the marketable plant part, substantial losses in quality and marketability of the crop result from the injury produced by the joint action of pollutants. The amount of foliar injury affects the amount of photosynthate produced by the plant. Thus, in many instances, foliar injury provides some indication of the potential for loss in weight, size, and number (yield) of the marketable plant part. Foliar-injury response from the joint action of pollutants needs continued study.

Since 1978, researchers have continued to use foliar injury as an indicator of the sensitivity of plant species and cultivars within a species to the joint action of O_3 and SO_2. Studies have included apple (Shertz et al., 1980), grape (Shertz et al. 1980b), radish, cucumber, and soybean (Beckerson and Hofstra, 1979b), begonia (Reinert and Nelson, 1980), and pea (Olszyk and Tibbitts, 1981). These results are summarized in Table 7-6. Although relatively high O_3 and SO_2 concentrations were used for only a few hours, most species displayed a synergistic injury response from the joint effects of the pollutants, supporting previous observations.

TABLE 7-6. FOLIAR INJURY RESPONSE OF VARIOUS PLANT SPECIES TO OZONE AND OZONE PLUS SULFUR DIOXIDE[a]

Species	Concentration[b], ppm O_3	Concentration[b], ppm SO_2	Exposure duration	Response	Foliar injury,% O_3	Foliar injury,% SO_2	Foliar injury,% $SO_2 + O_3$	Monitoring method[a]	Calibration method	Fumigation facility	Reference
Apple (Vance Delicious)	0.40	0.40	O_3-4 hr/day, 1 time SO_2-4 hr/day, 1 time	Foliar injury	24	8	26	O_3-Mast meter	KI	Controlled environment chambers	Shertz et al. (1980a)
(Imperial McIntosh)					30	9	22	SO_2-Not given	Permeation tubes		
(Golden Delicious)					27	19	19				
Grape (Ives)	0.40	0.40	O_3-4 hr/day, 1 time SO_2-4 hr/day	Foliar injury	27	18	47	O_3-Mast meter SO_2-Not given	KI Permeation tubes	Controlled environment chambers	Shertz et al. (1980b)
(Delaware)					1	1	4				
Radish	0.15	0.15	O_3-6 hr/day, 5 days SO_2-4 hr/day, 5 days	Foliar injury	13	1	30	O_3 -UV Dasibi SO_2-Conductivity	Not given Not given	Exposure chambers in environmentally controlled room	Beckerson and Hofstra (1979)
Cucumber					27	9	54				
Soybean					18	0	0				
Begonia (Schwabenland Red)	0.25	0.50	O_3-4 hr/day every 6 days, 4 times SO_2-4 hr/day every 6 days	Foliar injury	54	2	67	O_3-Chemiluminescence SO_2-Flame photometry	Monitor Labs Calibrator	CSTR in greenhouse	Reinert and Nelson (1980)
(Wisper 'O' Pink)					25	1	58				
(Fantasy)					2	0	13				
(Renaissance)					15	0	18				
(Turo)					8	0	12				
Pea	0.13	0.40	O_3-4 hr, 1 time SO_2-4 hr, 1 time	Foliar injury	0	0	32	O_3-Chemiluminescence SO_2-Thermoelectron (SO_2)	KI Gas-phase titration	Plexiglas chamber	Olszyk and Tibbitts (1981)

[a]Where column entry is blank, information is the same as above.

[b]Concentrations of the combination were the same as the single gases.

The chronic effects of the joint action of O_3 and SO_2 on the growth of radish, alfalfa, soybean, and tobacco (Table 7-7) were summarized in 1978 (U.S. Environmental Protection Agency, 1978). These four species represent a diverse group of plant species in terms of growth habit. Primary focus in earlier studies was on weight changes during the vegetative stage of growth, with the exception of one study (Heagle et al., 1974); however, radish root (hypocotyl), tobacco leaf weight, and alfalfa foliage (top) weight are the marketable portions of the plant. With the exception of alfalfa, the growth of each plant species was reduced in an additive manner by the joint action of the two pollutants. Soybean root (fresh weight) responded synergistically to the joint action of O_3 and SO_2 in one study (Tingey et al., 1973d).

The above data were obtained in greenhouse studies (except for Heagle et al., 1974). These data provided preliminary evidence that the joint action of O_3 and SO_2 at concentrations of 0.05 ppm and greater caused an additive reduction in plant yield. Additional studies of the joint action of O_3 and SO_2 on plant yield have been conducted since 1978 (Tables 7-8 and 7-9). More emphasis has been given to the influence of pollutant combinations on yield (weight, size, and numbers) as a measure of plant response, including the yield of flower, fruit, and seed portions of the plant (Table 7-8). Shew et al. (1982) exposed tomato to 0.2 ppm O_3 and SO_2 alone and in mixture, two times per week, 2 hours each time for 8 weeks. They demonstrated that the joint action of O_3 and SO_2 was synergistic, decreasing the weight of the largest fruit in each tomato cluster, but that the synergistic effects did not influence total fruit weight per plant.

Reinert and Nelson (1980) exposed five cultivars of begonia to 0.25 ppm O_3 and SO_2 alone and in combination for a total of 16 hours (4 hours per week) over a 4-week period. The joint action of O_3 plus SO_2 was antagonistic (cv. Schwabenland Red) and additive (cv. Fantasy), respectively, in producing a loss in flower weight. The mean yield (flower weight) from the joint effects of O_3 and SO_2 ranged from 1 percent (Schwabenland Red) to 15 percent (Fantasy) greater than the loss resulting from O_3 alone.

The joint action of O_3 and SO_2 on the growth and yield components of tall fescue was studied by Flagler and Younger (1982a). Fescue was exposed to O_3 concentrations of 0.0, 0.1, 0.2, and 0.3 ppm and 0.0 and 0.1 ppm SO_2 for 6 hours per day, once a week for 12 weeks. The joint action of SO_2 in the presence of increasing concentrations of O_3 caused additive decreases in

TABLE 7-7. GROWTH RESPONSE OF SELECTED PLANTS TO OZONE AND OZONE PLUS SULFUR DIOXIDE

Species	Concentration[a], ppm O_3	Concentration[a], ppm SO_2	Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted) O_3	Yield, % reduction from control (negative unless otherwise noted) SO_2	Yield, % reduction from control (negative unless otherwise noted) $SO_2 + O_3$	Monitoring Method	Calibration Method	Fumigation Facility	Reference
Radish (Cherry Belle)	0.05	0.05	8 hr/day, 5 days/wk, 5 wks	Top dry wt	10	0	10	O_3-Mast meter	KI	Chambers in greenhouse	Tingey et al. (1971)
				Root dry wt	50	17	55	SO_2-Conductivity	Colorimetric		
Alfalfa (Vernal)	0.05	0.05	8 hr/day, 5 days/wk 12 wk	Top dry wt	12	26	18	O_3-Mast meter	KI	Chambers in greenhouse	Tingey and Reinert (1975)
				Root dry wt	22	29	24	SO_2-Conductivity	Colorimetric		
Soybean (Dare)	0.05	0.05	7 hr/day, 5 days/wk 3 wk	Top fresh wt	2	+5	12	O_3-Mast meter	KI	Chambers in greenhouse	Tingey et al. (1973d)
				Root frest wt	3	0	24	SO_2-Conductivity	Colorimetric		
Soybean (Dare)	0.10	0.10	7 hr/day, 5 days/wk, until harvest	Top fresh wt	65	+3	52	O_3-Mast meter	KI	Field chambers	Heagle et al. (1974)
				Seed wt	54	4	63	SO_2-Flame photometry	Not given		
Tobacco (Bel-W_3)	0.05	0.05	7 hr/day, 5 days/wk, 4 wk	Leaf dry wt	1	14	30	O_3-Mast meter	KI	Chambers in greenhouse	Tingey and Reinert (1975)
								SO_2-Conductivity	Colorimetric		

[a]Concentrations of the combination were the same as the single gases.

TABLE 7-8. YIELD RESPONSES OF VARIOUS PLANT SPECIES TO OZONE AND OZONE PLUS SULFUR DIOXIDE

Species	Concentration[a], ppm O_3	Concentration[a], ppm SO_2	Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted) O_3	Yield, % reduction from control (negative unless otherwise noted) SO_2	Yield, % reduction from control (negative unless otherwise noted) $SO_2 + O_3$	Monitoring method[a]	Calibration method	Fumigation facility	Reference
Tomato (Walter)	0.20	0.20	O_3-4 hr/day, 2 day/wk, 8 wk	Largest fruit each cluster	1	2	18	O_3-Chemiluminescence	Known source Permeation tube	Chambers in greenhouse (CSTR)[b]	Shew et al. (1982)
			SO_2-4 hr/day, 2 day/wk, 8 wk	Total fruit	5	4	4	SO_2-Flame photometry			
Begonia (Schwabenland Red)	0.25	0.50	O_3-4 hr/day, every 6 days for 4 times, SO_2-4 hr/day every 6 days 4 for times	Flower wt	39	22	38	O_3-Chemiluminescence SO_2-Flame photometry	Known source Permeation tube	Chambers in greenhouse (CSTR)	Reinert and Nelson (1980)
(Wisper 'O' Pink)	0.25	0.50		Flower wt	22	+16	28				
(Fantasy)	0.25	0.50		Flower wt	6	9	21				
(Renaissance)	0.25	0.50		Flower wt	55	43	54				
(Turo)	0.25	0.50		Flower wt	+10	+11	4				
Snap bean (BBL 290) (BBL 274) (Astro)	0.065[b]	0.30	O_3-11 hr/day avg, 3 mo SO_2-6 hr/day, 5 day/wk, 5 wk	Green pod wt	2	16	44	O_3-Not given SO_2-Pulse fluorescence	Not given Permeation tube	Field chamber (open top)	Heggestad and Bennett (1981)
Tall fescue (Alta)	0.10	0.10	O_3 and SO_2 6 hr/day, once a week for 12 weeks	No. of tillers	+1	6	4	O_3-UV	UV photometry	Chambers in greenhouse (CSTR)	Flagler and Younger (1982a)
	0.20	0.10			6	6	+12				
	0.30	0.10			+5	6	19	SO_2-Pulse fluorescence	Permeation tube		
	0.10	0.10		Top dry wt	+3	5	18				
	0.20	0.10			19	5	19				
	0.30	0.10			18	5	53				
Alfalfa (Mesa-Sirsa)	0.05	0.05	O_3-6 hr/day, 68 days SO_2-24 hr/day, 68 days	Foliage dry wt	49		46	O_3 Mast meter	KI	Field chamber (closed top)	Neely et al. (1977)

[a]Concentrations of the combination were the same as the single gases.

[b]CSTR = Continuous stirred tank reactor exposure chamber.

TABLE 7-9. THE INFLUENCE OF MIXTURES OF OZONE AND SULFUR DIOXIDE ON SOYBEAN YIELD (grams OF SEED)

Seasonal 7 hr/day O_3 concentration, ppm	Seasonal 4 hr/day SO_2 concentration, ppm			
	0.00	0.026	0.085	0.367
0.00	412	438	426	286
0.55	381	318	329	237
0.068	318	313	294	192
0.085	273	238	233	189
0.106	246	250	198	154

[a]Each value is the mean of eight 1-m-row samples.

Heagle et al., 1983a.

fescue total dry weight, root dry weight and root-to-shoot ratio. For example, O_3 decreased total dry weight 49 percent at 0.3 ppm O_3; in the presence of SO_2 there was an additional 11 percent loss in total dry weight. Ozone and SO_2 acted synergistically to decrease the number of tillers in fescue but the synergism depended on the O_3 concentration. These studies were done in a charcoal-filtered-air greenhouse in CSTR exposure chambers.

Recently, studies of the combined action of O_3 and SO_2 have been conducted in open-top field chambers (Heagle et al., 1983a; Heggestad and Bennett, 1981) and large CSTR field chambers (Foster et al., 1983b; and Oshima, 1978). In these experiments, O_3 levels near ambient, as well as increasing O_3 concentrations above ambient, were used in combination with two or more concentrations of SO_2. Heagle et al. (1983a) exposed soybean to various concentrations of O_3 for 7 hr daily and 4 concentrations of SO_2 for 4 hours per day. Both gases were added for 111 days (Table 7-9). The high concentration of SO_2 decreased the amount of visible injury from increasing concentrations of O_3. The joint action of O_3 and SO_2 on soybean seed weight per meter of row at lower concentrations appeared to be additive, but as the concentrations of both pollutants increased there was an antagonistic $O_3 + SO_2$ interaction. The nature of the joint action was similar to that for visible injury: as SO_2 increased to 0.365 ppm, the loss of seed weight from increasing O_3 concentrations was less than at lower concentrations of SO_2. For example, at 0.365 ppm SO_2 and 0.085 ppm O_3 there was a 34 percent seed-weight loss compared to that at 0.365 ppm

SO_2 alone. At 0.026 ppm SO_2 and 0.085 ppm O_3 there was a 45 percent seed-weight loss, compared to that at 0.026 ppm SO_2 alone (Table 7-8). The two highest mean SO_2 concentrations were higher than usually occur in the United States (U.S. Environmental Protection Agency, 1983).

Heggestad and Bennett (1981) exposed three cultivars of bean to increasing concentrations of SO_2 (0.06, 0.12, 0.3 ppm) for 6 hours per day in charcoal-filtered and unfiltered ambient air, using open-top field chambers. The beans were exposed daily 5 days per week, for 31 days. Sulfur dioxide (0.30 ppm) reduced snap bean yields (all cultivars) in nonfiltered air (O_3) by 44 percent compared to a 16 percent reduction in charcoal-filtered air. At 0.06 ppm SO_2, the yield of cv. 'Astro' was reduced more in nonfiltered than in filtered air. The SO_2 concentrations used in this study, however, were higher than typically occur in the United States (U.S. Environmental Protection Agency, 1983).

In southern California, Oshima (1978) and Foster et al. (1983a,b) conducted studies to determine the joint action of SO_2 and photochemical oxidants. A range of photochemical oxidant concentrations was obtained by combining various proportions of charcoal-filtered ambient air containing oxidants yielding various concentrations of oxidants in ambient air and charcoal-filtered air which was added to the CSTR-type field exposure chambers. Sulfur dioxide (0.0 or 0.1 ppm) was added to the chambers for 6-hour intervals approximately 47 times over a 76-day period for beans (Oshima, 1978) and 4 to 5 days per week over a 10-week period for potato (Foster et al., 1983b). The kidney bean yield was less in the presence of ambient oxidant plus SO_2 except at the high oxidant concentrations, when the yields were more nearly similar. Similar studies with potato exposed to SO_2 and partially filtered ambient air containing O_3 resulted in no evidence of joint action on tuber yield (Foster et al., 1983b).

In summary, recent studies on the effects of O_3 and SO_2 on the yield of various plant species have found the effects of O_3 and SO_2 to be additive for begonia flower weight, fescue plant and root dry weight, soybean seed weight, and snap bean and green bean yield. Synergistic interaction was identified for the effects of O_3 and SO_2 on the largest tomato fruit in each cluster, the number of fescue tillers, and kidney bean yield. Examples of antagonistic joint action occurred in one cultivar of begonia and in soybean seed weight at the highest SO_2 concentration. These effects varied with the concentration of pollutants, the plant response measured, species, and cultivar. Thus, observations were significant enough to propose the following general concepts:

1. When concentrations of O_3 and SO_2 are below or at the threshold for visible injury, synergistic interaction may be a frequent occurrence.

2. As concentrations of O_3 and SO_2 increase in mixture above the injury threshold, yield loss from joint action may be additive.

3. When both pollutants are present in high concentrations, the joint action of O_3 and SO_2 may be antagonistic, such that further weight loss is miminal.

4. An analysis of ambient air monitoring data at various locations determined the frequency of the co-occurrence of pollutants pairs (O_3/SO_2, O_3/NO_2) during a 5-month summer season (May through September) (Lefohn and Tingey, 1984). Co-occurrence was defined as the simultaneous occurrence of hourly averaged concentrations of 0.05 ppm for both pollutants of the pair, Applying this criterion, most sites experienced 10 or fewer periods of co-occurrence during the 5-month period.

7.3.2.3.1.2 Ozone and Nitrogen Dioxide. Although the effects of NO_2 and O_3, alone and in mixture, have not generally been studied, recent reports comparing two- and three-pollutant mixture treatments include NO_2 plus O_3 combinations. Kress and Skelly (1982) have studied the responses of seven tree species to NO_2 (0.1 ppm) and O_3 (0.1 ppm) alone and in mixture for 6 hours per day, for 28 consecutive days (Table 7-10). Virginia and loblolly pine growth, as measured by plant height, was significantly suppressed by the O_3 + NO_2 treatment, but not by the individual pollutants. Nitrogen dioxide alone significantly suppressed root and total dry weight of sweetgum; however, the joint action of O_3 + NO_2 was antagonistic on sweetgum root and total dry weight and white ash root dry weight.

7.3.2.3.1.3 Ozone plus nitrogen dioxide and sulfur dioxide. The previous criteria document (U.S. Environmental Protection Agency, 1978) makes no reference to the effects of mixtures using three pollutants. Since then, however, experiments have been designed to study the effect of increasing concentrations of NO_2, SO_2, and O_3 in mixture (Table 7-11). Reinert and Gray (1981) exposed radish plants one time for 3 or 6 hours to 0.2 or 0.4 ppm of NO_2, SO_2, or O_3, or combinations. They found no interaction for either two- or three-gas

TABLE 7-10. YIELD RESPONSES OF SELECTED TREE SPECIES TO OZONE PLUS NITROGEN DIOXIDE[a]

Species	Concentration[b] ppm O_3	Concentration[b] ppm SO_2	Exposure Duration	Response	Height and top dry wt % reduction from control (negative unless otherwise noted) O_3	NO_2	O_3 + NO_3
Loblolly Pine	0.10	0.10	6 hr/day, 28 days	Height Growth	17	15	39
				Top Dry Wt	19	18	16
Loblolly Pine (6-13 x 2-8)[c]	0.10	0.10	6 hr/day, 28 days	Height Growth	25	11	24
				Top Dry Wt	9	10	4
Pitch Pine	0.10	0.10	6 hr/day, 28 days	Height Growth	14	16	26
				Top Dry Wt	+14	20	11
Virginia Pine	0.10	0.10	6 hr/day, 28 days	Height Growth	11	13	23
				Top Dry Wt	2	1	1
Sweetgum	0.10	0.10	6 hr/day, 28 days	Height Growth	27	32	28
				Top Dry Wt	30	25	19
White Ash	0.10	0.10	6 hr/day, 28 days	Height Growth	20	+5	16
				Top Dry Wt	37	1	37
Green Ash	0.10	0.10	6 hr/day, 28 days	Height Growth	19	+1	22
				Top Dry Wt	17	10	29
Willow Oak	0.10	0.10	6 hr/day, 28 days	Height Growth	5	10	14
				Top Dry Wt	+1	24	13

Source: Kress and Skelly, 1982

[a]Plants were exposed in continuously stirred tank reactor (CSTR) exposure chambers in a greenhouse. Ozone and NO_2 were monitored using chemiluminescent analyzers which were calibrated with known sources of each pollutant.

[b]Concentrations of the combination were the same as the single gases.

[c]Indicates seeds were from a full-sibling collection.

TABLE 7-11. YIELD OF VARIOUS PLANT SPECIES TO OZONE, SULFUR DIOXIDE, AND NITROGEN DIOXIDE

Species	Concentration[a] ppm O_3	SO_2	NO_2	Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted) O_3	SO_2	NO_2	SO_2+NO_2	O_3+SO_2	O_3+NO_2	$O_3+SO_2+NO_2$	Monitoring method	Calibration method	Fumigation facility[b]	Reference
Snap Bean	0.15	0.15	0.15	4 hr, 3 times/wk 4 wks	Green bean fresh wt	27	9	+12	20	6	25	27	O_3, NO_2-chemiluminescence; SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Reinert and Heck (1982)[c]
Marigold	0.30	0.30	0.30	3 hr/day, 3 days/wk, 3 wks	Flower wt	20	47	+16	13	23	+4	20	O_3, NO_2-chemiluminescence; SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Reinert and Sanders (1982)
Marigold	0.30	0.30	0.30	3 hr/day, 3 days/wk, 1 wk	Flower wt	41	49	23	47	25	39	20	O_3, NO_2-chemiluminescence SO_2 Flame photometry	Known source	Chambers in greenhouse (CSTR)	Sanders and Reinert (1982b)
Radish	0.30	0.30	0.30	3 hr/day, 3 days/wk, 1 wk	Hypocotyl	30	+21	+10	+16	43	33	65	O_3, NO_2-chemiluminescence SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Sanders and Reinert (1982b)
Radish	0.40	0.40	0.40	3 hr + 6 hr 1 time	Hypocotyl	20	4	0	13	24	23	36	O_3, NO_2-chemiluminescence SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Reinert and Gray (1981)
Azalea	0.25	0.25	0.25	3 hr/day, 6 times in a 4-wk period	Foliage	6	7	0	17	22	16	27	O_3, NO_2-chemiluminescence; SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Sanders and Reinert (1982a)

TABLE 7-11 (cont'd). YIELD OF VARIOUS PLANT SPECIES TO OZONE, SULFUR DIOXIDE, AND NITROGEN DIOXIDE

Species	Concentration[a] (ppm) O_3	SO_2	NO_2	Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted) O_3	SO_2	NO_2	SO_2+NO_2	O_3+SO_2	O_3+NO_2	$O_3+SO_2+NO_2$	Monitoring method	Calibration method	Fumigation facility[b]	Reference
Kentucky bluegrass (12 cultivars)	0.15	0.15	0.15	O_3-hr/day, 10 days SO_2-cont. 10 days NO_2-, continuous, 10 days	Leaf area	5	12	6	NT[d]	NT	NT	16	O_3, UV Dasibi SO_2, phase fluorescence NO_2, chemiluminescence	Not given exposure chamber	Plexiglas and Ormrod	Elkiey (1980)
Red top grass	0.15	0.15	0.15	SAA	Leaf area	14	12	12	NT	NT	NT	28				
Creeping bentgrass	0.15	0.15	0.15	SAA[e]	Leaf area	7	18	8	NT	NT	NT	26				
Colonial bentgrass	0.15	0.15	0.15	SAA	Leaf area	15	6	13	NT	NT	NT	27				
Red Fescue (2 cultivars)	0.15	0.15	0.15	SAA	Leaf area	16	0	0	NT	NT	NT	22				
Perennial Ryegrass	0.15	0.15	0.15	SAA	Leaf area	20	+7	2	NT	NT	NT	13				

[a]Concentrations of the combinations were the same as two single gases, except for bean exposed at 0.05 (0), 0.1 or 0.15 (SO) and 0.05 or 0.1 (NO_2).

[b]CSTR = Continuous stirred tank reactor exposure chamber.

[c]Derived from experimental data.

[d]NT = Exposure combination not tested.

[e]SAA = Exposure condition same as above.

mixtures, even though the decrease in hypocotyl weight by O_3 was further reduced by NO_2 alone, SO_2 alone, or NO_2 plus SO_2, which suggests an additive response. Reinert and Sanders (1982) and Sanders and Reinert (1982b) reported similar results in radish following repeated exposures at different ages.

Marigold was exposed at different ages for 3 hours to 0.3 ppm of each pollutant, three times per week for 1 week (Sanders and Reinert, 1982b). Ozone alone decreased flower dry weight but the interaction of NO_2 or O_3 with SO_2 was apparently antagonistic. Similar results were reported for marigold exposed repeatedly 3 days a week for 3 weeks. Reinert and Heck (1982) exposed snap beans 27 times intermittently for 3 hours each time over 6.5 weeks to increasing concentrations of SO_2 (0.0, 0.1, 0.15 ppm) and NO_2 (0.0, 0.05, 0.1 ppm) in the presence of 0.05 ppm O_3. Ozone alone decreased bean pod weight 10 percent, while NO_2 at 0.1 ppm, SO_2 at 0.15 ppm, and at O_3 0.05 ppm decreased pod weight by 31 percent. Reinert and Heck (1982) exposed 16-day-old radish plants one time for 3 hours to three concentrations (0.0, 0.2, and 0.4 ppm) or (0.1, 0.2, and 0.4 ppm) of NO_2, SO_2, and O_3 at all 27 (3 x 3 x 3) treatment combinations (Table 7-12). In both experiments, the reduction in size of radish hypocotyls was predominantly additive and linear within the range of concentrations used. The above studies were conducted primarily under greenhouse conditions but some of the species studied, such as marigold, tomato, and azalea, are grown commercially in greenhouses. The concentrations of SO_2 and NO_2 ($\leq$ 0.4 ppm) are below the concentration of each pollutant individually (SO_2, 0.5 ppm, and NO_2, 1 to 2 ppm) that causes visible injury for a single exposure (Tingey et al., 1971b).

Several turf grass species and cultivars were exposed to O_3, SO_2, and NO_2 individually, and the combination of the three pollutants combined to determine the effects on leaf area (Elkiey and Ormrod, 1980). The three-pollutant combination reduced the leaf area of only 4 of the 12 Kentucky bluegrass cultivars. The three-pollutant combination had no significant effect on red top, creeping bentgrass, and colonial bentgrass, but it did significantly reduce the leaf area of perennial ryegrass and one of the two red fescue cultivars.

The initial studies on the effects of mixtures of NO_2, SO_2, and O_3 have involved the co-occurrence of these pollutants. The sequential effects of pollutant mixtures need to be investigated. In addition, more monitoring data are needed for each of the three pollutants so that realistic occurrences and concentrations can be part of the experimental design for assessing plant response.

TABLE 7-12. THE EFFECTS OF NITROGEN DIOXIDE IN COMBINATION WITH SULFUR DIOXIDE OR OZONE, OR BOTH, ON RADISH ROOT; FRESH WEIGHT (GRAMS) AT THREE CONCENTRATIONS OF EACH GAS[a]

SO_2, ppm	O_3, ppm	Radish root fresh wt, g		
Experiment 1		NO_2, ppm		
		0.1	0.2	0.4
0.1	0.1	9.5	8.8	8.4
	0.2	7.3	7.7	4.6
	0.4	4.6	3.0	2.9
0.2	0.1	9.5	9.5	6.2
	0.2	6.3	5.3	5.1
	0.4	2.9	3.3	2.7
0.4	0.1	8.3	6.6	4.9
	0.2	5.6	5.0	3.9
	0.4	2.3	3.0	3.0
Experiment 2		NO_2, ppm		
		0.0	0.2	0.4
0	0	15.2	16.9	14.4
	0.2	12.4	11.0	9.6
	0.4	6.6	5.3	8.0
0.2	0	16.7	17.2	11.9
	0.2	11.2	7.3	7.6
	0.4	6.8	5.3	4.8
0.4	0	17.2	13.2	11.4
	0.2	9.5	7.2	5.8
	0.4	5.1	5.6	4.3

Source: Reinert and Heck (1982).

[a]Means represent 20 (exp. 1) or 12 (exp. 2) plants. Plants were exposed once for 3 hr at 16 days from seed and were harvested at 23 days from seed.

7.3.2.3.1.4 Ozone and other pollutants. Zinc and cadmium reacted synergistically with O_3 in producing visible injury and chlorophyll loss in garden cress and lettuce (Czuba and Ormrod, 1974). The combination of cadmium (Cd) and O_3 induced earlier development of necrosis and chlorosis and the injury was observed at lower O_3 plus cadmium levels than for the individual treatments (Czuba and Ormrod, 1981). Cadmium and nickel (Ni) concentrations of 1, 10, 100 μmol in the nutrient solution interacted to reduce root and shoot growth of peas (Ormrod, 1977). Ozone exposure increased the Cd and Ni effects but the increase was less than additive. Low concentrations of cadmium and nickel, however, tended to enhance O_3 phytotoxicity. The interaction of cadmium and O_3 was influenced by both concentration and the environmental conditions. Tomato plants grown at 0.25 and 0.75 mg Cd/ml developed only slight foliar injury when exposed to O_3 (0.20 ppm for 3 hours) under cloudy skies; whereas the Cd treatment alone had no significant effect (Harkov et al., 1979). In full sun there was extensive O_3 injury and the joint response was synergistic. The changes in the cellular ultrastructure of pea leaves resulting from exposure to ozone (0.50 ppm) increased when plants were grown in nutrient solutions containing 100 μmol nickel sulfate (Mitchell et al., 1979).

The limited published data indicate that heavy metals can increase the phytotoxic reactions of ozone. At the present time, it is not possible to assess the risk from the joint action of gaseous and heavy metal pollutants to vegetation. In industrial areas, along heavily travelled highways, and on crop lands fertilized with sludge, however, there is the possibility for interactive effects.

The results from pollutant interaction studies demonstrated that the joint action of O_3 with SO_2 or NO_2 or both decreased the yield of several crop species more than O_3 alone. Sulfur dioxide usually modified the response to O_3 in an additive way. Yield losses resulting from O_3 exposure were further decreased by SO_2 in radish (5 percent), alfalfa (6 percent), soybean seed weight (9 percent) and tobacco (7 percent). These effects were at concentrations of O_3 and $SO_2 \leq 0.05$ ppm and greater. At higher concentrations of O_3 and SO_2 (0.2 to 0.5 ppm), yield losses from O_3 exposure were further reduced by SO_2 in begonia flower weight 6 to 15 percent depending on the cultivar; in kidney bean 11 to 28 percent, depending on the O_3 concentration; in potato, 11 to 16 percent; in soybean seed weight, 11 to 12 percent; and fescue, $\leq$ 24 percent. Additional information concerning pollutant dose and frequency of exposure at which these effects take place is needed.

7.3.2.3.2 Chemical Sprays. A variety of agricultural chemicals commonly used by growers to control diseases and insects and other pests on crops, and research plantings can modify vegetational response to air pollutants (Reinert and Spurr, 1972; Sung and Moore, 1979). Certain fungicides, insecticides, nematicides, and herbicides have been found to change the sensitivity of plants to ozone.

Protection from or reduction of O_3 injury to vegetation is significant to growers of economically important crops in areas of high ozone concentrations. In addition, the control of O_3 injury to plants in the field can be of assistance to scientists attempting to determine how O_3 injures plants. The report by Kendrick et al. (1954) that fungicides used as sprays or dusts protected pinto bean foliage from O_3-induced plant damage alerted the scientific community to the fact that agricultural chemicals could protect vegetation from O_3 injury. Since that time, it has been shown that other chemicals, including ascorbic acid sprays (Freebairn, 1963; Freebairn and Taylor, 1960), antiozonants (Rich and Taylor, 1960), anti-transpirants (Gale and Hagan, 1966), stomatal regulators (Rich, 1964), growth regulators (Cathey and Heggestad, 1973), and some herbicides can offer some protection against ozone injury.

A comprehensive review of plant protectant sprays and their uses is found in Ozone and Other Photochemical Oxidants (National Research Council, 1977). The degree of plant protection obtained from O_3 injury and the species tested are listed in Table 7-13.

Nematicides increase the sensitivity of vegetation to O_3, but nematicides in combination with certain fungicides decrease sensitivity to O_3. Miller et al. (1976) noted that pinto bean and tobacco growing in sand or soil treated with the contract nematicides, phenamiphos, fensulfothion, aldicarb, and oxafothion were more sensitive to O_3. Adding benomyl or carboxin, both fungicides, to the soil containing the contact nematicides caused the plants to become highly resistant to O_3 injury. Benomyl or carboxin used alone also induced plant resistance to O_3 injury.

The influence of selected herbicides on the O_3 sensitivity of tobacco and other crop plants has been studied with differing results. Carney et al. (1973) demonstrated that pebulate increased O_3 injury to tobacco but that benefin decreased O_3 injury. The studies of Sung and Moore (1979), however, failed to confirm the observation that pebulate increases O_3 sensitivity. Sung and Moore suggested that the difference in results occurred either because

TABLE 7-13. PROTECTION OF PLANTS FROM OXIDANT INJURY BY APPLICATION OF PROTECTIVE CHEMICALS

Plant species	Pollutant protected from	Chemical (Concentration)[a]	Type of protectant	Degree of protection, %[b]
Bean, cultivar Pinto	Oxidant	K-Ascorbate (0.01 M)	Antioxidant	52
Petunia	Oxidant	K-Ascorbate (0.01 M)	Antioxidant	39
Tobacco	Oxidant	Zn-ethylenebisdithiocarbamate dust (variable)	Fungicide	44
Tobacco, cultivar White Gold	Oxidant	Phygon XL (variable)	Antioxidant	89
Tobacco, cultivar White Gold	Oxidant	Phygon XL (variable)	Antioxidant	78
Tobacco, cultivar White Gold	Oxidant	4,4-Dioctyldiphenylamine in butyl latex	Antioxidant	100
Bean, cultivar Pinto	Oxidant	Zineb (normal use)	Fungicide	91
Bean, cultivar Pinto	Ozone	Zineb (normal use)	Fungicide	97
Azalea	Oxidant	Benomyl (60-ppm drench)	Fungicide	96
Bean, cultivar Pinto	Ozone	Carboxin (2.3 ppm in soil)	Fungicide	95
Radish	Ozone	N-6-Benzyladenine (30-ppm spray)	Growth substance	100
Poinsettia	Ozone	Ancymidol (100-ppm spray)	Growth retardant	100
Poinsettia	Ozone (chronic)	Benomyl (500-ppm drench)	Fungicide	57
Bean, cultivar Pinto	Ozone	Folicote (0.5% spray)	Wax emulsion	92
Bean, cultivar Pinto	Ozone	Benomyl (5 ppm in nutrient solution)	Fungicide	97
Bean and cucumber	Ozone	Benomyl (80 ppm in soil)	Fungicide	94
Grape	Ozone	Benomyl (6.7 kg/ha, 6 times)	Fungicide	53
Bean, cultivars Tempo and Pinto	Ozone	Benomyl (0.25 to 0.36%, 4 weekly sprays)	Fungicide	75
Bean, cultivars Tempo and Pinto	Oxidant	Carboxin (10% granular as soil amendment, 8 g/5-m row)	Fungicide	100
Tobacco	Ozone (0.50 ppm, 2 hr)	Piperonylbutoxide (2 mM solution)	Insecticide	99
Tobacco	Ozone (0.35 ppm, 2 hr)	Safroxane	Insecticide	76
Bean, cultivar Tempo	Oxidant	Benomyl (0.24% spray)	Fungicide	32 to 41[c]
Grass, annual blue	Ozone (0.25 ppm, 2 hr)	Benomyl (60-ppm amendment)	Fungicide	85
Bean, cultivar Pinto	Ozone (0.30 ppm, 4 hr)	Triarimol	Fungicide	81
Bean, cultivar Pinto	Ozone (0.25 ppm, 4 hr)	Benomyl (1.60-μg/g soil amendment)	Fungicide	98
Bean, cultivar White	Ozone (0.13 to 0.50 ppm, 0.5 hr)	Ascorbic acid	Antioxidant	75
Petunia	Oxidant	SADH (0.5% spray)	Growth retardant	82
Tobacco	Oxidant	Benomyl (25-ppm drench)	Fungicide	68
Tobacco	Oxidant	Benomyl (0.18% spray)	Fungicide	59
Tobacco	Ozone	Peroxidase (0.10 ppm injected)	Enzyme	89

Source: Modified from National Research Council, 1977.

[a]These are applied as sprays unless otherwise noted.

[b]Percent reduction in plant injury from ozone as a result of the protectant treatment.

[c]Increase in yield by protectant application.

the plants used were of different ages or because the O_3 concentrations used in the respective experiments differed. Reilly and Moore (1982), however, stated that pebulate had no consistent effect upon tobacco sensitivity to O_3.

Benomyl, specifically, and fungicides in general were discussed extensively as plant protectants in the National Research Council report (1977) because they have been the most widely studied protectants. Benomyl (methyl-1-butylcarbamoyl-2-bensimidazolecarbamate) has been used as a foliar spray, soil drench, and a soil amendment (National Research Council, 1977) and was found to reduce O_3 injury in a wide range of plant species (Table 7-13). Benomyl, while usually offering protection against O_3 injury, does not prevent PAN injury (Pell, 1976; Pell and Gardner, 1975; Pell and Gardner, 1979).

Antioxidants, chemical compounds that prevent food spoilage and discoloration and prevent rubber from reacting with O_3, have also been found to reduce O_3 injury in vegetation (Kendrick et al., 1962). In agricultural practice, antioxidants are used as synergists with insecticides, herbicides, and fungicides to increase in their effectiveness. For example, antioxidants increase the potency of a certain insecticide by decreasing the rate at which insects are able to detoxify it.

Piperonyl butoxide (α-[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene), a synergist used with pyrethrum insecticides, is highly effective in protecting tobacco leaves from O_3 injury (Koiwai et al., 1974; Koiwai and Kisaki, 1976; Koiwai et al., 1977). Koiwai et al. (1977) determined that most compounds having a synergistic activity with pyrethrum insecticides are, in general, effective in preventing ozone injury to tobacco leaves. Rubin et al. (1980) tested the protective capability of piperonyl butoxide when applied to navy bean cultivars '0686' and '0670' and found that both cultivars were protected by piperonyl butoxide, but only if it was used as a spray, not as a soil treatment. Piperonyl butoxide was slightly phytotoxic, but the symptoms resulting from the spray were not similar to those characteristic of ozone injury. Santoflex 13, (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine), an antioxidant, is used to protect rubber from ozone attack. Gilbert et al. (1977) found that bean, muskmelon cultivar 'Delicious 51,' and tobacco cultivar 'Bel W-3' were protected by Santoflex dust against visible injury when they were exposed to concentrations of O_3 up to 0.35 ppm in chamber studies.

Ethylenediurea (EDU) [N-(2-(2-oxo-1-imidazolidinyl)ethyl)-N-phenylurea], an antioxidant, has been widely used to reduced O_3 injury to vegetation.

Pinto beans sprayed to run-off with 500 µg/ml EDU usually survived exposure to O_3 at concentrations of 0.8 ppm for 150 minutes without visible injury (Carnahan et al., 1978). Untreated plants exposed under the same conditions developed ozone injury symptoms over the entire surface area of the primary leaves.

Hofstra et al. (1978) found EDU to be more effective than benomyl or carboxin in suppressing O_3 injury on the highly sensitive navy bean growing in the field. It reduced bronzing, delayed leaf drop, and increased the yield up to 36 percent in plants exposed to hourly mean concentrations of O_3 at 0.1 to 0.3 ppm.

Pinto bean plants grown in pots received the greatest protection from O_3 injury when treated with EDU 3 to 7 days before a 6-hour exposure to O_3 concentrations of 0.10 to 0.76 ppm (Weidensaul, 1980). Plants received the most effective protection by EDU when O_3 concentrations were 0.41 ppm or higher. Foliage that had not yet been formed at the time the chemical was applied was not protected. The most extensive testing of the protective capabilities of EDU has been done by Cathey and Heggestad (1982a,b,c), who studied the effects of EDU (as either a foliar spray or soil drench) on the O_3 sensitivity of petunia (5 cultivars), chrysanthemum, and 44 other herbaceous species. In all cases they found that treatment with EDU reduced the O_3 injury. In addition to herbaceous species, EDU also reduced O_3 injury in woody vegetation (McClenahan, 1979; Cathey and Heggestad, 1982c).

Legassicke and Ormrod (1981) showed the effectiveness of EDU in reducing O_3 injury and increasing tomato yields in the field. For example, an EDU treatment (spray) increased the number of fruit on the cultivar 'Tiny Tim' and fruit size was increased in the cultivar 'New Yorker' in the O_3 treatments. In this study, the ambient O_3 concentration exceeded 0.08 ppm for 15 days during the growing season. A maximum of 0.14 ppm was recorded with a Dasibi O_3 monitor.

In an attempt to quantify the yield losses of potato crops attributable to O_3, Clarke et al. (1983) grew three potato cultivars ('Norland,' 'Norchip,' and 'Green Mountain') in the field for 2 years using standard commercial practices (1978, 1980). Half of the plants grown were protected with a drench of EDU at the rate of 6.7 kilograms of active ingredient gradient per hectare every 3 weeks from June to September. Foliage was inspected weekly. The order of foliar injury was 'Norland' > 'Norchip' > 'Green Mountain.' The

percentage leaf injury increased as the season progressed, but EDU-treated plants had significantly less injury than untreated plants. Oxidant concentrations were monitored continuously with a Mast meter. The effect of O_3 on potato yield was determined by comparing the EDU-treated with the untreated plants. Such a comparison indicated that in 1978, 'Norland' tuber yield was reduced 25 percent; in 1980, yield was reduced 24 percent. The cumulative oxidant dose (ppm-hr) for 1980 was nearly twice that of 1978. 'Norchip' showed a 31 percent loss in yield in 1980 and a 10 percent loss in 1978. 'Green Mountain' was relatively insensitive to O_3 injury.

Farmers and others growing crops in areas where high O_3 concentrations exist should be aware that agricultural chemicals commonly used to protect plants from a variety of fungi, insects, and nematodes can modify the response of the vegetation to O_3 exposure. Antioxidants used in insecticides and herbicides to increase their effectiveness can also change the way plants respond to O_3 exposure. In general, nematicides seem to increase O_3 sensitivity, while fungicides and antioxidants have a protective effect when sprayed or drenched onto crops. Studies with herbicides have shown no general trend. Because none of the chemical compounds that have been studied appear to function in the same way, it is not possible to generalize. At the present time, none of the protectants appear to be cost-effective to the extent that they can be generally prescribed for protecting plants from O_3 injury.

7.4 OZONE EXPOSURE AND RESPONSE

Plant responses to O_3 may be manifested as biochemical, physiological, visible injury, growth, yield, reproduction, and ecosystem effects. Biochemical and physiological alterations are the fundamental cause of all other effects, and were briefly described in section 7.3. Visible foliar symptoms are frequently the first indication of the effects of air pollution on vegetation, but they may be difficult to distinguish from other stress effects. Although functional leaves are required for plant growth and yield, the loss of leaf area is not always well correlated with yield reductions. This lack of correlation may occur, if, for example, the plant has more leaf area than required to maintain the yield, or if plant or environmental factors other than leaf area limit yield. The lack of correlation between visible injury and yield is most common when the plant foliage is not the usable or marketable

portion of the plant (yield). In this section, yield loss refers to the impairment of the intended use of the plant as described in section 7.2.5. Foliar injury on ornamental plants and leafy vegetables, effects on native species, reductions in fruit, grain, foliage, or root production by agricultural species and adverse changes in plant quality and aesthetic value are all considered yield loss. Reproductive capacities may be altered as a result of these responses. Effects on individual plants may lead to changes in populations and, eventually, ecosystem modification. The effects of O_3 on ecosystems are discussed in Chapter 8.

In the chapter on vegetational effects in the previous criteria document (U.S. Environmental Protection Agency, 1978), emphasis was primarily on visible injury and growth effects. Most of the growth effects discussed concerned plant parts other than those of primary importance for yield. This emphasis was dictated by the bulk of the data available at that time. The summary figures and tables in the previous criteria document (U.S. Environmental Protection Agency, 1978) emphasized foliar injury responses (Figures 7-3, 7-4, 7-5 and Table 7-14). The visible injury data were summarized by presenting limiting values (Figures 7-3, 7-4) (i.e., those concentrations below which visible injury was unlikely and presumably reduced growth and yield would not occur). Another approach was to determine the O_3 concentrations that would produce a trace (5 percent) of foliar injury at various time intervals (Figure 7-5; Table 7-14). The limiting values shown in Figures 7-3 and 7-4, were developed from a review of the literature available at that time (1976) and represented the lowest concentration and time reported to cause visible injury on various plant species. These data were based on more than 100 studies of agricultural crops and 18 studies for tree species. In the figures, the shaded areas represented the range of uncertainty in the data. Foliar injury was considered unlikely at doses below and to the left of the shaded areas. The limiting values were summarized as follows:

Agricultural crops:

0.20 to 0.41 ppm for 0.5 hour
0.10 to 0.25 ppm for 1.0 hour
0.04 to 0.09 ppm for 4.0 hour

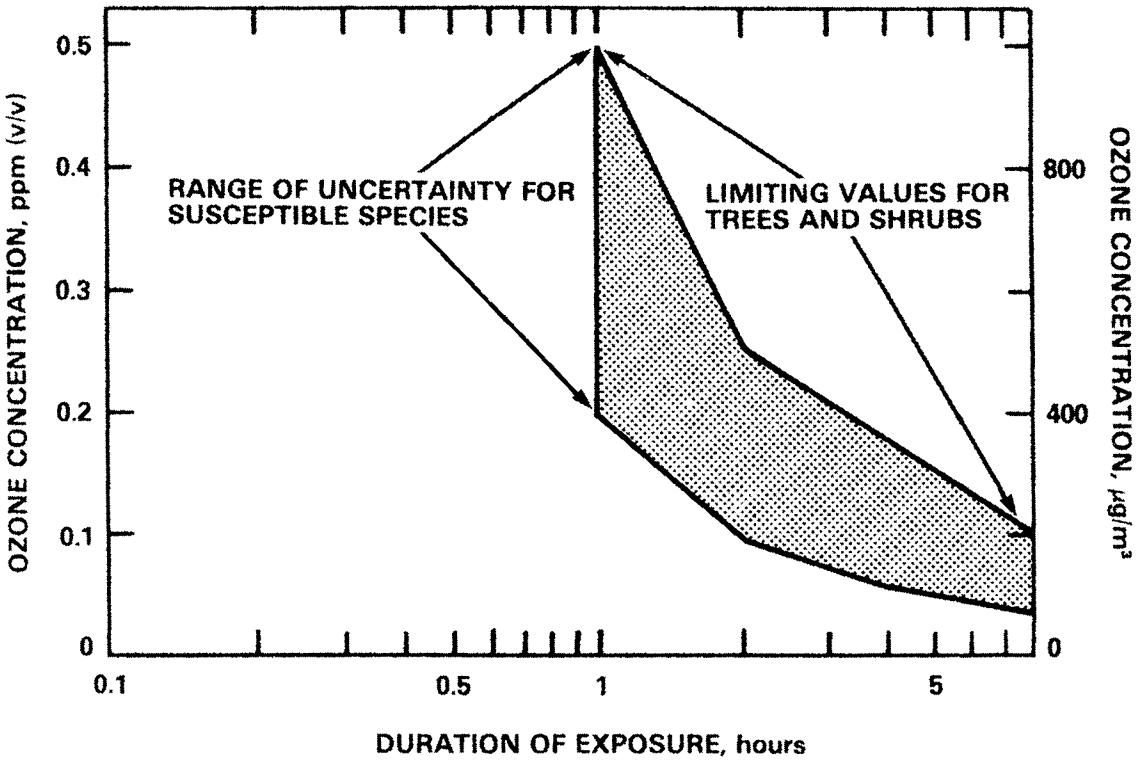

Figure 7-3. Limiting values for foliar injury to trees and shrubs by ozone.
Source: U.S. Environmental Protection Agency (1978).

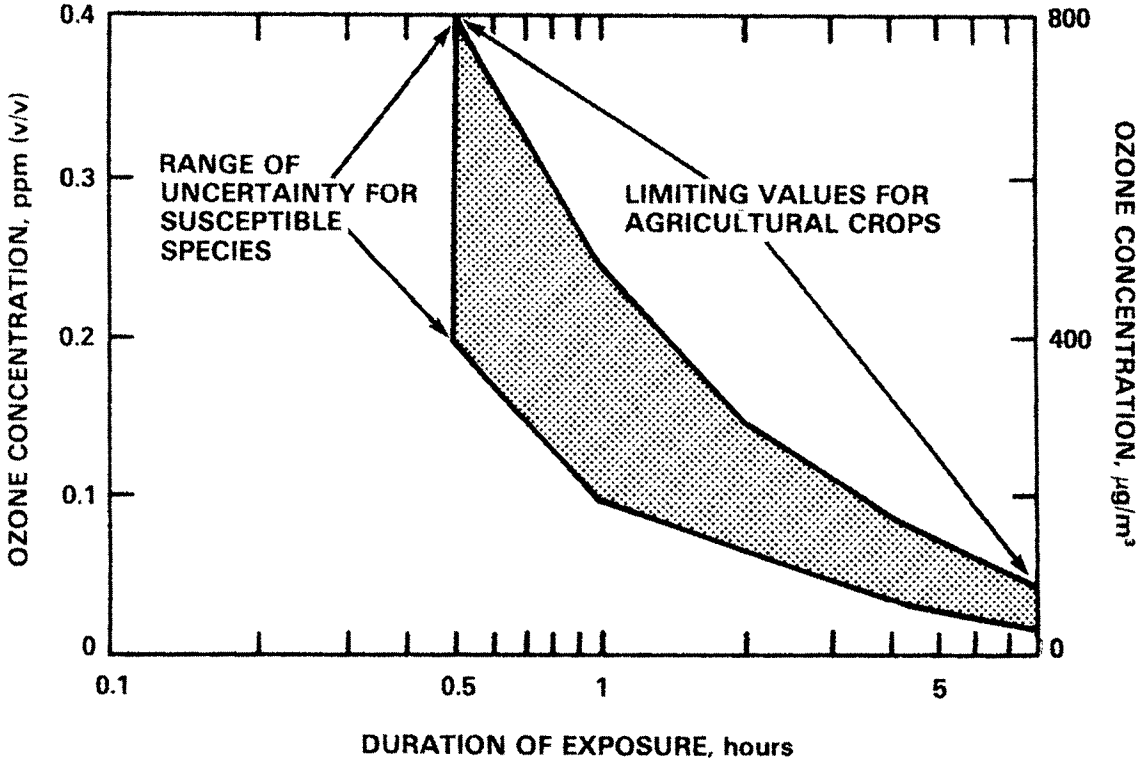

Figure 7-4. Limiting values for foliar injury to agricultural crops by ozone.
Source: U.S. Environmental Protection Agency (1978).

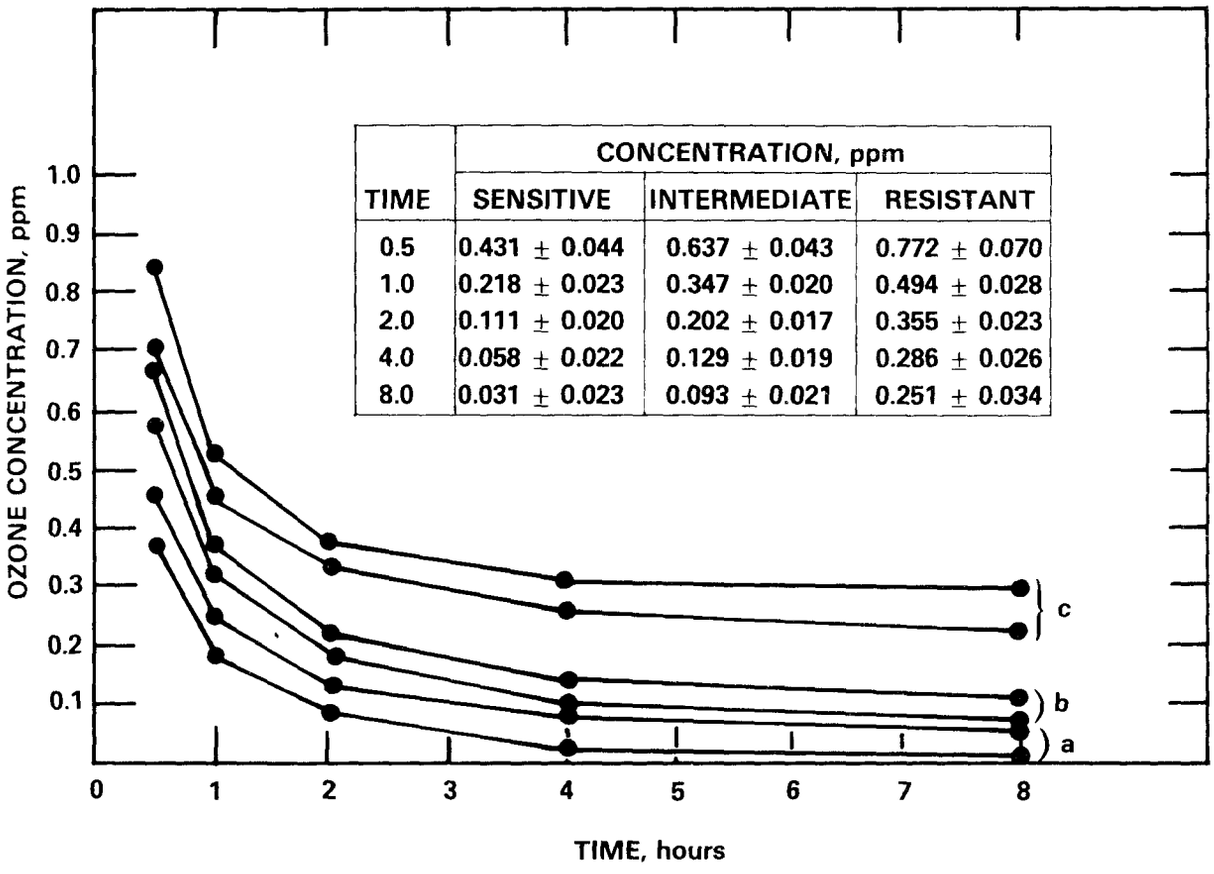

Figure 7-5. Ozone concentrations versus duration of exposure required to produce a 5 percent response in three different plant susceptibility groupings. The curves were generated by developing 95 percent confidence limits around the equations for all plants in each susceptibility grouping from Table 7-14. Curves: a = sensitive plants, b = intermediate plants, c = resistant plants.

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

TABLE 7-14. CONCENTRATION, TIME, AND RESPONSE EQUATIONS FOR THREE SUSCEPTIBILITY GROUPS AND FOR SELECTED PLANTS OR PLANT TYPES WITH RESPECT TO OZONE[a]

Plants	$(C = A_o + A_t I + A_2 T)$[b]			R^2[c]	Threshold concentration ppm[d]			Number data points	Mean values[e]			
					1 hr	4 hr	8 hr		Conc (C)., ppm	Time (T)., hr	Response (I)., %	Dose, ppm · hr
Sensitive:												
All plants	-0.0152	+0.00401	+0.213/T	0.57	0.22	0.06	0.03	471	0.29	1.74	45.4	0.503
Grasses	-0.0565	+0.00481	+0.291/T	0.74	0.26	0.04	0.01	71	0.37	1.66	50.9	0.608
Legumes	0.0452	+0.00361	+0.172/T	0.46	0.24	0.11	0.09	100	0.34	1.42	40.1	0.480
Tomato	-0.0823	+0.00431	+0.243/T	0.50	0.18	None	None	20	0.31	1.50	56.5	0.491
Oat	-0.0427	+0.00511	+0.273/T	0.76	0.26	0.05	0.02	30	0.37	1.66	40.2	0.611
Bean	-0.0090	+0.00301	+0.164/T	0.58	0.17	0.05	0.03	62	0.30	1.23	47.2	0.370
Tobacco	0.0245	+0.00341	+0.137/T	0.52	0.18	0.08	0.06	197	0.23	1.90	38.9	0.448
Intermediate:												
All Plants	0.0244	+0.00651	+0.290/T	0.74	0.35	0.13	0.09	373	0.37	1.67	27.0	0.625
Vegetables	-0.0079	+0.00641	+0.263/T	0.79	0.29	0.09	0.06	25	0.41	1.29	33.5	0.532
Grasses	0.0107	+0.00591	+0.292/T	0.82	0.33	0.11	0.09	68	0.39	1.61	31.0	0.625
Legumes	0.0116	+0.00741	+0.329/T	0.81	0.38	0.13	0.09	104	0.40	1.59	25.0	0.642
Perennial	0.0748	+0.00701	+0.237/T	0.77	0.35	0.17	0.14	27	0.36	1.91	22.9	0.687
Clover	-0.0099	+0.00711	+0.268/T	0.95	0.29	0.09	0.06	24	0.28	2.13	23.0	0.595
Wheat	-0.0036	+0.00811	+0.302/T	0.88	0.34	0.11	0.08	15	0.47	1.25	28.9	0.508
Tobacco	0.0631	+0.00871	+0.152/T	0.78	0.26	0.14	0.13	59	0.28	1.99	15.7	0.551
Resistant:												
All plants	0.1689	+0.00951	+0.278/T	0.51	0.50	0.27	0.25	291	0.45	1.55	10.6	0.696
Legumes	0.0890	+0.01081	+0.304/T	0.82	0.45	0.22	0.18	36	0.30	1.89	12.2	0.722
Grasses	0.1906	+0.01171	+0.263/T	0.55	0.51	0.31	0.20	13	0.45	1.47	6.5	0.655
Vegetables	0.1979	+0.01261	+0.107/T	0.70	0.38	0.29	0.20	16	0.55	1.50	17.8	0.819
Woody plants	0.2312	+0.00611	+0.208/T	0.45	0.47	0.31	0.30	46	0.39	2.50	7.8	0.905
Cucumber	0.1505	+0.01411	+0.106/T	0.83	0.33	0.25	0.23	18	0.41	1.41	13.3	0.581
Chrysanthemum	0.2060	+0.00521	+0.256/T	0.40	0.49	0.30	0.27	45	0.39	2.17	12.6	0.847

[a]Equations were developed from exposures limited in time (0.5 to 8 hr except for 2 to 12 hr points in the sensitive group) and denote acute responses of the plants. Concentrations range from 0.05 to 0.99 (1.0) ppm and responses from 0 to 99 (100)% of control (U.S. EPA, 1978).

[b]C is ozone concentration in ppm. I is percent injury. T is time in hours, and A_o, A_t, and A_2 are constants (partial regression coefficients) that are specific for pollutant plant species or group of species, and environmental conditions used.

[c]Multiple correlation coefficient squared, which represents the percent variation explained by the model.

[d]For 5 percent response in 1-, 4-, and 8-hr periods.

[e]From the computer analysis.

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

Trees and shrubs:

0.20 to 0.51 ppm for 1 hour

0.10 to 0.25 ppm for 2 hour

0.06 to 0.17 ppm for 4 hour

A concept similar to the limiting values for foliar injury was developed to present the O_3 concentrations and durations which could potentially reduce plant growth and yield (Figure 7-6). In the figure, the line displays the boundary of mean O_3 concentrations and exposure durations below which effects on growth and yield were not observed. Most of the data points represented effects on growth rather than yield, as defined in the present document (see section 7.2.5). The graphical analysis indicated that the lower limit for effects was a mean O_3 concentration of 0.05 ppm for exposure durations greater than 16 days. At exposure durations of less than 16 days, the O_3 response threshold increased to about 0.10 ppm at 10 days and 0.30 ppm at 6 days.

This revision of the criteria document will place greater emphasis on yield loss rather than just injury. Visible foliar injury will be considered for those plants in which the foliage is the marketable plant part (yield), for plants used for aesthetic purposes, and for plants used as bioindicators.

In the following portions of Section 7.4, the use of plants as bioindicators and effects on vascular and nonvascular plants will be discussed. Bioindicators are important, because they provide information about the site of potential O_3 impacts and may be useful in elucidating O_3 as a causative factor in yield loss.

7.4.1 Bioindicators of Ozone Exposure

Plants are known to respond differentially to the characteristics of the environments that they occupy (Treshow, 1980b). Temperature, moisture, solar radiation, elevation, and soil quality are obvious environmental features that affect the distribution and relative performance of vegetation. Because established plants are confined to a particular location, they depend primarily on that local environment to meet their requirements for growth and reproduction; therefore, plant growth and yield integrate all environmental factors. Thus, vegetation can act as a biological indicator of the environment, which includes air pollutants.

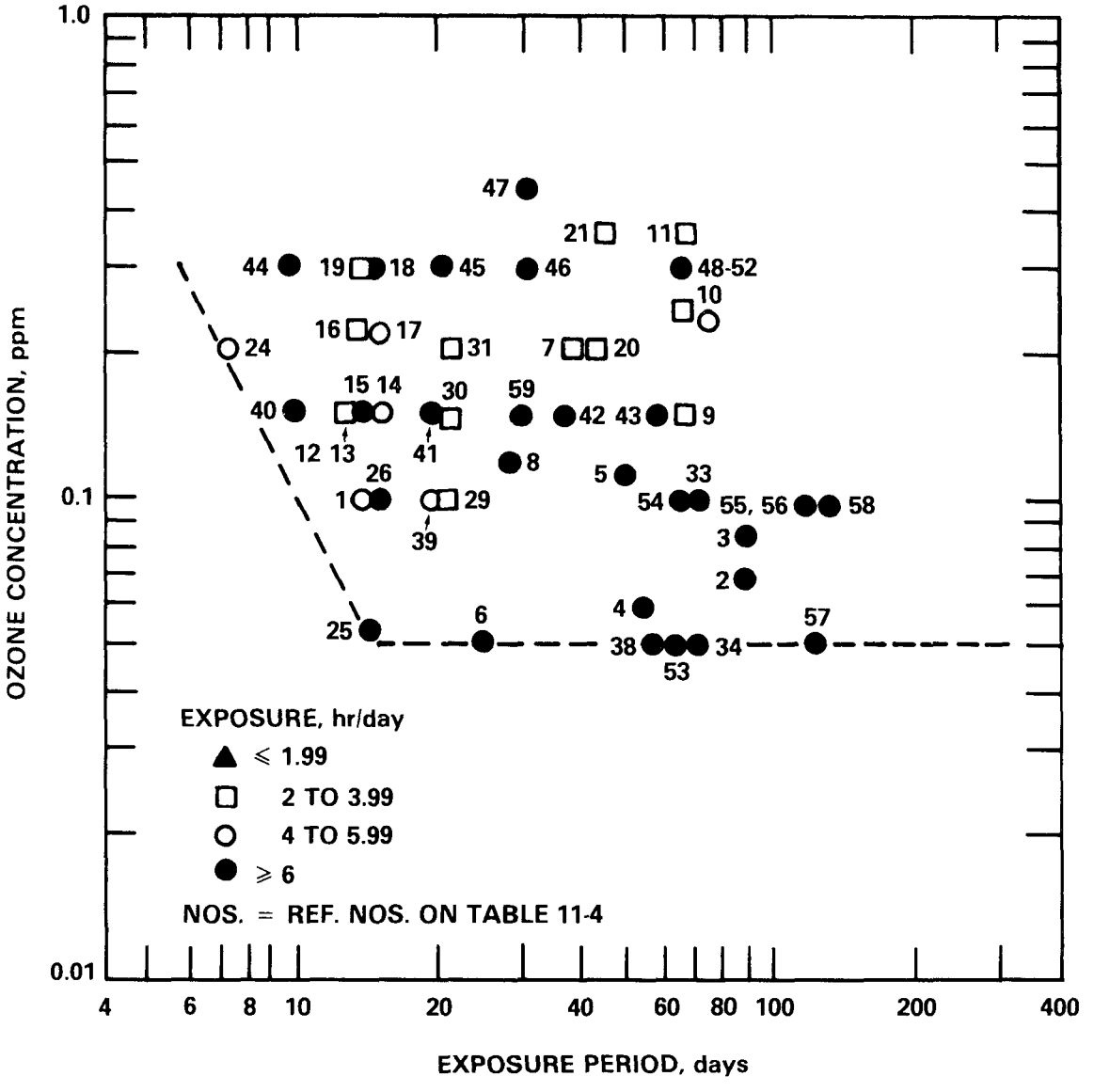

Figure 7-6. Relationship between ozone concentration, exposure duration, and reduction in plant growth or yield (see Table 7-18; also U.S. EPA, 1978).
Source: U.S. Environmental Protection Agency (1978).

Because organisms/plants growing in a particular environment are integrated products of that environment, they can provide important information about air pollution effects. A plant's response is the direct expression of the pollutant in that specific environment; physical methods provide only a measure of pollution occurrence and magnitude (Laurence, 1982). Therefore, bioindicators provide a direct method for understanding the risk that pollution presents to the biological components of the affected environment (Guderian, 1977). For this reason, there is renewed interest in biological methods for determining air pollution effects (Manning and Feder, 1980).

7.4.1.1 Bioindicator methods. As the use of plants to monitor air pollution has increased, methods have changed to better relate plant response to pollution exposure. Manning and Feder (1980) have summarized the important attributes of a bioindicator species. To perform predictably, the plants should be sensitive to a specific pollutant, genetically uniform, native or adaptable to the region, produce characteristic symptoms, grow indeterminately, and respond proportionally to pollutant exposure. To further minimize natural variation, efforts should be made to provide uniform soil and water conditions and ensure observation by trained personnel (Oshima et al., 1976; Posthumus, 1976, 1980). The aim of these measures is to standardize the plant and growing conditions so that effects of the pollutant are the major sources of variation in the subsequent analysis (Teng, 1982). During the past 10 years, substantial progress has been made towards improving our understanding of the variables affecting the performance of indicator species. Specific examples of these studies are summarized in this section.

7.4.1.2 Response of indicator species. Most early studies with indicator species focused on visible symptoms, the most obvious reaction of a plant to change in its environment. These responses included chlorosis or necrosis of tissues and typically represented the effects of an acute exposure to a single pollutant (Feder and Manning, 1979; Heck, 1966; Heggestad and Darley, 1969; Laurence, 1982). With the identification and application of very sensitive species such as Bel W-3 tobacco (Heggestad and Menser, 1962), means were gained to predictably identify progressively lower concentrations of O_3 (Feder, 1978). There is general agreement that this tobacco cultivar will predictably respond to an O_3 exposure above 0.04 ppm for 4 hr (Ashmore et al., 1978) when environmental conditions are favorable.

The symptoms caused by exposure to O_3 differ on broad-leaved (dicotyledonous) and narrow-leaved (monocotyledenous) plants. The foliage of dicotyledonous plants initially appears water soaked due to injury to palisade cell membranes (U.S. Environmental Protection Agency, 1976). These areas appear shiny or oily within hours of the exposure and with characteristic flecks or stipples when the water-soaked area dries (Figure 7-7). Flecks (Figure 7-8) are small lesions formed when groups of palisade and/or mesophyll cells die and the associated epidermal cells collapse (U.S. Environmental Protection Agency, 1976). They may be yellow or tan, and if the injury is extensive, the entire leaf surface may appear bronzed. Individual flecks may coalesce to form bifacial lesions that appear on both leaf surfaces. "Stipples" (Figure 7-7) are small groups of red, purple, or black pigmented palisade cells (U.S. Environmental Protection Agency, 1976). This symptom is viewed through the uninjured epidermal layer of the upper leaf surface. The leaf veins are also uninjured and form angular boundaries to the pigmented areas.

Monocotyledonous plants generally do not have differentiated mesophyll tissue, and ozone injury typically appears as chlorotic spots or white flecks between veins (U.S. Environmental Protection Agency, 1976). This injury may extend to form long white or yellow streaks between the parallel veins of sensitive plants and becomes most severe as leaf bands (Figure 7-9).

Ozone injury to the foliage of coniferous plants is described as chlorotic mottle and tipburn (U.S. Environmental Protection Agency, 1976). Small patches of needle tissue are injured and turn yellow. These areas are surrounded by healthy green tissue and the needle appears mottled (Figure 7-10). When the entire needle tip dies, it turns reddish brown and later gray. This tipburn is also a characteristic of O_3 injury. In both cases, it is usual for only current-year needles to be affected after acute exposures to O_3.

Long-term exposure to low pollutant concentrations may adversely affect plant health without producing visible symptoms. Chronic injury from this type of exposure may be represented by reductions in growth or yield caused by changes in photosynthesis, respiration, chlorophyl content, or other processes (Dochinger et al., 1970; Feder, 1978; Heck, 1966; Laurence, 1982; Posthumus, 1976).

7.4.1.3 Bioindicator Systems. Although many field biologists have identified certain plants as indicators of pollutants, few have published documentation of the sensitivity of specific plants to ambient O_3 in the field or in natural

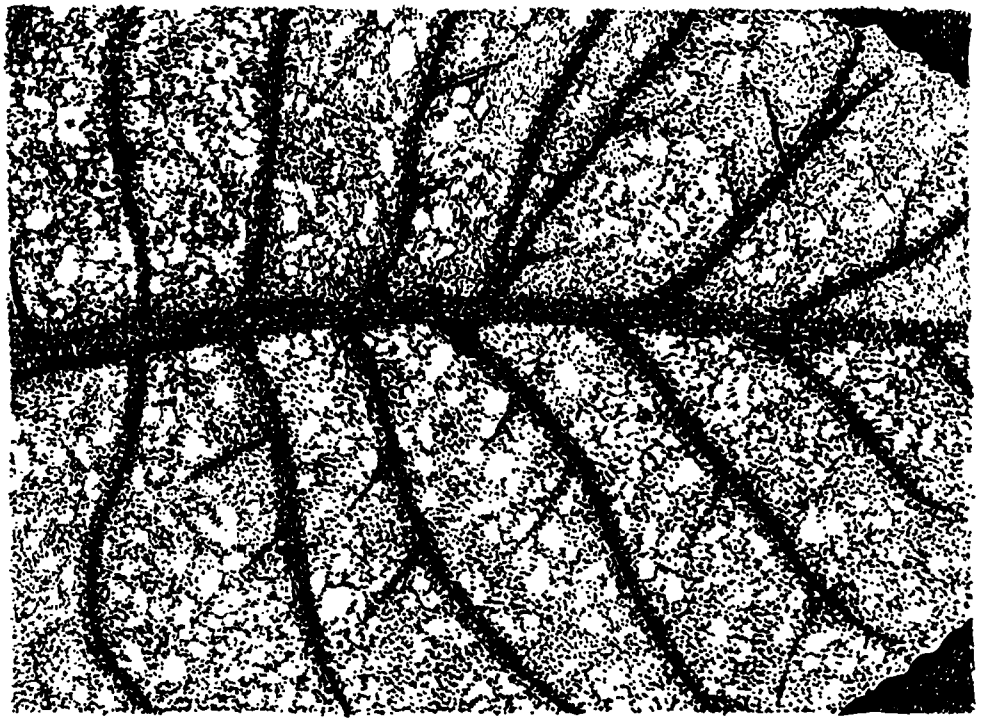

Figure 7-7. Ozone injury to Bel W-3 tobacco. Clear interveinal areas represent necrotic tissue (fleck and bifacial necrosis).

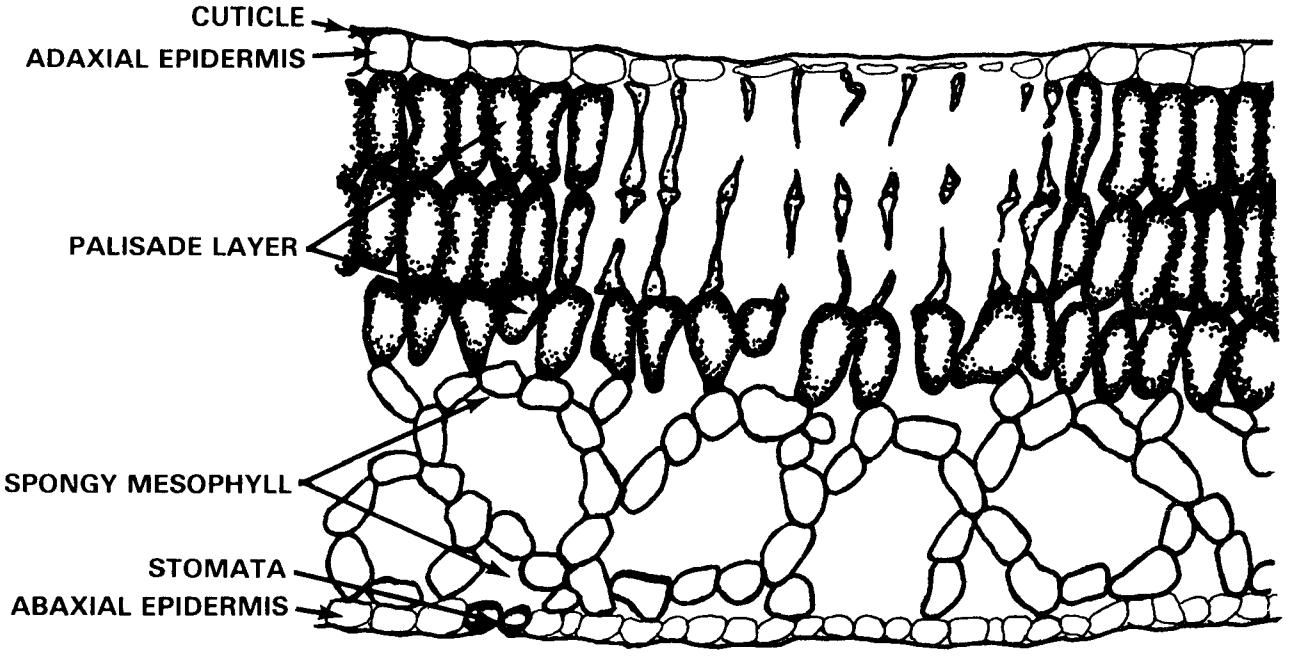

Figure 7-8. Schematic cross section of typical dicot leaf showing ozone injury to palisade cells and collapsed epidermal cells.

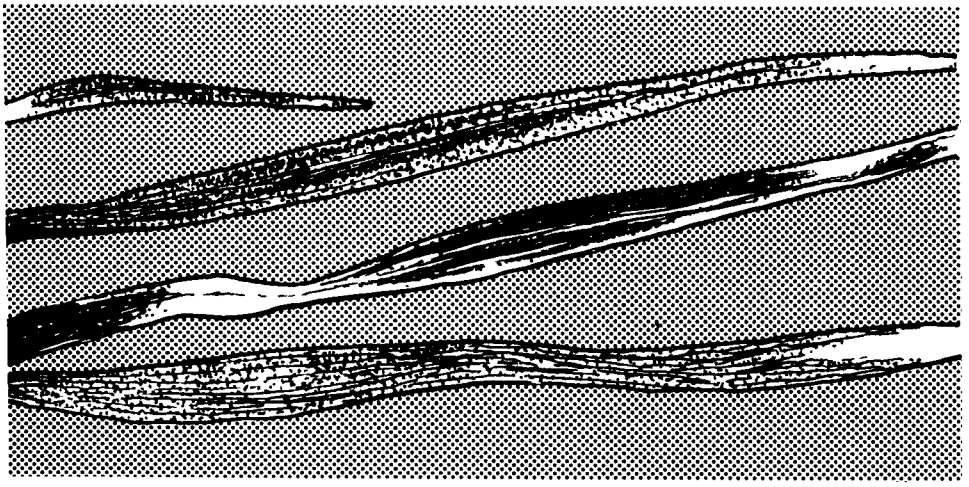

Figure 7-9. Ozone injury to oats. Clear areas represent bleached and necrotic tissue.

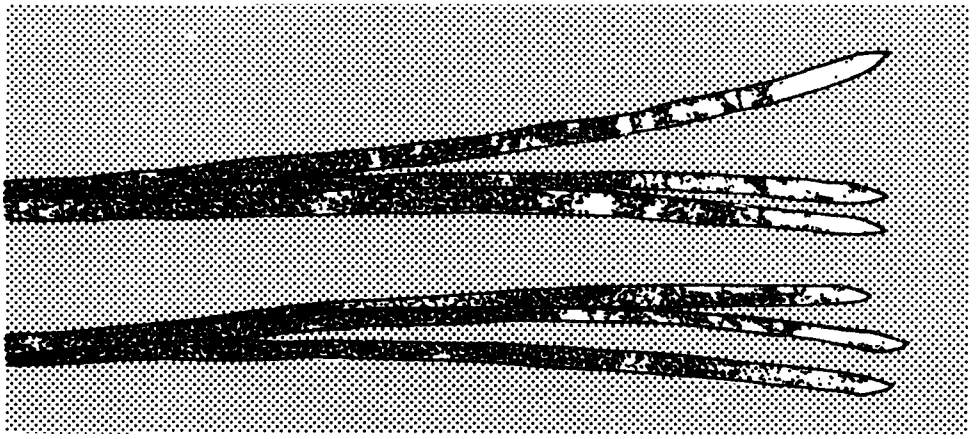

Figure 7-10. Ozone injury to needles of conifer. Clear areas represent injured tissue (chlorotic mottle and tipburn).

environments. Duchelle and Skelly (1981) characterized the response of milkweed to O_3 in both field and laboratory studies. This is a particularly valuable study, because it defines the response of a plant that has been classed as a sensitive bioindicator in the field and establishes a base line sensitivity that can be reevaluated in the future to detect possible changes in the frequency of sensitive individuals in the field. Benoit et al. (1982) reported on the radial growth of eastern white pine as an indicator of O_3 pollution. Similar results were obtained when ponderosa and Jeffrey pines were used as bioindicators in the southern California mountains (Miller, 1973). Although a good relationship between radial growth and observed O_3 sensitivity exists, it is probably realistic to only use this procedure to measure of long-term effects because of the detailed analyses of tree rings and precipitation patterns required. They were able to identify three classes of eastern white pine (sensitive, intermediate, and tolerant). Injury observed on those sensitive species would serve to indicate the extent of O_3 pollution.

There have been several reports of the use of plants in systems designed to detect the presence of elevated concentrations of ozone. Many early studies (Heck, 1966) were conducted to assess the spatial and temporal distribution of smog by using sensitive indicator plants. In most cases, poor correlations between measured oxidants and plant injury were found. With the identification of Bel W-3 tobacco as a sensitive indicator of elevated ambient O_3 concentrations (Heggestad and Menser, 1962), a new series of studies was conducted (e.g., Heck et al., 1969, Heck and Heagle, 1970; Jacobson and Feder, 1974; Naveh and Chaim, 1978; Goren and Donagi, 1979; Horsman, 1981; Ashmore et al., 1978; 1980; Bell and Cox, 1975). The most widespread network established to determine the spatial and temporal distribution of ambient oxidant induced injury on Bel-W3 tobacco was that described by Jacobson and Feder (1974). The bioindicators sites were located in nine states ranging from North Carolina to Maine. The authors observed both temporal and spatical variations in O_3 injury and concluded that Bel-W3 could be used to indicate the present of O_3 but would not reliably indicate the O_3 concentration. A major problem identified by the authors was the necessity of growing Bel W-3 plants under pollution-free conditions prior to their use.

Oshima (1974b) devised a bioindicator system for use in California that utilized pinto bean. In field trials, a strong and significant relationship was found between injury observed on bean leaves and average weekly ambient O_3

dose. His measure of O_3 dose consisted of a censored sum (hours greater than 0.1 ppm) of ambient O_3 concentrations obtained from nearby physical monitors. It would be feasible to use such a system on a large scale to at least qualitatively, if not quantitatively, assess spatial and temporal occurrence of phytotoxic concentrations of O_3.

In the Netherlands, bioindicators of air pollution have been in continuous use since 1954. Posthumus (1976) reported the results of a study to investigate the occurrence and distribution of O_3 by using Bel W-3 tobacco at 31 sites throughout the country. He reported, "It is possible to determine the place and time with the highest mean intensity or highest frequency of injury by O_3...". A "'fingerprint'" can be produced and, by comparing patterns from year to year, specific trends in the occurrence of pollution may be identified. He further concluded that, "The clear advantage of plants as indicators of air pollution is that these show the result of the action of the pollutants on living material", and added that, "In this way it could be a rather efficient and relatively inexpensive manner to follow trends in air pollution and to evaluate sanitation measures."

Nouchi and Aoki (1979) used morning glory as an indicator of photochemical oxidants (primarily O_3). In studies conducted both in the laboratory and field, they were able to model the effects of O_3 on leaf injury, including the effects of previously occurring exposures. Field verification of their model showed that they were able to determine (within acceptable margins of error) oxidant levels on a given day by using measurements of visible injury to morning glory. They emphasized however, that the most valuable use of their system was to characterize the frequency and spatial distribution of elevated oxidant concentrations.

The common theme in all these studies is that a good understanding of the occurrence of elevated O_3 concentration can be obtained by using the visible response of sensitive plants. While the methodology to biomonitor is still in the early stages of development, bioindicators have a certain value as integrators, by providing information on where, when, and how often O_3 concentrations may be reaching phytotoxic concentrations. The value of deploying networks of bioindicators has been demonstrated in the early detection of developing regional oxidant pollution problems, in identification of trends in pollutant occurrence, and in supplementing physical monitoring networks to provide additional information on the biological effects of pollution for the assessment of crop loss (Laurence, 1982).

7.4.1.4 Lichens as bioindicators of oxidant pollution. Lichens have been used extensively to index ambient air quality; there are many historic reports describing the frequency and diversity of these plants as a function of distance and direction from large sources of SO_2 and metal pollution (Guderian and Schoenbeck, 1971; LeBlanc and Rao, 1973; Schoenbeck, 1969; Skye, 1979). Because they lack roots and stomata, lichens depend more on and are more subject to the atmospheric component of their environment than are vascular plants. For this reason, they are generally noted for their sensitivity to air pollution (Laurence, 1982).

Until recently, there was little information describing the effects of O_3 on lichens in natural environments. Sigal and Nash (1983) have recently conducted an extensive study of lichen distribution relative to oxidant air pollution in southern California. Collections of lichens from regions of high (1300 hr >0.09 ppm, 1968-1974, San Bernadino Mountains) and low (Cuyamaca Rancho State Park) levels of oxidant pollution were compared with collections made in 1913. The frequency and cover of the current lichen communities in these regions were also compared with calculated levels of O_3 associated with injury to pines as reported earlier (National Research Council, 1977). Additionally, lichens from unaffected areas were transplanted to ecologically similar sites in affected areas.

In this multidimensional study, the authors found consistently high levels of injury to lichens in areas with high levels of O_3. In polluted areas, only 8 of 16 previously reported species were still present, and 4 were found only in trace amounts. This compared with 15 of 16 species still present in areas with low levels of O_3. Transplanted lichens performed poorly in areas where injury to pine was most extensive and calculated levels of O_3 were highest. The authors concluded that lichen communities in southern California were not adversely affected if the cumulative oxidant dose level was below about 300 ppm/hr per year. This dose was calculated with all concentrations greater than 0.04 ppm O_3 x time.

7.4.1.5 Published reports of visible injury of plants due to ambient ozone in the United States. When the phytotoxicity of O_3 was first being discussed in the late 1950's and early 1960's and when attempts to use plants as bioindicators of O_3 exposure were just beginning, many reports of ambient O_3 injury to plants were published. In the past 10 years, the number of published observations has decreased as scientists are reluctant to report "one more plant" or

"a new state" showing O_3 injury, and journals are equally reluctant to publish those reports.

There are published reports of O_3-induced visible injury to plants in at least 27 states of the United States (Table 7-15 and Figure 7-11). In addition, similar observations have been made for areas of Canada (Weaver and Jackson, 1968; MacDowell et al., 1964) and Mexico (DeBauer, 1972). Combined with the overseas reports previously mentioned, the magnitude of potential ozone pollution problems represented by injury to vegetation becomes apparent. There are no reports of visible O_3 injury to vegetation in the Great Plains, parts of the Rocky Mountain region, the Deep South, and a few states in the Northeast. The areas in which vegetation injury has been reported are generally near locations in which research is being conducted on the effects of air pollution on vegetation. The absence of reported injury is probably the result of a failure to look for it. It is quite likely that sensitive indicator plants would be injured in many of those areas.

Plants have been used to index various characteristics of the environments in which they grow. Ozone air pollution is an imposed environmental variable that can be detected and sometimes quantified by observing the specific response of sensitive plants. The occurrence of O_3 has been widely reported in the United States, the Netherlands, Great Britain, Germany, Japan, Israel, and Australia by observing foliar injury to selected sensitive species and cultivars/subspecies.

Biological methods for assessing the extent and intensity of O_3 air pollution have value beyond that provided by physical measurements. Bioindicators are integrators of their environment and can yield direct information about the effect a given pollutant exposure has on vegetation, subject to the joint influence of other environmental variables.

7.4.2 Microoorganism And Nonvascular Plant Response To Ozone Exposure

7.4.2.1 Microorganisms. Most studies with this group of organisms (bacteria and fungi) have used O_3 exposures that are higher than those that would be expected to occur in ambient air, often in excess of 1 ppm. Direct effects of ozone on microorganisms and, in some instances, their capacity to incite plant diseases have been reviewed by Laurence (1981) and Heagle (1973, 1982), and in section 7.3.2.1.3 of this document.

TABLE 7-15. A PARTIAL LISTING OF AMBIENT OZONE INJURY ON SENSITIVE VEGETATION REPORTED IN THE LITERATURE[a]

State	Plant	Reference
Arizona	Tobacco	National Research Council, 1977
California	Grape, bean, ponderosa pine	Richards et al., 1958; Oshima, 1974; Miller and Millecan, 1971
Connecticut	Tobacco	Jacobson and Feder, 1974
Delaware	Tobacco	Jacobson and Feder, 1974
Florida	Tobacco	Dean, 1963
Georgia	Tobacco	Walker and Barlow, 1974
Illinois	Soybean	Kress and Miller, 1983
Indiana	White pine	Usher and Williams, 1982
Kentucky	Tobacco	Menser, 1969
Maine	Tobacco	Jacobson and Feder, 1974
Maryland	Tobacco	Jacobson and Feder, 1974
Massachusetts	Tobacco	Jacobson and Feder, 1974
Michigan	Potato	Hooker et al., 1973
	Bean	Olson and Saettler, 1979
Minnesota	Soybean	Laurence et al., 1977
Missouri	Tobacco	Heck et al., 1969
New Jersey	Tobacco	Jacobson and Feder, 1974
New York	Tobacco	Jacobson and Feder, 1974
North Carolina	Tobacco	Jacobson and Feder, 1974
Ohio	Tobacco	Heck and Heagle, 1970
Pennsylvania	Tobacco	Jacobson and Feder, 1974
South Dakota	Tobacco	Gardner, 1973
Tennessee	Tobacco	Menser, 1969

TABLE 7-15. (continued)

State	Plant	Reference
Utah	Tobacco	Tingey and Hill, 1967
Virginia	Milkweed Potato	Duchelle and Skelly, 1981 Heggestad, 1973
Washington	Tobacco	National Research Council, 1977
West Virginia	White pine	Wood and Pennypacker, 1975
Wisconsin	Pine	Usher and Williams, 1982

[a]This is a partial listing designed to show the nationwide distribution. It is not complete in either the diversity of species injured or the number of reports of injury.

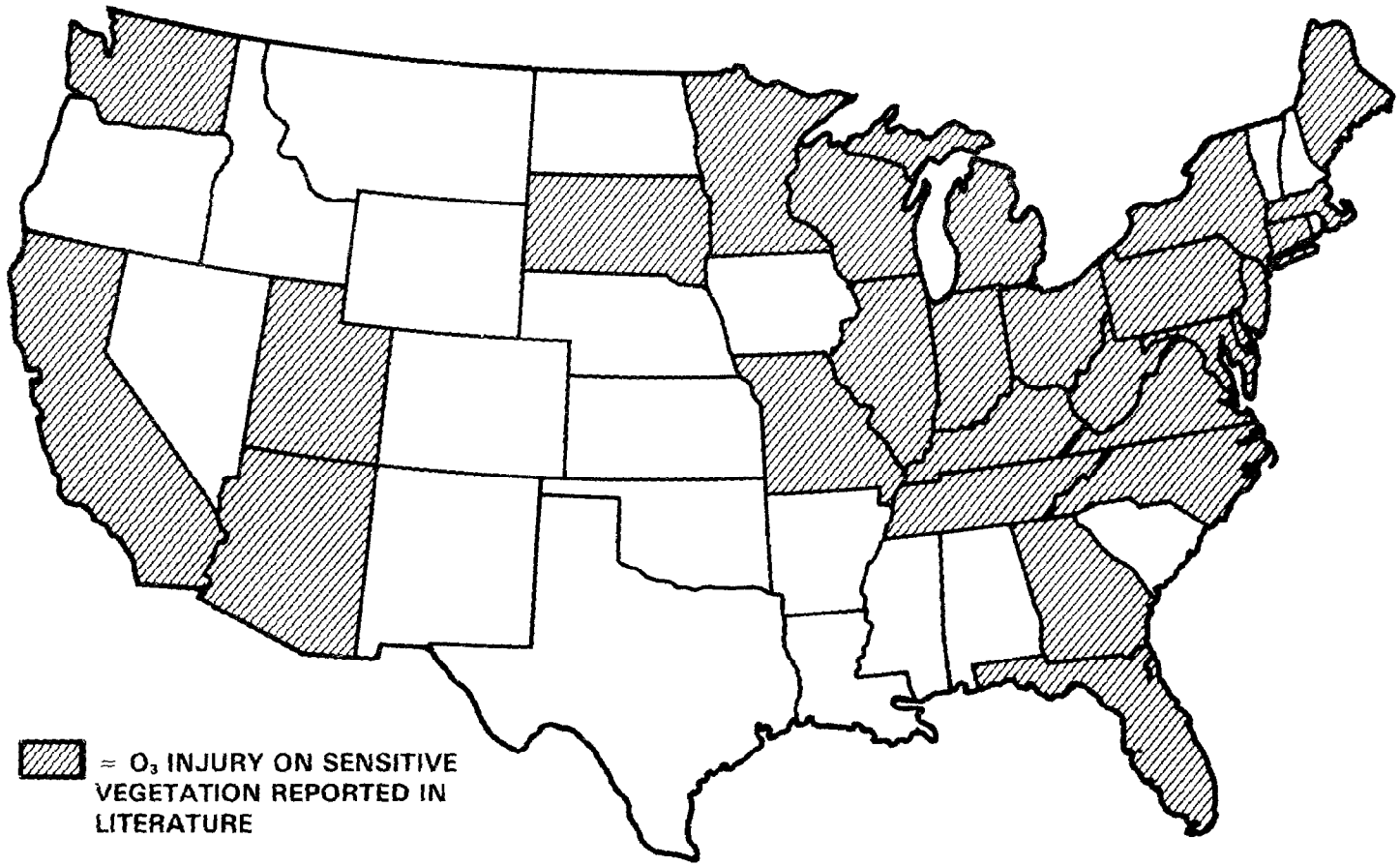

Figure 7-11. States in which some injury to vegetation has occured as reported in the published literature.

The O_3 concentration required for direct impact on microorganisms may be quite high. The data of Hibben and Stotsky (1969) are illustrative. These investigators examined the response of detached spores of 14 fungi to 0.1 to 1.0 ppm of O_3 for 1, 2, and 6 hr. The large pigmented spores of Chaetomium sp., Stemphylium sarcinaeforme, S. loti, and Alternaria sp. were not affected by 1.0 ppm. Germination of Trichoderma viride, Aspergillus terreus, A. niger, Pennicillium egyptiacum, Botrytis allii, and Rhizopus stolonifera spores were reduced by O_3 exposure, but only at concentrations above 0.5 ppm. The germination percentages in the small colorless spores of Fusarium oxysporum, Colletotrichum largenarium, Verticillium albo-atrum, and V. dahliae were reduced by 0.5 ppm and occasionally by concentrations of 0.25 ppm of O_3 for 4 to 6 hr; lower doses stimulated spore germination in some cases. The ability of ozone to reduce spore germination in fungi apparently depends on the species, spore type, morphology, moisture, and substrate. Moist spores were more sensitive than dry ones. Single-celled spores and those with thin cell walls were most sensitive.

Hibben and Stotsky (1969) found O_3 toxic to moist fungus spores of some species, even at concentrations of 0.1 ppm when applied for 28 hr. Exposure to 0.5 and 1.0 ppm reduced or prevented germination of spores of all species tested. Ozone at 0.1 ppm for 4 hr or at 1.0 ppm for 2 hr stopped apical cell division of conidiophores of Alternaria solani and caused collapse of the apical cell wall (Rich and Tomlinson, 1968).

Ozone can inhibit fungal growth on artificial media but rarely kills the fungus even at high concentrations. Differences in species sensitivity are known. In several fungi, exposure to O_3 (0.10 or 0.40 ppm for 4 hr) caused a 10 to 25 fold increase in sporulation (Heagle, 1973). The same author reported the effects of low exposures to O_3 on three obligate parasitic fungi. Germination of spores was not affected in any of these studies (Heagle, 1975). Reduced sporulation, germination, and pathogenicity of Botrytis cinerea were observed by Krause and Weidensaul (1978a,b) after exposure of the microorganism in vitro and in vivo to 0.30 ppm of O_3 for two 6-hr periods.

7.4.2.2 Lichens, mosses, and ferns. The effects of O_3 on lichens are not well known. Sigal and Nash (1983) recently completed a survey of lichens in southern California and compared their results to a collection made early in the 1900's. They found high levels of injury to pine trees. Lichen communities in non-polluted areas were similar in species composition to those observed early in the century, but those in heavily polluted areas had only 8 of

16 previously reported species present. They concluded that lichens were not adversely affected if the cumulative oxidant dose level was below about 300 ppm/hr.

In a laboratory study, Nash and Sigal (1979) fumigated two species of lichen (Parmelia sulcata and Hypogymnia enteromorpha) with O_3 at concentrations of 0.5 and 0.8 ppm for 12 hr. The former exhibited greater sensitivity than the latter, as measured by a reduction in gross photosynthesis. P. sulcata, which grows on black oak, is absent from the San Bernardino Mountains; H. enteromorpha is present but apparently deteriorating. The authors noted that for these species, the pattern observed in the laboratory is consistent with that found in field observations in Southern California, where extensive O_3 injury occurs. In another study (Ross and Nash, 1983), photosynthesis was decreased at O_3 concentrations of 0.1, 0.25, and 0.50 ppm for 12 hr in Pseudo parmelia caperata; however, effects were not found when Ramalina menziesei was exposed to concentrations of O_3 up to 0.5 ppm for 12 hr. Exposures of both species to ozone at 0.10 ppm for 6 hr/day on 5 consecutive days resulted in the same responses seen at the higher concentrations.

Very little is known about the responses of mosses and ferns to O_3. The information in the previous EPA document (U.S. Environmental Protection Agency, 1978) indicates that, based on published information, significant effects would not be expected at current ambient O_3 levels.

The responses of nonvascular plants to ozone have received little study. The study of Sigal and Nash (1983) is important, because it was performed under ambient conditions and comparisons could be made to previous lichen collections. Their data indicate that lichens are probably the most sensitive of nonvascular plants to O_3. In areas of high O_3 pollution, many species formerly present had been eliminated from the plant community, and lichens that were transplanted into the area performed poorly. Reports indicate that moist fungal spores were more sensitive to O_3 than dry spores, but these experiments were conducted under laboratory conditions some years ago. Inhibition of spore germination in the ambient environment has not been observed.

7.4.3 Losses in Vascular Plants Due to Ozone

This section will relate losses in plant yield to O_3 exposure. Exposures will be described as duration and O_3 concentrations, but the statistics used to characterize the exposure will take several forms. Yield loss is defined

as the impairment of the intended use of the plant (see Section 7.2.5) and includes aesthetic values, foliar injury, plant appearance, and losses in terms of number, size, or weight of the plant part that is normally harvested. Yield loss can also be defined as a change in physical appearance, chemical composition, or ability to withstand storage; collectively, these traits are termed crop quality.

7.4.3.1 Losses in aesthetic value and foliar yield. Losses in aesthetic value are difficult, if not impossible, to quantify. For example, because of its aesthetic value, the loss of or adverse effects on a specimen tree or shrub in a landscape planting will result in a much greater economic loss than the same impact on a tree or shrub of the same or similar species growing as a part of a natural plant community. Foliar symptoms which may decrease the value of an ornamental crop may occur on various types of plants (e.g., turfgrasses, floral foliage, ornamental trees, and shrubs) with or without concomitant growth reductions. The occurrence of foliar injury on other crops in which the foliage is the marketable plant part (e.g., spinach, cabbage, tobacco) can substantially reduce marketability and constitute a yield loss in economic (if not biologic) terms.

Petunia, geranium, and poinsettia were exposed to O_3 (up to 0.10 to 0.12 ppm for 6 hr/day) for 9 days (petunia), 8 days (geranium), and 50 days (poinsettia) (Cracker and Feder, 1972). Flower size was significantly reduced in all three species at a concentration of 0.10 to 0.12 ppm. Ozone decreased flower color in all three species: petunia (0.06 to 0.08 ppm), geranium (0.10 to 0.12 ppm), and poinsettia (0.02 to 0.04 ppm). All these changes in flower appearance (yield) occurred without visible injury to the plant leaves. Five begonia cultivars exposed to O_3 (0.25 ppm for 4 hr/day for a total of 16 hr over a 4-week period) varied in foliar injury from 2 to 54 percent (Table 7-16); flower size was also reduced (Reinert and Nelson, 1980).

Ozone injury on the foliage of ornamental trees and shrubs impairs their appearance and may reduce their value. Mean foliar injury on eight azalea cultivars exposed to 0.25 ppm of O_3 (six 3-hr fumigations) ranged from 0 to 24 percent (Sanders and Reinert, 1982a). Stem weight was significantly reduced for three of the cultivars (Table 7-16). Tree and shrub species have developed foliar injury following exposure to 0.20 ppm of O_3 for 5 hr (Davis et al., 1981). Visible injury to black cherry foliage occurred following a 4-hr exposure at 0.10 ppm and 2 hr at 0.19 ppm of O_3 (Davis et al., 1981). In an

TABLE 7-16. FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibrating method[c]	Fumigation facility[d]	Reference
Begonia (Schwabenland Red)	0.25	4 hr/day, every 6th day, 4 times	54 (39%* dec. in flower wt)	Chem	not given	GH-CSTR	Reinert and Nelson, 1980
(Whisper 'O' Pink)	0.25		25 (22%* dec. in flower wt)				
(Fantasy)	0.25		2 (6%* dec. in flower wt)				
(Renaissance)	0.25		15 (55%* dec. in flower wt)				
(Turo)	0.25		8 (10% inc. in flower wt)				
ORNAMENTAL TREES AND SHRUBS							
Hybrid poplar (Dorskamp)	0.041	12 hr/day, 23 wk	not given (1333%* inc leaf drop)	Chem	NBKI	GH-CH	Mooi, 1980
(Zeeland)	0.041		not given (692%* inc. leaf drop)				
Hinodegiri azalea	0.20	5 hr	33	Chem	NBKI	GC	Davis et al., 1981
Black Cherry	0.20		27				
American sycamore	0.20		26				
Hybrid poplar	0.20		20				

TABLE 7-16 (con't). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
Yellow poplar	0.20		19				
Black walnut	0.20		12				
Delaware Valley white azalea	0.20		12				
Black elder	0.20		11				
Spreading cotoneaster	0.20		4				
Austrian pine	0.20		0				
Eastern white pine	0.20		0				
Virginia pine	0.20		0				
Hinodegiri azalea	0.25	8 hr	95 (Severity index[e])	Chem	NBKI	GC	Davis and Coppolino, 1974
Korean azalea	0.25		70				
Tree-of-heaven	0.25		65				
Chinese elm	0.25		24				
Mock-orange, sweet	0.25		17				
Viburnum, tea	0.25		5				
Viburnum, linden	0.25		2				
American holly (♂)	0.25		0				
American holly (♀)	0.25		0				
Amur privet	0.25		0				

TABLE 7-16 (con't). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
Black gum	0.25		0				
Dense Anglogap yew	0.25		0				
Mountain-laurel kalmia	0.25		0				
Hete Japanese holly	0.25		0				
Hybrid poplar	0.25	12 hr/day, 24 days	not given (50%* inc. in leaf abscission)	Chem	Known O_3 source	GH-CSTR	Noble and Jensen, 1980
Azalea (Red Wing)	0.25	3 hr/day, 6 days over 4 wk	1 (32%* dec. stem dry wt)	Chem	Known O_3 source	GH-CSTR	Sanders and Reinert, 1982a
(Snow)	0.25		0				
(Glacier)	0.25		24				
(Hersey Red)	0.25		21 (44%* dec. stem dry wt)				
(Pink Gumpo)	0.25		0				
(Mme. Pericat)	0.25		4				
(Red Luann)	0.25		8 (25%* dec. stem dry wt)				
(Mrs. G.G. Gerbing)	0.25		9				

TABLE 7-16 (con't) FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
TURFGRASS							
Turfgrass (Meyer zoysiagrass)	0.20	2 hr	0	Mast	not given	CH	Richards et al., 1980
(Tufcote bermudagrass)	0.20		0				
(Merion bluegrass)	0.20		0				
(Kenblue bluegrass)	0.20		2				
(K-31 tall fescue)	0.20		7				
(NK-100 ryegrass)	0.20		9				
(Penncross bentgrass)	0.20		14				
(Pennlawn red fescue)	0.20		17				
(Annual bluegrass)	0.20		20				
Kentucky bluegrass (Newport)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	0 5				
(Sydsport)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	5 12				
(Merion)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	9 14				
(Fylking)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	9 14				
(Windsor)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	7 15				
(S. Dakota (certified)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	10 17				

TABLE 7-16 (con't). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury		Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
(Kenblue)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	12 17					
Kentucky bluegrass (Adelphi)	0.15	6 hr/day, 10 days	6		UV	not given	CH	Elkiey and Ormrod, 1980
(Baron)	0.15		0					
(Birka)	0.15		0					
(Cheri)	0.15		19					
(Fylking)	0.15		0					
(Merion)	0.15		9					
(Nugget)	0.15		8	(8% dec. in leaf area)				
(Plush)	0.15		0					
(Skofti)	0.15		0					
(Sydsport)	0.15		12					
(Touchdown)	0.15		0					
(Victa)	0.15		10					
Red top (Common)	0.15		40					
Creeping bentgrass (Penncross)	0.15		20					

TABLE 7-16 (con't). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
Colonial bentgrass (Exetes)	0.15		6				
Red fescue (Highlight)	0.15		2				
(Pennlawn)	0.15		6	(27%* dec. in leaf area)			
Perennial ryegrass	0.15	11 (20%* dec. in leaf area)					
FOLIAGE CROPS							
Tobacco	0.05	4 hr	0	Mast	NBKI	GH-CH	Tingey et al., 1973c
(Bel B)	0.10		0				
(White Gold)	0.05		0				
	0.10		0				
Cabbage (All Season)	0.05		0				
	0.10		0				
Spinach (Northland)	0.05		0				
	0.10		0				

TABLE 7-16 (con't). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
Spinach (America)	0.13	7 hr/day average for 30 days (0.08 ppm O_3 ambient air each day)	49 ($36\%^{ng}$ dec. in fresh wt)	Chem	NBKI	OT	Heagle et al., 1979b
(Winter Bloomsdale)	0.13		52 ($45\%^{ng}$ dec. in fresh wt)				
(Seven-R)	0.13		52 ($55\%^{ng}$ dec. in fresh wt)				
(Hybrid-424)	0.13		54 ($42\%^{ng}$ dec. in fresh wt)				
(Hybrid-7)	0.13		56 ($43\%^{ng}$ dec.) in fresh wt)				
(Viking)	0.13		58 ($44\%^{ng}$ dec. in fresh wt)				
(Dark Green Bloomsdale)	0.13		58 ($58\%^{ng}$ dec. in fresh wt)				
(Viroflay)	0.13		60 ($33\%^{ng}$ dec. in fresh wt)				
(Chesapeake)			63 ($42\%^{ng}$ dec. in fresh wt)				
(Hybrid-612)	0.13		65 ($61\%^{ng}$ dec. in fresh wt)				
(Dixie Market)	0.13		65 ($55\%^{ng}$ dec. in fresh wt)				

TABLE 7-16 (con't). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent foliar injury	Monitoring method[a]	Calibrating method[b]	Fumigation facility[c]	Reference
Tobacco (GC-166)	ambient air (Beltsville, MD)	11 wks	1	Mast	not given	field	Menser and Hodges, 1972
(CCC-E)			1				
(GC-172)			2				
(GC-169)			6				
(GC-18)			7				
(CCC-C)			10				
(GC-46)			10				
(CCC-L)			11				
(CCC-K)			11				
(GC-50)			11				
(CCC-M)			15				
(CCC-J)			18				
(CCC-S)			25				
(Bel-C)			55				

[a]Where a column entry is blank, the information is as above.

[b]chem = chemiluminescence; Mast = Mast oxidant meter (coulometric); UV = ultraviolet spectrometry.

[c]NBKI = neutral buffered potassium iodide.

[d]GH = greenhouse; GH-CSTR = continuous stirred tank reactor in a greenhouse; OT = open-top chamber; GC = growth chamber; CH = specially designed exposure chamber other than CSTR; GH-CH = exposure chamber in a greenhouse.

[e]severity index = [severity factor (0-5) x (% foliage injured) x (% population susceptible)] ÷ 100.

*significant at P = 0.05; ng = not given.

earlier study, several species were exposed to O_3 (0.25 ppm for 8 hr) and evaluated for foliar injury (Davis and Coppolino, 1974). Some common ornamentals (holly, privet, yew, laurel, linden) exhibited no foliar injury, but others (azalea, tree-of-heaven, elm) appeared to be relatively sensitive (Table 7-16).

For ornamental tree plantings, excessive leaf drop decreases the value and thus can be considered a yield loss. Ozone has been shown to induce significant defoliation in hybrid poplar. Mooi (1980) noted increases of about 7 and 13-fold in leaf drop of two poplar cultivars exposed to 0.041 ppm, 12 hr/day, for 23 weeks (Table 7-16). Noble and Jensen (1980) reported a 50 percent increase in leaf drop of hybrid poplar exposed to 0.25 ppm of O_3, 12 hr/day, for 24 days (Table 7-16).

Species and cultivars of turfgrass have exhibited foliar injury when exposed to 0.15 ppm of O_3 (6 hr/day, 10 days) (Elkiey and Ormrod, 1980). The extent of foliar injury was usually greater than the resultant growth inhibition. Ozone concentrations of 0.10 ppm for 3.5 hr/day for 4 days or 0.20 ppm for 2 hr were high enough to elicit injury in most turf grasses (Richards et al., 1980) (Table 7-16).

The appearance of the foliage on crops such as tobacco and spinach is important to their value and may affect marketability. Tobacco and spinach failed to exhibit visible injury after exposure to 0.05 or 0.10 ppm of O_3 for 4 hr (Tingey et al., 1973c) (Table 7-16). Eleven spinach cultivars exhibited 49 to 65 percent mean foliar injury (and 33 to 61 percent mean fresh weight reduction) when exposed in the field to a 7-hr seasonal mean O_3 concentration of 0.13 ppm (Heagle et al., 1979b) (Table 7-16). The physical appearance of cigar wrapper tobacco leaves may be very important to their value. Foliar injury from O_3 has been documented in the field (some cultivars are commonly used as bioindicators) and in controlled fumigations. Plants of commercial tobacco cultivars grown in ambient air at Beltsville, MD, exhibited 1 to 55 percent O_3 injury (Menser and Hodges, 1972) (Table 7-16). Ozone concentrations of 0.10 ppm for 2 hr induced up to 20 percent foliar symptoms.

The above data are examples of O_3-induced impairments in the appearance and aesthetic value of plants due to foliar injury. Such effects occur at concentrations as low as 0.041 ppm for several weeks or 0.10 ppm for 2 hr, and these effects can constitute a yield loss when marketability of the plants is decreased. The actual amount of yield loss due to decreased aesthetic value

or appearance may be more difficult to quantify than yield loss in weight or bulk. However, it is not unreasonable for such losses to be relatively greater than those due to loss in weight even though there may not be as much physical injury to the plant.

7.4.3.2 Yield Losses as Weight, Size, and Number. The previous criteria document (U.S. Environmental Protection Agency, 1978) summarized the effects of acute and chronic O_3 exposures with the primary focus on plant growth and a few reports which specifically studied yield loss (Tables 7-17, 7-18). Growth and yield reductions were observed in a diverse range of plant species at various exposure durations and O_3 concentrations. The majority of the studies were conducted in greenhouse or controlled-environment chambers with only a few studies conducted in the field. These data indicated that as the exposure duration increased, the mean O_3 concentrations at which growth effects occurred decreased. When the exposure duration exceeded 15 days (not continuous exposures), mean O_3 concentrations of 0.05 ppm and greater caused significant growth and yield reductions. In field studies, significant growth and yield reductions were observed in commercial varieties of sweet corn, soybean, and pine seedlings (Heagle et al., 1972; Heagle et al., 1974; Wilhour and Neely, 1977) when the seasonal 6-hr O_3 concentration was 0.10 ppm or greater. In another field study, significant growth and yield reductions occurred in alfalfa when the 7-hr seasonal mean O_3 concentration was 0.05 ppm or greater (Neely et al., 1977).

Yield losses are summarized in the following sections in terms of weight or size, and decrease in number from studies in which known amounts of O_3 were added to either charcoal-filtered or ambient air. The effects of ambient O_3 on yield are also presented.

7.4.3.2.1 Ozone addition studies. Ozone-induced yield-loss studies have used a variety of experimental approaches. Some studies have attempted to approximate typical agronomic conditions, and others have deviated from typical field practices in an attempt to have better control of the experimental conditions. Open-top chamber data will be discussed first, because most of these studies attempted to follow typical field practices. Results from experiments conducted under more controlled conditions (greenhouses, indoor chambers, potted plants) are discussed primarily as they relate to the field studies.

TABLE 7-17. EFFECTS OF SHORT-TERM EXPOSURES ON GROWTH AND YIELD OF SELECTED PLANTS[a]

Plant species	Ozone concentration ppm	Exposure time (hr)	Plant response, % reduction from control[b]
Begonia, cultivar White Tausendschon	0.10	2	5, avg. of 3 growth responses: shoot wt, flower wt, flower no.
	0.20	2	10, avg. of same responses
	0.40	2	19, avg. of same responses
	0.80	2	38, avg. of same responses
Petunia, cultivar Capri	0.10	2	9, avg. of same responses
	0.20	2	11, avg. of same responses
	0.40	2	21, avg. of same responses
	0.80	2	31, avg. of same responses
Coleus, cultivar Scarlet Rainbow	0.10	2	2, avg. of same responses
	0.20	2	17, avg. of same responses
	0.40	2	24, avg. of same responses
	0.80	2	39, avg. of same responses
Snapdragon, cultivar Floral Carpet, mixture	0.10	2	0, avg. of same responses
	0.20	2	6, avg. of same responses
	0.40	2	8, avg. of same responses
	0.80	2	16, avg. of same responses
Radish, cultivar Cavalier Cherry Belle	0.25	3	36, top dry wt (Cavalier) 38, root dry wt (Cherry Belle)
Radish	0.40	1.5(1)[c]	37, root dry wt
		1.5(2)[c]	63, root dry wt
		1.5(3)[c]	75, root dry wt
Cucumber, cultivar Ohio Mosiac	1.00	1	19, top dry wt (1% injury)
	1.00	4	37, top dry wt (18% injury)
Potato, cultivar Norland	1.00	4	0, tuber dry wt (no injury)
	1.00	4(3)[c]	30, tuber dry wt (injury severe)
Tomato, cultivar Fireball	0.50	1	15, plant dry wt (grown in moist soil)
	1.00	1	20, plant dry wt (grown in moist soil)
Tomato, cultivar Fireball	0.50	1	15, increase in plant dry wt (grown in dry soil)
	1.00	1	25, increase in plant wt (grown in dry soil)
Onion, cultivar Spartan Era	0.20	24	0, effect
	1.00	1	19, plant dry wt (no injury)
	1.00	4	49, plant dry wt
Tobacco, cultivar Bel W_3	0.30	2	48, chlorophyll content

[a]Taken from Ref. (U.S. Environmental Protection Agency, 1978).

[b]Unless otherwise noted.

[c]Number of exposures in parentheses.

TABLE 7-18. EFFECTS OF LONG-TERM, CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD, AND FOLIAR INJURY TO SELECTED PLANTS[a]

Plant species	Fig. 7-6[b] Nos.	Ozone concentration, $\mu g/m^3$ (ppm)	Exposure time	Plant response, % reduction from control
Lemna, duckweed	1	196 (0.10)	5/day, 14 days	100, flowering; 36, flowering (1 wk after exposure completed) 50, frond doubling rate
Carnation	2	98-177 (0.05-0.09)	24/day, 90 days	50, flowering (reduced vegetative growth)
Geranium	3	137-196 (0.07-0.10)	9.5/day, 90 days	50, flowering (shorter flower lasting time, reduced vegetative growth)
Petunia	4	98-137 (0.05-0.07)	24/day, 53 days	30, flower fresh wt
Poinsettia	5	196-235 (0.10-0.12)	6/day, 5 days/week, 10 weeks	39, bract size
Radish	6	98 (0.05)	8/day, 5 days/week, 5 weeks	54, root fresh wt 20, leaf fresh wt
		98 (0.05)	8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	63, root fresh wt 22, leaf fresh wt
Beet, garden	7	392 (0.20)	3/day, 38 days	50, top dry wt
Bean, cultivar Pinto	8	255 (0.13)	8/day, 28 days	79, top fresh wt 73, root fresh wt 70, height
Bean, cultivar Pinto	9	290 (0.15)	2/day, 63 days	33, plant wt; 46, pod fresh wt
	10	490 (0.25)	2/day, 63 days	95, plant dry wt; 99, pod fresh wt
	11	686 (0.35)	2/day, 63 days	97, plant dry wt; 100, pod fresh wt
Bean, cultivar Pinto	12	290 (0.15)	2/day, 14 days	8, leaf dry wt
	13	290 (0.15)	3/day, 14 days	8, leaf dry wt
	14	290 (0.15)	4/day, 14 days	23, leaf dry wt (Data available on whole plants, roots, leaves, injury, and three levels of soil (moisture stress)
	15	290 (0.15)	6/day, 14 days	49, leaf dry wt
	16	440 (0.225)	2/day, 14 days	44, leaf dry wt
Bean, cultivar Pinto	17	440 (0.225)	4/day, 14 days	68, leaf dry wt (Data available on whole plants, roots, leaves, injury, and three levels of soil (moisture stress)
	18	588 (0.30)	1/day, 14 days	40, leaf dry wt

TABLE 7-18 (con't). EFFECTS OF LONG-TERM, CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD AND FOLIAR INJURY TO SELECTED PLANTS[a]

Plant species	Fig. 7-6 Nos.	Ozone concentration $\mu g/m^3$ (ppm)	Exposure time	Plant response, % reduction from control
	19	588 (0.30)	3/day, 14 days	76, leaf dry wt
Tomato	20	392 (0.20)	2.5/day, 3 days/week 14 weeks	1, yield; 32 top dry wt; 11, root dry wt
	21	686 (0.35)	2.5/day, 3 days/week, 14 weeks	45, yield; 72, top dry wt; 59, root dry wt
Corn, sweet, cultivar Golden Jubilee	22	392 (0.20)	3/day, 3 days/week till harvest	13, kernel dry wt; 20, top dry wt; 24, root dry wt
	23	686 (0.35)	3/day, 3 days/week till harvest	20, kernel dry wt; 48, top dry wt; 54, root dry wt
Wheat, cultivar Arthur 71	24	392 (0.20)	4/day, 7 days (anthesis)	30, yield
Soybean	25	98 (0.05)	8/day, 5 days/week 3 weeks	13, foliar injury
			8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	16, foliar injury 20, root dry wt
Soybean	26	196 (0.10)	8/day, 5 days/week 3 weeks	21, top dry wt 9, root dry wt
Alfalfa	27	196 (0.10)	2/day, 21 days	16, top dry wt
	28	290 (0.15)	2/day, 21 days	26, top dry wt
	29	390 (0.20)	2 day, 21 days	39, top dry wt
Grass brome	30	290-647 (0.15-0.33)(varied)	4/day, 5 days/week growing season	83, biomass
Alfalfa[c]	31	196 (0.10)	6/day, 70 days	4, top dry wt, harvest 1 20, top dry wt, harvest 2 50, top dry wt, harvest 3
Alfalfa[c]	32	98 (0.05)	7/day, 68 days	30, top dry wt, harvest 1 50, top dry wt, harvest 2
Alfalfa	33	98 (0.05)	8/day, 5 days/week 12 weeks	18, top dry wt
Pine, eastern white	34	196 (0.10)	4/day, 5 days/week 4 weeks (mixture of O_3 and SO_2 for same periods)	3, needle mottle (over 2-3 days of exposure) 16, needle mottle

TABLE 7-18 (con't). EFFECTS OF LONG-TERM, CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD AND FOLIAR INJURY TO SELECTED PLANTS[a]

Plant species	Fig. 7-6 Nos.[b]	Ozone concentration $\mu g/m^3$ (ppm)	Exposure time	Plant response, % reduction from control
Pine, ponderosa	35	290 (0.15)	9/day, 10 days	4, photosynthesis
	36	290 (0.15)	9/day, 20 days	25, photosynthesis
Pine, ponderosa	37	290 (0.15)	9/day, 30 days	25, photosynthesis
	38	290 (0.15)	9/day, 60 days	34, photosynthesis
	39	588 (0.30)	9/day, 10 days	12, photosynthesis
	40	588 (0.30)	9/day, 20 days	50, photosynthesis
	41	588 (0.30)	9/day, 30 days	72, photosynthesis
	42	880-588 (0.30)	9/day, 30 days	85, photosynthesis
Poplar, yellow	43	588-880 (0.45)	9/day, 30 days 13 weeks	82, leaf drop; 0, height
Maple, silver	44	588 (0.30)	8/day, 5 days/week 13 weeks	50, leaf drop; 78, height
Ash, white	45	588 (0.30)	8/day, 5 days/week 13 weeks	66, leaf drop; 0, height
Sycamore	46	588 (0.30)	8/day, 5 days/week 13 weeks	0, leaf drop; 22, height
Maple, sugar	47	588 (0.30)	8/day, 5 days/week 13 weeks	28, leaf drop; 64, height
Corn, sweet, cultivar Golden Midget[c]	48	98 (0.05)	6/day, 64 days	9, kernel dry wt; 14, injury (12, avg. 4 yield responses)
	49	196 (0.10)	6/day, 64 days	45, 25, 35 for same responses
Pine, ponderosa[c]	50	196 (0.10)	6/day, 126 days	12, root length 21, stem dry wt; 26, root dry wt
Pine, western white[c]	51	196 (0.10)	6/day, 126 days	13, foilage dry wt 9, stem dry wt
Soybean, cultivar Dare[c]	52	98 (0.05)	6/day, 133 days	3, seed yield; 22, plant fresh wt; 19, injury, defoliation, no reduction in growth or yield
	53	196 (0.10)	6/day, 133 days	55, 65, 37 for same responses
Poplar, hybrid	54	290 (0.15)	8/day, 5 days/week 6 weeks	50, shoot dry wt; 56, leaf dry wt; 47, root dry wt

[a] From Ref. (U.S. Environmental Protection Agency, 1978).

[b] Numbers in this column are keyed to numbers in Fig. 7-6.

[c] Studies conducted under field conditions, except that plants were enclosed to ensure controlled pollutant doses. Plants grown under conditions making them more sensitive.

7.4.3.2.1.1 Open-top chamber studies. The data from experiments in open-top chambers provide information on O_3 exposure-yield response relationships for plants grown under near-normal field conditions. Each of the studies described in this section used charcoal-filtered air as the lowest O_3 level (control). To create a range of concentrations, O_3 was added to either charcoal-filtered air or to unfiltered air. In summarizing the data, yield loss was derived from the plant performance in charcoal-filtered air, although other reference concentrations could have been used. One of the experimental objectives of most of the studies was to develop exposure response relationships among O_3 concentration, exposure duration, and yield loss. To derive the exposure response functions, various regression techniques have been used. To estimate the impact of O_3 on yield at a common O_3 concentration for all the studies, the derived equations were used to estimate the yield loss at a particular exposure condition rather than individual means. Graphs of the exposure response equations and the data used to derive them are presented to show how well various models fit the experimental data.

The effects of O_3 on the yield of five soybean cultivars exposed to various O_3 concentrations at different NCLAN sites during different years are remarkably similar (Figure 7-12 A to D; Table 7-19). The yield reductions for the soybean cultivar Davis (Heagle et al., 1983a) were derived from a curvilinear (quadratic) regression approach which predicted a 24 percent reduction in seed weight per meter of row at a 7-hr mean seasonal O_3 concentration of 0.06 ppm and compared to a control of 0.025 ppm of O_3 (Figure 7-12a). However, this curve appears to overestimate the control yield. Based on interpolation of the treatment means, the reduction at 0.06 ppm should be about 13 percent. A yield reduction of 21 percent (0.06 ppm) was predicted for the soybean cultivar Corsoy (control = 0.022 ppm of O_3) based on a linear model (Figure 7-12d) (Kress and Miller, 1983). Plants infected with a virus appeared to be more resistant to O_3. However, no data from virus-free plants were used in developing the equation. Earlier studies (1977, 1978) which used the cultivar Davis grown in pots displayed smaller yield losses (Heagle and Heck, 1980; Heck et al., 1982a) (Figure 7-12b,c). Linear regression equations predicted yield reductions of 16 percent (0.06 ppm) (control = 0.025 ppm of O_3) in 1977, and 13 percent (0.06 ppm) (control = 0.024 ppm of O_3) in 1978. The apparent lesser sensitivity of Davis soybean in 1977 and 1978 may have resulted from a lower water availability, because the plants were grown in pots (Heagle et al., 1983a).

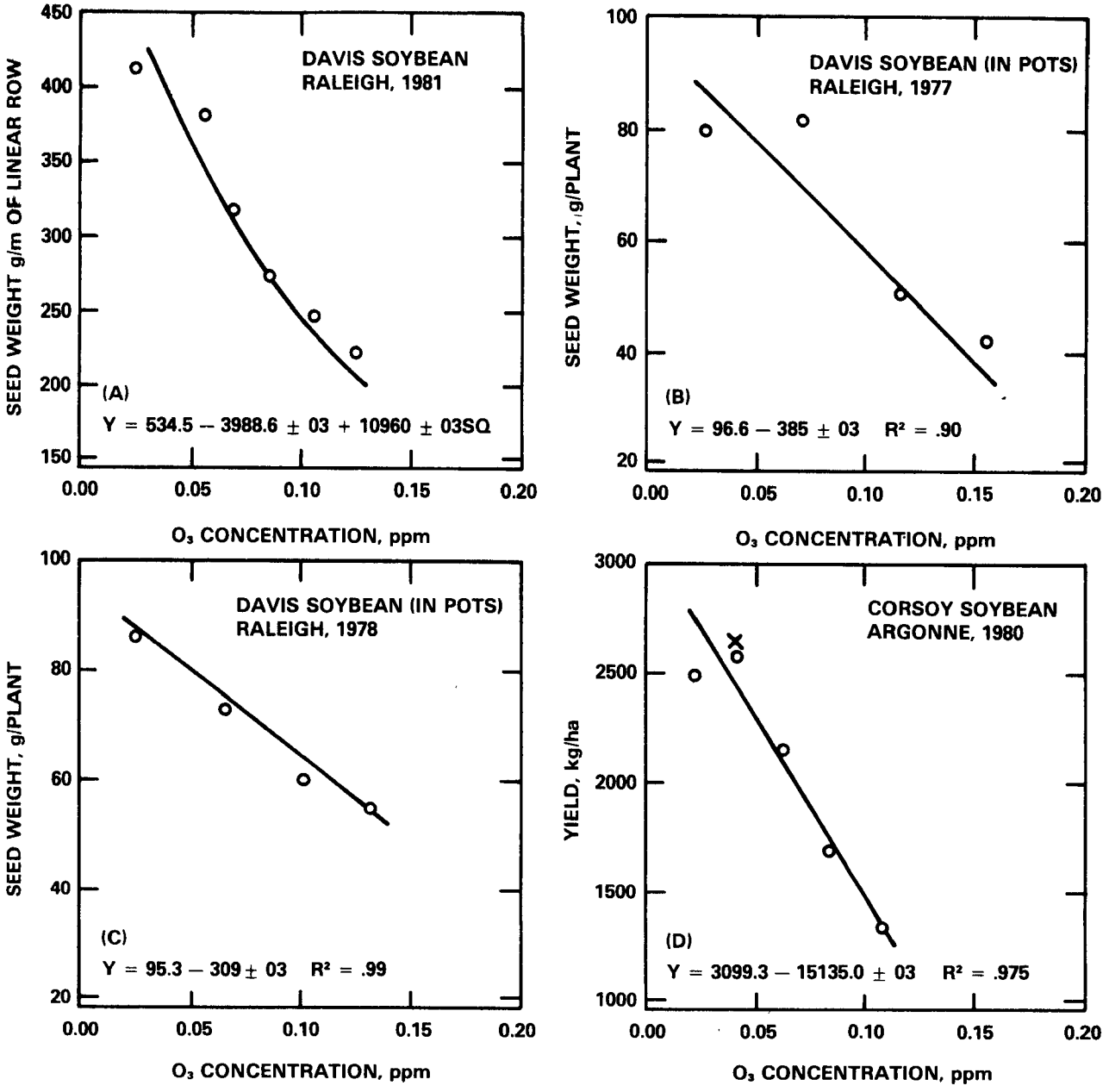

Figure 7-12. Effect of O_3 exposures on the yield of various legumes. O_3 concentration (ppm) is expressed as 7-hr seasonal mean. o indicates mean of plants in open top chambers; X indicates mean of plants in ambient air, which were not used in the regression analysis. (A) Data and regression equation from Heagle et at., 1983a. Each point is the mean of two plots; the regression equation was based on the individual plot values. (B) and (C) Data are from Heck et al., 1982. Similar equations were published in Heagle and Heck, 1980. Each point is the mean of two replications (chambers) with four plots per replication. (D) Data and regression equation are from Kress and Miller, 1983. Data and curve for yield in g/plant are also given in Heck et al., 1982. Each point is the mean of four plots; the regression equation was based on individual plot values.

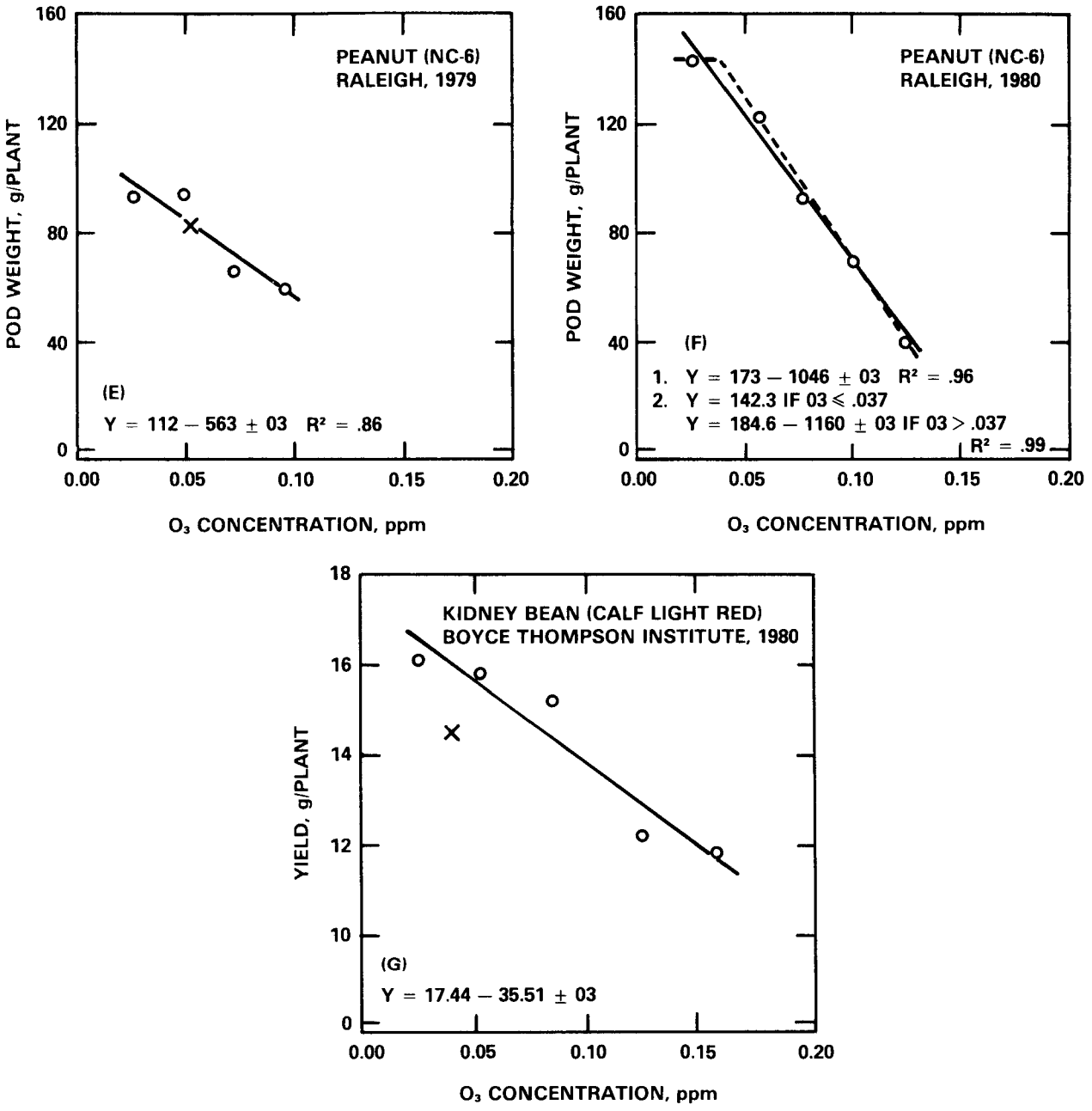

Figure 7-12. (continued) (E) Data and regression equation from Heagle et al., 1983b. Each point is the mean of two plots with 16 plants per plot. (F) Data and the straight line equation are found in Heagle et al., 1983b, and Heck et al., 1982. The plateau-linear equation is from Heck et al., 1982. (G) Data and regression equation are from Kohut and Laurence, 1983. The same data and another straight line regression are in Heck et al., 1982. Each point is the mean of three plots. Regression was performed on treatment means.

TABLE 7-19. OPEN-TOP CHAMBER EFFECTS AND WEIBULL PARAMETERS FOR INDIVIDUAL OZONE DOSE-CROP RESPONSE DATA SETS.[a]

Crop	Chamber Effect-$\hat{\alpha}_2$[b] g/plant		Weibull parameters for individual models[f] $\hat{\alpha}$ g/plant		$\hat{o}$, ppm		$\hat{c}$	
Soybean								
Corsoy[d]	-0.75	(0.92)	15.6	(1.23)	0.129	(0.01)	1.70	(0.53)
Davis[e]	-2.26	(5.25)	31.1	(4.63)	0.129	(0.02)	0.91	(0.29)
Essex[e]	7.51	(3.45)	18.7	(6.35)	0.309	(0.37)	0.76	(1.26)
Hodgson (F)[f]	1.28	(1.33)	15.2	(7.63)	0.207	(0.14)	0.50	(0.54)
Hodgson (P)[f]	0.14	(1.87)	15.5	(2.27)	0.153	(0.03)	1.57	(1.10)
Williams[e]	3.49	(2.36)	19.4	(3.77)	0.243	(0.17)	0.94	(0.95)
Common Response (cv)[g]	-		-		0.153	(0.007)	1.26	(0.18)
Corn								
Coker 16[h]	18.3	(8.67)	240	(5.90)	0.221	(0.05)	4.46	(2.83)
PAG 397	13.0	(7.38)	166	(3.80)	0.160	(0.00)	4.28	(0.72)
Pion. 3780	5.9	(6.28)	149	(3.90)	0.155	(0.00)	3.11	(0.46)
Common Response (cv)[g,h]	-		-		0.158	(0.00)	3.53	(0.57)
Wheat								
Blueboy II	0.93	(0.27)**	5.88	(0.22)	0.175	(0.02)	3.22	(1.33)
Coker 47-27	0.70	(0.23)*	5.19	(0.29)	0.171	(0.02)	2.06	(0.68)
Holly	0.75	(0.25)*	4.95	(0.17)	0.156	(0.01)	4.95	(2.03)
Oasis	0.32	(0.25)	4.48	(0.20)	0.186	(0.04)	3.20	(1.86)
Common Response (cv)[g]	-		-		0.174	(0.01)	2.90	(0.78)
Peanut								
NC-6	-48.1	(5.80)**	148	(4.70)	0.111	(0.00)	2.21	(0.23)
Cotton[i]								
Acala SJ-2(I)	-3.30	(3.72)	41.5	(4.90)	0.197	(0.02)	1.12	(0.42)
Kidney Bean								
Calif. Lt. Red.	1.44	(1.00)	16.5	(1.10)	0.287	(0.09)	1.77	(1.06)
Lettuce								
Empire	144	(181)	1245	(530)	0.098	(0.04)	1.22	(0.71)
Turnip								
Just Right	5.57	(0.70)**	10.89	(0.50)	0.090	(0.003)	3.05	(0.65)
Pu. Top W.G.	2.93	(0.45)**	6.22	(0.35)	0.095	(0.005)	2.51	(0.67)
Shogoin	2.56	(0.38)**	4.68	(0.33)	0.096	(0.006)	2.12	(0.64)
Tokyo Cr.	8.99	(2.09)**	15.25	(1.30)	0.094	(0.006)	3.94	(2.01)
Common Response (cv)[g]	-		-		0.093	(0.003)	2.75	(0.57

TABLE 7-19. OPEN-TOP CHAMBER EFFECTS AND WEIBULL PARAMETERS FOR INDIVIDUAL OZONE DOSE-CROP RESPONSE DATA SETS[a]

Crop	Chamber effect-$\hat{\alpha}_2$[b] (g/plant)	Weibull parameters for individual models[c] $\hat{\alpha}$ (g/plant)	$\hat{\sigma}$ (ppm)	$\hat{c}$
Spinach[j]				
America	-	21.2 (3.20)	0.142 (0.021)	1.65 (0.98)
Hybrid[g]	-	36.6 (4.90)	0.139 (0.017)	2.68 (1.70)
Viroflay	-	41.1 (5.80)	0.129 (0.017)	1.99 (1.06)
Winter Bloom.	-	20.8 (3.10)	0.127 (0.017)	2.07 (1.17)
Common Response (cv)[g]	-	-	0.135 (0.008)	2.08 (0.51)

[a]Table from Heck et al., 1983. The Weibull model is $Y = \alpha \exp[-(\frac{x}{\sigma})^c] + \varepsilon$. The standard error (SE) is shown in () for all data; all values are ±SE. The SE was calculated using the mean square error term from the analysis of variance.

[b]The α_2 is the predicted chamber effect (g/plant), the significance of α_2 was tested using a t-test; * and **, significantly different from zero at p=0.05 and p=0.01, respectively. Negative values correspond to situations in which AA plot yields were greater than those from corresponding chambered plots and vice versa.

[c]Weibull parameters: $\hat{\alpha}$ is the predicted yield (g/plant) at zero O_3; $\hat{\sigma}$ is the predicted O_3 concentration (ppm) at 67% yield reduction; $\hat{c}$ is the predicted shape of the curve and has no dimensions; and $\hat{\sigma}$ and $\hat{c}$ are common for all cultivars that are combined, but α is different for each cv; Weibull parameters are based on chambered plots only.

[d]These estimates were based on yields corrected by a covariance analysis for the effects of a virus infection and differ slightly from previously published information on this data set (Heck et al., 1982).

[e]For Davis, Essex, and Williams data sets, an SO_2 response was also measured.

[f]The Hodgson data were obtained from two designs in 1981; a full plot harvest (F) and a partial plot harvest (P), where some plants were removed before harvest.

[g]An F statistic was used as a test for the homogeneity of the proportional response part of the model, $\exp[-(\frac{x}{\sigma})^c]$; none of the F values were significant at P = 0.05, thus they were all homogeneous.

[h]Coker 16 was not included in the "Common Response" because the use of the Coker 16 data resulted in a highly significant F value (29.31), indicating a heterogeneous response.

[i]The cotton experiment utilized an irrigated (I) and droughted (D) treatment. These two designs gave a positive test for homogeneity using the Weibull function. However, the F statistic was large (3.2) and the analysis of variance showed an O_3 by soil moisture interaction. Thus, these data sets were not combined.

[j]AA plots were not used in this experiment.

More recently, NCLAN has used the Weibull equation to estimate O_3-induced yield reductions (Heck et al., 1983). The predicted yield reductions at 0.06 ppm were 18 percent (Essex), 18 to 22 percent (Hodgson), and 18 percent (Williams) (Table 7-19). In fact, the responses of the five cultivars from these studies were statistically homogeneous. Unfortunately, the raw data from which the equations for Essex, Hodgson, and Williams were developed were not presented.

Peanuts are among the more sensitive crops thus far tested in the NCLAN program (Heagle et al., 1983c). The peanut study was replicated over 2 years (Figure 7-12 e,f). In the first year, a linear regression equation predicted a 20 percent yield reduction (0.06 ppm) compared to a charcoal-filtered air control of 0.026 ppm O_3 mean 7-hr seasonal concentration; however, the O_3 effect was statistically significant at only $p = 0.13$. In the second year (1980), a 25 percent yield loss of marketable pod weight per plant (0.06 ppm), compared to a control concentration of 0.025 ppm, was predicted from the linear model. The authors suggested that the 1979 peanut crop was under greater moisture stress because of closer plant spacing, less irrigation, and constant air movement, which may have depressed plant growth and rendered the plants less sensitive to O_3. The data for 1980 were fit with linear, plateau-linear, and Weibull (Table 7-19) models, which predicted similar yield losses.

Kidney bean (California Light Red) appeared to be considerably less sensitive to O_3 than soybean (Kohut and Laurence, 1983). A linear regression equation predicted bean weight/plant yield reductions of 7 percent (0.06 ppm) compared to the control (0.025 ppm of O_3) (Figure 7-19). The predicted yield reductions from the Weibull equation (Heck et al., 1983) were similar, at 5 percent (0.06 ppm) (Table 7-19).

Winter wheat yield appeared to be relatively sensitive to O_3 based on the yield reductions of four cultivars (Table 7-20). The yields of all four cultivars were significantly reduced (11 to 25 percent) at 0.10 ppm of O_3, but only one cultivar was significantly affected (11 percent reduction) at 0.06 ppm of O_3 (Heagle et al., 1979c). These data were subsequently re-evaluated using quadratic (Heagle and Heck, 1980) and linear (Heck et al., 1982) regression models (Figure 7-13 a to d). Based on a visual inspection, the quadratic model fit the data better than the linear model for all cultivars. A plateau-linear model was used for one cultivar (Holly) but its fit did not appear better than that of the quadratic. At a seasonal 7-hr mean O_3 concentration of 0.06 ppm, the model predicted yield losses of 0.0 to 11 percent for the four cultivars. The yield reductions predicted by the Weibull equations were similar (Table 7-19).

TABLE 7-20. EFFECTS OF OZONE ADDED TO AMBIENT AIR IN OPEN-TOP CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration method	Reference
Field corn (Coker 16)	0.02	Beginning 25 days after planting for 88 days, Seasonal 7-hr average (0830-1530 ST)	Control	Chem.	1% NBKI	Heagle et al., 1979a
	0.07		+3, seed wt/plant; +2, wt/seed			
	0.11		4, seed wt/plant; 1, wt/seed			
	0.15		16*, seed wt/plant; 9*, wt/seed			
Field corn (Coker 16)	0.02	Beginning 25 days after planting for 88 days, Seasonal 7-hr average (0830-1530 ST)	Control	Chem.	1% NBKI	Heagle et al., 1979a
	0.15		12*, seed wt/plant; 15*, wt/seed			
(FR632 X FR619)	0.02		Control			
	0.15		37*, seed wt/plant; 25*, wt/seed			
(H95 X FR64A)	0.02		Control			
	0.15		40*, seed wt/plant; 30*, wt/seed			
Winter wheat (soft red) (Blueboy II)	0.03	Beginning when plants were 28 to 45 cm tall for 53 days Seasonal 7-hr average (0930-1530 ST)	Control	Chem.	1% NBKI	Heagle et al., 1979c
	0.06		2, seed wt/plant			
	0.10		15*, seed wt/plant			
	0.13		31*, seed wt/plant			
(Coker 47-27)	0.03		Control			
	0.06		11*, seed wt/plant			
	0.10		25*, seed wt/plant			
	0.13		43*, seed wt/plant			
(Holly)	0.03		Control			
	0.06		1, seed wt/plant			
	0.10		11*, seed wt/plant			
	0.13		33*, seed wt/plant			
(Oasis)	0.03		Control			
	0.06		1, seed wt/plant			
	0.10		11*, seed wt/plant			
	0.13		26*, seed wt/plant			

TABLE 7-20 (con't). EFFECTS OF OZONE ADDED TO AMBIENT AIR IN OPEN-TOP CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant Species	O_3 concentration, ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration method	Reference
Spinach (America)	0.024	Beginning 10 days after planting for 38 days, Seasonal 7-hr average (0820-1520 ST)	Control	Chem.	1% NBKI	Heagle et al., 1979b
	0.056		23, fresh wt of shoots			
	0.096		39*, fresh wt of shoots			
	0.129		70*, fresh wt of shoots			
(Winter Bloomsdale)	0.024		Control			
	0.056		19, fresh wt of shoots			
	0.096		44*, fresh wt of shoots			
	0.129		73*, fresh wt of shoots			
(Hybrid 7)	0.024		Control			
	0.056		4, fresh wt of shoots			
	0.096		35*, fresh wt of shoots			
	0.129		61*, fresh wt of shoots			
(Viroflay)	0.024		Control			
	0.056		26, fresh wt of shoots			
	0.096		35*, fresh wt of shoots			
	0.129		72*, fresh wt of shoots			
Soybean (Pots) (Forest)	0.025	Beginning 25 days after planting for 116 days, Seasonal 7-hr average (0820-1520 ST)	Control	Chem.	1% NBKI	Heagle and Letchworth, 1982
	0.101		32*, seed wt/plant			
(Ransom)	0.025		Control			
	0.101		20*, seed wt/plant			
(Davis)	0.025		Control			
	0.101		34*, seed wt/plant			
(Bragg)	0.025		Control			
	0.101		+4, seed wt/plant			

TABLE 7-20 (con't). EFFECTS OF OZONE ADDED TO AMBIENT AIR IN OPEN-TOP CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant species	O_3 concentration, ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring method	Calibration method	Reference
Soybean (plot) (Davis)	0.025 0.116	Beginning 23 days after planting for 116 days, Seasonal 7-hr average (0820-1520 ST)	Control 48*, seed wt/plant	Chem.	1% NBKI	Heagle et al., 1983b
(Davis)	0.023 0.098	Beginning 23 days after planting for 116 days, Seasonal 7-hr average (0820-1520 ST)	Control 28*, seed wt/plant			

[a]Where a column entry is blank the information is the same as above.

[b]Chem = chemiluminescence.

[c]1% NBKI = 1% neutral buffered potassium iodide.

*Significant effect at p = 0.05.

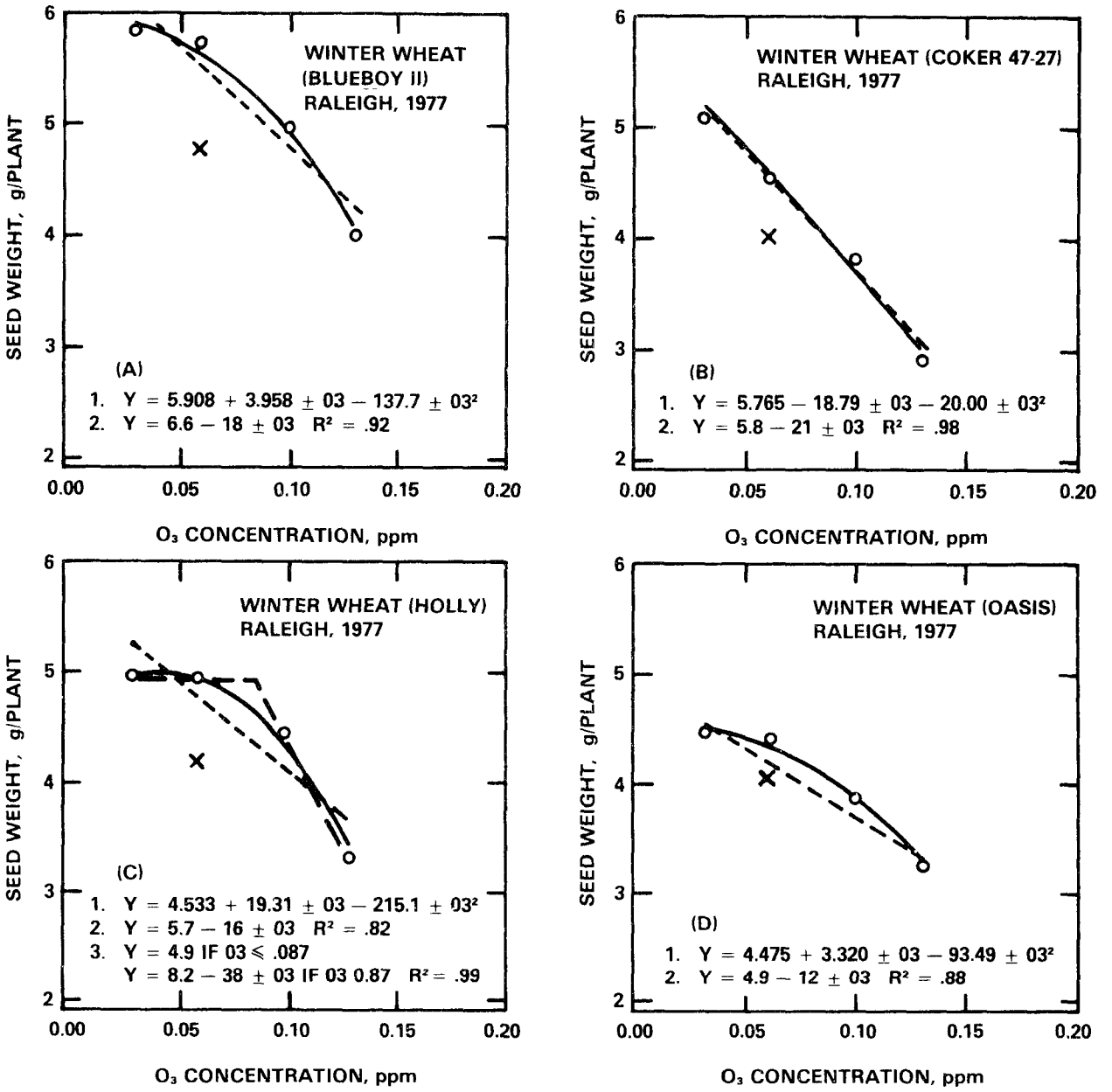

Figure 7-13. Effects of O_3 exposures on winter wheat and field corn yields. O_3 concentration is expressed as 7-hr seasonal mean. o indicates mean of plants in open top chambers; X indicates mean of plants in ambient air, which were not used in the regression analysis. (A-D) Data are from Heagle et al., 1979c. Quadratic equations are from Heagle and Heck, 1980. In Heagle and Heck, 1980 the data are presented as the yield per four plants; however, in this figure the values were divided by four to express yield on a per plant basis. All other equations are from Heck et al., 1982. Each point is the mean of 4 plots with 48 plants per plot.

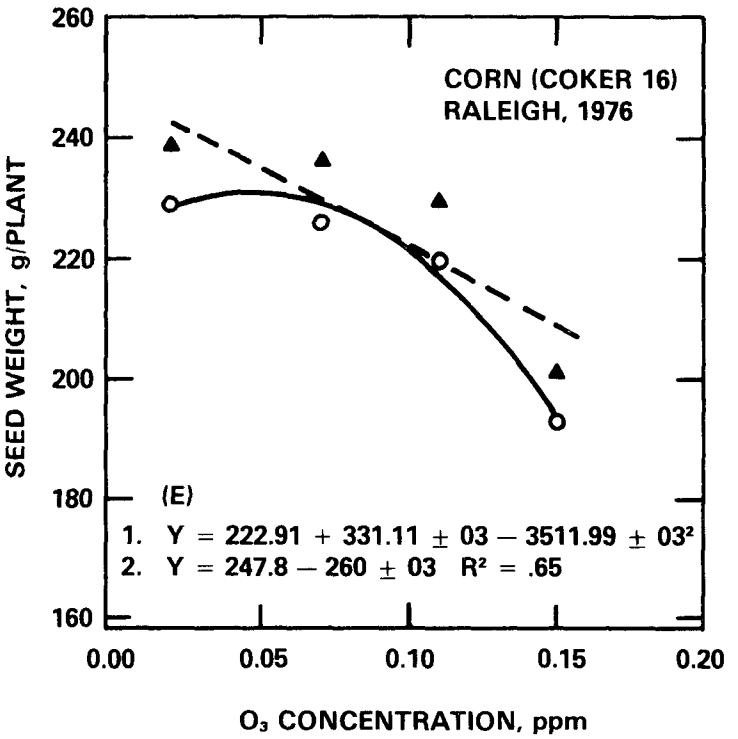

Figure 7-13. (continued) (E) Data are from Heagle et al., (1979a) with a correction for the yield at 0.07 ppm (personal communication, A.S. Heagle). The quadratic equation (solid line, o symbol) is from Heagle and Heck, 1980. Data point at the concentration of 0.07 is different from the original paper; the correction was based on information from A.S. Heagle. The straight line equation (dashed line, ▲ symbol), is from Heck et al., 1982. In developing the quadratic equation, the data from Heagle et al, 1979a, were divided by a factor of 1.045 to adjust the moisture content (Heagle, personal communication); for the linear equation the unadjusted data were used. ▲ indicates an adjusted treatment mean; y indicates the adjusted ambient plot mean. Each point is the mean of five plots with eight plants/plot.

Statistically, the yield responses of the four cultivars are uniform (Heck et al., 1983).

The effects of O_3 on the yield of field corn have been examined in two studies, but the results from one study have been reanalyzed three times and have thus been published in four different forms. First presented in tabular form with means comparison tests (Heagle et al., 1979a) (Table 7-20), the data for Coker 16 were subsequently analyzed using quadratic (Heagle and Heck, 1980) and linear (Heck et al., 1982) regression models (Figure 7-13e). Reductions in seed yield (g/plant) were originally shown to be 4 percent at 0.11 ppm and 16 percent at 0.15 ppm of O_3 when compared to a 0.02 ppm control (Table 7-20). The quadratic regression predicted a yield increase of 1 percent at 0.06 ppm and a yield reduction of 3 percent at 0.10 ppm (Figure 7-13e). The linear equation did not fit the data as well as the quadratic; therefore, it was not considered. The divergent yield reduction estimates resulting from different regression models illustrate the need to check the fit of the model to the data before using the equations to estimate yield reductions. The Weibull equation predicted yield reductions of 0.3 percent at 0.06 ppm of O_3 and 3 percent at 0.10 ppm of O_3 (Table 7-19). Heck et al. (1983) also derived Weibull equations for two other field corn hybrids (Table 7-19). Yield reductions of 5 percent at 0.06 ppm and 23 percent at 0.10 ppm were predicted for Pioneer 3780, and 2 percent at 0.06 ppm and 13 percent at 0.10 ppm of O_3 for PAG 397. These yield reductions were significantly greater than for Coker 16. It should be noted that the Weibull function does not allow for a yield stimulation at low O_3 concentrations, because the function has a maximum at zero and decreases with increasing O_3 concentrations.

Four cultivars of spinach appeared to be relatively sensitive to O_3 (Table 7-20). All cultivars exhibited significant yield reductions (35 to 44 percent) when exposed to 0.096 ppm of O_3 (7-hr seasonal mean) compared to a control of 0.024 ppm (Heagle et al., 1979b). Nonsignificant reductions of 4 to 26 percent were noted at 0.056 ppm of O_3 (Heagle et al., 1979b). The same data were subsequently subjected to regression analyses (Heck et al., 1982). Yield reductions predicted from the linear regressions for America, Hybrid 7, Viroflay, and Winter Bloomsdale, respectively were 19 percent, 18 percent, 21 percent, and 21 percent at 0.06 ppm (7-hr seasonal mean) (Figure 7-14 a-d). Weibull equations applied to the data predicted 17 percent, 9 percent, 7 percent, and 16 percent yield reductions, respectively, at 0.06 ppm (Table 7-19) (Heck et al., 1983). The four cultivars were not significantly different ($p = 0.05$) in their responses to O_3.

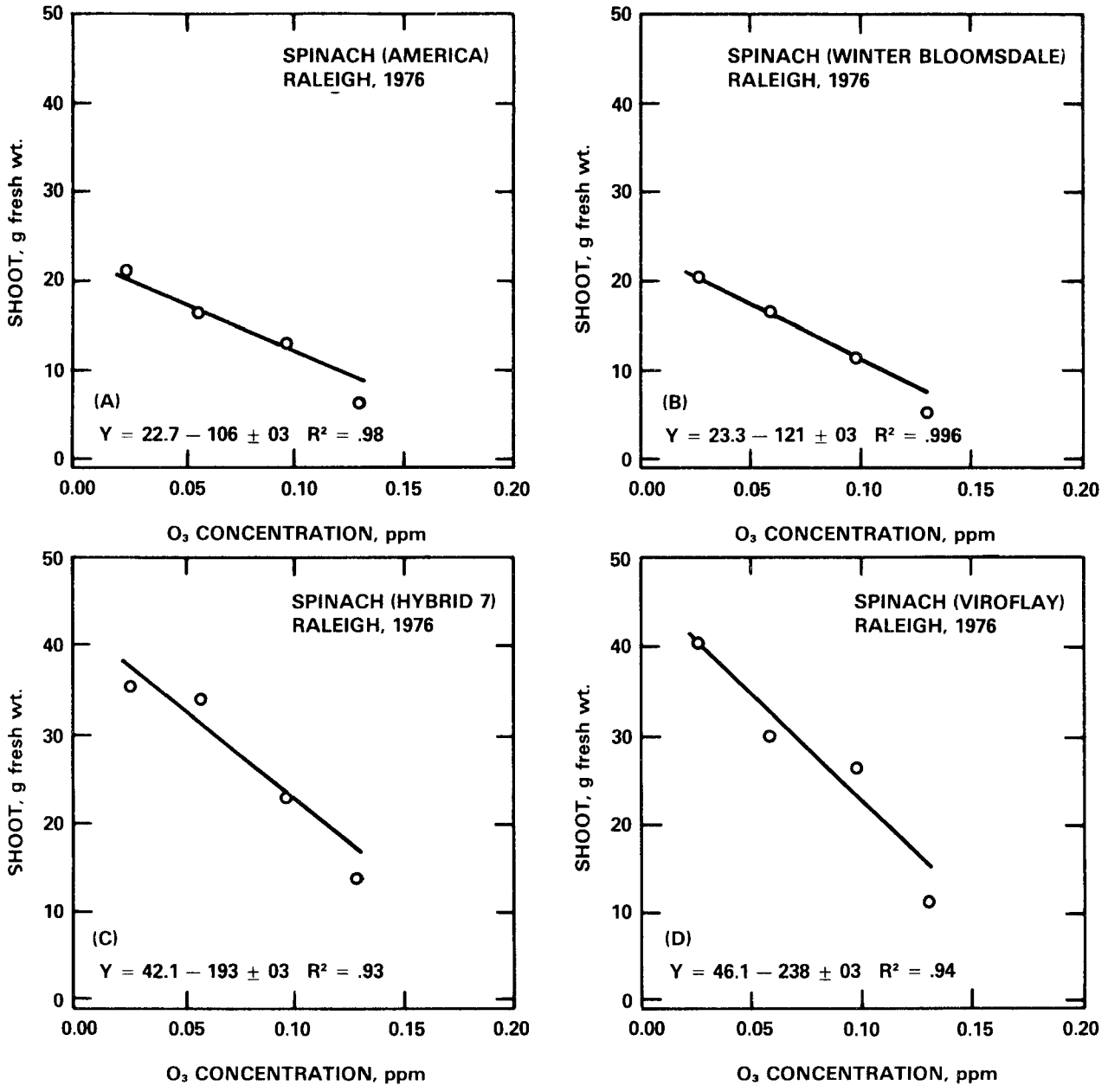

Figure 7-14. Effects of O_3 exposures on spinach and lettuce yields. O_3 concentration is expressed as 7-hr seasonal mean; o indicates mean of plants in open top chambers; indicates mean of plants in ambient air, which were used in the regression analysis. (A-D) Data are from Heagle et al., 1979b. Regression equations are from Heck et al., 1982. Another set of straight line equations is given in Heagle and Heck, 1980. Each point is the mean of four plots with four quadrants (two to three plants per quadrant) per plot.

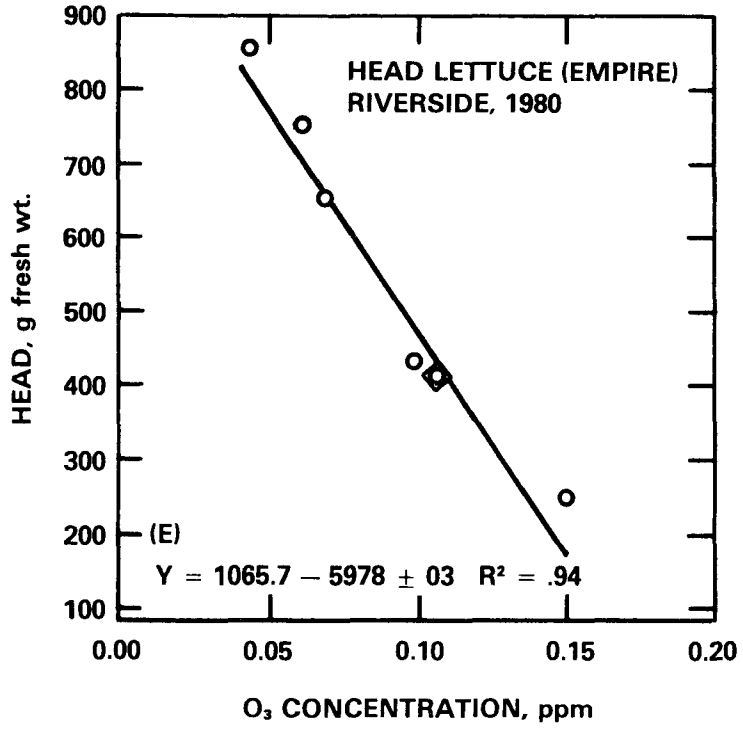

Figure 7-14. (continued) (E) Data and equations are from Heck et al., 1982. Each point is the mean of four plots.

The impact of O_3 on the yield of head lettuce was investigated by varying the amount of ambient O_3 filtered from the air to create a series of different O_3 exposure levels, and the data were analyzed with a linear regression model (Figure 7-14E) (Heck et al., 1982). The linear regression model predicted 13 percent and 42 percent yield reductions at 7-hr seasonal mean O_3 concentrations of 0.06 and 0.10 ppm, respectively. The Weibull model predicted similar yield reductions--17 percent (0.06 ppm) and 48 percent (0.10 ppm), the (Table 7-20) as the linear regression (Heck et al., 1983). At the test plots in southern California, the ambient O_3 (7-hr seasonal mean = 0.106 ppm) reduced the yield 47 percent when compared to a concentration in the charcoal-filtered chamber (control) of 0.043 ppm. The authors cautioned that the lettuce data should not be regarded as conclusive. Because there were high winds near the end of the study that stressed the plants, they were harvested before they reached full maturity. The yield response of Acala SJ-2 cotton to O_3 was evaluated with the Weibull model (Heck et al., 1983) (Table 7-19). Predicted yield reductions were 18 percent at 0.06 ppm of O_3 (7-hr seasonal mean) and 34 percent at 0.10 ppm of O_3.

Turnips were among the more sensitive crops tested by NCLAN (Heck et al., 1982). Four cultivars were tested. The absolute yields varied by three-fold among cultivars, with the yield of Shogun and Purple Top White Globe being especially low (Figure 7-15). The percent yield reductions due to O_3 were remarkably uniform among cultivars. The cultivar Shogoin exhibited a linear regression with an edible root fresh weight reduction of 35 percent (0.06 ppm) compared to a control of 0.014 ppm. More complex plateau-linear models accounted for significantly more of the variation than the linear models for the three other cultivars (Just Right, Purple Top White Globe, Tokyo Cross). With O_3 thresholds of 0.038, 0.034, and 0.054 ppm respectively the predicted yield reductions were 27 percent, 26 percent, and 14 percent at 7-hr seasonal mean O_3 concentrations of 0.06 ppm. The threshold value in a plateau-linear model is a statistical estimate of the O_3 concentration that must be exceeded before there will be a significant effect. The Weibull models predict nearly identical loss estimates (Table 7-19) and also demonstrate homogeneity among the cultivar responses to O_3 (Heck et al., 1983). [The turnip yield data should be used with caution (A.S. Heagle, personal communications -- to be published). Part of the yield loss was attributed to an acute injury episode from a low concentration of O_3 after a period of dark, cool, rainy weather. These data illustrate one of the problems with the 7-hr seasonal mean as a statistic to characterize the O_3 exposure.]

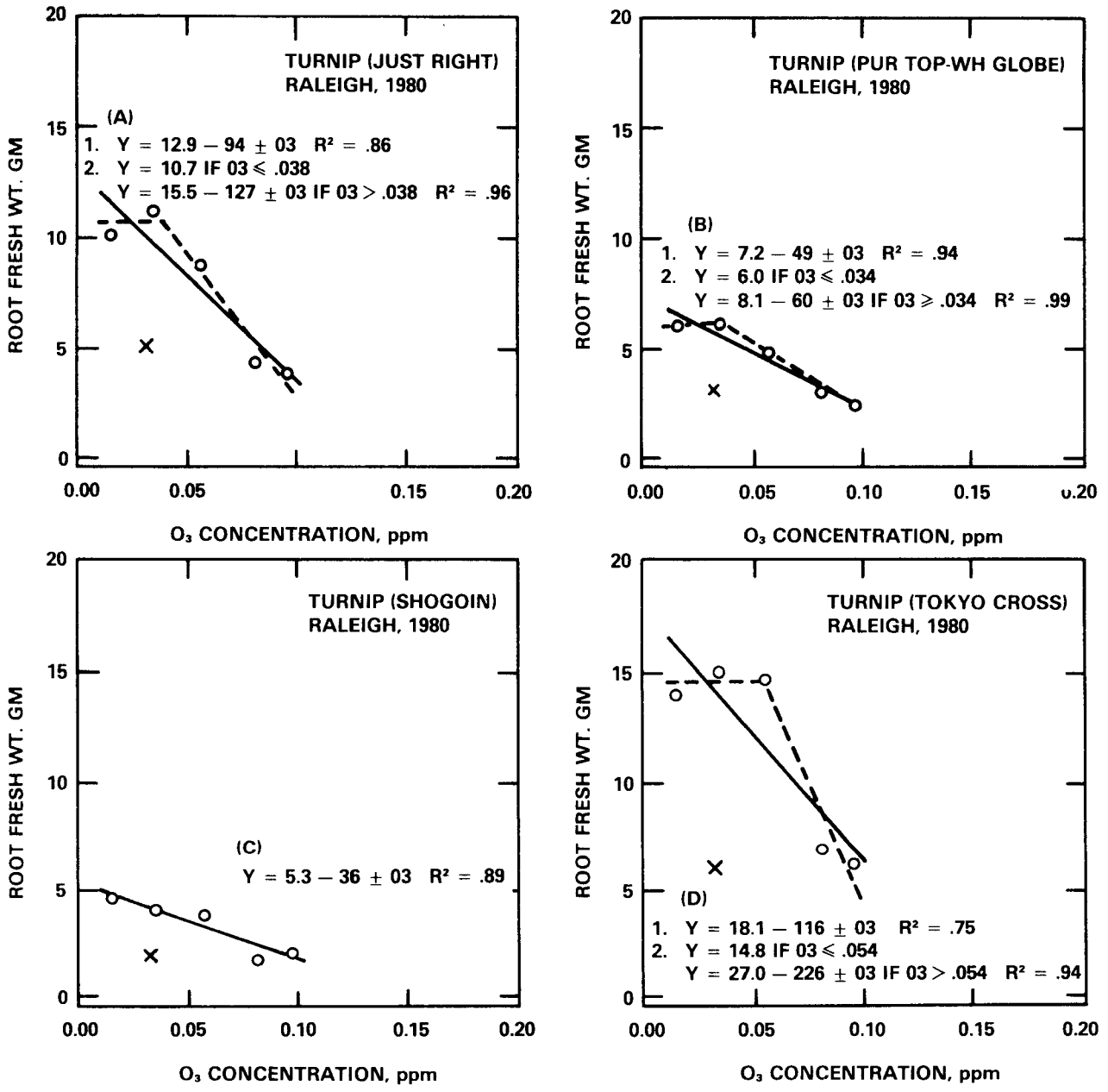

Figure 7-15. Effects of O_3 exposures on turnip yields. O_3 concentration is given as 7-hr seasonal mean. o indicates mean of plants in open top chambers; X indicates mean of plants in ambient air, which were not used in the regression analysis. (A-D) Data and all regression equations are from Heck et al., (1982). Each point is the mean of four plots.

In most of the open-top chamber studies, the potential chamber influence on the plant response was studied by comparing the yield of plants growing in open air plots without chambers with the yield from plants grown in chambers receiving nonfiltered air. No significant chamber effects were noted in any of the soybean studies (Figure 7-12), the kidney bean study (Figure 7-12), and the lettuce study (Figure 7-14). However, in the wheat (Figure 7-13) and turnip studies (Figure 7-15), the plants grew significantly better in the non-filtered chambers than ambient air plots. In 1979, peanuts yielded more in the nonfiltered chambers than in ambient air plots, but the difference was not significant. However, in 1980, the peanut plants yielded significantly less in the chambers (Figure 7-12). As part of the Weibull model evaluation, the predicted chamber effect was tested for all crops except spinach, with much the same results (Heck et al., 1983) (Table 7-19). In the peanut study, the relationship between the O_3 concentration and percent yield reduction was similar in both 1979 and 1980, despite a chamber effect in 1980. It is not known if the chamber effect modified the O_3 exposure response relationships in the turnip and wheat studies.

As part of an open-top chamber study, Heagle et al., (1983b) compared the yield of soybean plants growing directly in the soil with plants growing in pots placed in the soil. Over 2 years, virtually no differences in the percent yield reduction due to O_3 exposure were noted. Similar comparisons were made in studies with corn (Heagle et al., 1979a), wheat (Heagle et al., 1979c), and spinach (Heagle et al., 1979b), and in all of them, the percent yield reductions due to O_3 were similar whether the plants were in pots or directly in the soil. There was, however, a trend toward lesser sensitivity in pot-grown plants. The trend of pot-grown plants being less sensitive to O_3 than soil-grown plants is to be expected, because pot-grown plants, are probably subjected to more moisture stress than plants grown directly in soil. In most field studies in which the plants were grown directly in the soil, the investigators have attempted to provide sufficient water, so that water was not a limiting factor. This observation makes the results from the following study more relevant, in terms of typical conditions. Four cultivars of soybean grown in pots were exposed to 0.10 ppm of O_3 in open-top chambers (Heagle and Letchworth, 1982). Three of the cultivars (Forrest, Ransom, Davis) exhibited significant yield reductions that were similar to those estimated from previously mentioned studies (Figure 7-12, Table 7-20). One cultivar (Bragg) exhibited a slight yield increase.

7.4.3.2.1.2 Other field studies. Low concentrations of O_3 added to filtered air in field chambers induced yield reductions in a variety of plant species (Table 7-21). Alfalfa exhibited a 49 percent decrease in top dry weight when exposed to 0.05 ppm of O_3 for 68 days (Neely et al., 1977). Extended (several weeks) exposures to 0.10 ppm caused yield reductions in alfalfa (Neely et al., 1977), soybean (Heagle et al., 1974), sweet corn (Heagle et al., 1972), and ponderosa and western white pine (Wilhour and Neely, 1977). Stem specific gravity, an indicator of wood density and quality of several hybrid poplar clones, was consistently less in response to 0.15 ppm of O_3 12 hr/day for 102 days, but effects on height ranged from slight stimulations in four clones to a significant reduction in one clone (Patton, 1981).

7.4.3.2.1.3 Greenhouse and indoor chamber studies. The effects of O_3 on plant yield may be mediated by myriad genetic, cultural, and environmental factors (see section 5.3). The previously discussed studies have attempted to quantify plant responses to O_3 under ambient or normal environmental and cultural conditions. Several investigations on the yield responses of plants to O_3 have been performed under more controlled (to various degrees) conditions (Tables 7-22, 7-23). These exposures at 0.041 to 0.40 ppm of O_3 will be discussed as they relate to the previous studies.

Ozone caused significant yield reductions in exposures lasting several weeks (Table 7-23). At O_3 concentrations of 0.05 ppm or greater, the response varied among species. Hybrid poplar cuttings exhibited a 13-fold increase in leaf abscission in response to 0.041 ppm for 5 months (Mooi, 1980). American sycamore seedlings exhibited significant 9 percent height reduction (Kress et al., 1982b), and loblolly pine seedlings showed 18 percent height reductions (Kress and Skelly, 1982) at 0.05 ppm for 4 weeks. Several species showed no change in yield due to the 0.05 ppm exposure; however, there was also some yield stimulation (some significant). In the same hybrid poplar study discussed above (Mooi, 1980), there was a significant 14 percent increase in height accompanied by a slight decrease in stem dry weight. Yellow poplar and white ash seedlings exhibited significant 60 percent and 22 percent increases in height and total dry weight, respectively (Kress and Skelly, 1982). In general, slight growth stimulations are more common in hardwood tree species than in coniferous tree species (Kress and Skelly, 1982) (Table 7-23).

Significant yield reductions were noted for many species exposed to 0.05 to 0.10 ppm of O_3 for one to several weeks (Tables 7-22, 7-23). Carnations had significantly fewer flowers and flower buds when grown in air containing

TABLE 7-21. EFFECTS OF OZONE ADDED TO FILTERED AIR IN FIELD CHAMBERS ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration, ppm	Exposure duration[a]	Percent yield reduction from control[b]	Monitoring[c] method	Calibration[d] method	Fumigation[e] facility	Reference
Alfalfa	0.05	7 hr/day, 68 days	31, top dry wt, 1st harvest; 49* top dry wt, 2nd harvest 17, total protein, top, 1st harvest; 42*, total protein, top, 2nd harvest 32*, total nonstructural carbohydrate (TNC), 1st harvest (top) 55*, total nonstructural carbohydrate (TNC), 2nd harvest (top)	Mast	Known O_3 source 1% NBKI	FC-CT	Neely et al., 1977
Alfalfa	0.10	7 hr/day, 70 days	51*, top dry wt, final harvest 53*, total nonstructural carbohydrate (TNC), final harvest 38*, total protein, final harvest	Mast	Known O_3 source,	FC-CT 1% NBKI	Neely et al., 1977
Soybean (Dare)	0.05 0.10	6 hr/day, 133 days	3, seed wt/plant 55*, seed wt/plant	Mast	2% NBKI	FC-CT	Heagle et al., 1974
Sweet corn (Golden midget)	0.05 0.10	6 hr/day, 64 days	9, kernel dry wt 45*, kernel dry wt	Mast	2% NBKI	FC-CT	Heagle et al., 1972
(White midget)	0.05 0.10	6 hr/day, 71 days	0				
Douglas fir	0.10	6 hr/day, 126 days	6, height; 15, stem dry wt	Mast	Known O_3 source, 1% NBKI	FC-CT	Wilhour and Neely, 1977
Jeffrey pine	0.10		2, height; 2, stem dry wt				
Lodgepole pine	0.10		8, height, 8, stem dry wt				
Monterey pine	0.10		0, height; 0, stem dry wt				

TABLE 7-21 (con't) EFFECTS OF OZONE ADDED TO FILTERED AIR IN FIELD CHAMBERS ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration, ppm	Exposure duration[a]	Percent yield reduction from control[b]	Monitoring[c] method	Calibration[d] method	Fumigation[e] facility	Reference
Ponderosa pine	0.10		11, height, 21*, stem dry wt				
Shore pine	0.10		2, height; 6, stem dry wt				
Sugar pine	0.10		0, height; 0, stem dry wt				
Western white pine	0.10		0, height, 9*, stem dry wt				
Sitka spruce	0.10		0, height, 14, stem dry wt				
Hybrid poplar (252)	0.15	12 hr/day, 102 days	+16, height; 12*, stem specific gravity	UV	Known O_3 source	OT	Patton, 1981
(279)	0.15		23, height; 14*, stem specific gravity				
(346)	0.15		3, height; 6*, stem specific gravity				
(W5)	0.15		5, height; 12*, stem specific gravity				
(W87)	0.15		+19, height; 11*, stem specific gravity				
Hybrid poplar (42)	0.15	12 hr/day, 102 days	25, height; 8, stem specific gravity	UV	Known O_3 Source	OT	Patton, 1981
(50)	0.15		58*, height; 1, stem specific gravity				
(207)	0.15		+8, height; 7*, stem specific gravity				
(215)	0.15		+17, height; 11, stem specific gravity				

[a] Where a column entry is blank the information is the same as above.

[b] + = an increase above the control

[c] Mast = Mast meter (coulometric); UV = ultraviolet spectrometry

[d] NBKI = neutral buffered potassium iodide

[e] OT = open-top chamber; FC-CT = closed-top field chamber

* Significant at p = 0.05

TABLE 7-22 EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Pinto bean	0.15 0 25 0.35	2 hr/day, 63 days	44^{ng}, pod fresh wt 100^{ng}, pod fresh wt 100^{ng}, pod fresh wt	Mast	(not given)	Room	Hoffman et al., 1973
Sweet corn (Golden jubilee)	0 20 0.35	3 hr/day, 3 days/ wk, 8 wk	13*, ear fresh wt, 13*, kernel dry wt; +1300*, length of ear with shrivelled kernals	Mast	2% NBKI	GH	Oshima, 1973
	0.35	3 hr/day, 3 days/ wk, 8wk	22* kernel dry wt				
Wheat (Arthur 71)	0.20	4 hr/day, 7 days	30*, seed yield, 17*, kernel wt; 8, % seed set	Mast	(not given)	GC	Shannon and Mulchi, 1974
(Blueboy)	0.20	4 hr/day, 7 days	24, seed yield; 2, kernel wt; 22*, % seed set				
Radish (Cherry belle)	0.20 0.40	3 hr or 6 hr	6^{ng}, root fresh wt; 6^{ng}, root dry wt 38^{ng}, root fresh wt; 40^{ng}, root dry wt	Chem.	Known O_3 source	CH-CSTR	Reinert and Gray, 1981
Radish (Cavalier)	0.25	3 hr	33*, root dry wt (average of 4 pre- or post-fumigation temperature regimes)	Mast	(not given)		Adedipe and Omrod, 1974
(Cherry belle)	0.25	3 hr	37*, root dry wt (average of 4 pre- or post-fumigation temperature regimes)				
Beet	0.20	0.5 hr/day, 38 days 1 hr/day, 38 days 2 hr/day, 38 days 3 hr/day, 38 days	+9, storage root dry wt +2, storage root dry wt 40*, storage root dry wt 40*, storage root dry wt	Mast	(not given)	GC	Ogata and Maas, 1973

TABLE 7-22 (con't). EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Potato (Norland)	0.20	3 hr/day, every 2 wk, 120 days	20*, tuber no.; 25*, tuber wt; 13*, total solids	(not given)	(not given)	GC	Pell et al., 1980
(Kennebec)	0.20	3 hr/day, every 2 wk, 140 days	36*, tuber no.; 42*, tuber wt; 20*, total solids				
Pepper (M-75)	0.12 0.20	3 hr/day, 3 day/ wk, 11 wk	19*, dry wt/fruit; 20, no. mature fruit; 50*, dry wt/fruit; 53*, no mature fruit	Mast	UV	CH	Bennett et al., 1979
Tomato (Walter)	0.20	4 hr/day, 2 day/ wk, 13 wk	6, fruit fresh wt	Chem.	Known O_3 source	GH-CSTR	Shew et al., 1982
Cotton (Acala SJ-2)	0.25 0.25	6 hr/day, 2 day/ wk, 13 wk, 6 hr/ day, 2 day/wk, 18 wk	52*, no. of bolls; 62*, fiber dry wt; 55*, no. of bolls; 59*, fiber dry wt	UV	UV	CH	Oshima et al., 1979
Carnation (White sim)	0.05-0.09	24 hr/day, 12 days 23 days 44 days 56 days	74*, no. of flower buds 53*, no. of flower buds 46*, no. of flower buds 100*, no. of normal open flowers	Mast	(not given)	GH	Feder and Campbell, 1968
Coieus (Pastel rainbow)	0.10 0.20 0.40	2 hr 2 hr 2 hr	+3, flower no. 4, flower no. 8*, flower no.	Mast	(not given)	CH	Adedipe et al., 1972a
Snapdragons (Rocket mixture)	0.10 0.20 0.40	2 hr 2 hr 2 hr	+1, flower no. 10, flower no. 9, flower no.	Mast	(not given)	CH	
(Floral carpet formula mixture)	0.10 0.20 0.40	2 hr 2 hr 2 hr	+3, flower no. 2, flower no. 4, flower no.	Mast	(not given)	CH	

TABLE 7-22 (con't) EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Begonia (Linda)	0 10	2 hr	4, flower no	Mast	(not given)	CH	
	0.20	2 hr	9, flower no				
	0 40	2 hr	5, flower no.				
(Scarletta)	0.10	2 hr	+5, flower no.	Mast	-	CH	
	0.20	2 hr	+3, flower no.				
	0.40	2 hr	8*, flower no				
(White Tausendschon)	0.10	2 hr	5, flower no.	Mast	-	CH	
	0.20	2 hr	10, flower no.				
	0.40	2 hr	10, flower no.				
Petunia (Canadian All Double Mixture)	0.10	2 hr	0, flower no.	Mast	-	CH	
	0.20	2 hr	4, flower no.				
	0.40	2 hr	7, flower no.				
(Capri)	0.10	2 hr	7, flower no.	Mast	-	CH	
	0.20	2 hr	6, flower no.				
	0.40	2 hr	14*, flower no.				
(Bonanza)	0.10	2 hr	+3, flower no.	Mast	-	CH	
	0.20	2 hr	8, flower no.				
	0.40	2 hr	10, flower no.				
Coleus (Scarlet Rainbow)	0.10	2 hr	+3, flower no.	Mast	-	CH	
	0.20	2 hr	20*, flower no.				
	0.40	2 hr	28*, flower no.				
Begonia (Schwabenland red)	0.25	4 hr/day, 4 times once every 6 days	39*, flower wt; (54% foliar injury)	Chem.	(not given)	GH-CSTR	Reinert and Nelson, 1980
(Whisper-O-pink)	0.25	4 hr/day, 4 times once every 6 days	22*, flower wt, (25% foliar injury)	Chem.	-	GH-CSTR	

TABLE 7-22 (con't) EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
(Fantasy)	0.25	4 hr/day, 4 times once every 6 days	6*, flower wt; (2% foliar injury)	Chem.	-	GH-CSTR	
(Renaissance)	0.25		55*, flower wt; (15% foliar injury)	Chem.	-	GH-CSTR	
(Turo)	0.25		+10, flower wt; (8% foliar injury)	Chem.	-		GH-CSTR
Alfalfa (Moapa)	0.10 0.15 0.20	2 hr/day, 21 days 2 hr/day, 21 days 2 hr/day, 21 days	16*, top dry wt 26*, top dry wt 39*, top dry wt	Mast	(not given)	CH	Hoffman et al., 1975
Alfalfa (Moapa)	0.10 0.10	2 hr/day, 21 days 2 hr/day, 42 days	21*, top dry wt 20*, top dry wt	Mast	(not given)	CH	
Pasture grass (N.Z. grasslands)	0.09	4 hr/day, 5 days/ wk, 5 wk	20*, top dry wt	Chem.	(not given)	GC	Horsman et al., 1980
(Victorian)	0.09	4 hr/day, 5 days wk, 5 wk	14*, top dry wt	Chem.	(not given)	GC	
(Australian)	0.09	4 hr/day, 5 days wk, 5 wk	18*, top dry wt	Chem.	(not given)	GC	
Ladino clover (Tillman)	0.10	6 hr/day, 5 days	20*, shoot dry wt; 38*, shoot total nonstructural carbohydrate (TNC)	Chem.	2% NBKI	GH-CH	Blum et al., 1982
Tall fescue (Alta)	0.10 0.20 0.30 0.40	6 hr/day, 1 day/wk, 7 wk 6 hr/day, 1 day/wk, 7 wk	10, dry wt/plant 20, dry wt/plant significant linear 30, dry wt/plant	UV	UV	GH-CSTR	Flagler and Younger, 1982a

TABLE 7-22 (con't) EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concentration ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
(Fawn)	0.10	6 hr/day, 1 day/wk, 7 wk	regression, r = .98				
	0.20		9, dry wt/ plant				
	0.30	6 hr/day, 1 day/wk, 7 wk	18, dry wt/plant significant linear				
	0.40	6 hr/day, 1 day/wk, 7 wk	36, dry wt/ plant regression, r = .99				
(Kentucky-31)	0.10	6 hr/day, 1 day/wk, 12 wk	13, dry wt/plant	UV	UV	CH-CSTR	Flagler and Younger, 1982b
	0.20		27, dry wt/plant				
	0.30	6 hr/day, 1 day/wk, 12 wk	significant linear 40, dry wt/plant regression, r = .98				
	0.40		54, dry wt/plant				
Tall fescue (Alta)	0.10		+3, top dry wt				
	0.20		19, top dry wt				
	0.30		41, top dry wt				

[a] + = an increase above the control

[b] Chem. = chemiluminescence; Mast = Mast meter (coulombmetric); UV = ultraviolet spectrometry

[c] NBKI = neutral buffered potassium iodide

[d] GH = greenhouse; CSTR = continuous stirred tank reactor; GH=CSTR = CSTR in greenhouse; GC = controlled environment growth chamber; CH = manufactured chamber other than CSTR or GC; GH-CH = CH in greenhouse; Room = plant growth room.

*Significant at p = 0.05; ng = not given

TABLE 7-23. EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED TREE CROPS.

Plant species	O_3 concentration ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Poplar (Dorskamp)	0.041	12 hr/day, 5 mo	+14*, stem length; 12 stem dry wt; +1333, no. of dropped leaves; 6, total dry wt	Chem.	NBKI	GH-CH	Mooi, 1980
(Zeeland)	0.041	12 hr/day, 5 mo	2, stem length; 4, stem dry wt; +692, no. of dropped leaves; 0, total dry wt	Chem.	NBKI	GH-CH	Mooi, 1980
American Sycamore (16-SYC-19)	0.05	6 hr/day, 28 days	9*, height growth	Chem.	1% NBKI	CH	Kress et al., 1982b
(16-SYC-23)	0.05	6 hr/day, 28 day	2, height growth				
American Sycamore (16-SYC-19)	0.05	6 hr/day, 28 days	11, height growth	Chem.	1% NBKI	CSTR	Kress et al., 1982b
(16-SYC-23)	0.05	6 hr/day, 28 day	9*, height growth				
Sweetgum	0.05 0.10 0.15	6 hr/day, 28 days	+9, height growth; 10, total dry wt 29*, height growth; 26, total dry wt 45*, height growth; 42*, total dry wt	Chem.	Constant source, NBKI, UV	CSTR	Kress and Skelly, 1982
American Sycamore	0.05 0.10 0.15	6 hr/day, 28 days	+4, height growth; 23, total dry wt 27*, height growth; 61*, total dry wt 21*, height growth; 69*, total dry wt	Chem.	Constant source, NBKI, UV	CSTR	
White ash	0.05 0.10 0.15	6 hr/day, 28 days	+12, height growth; +22*, total dry wt 9, height growth; 9, total dry wt 15, height growth; 17*, total dry wt	Chem.	Constant source, NBKI, UV	CSTR	Kress and Skelly, 1982
Green ash	0.05 0.10 0.15	6 hr/day, 28 days	2, height growth; 14, total dry wt 24*, height growth, 28, total dry wt 30*, height growth; 33, total dry wt	Chem.	Constant source, NBKI, UV	CSTR	Kress and Skelly, 1982

TABLE 7-23 (con't). EFFECTS OF OZONE ADDED TO FILTERED AIR ON YIELD OF SELECTED TREE CROPS

Plant species	O_3 concentration, ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Willow oak	0.05 0.10	6 hr/day, 28 days	1, height growth; 2, total dry wt 4, height growth; 11, total dry wt	Chem.	constant source NBKI, UV	CSTR	Kress and Skelly 1982
Sugar maple	0.05 0.10 0.15	6 hr/day, 28 days	5, height growth; 2, total dry wt +8*, height growth; 7, total dry wt 12*, height growth; 41*, total dry wt	Chem.		CSTR	Kress and Skelly, 1982
Yellow poplar	0.05 0.10 0.15	6 hr/day, 28 days	+60*, height growth; +41, total dry wt +8, height growth; +5, total dry wt 12, height growth; +18, total dry wt	Chem.		CSTR	
Yellow poplar	0.10	12 hr/day, 48 days	19[ng], relative growth rate	Chem.	(not given)	CSTR	Jensen, 1981a
Cottonwood	0.10		59[ng], relative growth rate				
White ash	0.10		no significant effects				
White ash	0.10 0.20 0.30 0.40	4 hr/day, 1 day/wk, 9 wk	+13, total height; +7, shoot dry wt 0, total height; +5, shoot dry wt 0, total height; 11, shoot dry wt 0, total height; 14, shoot dry wt	(not given)	(not given)	(not given)	McClenahen, 1979
Black cherry	0.10 0.20 0.30 0.40		+16, total height; +15, shoot dry wt +5, total height; 4, shoot dry wt +3, total height; 4, shoot dry wt 28*, total height; 15, shoot dry wt	(not given)	(not given)	(not given)	McClenahen, 1979
Hybrid poplar (NS 207 + NE 211)	0.15	8 hr/day, 5 days/wk, 6 wk	50*, dry wt new shoots from terminal cuttings 62*, dry wt new shoots from basal cuttings	(not given)	(not given)	GH-CH	Jensen and Dochinger, 1974

TABLE 7-23 (con't). EFFECTS OF OZONE ADDED TO FILTERED AIR ON YIELD OF SELECTED TREE CROPS

Plant species	O_3 concentration, ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Hybrid poplar (207)	0.20 0 20	7 5 hr/day, 5 day/wk, 6 wk	5, height 8, height	(not given)	(not given)	CH	Jensen, 1979
Yellow birch	0.25	8 hr/day, 5 day/wk, 15 wk	9, height	MAST	NBKI	GH-CH	Jensen and Masters, 1975
White birch	0.25		34, height				
Bigtooth aspen	0 25		+7, height				
Eastern cottonwood	0.25						
Red maple (163 ME)	0.25	8 hr/day, 6 wk	18, height	MAST	1% NBKI	CH	Dochinger and Townsend, 1979
(167 NB)			32, height				
(128 OH)			37*, height				
Loblolly pine (4-5 x 523)	0.05	6 hr/day, 28 days	6, height growth	Chem.	1% NBKI	CH	Kress et al., 1982a
(14-5 x 517)	0.05						
Loblolly pine	0.05 0.10 0.15	6 hr/day, 28 days	18*, height growth; 14, total dry wt 27*, height growth; 22*, total dry wt 41*, height growth; 28*, total dry wt	Chem.	Constant source, NBKI, UV	CSTR	Kress and Skelly, 1982
Pitch pine	0.05 0.10 0.15	6 hr/day, 28 days	4, height growth; 8, total dry wt 13*, height growth; 19, total dry wt 26*, height growth, 24*, total dry wt				

TABLE 7-23 (con't). EFFECTS OF OZONE ADDED TO FILTERED AIR ON YIELD OF SELECTED TREE CROPS

Plant species	O_3 concentration, ppm	Exposure duration	Percent yield reduction from control[a]	Monitoring[b] method	Calibration[c] method	Fumigation[d] facility	Reference
Virginia pine	0.05	6 hr/day, 28 days	5, height growth; +2, total dry wt				
	0.10		11, height growth; 3, total dry wt				
	0.15		14, height growth; 13, total dry wt				
White spruce	0.25	8 hr/day, 5 day/wk, 15 wk	5, height	Mast	NBKI	GH-CH	Jensen and Masters, 1975
Japanese larch	0.25		+6, height	Mast	NBKI	GH-CH	

[a] + = an increase above the control

[b] Chem. = chemiluminescence; Mast = Mast meter (coulometric); UV = ultraviolet spectrometry

[c] NBKI = neutral buffered potassium iodide

[d] GH = greenhouse; CSTR = continuous stirred tank reactor; CH = manufactured chamber other than CSTR or GC; GH-CH = CH in greenhouse

*Significant at p = 0.05; ng = not given.

0.05 to 0.09 ppm of O_3 for 24 hr/day for 12 to 56 days (Feder and Campbell, 1968). Pasture grasses produced less top growth when exposed to 0.09 ppm of O_3 for 4 hr/day for 5 weeks (Horsman et al., 1980). Exposure response equations were developed for three fescue cultivars under greenhouse conditions (Flagler and Youngner, 1982a). Based on yield they found that the cultivar Kentucky 31 showed the largest yield decrease with increasing O_3 concentration; based on these data it was ranked most sensitive and Fawn the least sensitive of the three. Significant yield reductions (10 percent) were predicted for each of the cultivars at the following O_3 concentrations (ppm): 0.119 Kentucky 31), 0.10 (Alta), 0.11 (Fawn). The cultivars were exposed for 6 hours/day, 1 day/week for 7 weeks. Significant yield reductions have been noted for alfalfa, (Hoffman et al., 1975); clover (Blum et al., 1982), and loblolly pine, pitch pine, sweetgum, American sycamore, and green ash (Kress and Skelly, 1982) when exposed to 0.10 ppm of O_3 for various lengths of time. However, numerous studies reported no significant effects, and some have reported yield stimulations. Significant yield stimulations in response to 0.10 ppm of O_3 for 6 hr/day for 4 weeks have been noted for sugar maple (Kress and Skelly, 1982).

Ozone concentrations of 0.10 ppm O_3 and greater for several days to weeks generally caused yield reductions (Tables 7-21, 7-22), although some growth stimulations were noted at higher concentrations.

7.4.3.2.1.4 Effects of Ozone on Crop Quality. Quality is a broad term which includes many features such as chemical composition, physical appearance, taste, and ability to withstand storage and transport. All these features have economic importance.

Four types of experimental approaches were used to investigate the effects of O_3 or oxidants on crop quality: (1) field experiments in which the impact of ambient oxidants and charcoal-filtered air were contrasted; (2) field experiments in which ambient oxidant injury was prevented by using an antioxidant chemical spray; (3) field experiments in which O_3 was added to ambient or charcoal-filtered air; and (4) laboratory experiments in which potential effects were measured by exposing plants to O_3.

The effects of ambient oxidants were studied at three different locations (Riverside, California; Geneva, New York; and Beltsville, Maryland) to determine their impact on the quality of alfalfa, grape, and soybean (Thompson et al., 1976b; Musselman et al., 1978; Howell and Rose, 1980). Alfalfa plants experienced oxidant concentrations greater than 0.08 ppm between 25 and 60

percent and 0.12 ppm between 5 and 50 percent of daylight hours (measured with a Mast meter). Plants receiving ambient oxidants exhibited significant ($p = 0.05$ or 0.01) changes in a number of quality variables in some harvests. Ambient oxidants decreased crude fiber, β-carotene, and vitamin C; increased niacin; and had no effect on protein efficiency and nitrogen digestibility ratios (Thompson et al., 1976b). Grape crops receiving ambient oxidants suffered a 6 percent reduction in soluble solids ($p = 0.05$), which would reduce the value of this fruit for wine (Musselman et al., 1978); however, ozone concentrations were not measured at the Fredonia, NY site where grape experiments were conducted. Soybean seed quality exhibited small but significant ($p = 0.05$) changes: protein was increased 2 percent and oil was decreased 3.8 percent (Howell and Rose, 1980) when the plants were exposed to ambient oxidants at 0.08 ppm or greater and at 0.12 ppm or greater for 0.3 percent of the growing season (the experimental conditions for the seed quality study are reported in Howell et al., 1979). In addition to measuring yield in terms of biomass, some of the NCLAN studies have examined the quality of the yield. Corsoy soybeans exhibited a significant linear decrease ($R^2 = 0.81$) in percent oil content of seeds as the O_3 concentration increased. Concurrently, there was a significant increase in percentage of protein content with increasing O_3 concentration (Kress and Miller, 1983). Estimated changes resulting from a seasonal 7-hr average concentration of 0.10 ppm of O_3 were a 5 percent decrease in percent oil content and a 4 percent increase in percentage of protein content.

Clarke et al. (1983) grew potatoes in ambient air plots in central New Jersey; half the plants were treated with the antioxidant EDU to suppress O_3 effects. In 1980, the ambient oxidant dose was 110 ppm-hours. Specific gravity, a quality directly correlated with high quality of processed and tablestock potatoes, was 0.4 percent lower in non-EDU-treated plants ($p = 0.05$). In 1978, the ambient oxidant dose was 65 ppm-hours; changes in specific gravity were not detected. Foster et al. (1983a) found no difference in the specific gravity or total solids of potatoes exposed to ambient oxidants in open-top field chambers in California.

Alfalfa plants exposed to 0.10 ppm of O_3 (7 hr/day for 70 days) showed an increased protein and amino acid content per unit area, but a decrease in total protein and amino acid due to reduced dry matter production (Neely et al., 1977). Reductions were also noted in the β-carotene and total nonstructural carbohydrate.

Small trees from several clones of hybrid poplar have exhibited decreased stem specific gravity (a measure of wood quality which could result in reduced wood strength or reduced pulpwood value) when exposed to 0.15 ppm O_3 of for 12 hr/day for 102 days in open-top chambers (Patton, 1981).

A number of investigators have exposed greenhouse-grown crops to controlled doses of O_3 and subsequently measured the impact on crop composition. These results serve more as indicators of potential impact than predictors that effects would occur in a field environment. Results are summarized below.

Pippen et al. (1975) exposed cabbage, carrot, corn, lettuce, strawberry, and tomato to intermittent acute doses of O_3. Ozone concentrations ranged from 0.20 to 0.35 ppm for 2.5 to 6.5 hr, from 1 to 3 days per week from emergence to harvests. Plants were exposed to O_3 for 1.62 to 3.59 percent of the life cycle, depending on the species. Some of the species studied exhibited significant ($p = 0.05$) changes in quality in response to one or more of the O_3 regimes employed. Corn exhibited a decrease in solids, β-carotene, and carbohydrates, but total nitrogen and vitamin C levels increased. The niacin concentration increased in carrots and strawberries. Solids, fiber content, vitamin C, and thiamine were all reduced in tomato. Cabbage exhibited significant increases in total solids and vitamin C.

When greenhouse-grown potato plants were exposed to O_3 at a concentration of 0.20 ppm for 3 hr once every 2 weeks throughout the growth period, tubers exhibited a decrease in percent dry matter which is associated with a decrease in fluffiness of tablestock potatoes (Pell et al., 1980). Reducing sugars, associated with undesirable darkening of potato chips, increased in tubers harvested from plants exposed to O_3. Glycoalkaloids, compounds which can cause a bitter taste in potato tubers, either decreased or were unaffected by the O_3 treatment (Speroni et al., 1981).

The potential of O_3 to induce a series of estrogenic isoflavonoids was investigated in five different alfalfa cultivars (Hurwitz et al., 1979; Skärby and Pell, 1979; Jones and Pell, 1981). These biochemicals have been directly correlated with breeding disturbances in both domesticated and wild animal species. Coumestrol, daidzein, genistein, and formononetin, all with potentially adverse affects on crop quality, were not detected in greenhouse-grown alfalfa plants which received O_3 concentrations of 0.20 to 0.40 ppm (392 to 784 ug/m^3) for 3 hr. Ladino clover, another forage crop, exhibited reduced total nonstructural carbohydrate and generally increased mineral content

(except for sodium) when exposed to 0.10 ppm of O_3 (6 hr/day for 5 days) (Blum et al., 1982).

The impact of O_3 and ambient oxidants on crop quality has important implications from both health and economic perspectives. A reduction in nutritional value of food or forage such as reduced vitamin content or precursors to proteins, will be detrimental to the consumer. An adverse effect on a crop destined for processing, such as grapes for wine or potatoes for chips, will reduce the economic value of the crop. However, it is, at present, difficult to completely correlate these effects with the more conventional measures of O_3 effects on foliage and yield.

7.4.3.2.1.5 Effects of Ozone on Plant Reproduction. Ozone has been shown to affect the reproductive capacities of plants. The flowering and seed production of soybean plants was reduced by O_3 at 0.10 ppm (6 hr/day, 133 days) (Heagle et al., 1974). In sweet corn plants, seed production as estimated by percentage of ear filled was reduced when the plants were grown in an environment of 0.10 ppm of O_3 (6 hr/day, 64 days) (Heagle et al., 1972). Wheat plants exposed to 0.20 ppm of O_3 (4 hr/day, 7 days) at anthesis exhibited reduced percent seed set (Shannon and Mulchi, 1974). Reduced seed production of cotton plants exposed to 0.25 ppm O_3 (6 hr/day, 2 day/week, 13 weeks) was reported (Oshima et al., 1979). The number of tillers in three tall fescue cultivars increased slightly as O_3 was increased from 0.10 to 0.40 ppm (6 hr/day, 1 day/wk, 7 weeks) Flagler and Younger, 1982a). These data indicate that O_3 may decrease the reproductive capacity of plants. The reductions in seed production suggest an O_3 impact on fertilization processes. The observation that O_3 (0.05 ppm for 5.5 hr) reduced pollen germination (40 to 50 percent) in tobacco and petunia and pollen tube elongation in (Feder, 1968) supports this conclusion. Ozone also reduced the germination of corn pollen 60 (0.06 ppm) and 70 percent (0.12 ppm), respectively (Mumford et al., 1972). Plants were exposed to O_3 (0.06 or 0.12 ppm for 5.5 hr/day for 60 days) and the pollen was harvested daily as soon as it was mature and percent germination could be determined. Because the pollen was harvested as soon as it reached maturity, it is probable that the pollen was exposed to O_3 for only a short time period.

7.4.3.2.1.6 Relationship between foliar injury and yield loss. Because plant growth depends on their being functional leaves to conduct the photosynthesis required for plant growth, various studies have been conducted to determine the

association between foliar injury and yield for species in which the foliage is not part of the yield. Some investigations discussed in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) demonstrated yield loss with little or no foliar injury (Tingey and Reinert, 1975; Tingey et al., 1971a); others demonstrated significant foliar injury not accompanied by yield loss (Heagle et al., 1974; Oshima et al., 1975). Many other studies can be cited to illustrate the inconsistency of the relationship between foliar injury and yield loss when the foliage is not the yield component. Significant yield reductions with no foliar injury have been noted for American sycamore (Kress et al., 1982b), loblolly and pitch pine (Kress and Skelly, 1982), carnations (Feder and Campbell, 1968), and petunia and coleus (Adedipe et al., 1972a). With red maple seedlings, foliar injury was directly correlated with subsequent height reductions (Dochinger and Townsend, 1979). The relative sensitivities of two potato cultivars were reversed when judged on yield reductions rather than foliar injury (Pell et al., 1980). In a study comparing the effects of long- and short-term exposures, a long-term exposure (0.15 ppm for 8 hr day, 5 days/week for 6 weeks) resulted in 75 percent foliar injury and 50% growth reduction, whereas the short-term exposure (1.0 ppm for 2.4 or 8 hr) resulted in 70 percent foliar injury and no growth reduction (Jensen and Dochinger, 1974).

All of the studies in Table 7-20 reported foliar injury as well as yield responses. For field corn, foliar injury response was at lower concentrations than the yield effects, but with increased O_3 concentration, the percent yield reductions became greater than the percent foliar injury (Heagle et al., 1979a). For wheat, the increases in foliar injury were generally accompanied by decreases in yield, but foliar injury was not a good predictor of yield reduction. For example, at 0.06 ppm, the wheat cultivar Coker 47-27 had 5 percent foliar injury (compared to the control) and 11 percent yield reduction, but the cultivar Holly had 6 percent foliar injury and 1 percent yield reduction (Heagle et al., 1979c). There were no obvious relationships between foliar injury and shoot fresh or dry weight of spinach (Heagle et al., 1979b). In the soybean study also, relative cultivar injury did not predict relative yield response (Heagle and Letchworth, 1982). The cultivars Bragg and Ransom had equal amounts of foliar injury (35 percent) when exposed to 0.10 ppm of O_3, but Bragg yield increased 4 percent and Ransom yield decreased 20 percent.

The lack of correlation between foliar injury and yield reduction for many crops should not be surprising. Plants have evolved with a reserve capacity to cope with some level of stress, for example a plant species may develop more leaf area than that needed for maintaining yield. Therefore O_3 would not be expected to reduce plant yield unless its effects were sufficiently great to make some process limiting for plant yield. Yield would also be reduced if O_3 directly impacted the process limiting growth. Unless either of these two conditions are achieved, the plant may display a biological (phytotoxic) response to O_3 but the yield would not be impaired. However, for plants in which the foliage is the marketable portion (either for food or ornamental use) a phytotoxic impact on the foliage may reduce the yield without the plant weight being altered. These concepts imply that not all impacts of O_3 on plants are reflected in growth or yield reductions. Also O_3 would not impact plant growth or yield unless it made some process more limiting for growth or yield than the environmental factors that currently were controlling growth. These conditions suggest that there are combinations of O_3 concentration and exposure duration that the plant can experience which will not result in visible injury or reduced plant growth and yield. Numberous studies of many plant responses have demonstrated combinations of concentration and time that did not cause a significant effect.

Ozone can decrease the yield of a variety of crops. In the field, ozone addition studies performed primarily in open-top chambers provide the closest simulation of ambient conditions. The data show that yields of soybean, kidney bean, peanut, winter wheat, turnip, spinach, cotton, and lettuce decreased with increasing O_3 concentrations. Ozone concentrations (7-hr seasonal mean) currently occurring in ambient air (0.042 to 0.056 ppm) are estimated to cause up to 26 percent yield decrease of these crops. Of the crops studied by NCLAN (and similar studies), cotton, spinach, turnip, peanut, lettuce, and soybean are the most sensitive. Winter wheat and kidney bean appear to be somewhat less sensitive. Field corn is relatively tolerant.

It is more difficult to extrapolate data from studies conducted under more controlled conditions (greenhouse, growth chamber) to field conditions, except when plants are normally grown under these conditions (e.g., flower crops). However, the more controlled chamber data can serve to strengthen the demonstration of O_3 effects in the field. Concentrations of 0.05 ppm of O_3, in extended or repeated exposures, have been shown to cause yield reductions

in some species or cultivars, no effects in others, and increased yield in others. Concentrations of 0.10 ppm and above appear to more consistently cause yield reductions, although exceptions can be found (Tables 7-21, 7-22, 7-23).

The impact of O_3 on crop quality has important implications from both health and economic perspectives. A reduction in nutritional value of food or forage, such as reduced vitamin content or fewer protein precursors, can be detrimental to the consumer. An adverse effect on a crop destined for processing (e.g., grapes for wine or potatoes for chips) will reduce the economic value of the crop. It is, at present, difficult to completely correlate these effects with the more conventional measures of O_3 effects on foliage and yield.

7.4.3.2.2 Biomass and yield responses from ambient exposures. Determination of the effects of ambient air pollutants directly shows the impact of existing air quality on plant yield in the environment. Two basic types of studies are used to describe the effects of ambient exposures on plants. In one type, field observations are used to develop an association between O_3 exposure and plant response (growth or yield reductions or mortality). In the other type, the difference between plant yield in charcoal-filtered air and in ambient air (it may contain a single major pollutant or several) is used to indicate the impact of the pollutant; some type of exposure chamber is required for these studies. In either case, plants are exposed to pollutant concentrations at the frequency of occurrence found in the ambient air. When only a single pollutant is present and/or the study is conducted at a single location, the interpretation of the results is simplified. However, when the studies are conducted at different locations, differences in climatic and edaphic conditions, in addition to the pollutant time series that may influence the results and complicate the interpretation, can occur.

The previous criteria document (U.S. Environmental Protection Agency, 1978) reviewed the effects of O_3 in ambient air (Table 7-24). These studies utilized charcoal filtration in greenhouses or open-top chambers or simply correlated effects with the ambient O_3 concentrations. Leaf injury (sweet corn, tobacco, potato), yield reductions (citrus, grape, tobacco, cotton, potato), and quality changes (grape) were documented. It was concluded that ambient oxidants were causing decreased plant growth and yield.

More recently, studies have also been conducted to evaluate the yield of plants grown in the presence of photochemical oxidants (ambient air) versus

TABLE 7-24. EFFECTS OF OXIDANTS (OZONE) IN AMBIENT AIR ON GROWTH, YIELD, AND FOLIAR INJURY IN SELECTED PLANTS[a]

Plant species	Oxidant concentration, ppm	Duration of exposure	Plant response (reduction from control listed as %)	Location of study
Lemon	>0.10	Over growing season	32, yield 52, yield (leaf drop and other effects)	California
Orange	>0.10	148 hr/month average from March-October, 254 hr/month average from July-September	54, yield (other reductions found)	California
Grape, Zinfandel	≥0.25	Often over May-September growing season	12, yield (first year) 61, yield (second year) (increased sugar content) 47, yield (third year)	California
Corn, sweet	0.20-0.35	Hourly maximum for 3 to 4 days before injury	67, injury (10 cultivars, 5 unmarketable) 18, injury (13 cultivars) 1, injury (11 cultivars)	California
Bean, white	>0.08	9 hr	(Bronze color, necrotic stipple, premature) abscission)	Ontario, Canada
Tobacco, cultivar Bel W_3	0.02-0.03	6 to 8 hr	(Minimal injury)	Ohio
Tobacco, cultivar Bel W_3	>0.05	Often over growing season	22 (fresh wt), top 27 (fresh wt), root	North Carolina
Cotton, cultivar Acula	Ambient	Over growing season	7-20, lint + seed (3 locations, 1972) 5-29, lint + seed (3 locations, 1973)	California
Potato, 4 cultivars[b]	≥0.05	326 to 533 hr (2 years)	34-50, yield (2 years for 2 cultivars) 20-26, yield (1 year for 2 cultivars)	Maryland
Potato, cultivar Haig	0.15	3 consecutive days	95, injury (leaf area covered)	Delaware

[a]Table taken from National Reseach Council (1977).

[b]Greenhouse studies.

charcoal-filtered air (Table 7-25). Ozone induced significant yield reductions in tomato (33 percent at a mean concentration of 0.035 ppm), bean (26 percent at 0.041 ppm), soybean (average of four cultivars) (20 percent at O_3 concentrations > 0.05 ppm), two cultivars of sweet corn (9 percent and 28 percent at O_3 concentration > 0.08 ppm), and forbes, grasses, and sedges (31 percent at 0.052 in 1982; 20 percent at 0.051 in 1980; 15 percent at 0.035 in 1981) (Table 7-25). The yields of bean cultivars varied from a 5 percent increase to a 22 percent yield decrease in response to O_3 concentrations above 0.06 ppm O_3. Mean height of several tree species grown in air containing 0.052 ppm O_3 was reduced 12 to 67 percent (Table 7-25).

Some of the early ambient air studies in California incorporated multiple locations sited along an ambient O_3 gradient in a portion of the South Coast Air Basin, where phytotoxic pollutants other than O_3 occur only at extremely low concentrations (Oshima et al., 1976; Oshima et al., 1977a). These studies used a modified cumulative O_3 dose (sum of hourly averages above 0.10 ppm for the exposure period, ppm-hr) as a summary exposure statistic (Table 7-26). The dose calculation was further modified in the 1977 study by including only these pollutant concentrations present during daylight hours. In the 1976 study, the lowest dose was 2.64 ppm-hr, the equivalent of 0.11 ppm for 264 hr (1.26 hr/day) of the 5040-hr season. The highest dose was 55.52 ppm-hr, the equivalent of 0.111 ppm for each hour of the 5040-hr season. Alfalfa yield was reduced (10 percent) at a seasonal dose of 10.8 ppm-hr. Tomatoes were substantially more sensitive than alfalfa. The tomato yield was reduced at a seasonal dose of 4.2 ppm-hr.

Oshima (1978) designed and constructed an exposure facility (modified CSTR) by using chambers enclosed by a Teflon® film to minimize environmental alterations. The exposure system used proportional charcoal filtration of ambient air, thus retaining the ambient exposure properties at several pollutant concentrations. Ozone concentrations were expressed as cumulative dose (sum of hourly averages for the exposure period, ppm-hr) (see Section 7.2.2.1 and 7.4.3.3). Both Oshima (1978) and Foster et al. (1983b) (Table 7-26) were able to demonstrate yield losses in pot-grown red kidney bean and Centennial Russet potato, respectively, at low concentrations of ambient O_3. Potato yield was reduced (10 percent) at a seasonal dose of approximately 9.7 ppm-hr but a substantially higher dose (>51.6 ppm-hr) was required to impact the yield of red kidney beans. Many of the ambient concentrations used in both

TABLE 7-25. EFFECTS OF AMBIENT AIR IN OPEN-TOP CHAMBERS, OUTDOORS CSTR CHAMBERS, OR GREENHOUSE ON THE GROWTH AND YIELD OF SELECTED CROPS

Plant species	O_3 concentration, ppm	Exposure duration	Percent reduction from control	Location of study	Monitoring method[a]	Calibration method[b]	Fumigation facility[c]	Reference
Tomato (Fireball 861 VR)	0.035 (0.017-0.072)	99 day average (0600-2100)	33*, fruit fresh weight	New York	Mast	NBKI	OT	MacLean and Schneider, 1976
Bean (Tendergreen)	0.041 (0.017-0.090)	43 day average (0600-2100)	26*, pod fresh wt, 24*, number of pods		Mast	NBKI	OT	
Snap Bean (3 cultivars. Astro, BBL 274, BBL 290)	0.042	3 mo average (0900-2000)	1, pod weight	Maryland	(not given)	(not given)	OT	Heggestad and Bennett, 1981
Soybean (4 cultivars: Cutler, York, Clark, Dare)	>0.05	31% of hr between (0800-2200) from late June to mid-September over three summers, 5% of the time the concentration was above 0.08 ppm	20*, seed wt; 10*, wt/100 +2, % protein content, 4% oil content	Maryland	Mast	NBKI, known O_3 source	OT	Howell et al., 1979 Rose, 1980
Forbes, grasses, sedges	0.052	8 hr/day average (1000-1800), April-September, 1979	31, total above ground biomass	Virginia	Chem	Known O_3 source, UV	OT	Duchelle et al., 1983
	0.051 0.035	1980 1981	§ 20, total above ground biomass 15 total above ground biomass	Virginia	Chem			Skelly et al., 1982

TABLE 7-25 (con't) EFFECTS OF AMBIENT AIR IN OPEN-TOP CHAMBERS, OUTDOORS CSTR CHAMBERS, OR GREENHOUSE ON THE GROWTH AND YIELD OF SELECTED CROPS

Plant species	O_3 concentration, (ppm)	Exposure duration	Percent reduction from control	Location of study	Monitoring method[a]	Calibration method[b]	Fumigation facility[c]	Reference
Snap bean (Gallatin 50)	>0 06	Average 170 hr over 60 days exposure (1972-1974) (6 crops)	+5, pod fresh weight	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al., 1980
(BBL 290)	>0.06	Average 170 hr over 60 days exposure (1972-1974) (6 crops)	14*, pod fresh weight	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al , 1980
(Astro)	>0 06	Average 170 hr over 60 days exposure (1972-1974) (6 crops)	3, pod fresh weight	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al., 1980
(Astro)	>0.06	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	6, pod dry weight	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al , 1980
Snap bean (Gallatin 50)	>0.06	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	+1, pod dry weight	Maryland	Mast	1% NBKI Chem	OT	Heggestad et al , 1980
(BBL 290)	>0.06	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	10, pod dry weight	Maryland	Mast	1% NBKI Chem	OT	Heggestad et al , 1980
(BBL 274)	>0 06	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	22*, pod dry weight	Maryland	Mast	1% NBKI Chem	OT	Heggestad et al., 1980

TABLE 7-25. (con't). EFFECTS OF AMBIENT AIR IN OPEN-TOP CHAMBERS, OUTDOORS CSTR CHAMBERS, OR GREENHOUSE ON THE GROWTH AND YIELD OF SELECTED CROPS

Plant species	O_3 concentration, ppm	Exposure duration	Percent reduction from control	Location of study	Monitoring method[a]	Calibration method[b]	Fumigation facility[c]	Reference
Sweet corn (Bonanza)	>0.08	58% of hr (0600-2100) between 1 July and 6 September	9*, ear fresh wt; 10*, no. seeds/ear	California	Mast	UV	OT	Thompson et al., 1976
(Monarch Advance)	0.08		28*, ear fresh wt; 42*%, no. seeds/ear					

[a]chem = chemiluminescence; Mast = Mast oxidant meter (coulombmetric); UV = ultraviolet spectrometry.

[b]NBKI = neutral buffered potassium iodide; UV = ultraviolet spectrometry.

[c]OT = open-top chamber; CSTR = continuous stirred tank reactor.

*significant at p = 0.05; ng = not given.

§28*, total above ground biomass -- 3 yr average -- NF and open plot versus CF α significant at p = 0.05

TABLE 7-26. EXPOSURE-RESPONSE FUNCTIONS RELATING OZONE DOSE TO PLANT YIELD[a]

Plant species	Yield equation	Dose (ppm-hr) for predicted 10% Yield reduction[b]	Reference
Alfalfa[c] (Moapa 69)	y = 162.4 - 1.5 x Dose	10.8	Oshima et al., 1976
Tomato[c] (6718VF)	y = 9.742 - 0.23 x Dose	4.2	Oshima et al., 1977a
Potato (Centennial Russett)	y = 1530 - 15.8 x Dose	9.7	Foster et al., 1977a
Bean[c] (Red Kidney)	y = 306.7 - 33.33 x log x Dose	>51.6	Oshima, 1978

[a]The studies were conducted in California and plants were exposed to ambient O_3.

[b]For Alfalfa and tomato the hourly averages above 0.10 ppm were summed to compete the seasonal dose. For potato and bean hourly average O_3 concentrations for the duration of the study were summed to complete seasonal dose.

[c]The original equation was based on pphm-hr but for this table the regression coefficient was converted to ppm-hr for consistency with the data in the rest of the chapter.

studies were equivalent to ambient concentrations in cleaner regions of California and the eastern United States.

Another approach to estimating the effects of ambient O_3 has been the use of EDU, an antioxidant (Clarke et al., 1983; Foster et al., 1983a). EDU can protect plants from the effects of O_3 (see Section 7.3.2.2.2). By using this experimental approach, plants may be grown under completely normal field conditions without potential chamber effects. However, there is the potential for effects of other non-oxidant-type pollutants and the possibility of a direct EDU effect on yield. Foster et al. (1983a) determined that EDU applied in a greenhouse in the absence of O_3 had no effect on yield of Centennial Russet or White Rose potatoes. EDU-treated Centennial Russet plants exposed to ambient air yielded 19 percent more marketable yield than plants exposed to ambient photochemical oxidants but treated with EDU. White Rose yields were unaffected by EDU treatment. Ambient O_3 concentrations were not reported for either study.

Several studies have measured various plant effects and attempted to describe associations between ambient O_3 and O_3 injury symptoms or yield responses. Oxidant-induced changes in forest ecosystems of California, Virginia, and Utah are discussed in Chapter 8. Some specific references to these and other areas follow. Increasing O_3 sensitivity of ponderosa pine has been correlated with insect-induced mortality (Cobb and Stark, 1970). Over a 3-year period, 24 percent of 150 study trees died, of which 92 percent had exhibited severe foliar O_3 symptoms. No trees classed as healthy or slightly symptomatic died. In a mixed-conifer stand in the San Bernardino Mountains, radial growth for the 30-year period 1945 to 1975 decreased an average of 34 percent, 1 percent, and 4 percent in areas with severe, moderate, and no injury, respectively (Kickert et al., 1977). Concentrations of O_3 that "commonly exceeded 0.10 ppm" have been associated with foliar injury and defoliation.

Reduced growth of O_3-sensitive eastern white pine appears to be attributable to reduced foliar biomass, which results from shortened needles and premature needle loss (Mann et al., 1980). The annual radial growth was reduced 50 percent. The reduced foliar biomass and foliar symptoms were associated with several episodes of O_3 above 0.08 ppm. White pines exhibiting relatively severe symptoms (chlorosis, tipburn, short needles, premature defoliation) experienced a steady decline in average ring width (71 percent over

15 years) and a loss in capacity for recovery (McLaughlin et al., 1982). The annual radial growth of eastern white pine trees exhibiting symptoms of O_3 stress was 28 percent less than that of trees exhibiting few or no symptoms (Benoit et al., 1982). Field studies in the San Bernardino National Forest in California showed that during the last 30 years, ambient O_3 reduced the height growth of ponderosa pine by 25 percent, annual radial growth by 37 percent and the total volume of wood produced by 84 percent (Miller et al., 1982).

The research presented in this section demonstrates that ambient O_3 in many areas of this country can reduce plant yield. Although the most severe effects appear to occur in the South Coast Air Basin of California and the San Bernardino Mountains, areas with high ambient O_3 concentrations, other agricultural areas in the nation are impacted as well. Data presented in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) suggested that ambient O_3 reduced yields for orange (54 percent) grape (47 to 61 percent) and cotton (5 to 29 percent). Also, the yield of potatoes growing in the East were reduced 20-50 percent by ambient O_3. More recent research indicated similar yield reductions are still occurring throughout the country from ambient O_3 exposures. Recent open-top chamber studies have demonstrated losses in tomato (33 percent), bean (26 percent), soybean (20 percent), snap-bean (0 to 22 percent), sweet corn (9 percent), several tree species (12 to 67 percent), and forbes, grasses, and sedges (9 to 33 percent). Still other chamber studies have shown yield reductions in potato (42 percent) exposed to ambient photochemical oxidants. The use of chemical protectants such as (EDU) has demonstrated yield losses in potatoes ranging from 2 to 31 percent. Correlations of plant yield with ambient O_3 concentrations based on either an O_3 gradient or differential cultivar or species sensitivity have been used to predict ambient yield losses in alfalfa (53 percent), tomato (22 percent) and ponderosa and white pines.

7.4.3.3 Exposure-Response Relationships (Empirical Models)--Empirical exposure response models are mathematical functions that describe a relationship between pollutant exposure and a biological response. These models are very useful because the entire relationship defined between the range of exposures is quantitatively defined. This desirable property differentiates the models from the results of descriptive designs described in Section 5.4.3.2. In addition, empirical models are useful as research tools because they succinctly summarize relationships in the form of an equation.

Empirical response models describing plant yield losses from O_3 have two major uses that are distinctly different in theory and requirements.

1. Models are used for crop production forecasting. The unit used in the forecasts is yield per unit land area. Because this forecast's essentially biological errors introduced from aggregative methods and the exclusion of environmental, cultural, and edaphic variables must be dealt with if model estimates are to be reliable.

2. Models are used to interface biological systems with economic models. The units used as a measure of effect in an economic model are monetary (profit and loss). These models are driven by economic variables such as input and output substitutions, supply, demand, and associated price fluctuations, and regional linkages. Problems of aggregation methods and impacts of economically important variables are considered in terms of the economic units. Errors introduced by aggregation and exclusion of environmental variables also affect the results obtained by economic models.

The development of empirical models is the first and the least complex step in their use. It is the application of these models that is most apt to be misunderstood.

The available empirical models were developed by using various exposure techniques ranging from ambient gradients to highly controlled laboratory exposures; therefore they have different constraints on their application. Additionally, until the emergence of NCLAN (National Crop Loss Assessment Network) as a multi-site effort to develop credible crop-loss assessments, no organized effort to standardize developmental methodology had occurred. NCLAN represents the first organized effort to establish defensible crop-loss estimates on a national scale.

Only one empirical model was discussed in the dose-response section of the 1978 criteria document (U.S. Environmental Protection Agency, 1978). The Heck and Tingey (1971) injury model was used to derive tabular and graphic data predicting O_3 concentrations for specific amounts of foliar injury for a number of species. Most other discussion revolved around the limiting value concept used to relate O_3 concentrations from the existing data base. Many empirical models have been developed since the 1978 air quality document was published, and such models have expanded to the point that they are commonly used as tools in most areas of air pollution research.

There are different categories of empirical exposure-response models. Physiological models generally are used as research tools to summarize relationships and provide a quantitative means of comparing responses. Injury models predict leaf response at various levels of exposure, and growth models define biomass accumulation, canopy development, and growth of reproductive organs. Yield response models focus on the economically or biologically essential portion of plant growth.

7.4.3.3.1 Physiological models. This section is included to provide an example of the uses of physiological models in basic research, which is the primary area of their application. Physiological response models are used as effective research tools in summarizing relationships or allowing comparisons among species (Tingey et al., 1976; Coyne and Bingham, 1981). The slope of linear models offers a convenient means for comparison of plant species or populations within a species. Physiological processes are particularly amenable to quantification with functions. Use of these response models fulfills objectives quite different from those fulfilled by the predictive models required for yield-loss estimates.

7.4.3.3.2 Injury models. Injury models estimate the magnitude of foliar injury incurred from pollutant exposures or, in one case, the concentration of pollutant from the degree of injury (Table 7-27). These models have been used to compare air quality in different geographical areas (Goren and Donagi, 1980; Naveh and Chaim, 1978). Heck and Tingey (1971) developed a model that would estimate the O_3 concentration required to cause specific amounts of foliar injury (Table 7-27). This model was the source of tabular and graphic data presented in the dose-response section of the previous ozone criteria document (Environmental Protection Agency, 1978).

A major contribution to the evolution of injury models was the model developed by Larsen and Heck (1976). They presented a mathematical model based on the assumption that percent leaf injury was distributed lognormally as a function of pollutant concentration for a specific exposure duration. This model also has been used for black cherry (Davis et al., 1981) and Hodgson soybean (Pratt and Krupa, 1981). Both groups of investigators modified the Larsen and Heck model slightly by using a probit transformation of the dependent variable.

Nouchi and Aoki (1979) developed injury models for both short-term controlled exposures and long-term ambient exposures with morning glory (Table 7-27). They recognized that foliar injury did not have a linear relationship

TABLE 7-27. SUMMARY OF MODELS DESCRIBING THE RELATIONSHIP BETWEEN FOLIAR INJURY AND OZONE EXPOSURE

Model	Plant species	Reference
1. $y = a + bx$ y = injured leaves, area (%) x = ozone index (ppb x hr) a = -3.5 (winter), -0.38 (summer),+ -1.85 (fall) b = 0.0037 (winter), 0.0016 (summer), 0.0015 (fall)	Tobacco Bel-W3 Winter R^2 = 0.94 Summer R^2 0.98	Goren and Donagi, 1980
2. $P = P_k(1-e^{-kt})$ P_k = % injured leaves at time t P_k = equilibrium % of injured leaves k = constant determined by least squares	Tobacco Bel-W3 No correlation coefficient available	Naveh and Chaim, 1978
3. $C = A_0 + A_1I + A_2/t$ C = ozone concentration A_0, A_1, A_2 = regression coefficients I = percent foliar injury t = time of exposure	Selected species Range of R^2 = 0.85 to 0.35	Heck and Tingey, 1971
4. Z = -ln Mghr/ln Sg - p lnt/lnSg + lnC/lnSg Z = no. of standard deviations that the percentage of injury is from the median C = ozone concentration t = exposure duration Mghr = geometric mean concentration Sg = standard geometric deviation p = slope of the line on a logarithmic scale.	Selected species Range of R^2 = 0.96 to 0.58	Larsen and Heck, 1976
5. Model 5 Probit (y) = 1.3 lnc + 0.49 lnd + 0.77 where c = concentration in µl/l d = duration in hr y = % leaf surface injured	Soybean cv. Hodgson R^2 = 0.84	Pratt and Krupa, 1981

TABLE 7-27 (con't). SUMMARY OF MODELS DESCRIBING THE RELATIONSHIP BETWEEN FOLIAR INJURY AND OZONE EXPOSURE

Model	Plant species	Reference
6. Model 5 $PIF = 0.2174 + 2.2457 \ln c + 2.1378 \ln t$ where c = concentration in µl/l t = duration in hr PIF = Probit mean proportion of injured foliage/plant	Black cherry $R^2 = 0.77$	Davis et al., 1981
7. Short-term controlled fumigations $S = n \ln D + K$ where $D = (C^{m/n} \times t)$ and S is in the range 0 to 1 S = plant injury degree[b] C = concentration in ppm t = exposure duration in hr m = constant n = constant K = constant $S = 0.278 \ln D + 0.999$	Morning glory $R^2 = 0.97$	Nouchi and Aoki, 1979
8. Ambient conditions $S = n \ln D + A \ln D' + K'$ where $D = \Sigma_i C_i^{m/n}$ S = plant injury degree[b] C_i = hourly average concentration at the ith hour in ppm A lnD' = contribution to the injury on the day due to the effects of oxidant dosage up to the previous day A = constant K' = constant $S = 0.278 \ln D_j + 0.041 (\ln D_{j-1} + \ln D_{j-2} + \ln D_{j-3}) + 1.872$	Morning glory $R^2 = 0.70$	Nouchi and Aoki, 1979

Following information relates to model 1.

[a]Half the accumulating sum of average hourly O_3 concentration between the first value $\geq$ 40 ppb and the last value $\leq$ 40 ppb.

[b]Plant injury degree = (Σ% damaged leaf per leaf)/Σ area of the leaves that can be damaged to the maximum degree.

with the conventional dose statistic (concentration x time) and developed a powered dose (dose raised to some power) for the acute exposure model. Further, Nouchi and Aoki included a factor in the ambient model that incorporated the time-dependent contribution of previous O_3 exposures and modified the dose expression to account for the long-term variable exposures that characterize ambient O_3 episodes. These investigators were the only group that attempted to account for the effects of previous O_3 exposures on foliar injury in their model.

7.4.3.3.3 Growth models. Only a few empirical growth models quantify O_3-induced alterations in biomass accumulation and assimilate partitioning. Oshima et al. (1978; 1979) developed growth models for parsley and cotton and later refined the cotton model (Oshima and Gallavan, 1980). Growth models are used primarily for research purposes and are included in this report only as an example to indicate progress in quantifying O_3 growth responses.

7.4.3.3.4 Yield and loss models. Yield models are the most sought after and most difficult models to develop. These models are necessary for estimates of production and economic loss because they relate yield directly to pollutant exposure. The number and quality of yield models is increasing rapidly because of increased interest and the NCLAN program. Existing models are summarized in Table 7-28. A more detailed discussion of actual yield responses that were derived from many of these studies is presented in tabular and graphic form in Section 7.4.3.2.

Oshima and his coworkers developed predictive models to estimate yield-losses from O_3 within California. Using an ambient O_3 gradient in southern California, Oshima et al. (1976) developed both yield and yield-loss models for a clone of Moapa 69 alfalfa (Table 7-28). Multiple-regression techniques were used to test the relative contributions of O_3 and other meteorological variables to changes in alfalfa yield. Ozone was determined to be the greatest contributor to yield variation, it vastly overshadowed the contributions of the other tested variables. The O_3-yield function was then transformed to a predictive loss model using the intercept as the zero-loss reference value. Similar techniques were used to develop an O_3-loss model for fresh market tomatoes (Table 7-28) (Oshima et al., 1977a). This model incorporated the unique feature of transforming plant yield to economic packing container units. Tomato fruit yield was predicted as percent loss in marketable container units (flats or lugs) based on U.S. Department of Agriculture fruit size categories. The inclusion of the marketing criteria sharply increased the proportion of loss.

TABLE 7-28. SUMMARY OF MODELS OF OZONE YIELD AND LOSS

	Model	Crop	Reference
1. a)	Total fresh wt. function $y = a + bx$ $y = 162.4 - 0.015x$ y = fresh wt (g/plant) a = intercept x = ozone dose (pphm-hr > 10 pphm)	Alfalfa cv Moapa 69 $R^2 = 0.68$	Oshima et al., 1976
b)	Loss function - transformed from 1a by % loss = (a - wt)/a x 100 % Loss = $-1.068 \times 10^{-4} + 9.258 \times 10^{-3}x$ x = ozone dose (pphm-hr > 10 pphm)		
2. a)	Marketable fruit $y = [\sin(-0.0076x + 84.2816)]^2$ y = % fruit marketable USDA minimum size x = ozone dose (pphm-hr > 10 pphm)	Tomato VF 6718 $R^2 = 0.85$	Oshima et al., 1977a
b)	Yield function $y = 9.742 - 0.0023x$ y = container yield based on USDA fruit size and packing configuration x = ozone dose (pphm-hr > 10 pphm)	$R^2 = 0.62$	
c)	Loss function - transformed from 2b by % loss = (a - container yield)/a x 100 % Loss = $0 + 0.0232x$ x = ozone dose (pphm-hr > 10 pphm)		
3. a)	$y = a + bx$ y = yield (varies with crop) x = ozone exposure in seasonal 7 hr/day mean ozone concentrations (ppm) a = intercept b = slope	Selected crops R^2 statistics are not available	Heagle and Heck, 1980
b)	$y = a + b_0x + b_1x^2$ y = yield (varies with crop) x = ozone exposure in seasonal 7 hr/day mean ozone concentration (ppm) a = intercept b_0 and b_1 = regression coefficients		
4. a)	Linear yield function $y = b_0 + b_1x$ y = crop yield (g/plant) x = ozone exposure in seasonal 7 hr/d b_0 = intercept b_1 = slope	Selected crops range of R^2 = 0.99 to 0.65	Heck et al., 1982

TABLE 7-28 (con't). SUMMARY OF MODELS OF OZONE YIELD AND LOSS

Model	Crop	Reference
b) Plateau - linear yield function $y = b_0$ if $x \leq f$ $y = (b_0 - b_1 f) + b_1 x$ if $x > f$ y = crop yield (g/plant) x = ozone exposure in seasonal 7 hr/day mean concentration (ppm) f = threshold 7 hr/day mean concentration (ppm) b_0 = intercept b_1 = slope	range of R^2 = 0.99 to 0.94	
c) Loss function $y = \frac{100}{a} b_1 (0.025 - x)$ y = % yield reduction b_1 = regression coefficient from function 4a a = predicted yield from function 4a at 0.025 ppm 7 hr/day mean ozone concentration in g/plant x = ozone exposure in seasonal 7 hr/day mean ozone concentration		
5. Weibull function $y = \alpha \exp [- (x/\sigma)^c] + e$ y = yield α = hypothetical maximum yield at 0 ozone x = ozone dose in seasonal 7 hr/day mean ozone concentration in ppm σ = the ozone concentration when yield is 0.37 α c = dimensionless shape parameter	Selected crops parameters estimated from empirical data	Heck et al., 1983
6. a) Tuber weight yield function $y = a + bx$ $y = 1530 - 15.8D$ y = % tuber yield in g/plant D = ozone dose in ppm-hr	Potato cv Centennial Russet $R^2 = 0.77$	Foster et al., 1983b
b) Tuber number yield function $y = 34.3 - 0.318D$ y = tuber yield in number/plant D = ozone dose in ppm-hr	$R^2 = 0.62$	
c) Plant dry matter function $DM = 382 - 3.83D$ DM = total dry matter in g/plant D = ozone dose in ppm-hr	$R^2 = 0.73$	

Heagle and Heck (1980) developed both linear and quadratic yield models for cultivars of field corn, winter wheat, soybeans, and spinach (Table 7-28). The models were derived from open-top chamber experiments and used a seasonal 7 hr/day mean O_3 concentration to characterize O_3 exposures. These models were the precursors of those developed by NCLAN.

The first published yield models produced by NCLAN (Heck et al., 1982) were presented as either linear or plateau-linear functions (Table 7-28). The plateau-linear function combines two linear functions; the first with a slope of zero, depicting no response, and a second with a measurable slope. The intersection of the two functions can estimate a threshold value. A loss model was developed with the yield at 0.025 ppm (seasonal 7 hr/day mean O_3 concentration) as the reference zero-loss value. Yield functions were developed from open-top chamber data obtained by the regional research laboratories participating in the NCLAN program. Each model was developed with a standardized method monitored by a quality-control program. Yield-loss models were developed for cultivars of corn, soybean, kidney bean, head lettuce, peanut, spinach, turnip, and wheat. Some models included in this publication were generated from earlier experiments that involved the corn, wheat, and spinach models of Heagle et al. (1979a, 1979b, 1979c).

Recently, Heck et al. (1983) used a 3-parameter Weibull function to model NCLAN yield losses (Table 7-28). The Weibull function was selected because it could be used to represent a variety of functional forms, its parameters could be interpreted to be biologically meaningful, and it offered a method of summarizing species responses by developing a common proportional model. The Weibull modeling approach was subsequently used with NCLAN data previously modeled with linear, plateau-linear, or quadratic functional forms (Heck et al., 1983). In addition, a comparison of crop-loss estimates from the Weibull, linear, and plateau-linear models was completed using production estimates to project economic surplus figures for the Corn Belt (Ohio, Indiana, Illinois, Iowa, and Missouri). This comparison used a regional approach with relevant units (economic surplus) but did not address the impact of other regions or economic adjustments characteristic of more sophisticated estimates.

Foster et al. (1983b) produced yield and plant dry weight functions for Centennial Russet, an extremely sensitive potato cultivar. These models were developed using an ambient exposure facility composed of a series of large Teflon® chambers with O_3 exposure controlled by proportional filtration of ambient O_3.

A multi-point crop-loss technique was developed (Teng et al. as reported in Benson et al., 1982) and used to assess the impacts of O_3. Previously the multi-point models had been used to predict biotic yield losses (resulting from biotic pathogens) but the authors further refined this technique by summing daily multi-point loss models over a season to arrive at a seasonal loss for alfalfa (Table 7-29). When single harvest crops such as corn, wheat, and potato were used, the authors divided the seasonal exposure into 12 time steps and regressed final harvest on the exposure steps. However, this application of the model was seriously flawed because only one time series of O_3 exposures was used. Separating total O_3 exposure into several time steps creates a model with several colinear variables. The estimated coefficients of these variables are unstable. The alfalfa model is important because O_3 exposures were represented by multiple variables that indicate specific exposure periods, which may more closely approximate the ambient patterns of exposure than do the single summary statistics used by other researchers.

Three kinds of models have been used to describe yield and loss: linear, plateau-linear, and Weibull functions. These empirical models are intended to describe the behavior of plants in the absence of a known functional relationship between O_3 concentration and yield. Each type of model has strengths and limitations. The class of linear models, including straight line and quadratic equations, is very flexible because it can take on a large variety of shapes and can be used to approximate other functions and statistical methods for computing confidence bands (Draper and Smith, 1966). Straight line models are limited because they allow no curvature and they do not allow threshold levels below which no yield loss occurs. Quadratic models allow curvature and gradual changes in slope, but like straight line models, they do not allow plateau shapes or thresholds. They can, however describe situations in which low levels of a pollutant stimulate growth but higher levels cause yield reductions. Two nonlinear models have been used in attempts to describe situations in which response to O_3 has a threshold. Statistical theory for nonlinear models is not as well developed as that for linear models; consequently, confidence bands are not usually fit to nonlinear models. The two nonlinear models discussed are the plateau-linear and Weibull models. The plateau-linear model incorporates a threshold value but does not allow curvature of any increase in yield followed by a decrease. The Weibull model can take on a plateau shape followed by curved gradual decreases, but this model is limited, because above zero concentration, no decrease can be preceded by an increase.

TABLE 7-29. SUMMARY OF CROP-LOSS MODELS

Model		Loss criteria
General models		
1. $y = f(x_{ti})\ldots$	y = proportion of yield reduction x_i = dose parameter at time t_i	NA[a]
2. Net yield reduction is	$\sum_{i}^{n} ydt$ dt = time step n = maximum number of growing days	NA[a]
Functional models		
1. Alfalfa $y = ax + bx^2 + cx^3$ Range of R^2 = 0.99 to 0.13	y = daily yield loss (fresh wt) x = Σ hourly averages for 1 day a to c = regression coefficients	Loss = 1.0 - $\frac{\text{Biomass at site (x)}}{\text{Biomass at control site}}$
2. Corn $y = ax_1 + bx_2 \ldots 1x_{12}$ R^2 = 0.87	y = yield loss based on 100 kernel wt x_1 to x_{12} = ozone summary statistic for periods 1 to 12 calculated as: $\frac{\sum_{i=1}^{N} [(\Sigma\ hi/n)24]}{N}$ where: N = the number of days in a period (7 days) hi = ozone concentrations n = number of hours for which there are ozone concentrations a to 1 = regression coefficients	Loss = 10 - $\frac{\text{100 kernel yield for (x)}}{\text{100 kernel yield for control}}$

TABLE 7-29. SUMMARY OF CROP-LOSS MODELS

	Model	Loss criteria
3. Wheat $y = ax_1 + bx_2 \ldots gx_7$ $R^2 = 0.95$	y = yield loss based on 100 seed ct. x_1 to x_7 = ozone summary statistics for periods 1 to 7 calculated as: $\frac{\sum_{i=1}^{N} [(\Sigma\, hi/n)24]}{N}$ where: N is the number of days in a period (7) hi = ozone concentrations n = number of hours for which there are ozone concentrations a to g = regression coefficients	Loss = 1.0 - $\frac{\text{100 seed yield for (x)}}{\text{100 seed yield for carbon filtered treatment}}$
4. Potato $y = ax_1 + bx_2 + cx_3 + dx_4 + ex_5$ $R^2 = 0.93$	y = yield loss based on tuber wt/plant x_1 to x_5 = ozone summary statistic for periods 1 to 5 calculated as: $\frac{\sum_{i=1}^{N} [(\Sigma\, hi)]}{N}$ where: N = the number of days in a period (14 days) hi = hourly ozone concentrations in 1 day a to e = regression coefficients	Loss = 1.0 - $\frac{\text{tuber wt yield for (x)}}{\text{tuber wt yield for control treatment}}$

Source: Benson et al., 1982.

[a]NA = Not available.

All the yield and loss models presented have some common weaknesses for production forecasting. With the exception of Teng's model (Benson et al., 1982), none of the models uses a statistic that characterizes the episodic nature of ambient exposures. The multi-exposure variables used by Teng (Benson et al., 1982) partition the seasonal exposure into discrete periods, which account for some of the ambient fluctuations in O_3 levels. However, the temporal periods of exposure were preselected and did not correspond to natural fluctuations. Only the alfalfa model incorporated the daily variations in ambient exposures because of the nature of its yield.

An additional weakness common to all the yield loss models relates to their reference loss criteria. Every model presented uses the experimental data base to estimate its zero-loss reference value (Section 7.2.5). These values may bear no relationship to actual zero-loss values that are in the areas where the models are to be applied for production forecasting.

7.4.3.3.5 Interpreting exposure response models. Interpretation of exposure-response models requires an understanding of the subjects presented in Section 7.2. The loss models presented in Tables 7-28 and 7-29 were developed by means of a range of diverse exposure methods, exposure characterizations, experimental designs, and reference loss criteria. Despite their enormous differences, the models are mathematically very similar because all but the Weibull functions used linear or multiple linear regression techniques. All but the Weibull and quadratic models are linear functional forms, use percent as the unit of loss, and with the exception of Teng (Table 7-29), use a single independent variable to represent O_3 exposure. These models differ because they use several independent variables that represent periods of exposure within a season. For simplicity, these loss models can be represented by a general function:

$$Y = a + b(x) \qquad (7\text{-}2)$$

Y = yield loss;
a = the regression intercept;
b = regression coefficient; and
x = O_3 exposure representation.

The variable x represents O_3 exposure in the general model. The models presented in Tables 7-28 and 7-29 use different statistics to represent the O_3 exposure,

and as previously stated in Section 7.2.2, these statistics can not be readily transformed for comparison.

The y variable in the general model represents the dependent variable (yield loss). All models utilize percentages as loss units but calculate the loss percentages from different reference zero-loss values. Only a single model (Oshima et al., 1977a) used percentages calculated from commercial marketing criteria. All other models used biological yield parameters as the basis for converting to percent loss. The models used are the best available, and they serve to define the relationship between O_3 exposure and yield of specific crops. These models also serve as criteria used to develop simulation models designed to generate the coefficients necessary to drive more sophisticated crop production models described by Holt et al. (1979) or serve to focus research into areas required for rational crop-loss assessments (Teng and Oshima, 1982).

Use of a loss model requires O_3 exposure data in the appropriate format, good judgment to guide its application, and an appreciation of what the predicted value represents. The fresh market tomato loss model (Oshima et al., 1977a) can be used as an example.

$$\text{Loss} = 0.0232\ (O_3\ \text{dose}) \qquad (7\text{-}3)$$

This linear model predicts the loss in marketing container yield caused by seasonal O_3 exposure expressed as cumulative O_3 dose greater than 0.10 ppm. This model was developed from ambient plots along an O_3 gradient; therefore, it is representative of plot level yields. The zero reference level is the intercept of the yield model in Table 7-29.

This model requires information on the cumulative dose of O_3 exposure. Other exposure statistics, such as the seasonal 7-hr daily average used by NCLAN, cannot be used with this model. By calculating the O_3 doses for locations of interest, plot level predictions can be calculated. Using this model's exposure statistic, the hourly averages for each hour between 0700 to 2100 that had an O_3 concentration greater than 0.10 ppm were summed for the 4-month season to determine the O_3 dose.

Examples of loss calculations for three hypothetical locations are

Location	Ozone dose	Predicted loss
1	500 pphm-hr	11.6%
2	1000 pphm-hr	23.2%
3	1500 pphm-hr	34.8%

The predicted values can be used either to estimate losses in tomato production or to arrive at an estimate of economic crop loss. This distinction must be made because application of these loss estimates requires different procedures.

Ideally, the model would include an applications validation test wherein an independent data set of tomato losses at specific O_3 doses would be compared to predicted losses from the model to determine the precision of the estimates. If the three previously calculated location estimates represent three locations in the area of interest, the next procedure required is aggregation. The estimates represent three plots of plants grown in different O_3 exposure conditions. To represent tomato production on a larger scale, the plot level estimates must be aggregated to estimate field level production, the production from all fields in the area, and the production from the region that includes the three fields.

If an economic crop-loss assessment is required, the inputs into the economic model of choice are the estimates or the loss function. The three yield-loss estimates provide the basis for an economic transformation to profit or loss estimates, depending on the factors incorporated into the economic model. For instance, if they are inputs into the linear program, representative farm model used by NCLAN, then grower crop substitutions, alternate cultural practices, and other farm level options would be explored to determine predicted economic impact. The aggregation methods would be economically derived and would probably incorporate regional supply and demand, market price dynamics, and regional linkages. Alternative approaches such as econometric modeling might be selected in some instances.

Use of a yield-loss model is a process that requires adhering to the limitations and requirements of the model, having the required data necessary to drive the model, deciding on the specific application desired, and using the appropriate step to aggregate estimates to the organizational level required.

7.5 ECONOMIC ASSESSMENTS OF OZONE EFFECTS

Previous sections of this chapter discuss the potential negative effects of O_3 on crop yields. In view of the importance of U.S. agriculture for both domestic and world consumption of food and fiber, reductions in crop yield caused by O_3 could substantially affect human welfare. The plausibility of this premise has resulted in numerous attempts to assess, in monetary terms, the losses or benefits of O_3 control. The resulting estimates from these studies and their validity are discussed in this section.

7.5.1 Economic and Methodological Issues in Performing Assessments

Three procedures are used to assess crop loss caused by O_3. The ability to discriminate among these assessment types is important because their data requirements, informational content, and economic validity differ. The first method reports crop losses in physical units (reduction in crop production) for a given geographical unit (e.g., a state or region). These aggregate physical losses are typically estimated by extrapolating from crop dose-response models. Examples include the recent work by Loucks and Armentano (1982) and the "damage" model defined in Moskowitz et al. (1982). This type of assessment is not discussed further in this section because it does not report economic losses.

The second type of assessment translates physical losses into a dollar value by multiplying estimated yield or production losses by an assumed constant crop price. This procedure is commonly used for obtaining dollar estimates of O_3-induced crop losses. In this section, this approach is defined as the traditional procedure. As an economic assessment methodology, this approach has serious conceptual weaknesses that limit the validity of the estimates to very restrictive cases. Given these conceptual limitations, the pecuniary loss estimates obtained from the traditional approach should not be viewed as estimates of the economic consequences of O_3.

The third assessment type uses theoretically justified economic methodologies; therefore, the assessment may be viewed as economic rather than pecuniary. Such studies provide estimates of the benefits of O_3 control or the costs of air quality degradation by accounting for producer and consumer decision-making and associated responses. Assessments of this type usually address price changes caused by adjustments in production and the role of producer input and

output substitution strategies. Thus, the resulting estimates will more accurately reflect the true economic costs of O_3 where economic decision-making and markets are known to operate (e.g., agricultural production).

Dollar loss estimates arising from the last two assessment types are seldom distinguished in the popular press. However, economists generally discount the monetary estimates obtained from the traditional type of assessment. Leung et al. (1978) and Crocker (1982) have critiqued this approach.

The assessments of O_3-induced vegetation effects reported in the 1978 oxidant criteria document (U.S. Environmental Protection Agency, 1978) use the simplistic traditional procedure. Examples of this procedure for obtaining dollar estimates (as cited in the 1978 document) are reported in Table 7-30. The advantage of such an assessment is the relative ease with which dollar values may be obtained. This advantage must be weighed against the weak conceptual basis and the implications this has for the validity of the loss estimates.

TABLE 7-30. PRE-1978 ESTIMATES OF ECONOMIC LOSSES TO CROPS AND VEGETATION ATTRIBUTABLE TO OZONE AIR POLLUTION IN THE UNITED STATES

Area	Year	Estimated loss, $10^3	Comments
United States	1963	65,000	First approximation for commercial crops (SRIa)
		121,400	Revised SRI report to include ornamentals
California	1963	33,700	Revised SRI report
	1970	17,500	Does not include ornamentals or indirect costs
Pennsylvania	1963	6,300	Revised SRI report
	1969	9,600	Pa. survey; includes indirect costs
	1970	60	Pa. survey; includes indirect costs
New Jersey	1971	950	N.J. survey of a limited number of crops, based on visible injury
	1972	60	N.J. survey of a limited number of crops, based on visible injury
New England	1961	1,100	Mass. survey; primarily crops and ornamentals

Source: National Research Council, 1977 (Benedict et al., 1971. Cited in U.S. Environmental Protection Agency, 1978).

[a]SRI = Stanford Research Institute.

More comprehensive economic assessments, as exemplified by Leung et al. (1982), Benson et al. (1982), and Adams et al. (1982), attempt to account for market impacts of yield reductions. These studies use various techniques, as determined by the structure of the particular economic problem. However, each study explicitly measures crop price adjustments caused by changes in production (supply). This measurement provides estimates of the economic losses to both producers and consumers, and thus can suggest possible distributional consequences of O_3. In the Benson et al. (1982) and Adams et al. (1982) studies, results were compared with estimates obtained (from the same data) study explicitly measures crop price adjustments caused by changes in production (supply). This measurement provides estimates of the economic losses to both producers and consumers, and thus can suggest possible distributional consequences of O_3. In the Benson et al. (1982) and Adams et al. (1982) studies, results were compared with estimates obtained (from the same data) using the traditional procedure. The differences were moderate to large; the traditional procedure overestimated losses from air pollution when comparing an area with clean air to an area with ambient O_3. The specific magnitude of these differences is reported in Section 7.5.3.

The most appropriate measure of economic benefits or losses must be defined. The economic literature suggests that concepts of economic surplus are the appropriate measures of the effect of alternative policies on social well-being under certain restrictive assumptions (Mishan, 1964, 1971; Willig, 1976; Just et al., 1982). Following this reasoning, most economic assessments of policy issues measure changes in the economic surplus accruing to consumers (consumers' surplus) and producers (producers' quasi-rents). This surplus is generally defined as the difference between the total amount consumers would be willing to pay (or producers would be willing to accept) and the amount they actually pay (accept). Economic surplus also may be approximated geometrically as the triangle formed by the intersection of conventional demand and supply curves for the commodity in question. Adams et al. (1982), Leung et al. (1982), and Adams and McCarl (1984) define economic effects in these terms. In contrast, the traditional procedure, which ignores price effects and, implicitly, the demand curve, at best addresses only producer effects, with no attention paid to the fate of consumers. Thus, conceptually and empirically, a fundamental difference exists between losses measured by the traditional procedure and those obtained from more comprehensive economic assessments.

In addition to conceptual differences in methodologies, other factors also contribute to the wide range of loss estimates in the literature. These factors, which are primarily technical, are discussed in the following section.

7.5.2 Biological and Practical Issues in Performing Economic Assessments

In the 1978 criteria document (U.S. Environmental Protection Agency, 1978) and in Section 7.2.5 of this document, a distinction is made between injury (defined as any identifiable and measurable response of a plant to air pollution) and loss (defined as any measurable adverse effect on the desired or intended use of the plant). Such a distinction is made because the evaluation of the economic effects of O_3 exposure require that the plant be altered either quantitatively (yield) or qualitatively (market acceptability) so that its value is reduced. In some cases, exposure may result in injury, such as leaf necrosis, without affecting yield.

The need to obtain response data in terms of yield rather than injury has been noted by most economists doing assessment research (e.g., Leung et al., 1978; Adams and Crocker 1982a). Oshima and coworkers (Oshima, 1974, Oshima et al., 1976; Oshima and Gallavan, 1980) have worked extensively to develop methods for evaluating and reporting crop losses in terms of yield reduction. Oshima's dose-response function for alfalfa has been used as the basis for several estimates of the dollar loss resulting from O_3 exposure. The recent work resulting from NCLAN (Heck et al., 1982a) also provides response information that can be easily used for economic assessments. Preliminary NCLAN response studies are used to derive some of the loss estimates reported in this document and serve as the primary data source for ongoing assessments.

Biological data on yield response to O_3 are important inputs to economic assessments of crop damage. As noted in Section 7.4.3.3, these data also are the most difficult biological loss models to develop. Prior to the availability of NCLAN data, economists and other assessors who needed such information either extrapolated data from a narrow set of existing response functions reported in the plant science literature or estimated these relationships from secondary data on production and air quality. The credibility of these extrapolation or estimation procedures and their implications in terms of the resultant economic loss estimates are ill-defined. Thus, the biological and air quality data used in these economic assessments, along with misspecified or overly simplified economic models, must be recognized as a potentially critical source of uncertainty in resulting loss estimates.

Some of the data problems mentioned above have contributed to the highly divergent loss estimates reported for O_3 (Table 7-31). In addition to the role that different assessment methodologies play in loss estimates, the divergences also may be attributed to specific biological and air quality data problems:

1. Few data or no data on O_3-induced crop losses for the crops under investigation. As noted above, lack of such data has caused assessors to (a) extrapolate from available foliar-injury estimates to obtain questionable yield-reduction estimates, (b) extrapolate from one crop response for which data are available to crops where no data exist; and (c) extrapolate from site and cultivar specific responses to other regions and cultivars.

2. The use of different crops, regions, and time periods in the analyses. Crop prices, production levels, and O_3 exposure vary geographically and temporally, with resultant changes in loss estimates.

3. The use of different background ambient levels to portray "clean air." When used in combination with a standardized dose-response function, the use of different background levels provides different yield-reduction estimates and ultimately different dollar-loss estimates.

4. The difficulty of extrapolating from controlled-chamber experiments to agronomic regions with all the required assumptions regarding soil type, precipitation regimes, oxidant exposure patterns, solar radiation levels, and interactions among these edaphic and climatic variables.

5. The use of different measures of dose or exposure. The recent NCLAN experiments standardize dose as the seasonal 7-hr average in parts per million. Other researchers use cumulative dose (e.g., hours of exposure to concentrations exceeding 0.10 ppm) or some other measure. The statistical link between these various dose measures and their correspondence to actual levels of plant exposure need to be better understood.

The impact of the above factors on dollar estimates may be seen in a brief chronological review of loss assessments. The earliest estimates of dollar losses were largely subjective because credible data on yield losses were not available, and the traditional procedure for calculating dollar losses was used. For example, figures of $3 to $4 million in California and $18 million on the East Coast (National Research Council, 1977) were later

TABLE 7-31. SUMMARY OF RECENT REGIONAL OZONE CONTROL BENEFITS ESTIMATES

Region	Reference	Annual benefits or loss estimate, $ million	Comments
Southern California	Adams et al., 1982	45	Losses estimated as economic surplus in 1976 dollars for 14 annual crops. Employs mathematical programming model to compare 0.04 ppm ozone assumption with 1976 ambient levels.
South Coast Air Basin (California)	Leung et al., 1982	93-103 (300)[a]	Losses estimated as economic surplus in 1975 dollars for citrus, avacados, and selected annual crops. Employs econometric procedures to compare "clear air case" (no oxidant pollution) with ambient levels.
Ohio River Basin	Page et al., 1982	278[b] (6,960)[c]	Losses estimated as producer losses for corn, soybean, and wheat in 1976 dollars. Region includes Illinois, Indiana, Ohio, Kentucky, West Virginia, and Pennsylvania.
Minnesota	Benson et al., 1982	30.5[d]	Losses estimated in 1980 dollars for corn, alfalfa, and wheat under alternative ozone assumptions. Uses dynamic loss functions incorporating crop growth stage and ozone episodes. Farm level dollar losses obtained from econometric model of national commodity markets national.
Corn Belt	Adams and McCarl, 1984	688	Uses a sectoral model of U.S. agriculture to record economic effects of changes in yields of corn, soybean, and wheat because of alternative oxidant standards. Benefits include effects on both consumer and producer of a federal ozone standard (0.08 ppm).
Illinois	Mjelde et al., 1984	55-200[e]	Uses cost functions to measure effect of ozone on producers' profits. Aggregate effect over corn, soybean, and wheat for 4 years assuming a 25-percent reduction in ambient ozone.

[a]Estimate of direct and indirect losses for entire state.

[b]Estimated annual equivalent loss caused by oxidants.

[c]Present value of losses caused by ozone for 25-year period (1976-2000).

[d]Worst case ozone situation (ignores production effects outside Minnesota). If other regions included in analysis, worsening of ozone increases total gross returns to Minnesota producers by $67 million because of inelastic nature of commodity demand.

[e]Range of economic benefits caused by a 25-percent reduction in ozone from ambient levels over a 4-year period (1978-1981).

raised to $500 million on the basis of increased awareness of potential pollution effects on plants and of additional sensitive species. Starting in 1969, some states and regions developed estimates of loss caused by oxidant pollution. Most of these surveys estimated yield reductions on the basis of foliar injury, and they made no direct assessments of growth or yield, although subjective estimates of damage were obtained.

The first national assessment (Benedict et al. 1971) used data from controlled exposure of various crops and data from simulated reaction chambers to estimate the effects of O_3 and other oxidants. This Stanford Research Institute (SRI) model estimated that the 1969 economic crop loss caused by O_3 exposure was about $125 million. Increased crop values, better air quality data, and more complete crop dose-response coverage have raised the dollar-loss estimates in recent years. Results of the SRI model and other estimates compiled before 1978 are summarized in Table 7-30; when compared with national estimates generated from more recent analyses (Table 7-31), a general escalation in dollar estimates is observed.

The relative contribution of better economic methodologies can not be sorted out vis-á-vis better biological data. However, in a reanalysis of the results of Adams et al. (1982), Crocker (1982) suggests that adequate economic representation may contribute as much as accurate biological data to reliable measure of benefits. In this particular case, estimates of the ultimate benefits of air pollution control hinge as much on an adequate representation of producer and consumer reactions as on the magnitude of the change in biological yield. The implication is that an accurate portrayal of both biological and economic responses is critical. Studies lacking in either category should be reviewed as incomplete.

7.5.3 A Review of Economic Assessments of Ozone Effects on Agriculture

Both regional and national assessments are found in the post-1978 literature. While each type of assessment can provide useful information, the geographical scale has implications for the validity and tractability of alternative assessment techniques. For this reason, regional and national studies are discussed separately. Only the third type of methodology (economic assessment) is presented in the regional review. In the review of studies at the national level, analyses using both traditional and economic approaches are discussed. This approach responds to the importance that the popular

press normally attaches to any nationwide estimate of pollution damage and the resultant need to describe any limitations inherent in the underlying analyses. The emphasis of the critique is on how well the assessments conform to economic realities. However, the studies also may be lacking in their biological basis.

7.5.3.1 Regional Loss Estimates. Most of the economic assessments of agricultural losses since 1978 have focused on regional losses. This focus may be caused by the relative abundance of data on crop response and air quality for selected regions, as well as by the obvious importance of certain agricultural regions (e.g., the Corn Belt and California). While estimates of regional losses are not adequate for evaluation of the national impact of alternative ozone levels, such studies can provide useful information on alternative economic methodologies. Also, regional loss estimates may indicate a lower bound on national losses if that region produces a dominant share of major commodities (e.g., the Corn Belt for corn and soybean). Finally, regional studies can measure the effects of O_3 on the regional economy. Loss or benefit estimates for regional studies are presented in Table 7-31.

Several regional studies have focused on southern California because this region has high O_3 levels and an important agricultural economy. Adams et al. (1982) assessed the impact of O_3 on 14 annual vegetable and field crops in four agricultural subregions of central and southern California for 1976 by using a mathematical programming model of California agriculture. The model predicted the effects of changed O_3 levels on the welfare of both producers and consumers. Ozone-induced reductions in yield were estimated for most crops from the Larsen-Heck foliar injury models. Foliar injury was then converted to yield loss using Millecan's "rule of thumb" (1971). A cumulative dose exposure-response model (Oshima et al., 1976) was used to estimate yield loss for tomatoes. These yield data, which at best are approximations, were incorporated into the economic model. This model also included a system of linear-demand functions used to measure price changes associated with production changes. The model was calibrated against 1976 production data to establish the model's general accuracy. The researchers then estimated the 1976 crop production and price by assuming that the 1976 national ambient air quality standard, 0.08 ppm, not to be exceeded more than one day per year, had been achieved.

As a percentage of total crop value (about $1.5 billion), the estimated losses caused by air pollution that exceeded the federal standard were found to be relatively small--$45.2 million (see Table 7-31). In terms of distributional consequences, meeting the 1976 standard would have increased 1976 agricultural income (quasi-rents) by $35.1 million and consumers' welfare (ordinary consumer surplus) by $10.1 million. To provide a comparison, the authors also applied the traditional method of computing losses (multiplying the estimated difference between actual and potential yield by market price) and obtained a total estimated loss of $52.5 million. While the empirical difference between the methods appears small, the traditional procedure measures only the effects on producers. Thus, if this latter figure ($52.5 million) is compared with the producer loss from the economic analysis ($35.1 million), the difference is approximately a 50 percent greater loss estimate for the traditional approach.

Leung et al. (1982) estimated O_3 damage to nine annual and perennial crops in the California South Coast Air Basin. These nine crops represent about 40 percent of the value of crop production in the region. Crop yields for 1963 through 1975 were obtained from county agricultural commissioners' reports of yields realized by farmers. Principal component analysis (PCA), a technique in which highly correlated variables are replaced with one or two components that contain most of the information of the original variables, was used to transform monthly environmental data (e.g., O_3 concentration, temperature, relative humidity, and precipitation) into yearly indices. Then yield was regressed on these indices using linear regression procedures. Finally, 1975 crop-yield reductions were estimated by calculating differences between actual yields (with 1975 levels of O_3) and yields predicted at zero-ozone concentration.

Leung et al. (1982) calculated changes in consumer surplus and producer surplus to approximate the welfare effects of changes in agricultural supply caused by air pollution. Estimated 1976 losses of consumer and producer surplus from O_3 exposure were $103 million.

Finally, the estimate of crop loss was subjected to input-output analysis (which traces the economy-wide effects of changes in a single economic variable) to determine the indirect impact on related economic sectors in California. Leung et al. (1982) estimated that the indirect loss of sales caused by O_3 damage was $276 million in the study region and $36.6 million in the rest of

the state. These figures translate into lost income (value added) of $117 million in the region and $14.1 million in the rest of the state. Associated employment losses were 9525 person-years (region) and 667 person-years (state).

While the Leung et al. analysis represents an innovative attempt to overcome some data and statistical problems that have plagued economic assessments of pollution damage, a number of potential limitations need to be recognized. First, by assuming a zero background O_3 concentration, the anthropogenically induced economic losses are overstated if the background or biogenic levels exceed zero level. While the issue of what is a precise background O_3 level is not available in the literature, some researchers have suggested that the background O_3 concentration should range from 0.025 to 0.035 ppm (7-hour seasonal mean). Second, the use of PCA has not overcome the statistical problems of extrapolation beyond the range of data for some functions as well as the continued presence of multicollinearity. Finally, given the national linkages involved in California agriculture, the use of a regional input-output model for agriculture may be overstating multipliers, and hence influencing the regional economic effects.

Losses within the Ohio River Basin (Illinois, Indiana, Ohio, Kentucky, West Virginia, and Pennsylvania) were estimated by Page et al. (1982). The region is a major producer of corn, soybean, and wheat; it also experiences oxidant levels that depress crop yields. While the study examined two pollutants, SO_2 and O_3, the largest losses (approximately 98%) were attributed to O_3.

The yield reduction data were derived from Loucks and Armentano (1982). Economic losses were measured at the producer level as changes in producers' income (quasi-rents) between clean air and ambient O_3 levels. The net present value of O_3-induced losses across the various loss scenarios for the period (1976 to 2000) is approximately $6.8 billion, or an annual equivalent of $278 million. Most of these losses accrue to the states with the largest agricultural production, Illinois and Indiana. The yield data used to generate these economic estimates have problems that are similar to those noted earlier, and they do not conform well to the subsequent experimental data generated within the NCLAN program.

Benson et al. (1982) provide economic-loss estimates for Minnesota. The biological basis for the study is summarized in Section 7.4.3.2. The authors evaluate O_3-induced crop losses for alfalfa, wheat, and corn through application of dynamic loss functions that specifically account for crop development

and episodic exposure. The loss functions are then evaluated at the county level with actual or simulated 1980 O_3 data.

The potential yield losses for each county are aggregated to provide a statewide crop loss. A national econometric model is then used to convert yield (production) adjustments for each crop into dollar losses, under two alternative supply assumptions: (1) O_3 and crop production are unchanged in areas outside of Minnesota and (2) O_3 changes nationwide. In the second case, the analysts account for supply and demand relationships for each crop as affected by production changes in all regions. The two assumptions gave highly divergent estimates of losses to Minnesota producers. For example, the estimated dollar loss attributable to a worst case O_3 level obtained from the first assumption is approximately $30.5 million in 1980 dollars. But when the econometric model accounts for price changes resulting from production changes in all regions, there is a $67 million gain to Minnesota producers in the short run if O_3 levels increased (in Minnesota as well as other production areas). This gain is caused by the rise in prices associated with reduced supply. These results and similar observations from Adams et al. (1982) and Leung et al. (1982) suggest the importance of using assessment methodologies that account for regional market linkages and resultant price effects.

Mjelde et al. (1984) estimated the effects of O_3 on Illinois cash grain farms by measuring cost functions for individual farms that experience varying levels of O_3. In addition to measuring the direct economic consequences of O_3 on farmers' incomes, this analysis demonstrated the methodological utility of the cost function approach, under some fairly restrictive conditions.

One of the primary objectives of the study was to test whether a meaningful link could be established between the physical loss estimates obtained under controlled experimentation and response information inherent in observed economic behavior (i.e., farmers' cost data). Mjelde et al. (1984) developed profit and cost functions for Illinois grain farms. These profit functions were estimated from a large sample of detailed cost and production data for Illinois farms and incorporate environmental variables (i.e., O_3, temperature, and rainfall) as well as the traditional economic variables.

In most specifications, O_3 has a negative and significant (at the 5 percent level) impact on profit. When direct production effects of O_3 are compared with NCLAN results obtained in Illinois, the production responses appear to be comparable. For a 25 percent increase in O_3, it is estimated that

output for the three crops would decline 3.3 percent. The same 25 percent increase using the NCLAN data indicates an 11.7 percent and 3.7 percent decrease in output for two cultivars of soybean. For two corn cultivars, output would decline between 1.4 and 0.6 percent. The Dixon et al. (1983) estimate (3.3 percent) lies between these estimates.

Mjelde et al. (1984) calculated that O_3 resulted in an aggregate loss in profits to Illinois farmers of approximately $200 million in 1980. This result seems consistent with some previous loss estimates (Heck et al., 1983; Page et al., 1982). The procedure applied by Mjelde et al. (1984) provides encouraging preliminary results; however, certain caveats need to be noted. First, the authors had abundant economic and air quality data. Similarly detailed data probably would not exist at the national level. In addition, a number of statistical and estimation problems occurred. Even though some of these problems were resolved, the stability of the coefficients in several specifications is suspect and thus reinforces some well-recognized difficulties that result from using secondary data to statistically sort out the effect of one environmental variable from among the many that affect yield.

A study of O_3 effects on Corn Belt agriculture by Adams and McCarl (1984) uses a mathematical programming model to measure effects of alternative oxidant standards on producers and consumers. Changes in yields for corn, soybean, and wheat associated with NCLAN response data provide the basis for regulatory impact analysis. The results of the analysis suggest that a reduction in oxidants from the present Federal standard of 0.12 ppm to 0.08 ppm would provide a net benefit of $668 million. Conversely, relaxing the standard to 0.16 ppm would result in a loss to consumers and producers of approximately $2.0 billion. The results of this analysis are consistent with distributional shifts that are associated with changes in supply when the demand is inelastic. The 0.08 ppm scenario benefits consumers at the expense of producers, whereas the 0.16 ppm assumption results in the opposite situation.

The authors also performed extensive sensitivity analyses to measure the effect of different yield data (predicted yield changes) on the economic estimates. The results of these analyses indicate that the effect of the biological data on economic estimates varies dramatically. In cases where little or no prior information on the effects of O_3 or O_3 interactions on a given crop exists and extrapolations across crops are used to approximate these effects, the difference between these economic estimates and those economic estimates

derived from data generated specifically for the crops in question (e.g., the NCLAN data) is quite large. Conversely, when some data exist, such as the NCLAN data for a given crop, and additional response data are generated for the same crop, the effect of added precision tends to be less important. One implication of this analysis is that the error within some early economic estimates that were based on biological responses extrapolated from other crops or were not cross-checked against experimental data may be quite large.

7.5.3.2 National Loss Estimates. Properly structured national analyses overcome a fundamental limitation of regional analyses by providing a more comprehensive accounting of economic link between regional production (supply) and national demand. However, national assessments require more data and therefore are more costly. Moreover, yield loss data become more questionable as they are extrapolated farther beyond the experiments from which they are derived. As a result of these difficulties, fewer estimates of oxidant damages exist at the national level than at the regional level. Several of these national estimates use the traditional approach to quantify damages.

The principal improvements in current national assessments over those appearing in the 1978 air quality criteria document (U.S. Environmental Protection Agency, 1978) include more complete dose-response information for an increasing number of major commodities and more complete air quality data. National estimates of O_3 damages are summarized in Table 7-32. As indicated, the range of damages falls between $1.8 and $3.0 billion. However, such relative consistency does not imply that this amount is the range of national agricultural losses; because the analyses are based on somewhat different crops, yield responses, and alternative assessment approaches.

The recent national estimates of oxidant damages to vegetation include an updated version of the Benedict et al. (1971) study. This SRI study Ryan et al. (1981) provides estimates of dollar losses to major agricultural crops caused by oxidants and SO_2. For oxidants, 16 crops with demonstrated oxidant sensitivity serve as the empirical base. The principal differences between Benedict et al. (1971) and the SRI effort include the use of a wider range of dose-response functions drawn from more recent literature, updated data on crop production from the 1974 Census of Agriculture, and updated data on air quality and crop prices.

Using alternative response functions and county-level data on air quality the loss in potential yield is estimated for 531 counties, around the United

TABLE 7-32. SUMMARY OF RECENT NATIONAL DAMAGE ESTIMATES FOR OZONE

Study	Crops	Annual loss estimates	Comments
Stanford Research Institute (1981)	Corn, soybean, alfalfa, and 13 other annual crops	$1.8 billion	Updated version of SRI[a] model. Loss measured in 1980 dollars for 531 counties.
Shriner et al. (1982) (Office of Technology Assessment)	Corn, soybean, wheat, peanut	$3.0 billion	Losses estimated in 1978 dollars, measured at producer level. Assumes a background or clean air oxidant level of 0.025 ppm ozone.
Adams and Crocker (1982b)	Corn, soybean, cotton	$2.2 billion	Losses measured in 1980 dollars using economic surplus. Loss represents difference between current production and production if a background ozone level of 0.040 ppm had been achieved.

[a]SRI = Stanford Research Institute.

Source: Ryan et al., 1981.

States, not in compliance with the current 1984 national ambient air quality standard for ozone (0.12 ppm). Yield loss is then translated to dollar loss by multiplying the decrease in production by the 1980 crop price for each commodity. The resulting potential benefit of implementing the secondary standard for oxidants is $1.8 billion (in 1980 dollars). This estimate is much higher than the previous SRI damage estimate (Table 7-31), thus, it reflects the sensitivity of these estimates to the data assumptions and time period employed.

A national assessment by Shriner et al. (1982) for the Office of Technology Assessment estimated the losses accruing to ambient O_3 levels for corn, soybean, wheat, and peanut. The study employed dose-response data from recent NCLAN experiments. It simulated county-level ambient O_3 data interpolated by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, N.C., from available SAROAD monitoring sites (U.S. Environmental Protection Agency, 1983). Percentage reductions in crop yield were calculated against a base (assumed background) ozone level of 0.025 ppm ambient concentration. The basis for these calculated reductions is NCLAN and other data cited in Heck et al. (1982).

Shriner et al. converted physical reduction in county production for each crop to dollar loss by multiplying this production by the county-level price. For the United States, the aggregate loss (difference between value of production at ambient levels and value of production at 0.025 ppm) was estimated to be approximately $3 billion. Both this study and the updated SRI study have conceptual problems concerning the structure of the economic problem and extrapolation of biological data from relatively few sites and cultivars.

Another estimate of nationwide damages was developed by Adams and Crocker (1982b). They used information on O_3 effects as a surrogate for the effects of acid deposition on agricultural systems. The primary aim of this approach was to determine the sensitivity of economic loss to additional information on dose-response relationships. However, the analysis also leads to an estimate of O_3 damage to three crops representing about 60 percent of the value of U.S. crop output (corn for grain, soybean, and cotton). The authors noted that their numerical example, is plausible; however, when it is measured against the gross value of these crops, the result is highly conditional given the uncertainties associated with the biological and air quality data used to derive the national production effects.

In developing their estimates, Adams and Crocker used O_3 dose-response functions derived from NCLAN results (Heck et al., 1982). They directly estimated farm-level demand and supply relationships. Demand was assumed to be a linear function, and farm-level price depended on quantity consumed and per capita income. Quantity supplied was assumed to be a function of prices of the same and competing commoditites in the preceding time period. The response data, combined with the demand and supply structure of the commodity markets in question, were used to estimate the benefits (economic surplus) of progressively more stringent control schemes. The estimated economic consequences of the difference between ambient ozone levels associated with the 1979 national ambient air quality standard of 0.12 ppm (not to be exceeded more than 1 day/yr) and a hypothetical standard of 0.08 ppm (assuming that all areas of the United States just met the 0.12 ppm standard) was approximately $2.2 billion. Specifically, by using a log-normal distribution of ozone concentrations, the authors assumed that a 7-hr seasonal mean ozone level of 0.04 ppm was approximately equivalent to an ambient level that would just comply with a federal standard of 0.08 ppm (second hourly maximum). This correspondence between a seasonal 7-hr average and a second hourly maximum (federal standard) is drawn from Heck et al. (1982a).

These estimates of benefits from decreasing ambient ozone levels are conditional on the assumed log-normal distribution of ozone events and the assumption that all regions would not exceed that level. The analysis assumes that O_3 levels with each standard are uniform across all crop-production areas. If the actual concentrations are lower in most agricultural areas, then the benefits accruing to the meeting of national standards would be overstated. Improved data on O_3 concentrations within growing areas, more complete economic modeling of producer behavior, and resolution of the uncertainties associated with the simple dose-response functions are needed to reduce potential errors in the economic estimates generated from this type of assessment.

7.5.4 An Overview of Current Loss Assessments

The ability to assess O_3 damage to agricultural crops has been enhanced by recent improvements in dose-response measurements and air quality data. As Section 7.2.5 of this document indicates, the plant science literature contains dose-response functions (where response is measured in yield) for many major agricultural commodities, primarily as a result of the NCLAN program. While

cultivar coverage remains sparse for some crops and important edaphic-climatic interactions are superficially addressed, these simple dose-response relationships are superior to the data underlying loss estimates reported in the 1978 criteria document (U.S. Environmental Protection Agency, 1978). In addition, air quality data for rural areas are slowly improving as monitoring expands. Interpolative procedures, as used by Shriner et al. (1982), might fill existing gaps in air quality data. However, much of the improved information postdates the economic assessments found in current literature.

This review of recent agricultural assessment efforts indicates that increased applications of techniques are consistent with economic theory. Consequently, they produce more defensible estimates of economic benefits. This same review, however, indicates that treatment of some economic issues is still incomplete. These deficiencies include the need to account for input and output substitution effects through time and across regions, the need to measure damages to perennial crops (fruits, nuts, and timber), and the need to account for other long-term and dynamic adjustments to chronic pollution effects, such as interactions between insect and disease injury and O_3 as well as interactions between crop inputs (pesticides and fertilizer) and O_3. Researchers should also assess the link between intermediate products and final products (e.g., the relationship between feed grains and livestock production) and the problems of evaluating economic damages to nonmarketed plants (e.g., as manifested through aesthetic effects on forest ecosystems).

Additional technical issues require resolution before economic assessments can be meaningfully compared. As noted earlier, the appropriate measure of dose is an important issue. While the current NCLAN experimental design uses the seasonal 7-hr mean concentration, other dose measurements may better characterize plant response. The use of standard dose measurements would ease comparisons across studies. Further, the validity of extrapolating site-specific response data across regions is not resolved. Another important issue concerns the definition of background (clean air) O_3 levels. The air quality literature does not present a consensus on the relative importance of biogenic, anthropogenic, and stratospheric sources in rural areas.

The most recent estimates of national damage (Table 7-32) exceed those found in the 1978 criteria document on oxidants. Two of these recent studies employ the simple traditional approach; therefore, their increase in damage estimates is largely caused by the increased crop coverage, somewhat greater

recognition of effects as reported in the recent literature, different quality assumptions, and the use of different base-dollars (i.e., 1980 dollars vs. 1970 dollars). As a percentage of total crop value, the loss estimates range from 4 to 6 percent. This range is comparable with estimates of crop losses from sources such as those reported in Boyer (1982) but far less than the $25 billion annual loss attributed by the U.S. Department of Agriculture (1965) to insect and disease damage.

In conclusion, the current dollar estimates of crop damage are useful primarily as indicators of magnitudes. A full accounting of the economic mechanisms underlying agricultural production is required to provide definitive estimates of the extent of agricultural losses. Ideally, such an accounting must address both annual and perennial crops (agronomic and horticultural) and the associated dynamic adjustments of agricultural production. The effects on intermediate consumers (such as livestock growers and food processors) and final consumers (both domestic and foreign) must also be addressed. The physical and economic effects of O_3 on ornamentals have not been addressed. Also, improved rural air quality data and procedures for obtaining regionally averaged yield responses are needed. None of the literature citations in this section meets all the criteria of an ideal bioeconomic assessment, and all give some misrepresentation to economic importance.

7.6 MODE OF PEROXYACETYL NITRATE (PAN) ACTION ON PLANTS

The sequence of events inducing vascular plant response to PAN is essentially identical to that described for O_3 (Section 7.3). PAN enters the leaf tissue through open stomata and dissolves in the aqueous layer surrounding the substomatal chamber (Figure 7-1). Hill (1971) reported that PAN was relatively insoluble and the rate of absorption by an alfalfa canopy was approximately one-half that for O_3. The absorption rate depends upon the plant's ability to metabolize, translocate, or otherwise remove the active pollutant species from the absorbing solution, as well as on the solubility of PAN. Thus, the flux of PAN into the inner leaf tissues is influenced by many physical, biochemical, and physiological factors. The equation used to describe O_3 flux (Section 7.3) also can be directly applied to describe the flux of PAN into the leaf.

PAN is highly unstable, and if it comes in contact with an aqueous solution, breakdown occurs rapidly (Mudd, 1975). According to Nicksic et al. (1967) and Stephens (1967), the breakdown of PAN in aqueous solution yields acetate, nitrite, oxygen, and water. The pathway of PAN absorption and reaction within the leaf tissue is not adequately described to explain why cells at a specific stage of physiological development are highly susceptible while adjacent cells are relatively tolerant. The magnitude of PAN injury is influenced by the stage of tissue development, succulence of the tissues, and conditions of the macro- and microclimate. Injury is manifested in several ways. The most evident injury is necrosis of rather specific areas of the lower and upper leaf surfaces. This characteristic symptom expression may be accompanied by leaf distortion, premature senescence, and defoliation (Taylor, 1969). Experimental evidence shows that yield may be suppressed in the absence of visible injury symptoms (Thompson and Kats, 1975; Temple, 1982). PAN-type symptoms have been reported from California, the eastern United States, Canada, Japan, and the Netherlands (Table 7-33). The smog, photochemical smog, or oxidant injury symptoms described by Middleton et al. (1950), Went (1955), and by other researchers working with polluted ambient air in California preceding about 1960 were identical to injury symptoms subsequently produced with synthesized PAN (Taylor et al., 1961; Taylor, 1969). Frequently, the injury symptoms are sufficient to significantly reduce quality of leafy vegetables and ornamental crops, but they are seldom associated with suppressed growth or yield.

The phytotoxicity of PAN and processes of injury development will be discussed in the following sections. The discussion will be limited to PAN, the most common member of a series of homologs that increase in phytotoxicity with molecular weight. Many of the biochemical and physiological studies with PAN and its homologs were conducted with concentrations that exceed those encountered in ambient air. However, the studies were conducted to identify responses that might be more difficult to detect at lower concentrations. For unknown reasons, most vegetation grown in glasshouses and growth chambers is considerably less sensitive to synthesized PAN than comparable plants grown and exposed to PAN and the total pollutant complex found in the field (Taylor, 1969).

7.6.1 Biochemical and Physiological Responses to PAN

As with O_3 (Section 7.3.1), the phytotoxic effects of PAN occur only when a sufficient amount of the gas diffuses into susceptible regions of the leaf

TABLE 7-33. GEOGRAPHIC OCCURRENCE OF PAN (OXIDANT) INJURY ON PLANTS

Area	Species injured	Reference
California[a]		Middleton and Haagen-Smit (1961)
	Bean spinach, Romaine lettuce	
Washington		
Missouri		
Illinois		
Colorado		
Utah	Oat, petunia, tomato, Swiss chard, sugar beet	Tingey and Hill (1967)
Baltimore, MD	Tobacco	Went (1955)
Philadelphia, PA	Garden plants	
New York City, NY		
The Netherlands[a]	Little-leaf nettle, petunia, annual bluegrass	Floor and Posthumus (1977)
Japan[a]	Various species	Fukuda and Terakado (1974)
	Spinach, French bean, lettuce	Sawada et al. (1974)
Canada	Tomato	Pearson et al. (1974)

[a]Monitoring data for PAN in southern California, the Netherlands, and Japan were available to corroborate the reports of PAN-type symptoms observed in those areas.

interior and encounters the plasmalemma or passes into the liquid phase of the cells. Once deposited on the wet cell surface, the gas will begin to break down and the degradation products and/or PAN molecules will move by diffusion or bulk flow to sites of action (Mudd, 1975). The target sites may include the cell membrane, chloroplast, cytoplasm, and various cell organelles.

7.6.1.1 Gas-Phase Movement into the Leaf. The primary entry port for PAN into leaf tissue is through open stomata. As indicated in Section 7.3.1.1, the influence of O_3 on stomatal movement has received considerable attention, but relatively little effort has been made to determine if PAN will also induce stomatal closure. Starkey et al. (1981) reported that a PAN-susceptible variety of bean, exposed to 80 ppb PAN for 0.5 hr, developed drought stress symptoms, but a tolerant variety showed no effect. This finding suggests that PAN may have stimulated stomatal opening to allow a greater rate of transpiration. Metzler and Pell (1980) found that pinto bean plants exposed to subthreshold levels of PAN (54 ppb for 1 hr) developed no macroscopic injury and showed no effects on stomatal conductance. At the injury threshold (70 ppb for 1 hr) and above, abaxial glazing developed and stomatal conductance increased. Temple (1982) observed no effects on stomatal conductance at concentrations of 25 and 50 ppb PAN after tomato leaves were exposed for 2 hr. In this study, 0.20 ppm O_3, in combination with the two concentrations of PAN, did suppress stomatal conductance when tomato plants were exposed for 2 hr.

The size of stomatal pores and number of stomata per unit area of leaf vary greatly according to plant species. Many plants have stomata in both surfaces of the leaf, whereas others have stomata only in the lower surface. As a general rule, stomata occur in larger numbers per leaf area near the apex of the leaf and become less numerous toward the base of the leaf. Although plants shown to be most susceptible to PAN are among those that have stomata in both leaf surfaces, no correlation between susceptibility and number or size of stomata has been demonstrated.

7.6.1.2 Biochemical and Physiological Responses. PAN is a highly specific phytotoxic agent that attacks leaf tissue at a fairly specific stage of physiological development and is most injurious to succulent, rapidly expanding tissues of herbaceous foliage (Noble, 1955; Taylor and MacLean, 1970). Concentrations of 14 to 15 ppb (maximum) under field conditions have been observed to produce PAN-type injury on susceptible crops (Taylor, 1969; Temple, 1982). Fukuda and Terakado (1974) reported that petunia plants under field conditions

developed silvering and bronzing on the lower leaf surface when the maximum PAN concentrations ranged from 3.0 to 6.7 ppb. The most serious observed damage occurred when a PAN concentration of more than 5 ppb continued for 7 hr. Because PAN is phytotoxic at very low concentrations, Mudd (1963) concluded that the most likely target in plant cells must be some enzyme system. Much of the early work with enzymes involved the use of relatively high PAN concentrations to demonstrate reactive sites in the metabolic pathways.

Ordin (1962) observed that growth of oat coleoptile sections, which involved cell expansion rather than initiation of new cells, was inhibited by PAN. He found that fumigation with 1.1 ppm PAN for 6 hr resulted in 32 percent inhibition of growth and 45 percent inhibition of glucose absorption from the solution. Fumigations were accomplished by floating the oat coleoptiles in a solution and bubbling PAN through the solution. There was no way to determine how much PAN the coleoptiles actually encountered. The response suggested that PAN interfered with metabolism of cell wall sugars. Subsequently, Ordin and Hall (1967) found that cellulose synthetase was inhibited, and Ordin et al. (1967) reported that the enzyme phosphoglucomutase was inhibited when coleoptile tissue was exposed to PAN. The treatment consisted of bubbling 50 ppm PAN for 4 hr at a rate of 400 ml/min through 100 ml of solution in which the coleoptiles were floating.

Using in vitro procedures, Mudd and Dugger (1963) showed that PAN oxidized NADH and NADPH. Mudd (1966) and Mudd et al. (1966) found that enzymes with free-SH groups were inactivated, but enzymes with no free SH groups were resistant to PAN. The amount of PAN used in these studies was not reported. Hanson and Stewart (1970) observed that exposure to 50 ppb PAN for 1 to 4 hr inhibited mobilization of starch in darkness, implying that the phosphorylase reaction was inhibited. Such a response could seriously interfere with photosynthate partitioning and inhibit growth and development. The reaction deserves further investigation.

Thomson et al. (1965) showed that PAN (1000 ppb for 30 min) or its degradation products caused crystallization and other disruptions in the chloroplast stroma that were similar to the effects of dessication. These observations suggest that PAN affected the permeability of the chloroplast membrane in much the same way as its reaction with the plasmalemma, which allowed leakage of cell contents.

PAN enters leaf tissue through open stomata and is rapidly dissolved in the aqueous covering of substomatal cells. PAN and its degradation products are transported through the cell wall and cell membrane into the aqueous cell contents. Permeability of the cell membrane is disrupted, thus allowing leakage into the intercellular spaces. Similarly, permeability of the chloroplast membrane is disrupted, thereby inducing plasmolytic-type characteristics to develop. PAN inactivates enzymes containing sulfhydryl groups. Visible injury from PAN results when mesophyll cells are killed and shrink causing dessication and death of the epidermal tissue. A degree of chlorosis is often visible on the upper leaf surface as the chloroplasts in living cells are destroyed.

The destruction of chloroplasts (Thomson, 1965) and disruption of biochemical and physiological systems (Ordin and Hall, 1967; Ordin et al., 1967; Mudd, 1966; Hanson and Stewart, 1970) can be expected to adversely affect growth and yield as well as the aesthetic qualities of the vegetation. Inactivation of enzymes can suppress growth, as demonstrated with oat coleoptiles, and may interfere with photosynthate, as demonstrated by inhibition of starch mobilization in the dark, and interfere with other metabolic processes.

7.6.2 Factors that Modify Plant Response to PAN

Plant response to PAN and many other environmental stresses is conditioned by complex, interacting internal and external factors (U.S. Environmental Protection Agency, 1978). External physical factors such as temperature, light conditions, humidity, and edaphic factors can influence plant response to PAN. Similarly, biological variables such as genetic differences, physiological stage of tissue development, and rate of plant growth can affect plant response.

7.6.2.1 Biological Factors. Trees and other woody species are apparently quite resistant to foliar injury from PAN (Davis, 1975; Davis, 1977; Taylor, 1969). Foliar injury has been produced only once or twice by fumigations with extremely high concentrations of PAN (1 ppm for several hours), and injury to these species in the field has not been reported. Variations in susceptibility to PAN within herbaceous species have been observed in the field and have been demonstrated for some crops with synthesized PAN.

Genetically controlled variation in response to PAN has been observed under field conditions and has been verified by controlled fumigations. Drummond (1972) exposed 28 F_1 varieties of petunia plants to 150 ppb PAN for

1 hr and found highly significant differences in susceptibility. Feder et al. (1969) used six varieties of petunia that are common in the Boston area to determine the genetic variation in susceptibility to PAN injury. Exposures were for 1 hr to concentrations of 120, 250, and 500 ppb. High concentrations were used to ensure that all varieties developed some injury. Feder et al. found that the types of petunia varied significantly in their response to PAN. They concluded that a variety that was resistant to one pollutant was also resistant to other pollutants. Studies by Hanson et al. (1976) showed that petunia varieties that are susceptible to PAN were not necessarily susceptible to ozone. Their studies were conducted with ambient air at Arcadia, California, using characteristic leaf injury symptoms to determine susceptibility. Fumigations with synthesized PAN using concentrations of 86 and 120 ppb and combinations of exposure periods of 1, 1.5, 2, and 2.5 hr were conducted to verify results from the ambient air studies. The objective of the study was to determine the relative susceptibility of 49 siblings from a complete diallel cross of seven commercial inbred lines of pink flowered petunia. DeVos et al. (1980) used inbred parents of White Cascade, a susceptible F_1 hybrid, and Coral Magic, a resistant hybrid, to study inheritance of PAN resistance. Plants were exposed to 150 ppb PAN for 1.5 hr in controlled environment chambers. Significant genetic variation was detected, but there was large genotype-by-environment interaction. Starkey et al. (1976) exposed 10 varieties of bean for 2 hr to 120 or 150 ppb PAN to observe the injury symptomology and determine varietal susceptibility.

Middleton et al. (1950) first described smog injury (PAN type) and listed endive, lettuce, romaine lettuce, and spinach as extremely susceptible, whereas carrot and members of the cabbage and melon family were tolerant or resistant. This general ranking of susceptibility is still acceptable for PAN. Specific varieties of petunia, bean, Swiss chard, oats, and cos lettuce have been selected, because of their susceptibility, for controlled fumigation studies. Tomato was originally listed as only slightly susceptible to smog, but it is now known that many varieties are highly susceptible.

Sensitive plants show a characteristic pattern of injury when they are exposed to PAN. The pattern described from field observations in Los Angeles County, California, by Noble (1955), Juhren et al. (1957), and Glater et al. (1962) indicates that leaves of different ages show damage in different positions. A similar description of PAN injury confirms that susceptibility is

related to specific physiological stage and foliage development (Taylor, 1969; Taylor and MacLean, 1970; Noble, 1955; and Glater et al., 1962), but the causal factors involved in this selective sensitivity phenomenon have not been identified.

7.6.2.2 Physical Factors. The light-exposure regime to which plants are subjected before, during, and after exposure to phytotoxic concentrations of PAN will significantly affect response (Taylor et al., 1961). Brief dark periods preceding exposure and immediately following exposure can reduce or even prevent the development of visible symptoms of injury. Maximum injury occurs when plants are exposed in full sunlight. Dugger et al. (1963) determined that the maximum quantum responsivity to PAN occurred in the 420 to 480 nm range. There was no evidence to indicate participation of chlorophylls or phytochrome in the sensitization phenomenon.

Juhren et al. (1957) found that plants were most susceptible to oxidant injury (PAN-type symptoms) when grown under 8 hr photoperiods, and injury decreased with photoperiods of 12 to 16 hr. This observation may help to explain why symptoms of PAN injury are most prominant in late fall, winter, and spring in southern California. Juhren also found that the greatest oxidant injury occurred at 25° to 20°C day/night temperatures. The oxidant injury symptoms described by Juhren et al. (1957), Middleton and Haagen-Smit (1961), Middleton et al. (1950), and others during the period from 1951 to 1961 were identical with those later shown to be induced by PAN.

The effects of relative humidity, air temperature, and edaphic factors have not been investigated extensively, but some observations have been reported. There is no cohesive evidence relative to the significance of relative humidity and plant susceptibility, but PAN injury to vegetation in the South Coast Air Basin of California occurs most frequently when relative humidity is 50 percent or above (Taylor, 1974).

Field observations in southern California, where irrigation is essential for crop production, revealed that crops growing under soil moisture deficits developed few or no O_3 or PAN-type injury symptoms during a severe smog attack, while adjacent, recently irrigated crops were severely injured (Taylor, 1974). Similarly, the author observed increased tolerance of beans and tobacco to O_3 and PAN when potted test plants were inadvertently allowed to wilt briefly during the day preceding fumigation, even though the plants were watered several hours before treatment and appeared to be normal. Oertli (1959) reported

increased tolerance of sunflower plants to oxidant air pollutants (PAN-type symptoms) with increasing salinity and soil moisture stress.

Very little information is available on the effects of nutrition on plant response to PAN. The few available reports are contradictive; they suggest that injury may be enhanced by addition of nitrogen when it is deficient but a luxury amount may not increase injury and may even suppress it (Taylor, 1974).

7.6.2.3 Chemical Factors. The effectiveness of chemical additives applied for pest control and specifically for the prevention of oxidant air pollutant injury has been studied by Freebairn and Taylor (1960), Pell (1976), Pell and Gardner (1975), and Pell and Gardner (1979). These studies were made to determine if cultural practices could be modified to mediate the effects of PAN and other oxidant air pollutants. None of the chemical treatments have been sufficiently effective in preventing or reducing PAN injury to encourage general grower use.

Phytotoxicants seldom occur alone in the atmosphere; consequently, interactions may occur to enhance or suppress the development of vegetation injury. A synergistic response from nitrogen oxides, O_3, and PAN in combination could significantly increase plant response.

7.6.2.3.1 Pollutant interactions. Although O_3 was identified as a major chemical component of the photochemical oxidant complex in the 1950's, its importance as a phytotoxicant was not recognized before the 1960's. Descriptions of injury symptoms observed in the field were identical to those subsequently produced by fumigations with PAN. The fumigations conducted before 1960 used reaction products of O_3 and hydrocarbons in an attempt to reproduce the PAN type injury symptoms. PAN is rarely present by itself in the photochemically polluted atmosphere (Oshima et al., 1974; Penkett et al., 1977). However, PAN is almost always present when O_3 occurs; the ratio of O_3 to PAN in southern California has been reported to be about 10:1 (Taylor, 1969), and at Calgary the ratio was reported to vary according to atmospheric conditions (Peake and Sandhu, 1983). Conversely, PAN is about 10 times more phytotoxic than O_3 (Taylor and MacLean, 1970; Pell, 1976; Darley et al., 1963).

Interactions involving plant exposure to mixtures of PAN and O_3 in polluted atmospheres probably occur, but the few published reports of controlled PAN + O_3 interaction studies with plants have shown variable and inconsistent effects on symptom type and intensity of injury. Kohut et al. (1976) found O_3 (0.18 ppm) + PAN (180 ppb) treatments for 4 hr in midday produced O_3-type

symptoms on hybrid poplar seedlings, but the amount of injury was highly variable. Davis (1977) found that ponderosa pine seedlings that were exposed to an O_3 (0.40 ppm) + PAN (200 ppb) combination for 4 hr developed significantly less injury than those exposed to O_3 alone. Kohut and Davis (1978) reported greater-than-additive O_3-type injury on bean leaves exposed to the O_3 (0.30 ppm) + PAN (50 ppb) combination for 4 hr, but PAN injury was almost completely suppressed. In a study of the protective effects of benomyl on bean plants exposed to 0.25 ppm O_3 and 150 ppb PAN for 3 hr, Pell (1976) found that the combination of O_3 and PAN produced more injury than PAN alone.

Posthumus (1977) exposed little-leaf nettle and annual bluegrass to O_3 (0.17 ppm) and PAN (50 ppb) singly and in combination for 2 hr in either the morning or afternoon. The combination induced more foliar injury in the morning than in the afternoon. However, there was no clear increase or decrease in the foliar injury in the plants exposed to the combination compared to the injury from the single gases. More recent studies with little-leaf nettle (Tonneijck, 1984) show that no interaction between O_3 and PAN was detected when both were applied at their respective injury threshold concentrations. However, the pollutant combination caused less than additive injury when the PAN concentration exceeded the injury threshold concentration. Matsushima (1971) reported additive or less than additive injury from combinations of PAN and sulfur dioxide. Nouchi et al. (1984) exposed petunia and bean plants for 4 hr to mixtures of O_3 and PAN to assess effects on visible symptoms of injury. Ozone concentrations for the petunia study were 0, 0.10, 0.20, 0.30, and 0.40 ppm and PAN concentrations were 0, 10, 20, 30, and 40 ppb. In the bean study, O_3 concentrations were 0, 0.15, 0.20, 0.30, and 0.40 ppm, and PAN concentrations were 0, 30, 45, 65, 85, and 100 ppb. For PAN alone, injury symptoms appeared on petunia at 20 ppb PAN, and with bean, injury appeared at 30 ppb PAN. The percent of foliar injury was greatest when plants were exposed to PAN alone, and the percent injury decreased as the O_3 concentration increased. Temple (1982) found that the response of four varieties of tomato plants to PAN-O_3 mixtures was variable. He exposed the plants to a combination of 0, 25, and 50 ppb PAN and 0, 0.10, and 0.20 ppm O_3 for 4 hr once a week for 3 weeks.

7.6.2.3.2 Chemical sprays and nutrients. Reports in the early literature indicated that efforts were made to find chemicals that would prevent or reduce foliage injury induced by the photochemical oxidant air pollutants

(Section 7.3.2.3.2). The experiments included dust or spray applications to the foliage and applications through the soil. In most of these studies, no differentiation was made between O_3- and PAN-type symptoms.

Chemicals tested for effectiveness in controlling "oxidant" injury included various formulations of ascorbic acid (vitamin C); several types of carbamate fungicides; benomyl; and ethylene diurea. None of these treatments consistently protected vegetation used in the tests to the extent that they could be used commercially. Benomyl showed some promise as a protectant in earlier studies, but results were variable. Pell (1976) found that use of benomyl as a soil treatment did not protect the primary leaves of pinto bean from PAN injury, and at some concentrations it may have stimulated injury. The plants were exposed to 150 ppb PAN or to 150 ppb PAN and 0.25 ppm O_3 for 3 hr. In subsequent studies, Pell and Gardner (1979) found that soil drenched with benomyl increased PAN injury on petunia plants, and the most PAN-sensitive variety exposed to 150 ppb PAN for 1.5 hr was particularly affected.

Imbalance of available plant nutrients has been suggested as a factor that may influence plant response to some air pollutants. No studies have been made to investigate the importance of this factor to PAN injury. However, general observations in the field and in controlled experiments have indicated that PAN injury is enhanced by all physical and chemical factors that promote optimum plant growth.

Plant response to PAN is influenced by light quality, intensity, and timing relative to PAN exposure. However, chlorophylls and phytochrome do not appear to participate in the sensitization process. Air temperature, photoperiod, and water potential in the foliage can influence response to PAN.

Woody perennials are much less sensitive to PAN than are the succulent herbaceous species. Sensitivity of varieties within a plant species is genetically controlled, but the genetic process through which the differential sensitivity occurs has not been identified.

PAN may interact with other air pollutants, particularly O_3, to enhance phytotoxicity, but the experimental results are variable. Chemical additives that are applied to the foliage and through the soil have provided variable results as protectants from PAN. Some may even enhance sensitivity. Plant nutrient balance and soil moisture conditions that are optimum for growth and development also are usually optimum for PAN sensitivity.

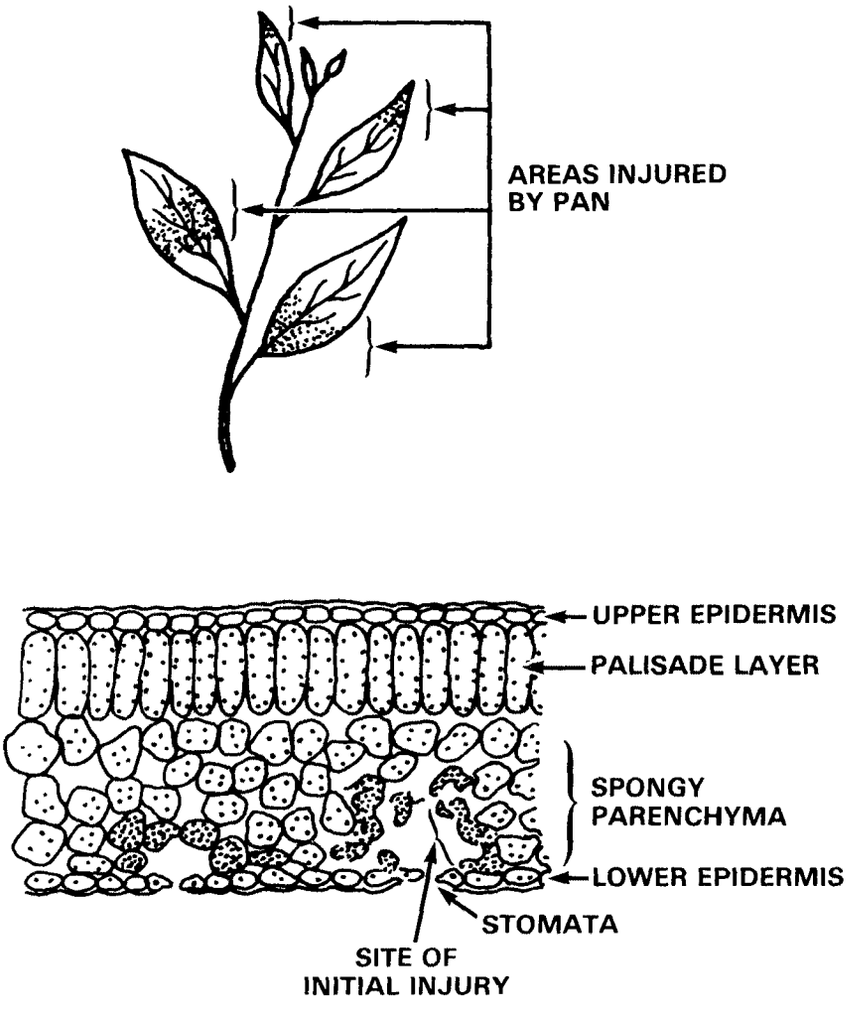

Figure 7-16. PAN injury. Note position effect with age of leaf. On sectioning, initial collapse is in the region of a stomata.

Source: Brandt (1962).

7.7 PAN EXPOSURE AND RESPONSE

Initial PAN-injury symptoms, which fully develop during the 24 to 72 hr following exposure, are a glazed, bronzed, or metallic sheen on the lower (abaxial) leaf surface. These symptoms are identical to those described on five garden species exposed to gaseous air pollutants in the Los Angeles area, (Middleton et al., 1950). The oxidant or PAN symptoms were clearly distinct from those produced by O_3, which typically caused upper surface necrotic stipple or fleck chlorosis or bifacial necrosis on susceptible species (Temple, 1982). Transverse bands of bleached, necrotic tissue and glaze and bronze on the lower surface (Noble, 1955) are characteristic of the PAN injury syndrome (Taylor, 1969). Most sensitive plant species develop diffuse transverse bands of injury in regions where the tissue is in identical stages of physiological development (Figure 7-16). This phenomenon results in injury at the apex of the youngest susceptible leaf and at regions nearer the base of the next successively older three or four leaves. Exposure on successive days results in a series of two or more injured bands separated by bands of healthy tissue, demonstrating that the stage of high susceptibility lasts for only a relatively short period (Noble, 1965). Some leaves, such as the two primary leaves on bean plants, do not develop the bands; the injury may be distributed at random or as a solid cover over the entire lower surface.

Ordin and Propst (1962) demonstrated that the auxin IAA in oat coleoptiles was completely inactivated when 1.3 ppm PAN was passed through the solution in which they were suspended for 3 hr. Similarly, enzyme activity was inhibited by exposures to 1 ppm PAN for 1 hr (Ordin et al., 1971) and to 125 ppm for 6 min (Mudd, 1963). Thomson et al. (1965) found that exposure to 1 ppm PAN for 30 min damaged leaves of pinto bean, and chloroplasts were markedly altered as the damage developed. The cell membranes were disrupted and the cell contents clumped together in a large mass. Dugger et al. (1965) reported that PAN inhibited ATP and NADPH formation and the fixation of $C^{14}O_2$, thus inhibiting the photosynthesis of carbohydrates. These biochemical and physiological studies were conducted with high concentrations of PAN (1 ppm and above) which far exceed those found in the atmosphere, but they demonstrate that reactions essential for plant growth and development may be inhibited.

The response of plants to PAN was summarized in Chapter 11 of the criteria document for photochemical oxidants published in 1978 (U.S. Environmental Protection Agency, 1978). Figure 7-17 graphically presents the estimated

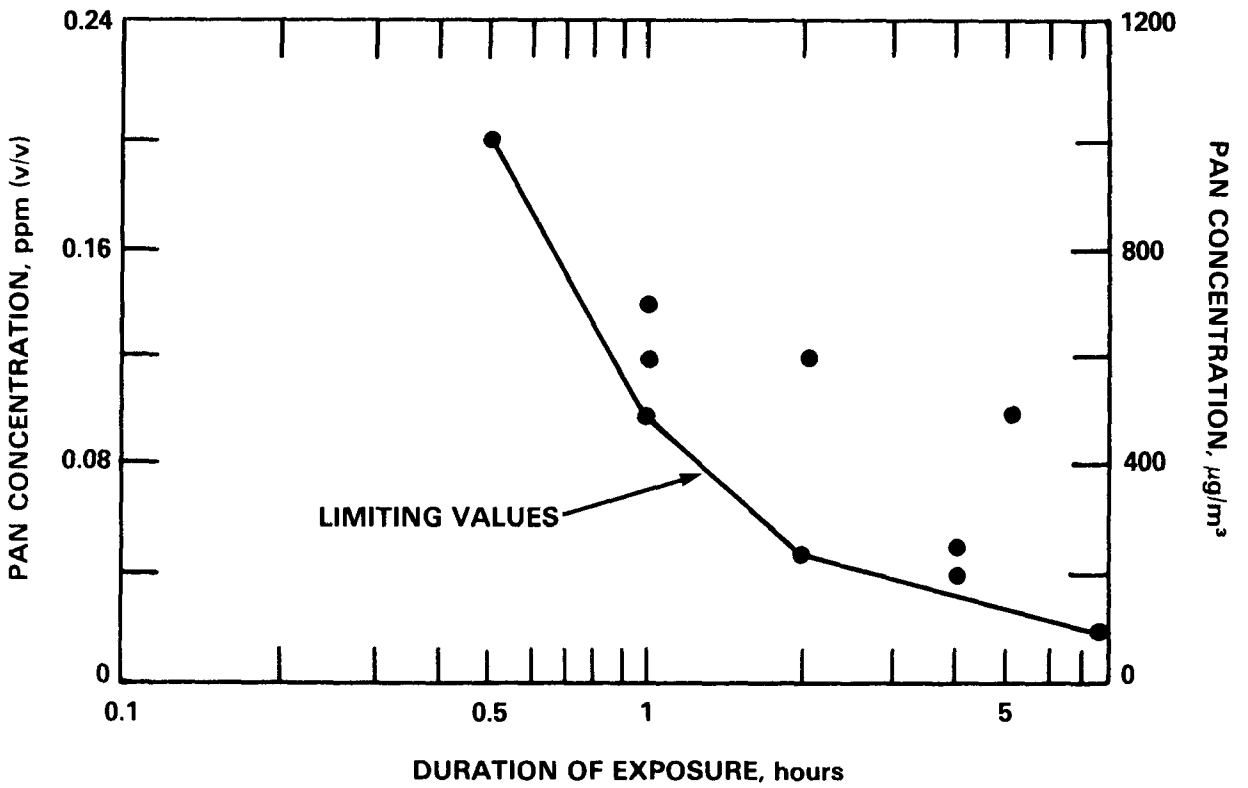

Figure 7-17. Dose-response relationships and limiting values for foliar injury to vegetation by peroxyacetylnitrate (PAN).

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

limiting values for PAN injury as calculated by Jacobson (1977) and presented by the U.S. Environmental Protection Agency (1978). Susceptible plants exposed to doses in the region above and to the right of the data points have a low risk for development of visible injury symptoms. Those plants exposed to doses to the left and below the data points are at greater risk of developing injury symptoms. This illustration was based on a limited amount of information and the data were produced by controlled fumigation with synthesized PAN. Plants growing and exposed under ambient field conditions may be at greater risk than indicated by the illustration. This chapter indicates that PAN is one member of a family of highly phytotoxic, gaseous compounds in the photochemical oxidant complex. Acute responses of plants to O_3 and PAN result from disruption of normal cell structure and processes. The biochemical and physiological effects of PAN are less understood than those for O_3. Plant growth and yield response to PAN exposure was recognized in Chapter 11 of the previous criteria document (U.S. Environmental Protection Agency, 1978), but this response was associated with visible injury symptoms. The concept of limiting values (i.e., those concentrations below which foliar injury and, presumably, reduced growth and yield would not occur) was used to illustrate potentially harmful exposures. The range of limiting values for PAN was

100 $\mu g/m^3$ (200 ppb) for 0.5 hr
500 $\mu g/m^3$ (100 ppb) for 1 hr
175 $\mu g/m^3$ (35 ppb) for 4 hr

Studies using little-leaf nettle showed the limiting values proposed by Jacobson (1977) were insufficient to protect that species from PAN injury (Tonneijck, 1984). In this species the limiting values would need to be reduced 30 to 40 percent to prevent foliar injury.

Physical and biological factors involved in visible injury development and the studies of biochemical and physiological responses produced by PAN exposure were discussed briefly in the 1978 criteria document for oxidant air pollutants (U.S. Environmental Protection Agency, 1978). However, primarily because of the deficiency of supporting experimental data, the potential for growth and yield responses to intermittent PAN exposures was not discussed.

While the deficiency of supporting data for growth and yield response to PAN exposures, the intent in this revision of the criteria document is to emphasize yield and growth effects with and without extensive visible symptom

development. This section focuses on yield loss as described in Section 7.2. Foliar injury is an important factor as a bioindicator (see Section 7.7.1) and as a yield loss factor reported periodically in southern California during the past 30 years.

7.7.1 Bioindicators of PAN Exposure

Foliar injury symptoms frequently seriously reduce market value and in some instances render the product unmarketable. These symptoms also may destroy a significant amount of photosynthetically active leaf tissue. The injury symptom syndrome can serve as a very important indicator that damaging PAN exposures have occurred, and the effect may be considerably greater than the actual tissue destruction observed.

The concept of using bioindicators to assess the impact of air pollutants and the methodology involved are presented in Section 7.4.1. The PAN injury symptoms that are most useful in field diagnosis are the diffuse transverse bands of injury, which may be visible only on the lower leaf surface or on both surfaces, and the glazing, silvering, bronzing, and/or metallic sheen on the lower leaf surface. Recognition of PAN injury in the field is not always a simple process because a type of lower leaf surface glaze and bronze may be produced by other factors such as cold temperatures, insects (mites), and other air pollutants: O_3, hydrochloric acid (HCl), SO_2, hydrofluoric acid (HF)). In making field assessments, it is important that the observer know the relative susceptibility of the crop and the native and ornamental species in the area and that as many different species as possible be examined.

Noble (1965) reported on a 6-year study in southern California designed to use plant indicators to identify injury induced by air pollutants. He used six agricultural crops and two weed species widely distributed in the area. The study revealed that annual blue grass (meadowgrass) was a very good indicator for PAN. Posthumus (1977) found that little-leaf nettle and annual bluegrass developed characteristic PAN-type injury symptoms when exposed to about 50 ppb PAN, and he suggested that these wild species might be accurate indicators. Sawada et al. (1974) used 16 plant species in a survey for O_3 and PAN injury and observed PAN injury on 28 percent of the 138 plants used in the study.

Field surveys in southwestern Ontario, Canada (Pearson et al., 1974) revealed PAN-type injury symptoms on tomato crops. On the basis of these

symptoms and the meteorological conditions that occurred during their development, the authors concluded that the air pollutants probably originated in the Cleveland area. Bioindicators should be used cautiously when monitoring data are not available as verification and when observations are made on a single plant species. Lewis and Brennan (1978) reported PAN-type injury on petunia leaves exposed to mixtures of O_3 and SO_2. Wood and Drummond (1974) suggested that PAN-type injury may be caused by interactions of PAN and other phytotoxicants or perhaps by a single pollutant such as HCl.

Field observations and diagnosis provide an important means of determining if a PAN problem exists and they give some indication of its importance. PAN can be measured chromatographically, but the instrument can be calibrated only with known concentrations of PAN. The problems associated with its synthesis, dilution, and measurement of the calibration gases has discouraged the establishment of monitors for long-term use. Plant-damaging exposures of PAN can be verified with monitoring instrumentation in only a very few locations. Therefore, the ability to recognize and evaluate PAN injury symptoms in the field is very important. PAN is produced in the same photochemical process as O_3, and at locations where both are monitored continuously. With very few brief exceptions, they occur simultaneously in oxidant-polluted atmosphere.

PAN-type oxidant foliar injury has been reported in more than half of the counties in California, in several states, and in several foreign countries. Went (1955) reported PAN-type injury in some European and South American cities as well as in several cities in the eastern United States. Locations at which PAN injury was observed on vegetation in the United States are presented in Table 7-33.

Bioindicators have been used successfully to show that phytotoxic levels of PAN have occurred. In addition to observations for the presence of a syndrome of injury symptoms, it may be necessary to observe a plant community that contains both susceptible and tolerant species. Researchers have cautioned that injury symptoms that resemble those attributed to PAN can be produced by other pollutants and by certain adverse environmental conditions.

7.7.2 Nonvascular Plant Response to PAN Exposure

Gross and Dugger (1969) examined the effects of PAN on algae (Chlamydomonas reinhardtii) by measuring growth, photosynthesis, respiration, and pigment content of the cells. PAN was bubbled through a liquid medium containing the

algal cells, and treatment usually lasted for several minutes. The gaseous mixture usually contained an average PAN concentration of 125 ppm in nitrogen (N_2), and treatment dose was expressed in nanomoles. Exposures ranged from 20 nanomoles to 250 nanomoles. The study results indicated that both autotrophic and heterotrophic growth was inhibited, photosynthesis and respiration were adversely affected, and photosynthesis was more severely affected than respiration. The results also indicated that carotenoids were destroyed and that there was destruction of both chlorophylls, although chlorophyll a was more stable than chlorophyll b. Gross and Dugger (1969) also reported that PAN lowered the free sulfhydryl content of the cells.

Field studies of the lichen populations in the southern California mountains indicated trends in community parameters that inferred that oxidant air pollutants had a deleterious effect on lichens (Sigal and Taylor, 1979). They fumigated three species for 4 hr/day for 8 days with 50 ppb PAN. In one experiment, the lichens were fumigated for only 7 days with 100 ppb PAN. Response to PAN, evaluated as reduction in gross photosynthesis, indicated that Parmelia sulcata was more sensitive than Hypogymnia enteromorphia, and Collema nigrescens was not affected. Photosynthesis was inhibited in Parmelia sulcata, probably inhibited in Hypogymnia entermospha (results were highly variable), and appeared not to be affected in Collema nigrescens.

PAN was apparently destructive to chlorophyll and carotenoids in a species of algae. Treatments also adversely affected photosynthesis and respiration and suppressed growth. The difference in gross photosynthesis response to PAN fumigations exhibited by three lichen species tended to indicate that PAN, along with other pollutants, may be detrimental to lichen populations.

7.7.3 Losses in Vascular Plants Caused by PAN

The term loss is used in this section to mean loss in the intended use or value of vegetation caused by PAN injury. The loss may be a reduction in amount of marketable product or a loss resulting from aesthetic degradation.

7.7.3.1 Losses in Aesthetic Use and Foliar Yield. Various types of petunias are used as bedding plants. This species is highly susceptible to PAN injury, and although monetary losses have not been reported, it is obvious that they have been heavy in the wholesale industry, retail market, and to the consumer. Although such information is not reported in the literature, attempts have been made to produce plants outside heavily polluted areas and transport them

to the market. This practice was only partly successful because substantial foliar injury usually developed after delivery to retail outlets and before retail sale. While the petunia is one of the most susceptible species, other ornamentals that are planted for foliage and blossoms also are affected. No evidence indicates that the petals or other blossom parts are injured by PAN.

Several vegetable crops such as leaf lettuce, spinach, mustard greens, table beets, endive, and romaine lettuce are grown and marketed for their foliage. Some of these crops are grown in close proximity to metropolitan areas and marketed as specialty crops. These species are harvested early in the morning and are supplied, at relatively high prices, to restaurants and specialty stores. After a heavy PAN attack, entire crops in some areas are not marketable, and others require expensive hand work to sort and trim the product to make them acceptable. No reliable assessment of such losses has been made, but losses of several hundred thousand dollars per year in the Los Angeles area have been suggested (Middleton et al., 1950).

The indirect effect of PAN on plant growth resulting from destruction of leaf tissue has not been measured. However, destruction of a significant amount of leaf area caused by the necrotic bands and damage to the lower epidermis and increased defoliation of deciduous plants should be expected to suppress growth. Earlier reports indicated that growth and yield by most plants are not measurably affected until the loss of photosynthetic surface exceeds 5 percent (Thomas and Hendricks, 1956). Plants that rapidly replace foliage (e.g., grasses) might be expected to express less growth reduction because of foliage loss than plants that retain their foliage for several years (e.g., citrus trees) and replace the lost foliage more slowly.

Thompson and Kats (1975) reported a trend toward reduced yield of mature navel orange fruit when branches of mature trees were enclosed and fumigated with PAN dosages equivalent to those occurring in the Riverside, California area. PAN treatments consisted of carbon-filtered air, ambient air, and carbon-filtered air plus additions of PAN adjusted to simulate concentrations monitored in the ambient air at Riverside. The continuous treatments were administered for 9 months. Tree growth also was suppressed, presumably because of lost photosynthetically active tissue when leaf drop was stimulated.

Middleton et al. (1950) estimated the dollar loss for 11 crops in Los Angeles County, California during the 1949 growing season to be $479,495. The foliar symptoms described as the cause of this loss were identical with those

later found to be caused by PAN (Taylor et al., 1960). Though O_3 was undoubtedly a component of the smog described in 1950, symptoms of O_3 injury were not included in the injury symptom syndrome implicated in the crop losses. Oshima et al. (1974) did not attempt to estimate monetary loss after the severe PAN attack. In Los Angeles and San Bernardino Counties, the crop could be marketed after extensive trimming. Assessment of economic loss due to PAN has not been attempted in recent years.

7.7.3.2.1. PAN addition studies. Based on PAN addition studies, Temple (1982) concluded that the potentially phytotoxic episodes could be defined as concentrations greater than 15 ppb for 4 hr in the morning or greater than 25 ppb for 4 hr in the afternoon. His experiments were conducted in Teflon®-covered CSTR chambers in a greenhouse. PAN concentrations of approximately 14 ppb for 4 hr in ambient air are sufficient to produce foliar injury on susceptible plants growing in the field (Taylor, 1969). However, in chamber studies, approximately two to three times this dose is required to induce injury symptoms (Posthumus, 1977). Because of this discrepancy between chamber and field studies, it is inappropriate to relate responses obtained in chambers using synthesized PAN to responses expected in the field.

Exposure of lettuce and Swiss chard to 0, 25, and 50 ppb PAN for 4 hr/day once a week for up to 4 weeks caused no visible leaf injury and appeared to have little, if any, effect on plant growth (Temple, 1982). PAN by itself or in combination with O_3 had no effect on stomatal conductance. Temple found that PAN and O_3 alone and in combination reduced growth of four tomato varieties and altered partitioning of photosynthate between roots and shoots. He exposed the plants to 0, 0.1, and 0.2 ppm O_3 and 0, 25, and 50 ppb PAN, alone and in all combinations, for 4 hr/day once a week for 3 weeks. No PAN-type visible injury developed on the tomato plants, and this exposure had no effect on expression of O_3 injury. The PAN treatments had no effect on stomatal conductance, but 0.2 ppm O_3 reduced stomatal conductance in all four varieties. Results from two separate experiments were erratic, perhaps because the studies were conducted at different times of the year, but the evidence that the root/shoot ratio was altered suggests that further study is needed.

Greenhouse-grown plants (radish, lettuce, chard, oat, tomato, pinto bean, beet, and barley) representing root, foliage, fruit and seed crops were exposed to PAN (0, 5, 10, 20, or 40 ppb) for 4 hr/day, twice per week from germination to maturity of the harvestable crop (Taylor et al., 1983). Significant yield

reductions were observed only in lettuce (Empire) and chard; the threshold for yield reduction appeared to be between 10 and 20 ppb. Yield was reduced 13 percent in lettuce and 23 percent in chard exposed to 40 ppb. Of all the crops tested, only pinto bean developed a significant amount of foliar injury and only after exposure to 40 ppb; this sensitivity persisted throughout the developmental cycle of the crop. The results indicate that PAN at concentrations below the visible injury threshold can cause significant yield reductions in sensitive cultivars of leafy (foliage) crops.

Field observations in southern California during the past 30 years have revealed that severe visible PAN injury seldom appears during mid-summer, even though higher dosages and concentrations occur during the four summer months (Temple and Taylor, 1983). Ozone dosage also is highest during this period. To effectively assess the impact of PAN, in the presence and absence of visible symptoms, experiments should be designed to use O_3 and PAN mixtures, be conducted in as near full sunlight as possible, and be able to simulate fall and spring environmental conditions limited to those periods.

Youngner and Nudge (1980) measured the relative susceptibility of cultivars of 10 turf grass species to 50 ppb PAN and to 0.5 ppm O_3. They reported a significant variation in amounts of foliar injury and noted that warm-season grasses were more tolerant of both O_3 and PAN than were the cool-season grasses.

PAN is an important component of the oxidant air pollutant complex because of its extreme reactivity with biological materials (Mudd, 1975). PAN reacts strongly with sulfhydryl groups in enzymes (Mudd, 1963) and with low-molecular-weight, sulfur-containing compounds such as amino acids (Leh and Mudd, 1974). The occurrence of severe foliar injury symptoms on susceptible species in the field and during controlled experiments with synthesized PAN is well documented (Bobrov, 1955; Taylor, 1969; and Taylor and MacLean, 1970). Photosynthetic processes are disrupted when isolated chloroplasts are exposed to high PAN concentrations (Dugger et al., 1965).

Evidence of plant growth suppression following intermittant exposure to PAN at concentrations comparable to those found in ambient polluted air without visible leaf injury symptoms has been reported (Thompson and Kats, 1975; Temple, 1982).

7.7.3.3 Biomass and Yield Responses from Ambient Exposures. Substantial yield losses caused by ambient PAN exposures occur in southern California and on occasion in the highly productive central valley of the state. The

losses are most evident in leafy vegetable (salad) crops and herbaceous ornamentals and is due primarily to the damaged crop not being aesthetically acceptable on the market. Suppression of plant growth and reproduction because of exposure to PAN alone cannot be substantiated under ambient conditions because O_3 and PAN are present simultaneously, and no effective filter is available to separate them. Consequently, all of the crop responses under ambient conditions are the result of O_3 and PAN mixtures.

Root crops such as radish, table beet, and sugar beet develop foliar symptoms of PAN injury, but no substantiated evidence indicates that production of marketable roots is affected. Similarly, barley and oats growing in the field develop characteristic transverse necrotic bands on the foliage, but no evidence exists that the grain crop was affected.

A trend toward reduced fruit production of navel oranges was reported when tree limbs were exposed to synthesized PAN in a system designed to simulate ambient conditions for a full year. This response has not been substantiated with other crops or repeated with navel orange. The inability to separate PAN and O_3 under ambient conditions, difficulties in synthesizing large quantities of a strongly reactive compound, and knowledge that greenhouse and fumigation chamber environments greatly increase plant tolerance to PAN have discouraged attempts to conduct the long-term experiments necessary for crop growth and yield assessment.

Characteristic foliar injury consisting of necrotic transverse bands, chlorotic bands, lower-surface glazing and bronzing, and leaf distortion occur when sensitive plants are exposed to 14 to 15 ppb PAN under ambient field conditions. Two to three times this concentration is required to cause injury when plants are exposed in chambers. Injured crops of lettuce, spinach and other susceptible leafy crops often become a complete loss in southern California and parts of the San Joaquin Valley.

The injury symptom syndrome for smog or photochemical oxidants described in the literature preceding about 1960 is identical with the injury produced by PAN. Certainly O_3 was present in the atmosphere and was responsible for injury to vegetation, but the description of injury observed in the field during early studies of oxidant air pollutants did not include those symptoms attributed to O_3. Early estimates of crop loss in southern California were based on PAN-type symptoms.

After PAN was identified and a technique for synthesizing it was developed, studies were initiated to determine the susceptibility of species and to identify the mode of action once PAN entered leaf tissue. These early studies established that a high concentration, two to three or more times greater than that usually measured in the atmosphere, could inhibit enzyme activity and particularly those enzymes containing sulfhydryl groups. The studies revealed auxin IAA activity in oat coleoptile was inhibited, and growth by cell expansion was suppressed.

Evidence has been presented to show that PAN is absorbed in the aqueous layer surrounding internal leaf tissues and PAN or its degradation products are transported through the cell wall and plasmalemma where organelles are attacked. The evidence indicates that PAN disrupts permeability of the plasmalemma and plastid membrane, thus allowing leakage and plasmolysis. Disruption of organelles and inhibition of enzymes are the primary causes of the reported suppression of apparent photosynthesis.

Extensive studies have shown that species and varietal variation in susceptibility to PAN is controlled genetically. The complexity of the genetic influence has not been adequately described.

Under field conditions, injury symptoms may be produced on susceptible species when PAN concentrations are approximately 15 ppb for 4 hr; in most instances, 36 to 72 hr are required for the symptoms to fully develop. Susceptibility is influenced by genetic, edaphic, and other environmental conditions. Light conditions before, during, and immediately after exposure may influence plant response to PAN. In general, environmental conditions (e.g., soil moisture, nutrition, temperature, relative humidity, and light exposure) that are conducive to producing optimum plant growth also increase plant susceptibility.

The visible symptoms of PAN injury are glazing, silvering, and/or bronzing on the lower surface, usually in a diffuse transverse band across the lower surface of rapidly expanding leaves. As the PAN concentration increases, the injury may extend through the leaf to produce chlorotic or collapsed necrotic transverse bands of injury. The bands provide evidence that tissue at a specific stage of development is most susceptible to injury. The bands are located closer to the leaf base as the age of the expanding leaf increases.

Estimates of damage or crop loss have been based on the significance of leaf injury. Ornamentals and leafy vegetables whose market value is related

to appearance are often severely damaged. Individual growers may lose an entire crop, while in other instances, extensive trimming is required to produce a marketable product, thus reducing profits. Some studies have indicated that growth and yield may be suppressed by PAN even when visible symptoms do not develop. However, only a few such studies have been conducted and results have been too variable to conclusively state that yield of fruit and seed is reduced significantly in the absence of visible symptoms.

Interactions between PAN and O_3 and between PAN and SO_2 have been studied by several researchers. In some instances, synergistic responses have been reported, but variability is too great to conclusively state that such responses usually occur. However, with PAN concentrations near and at ambient levels, the studies indicated that PAN and O_3 do not interact or the resultant injury is less than would be expected if the effects were additive.

7.8 SUMMARY

Plant growth and yield are the end products of a series of biochemical and physiological processes related to uptake, assimilation, biosynthesis, and translocation. Sunlight (photosynthetic energy) drives the assimilation process that converts carbon dioxide into the organic compounds necessary for plant growth and development. In addition to the compounds obtained through photosynthesis, the plants must extract the essential mineral nutrients and water from the soil. The various plant organs convert these raw materials (carbon dioxide, mineral nutrients, and water) into the wide array of compounds that are required for plant growth and yield. These biosynthetic reactions occur in various plant organs, and their products are translocated through the plant. A disruption or reduction in the rates of uptake, assimilation, or the subsequent biochemical reactions can be reflected in reduced plant growth and yield.

In general, O_3 or PAN would be expected to reduce plant growth and yield only if it directly impacted the process that was limiting plant growth or if it caused some other processes to limit growth. An effect on plant growth and yield would not occur unless O_3 or PAN caused some processes to limit growth to the extent that environmental factors controlling plant growth were ineffective.

Ozone and PAN enter into the plant through its foliage, and this is the primary site where they exert their phytotoxic effects. To penetrate into active sites within the leaf, these gases must diffuse through small pores (stomata), which partially control the amount of O_3 and PAN entering the leaf, diffuse through the intercellular spaces, and dissolve in the hydrated cell surfaces.

The photochemical oxidant air pollutants, i.e., O_3 and PAN, and other gaseous air pollutants are phytotoxic only if they reach the active sites within the leaf. If the rate of pollutant uptake is small and the plant is able to detoxify or metabolize the pollutant (or its decomposition products) or repair or compensate for the impact, injury will not occur. Injury and the resulting effects on growth and yield will occur only when the uptake of O_3 or PAN exceeds the rate at which the plant is able to detoxify or metabolize the phytotoxins or repair the cellular disturbances. These physiological and biochemical events also are reflected in the observations that plants can tolerate specific concentrations of O_3 or PAN for specific time periods without inducing visible injury or measurable effects on plant growth and yield.

Some of the initial responses to O_3 include increased membrane permeability (both cell and organelle membranes), alterations in the activities of specific enzymes, and changes in various metabolic pools. Altered membrane permeability results in leakage of water and ions from the cells and disorganization of organelles, and cells become plasmolyzed. In addition, stress ethylene production is stimulated, and there are increases in secondary metabolites such as phenolic compounds. The appearance of visible foliar injury has been associated with elevated concentrations of phenols.

Ozone inhibits photosynthesis and alters partitioning of photosynthate. In various plant species, photosynthesis was significantly decreased by O_3 at concentrations of 0.05 ppm for 4 hr, 0.1 ppm for 1 hr, or 0.2 ppm for 1 hr (Table 7-1). Higher O_3 concentrations or longer exposure durations also reduced photosynthesis. The enzyme responsible for photosynthesis (RuBP carboxylase) was inhibited by 0.12 ppm O_3 for 2 hr in whole plants. These reductions in photosynthesis occurred at O_3 levels and exposure durations that occur in the ambient air. An inhibition in photosynthesis decreases the synthesis of the primary components needed for plant growth.

In addition to reducing the amount of material produced during photosynthesis, O_3 can alter the transport and allocation of the remaining photosynthetic

material. For example, the root growth of radish was reduced more than the top growth (0.05 ppm O_3, 8 hr/day, 5 days/week for 5 weeks). In ponderosa pine, the storage of sugars in the roots was depressed by O_3 (0.1 ppm, 6 hr/day for 16 weeks). Rye grass plants exposed to O_3 (0.09 ppm, 8 hr/day for 16 weeks) exhibited a 22 percent reduction in the root/shoot ratio. In addition to these examples, numerous studies have confirmed the observation that O_3 impacts root growth more than foliage growth even though the foliage is the primary site of O_3 action. These effects on photosynthesis and translocation may explain the yield reductions observed in other studies. The nature of the relationship between inhibition of photosynthesis and yield reduction is not well understood.

Many biological, physical, and chemical factors influence plant responses to O_3. Differential plant response to O_3 is an inherited trait. Genetic variance in O_3 response appears to be complex; it involves a number of genes. While each plant has a potential genetically determined susceptibility to O_3, the manifestation of that potential depends upon the physiological sensitivity of the plant. Although differential O_3 sensitivity has been documented for numerous species, most studies that have developed exposure-response relationships or attempted to assess the economic impacts of O_3 on crop productions have used only one or a few cultivars. Many biological, physical, and chemical factors contribute to the determination of the plant physiology. The developmental stage of the leaf and the plant influences sensitivity. Although interspecific variation has been observed, in general, leaves approaching maximum expansion seem to be most sensitive to O_3. Study results indicate that young plants and those approaching senescence are more sensitive to O_3 than plants at intermediate ages.

In both ambient environment and chamber studies, O_3 stimulates premature senescence and leaf drop. This premature leaf drop decreases the time that a leaf can contribute to plant growth and yield. Part of the O_3-induced effects on plant yield may result from premature senescence.

The biological environment of the plant also affects O_3 response in plants. Studies demonstrate that interaction exists between O_3 and plant pests, as reflected in plant response. Most laboratory evidence indicates that O_3 (at ambient concentrations or higher for 4 hr or more) inhibits infections by pathogens and subsequent disease development; however, increases in disease development were noted in certain cases. These increases most often

occurred with stress pathogens such as Botrytis blight of potatoes or onions or annosus root rot of ponderosa and Jeffrey pine. Also, O_3 can modify plant-insect relationships; this is best illustrated by studies conducted in the San Bernardino Mountains in California. Pines impacted by O_3 were more susceptible to invasion by bark beetles. Little evidence exists to indicate that O_3 causes significant direct effects on microorganisms. Given the importance of plant diseases and insects in agricultural and forestry production systems, relatively small changes in the incidence and severity of plant pest problems could add significantly to O_3-related losses in quality, quantity, or function of agro- or natural ecosystems.

The physical environment around a plant influences its sensitivity to O_3. Studies of the influence of physical factors on plant sensitivity to O_3 are limited. For some factors, a general trend exists across species, but for other factors, the responses vary among species. For example, light intensity and temperature significantly influence plant sensitivity but there is no clear trend among species. In contrast, plants became more sensitive to O_3 with increasing relative humidity, while plants that are water stressed become more tolerant to O_3. When the water stress is relieved, the plants regain their O_3 sensitivity. The influence of water stress has been confirmed in both field and laboratory studies, but the results are limited primarily to visible injury. The influence of relative humidity and soil moisture stress is related to their effects on stomatal opening, which influences the amount of O_3 entering the plant. While studies reveal that plants growing with different soil fertility regimes vary in O_3 sensitivity, it is not clear how nutritional status for most nutrients influences plant sensitivity. Plants that are low in calcium are highly sensitive to O_3. As the tissue calcium levels are increased from deficient to sufficient, the plants become more tolerant of O_3. This response probably is related to the role of calcium in maintaining membrane function.

Concern for the effects of pollutant mixtures on vegetation originated with the observation that noninjurious concentrations of O_3 and SO_2 induced foliar injury when the pollutants were combined. Since that time, numerous studies have been conducted to determine the effects of combinations of O_3 and SO_2 on visible injury and plant growth and yield. For visible injury, the majority of the studies showed that concentrations of O_3 and SO_2 (0.05 to 0.20 ppm for 1 to a few hours) generally acted synergistically in causing

visible injury. However, there were exceptions. Greenhouse studies showed that the effects of mixtures of O_3 and SO_2 on plant growth were in most cases additive or antagonistic. Recent studies conducted in the field found that SO_2 and O_3 interacted to reduce plant growth. However, this effect was found only at unusually high SO_2 concentrations. At more typical SO_2 concentrations, the effect of O_3 was not influenced by SO_2. Preliminary analysis of air monitoring information for locations that co-monitored both pollutants showed that at most sites, there were no more than 10 co-occurrences of O_3 and SO_2 (concentrations of 0.05 ppm or greater of each gas), during the 5-month period of May to September. Based on these data, the majority of the studies of the effects of O_3 and SO_2 on plant growth have used exposure regimes that are more severe than those that occur in ambient air.

Some studies have investigated the effects of O_3 and NO_2, but the results are too limited to allow any general conclusions. Preliminary studies have used mixtures of O_3, SO_2, and NO_2. The results of these studies indicated that the addition of the other gases caused a greater effect than O_3 alone. Limited studies have investigated the interaction of O_3 and heavy metals. In general, when plants are exposed to heavy metals and O_3, the heavy metals seem to make the plant more sensitive to O_3.

Commercial farming practices incorporate the use of a spectrum of pesticides. Interactions between O_3 and several pesticides have been documented. The most notable example is the protective role of the systemic fungicide benomyl with a diversity of plant species. However, the extent of the protection is such that these chemicals are not normally used to reduce O_3 injury in the field.

Plants have been used extensively to index various characteristics of the environments in which they grow. Ozone is an imposed environmental variable that can be detected and sometimes quantified by observing the specific response of sensitive plants. The occurrence of O_3 has been confirmed in the United States, the Netherlands, Great Britain, Germany, Japan, Israel, and Australia by observing foliar injury to selected plant species and cultivars.

Biological methods for assessing the extent and intensity of O_3 have a value beyond that provided by physical measurements. Bioindicators are integrators of their environment and can provide direct information on the effect a given pollutant dose has on vegetation, subject to the joint influence of other environmental variables.

The response of nonvascular plants to O_3 has received little study, but the available data suggest that microorganisms, mosses, and ferns are not impacted at present ambient concentrations. Studies conducted in southern California have shown a loss in the number of lichen species in areas experiencing elevated levels of photochemical oxidant air pollution.

Various summary statistics have been used to characterize the pollutant exposure regime that plants experience. The summary statistics ranged from the cumulative dose (ppm/hr) to means using various averaging times. These exposure statistics are not readily interconvertible. The currently used exposure statistics do not characterize the impact of pollutant episodes at specific, and perhaps critical periods during plant growth.

When pollutant concentrations exceed a given concentration for a specific time period, plants will be impacted by O_3. Various studies and lines of evidence indicate that concentration is more important than exposure duration in causing an effect. Initial studies have shown that plants that experience an episodic exposure are more impacted than plants that receive a constant exposure at the same dose.

The yield losses discussed in Section 7.4.3 dealt with effects on the intended use of the plant. Yield loss ranged from foliar injury (for those plants where the foliage is the important yield component) to losses in weight, size, or number and changes in plant quality. The previous criteria document (U.S. Environmental Protection Agency, 1978) summarized earlier research by presenting O_3 concentrations and exposure durations that could potentially reduce yield (Figure 7-6). That document displays a boundary of O_3 concentration and exposure periods below which O_3 effects would not be expected. The lower O_3 limit for an effect was 0.05 ppm for exposure durations of 16 days (2 to 8 hr/day) or greater. At exposure durations of less than 16 days, the O_3 response threshold was increased to about 0.10 ppm at 10 days and 0.30 ppm for 6 days.

A summary of foliar injury effects is presented in Table 7-34, which lists concentrations that can produce 5 percent or 20 percent injury to sensitive, intermediate, or tolerant plants. That summary predicts effects (foliar injury) on sensitive plants resulting from 8-hr exposures to 0.02 to 0.04 ppm (5 percent) or 0.06 to 0.12 ppm (20 percent).

Studies have been conducted with the frequent use of open-top field chambers to estimate the impact of O_3 on plant yield for important cultivars

TABLE 7-34. OZONE CONCENTRATIONS FOR SHORT-TERM EXPOSURES THAT PRODUCE 5 OR 20 PERCENT INJURY TO VEGETATION GROWN UNDER SENSITIVE CONDITIONS[a]

Exposure time, hr	Ozone concentrations that may produce 5% (20%) injury, ppm[b]		
	Sensitive plants	Intermediate plants	Tolerant plants
0.5	0.35 - 0.50 (0.45 - 0.60)	0.55 - 0.70 (0.65 - 0.85)	≥0.70 (0.85)
1.0	0.15 - 0.25 (0.20 - 0.35)	0.25 - 0.40 (0.35 - 0.55)	≥0.40 (0.55)
2.0	0.09 - 0.15 (0.12 - 0.25)	0.15 - 0.25 (0.25 - 0.35)	≥0.30 (0.40)
4.0	0.04 - 0.09 (0.10 - 0.15)	0.10 - 0.15 (0.15 - 0.30)	≥0.25 (0.35)
8.0	0.02 - 0.04 (0.06 - 0.12)	0.07 - 0.12 (0.15 - 0.25)	≥0.20 (0.30)

[a]Data developed from analysis of acute responses shown in Table 11-18 from U.S. Environmental Protection Agency, 1978. The concentrations in parenthesis represent the 20 percent injury level.

[b]1 ppm = 1960 $\mu g/m^3$.

of major crops. These studies can be grouped into two classes, depending on the methods used for data analysis: (1) those studies that developed predictive equations relating O_3 exposures to plant response, and (2) those studies that compared discrete treatment levels to a control. The first approach has the advantage that the models can be used to interpolate results between treatment levels.

To summarize the results from studies that developed exposure-response equations, these equations were used to estimate the O_3 concentrations that caused 10 and 30 percent reductions in yield (Table 7-35). For several species and cultivars, several models were fit to the same original data. In general, when several models were fit to the same data, the models then tended to predict similar concentrations. However, in cases involving corn, turnip, or winter wheat, the linear model tended to underestimate the O_3 concentrations. The linear models were more likely to show systematic deviations from the data than the models that allowed curvature. The similarity among the estimated

TABLE 7-35. 7-HOUR SEASONAL AVERAGE O_3 CONCENTRATIONS AT WHICH YIELD LOSSES OF 10 PERCENT OR 30 PERCENT ARE PREDICTED FROM EXPOSURE RESPONSE MODELS

Plant	Model	Control O_3 concentration[a]	Yield Percent	Loss Percent
Grains/Seeds				
Soybean				
Corsoy	kg/ha = 3099.3 - 15135 O_3	0.022	0.040	0.077
Corsoy	g/plant = 15.6 exp $[-(O_3/0.129)^{1.70}]$	0.022	0.043	0.076
Davis	seed wt/m = 534.5 - 3988.6 O_3 + 10,960 O_3* O_3	0.025	0.038	0.070
Davis	g/plant = 31.1 exp $[-(O_3/0.129)^{0.91}]$	0.025	0.038	0.071
Essex	g/plant = 18.7 exp $[-(O_3/0.309)^{0.76}]$	0.014	0.037	0.109
Hodgson-F[b]	g/plant = 15.2 exp $[-(O_3/0.207)^{0.50}]$	0.017	0.039	0.096
Hodgson-P[b]	g/plant = 15.5 exp $[-(O_3/0.153)^{1.57}]$	0.017	0.043	0.084
Williams	g/plant = 19.4 exp $[-(O_3/0.243)^{0.94}]$	0.014	0.038	0.098
Peanut - 1979	pod wt/plant = 112 - 563 O_3	0.026	0.043	0.078
Peanut - 1980[c]	pod wt/plant = 173 - 1046 O_3	0.025	0.039	0.067
Peanut - 1980	pod wt/plant = 142.3 if $O_3 \leq 0.037$; = 184.6 - 1160 O_3 if $O_3 > 0.037$	0.025	0.049	0.073
Peanut - 1980	g/plant = 148 exp $[-(O_3/0.186)^{3.20}]$	0.025	0.046	0.073
Kidney bean	seed wt/plant = 17.44 - 35.51 O_3	0.025	0.072	0.165
Kidney bean	g/plant = 16.5 exp $[-(O_3/0.287)^{1.77}]$	0.025	0.086	0.164

TABLE 7-35. 7-HOUR SEASONAL AVERAGE O_3 CONCENTRATIONS AT WHICH YIELD LOSSES OF 10 PERCENT OR 30 PERCENT ARE PREDICTED FROM EXPOSURE RESPONSE MODELS

Plant	Model	Control O_3 concentration[a]	Yield Loss Percent	
			Percent	Percent
Field corn				
(Coker 16)[c]	g/plant 247.8 - 260* O_3	0.02	0.113	0.300
(Coker 16)	g/plant = 222.91 + 331.11 O_3 - 3511.99 O_3* O_3	0.02	0.132	---
(Coker 16)	g/plant = 240 exp $[-(O_3/0.221)^{4.46}]$	0.02	0.133	0.175
(PAG 397)	g/plant = 166 exp $[-(O_3/0.160)^{4.28}]$	0.15	0.095	0.126
(Pioneer 3780)	g/plant = 149 exp $[-(O_3/0.155)^{3.11}]$	0.15	0.075	0.111
Winter wheat				
(Blueboy II)[c]	g/plant = 6.6 - 18 O_3	0.03	0.063	0.131
(Blueboy II)	g/plant - 5.908 + 3.958 O_3 - 137.7 O_3^2	0.03	0.0817	0.129
(Blueboy II)	g/plant = 5.88 exp $[-(O_3/0.175)^{3.22}]$	0.03	0.088	0.127
(Coker 47-27)[c]	g/plant = 5.8 - 21 O_3	0.03	0.055	0.104
(Coker 47-27)	g/plant = 5.765 - 18.79 O_3 - 20.00 O_3^2	0.03	0.055	0.103
(Coker 47-27)	g/plant = 5.19 exp $[-(O_3/0.171)^{2.06}]$	0.03	0.064	0.107
(Holly)[c]	g/plant = 5.7 - 16 O_3	0.03	0.063	0.128
(Holly)	g/plant = 4.533 + 19.31 O_3 - 215.1 O_3^2	0.03	0.095	0.129
(Holly)	g/plant = 4.95 exp $[-(O_3/0.156)^{4.95}]$	0.03	0.099	0.127
(Holly)	g/plant = 4.9 if $x \leq 0.087$ = 8.2 -38 $\bar{O}_3$ if $O_3 > 0.087$	0.03	0.100	0.126

TABLE 7-35. 7-HOUR SEASONAL AVERAGE O_3 CONCENTRATIONS AT WHICH YIELD LOSSES OF 10 PERCENT OR 30 PERCENT ARE PREDICTED FROM EXPOSURE RESPONSE MODELS

Plant	Model	Control O_3 concentration[a]	Yield Loss	
			Percent	Percent
(Oasis)[c]	g/plant = 4.9 - 12 O_3	0.03	0.068	0.143
(Oasis)	g/plant = 4.475 + 3.320 O_3 - 93.49 O_3^2	0.03	0.088	0.138
(Oasis)	g/plant = 4.88 exp $[-(O_3/0.186)^{3.20}]$	0.03	0.093	0.135
Cotton	g/plant = 41.5 exp $[-(O_3/0.197)^{1.12}]$	0.018	0.041	0.092
Root crops				
Turnip (Just Right)[c]	edible root wt/plant = 12.9 - 94 O_3	0.014	0.026	0.051
(Just Right)	edible root wt/plant = 10.7 if $O_3 \leq 0.038$ = 15.5 - 127 O_3 if $O_3 > 0.038$	0.014	0.046	0.063
(Just Right)	g/plant = 10.89 exp $[-(O_3/0.090)^{3.05}]$	0.014	0.043	0.064
(Purple Top White Globe)[c]	edible root wt/plant = 7.2 - 49 O_3	0.014	0.027	0.054
(Purple Top White Globe)	edible root wt/plant = 6.0 if $O_3 \leq 0.034$ = 8.1 - 60 O_3 > 0.034	0.014	0.045	0.065
(Purple Top White Globe)	g/plant = 6.22 exp $[-(O_3/0.095)^{2.51}]$	0.014	0.040	0.064
(Shogoin)	edible root wt/plant = 5.3 - 36 O_3	0.014	0.027	0.054
(Shogoin)	g/plant = 4.68 exp $[-(O_3/0.096)^{2.12}]$	0.014	0.036	0.060
(Tokyo Cross)[c]	edible root wt/plant = 18.1 - 116 O_3	0.014	0.028	0.057

TABLE 7-35. 7-HOUR SEASONAL AVERAGE O_3 CONCENTRATIONS AT WHICH YIELD LOSSES OF 10 PERCENT OR 30 PERCENT ARE PREDICTED FROM EXPOSURE RESPONSE MODELS

Plant	Model	Control O_3 concentration[a]	Yield Loss Percent	Yield Loss Percent
(Tokyo Cross)	edible root wt/plant = 14.8 if $O_3 \leq 0.054$ ≈ 27.0 - 226 O_3 if $O_3 > 0.054$	0.014	0.061	0.074
(Tokyo Cross)	g/plant = 15.25 exp $[-(O_3/0.094)^{3.94}]$	0.014	0.053	0.072
Foliage crops				
Lettuce	fresh head wt/plant = 1065.7 - 5978 O_3	0.043	0.057	0.084
Lettuce	g/plant = 1245 exp $[-(O_3/0.098)^{1.22}]$	0.043	0.053	0.075
Spinach (America)	g/plant = 22.7 -106 O_3	0.024	0.043	0.081
(America)	g/plant = 21.2 exp $[-(O_3/0.142)^{1.65}]$	0.024	0.046	0.082
(Winter Bloomsdale)	g/plant = 23.3 - 121 O_3	0.024	0.041	0.075
(Winter Bloomsdale)	g/plant = 20.8 exp $[-(O_3/0.127)^{2.07}]$	0.024	0.049	0.080
(Hybrid 7)	g/plant = 42.1 - 193 O_3	0.024	0.043	0.082
(Hybrid 7)	g/plant = 36.6 exp $[-(O_3/0.139)^{2.68}]$	0.024	0.060	0.095
(Viroflay)	g/plant = 46.1 - 238 O_3	0.024	0.041	0.075
(Viroflay)	g/plant = 41.1 exp $[-(O_3/0.129)^{1.99}]$	0.024	0.048	0.080

[a]The O_3 concentration is expressed as the 7-hour seasonal mean.

[b]The Hodgson data were obtained from two designs in 1981: a full harvest (F) and a partial plot harvest (P) where some plants were removed before harvest.

[c]This model did not fit the data well and tended to underestimate the O_3 concentrations that cause yield losses.

concentrations suggests that the predicted values are more influenced by the original input data than by the model fit to the data. The relative responses of five major crops to O_3, based on the Weibull model combined data sets, are presented in Figure 7-18.

A brief review of the yield response data summarized (Table 5-36) indicate that significant yield reductions (10 percent) were predicted when the 7-hour seasonal mean O_3 concentration exceeded 0.04 to 0.05 ppm. Studies with fescue cultivars predicted significant yield reductions when the plants were exposed to 0.10 ppm O_3 for 6 hours/week for 7 weeks.

To summarize the data from studies that used discrete treatments, the lowest concentration that significantly reduced yield was determined from the author's analysis (Table 7-36). The lowest concentration reported to cause a significant yield reduction was frequently the lowest concentration used in the study. Given the experimental design, it was not always possible to estimate if significant yield reductions could have occurred at lower O_3 concentrations. In general, the data indicate that O_3 concentrations of 0.10 ppm for a few hours per day for several days to weeks generally induced significant yield reductions. Although from this analysis it appears that higher O_3 concentrations were required to cause a yield reduction than the concentrations estimated by the regression approaches, it should be noted that the concentrations derived from the regression studies were based on a 10 percent yield loss, but in the studies that used discrete treatments the 0.10 ppm concentration frequently caused greater mean yield losses (10 to 50 percent).

The data from the previous criteria document (U.S. Environmental Protection Agency, 1978) developed limiting values which suggested that O_3 concentrations of 0.04 to 0.06 ppm for 4 hours or more were likely to injure plant foliage. The growth data summarized in the document indicated that plant growth and yield can be reduced at O_3 concentrations of 0.05 to 0.08 ppm for several hours/day. These concentrations are similar to the concentrations 0.04 to 0.07 shown to reduce plant yield in field studies and ambient air studies in this chapter.

Studies have shown that the ambient air in various parts of the United States is sufficiently polluted that crop growth yield is being reduced. For example, losses have been reported in tomato (33 percent at 0.035 ppm), bean (26 percent at 0.041 ppm), soybean (20 percent at 0.05 ppm), snapbean (10 to 22 percent at 0.06 ppm), forest trees (12 to 67 percent at 0.052 ppm), and

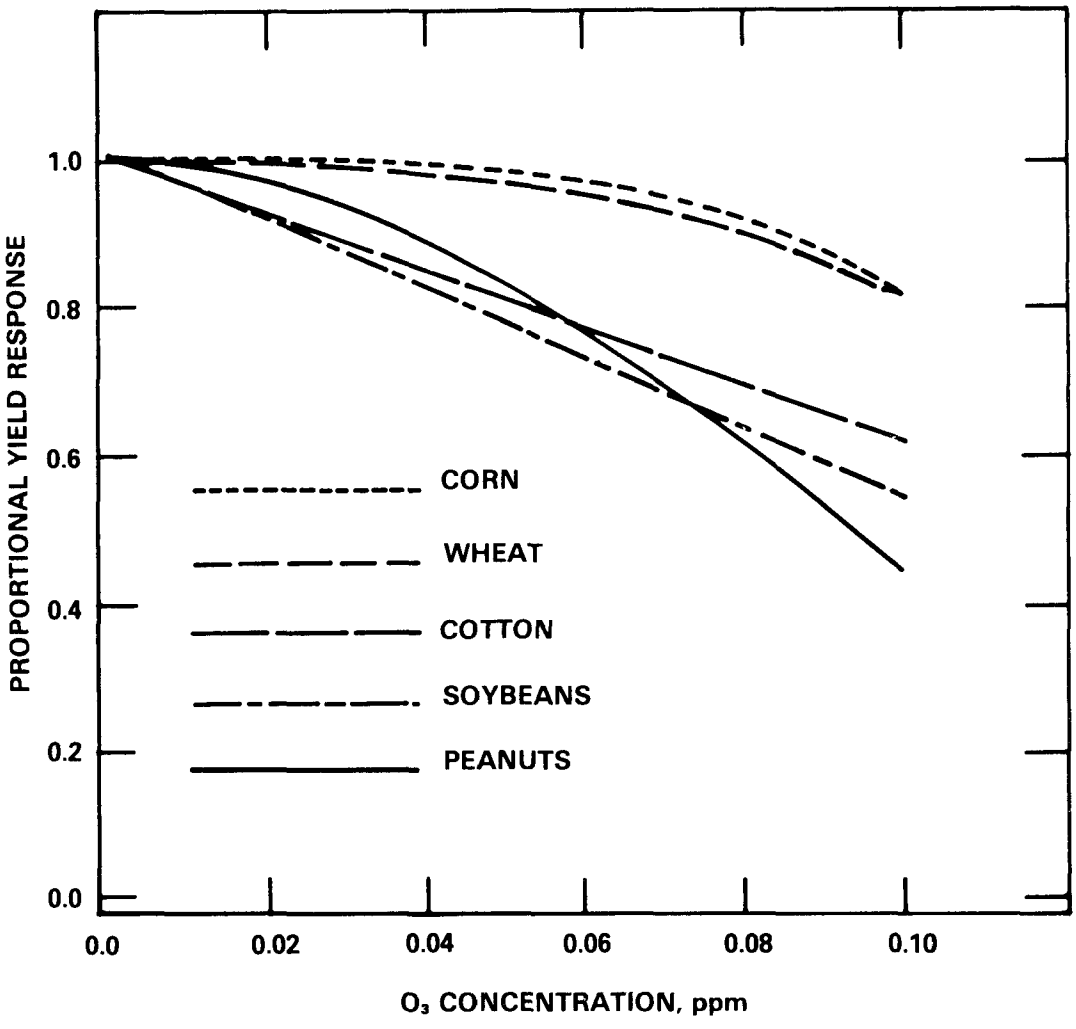

Figure 7-18. Relative O_3-induced yield reduction of selected crops as predicted by the Weibull model (Heck et al., 1983).

TABLE 7-36. OZONE CONCENTRATIONS AT WHICH SIGNIFICANT YIELD LOSSES HAVE BEEN NOTED FOR A VARIETY OF PLANT SPECIES EXPOSED TO O_3 UNDER VARIOUS EXPERIMENTAL CONDITIONS

Plant species	Exposure duration	Yield reduction, % of control	O_3 concentration
Alfalfa	7 hr/day, 70 days	51, top dry wt	0.10
Alfalfa	2 hr/day, 21 days	16, top dry wt	0.10
Pasture grass	4 hr/day, 5 days/wk, 5 wk	20, top dry wt	0.09
Ladino clover	6 hr/day, 5 days	20, shoot dry wt	0.10
Soybean	6 hr/day, 133 days	55, seed wt/plant	0.10
Sweet corn	6 hr/day, 64 days	45, seed wt/plant	0.10
Sweet corn	3 hr/day, 3 days/wk, 8 wk	13, ear fresh wt	0.20
Wheat	4 hr/day, 7 days	30, seed yield	0.20
Radish	3 hr	33, root dry wt	0.25
Beet	2 hr/day, 38 days	40, storage root dry wt	0.20
Potato	3 hr/day, once every 2 wk, 120 days	25, tuber wt	0.20
Pepper	3 hr/day, 3 days/wk, 11 wk	19, fruit dry wt	0.12
Cotton	6 hr/day, 2 day/wk, 13 wk	62, fiber dry wt	0.25
Carnation	24 hr/day, 12 days	74, number of flower buds	0.05 - 0.09
Coleus	2 hr	20, flower no.	0.20
Begonia	4 hr/day, 4 times once every 6 days over 24 days	55, flower wt	0.25

TABLE 7-36. OZONE CONCENTRATIONS AT WHICH SIGNIFICANT YIELD LOSSES HAVE BEEN NOTED FOR A VARIETY OF PLANT SPECIES EXPOSED TO O_3 UNDER VARIOUS EXPERIMENTAL CONDITIONS

Plant species	Exposure duration	Yield reduction, % of control	O_3 concentration
Ponderosa pine	6 hr/day, 126 days	21, stem dry wt	0.10
Western white pine	6 hr/day, 126 days	9, stem dry wt	0.10
Loblolly pine	6 hr/day, 28 day	18, height growth	0.05
Pitch pine	6 hr/day, 28 days	13, height growth	0.10
Poplar	12 hr/day, 5 mo	+1333, leaf abscission	0.041
Hybrid poplar	12 hr/day, 102 days	58, height growth	0.15
Hybrid poplar	8 hr/day, 5 day/wk, 6 wk	50, shoot dry wt	0.15
Red maple	8 hr/day, 6 wk	37, height growth	0.25
American sycamore	6 hr/day, 28 days	9, height growth	0.05
Sweetgum	6 hr/day, 28 days	29, height growth	0.10
White ash	6 hr/day, 28 days	17, total dry wt	0.15
Green ash	6 hr/dat, 28 days	24, height growth	0.10
Willow oak	6 hr/day, 28 days	19, height growth	0.15
Sugar maple	6 hr/day, 28 days	12, height growth	0.15

ground cover species (9 to 33 percent at 0.051 ppm) exposed for several weeks or several months. Studies of eastern white pine and ponderosa pine showed that ambient O_3 reduced the annual radial growth of the trees by 30 to 70 percent. Such a reduction can have a significant impact on wood production.

Some effects on crop quality have been shown in a few of the O_3 addition and ambient air studies. Ambient O_3 in the East (soybean, potato, grapes) and West (sweet corn, alfalfa) have affected product quality. Ozone addition studies reported altered crop quality at 0.10 ppm for alfalfa and clover and at 0.20 ppm for potato, sweet corn, carrot, tomato, and cabbage. Reduced reproductive capacities have also been suggested at O_3 concentrations of 0.05 to 0.10 ppm.

Ozone has been identified as the most important air pollutant in terms of reduced agricultural yields. In view of the importance of U.S. agriculture to both domestic and world consumption of food and fiber, major reductions in supply could have substantial consequences. Numerous studies have attempted to assess dollar losses resulting from ambient O_3 or the benefits of O_3 control. The most recent estimates of ambient O_3 damage to agriculture range from $30 million to $250 million for selected regions and from approximately $2 billion to $3 billion at the national level. These values typically exceed the estimates found in the 1978 criteria document on photochemical oxidants. This increase in damage estimates is partially caused by the increased crop coverage, somewhat greater recognition of O_3 effects as reported in the more recent response literature, different air quality assumptions, and the use of different base-dollars (e.g., 1980 dollars vs. 1970 dollars).

PAN is highly reactive chemically and with biological systems. It is produced photochemically in the same reaction that produces O_3. Both compounds coexist in the photochemical oxidant air pollutant complex. The effects of PAN were a concern in southern California for almost 20 yr before the phytotoxicity of O_3 under ambient conditions was identified.

The characteristic lower surface glazing and bronzing and transverse necrotic or chlorotic bands on foliage associated with PAN exposure have been reported in several states of these United States and in The Netherlands, Japan, and Canada. Monitoring data have revealed even wider distribution of the air pollutant.

Crops and ornamentals marketed for their foliage have frequently been rendered non-marketable or have suffered significant loss of value from ambient

exposures. After severe PAN damage entire crops may be unmarketable, or extensive hand work is required to remove the injured leaves before the crop may be marketed. Losses of fruit, seed, root, and total biomass in other types of crops have not been well evaluated, primarily because experimental data are not available to make such an assessment. The growth, development, and reproductive responses to PAN under ambient conditions are difficult to determine because they cannot be separated from responses to ambient O_3. Long-term experiments designed to measure growth and development responses are difficult to conduct because (1) PAN is highly reactive chemically and difficult to store; (2) generation of PAN is slow and time-consuming; (3) when PAN is condensed in liquid form, it is highly explosive; and (4) plants grown in greenhouses and exposed in chambers are much less responsive to PAN than are plants growing in the field and exposed under ambient conditions.

Growth suppression of navel orange trees exposed for a year to PAN under conditions designed to simulate ambient conditions was reported. Similarly, three and four 4-hr exposures on successive weeks were reported to reduce growth and disrupt photosynthate partitioning in four tomato varieties. Studies with lettuce and Swiss chard indicated that these crops could sustain significant yield losses of 13 percent (lettuce) and 23 percent (Swiss chard) without visible injury symptoms. The plants were exposed to 40 ppb for 4 hour/day, twice week from germination to crop maturity.

A comparison of PAN concentrations likely to cause either visible injury or reduced yield with the measured ambient concentrations (Chapter 6) indicates that it is unlikely that PAN effects will occur to plants in the United States except in some areas of California and possibly a few other localized areas.

PAN reacts with sulfhydryl (SH) groups and has been reported to inhibit SH containing enzymes. PAN was reported to inhibit cell expansion in oat coleoptile. High concentrations disrupted the photosynthesis process in isolated spinach chloroplasts.

Limited studies have been conducted with mixtures of PAN and O_3. When high concentrations of both gases were used, no clear trend was observed. But when PAN concentrations near and at ambient levels were used, the studies indicated that PAN and O_3 do not interact or that the resultant injury was less than would be expected if the effects were additive.

No data have shown that woody species or native vegetation are injured by ambient concentrations of PAN. However, the characteristic PAN-type injury

symptoms have been observed on the foliage of several weed and grass species. Such plants are frequently used as bioindicators to determine if injurious doses of PAN have occurred and to generally establish when the episode occurred and what concentrations were involved.

7.9 REFERENCES

Adams, R. M.; Crocker, T. D. (1982a) Dose-response information and environmental damage assessments: An economic perspective. J. Air Pollut. Control Assoc. 32: 1062-1067.

Adams, R. M.; Crocker, T. D. (1982b) Economically relevant response estimation and the value of information: The case of acid deposition. In: Crocker, T. D., ed. The economics of acid deposition. Ann Arbor, MI: Ann Arbor Science Press.

Adams, R. M.; McCarl, B.A. (1984) Assessing the benefits of alternative oxidant standards on agriculture: The role of response information. J. Environ. Econ. Manage. (In press).

Adams, R. M.; Crocker, T. D.; Thanavibulchai, N. (1982) An economic assessment of air pollution damages to selected annual crops in southern California. J. Environ. Econ. Manage. 9: 42-58.

Adedipe, N. O.; Ormrod, D. P. (1974) Ozone induced growth suppression in radish plants in relation to pre- and post-fumigation temperatures. Z. Pflanzen Physiol. 71: 281-287.

Adedipe, N. O.; Barrett, R. E.; Ormrod, D. P. (1972) Phytotoxicity and growth responses of ornamental bedding plants to ozone and sulfur dioxide. J. Am. Soc. Hortic. Sci. 97: 341-345.

Anderson, V. L.; McLean, R. A. (1974). Design of experiments: A realistic approach. New York, NY: Marcel Dekker, Inc.

Ashmore, M. R. (1984) Effects of ozone on vegetation in the United Kingdom. Proceedings of the OECD Workshop on Ozone, Gothenburg, Sweden.

Ashmore, M. R.; Bell, J. N. B.; Reily, C. L. (1978) A survey of ozone levels in the British Isles using indicator plants. Nature 276: 813-815.

Ashmore, M. R.; Bell, J. N. B.; Reily, C. L. (1980) The distribution of phytotoxic ozone in the British Isles. Environ. Pollut. Series B: 195-216.

Athanassious, R. (1980) Ozone effects on radish (Raphanus sativus L. cv. cherry belle). Foliar sensitivity as related to metabolite levels and cell architecture. Z. Pflanzenphysiol. Bd. 97: 183-187.

Aycock, M. K., Jr. (1972) Combining estimates for weather fleck in Nicotiana tabacum L. Crop Sci. 12: 672-674.

Barnes, R. L. (1972a) Effects of chronic exposure to ozone on photosynthesis and respiration of pines. Environ. Pollut. 3: 133-138.

Barnes, R. L. (1972b) Effects of chronic exposure to ozone on soluble sugar and ascorbic acid contents of pine seedlings. Can. J. Bot. 50: 215-219.

Beckerson, D. W.; Hofstra, G. (1979) Response of leaf diffusive resistance of radish, cucumber, and soybean to O_3 and SO_2 singly or in combination. Atmos. Environ. 13: 1263-1268.

Beckerson, D. W.; Hofstra, G.; Wukasch, R. (1979) The relative sensitivities of 33 bean cultivars to ozone and sulfur dioxide, singly or in combination, in controlled exposures and to oxidants in the field. Plant Dis. Rep. 63: 478-482.

Benedict, H. M.; Miller, C. J.; Olson, R. E. (1971) Economic impact of air pollutants on plants in the United States. Research Triangle Park, NC: U.S. Environmental Protection Agency; APTD-0953.

Bennett, J. H.; Hill, A. C. (1974) Acute inhibition of apparent photosynthesis. In: Dugger, J., ed. Air pollution effects on plant growth. Washington, DC: American Chemical Society; ACS Symposium Series 3.

Bennett, J. P.; Oshima, R. J. (1976) Carrot injury and yield responses to ozone. J. Am. Soc. Hort. Sci. 101: 638-639.

Bennett, J. P.; Runneckles, V. C. (1977) Effects of low levels of ozone on growth of crimson clover and annual ryegrass. Crop Sci. 17: 443-444.

Bennett, J. H.; Lee, E. H.; Heggestad, H. E. (1978) Apparent photosynthesis in leaf stomatal diffusion in EDU treated ozone-sensitive bean plants. In: M. Abdel-Raymen, ed. Proceedings 5th Annu. Plant Growth Regulation Working Group, Ageway, Inc. Syracuse, NY., pp. 242-246.

Bennett, J. P.; Oshima, R. J.; Lippert, L. F. (1979) Effects of ozone on injury and dry matter partitioning in pepper plants. Environ. Exp. Bot. 19: 33-39.

Benoit, L. F.; Skelly, J. M.; Moore, L. D.; Dochinger, L. S. (1982) Radial growth reductions in Pinus strobus L. correlated with foliar ozone sensitivity as an indicator of ozone induced losses in eastern forests. Can. J. For. Res. 12: 673-678.

Benson, E. J.; Krupa, S.; Teng, P. S.; Welsch, P. E. (1982) Economic assessment of air pollution damages to agricultural and silvicultural crops. In: Minnesota final report to Minnesota Pollution Control Agency. University of Minnesota, St. Paul.

Berry, C. R. (1971) Relative sensitivity of red, jack, and white pine seedlings to ozone and sulfur dioxide. Phytopathology 61: 231-232.

Bingham, G. E.; Coyne, P. I. (1977) A portable, temperature-controlled, steady-state porometer for field measurements of transpiration and photosynthesis. Photosynthetica 11: 148-160.

Bisessar, S. (1982) Effect of ozone, antioxidant protection, and early blight on potato in the field. J. Amer. Soc. Hort. Sci. 107: 597-599.

Bissessar, S.; Temple, P. J. (1977) Reduced ozone injury on virus-infected tobacco in the field. Plant Dis. Rep. 61: 961-963.

Black, V. J.; Ormrod, D. P.; Unsworth, M. H. (1982) Effects of low concentrations of ozone singly and in combination with sulfur dioxide on net photosynthesis rates of Vicia faba L. J. Exp. Bot. 33: 1302-1311.

Blum, U. T.; Heck, W. W. (1980) Effects of acute ozone exposures on snap bean at various stages of its life cycle. Environ. Exp. Bot. 20: 73-85.

Blum, U. T.; Tingey, D. T. (1977) A study of the potential ways in which ozone could reduce root growth and modulation of soybean. Atmos. Environ. 11: 737-739.

Blum, U. T.; Smith, G. R.; Fites, R. C. (1982) Effects of multiple O_3 exposures on carbohydrate and mineral contents of Ladino clover. Env. Exp. Bot. 22: 143-154.

Bobrov, R. A. (1955) The leaf structure of Poa annua with observations on its smog sensitivity in Los Angeles County. Amer. J. Bot. 42: 467-474.

Botkin, D. B.; Smith, W. H.; Carlson, R. W.; Smith, T. L. (1972) Effects of ozone on white pine saplings: Variation in inhibition and recovery of net photosynthesis. Environ. Pollut. 3: 273-289.

Box, G. E. P.; Hunger, W. G.; Hunter, J. S. (1978) Statistics for experimenters. New York, NY: John Wiley and Sons, Inc.

Boyer, J. S. (1982) Plant productivity and environment. Science 218: 443.

Brandt, C. S. (1962) Effects of air pollution on plants. In: Stern, A. C., ed. Air pollution. Vol. I. New York, NY: Academic Press; pp. 255-281.

Brennan, E. (1975) On exclusion as the mechanism of ozone resistance of virus-infected plants. Phytopathology 65: 1054-1055.

Brennan, E.; Halisky, P. M. (1970) Response of turfgrass cultivars to ozone and sulfur dioxide in the atmosphere. Phytopathology 60: 1544-1546.

Brennan, E.; Leone, I. A. (1969) Suppression of ozone toxicity symptoms in virus-infected tobacco. Phytopathology 59: 263-264.

Brennan, E.; Leone, I. A. (1970) The response of English holly selections to ozone and sulfur dioxide. Holly Lett. 37: 6-7.

Brennan, E.; Leone, I. A. (1972) Chrysanthemum response to sulfur dioxide and ozone. Plant Dis. Rep. 56: 85-87.

Brennan, E.; Leone, I. A.; Daines, R. H. (1964) The importance of variety in ozone plant damage. Plant Dis. Rep. 48: 923-924.

Brennan, E.; Leone, I. A.; Halisky, P. M. (1969) Response of forage legumes to ozone fumigations. Phytopathology 59: 1458-1459.

Butler, L. K.; Tibbitts, T. W. (1979) Stomatal mechanisms determining genetic resistance to ozone in Phaseolus vulgaris L. J. Am. Soc. Hort. Sci. 104: 213-216.

Butler, L. K.; Tibbitts, T. W.; Bliss, F. A. (1979) Inheritance of resistance to ozone in Phaseolus vulgaris L. J. Am. Soc. Hort. Sci. 104: 211-213.

Cameron, J. W. (1975) Inheritance in sweet corn for resistance to acute ozone injury. J. Am. Soc. Hort. Sci. 100: 577-579.

Carlson, R. W. (1979) Reduction in the photosynthetic rate of Acer, Quercus, and Fraxinus species caused by sulphur dioxide and ozone. Environ. Pollut. 18: 159-170.

Carnahan, J. E.; Jenner, E. L.; Wat, E. K. W. (1978) Prevention of ozone injury to plants by a new protective chemical. Phytopathology 68: 1225-1229.

Carney, A. W.; Stephenson, G. R.; Ormrod, D. P.; Ashton, G. C. (1973) Ozone-herbicide interactions in crop plants. Weed Sci. 21: 508-511.

Cathey, H. M.; Heggestad, H. E. (1972) Reduction of ozone damage to Petunia hybrida Vilm. by use of growth-regulating chemicals and tolerance cultivars. J. Amer. Soc. Hort. Sci. 97: 695-700.

Cathey, H. M.; Heggestad, H. E. (1973) Effects of growth retardants and fumigations with ozone and sulfur dioxide on growth and flowering of Euphorbia pulchurima Willd. J. Amer. Soc. Hort. Sci. 98: 3-7.

Cathey, H. M.; Heggestad, H. E. (1982a) Ozone and sulfur dioxide sensitivity of petunia: Modification by ethylenediurea. J. Amer. Soc. Hort. Sci. 107: 1028-1035.

Cathey, H. M.; Heggestad, H. E. (1982b) Ozone sensitivity of herbaceous plants: Modification by ethylenediurea. J. Amer. Soc. Hort. Sci. 107: 1035-1042.

Cathey, H. M.; Heggestad, H. E. (1982c) Ozone sensitivity of woody plants: Modification by ethylenediurea. J. Amer. Soc. Hort. Sci. 107: 1042-1045.

Christensen, E.; Giese, A. C. (1954) Changes in absorption spectra of nucleic acids and their derivatives following exposure of ozone to ultraviolet radiation. Arch. Biochem. Biophys: 51: 208-216.

Clarke, B. B.; Henninger, M. R.; Brennan, E. (1983) An assessment of potato losses caused by oxidant air pollution in New Jersey. Phytopathology 73: 104-108.

Clayberg, C. D. (1971) Screening tomatoes for ozone resistance. Hort. Sci. 6: 396-397.

Cobb, F. W. Jr.; Stark, R. W. (1970) Decline and mortality of smog-injured ponderosa pine. J. For. 68: 147-149.

Cochran, W. G.; Cox, G. M. (1957) Experimental designs. 2nd Ed. New York, NY: John Wiley and Sons, Inc.

Costonis, A. C.; Sinclair, W. A. (1972) Susceptibility of healthy and ozone-injured needles of Pinus strobus to invasion by Lophodermium pinastri and Aureobasidium pullalans. Eur. J. For. Path. 2: 65-73.

Coulson, C. L.; Heath, R. L. (1974) Inhibition of the photosynthetic capacity of isolated choloroplasts by ozone. Plant Physiol. 53: 32-38.

Coyne, P. E.; Bingham, G. E. (1978) Photosynthesis and stomatal light responses in snap beans exposed to hydrogen sulfide in ozone. J. Air Pollut. Control Assoc. 28: 1119-1123.

Coyne, P. E.; Bingham, G. E. (1981) Comparative ozone dose response of gas exchange in a ponderosa pine stand exposed to long-term fumigations. J. Air Pollut. Control Assoc. 31: 38-41.

Craker, L. E.; Feder, W. A. (1972) Development of the inflorescence in petunia, geranium, and poinsettia under ozone stress. Hort. Sci. 7: 59-60.

Crocker, T. D. (1982) Pollution damage to managed ecosystems. In: Jackson, J. S.; Miller, A. A., eds. Economic assessments in effects of air pollution on farm commodities. Izaak Walton League of America; Washington, DC; pp. 103-124.

Czuba, M.; Ormrod, D. P. (1974) Effects of cadmium and zinc on ozone induced phytotoxicity in cress and lettuce. Can. J. Bot. 52: 645-649.

Czuba, M.; Ormrod, D. P. (1981) Cadmium concentrations in cress shoots in relation to cadmium-enhanced ozone phytotoxicity. Environ. Poll. 25: 67-76.

Darley, E. F.; Dugger, W. M.; Mudd, J. B.; Ordin, L.; Taylor, O. C.; Stephens, E. R. (1963) Plant damage by pollution derived from automobiles. Arch. Environ. Health 6: 761-770.

Davis, D. D. (1975) Resistance of young ponderosa pine seedlings to acute doses of PAN. Plant Dis. Rept. 59: 183-184.

Davis, D. D. (1977) Response of ponderosa pine primary needles to separate and simultaneous ozone and PAN exposures. Plant Dis. Rep. 61: 640-644.

Davis, D. D.; Coppolino, J. B. (1974) Relative ozone susceptibility of selected woody ornamentals. Hort. Sci. 9: 537-539.

Davis, D. D.; Coppolino, J. B. (1976) Ozone susceptibility of selected woody shrubs and vines. Plant Dis. Rep. 60: 876-878.

Davis, D. D; Kress, L. (1974) The relative susceptibility of ten bean varieties to ozone. Plant Dis. Rep. 58: 14-16.

Davis, D. D.; Smith, S. H. (1975) Bean common mosaic virus reduces ozone sensitivity of pinto bean. Environ. Pollut. 9: 97-101.

Davis, D. D.; Smith, S. H. (1976) Reduction of ozone sensitivity of pinto bean by virus-induced local lesions. Plant Dis. Rep. 60: 31-34.

Davis, D. D.; Wood, F. A. (1972) The relative susceptibility of eighteen coniferous species to ozone. Phytopathology 62: 14-19.

Davis, D. D.; Umbach, D. M.; Coppolino, J. B. (1981) Susceptibility of tree and shrub species and response of black cherry foliage to ozone. Plant Dis. 65: 904-907.

Davis, J. M.; Rogers, H. H. (1980) Wind tunnel testing of open-top field chambers for plant affects assessment. J. Air Pollut. Control Assoc. 30: 905-908.

Dean, C. E. (1963) Weather fleck on Florida shadegrown tobacco. Tob. Sci. 7: 41-45.

Dean, C. E. (1972) Stomate density and size as related to ozone-induced weather fleck in tobacco. Crop Sci. 12: 547-548.

DeBauer, L. I. (1972) Uso de plantas indicadoras en la determinacion de aeropolutos en la Cuidad de Mexico. Phytopathology 62: 753.

de Cormis, L.; Borte, J.; Tisne, A. (1975) Technique experimentale permettant l'etude de l'incidence sur la vegetation d'une pollution par le dioxyde de soufie applique en permanence et a dose subnecrotique. Pollut. Atmos. 17(16): 103-107.

DeVos, N. E.; Hill, R. R., Jr.; Hepler, R. W.; Pell, E. J.; Craig, R. (1980) Inheritance of peroxyacetyl nitrate resistance in petunia. J. Am. Soc. Hort. Sci. 105: 157-160.

DeVos, N. E.; Hill, R. R. Jr.; Pell, E. J.; Cole, R. H. (1982) Quantitative inheritance of ozone resistance in potato. Crop Sci. 22: 992-995.

DeVos, N. E.; Pell, E. J.; Hill, R. R., Jr.; Cole, R. H. (1983) Laboratory versus field response of potato genotypes to oxidant stress. Plant Dis. 67: 173-176.

Dijak, M.; Ormrod, D. P. (1982) Some physiological and anatomical characteristics associated with differential ozone sensitivity among pea cultivar. Environ. Exp. Bot. 22: 395-402.

Dixon, B. L.; Garcia, P.; Mjelde, J. W.; Adams, R. M. (1983) Estimation of the economic cost of ozone on Illinois cash grain farms. Urbana, IL: Illinois Agricultural Experiment Station Research Report (in press).

Dochinger, L. S.; Bender, F. W.; Fox, F. L.; Heck, W. W. (1970) Chlorotic dwarf of eastern white pine caused by an ozone and sulphur dioxide interactin. Nature 225: 476.

Dochinger, L. S.; Townsend, A. M. (1979) Effects of roadside deicer salts and ozone on red maple progenies. Environ. Pollut. 19: 229-237.

Draper, N. R.; Smith, H. 1966. Applied regression analysis. New York, NY: John Wiley and Sons, Inc.

Drummond, D. D. (1972) The effect of peroxyacetyl nitrate on petunia (Petunia hybrida Vilm): An abstract of a Ph.D. thesis in plant pathology. Dept. of Plant Pathology, The Pennsylvania State University, PA.

Duchelle, S. F.; Skelly, J. M. (1981) Response of common milkweed to oxidant air pollution in the Shenandoah National Park in Virginia. Plant Dis. 65: 661-662.

Duchelle, S. F.; Skelly, J. M.; Chevone, B. I. (1982) Oxidant effects on forest tree seedling growth in the Appalachian Mountains. Water, Air, Soil Pollut. 18: 363-373.

Duchelle, S. F.; Skelly, J. M.; Charick, T. L.; Chevone, B. I.; Yang, Y. S.; Nellessen, J. E. (1983) Effects of ozone on the productivity of natural vegetation in a high meadow of the Shenandoah National Park of Virginia. J. Environ. Manage. 17: 299-308.

Dugger, W. M. Jr.; Ting, I. P. (1968) The effect of peroxyacetyl nitrate on plants: Photoreductive reactions and susceptibility of bean plants to PAN. Phytopathology 58: 1102-1107.

Dugger, W. M., Jr.; Mudd, J. B.; Koukol, J. (1965) Effect of PAN on certain photosynthetic reactions. Arch. Environ. Health. 10: 195-200.

Dugger, W. M. Jr.; Taylor, O. C.; Klein, W. H.; Shropshire, W. (1963) Action spectrum of peroxyacetyl nitrate damage to bean plants. Nature (London) 198: 75-76.

Dunning, J. A.; Heck, W. W. (1973) Response of pinto bean and tobacco to ozone as conditioned by light intensity and/or humidity. Environ. Sci. Technol. 7: 824-826.

Dunning, J. A.; Heck, W. W. (1977) Response of bean and tobacco to ozone: Effect of light intensity, temperature and relative humidity. J. Air Pollut. Control Assoc. 27: 882-886.

Dunning, J. A.; Heck, W. W.; Tingey, D. T. (1974) Foliar sensitivity of pinto bean and soybean to ozone as affected by temperature, potassium nutrition and ozone dose. Water, Air, Soil Pollut. 3: 305-313.

Edinger, J. G.; McCutchan, M. H.; Miller, P. R.; Ryan, B. C.; Schroeder, M. J.; Behar, J. V. (1972) Penetration and duration of oxidant air pollution in the South Coast Air Basin of California. J. Air Pollut. Control Assoc. 22: 882-886.

Elkiey, T.; Ormrod, D. P. (1980) Response of turfgrass cultivars to ozone, sulfur dioxide, nitrogen dioxide, or their mixture. J. Am. Soc. Hort. Sci. 105: 664-668.

Elkiey, T.; Ormrod, D. P. (1981) Absorption of ozone, sulphur dioxide, and nitrogen dioxide by petunia plants. Environ. Experi. Bot. 21: 63-70.

Engle, R. L.; Gabelman, W. H. (1966) Inheritance and mechanism for resistance to ozone damage in onion, Allium cepa L. J. Am. Soc. Hort. Sci. 89: 423-430.

Ensing, J.; Hofstra, G. (1982) Impact of the air pollutant ozone on acetylene reduction and shoot growth of red clover. Can. J. Plant Pathol. 4: 237-242.

Evans, L. S.; Ting, I. P. (1974) Ozone sensitivity of leaves: Relationship to leaf water content, gas transfer resistance, and anatomical characteristics. Am. J. Bot. 61: 592-597.

Feder, W. A. (1968) Reduction in tobacco pollen germination and tube elongation induced by low levels of ozone. Science 160: 1122.

Feder, W. A. (1978) Plants as bioassay systems for monitoring atmospheric pollutants. Environ. Health Perspectives 27: 139-147.

Feder, W. A.; Campbell, F. J. (1968) Influence of low levels of ozone on flowering of carnations. Phytopathology 58: 1038-1039.

Feder, W. A.; Manning, W. J. (1979) Living plants as indicators and monitors. In: Heck, W. W., Krupa, S. V., and Linzon, S. N., eds. Handbook of methodology for the assessment of air pollution effects on vegetation. Pittsburgh, PA: Air Pollution Control Assoc.

Feder, W. A.; Fox, F. L.; Heck, W. W.; Campbell, F. J. (1969) Varietal responses of petunia to several air pollutants. Plant Dis. Rep. 53: 506-510.

Flagler, R. B.; Youngner, V. B. (1982a) Ozone and sulfur dioxide effects on tall fescue: Growth and yield responses. Vol. I. J. Environ. Qual. 11: 386-389.

Flagler, R. B.; Youngner, V. B. (1982b) Ozone and sulfur dioxide effects on three tall fescue cultivars. J. Environ. Qual. 11: 413-416.

Floor, H.; Posthumus, A. C. (1977) Biologische erfassung von ozon-lund PAN-immissionen in den niederlanden 1973, 1974, and 1975. VDI-Berichte 270: 183-190.

Fong, F.; Heath, R. L. (1981) Lipid content in the primary leaf of bean (Phaseolus vulgaris) after ozone fumigation. Z. Pflanzenphysiol. 104: 109-115.

Foster, K. W.; Timm, H.; Labanauskas, C. K.; Oshima, R. J. (1983b) Effects of ozone and sulfur dioxide on tuber yield and quality of potatoes. J. Environ. Qual. 12: 75-80.

Foster, K. W.; Guerard, J. P.; Oshima, R. J.; Bishop, J. C.; Timm, H. (1983a) Differential ozone susceptibility of centennial russet and white rose potato as demonstrated by fumigation and antioxidant treatments. Amer. Pot. J. 60: 127-139.

Freebairn, H. T. (1963) Uptake and movement of $1\text{-}C^{14}$ ascorbic acid in bean leaves. Physiol. Plant. 16: 517-522.

Freebairn, H. T.; Taylor, O. C. (1960) Prevention of plant damage from airborne oxidizing agents. Proc. Amer. Soc. Hort. Sci. 76: 693-699.

Freeman, A. M., III (1979) The benefits of environmental improvement. Baltimore, MD: The Johns Hopkins University Press.

Fujiwara, T.; Ishikawa, H. (1976) Actual effects of combination of sulfur dioxide, nitrogen dioxide and ozone on some plants (in Japanese with English summary). Bull. Bio-Environ. Lab., No. 476001. 1019 pp.

Fukuda, H.; and Terakado, K. (1974) On the damages of plants due to peroxyacyl nitrates (PAN). Tokyo Nogyo Shikenjo Sokuho, Feb. 1974, pp. 35-36. (English abstract).

Furukawa, A.; Kadota, M. (1975) Effects of ozone on photosynthesis and respiration in poplar leaves. Environ. Control Biol. 13: 1-7.

Gale, J.; Hagan, R. M. (1966) Plant antitranspirents. Anna. Rev. Plant Physiol. 17: 269-282.

Gardner, W. S. (1973) Ozone injury to tobacco plants in South Dakota. Plant Dis. Rep. 57: 106-110.

Gesalman, C. M.; Davis, D. D. (1978) Ozone susceptibility for ten azalea cultivars as related to stomata frequency or conductance. J. Am. Soc. Hort. Sci. 103: 489-491.

Georgopoulos, P. G.; Seinfeld, J. H. (1982) Statistical distribution of air pollutant concentrations. Environ. Sci. Tech. 16: 401A-416A.

Gilbert, M. D.; Elfving, D. C.; Lisk, D. J. (1977) Protection of plants against ozone using the antiozonant N-(1,3-dimethylbutyl)-N'phenyl-p-phenylenediamine. Bull. Environ. Contam. Toxicol. 18: 783-786.

Glater, R. B.; Solberg, R. A.; Scott, F. M. (1962) A developmental study of the leaves of Nicotiana glutinosa as related to their smog-sensitivity. Am. J. Bot. 49: 954-970.

Goren, A. I.; Donagi, A. E. (1979) Use of Bel-W3 tobacco as indicator plant for atmospheric ozone during different seasons in the coastal zone of Israel. Int. J. Biometeorol. 23: 331-335.

Goren, A. I.; Donagi, A. E. (1980) Assessment of atmospheric ozone levels in Israel through foliar injury to Bel-W3 tobacco plants. Oecologia 44: 418-421.

Gross, R. E.; Dugger, W. M. (1969) Responses of Chlamydomonas reinhardtia to peroxyacetyl nitrate. Environ. Res. 2: 256-266.

Grosso, J. J., Menser, H. A., Jr.; Hodges, G. H.; McKinney, H. H. (1971) Effects of air pollutants on Nicotiana cultivars and species used for virus studies. Phytopathology 61: 945-950.

Guderian, R. (1977) Air pollution: Phytotoxicity of acidic gases and its significance in air pollution control. In: Ecological studies 22. Chapter 4. Springer-Verlag, Berlin.

Guderian, R.; Schoenbeck, H. (1971) Recent results for recognition and monitoring of air pollution with the aid of plants. In: Englund, H. M.; Beery, W. T., eds. Proceedings of the second international clean air congress; December 1970; Washington, DC. New York, NY: Academic Press; pp. 266-273.

Hanson, G. P. (1972) Relative air pollution sensitivity of some Los Angeles Arboretum plants. Lasca Leaves 22: 86-89.

Hanson, G. P.; Stewart, W. S. (1970) Photochemical oxidants: Effect on starch hydrolysis in leaves. Science 168: 1223-1224.

Hanson, G. P.; Addis, D. H.; Thorne, L. (1976) Inheritance of photochemical air pollution tolerance in petunia. Can. J. Genet. Cytol. 18: 579-592.

Hanson, G. P.; Thorne, L.; Addis, D. H. (1975) Ozone sensitivity of Petunia hybrida Vilm. as related to physiological age. J. Am. Soc. Hort. Sci. 100: 188-190.

Harkov, R.; Brennan, E. (1980) The influence of soil fertility and water stress on the ozone response of hybrid poplar trees. Phytopathology 70: 991-994.

Harkov, R.; Clarke, B.; Brennan, E. (1979) Cadmium contamination may modify response of tomato to atmospheric ozone. J. Air Pollut. Cont. Assoc. 29: 1247-1249.

Harris, M. J.; Heath, R. L. (1981) Ozone sensitivity in sweet corn (Zea mays L.) plants: A possible relationship to water balance. Plant Physiol. 68: 885-890.

Heagle, A. S. (1970) Effect of low-level ozone fumigations on crown rust of oats. Phytopathology 60: 252-254.

Heagle, A. S. (1973) Interactions between air pollutants and plant parasites. Phytopathology 11: 365-388.

Heagle, A. S. (1975) Response of three obligate parasites to ozone. Environ. Pollut. 9: 91-95.

Heagle, A. S. (1977) Effect of ozone on parasitism of corn by Helminthosporium maydis. Phytopathology 67(5): 616-618.

Heagle, A. S. (1979a) Effects of growth media, fertilizer rate and hour and season of exposure on sensitivity of four soybean cultivars to ozone. Environ. Pollut. 18: 313-322.

Heagle, A. S. (1979b) Ranking of soybean cultivars for resistance to ozone using different ozone doses and response measures. Environ. Pollut. 19: 1-10.

Heagle, A. S. (1982) Interactions between air pollutants and parasitic plant diseases. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London, England: Butterworths Scientific; pp. 333-348.

Heagle, A. S.; Heck, W. W. (1980) Field methods to assess crop losses due to oxidant air pollutants. In: Teng, P. S.; Krupa, S. V. eds. Crop loss assessment: Proceedings of E. C. Stakman commemorative symposium. University of Minnesota, Agricultural Experimental Station; Miscellaneous Publication No. 7; pp. 296-305.

Heagle, A. S.; Heck, W. W. (1974) Predisposition of tobacco to oxidant air pollution injury by a previous exposure to oxidants. Environ. Pollut. 7: 247-251.

Heagle, A. S.; Johnston, J. W. (1979) Variable responses of soybean to mixtures of ozone and sulfur dioxide. J. Air Pollut. Control Assoc. 29: 729-732.

Heagle, A. S.; Key, L. W. (1973a) Effect of ozone on the wheat stem rust fungus. Phytopathology 63: 397-400.

Heagle, A. S.; Key, L. W. (1973b) Effect of Puccinia graminis f. sp. tritici on ozone injury in wheat. Phytopathology 63: 609-613.

Heagle, A. S.; Letchworth, M. B. (1982) Relationships among injury, growth, and yield responses of soybean cultivars exposed to ozone at different light intensities. J. Environ. Qual. 11: 690-694.

Heagle, A. S.; Philbeck, R. B. (1979) Exposure techniques. In: Heck, W. W.; Krupa, S. V.; Linzon, S. N., eds. Methodology for the assessment of air pollution effects on vegetation: APCA specialty conference proceedings. Pittsburgh, PA: Air Pollution Control Association; pp. 6-2 to 6-18.

Heagle, A. S.; Strickland, A. (1972) Reaction of Erysiphe graminis f. sp. hordei to low levels of ozone. Phytopathology 62: 1144-1148.

Heagle, A. S.; Body, D. E.; Heck, W. W. (1973) An open-top field chamber to assess the impact of air pollution on plants. J. Environ. Qual. 2: 365-368.

Heagle, A. S., Body, D. E.; Neely, G. E. (1974) Injury and yield responses of soybean to chronic doses of ozone and sulfur dioxide in the field. Phytopathology 64: 132-136.

Heagle, A. S.; Body, D. E.; Pounds, E. K. (1972) Effect of ozone on yield of sweet corn. Phytopathology 62: 683-687.

Heagle, A. S.; Letchworth, M. B.; Mitchell, C. A. (1983a) Effects of growth medium and fertilizer rate on the yield response of soybeans exposed to chronic doses of ozone. Phytopathology 73: 134-139.

Heagle, A. S.; Letchworth, M. B.; Mitchell, C. A. (1983b) Injury and yield responses of peanuts to chronic doses of ozone in open-top field chambers. Phytopathology 73: 551-555.

Heagle, A. S.; Heck, W. W.; Rawlings, J. O.; Philbeck, R. B. (1983) Effects of chronic doses of ozone and sulfur dioxide on injury and yield of soybeans in open-top chambers. Crop Science 26: 1184-1191.

Heagle, A. S.; Philbeck, R. B.; Knott, W. M. (1979a) Thresholds for injury growth, and yield loss caused by ozone or field corn hybrids. Phytopathology 69: 21-26.

Heagle, A. S.; Philbeck, R. B.; Letchworth, M. B. (1979b) Injury and yield response of spinach cultivars to chronic doses of ozone in open-top field chambers. J. Environ. Qual. 8: 268-273.

Heagle, A. S.; Spencer, S.; Letchworth, M. B. (1979c) Yield response of winter wheat to chronic doses of ozone. Can. J. Bot. 57: 1999-2005.

Heagle, A. S.; Philbeck, R. B.; Rogers, H. H.; Letchworth, M .B. (1979d) Dispensing and monitoring ozone in open-top field chambers for plant-effect studies. Phytopathology 69: 15-20.

Heath, R. L. (1975) Ozone. In: Mudd, J. B.; Kozlowski, T. T. eds. Responses of plants to air pollution. New York, NY: Academic Press, Inc.; pp. 23-55.

Heath, R. L. (1980) Initial events in injury to plants by air pollutants. Ann. Rev. Plant Physiol. 31: 395-431.

Heck, W. W. (1966) The use of plants as indicators of air pollution. Air and Water Pollut. 10: 99-111.

Heck, W. W. (1968) Factors influencing expression of oxidant damage to plants. Ann. Rev. Phytopathol. 6: 165-188.

Heck, W. W.; Heagle, A. S. (1970) Measurement of photochemical air pollution with a sensitive monitoring plant. J. Air Pollut. Control Assoc. 20: 97-99.

Heck, W. W.; Tingey, D. T. (1971) Ozone time-concentration model to predict acute foliar injury. In: Englund, H. M.; Beery, W. T. eds. Proceedings of the Second International Clean Air Congress. New York: Academic Press; pp. 249-255.

Heck, W. W.; Dunning, J. A.; Hindawi, I. J. (1966) Ozone: Nonlinear relation of dose and injury to plants. Science 151: 511-515.

Heck, W. W.; Dunning, J. A.; Johnson, H. (1968) Design of a simple plant exposure chamber. U.S. Department of Health, Education, and Welfare, National Center Air Pollution Control; Publication APTD-68-6, 24 pp.

Heck, W. W.; Larsen, R. I.; Heagle, A. S. (1980) Measuring the acute dose-response of plants to ozone. In: Assessment of losses which constrain production and crop improvement in agriculture and forests: Proceedings of the E. C. Stakman commemorative symposium. St. Paul, MN: University of Minnesota, Agricultural Experimental Station; Miscellaneous Publication No. 7-1980; pp. 32-49.

Heck, W. W.; Philbeck, R. B.; Dunning, J. A. (1978) A continuous stirred tank reactor (CSTR) system for exposing plants to gaseous air contaminants: Principles, specifications, construction and operation. U.S. Department of Agriculture; Agriculture Research Series 181. Washington, DC: U.S. Government Printing Office.

Heck, W. W.; Fox, F. L.; Brandt, C. S.; Dunning, J. A. (1969) Tobacco, a sensitive monitor for photochemical air pollution. U.S. Department of Health, Education, and Welfare; National Air Pollution Control Administration Publication No. AP-55.

Heck, W. W.; Taylor, O. C.; Adams, R.; Bingham, G.; Miller, J.; Preston, E.; Weinstein, L. (1982) Assessment of crop loss from ozone. J. Air Pollut. Control Assoc. 32:353-361.

Heck, W. W.; Adams, R. M.; Cure, W. W.; Heagle, A. S.; Heggestad, H. E.; Kohut, R. J.; Kress, L. W.; Rawlings, I. O; Taylor, O. C. (1983) A reassessment of crop loss from ozone. Environ. Sci. Tech. 17: 573A-581A.

Heggestad, H. E. (1973) Photochemical air pollution injury to potatoes in the Atlantic coastal states. Amer. Potato J. 50: 315-328.

Heggestad, H. E.; Bennett, J. H. (1981) Photochemical oxidants potentiate yield losses in snap beans attributable to sulfur dioxide. Science 213: 1008-1010.

Heggestad, H. E.; Darley, E. F. (1969) Plants as indicators for air pollutants ozone and PAN. In: Air pollution proceedings of the first European Congress on the influence of air pollution on plants and animals. Wageningen, The Netherlands: Center for Agricultural Publishing Documentation; pp. 1968: 329-355.

Heggestad, H. E.; Menser, H. A. (1962) Leaf spot-sensitive tobacco strain Bel-W3, a biological indicator of the air pollutant ozone. Phytopathology 52: 735.

Heggestad, H. E.; Middleton, J. T. (1959) Ozone in high concentrations as cause of tobacco leaf injury. Science 129: 208-210.

Heggestad, H. E.; Burleson, R. F.; Middleton, J. T.; Darley, E. F. (1964) Leaf injury on tobacco varieties resulting from ozone, ozonated hexene-1, and ambient air of metropolitan areas. Int. J. Air Water Pollut. 8: 1-10.

Heggestad, H. E.; Heagle, A. S.; Bennett, J. H.; Koch, E. J. (1980) The effects of photochemical oxidants on the yield of snap beans. Atmos. Environ. 14: 317-326.

Henderson, W. R.; Reinert, R. A. (1979) Yield response of four fresh market tomato cultivars after acute ozone exposure in the seedling stage. J. Am. Soc. Hort. Sci. 104: 754-759.

Hibben, C. R. (1966) Sensitivity of fungal spores to sulphur dioxide and ozone. Phytopathology 56: 880-881.

Hibben, C. R. (1969) Ozone toxicity to sugar maple. Phytopathology 59:1423-1428.

Hibben, C. R.; Stotzky, G. (1969) Effects of ozone on the germination of fungus spores. Can. J. Microbiol. 15: 1187-1196.

Hibben, C. R.; Taylor, M. P. (1975) Ozone and sulphur dioxide effects on the lilac powdery mildew fungus. Environ. Pollut. 9: 107-114.

Hill, A. C. (1971) Vegetation: A sink for atmospheric pollutants. J. Air Pollut. Control Assoc. 21: 341-356.

Hodges, G. H.; Menser, H. A.; Ogden, W. B. (1971) Susceptibility of Wisconsin Havana tobacco cultivars to air pollutants. Agron. J. 63: 107-111.

Hofstra, G.; Beckerson, D. W. (1981) Foliar responses of five plant species to ozone and a sulphur dioxide/ozone mixture after a sulphur dioxide pre-exposure. Atmos. Environ 15: 383-389.

Hofstra, G.; Ormrod, D. P. (1977) Ozone and sulphur dioxide interaction in white bean and soybean. Can. J. Plant Sci. 57: 1193-1198.

Hofstra, G.; Littlejohns, D. A.; Wukasch, R. T. (1978) The efficiency of the antioxidant ethylene-dioxide (EDU) compared to carboxin and benomyl in reducing yield losses from ozone in navy bean. Plant. Dis. Rep. 62: 350-352.

Hoffman, G. J.; Maas, E. V.; Rawlins, S. L. (1973) Salinity-ozone interactive effects on yield and water relations of pinto bean. J. Environ. Qual. 2: 148-152.

Hoffman, G. J.; Maas, E. V.; Rawlins, S. L. (1975) Salinity-ozone interactive effects on alfalfa yield and water relations. J. Environ. Qual. 4: 326-331.

Hoigne, J.; Bader, H. (1975) Ozonation of water: Role of hydroxyl radicals as oxidizing intermediates. Science 190: 782-784.

Holt, D. A.; Daughtry, C. S. T.; Dale, R. F.; Hollinger, S. E.; Reetz, H. F.; Nelson, W. L.; Postage R. (1979) Separating soil, management, and weather effects in large area yield prediction. In: Peart, R., ed. Proceedings of biological systems simulation group workshop on crop simulation. West Lafayette, IN: Purdue University.

Hooker, W. J.; Yang, T. C.; Potter, H. S. (1973) Air pollution injury of potato in Michigan. Amer. Potato J. 50:151-161.

Horsman, D. C. (1981) A survey of ozone in Melbourne using tobacco as an indicator plant. Environ. Pollut. Series B: 69-77.

Horsman, D. C.; Nicholls, A. O.; Calder, D. M. (1980) Growth responses of Dactylis glomerata, Lolium perenne, and Phalaris aquatica to chronic ozone exposure. Aust. J. Plant Physiol. 7: 511-517.

Houston, D. B. (1974) Response of selected Pinus strobus L. clones to fumigations with sulfur dioxide and ozone. Can. J. For. Res. 4: 65-68.

Howell, R. K.; Graham, J. H. (1977) Interaction of ozone and bacterial leafspot on alfalfa. Plant Dis. Rep. 61:565-567.

Howell, R. K.; Kremer, D. F. (1973) The chemistry and physiology of pigmentation of leaves injured by air pollution. J. Environ. Qual. 2: 434-438.

Howell, R. K.; Rose, L. P. (1980) Residual air pollution effects on soybean seed quality. Plant Dis. 64: 385-386.

Howell, R. K.; Thomas, C. A. (1972) Relative tolerances of twelve safflower cultivars to ozone. Plant Dis. Rep. 56: 195-197.

Howell, R. K.; Devine, T. E.; Hanson, C. H. (1971) Resistance of selected alfalfa strains to ozone. Crop Sci. 11: 114-115.

Howell, R. K.; Kock, E. J.; Rose, L. P. (1979) Field assessment of air pollution-induced soybean yield losses. Agron. J. 71: 285-288.

Huang, T. R.; Aycock, M. D., Jr.; Mulchi, C. L. (1975) Heterosis and combining ability estimates for air pollution damage, primarily ozone in Maryland tobacco. Crop Sci. 15: 785-789.

Hucl, P.; Beyersdorf, W. D. (1982) The inheritance of ozone sensitivity in selected Phaseolus vulgaris L. populations. Can. J. Plant Sci. 62: 861-865.

Hughes, P. R.; Laurence, J. A. (1984) Relationship of biochemical effects of air pollutants on plants to environmental problems: Insect and microbial interactions. In: Koziol, M. J.; Whatley, F. R., eds., Gaseous air pollutants and plant metabolism, London, England: Butterworth Scientific; pp. 361-377.

Hurwitz, B.; Pell, E. J.; Sherwood, R. T. (1979) Status of coumesterol and 4', 7-dihydroxy flavone in alfalfa foliate exposed to ozone. Phytopathology 69: 810-813.

Jacobson, J. S. (1977) The effects of photochemical oxidants on vegetation. In: Ozone und Begleitsubstanzen im photochemischen Smog. VDI Ber. 270: 163-173.

Jacobson, J. S. (1982) Ozone and the growth and productivity of agricultural crops. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London, England: Butterworth Scientif pp. 293-304.

Jacobson, J. S.; Colavito, L. J. (1976) The combined effect of sulfur dioxide and ozone on bean and tobacco plants. Environ. Exp. Bot. 16: 277-285.

Jacobson, J. S.; Feder, W. A. (1974) A regional network for environmental monitoring: Atmospheric oxidant concentrations and foliar injury for tobacco indicator plants in the Eastern United States. Amherst, MA: Massachusetts Agricultural Experiment Station College of Food and Natural Resources; Bulletin No. 604.

James, C. (1980) Economic, social and political implications of crop losses: A holistic framework for loss assessment in agricultural systems. In: Crop loss assessment proceedings. E. C. Stakman Comm. Symposium, Univ. of Minnesota, Agr. Expt. Miscellaneous Publication No. 7; pp. 10-16.

James, R. L.; Cobb, F. W., Jr.; Miller, P. R.; Parmeter, J. R., Jr. (1980) Effects of oxidant air pollution on susceptibility of pine roots to Fomes annosus. Phytopathology 70:560-563.

James, R. L.; Cobb, F. W., Jr.; Wilcox, W. W.; Rowney, D. L. (1980) Effects of photochemical oxidant injury to ponderosa and Jeffrey pines on susceptibility of freshly cut stumps to Fomes annosus. Phytopathology 70:704-708.

Jensen, K. F. (1973) Response of nine forest tree species to chronic ozone fumigation. Plant Dis. Rep. 57: 914-917.

Jensen, K. F. (1979) A comparison of height growth and leaf parameters of hybrid poplar cuttings grown in ozone-fumigated atmospheres. U.S. Department of Agriculture; Forest Service Research Paper NE-446.

Jensen, K. F. (1981a) Air pollutants affect the relative growth rate of hardwood seedlings. U.S. Department of Agriculture; Forestry Service Research Paper NE-470.

Jensen, K. F.; Dochinger, L. S. (1974) Responses of hybrid poplar cuttings to chronic and acute levels of ozone. Environ. Pollut. 6: 289-295.

Jensen, K. F.; Masters, R. G. (1975) Growth of six woody species fumigated with ozone. Plant Dis. Rep. 59: 760-762.

Jones, J. V.; Pell, E. J. (1981) The influence of ozone on the presence of isoflavone in alfalfa foliage. J. Air Pollut. Control Assoc. 31: 885-886.

Johnston, J. W.; Heagle, A. S. (1982) Response of chronically ozonated soybean plants to an acute ozone exposure. Phytopathology 72: 387-389.

Juhren, M.; Noble, W.; Went, F. W. (1957) The standardization of Poa annua as an indicator of smog concentrations. I. Effects of temperature, photoperiod, and light intensity during growth of the test-plants. Plant Physiol. 32: 576-586.

Just, R. E.; Hueth, D. L.; Schmitz, A. (1982) Applied welfare economics and public policy. New York, NY: Prentice-Hall.

Karnosky, D. F. (1977) Evidence of genetic control of response to sulfur dioxide and ozone in Populus tremuloides. Can. J. For. Res. 7: 437-440.

Kats, G.; Thompson, C. R.; Kuby, W. C. (1976) Improved ventilation of open-top greenhouses. J. Air Pollut. Control Assoc. 26: 1089-1090.

Keen, N. T.; Taylor, O. C. (1975) Ozone injury in soybeans isoflavone accumulation is related to necrosis. Plant Physiol. 55: 731-733.

Kelleher, T. J.; Feder, W. A. (1978) Phytotoxic concentrations of ozone on Nantucket Island: Long range transport from the middle Atlantic states over the open ocean confirmed by bioassay with ozone-sensitive tobacco plants. Environ. Pollut. 17: 187-194.

Kendrick, J. B., Jr.; Darley, E. F.; Middleton, J. T. (1962) Chemotherapy for oxidant and ozone-induced plant damage. Int. J. Air Water Pollut. 6: 391-402.

Kendrick, J. B. Jr.; Middleton, J. T.; Darley, E. F. (1954) Chemical protection of plants from ozonated olefin (smog) injury. Phytopathology 44: 494-495.

Kickert, R. N.; McBride, J. R.; Miller, P. R.; Ohmart, C. P.; Arkley, R. J.; Dahlsten, D. L.; Cobb, F. W.; Cobb, Jr.; Parmeter, J. R., Jr.; Luck, R. F.; Taylor, O. C. (1977) Photochemical oxidant air pollution effects on a mixed conifer forest ecosystem. Taylor, O. C., ed. U.S. Environmental Protection Agency; Final report, Contract No. 68-03-2442.

Kohut, R. J.; Davis, D. D. (1978) Response of pinto bean to simultaneous exposure to ozone and PAN. Phytopathology 68: 567-569.

Kohut, R.; Laurence, J. A. (1983) Yield response of red kidney bean to incremental ozone concentrations in the field. Environ. Pollut. (Ser. A) 32: 233-240.

Kohut, R. J.; Davis, D. D.; Merrill, W. (1976) Response of hybrid poplar to simultaneous exposure to ozone and PAN. Plant Dis. Reprtr. 60: 777-780.

Koiwai, A.; Kisaki, T. (1976) Effect of ozone on photosystem II of tobacco chloroplasts in the presence of piperonyl butoxide. Plant Cell Physiol. 17: 1199-1207.

Koiwai, A.; Fukuda, M., Kisaki, T. (1977) Effect of piperonyl butoxide and diphenylamine on lipid peroxidation in ozonated chloroplasts. Plant Cell Physiol. 18: 127-139.

Koiwai, A.; Kitano, H.; Fukedo, M.; Kisaki, T. (1974) Methylenedioxy-phenyl and its related compounds as protectants against ozone injury to plants. Agr. Biol. Chem. 38: 301-307.

Koritz, H. K.; Went, F. W. (1953) The physiological action of smog on plants. I. Initial growth and transpiration studies. Plant Physiol. 28: 50-62.

Koukol, J.; Dugger, W. M., Jr. (1967) Anthocyanin formation as a response to ozone and smog treatment in Rumex crispus L. Plant Physiol. 42: 1023-1024.

Krause, C. R.; Weidensual, T. C. (1978a) Effects of ozone on the sporulation, germination, and pathogenicity of Botrytis cinerea. Phytopathology 18: 195-198.

Krause, C. R.; Weidensaul, T. C. (1978b) Ultrastructural effects of ozone on the host-parasite relationship of Botrytis cinerea and Pelargonium hortorum. Phytopathology 68: 301-307.

Kress, L. W.; Miller, J. E. (1983) Impact of ozone on soybean yield. J. Environ. Qual. 12: 276-281.

Kress, L. W.; Skelly, J. M. (1982) Response of several eastern forest tree species to chronic doses of ozone and nitrogen dioxide. Plant Dis. 66: 1149-1152.

Kress, L. W.; Skelly, J. M.; Hinkelmann, K. H. (1982a) Growth impact of O_3, NO_2, and/or SO_2 on Pinus taeda. Environ. Monit. Assess. 1: 229-239.

Kress, L. W.; Skelly, J. M.; Hinkelmann, K. H. (1982b) Growth impact of O_3, NO_2, and/or SO_2 on Platanus occidentalis. Agric. Environ. In press.

Larsen, R. I.; Heck, W. W. (1976) An air quality data analysis system for interrelating effects, standards, and needed source reduction: Part 3. Vegetation injury. J. Air Pollut. Control Assoc. 26: 325-333.

Laurence, J. A. (1981) Effects of air pollutants on plant pathogen interaction. J. Plant Dis. Prot. 87: 441-445.

Laurence, J. A. (1982) Development of a biological air quality indexing system. Report to the Minnesota Environmental Quality Board, Contract No. 10089, St. Paul, MN.

Laurence, J. A.; Wood, F. A. (1978a). Effects of ozone on infection of soybean by Pseudomonas glycina. Phytopathology 68: 441-445.

Laurence, J. A.; Wood, F. A. (1978b) Effect of ozone on infection of wild strawberry by Xanthomonas fragariae. Phytopathology 68: 689-692.

Laurence, J. A.; Wood, F. A.; Krupa, S. V. (1977) Possible transport of ozone and ozone precursors. Proc. Am. Phytopathol. Soc. 4: 31.

Laurence, J. A.; MacLean, D. C.; Schneider, R. E.; Hansen, K. S. (1982) Field tests of a linear gradient system for exposures of row crops to SO_2 and HF. Water Air Soil Pollut. 17: 399-407.

LeBlanc, F.; Rao, D. N. (1973) Effects of sulphur dioxide on lichen and moss transplants. Ecology 54: 612-617.

Lee, J. J.; Preston, E. M.; Lewis, R. A. (1978) A system for the experimental evaluation of the ecological effects of sulfur dioxide. In: ACS proceedings of the 4th joint conference on sensing of environmental pollutants; pp. 49-53.

Lefohn, A. S.; Tingey, D. T. (1984) The co-occurrence of potentially phytotoxic concentrations of various gaseous air pollutants. Atmos. Environ. In Press.

Legassicke, B. C.; Ormrod, D. P. (1981) Suppression of ozone-injury on tomatoes by ethylene divea in controlled environments and in the field. Hort. Science 16: 183-184.

Legge, A. H.; Savage, D. S.; Walker, R. B. (1979) Special techniques: A portable gas-exchange leaf chamber. In: Heck, W. W.; Krupa, S. V.; Linzon, S. N., eds. Handbook of methodology for the assessment of air pollution effects on vegetation: Air Pollution Control Association specialty conference proceedings. Pittsburgh, PA: Air Pollution Control Association; pp. 16-13 to 16-24.

Leh, F.; Mudd, J. B. (1974) Reaction of peroxyacetyl nitrate with cystine, cystine, methiomine, lipoic acid, papain and lysozyme. Arch. Biochem. Biophys. 161: 216-221.

Letchworth, M. B.; Blum, U. (1977). Effects of acute ozone exposure on growth, nodulation, and nitrogen content of ladino clover. Environ. Pollut. 14: 303-312.

Leung, S. K.; Reed, W.; Cauchois, S.; Howitt, R. (1978) Methodologies for valuation of agricultural crop yield changes: a review. Corvallis, OR: U.S. Environmental Protection Agency, Corvallis Environmental Research Laboratory; EPA Report No. EPA-600/5-5-78-018.

Leung, S. K.; Reed, W.; Geng, S. (1982) Estimates of ozone damage to selected crops grown in southern California. J. Air Pollut. Control Assoc. 32 (2): 160-164.

Loucks, O. L.; Armentano, T. V. (1982) Estimating crop yield effects from ambient air pollutants in the Ohio River Valley. J. Air Pollut. Control Assoc. 32: 146-150.

Ludlow, M. M. (1980) Adaptive significance of stomatal responses to water stress. In: Turner, N.C.; Kramer, P. J., eds. Adaptation of plants to water and high temperature stress. New York: Wiley-Interscience Publication; pp. 123-128.

MacDowall, F. D. H. (1965) Predisposition of tobacco to ozone damage. Can. J. Plant Sci. 45: 1-12.

MacDowall, F. D. H.; Cole, A. F. (1971) Threshold and synergistic damage to tobacco by ozone and sulfur dioxide. Atmos. Environ. 5: 553-559.

MacDowall, F. D. H.; Mukammal, E. I.; Cole, A. F. W. (1964) Direct correlation of air polluting ozone and tobacco weather fleck. Can. J. Plant Sci. 44: 410-417.

MacLean, D. C.; Schneider, P. E. (1976) Photochemical oxidants in Yonkers, New York. J. Environ. Qual. 5: 75-78.

Magie, R. O. (1960) Controlling gladiolus botrytis bud rot with ozone gas. Proc. Fla. State Hortic. Soc. 73: 373-375.

Male, L.; Preston, E.; Neely, G. (1983) Yield responses curves of crops exposed to SO_2 time series. Atmos. Environ. 17: 1589-1593.

Mandl, R. L.; Weinstein, L. H.; McCune, D. C.; Keveny, M. (1973) A cylindrical open-top chamber for the exposure of plants to air pollutants in the field. J. Environ. Qual. 2: 132-135.

Mann, L. K.; McLaughlin, S. B.; Shriner, D. S. (1980) Seasonal physiological responses of white pine under chronic air pollution stress. Environ. Exp. Bot. 20: 99-105.

Manning, W. J. (1975) Interactions between air pollutants and fungal, bacterial and viral plant pathogens. Environ. Pollut. 9: 87-89.

Manning, W. J.; Feder, W. A. (1980) Biomonitoring Air Pollutants with Plants. Applied Science Publishers, London. 142 p.

Manning, W. J.; Feder, W. A.; Perkins, I.; Glickman, M. (1969) Ozone injury and infection of potato leaves by Botrytis cinerea. Plant Dis. Rep. 53: 691-693.

Manning, W. J.; Feder, W. A.; Perkins, I. (1970a) Ozone and infection of geranium flowers by Botrytis cinerea. Phytopathology 60: 1302.

Manning, W. J.; Feder, W. A.; Perkins, I. (1970b) Ozone injury increases infection of geranium leaves by Botrytis cinerea. Phytopathology 60: 669-670.

Manning, W. J.; Feder, W. A.; Papia, P. M.; Perkins, I. (1971a). Effect of low levels of ozone on growth and susceptibility of cabbage plants to Fusarium oxysporum F. sp. conglutinans. Plant Dis. Rep. 55: 47-49.

Manning, W. J.; Feder, W. A.; Papia, P. M.; Perkins, I. (1971b). Influence of foliar ozone injury on root development and root surface fungi of pinto bean plants. Environ. Pollut. 1: 305-312.

Manning, W. J.; Feder, W. A.; Perkins, I. (1972) Effects of Botrytis and ozone on bracts and flowers of poinsettia cultivars. Plant Dis. Rep. 56: 1302.

Manning, W. J.; Feder, W. A.; Perkins, I. (1973a) Response of poinsettia cultivars to several concentration of ozone. Plant Dis. Rep. 57: 774-775.

Manning, W. J.; Feder, W. A.; Vardaro, P. M. (1973b) Benomyl in soil and response of pinto bean plants to repeated exposures to a low level of ozone. Phytopathology 63: 1539-1540.

Manning, W. J.; Feder, W. A.; Vardaro, P. M. (1974) Suppression of oxidant injury by benomyl: effects on yields of bean cultivars in field. J. Environ. Qual. 2: 1-3.

Matsushima, J. (1971) On composite harm to plants by sulfurous acid gas and oxidant. Sangyo Kogai 7:218-224. (English abstract).

McClenahen, J. R. (1979) Effects of ethylene diurea and ozone on the growth of the tree seedlings. Plant Dis. Rep. 63: 320-323.

McCool, P. M.; Menge, J. A. (1983) Influence of ozone on carbon partitioning in tomato: Potential role of carbon flow in regulation of the mycorrhizal symbosis under conditions of stress. New Phytologist 94: 241-247.

McCool, P. M.; Menge, J. A.; Taylor, O. C. (1979) Effects of ozone and HCl gas on the development of the mycorrhizal fungus Glomus faciculatus and growth of 'Troyer' citrange. J. Amer. Soc. Hort. Sci. 104151-154.

McCool, P. M.; Menge, J. A.; Taylor, O. C. (1982) Effect of ozone injury and light stress on response of tomato to infection by the vesicular-arbuscular mycorrihizal fungus, Glomus fasiculatus. J. Amer. Soc. Hort. Sci. 107: 839-842.

McLaughlin, S. B.; Taylor, G. E. (1980) Relative humidity: important modifier of pollutant uptake by plants. Science 22: 167-169.

McLaughlin, S. B.; Shriner, D. S.; McConathy, R. K.; Mann, L. K. (1979) The effects of SO_2 dosage kinetics and exposure frequency on photosynthesis and transpiration of kidney beans (Phaseolus vulgaris L.). Environ. Exp. Bot. 19: 179-91.

McLaughlin, S. B.; McConathy, R. K.; Duvick, D.; Mann, L. K. (1982) Effects of chronic air pollution stress on photosynthesis, carbon allocation, and growth of white pine trees. For. Sci. 28: 60-70.

Meiners, J. P.; Heggestad, H. E. (1979) Evaluation of snap bean cultivars for resistance to ambient oxidants in field plots and to ozone in chambers. Plant Dis. Rep. 63: 273-277.

Menser, H. A., Jr. (1969) Effects of air pollution on tobacco cultivars grown in several sites. Tobacco Sci. 169: 699-704.

Menser, H. A.; Heggestad, H. E. (1966) Ozone and sulfur dioxide synergism: injury to tobacco plants. Science 153: 424-425.

Menser, H.A.; Hodges, G. H. (1970) Effects of air pollutants on burley tobacco cultivars. Agron. J. 62: 265-269.

Menser, H. A.; Hodges, G. H. (1972) Oxidant injury to shade tobacco cultivars developed in Connecticut for weather fleck resistance. Agron. J. 64: 189-192.

Menser, H. A.; Street, O. E. (1962) Effects of air pollution, nitrogen levels, supplemental irrigation, and plant spacing on weather fleck and leaf losses of Maryland tobacco. Tobacco 155: 192-196.

Metzler, J. T.; Pell, E. J. (1980) The impact of peroxyacetyl nitrate on conductance of bean leaves and on associated cellular and foliar symptom expression. Phytopathology 70: 934-938.

Middleton, J. T.; Haagen-Smit, A. (1961) The occurrence, distribution and significance of photochemical air pollution in the United States, Canada, and Mexico. J. Air Pollut. Control Assoc. 11: 129-134.

Middleton, J. T.; Paulus, A. O. (1965) The identification and distribution of air pollutants through plant response. AMA Arch. Ind. Health 14: 526-532.

Middleton, J. T.; Kendrick, J. B., Jr.; Schwalm, H. W. (1950) Injury to herbaceous plants by smog or air pollution. Plant Dis. Rep. 34: 245-252.

Middleton, J. T.; Crafts, A. S.; Brewer, R. F.; Taylor, O. C. (1956) Plant damage by air pollution. Calif. Agric. 10: 9-12.

Middleton, J. T.; Darley, E. F.; Brewer, R. F. (1958) Damage to vegetation from polluted atmosphere. J. Air Pollut. Control Assoc. 8: 9-15.

Millecan, A. A. (1971) A survey and assessment of air pollution damage to California vegetation in 1970. Research Triangle Park, NC: U.S. Environmental Protection Agency, Air Pollution Control Office; APTD-0694.

Miller, C. A.; Davis, D. D. (1981a) Effect of temperature on stomatal conductance and ozone injury of pinto bean leaves. Plant Dis. 65: 750-751.

Miller, C. A.; Davis, D. D. (1981b) Response of pinto bean plants exposed to O_3, SO_2, or mixtures at varying temperatures. HortScience 16: 548-550.

Miller, J. E.; Sprugel, D. G.; Muller, R. N.; Smith, H. J.; Xerikos, P. B. (1980) Open-air fumigation system for investigating sulfur dioxide effects on corps. Phytopathology 78: 1124-1128.

Miller, P. R. (1973) Oxidant-induced community changes in a mixed conifer forest. IN: Naegle, J. A., ed. Air pollution damage to vegetation. Washington, DC: American Chemical Society; pp 101-117. Advances in Chemistry Series No. 122.

Miller, P. R.; Millecan, A. A. (1971) Extent of oxidant air pollution damage to some pines and other conifers in California. Plant Dis. Rep. 55: 555-559.

Miller, P. R.; Parmeter, J. R., Jr.; Flick, R. B.; Martinze, C. W. (1969) Ozone dosage response of ponderosa pine seedlings. J. Air Pollut. Control Assoc. 19: 435-438.

Miller, P. R.; McCutchan, M. H.; Millegan, H. P. (1972) Oxidant air pollution in the central valley, Sierra Nevada foothills and Mineral King Valley of California. Atmos. Environ. 6: 623-633.

Miller, P. R.; Taylor, O. C.; Wilhour, R. G. (1982) Oxidant air pollution effects on a western coniferous forest ecosystem. U.S. Environmental Protection Agency, EPA-600/D-82/276, Corvallis, OR, 10 pp.

Miller, P. M.; Tomlinson, H.; Taylor, G. S. (1976) Reducing severity of ozone damage to tobacco and beans by combining benomyl or carboxin with contact nematicides. Plant Dis. Rep. 60: 433-436.

Miller, V. L.; Howell, R. K.; Caldwell, B. E. (1974) Relative sensitivity of soybean genotypes to ozone and sulfur dioxide. J. Environ. Qual. 3: 35-37.

Mishan, E. J. (1964) Welfare economics; five introductory essays. New York: Random House.

Mishan, E. J. (1971) Cost-benefit analysis: an introduction. New York: Praeger.

Mitchell, A., Ormrod, D. P., Dietrich, H. F. (1979) Ozone and nickel effects on pea leaf cell ultrastructure. Bull. Environ. Contam. Toxicol. 22: 379-385.

Mjelde, J. W.; Adams, R. M.; Dixon, B. L.; Garcia, P. (1984) Using farmers' actions to measure crop loss due to air pollution. JAPCA (In Press).

Mooi, J. (1980) Influence of ozone on the growth of two poplar cultivars. Plant Dis. 64: 772-773.

Moskowitz, P. D.; Medeiros, W. H.; Morris. S. C.; Coveney, E. A. (1981) Oxidant air pollution: estimated effects on U.S. vegetation in 1969 and 1974. Upton, NY: Brookhaven National Laboratory; BNL 51327.

Moskowitz, P. D.; Coveney, E. A.; Medeiros, W. H.; Morris. S. C. (1982) Oxidant air pollution: a model for estimating effects on U.S. vegetations. J. Air Pollut. Control Assoc. 32: 155-160.

Moyer, J. W.; Smith, S. H. (1975) Oxidant injury reduction on tobacco induced by tobacco etch virus infection. Environ. Pollut. 9: 103-1-06.

Moyer, J. W.; Cole, Jr., H.; Lacasse, N. L. (1974a) Reduction of ozone injury on Poa annua by benomyl and thiophanate. Plant Dis. Rep. 58: 41-44.

Moyer, J. W.; Cole Jr., H.; Lacasse, N. L. (1974b) Suppression of naturally occurring oxidant injury on azalea plants by drench or foliar spray treatment with benzimidazo or oxathiin compounds. Plant Dis. Rep. 58: 136-138.

Mudd, J. B. (1963) Enzyme inactivation by peroxyacetyl nitrate. Arch. Biochem. Biophys. 102: 59-65.

Mudd, J. B. (1966) Reaction of peroxyacetyl nitrate with glutathione. J. Biol. Chem. 241: 4077-4080.

Mudd, J. B. (1975) Peroxyacyl nitrates. In: Mudd, J. B.; Kozlowski, T. T., eds. Response of plants to air pollutants. New York, NY: Academic Press, Inc.; pp. 97-119.

Mudd, J. B. (1982) Effects of oxidants on metabolic function. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London, England: Butterworth Scientific; pp. 189-203.

Mudd, J. B.; Dugger, W. M. (1963) The oxidation of reduced pyridine nucleotides by peroxyacetyl nitrates. Arch. Biochem. Biophys. 102: 52-58.

Mudd, J. B.; McManus, T. T. (1969) Products of the reaction of peroxyacetyl nitrate with sulfhydryl compounds. Arch. Biochem. Biophys. 132: 237-241.

Mudd, J. B.; Leavitt, R.; Kersey, W. H. (1966) Reaction of peroxyacetyl nitrate with sulfhydryl groups of proteins. J. Biol. Chem. 241: 4081-4085.

Mumford, R. A.; Lipke, H.; Laufer, D. A.; Feder, W. A. (1972) Ozone-induced changes in corn pollen. Environ. Sci. Technol. 6: 427-430.

Musselman, R. C.; Kender, W. J.; Crowe, D. E. (1978) Determining air pollutant effects on growth and productivity of "concord" grapevines using open-top chambers. J. Am. Hortic. Sci. 103: 645-648.

Musselman, R. C., Oshima, R. J.; Gallavan, R. E. (1983) Significance of pollutant concentration distribution in the response of red kidney beans to ozone. J. Amer. Soc. Hortic. Sci. 108: 347-351.

Naegele, J. A.; Feder, W. A.; Brandt, C. J. (1972) Assessment of air pollution damage to vegetation in New England: July 1971 - July 1972. Research Triangle Park, NC: U.S. Environmental Protection Agency; Final Report No. EPA-R5-72-009.

Nakamura, H.; Matsunaka, S. (1974) Indicator plants for air pollutants. (1) Susceptibility of morning glory to photochemical oxidants: Varietal difference and effect of environmental factors. Nippon Sakumotsu Gakkai Kiji 43: 517-522.

Nakamura, H.; Saka, H. (1978) Photochemical oxidants injury in rice plants: 3. Effect of ozone on physiological activities in rice plants. Jpn. J. Crop. Sci. 47: 707-714.

Nash, III, T. H.; Sigal, L. L. (1979) Gross photosynthetic response of lichens to short-term ozone fumigations. Bryologist 82: 280-285.

National Research Council. (1977) Ozone and other photochemical ozidants. Washington, DC: National Academy of Sciences; pp. 437-585.

Naveh, Z.; Chaim, S. (1978) Atmospheric oxidant concentrations in Israel as manifested by foliar injury in Bel-W3 tobacco plants. Environ. Pollut. 16: 249-262.

Neely, G. E.; D. T. Tingey; R. G. Wilhour; (1977) Effects of ozone and sulfur dioxide singly and in combination on yield, quality and N-fixation of alfalfa. In: Dimitriades, B., ed. International Conference on Photochemical Oxidant Pollution and its Control: Proceedings, Volume II. EPA-600/3-77-001b. Research Triangle Park, NC: U.S. Environmental Protection Agency; pp. 663-673.

Nicksic, S. W.; Harkins, J.; Mueller, P. K. (1967) Some analyses for PAN and studies of its structure. Atmos. Environ. 1: 11-18.

Noble, R. D.; Jensen, K. F. (1980) Effects of sulfur dioxide and ozone on growth of hybrid poplar leaves. Am. J. Bot. 67: 1005-1009.

Noble, R. D.; Pechak, D.; Jensen, K. (1980) Ozone effects on the ultrastructure of the chloroplasts from hybrid poplar leaves. Micron 11: 13-14.

Noble, W. M. (1955) Air pollution effects: pattern of damage produced on vegetation by smog. J. Agric. Food Chem. 3: 330-332.

Noble, W. M. (1965) Smog damage to plants. LASCA Leaves. 15: 1-18.

Noble, W. M.; Wright, L. A. (1958) Air pollution with relation to agronomic crops. II. A bioassay approach to the study of air pollution. Agron. J. 50: 551-553.

Noland, T. L.; Kozlowski. T. T. (1979) Influence of potassium nutrition on susceptibility of silver maple to ozone. Can. J. For. Res. 9: 501-503.

Nouchi, I.; Aoki, K. (1979) Morning glory as a photochemical oxidant indicator. Environ. Pollut. 18: 289-303.

Nouchi, I.; Mayumi, H.; Yamazoe, F. (1984) Foliar injury response of petunia and kidney bean to simultaneous and alternate exposure to ozone and PAN. Atmos. Environ. 18: 453-460.

O'Connor, J. A.; Parbery, D. G.; Strauss, W. (1975) The effects of phytotoxic gases on native Australian plant species: part 2. Acute injury due to ozone. Environ. Pollut. 9: 181-192.

Ogata, G.; Maas, E. V. (1973) Interactive effects of salinity and ozone on growth and yield of garden beet. J. Environ. Qual. 2: 518-520.

Olson, B.; Saettler, A. W. (1979) Interaction of ozone and common bacterial blight in two dry bean cultivars. In: Proceedings of the IX international congress of plant protection; Aug. 1979; Washington, DC. Abstract 192.

Olszyk, D. M.; Tibbitts, T. W. (1981) Stomatal response and leaf injury of Pisum sativum L. with SO_2 and O_3 exposures. Plant Physiol. 67: 539-544.

Olszyk, D. M.; Tibbitts, T. W.; Hertzberg, W. M. (1980) Environment in open-top field chambers utilized for air pollution studies. J. Environ. Qual. 9: 610-615.

Ordin, L. (1962) Effect of peroxyacetyl nitrate on growth and cell wall metabolism of Avena coleoptile sections. Plant Physiol. 37: 603-608.

Ordin, L.; Hall, M. A. (1967) Studies on cellulose synthesis of a cell-free oat coleoptile enzyme system: Inactivation by air pollutant oxidants. Plant Physiol. 42: 205-212.

Ordin, L.; Propst, B. (1962) Effect of air-borne oxidants on biological activity of indole acetic acid. Bot. Gazette 123: 170-174.

Ordin, L.; Hall, M. A.; Katz, M. (1967) Peroxyacetyl nitratic-induced inhibition of cell wall metabolism. J. Air Pollut. Contr. Ass. 17: 811-815.

Ordin, L.; Garber, J. J.; Kindinger, J. I., Whitmore, S. A.; Greve, C.; Taylor, O. C. (1971) Effect of peroxyacetyl nitrate (PAN) in vivo on tobacco leaf polysaccharide synthetic pathway enzymes. Environ. Sci. Technol. 5:621-626.

Ormrod, D. P. (1977) Cadmium and nickel effects on growth and ozone sensitivity of pea. Water Air Soil Pollut. 8: 263-270.

Ormrod, D. P. (1982). Air pollutant interactions in mixtures. In: Unsworth, M. H.; Ormrod, D. P.; eds. Effects of air pollution in agriculture and horticulture. London: Butterworths; pages 307-331.

Ormrod, D. P.; Kemp, W. G. (1979) Ozone response of tomato plants infected with cucumber mosaic virus and/or tobacco mosaic virus. Can. J. Plant Sci. 59: 1077-1083.

Ormrod, D. P.; Adedipe, N. O.; Hofstra, G. (1971) Responses of cucumber, onion, and potato cultivars to ozone. Can. J. Plant Sci. 51:283-288.

Ormrod, D. P.; Black, V. J.; Unsworth, M. H. (1981) Depression of net photosynthesis in Vicia faba L. exposed to sulphur dioxide and ozone. Nature 291: 585-586.

Ormrod, D. P.; Tingey, D. T.; Gumpertz, M. L.; Olszyk, D. M. (1984) Utilization of a response surface technique in the study of plant responses to ozone and sulfur dioxide mixtures. Plant Physiology (In Press).

Oshima, R. J. (1973) Effect of ozone on a commercial sweet corn variety. Plant Dis. Rep. 57: 719-723.

Oshima, R. J. (1974a) Development of a system for evaluating and reporting economic crop losses caused by air pollution in California; II; Yield study. IIA. Prototype ozone dosage - crop loss conversion function. Sacramento, CA: State of California, Department of Food and Agriculture.

Oshima, R. J. (1974b) A viable system of biological indicators for monitoring air pollutants. J. Air. Pollut. Control Assoc. 24: 576-578.

Oshima, R. J. (1975) Development of a system for evaluating and reporting economic crop losses by air pollution in California. Final report to California Air Resources Board; Agreement No. ARB-3-690.

Oshima, R. J. (1978) The impact of sulfur dioxide on vegetation: a sulfur dioxide-ozone response model. California Air Resources Board; Final Report; Agreement No. A6-162-30.

Oshima, R. J. (1979) The impact of sulfur dioxide on a processing tomato stressed with chronic ambient ozone. California Air Resources Board Agreement No. A7-141-30 74p.

Oshima, R. J.; Gallavan, R. (1980) Experimental designs for the quantification of crop growth and yield responses from air pollutants. In: Teng, P. S.; Krupa, S. V., eds. Crop loss assessment: proceedings of the E. C. Stakman commemorative symposium. St. Paul, MN: University of Minnesota, Agricultural Experimental Station; Miscellaneous Publication No. 7; pp. 63-70.

Oshima, R. J.; Taylor, O. C.; Cardiff, E. A. (1974) Severe air pollution episode in south coast basin. Calif. Agric. 28: 12-13.

Oshima, R. J.; Taylor, O. C.; Braegelmann, P. K.; Baldwin, D. W. (1975) Effect of ozone on the yield and plant biomass of a commercial variety of tomato. J. Environ. Qual. 4: 463-464.

Oshima, R. J.; Poe, M. P.; Braegelmann, P. K.; Baldwin, D. W.; Van Way, V. (1976) Ozone dosage-crop loss function for alfalfa: a standardized method for assessing crop losses from air pollutants. J. Air Pollut. Control Assoc. 26: 861-865.

Oshima, R. J.; Braegelmann, P. K.; Baldwin, D. W.; Van Way, V.; Taylor, O. C. (1977a) Reduction of tomato fruit size and yield by ozone. J. Am. Soc. Hortic. Sci. 102: 289-293.

Oshima, R. J.; Braegelmann, P. K.; Baldwin, D. W.; Van Way, V.; Taylor, O. C. (1977b) Responses of five cultivars of fresh market tomato to ozone: a contrast of cultivar screening with foliar injury and yield. J. Am. Soc. Hortic. Sci. 102: 286-289.

Oshima, R. J.; Bennett, J. P.; Braegelmann, P. K. (1978) Effect of ozone on growth and assimilate partitioning in parsley. J. Am. Soc. Hortic. Sci. 103: 348-350.

Oshima, R. J.; Braegelmann, P. K.; Flagler, R. B.; Teso, R. R. (1979) The effects of ozone on the growth, yield, and partitioning of dry matter in cotton. J. Environ. Qual. 8: 474-479.

Page, W. P., Arbogast, G.; Fabian, R. G.; Ciecka, J. (1982) Estimation of economic losses to the agricultural sector from airborne residuals in the Ohio River Basin. J. Air Pollut. Control Assoc. 32: 151-154.

Patton, R. L. (1981) Effects of ozone and sulfur dioxide on height and stem specific gravity of Populus Hybrids. For. Sci. Res. Pop. NE-471. 4 pp.

Peak, M. J.; Belser, W. L. (1969) Some effects of the air pollutant peroxy-acetyl nitrate upon deoxyribonucleic acid and upon necleic acid bases. Atmos. Environ. 3: 385-397.

Peake, E.; Sandhu, H. S. (1983) The formation of ozone and peroxyacetyl nitrate (PAN) in the urban atmospheres of Alberta. Can J. Chem. 61: 927-935.

Pearson, R. G.; Drummond, D. B.; McIlveen, W. D.; Linzon, S. N. (1974) PAN type injury to tomato crops in southwestern Ontario. Plant Dis. Rep. 58: 1105-1108.

Pell, E. G. (1973) Survey and assessment of air pollution damage to vegetation in New Jersey. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA-R5-73-022; p. 36.

Pell, E. J. (1976) Influence of benomyl soil treatment on pinto bean plants exposed to peroxyacetyl nitrate and ozone. Phytopathology 66: 731-733.

Pell, E. J. (1979) How air pollutants induce disease. In: Horsfall, J.; Cowling, E., eds. Plant disease. Vol. IV. New York, NY: Academic Press, Inc.; pp. 273-292.

Pell, E. J.; Brennan, E. (1973) Changes in respiration, photosynthesis, adenosine 5'-triphosphate, and total adenylate content of ozonated pinto bean foliage as they relate to symptoms expression. Plant Physiol. 51: 378-381.

Pell, E. J.; Gardner, W. (1975) Benomyl stimulation of peroxyacetyl nitrate injury to petunia. Abstract. Proc. Am. Phytopathol. Soc. 2: 29.

Pell, E. J.; Gardner, W. (1979) Enhancement of peroxyacetyl nitrate injury to petunia foliage by benomyl. J. Hortic. Sci. 14: 61-62.

Pell, E. J.; Pearson, N. S. (1983) Ozone-induced reduction in quantity of ribulose-1, 5-biphosphate carboxylase in alfalfa foliage. Plant Physiol. 73: 185-187.

Pell, E. J.; Weissberger, W. C. (1976) Histopathological characterization of ozone injury to soybean foliage. Phytopathology 66: 856-861.

Pell, E. J.; Lukezic, F. L.; Levine, R. G.; Weissberger, W. C. (1977) Response of soybean foliage to reciprocal challenges by ozone and a hypersensitive-response-inducing Pseudomonad. Phytopathology 67: 1342-1345.

Pell, E. J.; Weissberger, W. C.; Speroni, J. J. (1980) Impact of ozone on quantity and quality of greenhouse-grown potato plants. Environ. Sci. Technol. 14: 568-571.

Pellissier, M; Lacasse, N. L.; Cole, H., Jr.; (1971) Uptake of benomyl by bean plants. Abstract. Phytopathology 61: 132.

Pelz, E. (1962) The individual smoke resistance of spruce. Wiss. Z. Tech. Univ. Dresden 11: 595-600.

Penkett, S. A.; Sandalls, F. J.; Jones, B. M. R. (1977) PAN measurements in England--analytical methods and results. VDI-Berichte. 270: 47-54.

Pimentel, D. (1976) World food crisis: energy and pests bulletin. Entomol. Soc. Am. 22: 20-26.

Pippen, E. L.; Potter, A. L.; Randall, U. A.; Ng, K. C.; Reuter, R. W.; Morgan, A. L. (1975) Effect of ozone fumigation on crop composition. J. Food Sci. 40: 672-676.

Posthumus, A. C. (1976) The use of higher plants as indicators for air pollution in the Netherlands. In: Karenlampi, L. (ed.) Proceedings of the Kuopio meeting on plant damages caused by air pollution; Kuopio; pp. 115-120.

Posthumus, A. C. (1977) Experimentalle unterserchungen der wirkung von ozon und peroxyacetyl-nitrat PAN auf pflanzen. VDI - Berichte. 270: 153-161.

Posthumus, A. C. (1980) Monitoring levels and effects of air-borne pollutants on vegetation use of biological indicators and other methods national and international programmes. United Nations Economic Commission for Europe. Papers presented to the symposium on the effects of airborne pollution on vegetation. Warsaw, Poland.

Povilaitis, B. (1967) Gene effects of tolerance to weather fleck in tobacco. Can. J. Genet. Cytol. 9: 327-334.

Pratt, G. C. (1982) Effects of ozone and sulfur dioxide on soybeans. Ph.D. Thesis, University of Minnesota, Minneapolis, MN.

Pratt, G. C.; Krupa, S. V. (1979) Interaction between ozone and certain biopathogens on soybean cultivar Hodgson. In: Proceedings of the XI international congress of plant protection; Washington, DC; Abstract 196.

Pratt, G. C.; Krupa, S. V. (1981) Soybean cultivar Hodgson response to ozone. Phtopathology 71: 1129-1132.

Pryor, W. A.; Prier, D. G.; Church, D. F. (1981) Radical production from the interaction of ozone and PUFA as demonstrated by electron spin resonance spin-trapping technique. Environ. Res. 24: 42-52.

Purvis, A. C. (1978) Differential effects of ozone on in vivo nitrate reduction in soybean cultivars. I. Response to exogenous sugars. Can. J. Bot. 56: 1540-1544.

Rajput, C. B. S.; Ormrod, D. P. (1976) Response of eggplant cultivars to ozone. HortScience 11: 462-463.

Reich, P. B. (1984) Effects of low concentrations of O_3 on net photosynthesis, dark respiration, and chlorophyll contents in aging hybrid poplar leaves. Plant Physiol. 73: 291-296.

Reich, P. B.; Amundson, R. G.; Lassoie, J. P. (1980) Multiple pollutant fumigations under or near ambient environmental conditions using a linear gradient technique. In: Miller, P. R., ed. Symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems. U.S. Department of Agriculture, Forest Service; General Technical Report PSW-43; p. 247.

Reilly, J. J.; Moore, T. D. (1982) Influence of selected herbicides on ozone injury in tobacco (Nicotiana tabacum). Weed Sci. 30: 260-263.

Reinert, R. A. (1975) Monitoring, detecting, and effects of air pollutants on horticultural corps: sensitivity of genera and species. HortScience 10: 495-500.

Reinert, R. A.; Gooding, G. V., Jr.; (1978) Effect of ozone and tobacco streak virus alone and in combination on Nicotiana tabacum. Phytopathology 6: 15-17.

Reinert, R. A.; Gray, T. N. (1981) The response of radish to nitrogen dioxide, sulfur dioxide, and ozone, alone and in combination. J. Environ. Qual. 10: 240-243.

Reinert, R. A.; Heck, W. W. (1982) Effects of nitrogen dioxide in combination with sulfur dioxide and ozone on selected corps. In: Schneider, T.; Grant, L., eds. Air pollution by nitrogen oxides. Amsterdam, the Netherlands: Elsevier Scientific; pp. 533-546.

Reinert, R. A.; Henderson, W. R. (1980) Foliar injury and growth of tomato cultivars as influenced by ozone dose and plant age. J. Am. Soc. Hortic. Sci. 105: 322-324.

Reinert, R. A.; Nelson, P. V. (1979) Sensitivity and growth of twelve elatior begonia cultivars to ozone. HortScience 14: 747-748.

Reinert, R. A.; Nelson, P. V. (1980) Sensitivity and growth of five elatior begonia cultivars to SO_2 and O_3, alone and in combination. J. Am. Soc. Hortic. Sci. 105: 721-723.

Reinert, R. A.; Sanders, J. S. (1982) Growth of radish and marigold following repeated exposure to nitrogen dioxide, sulfur dioxide, and ozone. Plant Dis. 66: 122-124.

Reinert, R. A.; Spurr, H. W., Jr.; (1972) Differential effect of fungicides on ozone injury and brown spot disease of tobacco. J. Environ. Qual. 1: 450-452.

Reinert, R. A.; Weber, D. W. (1980) Ozone and sulfur dioxide-induced changes in soybean growth. Phytopathology 70: 914-916.

Reinert, R. A.; Tingey, D. T.; Carter, H. B. (1972) Ozone-induced foliar injury in lettuce and radish cultivars. J. Amer. Soc. Hort. Sci. 97: 711-714.

Reinert, R. A.; Heagle, A. S.; Heck, W. W. (1975) Plant responses to pollutant combinations. Mudd, B.; Kozlowski, T. T., eds. Responses of plants to air pollution. New York, NY: Academic Press, Inc.; pp. 159-177.

Reinert, R. A.; Shriner, D. S.; Rawlings, J. O. (1982) Response of radish to NO_2, SO_2, and O_3 in combination at three concentrations. J. Environ. Qual. 11: 52-57.

Rich, S. (1964) Ozone damage to plants. In: Ann. Rev. Phytopathology, Palo Alto, CA; pp. 253-266.

Rich, S.; Taylor, G. S. (1960) Antiozonants to protect plants from ozone damage. Science 132: 150-151.

Rich, S.; Tomlinson, H. (1968) Effects of ozone on conidiophores and conidia of Alternaria solani. Phytopathology 58: 444-446.

Rich, S.; Turner, N. C. (1972) Importance of moisture on stomatal behavior of plants subjected to ozone. J. Air Pollut. Control Assoc. 22: 718-721.

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

Richards, G. A.; Mulchi, C. L.; Hall, J. R. (1980) Influence of plant maturity on the sensitivity of turfgrass species to ozone. J. Environ. Qual. 9: 49-53.

Ridley, J. D.; Sims, Jr., E. T. (1966) Preliminary investigations on the use of ozone to extend the self-life and maintain the market quality of peaches and strawberries. Clemson, SC: Clemson University; South Carolina Agricultural Experiment Station Research Series No. 70.

Rist, D. L.; Lorbeer, J. W. (1981) Interactions of ozone, foliar fungi and the surface of the leaf. In: Blakeman, J. P., ed. Microbial ecology of the phylloplane. London: Academic Press; pp. 305-327.

Rogers, H. H.; Jeffries, H. E.; Stahel, E. P.; Heck, W. W.; Ripperton, L. A.; Witherspoon, A. M. (1977) Measuring air pollution uptake by plants: a direct kinetic technique. J. Air Pollut. Control Assoc. 27: 1192-1197.

Roose, M. L.; Bradshaw, A. D.; Roberts, T. M. (1982) Evolution of resistance to gaseous air pollutants. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London: Butterworth Scientific; pp. 379-409.

Ro-Poulsen, H.; Mortensen, L.; Johnsen, I. (1984) Effects of ozone on some Danish agronomic crops. Proceedings of the OECD Workshop on Ozone, Gothenburg, Sweden.

Ross, L. J.; Nash, T. H., III (1983) Effect of ozone on gross photosynthesis of lichens. Environ. Exp. Bot. 23:71-77.

Rubin, B.; Leavitt, J.R.C.; Penner, D. Saettler, A.W. (1980) Interaction of antoxidants with ozone and herbicide stress. Bull. Environ. Contam. Toxicol. 25: 623-629.

Runneckles, V. C.; Rosen, P. M. (1977) Effects of ambient ozone pretreatment on transpiration and susceptibility to ozone injury. Can. J. Bot. 55: 193-197.

Ryan, J. W.; Loehman, E.; Lee, W.; Trondsen, E.; Bland, M.; Goen, R.; Ludwig, F.; Eger, T.; Eigsti, S.; Conley, D.; Cummings, R. (1981) An estimate of the nonhealth benefits of meeting the secondary national ambient air quality standards [Final report for the National Commission on Air Quality]. Menlo Park, CA: SRI International; Project No. 2094.

Sanders, J. A.; Reinert, R. A. (1982a) Screening azalea cultivars for sensitivity to nitrogen dioxide, sulfur dioxide and ozone alone and in mixtures. J. Amer. Soc. Hort. Sci. 107: 87-90.

Sanders, J. S.; Reinert, R. A. (1982b) Weight changes of radish and marigold exposed at three ages to NO_2, SO_2 and O_3 alone and in mixture. J. Amer. Soc. Hort. Soc. 107: 726-730.

Santamour, F. S., Jr. (1969) Air pollution studies on Platanus and American elm seedlings. Plant Dis. Rep. 53: 482-484.

Sawada, I.; Date, N.; Fukuota, S.; Iizima, I.; Yoneyama, T.; Oodaira, T. (1974) On the plant damage due to ozone and PAN at the occurrence of oxidants with high concentration. J. Japan. Soc. Air Pollut. 9: 364. (English abs.).

Schoenbeck, H. (1969) A method for determining the biological effects of air pollution by transplanted lichens. Staub-Reinhalt. Luft 29: 17-21.

Scott, D. B. M.; Lesher, E. C. (1963) Effect of ozone on survival and permeability of Escherichia coli. J. Bacteriol. 85: 567576.

Seidman, G.; Hindawl, I. J.; Heck, W. W. (1965) Environmental conditions affect-ing the use of plants as indicators of air pollution. J. Air Pollut. Control Assoc. 15: 168-170.

Shannon, J. G.; Mulchi, C. L. (1974) Ozone damage to wheat varieties at anthesis. Crop Sci. 14: 335337.

Shertz, R. D.; Kender, W. J.; Musselmann, R. C. (1980a) Foliar response and growth of apple trees following exposure to ozone and sulfur dioxide. J. Am. Soc. Hortic. Sci. 105: 594598.

Shertz, R. D.; Kender, W. D.; Musselman, R. D. (1980b). Effects of ozone and sulfur dioxide on grapevines. Scientia Horticulturae 13: 37-45.

Shew, B. B., R. A. Reinert and R. R. Barker. (1982). Response of tomatoes to ozone, sulfur dioxide, and infection by Pratylenchus penetrans. Phytopathology 72: 822-825.

Shriner, D. S.; Cure, W. W.; Heagle, A. S.; Heck, W. W.; Johnson, D. W.; Olson, R. J.; Skelly, J. M. (1982) An analysis of potential agriculture and forestry impacts of long-range transport air pollutants. Oak Ridge, TN: Oak Ridge National Laboratory: ORNL Report No. 5910.

Sigal, L. L.; Nash, T. H., III. (1983) Lichen communities on conifers in southern California mountains: An ecological survey relative to oxidant air pollution. Ecology 64: 1343-1354.

Sigal, L. L.; Taylor, O. C. (1979) Preliminary studies of the gross photosynthetic response of lichens to peroxyacetyl nitrate fumigations. The Bryologyst 82: 564-575.

Skärby, L. (1984) Studies of ozone effects on crops and forest trees in Sweden. Proceedings of the OECD Workshop on Ozone, Gothenburg, Sweden.

Skärby, L.; Pell, E. J. (1979) Concentration of coumestrol and 4', 7-dihydroxylflavone in four alfalfa cultivars after ozone exposure. J. Environ. Qual. 8: 285-286.

Skelly, J. M. (1980) Photochemical oxidant impact on Mediterranean and temperate forest ecosystems: real and potential effects. In: Miller, P. R., ed. Proceedings of symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June 1980; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture Forest Service: pp. 3851. Available from: NTIS, Springfield, VA; PB 813372.

Skelly, J. M.; Croghan, C. F.; Hayes, E. M. (1977) Oxidant levels in remote mountainous areas of southwestern Virginia and their effects on native white pine (Pinus strobus L.). In: International conference on photochemical oxidant pollution and its control. Proceedings, Volume II. B. Dimitriades, ed. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA-600/3-77-001b; pp. 611-620.

Skelly, J. M.; Chevonl, B. I.; Yang, Y. S. (1982) Effects of ambient concentrations of air pollutants on vegetation indigenous to the Blue Ridge Mountains of Virginia. In: Proceedings of American Water Resources Association meeting; June 1982; Denver, CO.

Skye, E. (1979) Lichens as biological indicators of air pollution. Ann. Rev. Phytopathol. 17: 325-341.

Speroni, J. J.; Pell, E. J.; Weisberger, W. C. (1981) Glycoalkaloid levels in potato tubers and leaves after intermittent plant exposure to ozone. Am. Potato J. 58: 407-414.

Stan, H.; Schicker, S.; Kassner, H. (1981) Stress ethylene evolution of bean plants a parameter indicating ozone pollution. Atmos. Environ. 15: 391-395.

Stark, R. W.; Miller, P. R.; Cobb, Jr., D. L.; Wood, D. L.; Parmeter, Jr., J. R. (1968) Photochemical oxidant injury and bark beetle (Coleoptera: Scolytidea) infestation of ponderosa pine. I. Incidence of bark beetle infestation in injured trees. Hilgardia 39: 121126.

Starkey, T. E.; Davis, D. D.; Merrill, W. (1976) Symptomatology and susceptibility of ten bean varieties exposed to peroxyacetyl nitrate. Plant Dis. Rep. 60: 480-548.

Starkey, T. E.; Davis, D. D.; Pell, E. J.; Merrill, W. (1981) Influence of peroxyacetyl nitrate (PAN) on water stress in bean plants, HortScience 16: 547-548.

Steiner, K. C.; Davis, D. D. (1979) Variation among Fraxinus families in foliar response to ozone. Can. J. For. Res. 9: 106-109.

Stephens, E. R. (1967) The formation of molecular oxygen by alkaline hydrolyses of peroxyacetyl nitrate. Atmos. Environ. 1: 19-20.

Stephens, E. R. (1969) The formation, reactions, and properties of peroxyacyl nitrates (PAN_s) in photochemical air pollution. Adv. Environ. Sci. 1:119-146.

Stephens, E. R.; Hanst, P. L.; Doerr, R. C.; Scott, W. E. (1956) Reactions of nitrogen dioxide and organic compounds in air. Ind. Eng. Chem. 48: 1498-1504.

Stephens, E. R.; Darley, E. F.; Taylor, O. C.; Scott, W. E. (1961). Photochemical reaction products in air pollution. Int. J. Air Water Pollut. 4: 79-100.

Sung, C. H.; Chen, H. H.; Street, P. E.; Yang, Y. L. (1971) Gene effects for tolerance to weather fleck in tobacco. Taiwan Agric. Quart. 7: 173-181.

Sung, S. J. S.; Moore, L. P. (1979) The influence of three herbicides on the sensitivity of greenhouse-grown flue-cured tobacco (Nicotiana tabacum) plants to ozone. Weed Sci. 27: 167173.

Swanson, E. S.; Thompson, W. W.; Mudd, J. B. (1973) The effects of ozone on leaf cell membranes. Can. J. Bot. 51: 1213-1219.

Taylor, Jr., G. E.; Murdy, W. H. (1975) Population differentiation of an annual plant species, Geranium carolinianum L., in response to sulfur dioxide. Bot. Gaz. 136: 212-215.

Taylor, Jr., G. E.; McLaughlin, S. B.; Shriner, D. S. (1982a) Effective pollutant dose. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London: Butterworth Scientific; pp. 458-460.

Taylor, Jr., G. E.; Tingey, D. T.; Ratsch, H. C. (1982b) Ozone flux in Glycine max (L.) Merr.: sites of regulation and relationship to leaf injury. Oecologia 53: 179-186.

Taylor, O. C. (1969) Importance of peroxyacetyl nitrate (PAN) as a phytotoxic air pollutant. J. Air Pollut. Control Assoc. 19:347-351.

Taylor, O. C. (1974) Air pollutant effects influenced by plant-environmental interaction. In: Air pollution effects on plant growth. Dugger, W. M., ed. Am. Chem. Soc. Symposium Series 3: 1-7.

Taylor, O. C.; MacLean, D. C. (1970) Nitrogen oxides and the peroxyacyl nitrates. In: Jacobson, J. S.; Hill, A. C., eds. Recognition of air pollution injury to vegetation a pictorial atlas. Pittsburgh, PA: Air Pollution Control Association; Informative Report No. 1; pp. E1-E14.

Taylor, O. C.; Stephens, E. R.; Darley, E. F.; Cardiff, E. A. (1960) Effects of air-borne oxidants on leaves of pinto bean and petunia. Amer. Soc. Hort. Sci. 75: 435-444.

Taylor, O. C.; Dugger, W. M.; Cardiff, E. A.; Darley, E. F. (1961) Interaction of light and atmospheric photochemical products (SMOG) within plants. Nature 192: 814-816.

Taylor, O. C.; Temple, P. J.; Thill, A. J. (1983) Growth and yield responses of selected crops to peroxyacetyl nitrate. HortScience 18:861-863.

Temple, P. J. (1982) Effects of peroxyacetyl nitrate (PAN) on growth of plants. Ph.D. Dissertation. Dept. of Botany and Plant Sciences. Univ. of Calif. Riverside, CA.

Temple, P. J.; Bisessar, S. (1979) Response of white bean to bacterial blight, ozone, and antioxidant protection in the field. Phytopathology 69: 101-103.

Temple, P. J.; Taylor, O. C. (1983) World-wide ambient measurements of peroxyacetyl nitrate (PAN) and implications for plant injury. Atmos. Environ. 17: 1583-1587.

Teng, P. S. (1982) Development of a biological air quality indexing system. In: Laurence, J. A., ed. Report to the Minnesota Environmental Quality Board. Contract No. 10089. St. Paul, MN.

Teng, P. S.; Oshima, R. J. (1982) Identification and assessment of losses. In: Kommedahl T. H.; Williams, P. H., eds. Challenging problems in plant health. American Phytopathological Society.

Thomas, M. D. (1961) Effects of air pollution on plants. Air Pollution World Health Organization Monograph Series No. 46. New York, NY: Columbia University Press. pp. 233-278.

Thomas, M. D.; Hendricks, R. H. (1956) Effect of air pollution on plants. In: Magill, P. L.; Holden, E. R.; Ackley, C., eds. Air pollution handbook. New York, NY: McGraw-Hill Book Co.; pp. 9-1 to 9-44.

Thompson, C. R.; Taylor, O. C. (1966) Plastic-covered greenhouses supply controlled atmospheres to citrus trees. Trans. Am. Soc. Agric. Eng. 9: 338-342.

Thompson, C. R.; Kats, G. (1975) Effects of ambient concentrations of peroxyacetyl nitrate on navel orange trees. Environ. Sci. and Tech. 9: 35-38.

Thompson, C. R.; Kats, G.; Cameron, J. W. (1976a) Effects of photochemical air pollutants on growth, yield, and ear characters of two sweet corn hybrids. J. Environ. Qual. 5: 410-412.

Thompson, C. R.; Kats, G.; Pippen, E. L.; Isom, W. H. (1976b) Effect of photochemical air pollution on two varieties of alfalfa. Environ. Sci. Technol. 10: 1237-1241.

Thomson, W. W. (1975) Effects of air pollutants on plant ultrastructure. In: Mudd, J. B.; Kozlowski, T. T., eds. Responses of plants to air pollution. New York. NY: Academic Press, Inc.; pp. 179-194.

Thomson, W. W.; Dugger, W. M.; Palmer, R. L. (1965) Effects of peroxyacetyl nitrate on ultrastructure of chloroplasts. Bot. Gaz. 126: 66-72.

Ting, I. P. ; Dugger, Jr., W. M. (1968) Factors affecting ozone sensitivity and susceptibility of cotton plants. J. Air Pollut. Control Assoc. 18: 810-813.

Tingey, D. T. (1974) Ozone-induced alterations in the metabolite pools and enzyme activities of plants. In: Dugger, M., ed. Air pollution effects on plant growth. American Chemical Society Symposium Series 3; Washington, DC: American Chemical Society; pp. 40-57.

Tingey, D. T. (1977) Ozone-induced alterations in plant growth and metabolism. In: Dimitriades, B., ed. International conference on photochemical oxidant pollution and its control: proceedings, Volume II; January 1977. Research Triangle Park, NC: U.S. Environmental Protection Agency; pp. 601-609; EPA Report no. EPA600/377001b.

Tingey, D. T. (1980) Stress ethylene production: a measure of plant response to stress. HortScience 15: 630-633.

Tingey, D. T.; Blum, U. (1973) Effects of ozone on soybean nodules. J. Environ. Qual. 2: 341-342.

Tingey, D. C.; Hill, A. C. (1967) The occurrence of photochemical phytotoxicants in the Salt Lake Valley. Proc. Utah Acad. Sci. Arts Lett. 55: 387-395.

Tingey, D. T.; Reinert, R. A. (1975) The effect of ozone and sulfur dioxide singly and in combination on plant growth. Environ. Pollut. 9: 117-125.

Tingey, D. T.; Heck, W. W.; Reinert, R. A. (1971a) Effect of low concentrations of ozone and sulfur dioxide on foliage, growth and yield of radish. J. Am. Soc. Hort. Sci. 96: 369-371.

Tingey, D. T.; Reinert, R. A.; Dunning, J. A.; Heck, W. W. (1971b) Vegetation injury from the interaction of nitrogen dioxide and sulfur dioxide. Phytopathology 71: 1506-1511.

Tingey, D. T.; Reinhert, R. A.; Carter, H. B. (1972) Soybean cultivars: acute foliar response to ozone. Crop Sci. 12: 269-270.

Tingey, D. T.; Dunning, J. A.; Jividen, G. M. (1973a) Radish root growth reduced by acute ozone exposure. Proc. Third international clean air congress VDI-Verlog. GMBH, Dusseldorf, Federal Republic of Germany; A154-A156.

Tingey, D. T.; Fites, R. C.; Wickliff, C. (1973b) Ozone alteration in nitrate reduction in soybean. Physiol. Plant. 29: 33-38.

Tingey, D. T.; Reinert, R. A.; Dunning, J. A.; Heck, W. W. (1973c) Foliar injury responses of eleven plant species to ozone/sulfur dioxide mixtures. Atmos. Environ. 7: 201-208.

Tingey, D. T.; Reinert, R. A.; Wickliff, C.; Heck W. W. (1973d). Chronic ozone or sulfur dioxide exposures or both affect the early vegetative growth of soybean. Can. J. Plant Sci. 53: 875-879.

Tingey, D. T.; Fites, R. C.; Wickliff, C. (1975) Activity changes in selected enzymes from soybean leaves following ozone exposure. Physiol. Plant. 33: 316-320.

Tingey, D. T.; Standley, C.; Field, R. W. (1976) Stress ethylene evolution: a measure of ozone effects on plants. Atmos. Environ. 10: 969-974.

Tingey, D. T.; Manning, M; Grothaus, L. C.; Burns, W. F. (1979) The influence of light and temperature on isoprene emission rates from live oak. Physiol. Plant. 47: 112-118.

Tingey, D. T.; Taylor, Jr., G. E. (1982a) Variation in plant response to ozone: a conceptual model of physiological events. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London: Butterworth Scientific; pp. 113-138.

Tingey, D. T.; Thutt, G. L.; Gumpertz, M. L.; Hogsett, W. E. (1982b) Plant water status influences ozone sensitivity of bean plants. Agric. Environ. 8: (In press).

Todd, A. W. (1958) Effects of low concentrations of ozone on enzymes catalase, peroxidase, papain and urease. Physiol. Plant. 11: 457-463.

Tonneijck, A. E. G. (1984) Effects of peroxyacetyl nitrate (PAN) and ozone on some plant species. Proceedings of the OECD Workshop on Ozone, Gothenburg, Sweden.

Treshow, M. (1980a) Interactions of air pollutants and plant disease. In: Miller, P. R., ed. Proceedings of symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June 1980; Riverside, CA. Berkeley, CA; U.S. Department of Agriculture Forest Service, pp. 103-109. Available from: NTIS, Springfield, VA Pb81-3372.

Treshow, M. (1980b) Pollution effects on plant distribution. Environ. Conserv. 7: 279-286.

Trevathan, L. E.; Moore, L. D. (1976) Calcium nutrition in relation to ozone damage of flue-cured tobacco. Tobacco Sci. 82: 96-97.

Trevathan, L. E.; Moore, L. D.; Orcutt, D. M. (1979) Symptom expression and free sterol and fatty acid composition of flue-cured tobacco plants exposed to ozone. Phytopathology 69: 582-585.

Uhring, J. (1978) Leaf anatomy of petunia in relation to pollution damage. J. Am. Soc. Hortic. Sci. 103: 23-27.

Unsworth, M. H.; Heagle, A. S.; Heck, W. W. (1984) Gas exchange in open-top field chambers - II. Resistance to ozone uptake by soybeans. Atmos. Environ. 18: 381-385.

Unsworth, M. H.; Heagle, A. S.; Heck, W. W. (1984) Gas exchange in open-top field chambers - I. Measurement and analysis of atmospheric resistances to gas exchange. Atmos. Environ. 18: 373-380.

U. S. Environmental Protection Agency. (1976) Diagnosing vegetation injury caused by air pollution. Hicks, D. R., ed. EPA Contract Publication No. 68-02-1344.

U. S. Environmental Protection Agency. (1978) Air quality criteria for ozone and other photochemical oxidants. Research Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office; EPA report no. EPA-600/8-78-004. Available from: NTIS, Springfield, VA; PB80-124753.

U. S. Environmental Protection Agency. (1982) Air quality criteria for oxides of nitrogen. Research Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office; EPA report no. EPA-600/8-82-026F. Available from: NTIS, Springfield, VA; PB83-163337.

U. S. Environmental Protection Agency. (1983) Air quality data - 1982 annual statistics. Research Triangle Park, NC: U.S. Environmental Protection Agency Office of Air Quality Planning and Standards; EPA report no. EPA-450/4-83-016. Available from: NTIS, Springfield, VA; PB83-239830.

Usher, R. W.; Williams, W. T. (1982) Air pollution toxicity to eastern white pine in Indiana and Wisconsin. Plant Dis. 66: 199-204.

Vargo, R. H.; Pell, E. J.; Smith, S. H. (1978) Induced resistance to ozone injury of soybean by tobacco ringspot virus. Phytopathology 68: 15-17.

Walker, J. T.; Barlow, T. C. (1974) Response of indicator plants to O_3 levels in Georgia. Phytopatology 64: 1122-1127.

Wamsley, L.; Ashmore, M.L.; Bell, J. N. B. (1980) Adaptation of radish Raphanus sativus L. in response to continuous exposure to ozone. Environ. Pollut. 23: 165-177.

Weaver, E. M.; Jackson, H. O. (1968) Relationship between bronzing in white beans and phytotoxic levels of atmospheric ozone in Ontario. Can. J. Plant Sci. 48: 561-568.

Weber, D. E.; Reinert, R. A.; Barker, K. R. (1979) Ozone and sulfur dioxide effects on reproduction and host-parasite relationships of nematodes. Phytopathology 69: 624-628.

Weidensaul, T. C. (1980) N-2-(2-oxo-1-imidazolidinyl)ethyl-N'-phenylurea as a protectant against ozone injury to laboratory fumigated pinto bean plants. Phytopathology 70: 42-45.

Weidensaul, T. C.; Darling, S. L. (1979) Effects of ozone and sulfur dioxide on the host-pathogen relationship of Scotch pine and Scirrhia acicola. Phytopathology 69: 939-941.

Went, F. W. (1955) Air Pollution. Sci. Am. 192: 62-70.

Wilhour, R. G.; Neely, G. E. (1977) Growth response of conifer seedlings to low ozone concentrations. In: Dimitriades, B., ed. International conference on photochemical oxidant pollution and its control: proceedings, vol. II; January; Research Triangle Park. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA report no. EPA-600/3-77-001b; pp. 635-645. Available from: NTIS, Springfield, VA; PB264233.

Winner, W. E.; Mooney, H. A. (1980) Ecology of SO_2 resistance: I. Effects of fumigations on gas exchange of deciduous and evergreen shrub. Oecologia 44: 290-295.

Wood, F. A.; Drummond, D. B. (1974) Response of eight cultivars of chrysanthemum to peroxyacetyl nitrate. Phytopathology 64: 897-898.

Wood, F. A.; Pennypacker, S. P. (1975) Evaluation of the effects of air pollution on vegetation in the M. T. Storm, West Virginia-Oakland, Maryland area. 68th Annual Meeting, Air Pollution Control Association, Boston, MA; Paper 75-21.1.

Wukasch, R. T.; Hofstra, G. (1977a) Ozone and Botrytis interactions in onion-leaf dieback: open-top chamber studies. Phytopathology 67: 1080-1084.

Wukasch, R. T.; Hofstra, G. (1977b) Ozone and Botrytis spp. interaction in onion-leaf dieback: field studies. J. Am. Soc. Hort. Sci. 102: 543-546.

Yamazoe, F.; Mayumi, H. (1977) Vegetation injury from interaction of mixed air pollutants. Proceedings: international clean air congress; 4: Tokyo, Japan.

Yang, Y. S.; Kelly, J. M.; Chevone, B. I.; Birch, J. B. (1983) Effects of long-term ozone exposure on photosynthesis and dark respiration of eastern white pine. Environ. Sci. Technol: 17: 371-373.

Yarwood, C. E.; Middleton, J. T. (1954) Smog injury and rust infection. Plant Physiol. 29: 393-395.

Youngner, V. E.; Nudge, F. J. (1980) Air pollution oxidant effects on cool-season and warm-season turfgrasses. Agron. J. 72: 169-170.

Zadoks, J. C. (1980) Yields, losses and costs of crop protection - three views, with special reference to wheat growing in the Netherlands. In: Crop loss assessment. University of Minnesota, Agricultural Experiment Station; Miscellaneous Publication No. 7; pp. 17-23.

APPENDIX A

COLLOQUIAL AND LATIN NAMES OF PLANTS DISCUSSED IN THE CHAPTER

APPENDIX A. COLLOQUIAL AND LATIN NAMES OF PLANTS DISCUSSED IN THE CHAPTER

Colloquial Name	Latin name
Alfalfa	*Medicago sativa* L.
Ash	
Green	*Fraxinus pennsylvanica* Marsh.
White	*Fraxinus americana* L.
Aspen	
Bigtooth	*Populus grandidentata* Michx.
Azalea	
Delaware valley white	*Rhododendron mucronatum* Don.
Hinodegiri	*Rhododendron obtusum* Planch.
Korean	*Rhododendron poukhanensis* Leveille
Barley	*Hordeum vulgare* L.
Bean	*Phaseolus vulgaris* L.
var. - French	
Green snapbean	
Navy	
Pinto	
Red kidney	
Snapbean	
White	
Bean	
Broad	*Vicia faba* L.
Beet	*Beta vulgaris* L.
Garden	
Sugar	
Begonia	*Begonia semperflorens* Link and Otto
Begonia	*Begonia* X *hiemalis* Fotsch.
Birch	
White	*Betula papyrifera* Marsh.
Yellow	*Betula alleghaniensis* Britton
Cabbage	*Brassica oleracea capitata* L.
Carnation	*Dianthus caryophyllus* L.
Carrot	*Daucus carota* var. *sativa* DC.

APPENDIX A. (continued)

Colloquial Name	Latin name
Chard Swiss	Beta vulgaris var. cicla L.
Cherry Black	Prunus serotina Ehrh.
Chrysanthemum	Chrysanthemum morifolium Ramat.
Citrus	Citrus sp.
Clover Landino	Trifolium repens L.
Coleus	Coleus blumei Benth.
Corn Field Sweet	Zea mays L.
Cotoneaster	Cotoneaster divaricata Rehd.
Cotton	Gossypium hirsutum L.
Cottonwood Eastern	Populus deltoides Bartr.
Elder Black	Sambucus nigra L.
Elm Chinese	Ulmus parvifolia Jacq.
Endive	Cichorium endiva L.
Fir Douglas	Pseudotsuga menziesii (Mirb.) Franco.
Geranium	Pelargonium hortorum Bailey
Grape	Vitis vinifera L.
Grape	Vitis labrusca L.
Gum Black	Nyssa sylvatica Marsh.
Hemlock Eastern	Tsuga canadensis (L.) Carr.

APPENDIX A. (continued)

Colloquial Name	Latin name
Holly	
American	Ilex opaca Ait.
Japanese	Ilex crenata Thunb.
Larch	
Japanese	Larix leptolepis Gord.
Lettuce	
var.-Cos (Romaine)	Lactuca sativa L.
Linden	
American	Tilia americana L.
Locust	
Black	Robinia pseudoacacia L.
Maple	
Red	Acer rubrum L.
Sugar	Acer saccharum L.
Marigold	Tagetes erecta L.
Milkweed	Asclepias syriaca L.
Morning glory	Ipomea nil Roth.
Mountain laurel	Kalmia latifolia L.
Muskmelon	Cucumis melo L.
Mustard	Brassica migra (J.) Koch
Nettle (little leaf)	Urtica urens L.
Oak	
Black	Quercus velutina Lam.
California black	Quercus kelloggii Newb.
Willow	Quercus phellos L.
Oat	Avena sativa L.
Onion	
Australian	Allium cepa L.
Pasture grass	
Australian	Phalaris aquatica
Grasslands	Dactylis glomerata L.
Victorian	Lolium perenne L.

APPENDIX A. (continued)

Colloquial Name	Latin name
Peanut	*Arachis hypogea* L.
Pepper	*Capsicum annuum* L.
Petunia	*Petunia hybrida* Vilm.
Pine	
Austrian	*Pinus nigra* Arnold
Eastern white	*Pinus strobus* L.
Jeffrey	*Pinus jeffreyi* Grev. and Balf.
Loblolly	*Pinus taeda* L.
Lodgepole	*Pinus contorta* var. *murrayana* (Balf.) Critch
Monterey	*Pinus radiata* D. Don
Pitch	*Pinus rigida* Mill.
Ponderosa	*Pinus ponderosa* Laws.
Scotch	*Pinus sylvestris* L.
Shore	*Pinus contorta* var. *contorta* Dougl. ex Laud
Slash	*Pinus elliotti* Englem. ex Vasey
Sugar	*Pinus lambertiana* Dougl.
Table mountain	*Pinus pungens* Lamb.
Virginia	*Pinus virginiana* Mill.
Western white	*Pinus monticola* Dougl.
Poinsettia	*Euphorbia pulcherrima* Wildenow
Poplar	*Populus* X *euramericana*
Hybrid poplar	*Populus* sp.
Hybrid poplar	*Populus maximowiczii* X *trichocarpa*
Hybrid poplar	*Populus deltoides* X *trichocarpa*
Potato	*Solanum tuberosum* L.
Privet	
Amur	*Ligustrum amurense* Carr.
Radish	*Raphanus sativus* L.
Snapdragon	*Antirrhinum majus* L.
Soybean	*Glycine max* (L.) Merr.
Spinach	*Spinacia oleracea* L.
Spruce	
Sitka	*Picea sitchensis* (Bong.) Carr.
White	*Picea glauca* (Moench) Voss

APPENDIX A. (continued)

Colloquial Name	Latin name
Strawberry	Fragaria chiloensis var. ananassa Bailey
Sunflower	Helianthus anuus L.
Sweetgum	Liquidambar styraciflua L.
Sweet mock-orange	Philadelphus coronarius L.
Sycamore	
American	Platanus occidentalis L.
Tomato	Lycopersicon esculentum Mill.
Tree-of-heaven	Ailanthus altissima Swingle
Turfgrass	
Annual bluegrass	Poa annua L.
Bermudagrass	Cynodon dactylon L., Pers.
Colonial bentgrass	Agrostis tenuis Sibth.
Creeping bentgrass	Agrostis palustris Huds.
Kentucky bluegrass	Poa pratensis L.
Red fescue	Festuca rubra Gaud.
Red top	Agrostis alba L.
Ryegrass	Lolium perenne L.
Tall fescue	Festuca arundinaceae Schreb.
Zoysiagrass	Zoysia japonica Steud.
Turnip	Brassica rapa L.
Viburnun	
Tea viburnun	Viburnum setigerum Hance
Linden viburnum	Viburnum dilatatum Thunb.
Walnut	Juglans nigra L.
Black	
Wild strawberry	Fragaria virginiana Duchesne
Wheat	
Winter	Triticum aestivum L.
Yellow poplar (Tulip poplar)	Liriodendron tulipifera L.
Yew	Taxus X media Rehd.

APPENDIX B

SPECIES THAT HAVE BEEN EXPOSED TO OZONE TO DETERMINE DIFFERENTIAL RESPONSES OF GERMPLASM TO PHOTOCHEMICAL PRODUCTS

APPENDIX B. SPECIES THAT HAVE BEEN EXPOSED TO OZONE TO DETERMINE DIFFERENTIAL RESPONSES OF GERMPLASM TO PHOTOCHEMICAL PRODUCTS

Species	References
Alfalfa	Howell et al., 1971
Azalea	Gesalman and Davis, 1978
Bean	Butler and Tibbitts, 1979 Davis and Kress, 1974 Meiners and Heggestad, 1979 Heggestad et al., 1980
Begonia	Reinert and Nelson, 1979 Adedipe, 1972
Chrysanthemum	Wood and Drummond, 1974 Brennan and Leone, 1972
Cucumber	Ormrod et al., 1971
Eggplant	Rajput and Ormrod, 1976
English holly	Brennan and Leone, 1970
Forage legumes	Brennan et al., 1969
Grape	Richards et al., 1958
Lettuce	Reinert et al., 1972
Morning glory	Nakamura and Matsunaka, 1974
Oat	Brennan et al., 1964
Petunia	Feder et al., 1969 Cathey and Heggestad, 1972 Elkiey and Ormrod, 1980
Pine	Berry, 1971 Houston, 1974
Poplar	Karnosky, 1977
Poinsettia	Manning et al., 1973
Potato	Heggestad, 1973a DeVos et al., 1982

APPENDIX B. (continued)

Species	References
Radish	Reinert et al., 1972
Safflower	Howell and Thomas, 1972
Soybean	Tingey et al., 1972 Miller et al., 1974 Heagle and Letchworth, 1982
Spinach	Manning et al., 1972
Sugar maple	Hibben, 1969
Tobacco	Dean, 1963 Grosso et al., 1971 Heggestad et al., 1964 Huang et al., 1975
Tomato	Clayberg, 1971 Reinert and Henderson, 1980
Turfgrasses	Brennan and Halisky, 1970
Wheat	Heagle et al., 1979c
Woody species (general)	Davis and Coppolino, 1974; 1976 Davis and Wood, 1972 Hanson, 1972 Jensen, 1973 O'Connor et al., 1975 Wilhour and Neely, 1977

8. EFFECT OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS ON NATURAL AND AGROECOSYSTEMS

8.1 INTRODUCTION

Organisms do not live alone; each species exists as a breeding population. These populations live together to form communities that interact with their environment and each other to create ecosystems. Chapter 7 discusses the response of individual species and subspecies of plants to ozone (O_3) and peroxyacetyl nitrate (PAN) exposure. The responses of terrestrial vegetation to O_3 and PAN may be envisioned as a continuum ranging from the molecular, to the organismal, to the ecosystem level. Ecosystems respond to stress in a different manner from individuals. In this chapter, the responses of ecosystems to O_3 stress will be emphasized. Ecosystems in both the western and eastern United States have been under stress from O_3 transported from sources many kilometers away for more than three decades. No attempts have been made to examine an ecosystem response to PAN. Controlled fumigations with PAN, as well as field observations, have been confined to assessing the response of a few sensitive plant species.

8.2. ECOSYSTEMS: THE POTENTIAL FOR INDIRECT EFFECTS

8.2.1 Interwoven Structure, Boundaries, and Social Value

An ecosystem is an integrated unit of nature consisting of interacting plants and animals in a given area (the community) whose survival depends on the maintenance of biotic (living) and abiotic (nonliving) structures and functions. An ecosystem does not have to be isolated, but usually has definable limits within which are the integrated functions of energy flow, nutrient cycling, and water flux (Odum, 1969; Odum, 1971a; Jordan and Medina, 1977). The functions of energy flow and nutrient cycling among the biotic and abiotic components form definite patterns that lead to clearly defined trophic structures (food webs) and biotic diversity.

Ecosystems may be large or small, natural or human-made, and are not characterized by common physical dimensions or structures, but are characterized by the common processes of energy flow and chemical cycling (Botkin and Keller, 1982; Odum, 1969; Odum, 1971a). In all cases they have boundaries and may be delimited in several ways. Geographic, topographic, hydrologic, taxonomic, or energy boundaries have been used. Boundaries between adjacent

ecosystems may be obvious and distinctive, as when terrestrial and aquatic systems are juxtaposed, or they may be gradual and poorly defined, as in the transitional zone of scattered trees and grass between a forest and open grassland. Irrespective of the ease of boundary delimitation, there is always some flow of energy and materials from one ecosystem to adjacent ecosystems. All ecosystems are open and capable of responding to changes in the movement of energy and materials from adjacent environments as well as to changes in their own environment (Cox and Atkins, 1979).

A forest, fallen log, agricultural field, river, or lake is an ecosystem. Terrestrial ecosystems are associations or communities of land-dwelling plant and animal (including human) species and their environments. Of particular interest from the standpoint of air pollution impacts are forest and agricultural ecosystems. These systems not only hold obvious economic significance for human society; they also represent the even more fundamental fact that human life depends ultimately on such systems. Without plants fixing energy and essential elements to form the base of the food chain, humans could not survive. On the other hand, animals and microorganisms (consumers and decomposers) are essential to assure cycling of the essential elements. Thus, any effects of atmospheric pollutants on terrestrial ecosystems or their components deserve careful attention.

Natural and agricultural ecosystems possess the same basic functional components, require energy flow and mineral cycling for maintenance, and are subject to the dominating influences of climate and substrate. Natural ecosystems vary in diversity from simple systems with few species to complex systems with many species. Their populations also vary in genetic composition, age, and species diversity. They are self-regulating and self-perpetuating. Agroecosystems, on the other hand, are highly manipulated monocultures of similar genetic and age composition and are unable to maintain themselves without the addition of nutrients, energy, and human effort; opportunistic native and imported species may invade the sites. The manipulation of monocultures is designed to concentrate ecosystem productivity into a particular species to maximize its yield (e.g., corn, wheat, soybeans) for the benefit of humans (Cox and Atkins, 1979).

As cultural treatments intensify, the dollar value placed by humans on the products of the ecosystem generally increases, and biological diversity typically decreases. For example, wilderness forest areas and national parks

are high in biological diversity, and human management effort is low. Corn fields, wheat fields, lawns, and city parks are low in diversity and are highly managed (Figure 8-1). Natural forests managed as wilderness areas may have products of little direct dollar value, but they provide critically important (although unpriced) benefits to society, such as soil stabilization, enhanced water quality, nutrient conservation, energy conservation, gene preservation, and amenity and aesthetic functions (Bormann, 1976; Hutchinson et al., 1982; National Research Council, 1980; Smith, W. H., 1970; Westman, 1977). It is extremely important to recognize that societal benefits derived from natural ecosystems, such as forests, are commonly obtained without investment of appreciable direct dollar expenditures or intensive management. The benefits provided by forests are powered by solar energy. When forests are removed, these benefits are no longer available. They must be replaced by

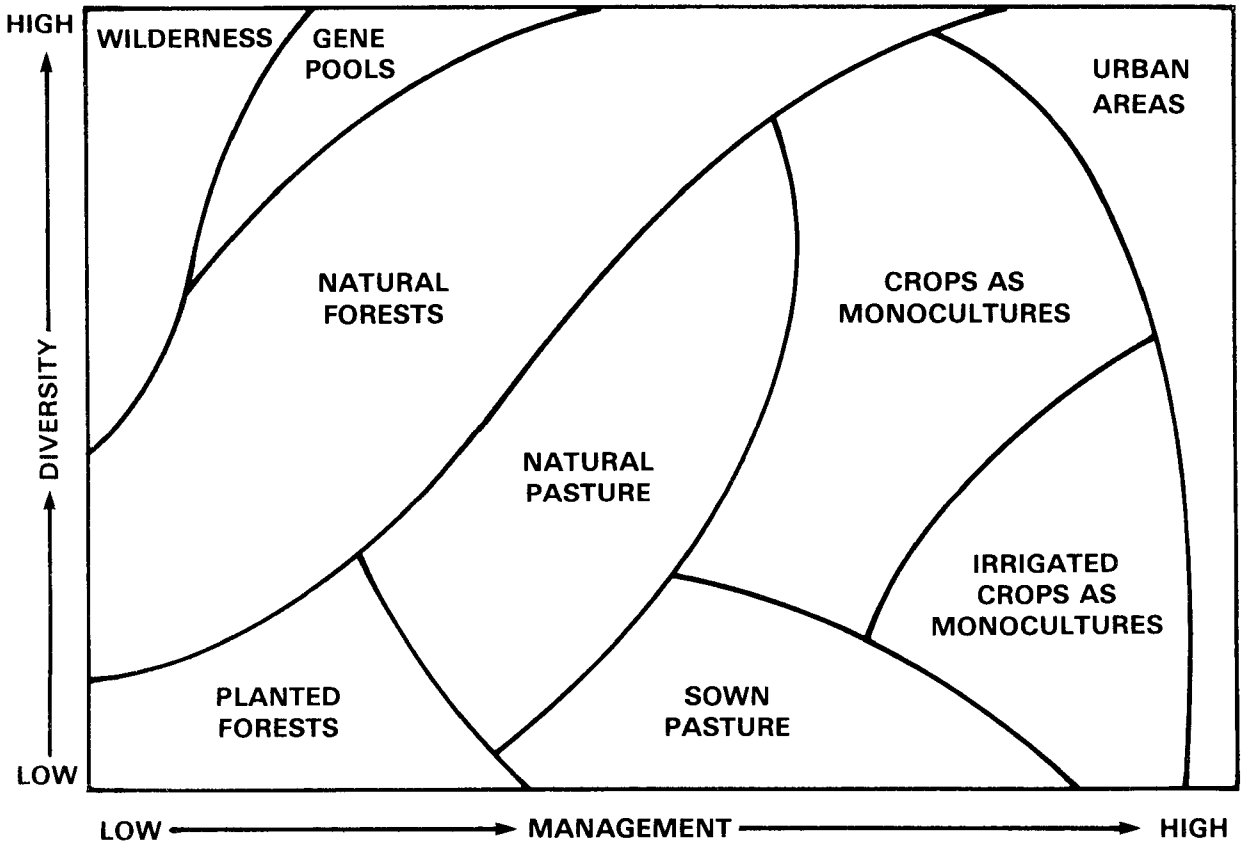

Figure 8-1. The relationship of several managed ecosystems in terms of degree of management and biological diversity.
Source: Smith and Hill (1975).

extensive and continuing investments of fossil fuels and other natural resources by humans if the quality of life is to be maintained. When forests are lost, replacements for wood products must be found, erosion control works built, reservoirs enlarged, air pollution control technology upgraded, flood control works installed, water purification plants improved, air conditioning increased, and new recreational facilities provided. These substitutes could produce an enormous tax burden, a drain on the world's remaining supply of natural resources, and an increased stress on the remaining natural systems. (Bormann and Smith, 1980).

8.2.2 Ecosystem Components: Internal Structure

The living (biotic) components of ecosystems are populations of either autotrophs (producers) or heterotrophs (consumers and decomposers). Autotrophs, predominantly green plants, are capable of synthesizing their own food from simple compounds by capturing the sun's energy and are, therefore, in the first trophic level. The biomass (total organic matter) accumulation at this trophic level is termed primary production. In a forest ecosystem, this is the addition of new organic matter through the growth of trees, shrubs, and herbs.

Heterotrophs (consumers and decomposers) require preformed food materials. Consumers are organisms that feed on other organisms and constitute all trophic levels above the first. In morphology and size, they are extremely variable, ranging from single-celled microscopic forms to large mammals. Consumers that rely directly on green plants for food are herbivores and are usually placed in the second trophic level; those that ingest herbivores or each other are carnivores. Decomposers are capable of degrading complex compounds and utilizing some of the decomposition products as their own food source while releasing inorganic substances for use by other organisms. Decomposers are organisms such as litter-feeding invertebrates, bacteria, fungi, and protozoa (Odum, 1971b; Botkin and Keller, 1982; Smith, R. L., 1980). Autotrophs and heterotrophs (producers, consumers and decomposers) all live together as populations of interacting organisms. "Genetically, individuals are members of their local populations; ecologically, they are members of a community and an ecosystem" (Billings, 1978). The number of species in a given ecosystem is variable. Desert ecosystems have fewer species than do forests. Most natural ecosystems have more species than do agricultural ecosystems. The number of species in a given ecosystem may change as the system matures.

The living components of an ecosystem cannot function without the nonliving (abiotic) components. All green plants require the energy of the sun (an abiotic component) to make their own food. Other abiotic components utilized by green plants in food formation include carbon dioxide, from the air, and water and minerals (calcium, phosphorus, magnesium, iron), primarily from the soil. Because virtually all other biotic components depend on green plants, the energy and minerals used by the plants are passed through the ecosystem as organic matter via the processes of energy flow and mineral cycling. Thus, ecosystem components become organized into structural patterns based on feeding steps (trophic levels). Food chains form when organisms eat and are eaten. Chains become complex food webs when the food source is shared. For example, a food web is formed when some animals are consumed by several predators or when the same plants are eaten by a variety of herbivores. The unidirectional movement of energy and the biogeochemical cycling of nutrients through the highly structured interrelationships that have developed among the various components unite the ecosystem into a complex, interacting system of physical, chemical, and biological elements. Temperature, precipitation, radiation, barometric pressure, climate, and pollution are additional abiotic factors that influence ecosystem components and thus they influence the flow of energy and cycling of minerals through the system as well (Odum, 1971a,b; Botkin and Keller, 1982; Smith, R.L., 1980).

8.2.3 Response to Stress

Forests, prairies, marshes, and ponds or lakes, natural ecosystems in existence today, are the culmination of years of gradual community development known as succession. Adaptation, adjustment and evolution occur with time as the biotic and abiotic components of the communities interact. Some organisms die, and others reproduce and replace them. Energy and mineral nutrients continually move through the food webs that have been established. In time the communities arrive at some form of steady state and are more or less self-maintaining as long as the abiotic factors remain constant. Through succession, ecosystems evolve toward the most stable state possible within the constraints of the environment (Odum, 1971a, b; Cox and Atkins, 1979; Smith, R. L., 1980).

Disturbances do occur. Fire, drought, windstorms, disease, and pollution perturb the ecosystems. Ecosystems can respond to these stresses only through

the response of the populations of organisms of which they are composed (Smith, R. L., 1980). The individual organisms of a population sensitive to environmental changes are removed. Therefore, the capacity of an ecosystem to maintain internal stability is determined by the ability of individual organisms to adjust their physiology or behavior to change. The capacity of organisms to withstand change or injury from weather extremes, fires, storms, pesticides, or polluted air follows the principle of limiting factors (Billings, 1978; Odum, 1971; Smith, R. L., 1980). According to this principle, for each physical factor in the environment there exists for each organism a minimum and a maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and in extreme cases, a species (Billings, 1978; Smith, R. L., 1980; Odum, 1971a). The range of tolerance of an organism may be broad for one factor and narrow for another. The tolerance limit for each species is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth, or growth form of an organism. Limiting factors are, therefore, those which, when scarce or overabundant, limit the growth, reproduction, and/or distribution of an organism (Billings, 1978; Smith, R. L., 1980; Odum, 1971a). The success with which an organism copes with environmental change is determined by its ability to produce reproducing offspring. The size and success of a population depend on the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that are tolerant of or adapt best to stress contribute most to future generations, because they have the greatest number of progeny in the population (Woodwell, 1970; Odum, 1971a; Smith, R. L., 1980; Roose et al., 1982).

Some plant populations have the capacity to evolve resistance (tolerance) to environmental stress. Sensitive plants in a population die or are unable to compete with resistant plants, so do not reproduce. The resistant plants reproduce and in time resistant populations develop. Resistance refers to the relative ability of organisms of the same genetic composition (genotype) to maintain normal growth and remain free from injury in a given polluted environment. Resistance is quantitative rather than qualitative, as resistance need not be complete (Roose et al., 1982). The rapidity with which a population

develops resistance depends on the selection pressure, i.e., the period of exposure to the stress.

Plants exposed continuously to heavy metals over time develop populations resistant to the stress. Selection by both air pollutants and herbicides tends to be episodic (Roose et al., 1982). Acute injury from air pollution resembles that from herbicides in that selection for resistance occurs only for short periods of time. Chronic air pollution more closely resembles soil contaminated with heavy metals in that the plants experience the polluted environment for a considerable portion of their lives. Resistance in either situation depends on the resistant or tolerant genotype being present in the plants that are growing in unpolluted air (Roose et al., 1982).

Variability in tolerance or resistance to air pollutants appears to be common in most species of plants. The differential sensitivity of plants is discussed in Chapter 7, in sections of the document that follow, by Roose et al. (1982), and in numerous other publications. Annual plants are capable of altering the genetic composition of the entire population every year. Perennial plants adapt and express their resistance through differential growth and the survival of the resistant genotype without sexual reproduction. Variability in resistance of ponderosa pine (Pinus ponderosa Doug. ex. Laws) and eastern white pine (Pinus strobus L.) is discussed in the sections that follow.

Competition increases selection for resistance under polluted conditions and selection against resistance under less polluted conditions. Studies using heavy metals and herbicides indicate that once the stress is removed and plants are growing in a pollutant-free environment, the pollutant-resistant plants tend to decline in number (Roose et al., 1982). This evidence is corroborated by observations of ecosystems functioning under specific natural environments. Certain terrestrial ecosystems require a major disturbance (e.g., fire, drought, and windstorms) to retain their characteristics (Vogel, 1980; Smith, W. H., 1980). In the absence of disturbance, some ecosystems appear to degrade, lose nutrients, become less productive, and have fewer species with a smaller biomass (Woodwell, 1970; Gorham et al., 1979).

Two groups of organisms particularly critical to the maintenance of an ecosystem are the producers, through which solar energy, carbon, and other nutrients enter living systems, and the decomposers, through which nutrients bound up in other organisms are released for reuse. Loss of either of these groups results in the collapse of the entire system (Ehrlich and Mooney, 1983).

The ecosystems that are particularly vulnerable are those in which a single species appears to be the primary controller of energy flow and nutrient movement, a redwood forest, for example. Controller species vary from ecosystem to ecosystem, and the differential sensitivity of these species will determine the extent to which injury occurs and how critical it is to the ecosystem.

Existing studies indicate that changes occurring within ecosystems, in response to pollution or other disturbances, follow definite patterns that are similar even in different ecosystems. It is possible, therefore, to predict the basic biotic responses of an ecosystem to disturbances caused by environmental stress (Woodwell, 1970; Woodwell, 1962). These responses to disturbance are (1) removal of sensitive organisms at the species and subspecies level due to differential kill; (2) reduction in the number of plants and animals (standing crop); (3) inhibition of growth or reduction in productivity; (4) disruption of food chains; (5) return to a previous state of development; and (6) modification in the rates of nutrient cycling.

Not all ecosystems respond in the same way to stress. Some ecosystems may be more sensitive to a given perturbation at one stage of development than at another. Organisms can exist only within their range of tolerance. Some populations of organisms, annual plants, insects, and mice, for example, respond rapidly to environmental change. They increase in numbers under favorable conditions and decline rapidly when conditions are unfavorable. Populations of other organisms, such as trees and wolves, fluctuate less in response to favorable or unfavorable conditions by showing little variation in the rates of reproduction and death. Adaptation is the ability of an organism to conform to its environment. Ecosystem stability ultimately is based on the adaptability of organisms that compose it. Stability may be associated with the ability of a system to return to an equilibrium state after a temporary disturbance (Holling, 1973). The less it varies from and the faster it returns to its original state, the more stable the system (Smith, R. L., 1980). Stability also involves persistence, the ability of the populations of an ecosystem to persist through time. Persistence involves resilience, the ability of an ecosystem to absorb changes. Although individual populations within a system may fluctuate greatly in response to environmental changes, the system may be highly resilient (Holling, 1973; Smith, R. L., 1980). Contrasted with resilience is resistance, the ability of a system, because of its structure, to resist changes from disturbances. Typically, the most

resistant ecosystems have large living components, trees for example, and store nutrients and energy in the standing biomass. Resistant systems such as forests, once highly disturbed, are very slow in returning to their original state (Smith, R. L., 1980). Perturbation typically causes retrogression, a return to an earlier and more simplified successional stage of ecosystem development. Both diversity and structure are changed. Complex communities become less complex (Whittaker and Woodwell, 1978; Woodwell, 1970). Too frequent disturbance, or natural disturbance combined or supplemented with anthropogenic disturbance (e.g., air pollution) may cause a system to change slowly or to disappear. With moderate rates of disturbance, ecosystems may be most productive and have the largest number of species and biomass.

8.3 RESPONSE TO OZONE

8.3.1 Effects on Plant Processes

The impact of O_3 and atmospheric pollutants on the environment has stimulated the interest of the general public and scientists as well. The effects of such disturbances on ecosystem structure and function have been the subject of numerous publications (Curtis, 1956; Miller and McBride, 1975; Cairns, 1980; National Research Council, 1977; Research Foundation, State University of New York, 1980; Johnson and Siccama, 1983; McLaughlin et al., 1982). The vegetational effects of O_3 can be viewed as a continuum that begins at the molecular, continues through the organismal and terminates at the ecosystem level of organization (Figure 8-2). The alteration of biochemical and physiological processes are the fundamental cause of all other effects. The reaction of O_3, or its decomposition products, with cellular components may increase membrane permeability, alter the activity of specific enzymes and change metabolic pathways. Visible foliar injury, premature senescence, reduced photosynthesis, plant vigor, and yield and/or growth are manifestations of cellular injury. Death may result (Chapter 7).

The ecosystem processes of energy flow and nutrient cycling are directly involved in plant growth and reproduction (yield) through the processes of assimilation, nutrient uptake, biosynthesis, and translocation. During assimilation, through the process of photosynthesis, carbon dioxide is converted into organic compounds for use by the plant. Nutrients and water enter plants through the roots. The raw materials formed during assimilation (sugars and

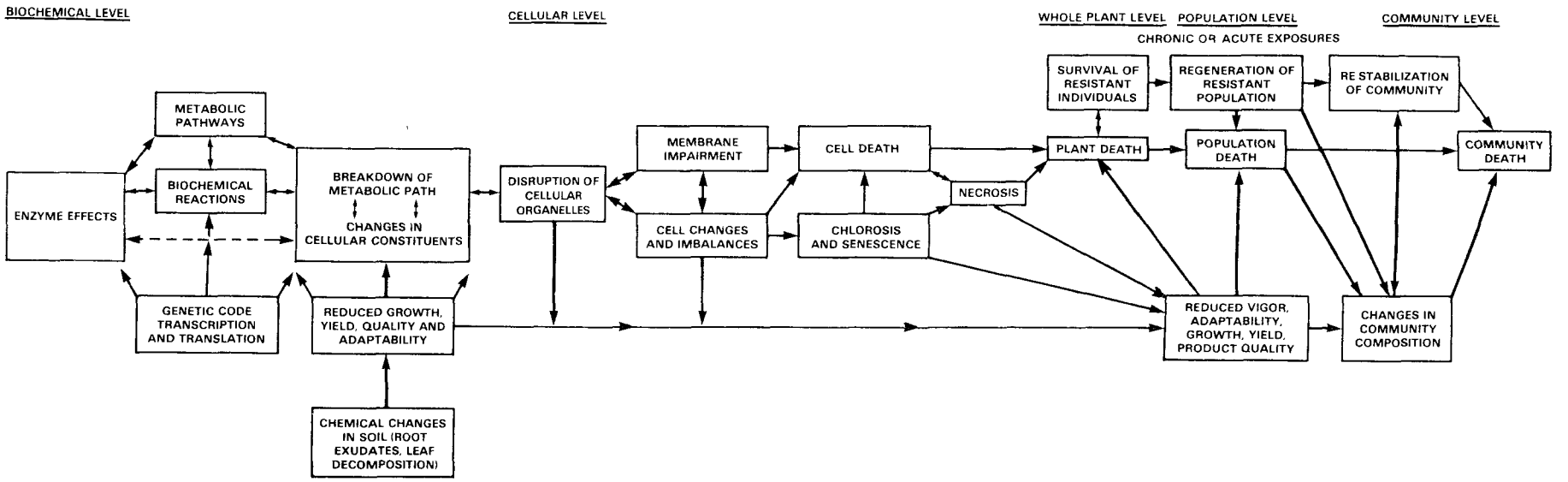

Figure 8-2. Conceptual sequence of levels showing continuum of plant responses. Source: Adapted from Heck (1973).

starches) and the nutrients and water taken up by the roots are, through biosynthesis in the various plant organs, converted into a wide array of compounds required for plant growth and reproduction. The products of biosynthesis are translocated throughout the plant. A disruption or reduction in the rate of assimilation, uptake, or the subsequent biochemical reactions, as frequently occurs under O_3 exposure, can be reflected in reduced plant growth and reproduction (Chapter 7).

Plant response to O_3 is also influenced by biological, physical, and chemical variables. Success of a population of plants or animals in any environment depends on its genetic diversity, the presence of particular gene combinations and variations among individuals in the population that give a species or taxon the capacity to adapt to environmental changes. Plants in a given population (e.g., trees in a stand of ponderosa pine) will not respond equally to O_3 exposure because of genetic diversity in the sensitivity of individual plants and the environmental heterogeneity of the habitat. Differential plant response is an inherited trait. Plants at different ages, or growing under different temperature, humidity, light intensity, or soil moisture regimes will respond differently to equivalent O_3 exposures. The developmental stage of both leaf and plant influences O_3 sensitivity. Leaves approaching maximum expansion appear to be most sensitive. Evidence indicates that young plants and those approaching senescence are more sensitive to O_3 exposure than those of intermediate ages. The presence of several pollutants, chemical sprays, biological pests, as well as soil moisture and fertility all contribute to the magnitude of plant response (Chapter 7).

Ozone inhibits photosynthesis, decreases formation of organic compounds needed for plant growth, and can alter the transport and allocation of the decreased products of photosynthesis so that sugar storage and root growth are reduced (Chapter 7). Concentrations of 0.05 ppm for 4 hr, 0.1 ppm for 1 hr, or 0.2 ppm for 1 hr significantly decreased photosynthesis in a variety of plant species. Higher concentrations or longer exposure durations also reduced photosynthesis (Chapter 7, Table 7-1). Specifically, exposure of 3-year-old ponderosa pine seedlings under controlled conditions to concentrations of 0.15, 0.30, and 0.40 ppm 9 hr/day for 30 days reduced photosynthesis by 10, 70, and 85 percent, respectively (Miller et al., 1969). The maximum photosynthetic rates and stomatal conductance among three injury classes (I, slight; II, moderate; III, severe) of ponderosa pine trees were compared in relation

to cumulative incident O_3 concentrations (Coyne and Bingham, 1981). Trees of an approximately even-aged (18 yr) stand and growing in a similar environment exhibited a continuum of O_3-related foliar injury symptoms that ranged from severe to slight, an indication of genetically related differential sensitivity to O_3. Differential photosynthetic and stomatal responses compared well with the O_3 injury classification mentioned above. The decline in photosynthesis and stomatal function normally associated with aging was accelerated as O_3 injury symptoms increased. Photosynthesis in all three age classes was reduced to about 10 percent of the maximum rate observed in class I current needles by incident exposures of approximately 800, 700, and 450 ppm-hr. When compared with Class I, photosynthesis declined most rapidly in the sensitive (Class III) trees. Photosynthetic rates were always higher in the trees with the fewest injured needles. Premature senescence and abscission of needles occurred soon after photosynthesis reached its lowest level. Losses in photosynthetic capacity in all trees and needle ages exceeded reductions in stomatal conductance, suggesting injury to the mesophyll, or carboxylation, or excitation of components of the CO_2 diffusion pathway was greater than injury to the stomata (Coyne and Bingham, 1981). Three sensitivity classes have also been observed in white pine (Pinus strobus L). Yang et al. (1983) studied the effect of O_3 exposure on photosynthesis in three clones of white pine with differing O_3 sensitivities. Under controlled conditions, the clones were exposed to concentrations of 0.00, 0.10, 0.20, and 0.30 ppm 4 hr/day for 50 consecutive days. By day 10, photosynthesis in the sensitive plants exposed to 0.30 ppm was significantly reduced. By day 20, photosynthesis in the sensitive plants at all concentrations was reduced. At the end of 50 days, net photosynthesis in the sensitive clone exposed to 0.10, 0.20, and 0.30 ppm was reduced from the control by 24, 42, and 51 percent respectively. Photosynthesis in the intermediately sensitive clone was reduced 6, 14, and 10 percent. The insensitive clone varied from the control at the 20-, 30- and 40-day periods, but had nearly recovered by 50 days. Decrease in the rates of photosynthesis was closely associated with visible needle injury, premature senescence and reduction of biomass in the sensitive clones. Reduction in biomass was associated with the effect of O_3 exposure upon the rate of photosynthesis, with plant metabolism and with injury to the assimilatory apparatus of the plants.

In each of the studies discussed above, O_3 exposure alters photosynthesis and other physiological and biochemical processes. Diminished photosynthetic

capacity results in decreased carbohydrates for plant use in growth, storage, reproduction, and injury repair. The trees are weakened as a result and more susceptible to disease. Ultimately, the alteration and change of plant processes will, if continued, be reflected in the ecosystem processes of energy flow and nutrient cycling.

8.3.2 Effects on Species Composition and Succession

Ozone stress has been shown to affect species composition and succession in forests and other plant communities in both the western and eastern United States. Ozone exerts selection pressure on sensitive species by causing their demise or by weakening them and making them less competitive. Ozone-tolerant species may then replace them in the plant communities. Disruption of food chains, modification of the rates of nutrient cycling, and a less stable community can result.

Cobb and Stark (1970) concluded that if the air pollution transported from the Los Angeles Basin to the San Bernardino Mountains continued unabated, there would be a conversion from the well-stocked forests dominated by ponderosa pine (Pinus ponderosa Dougl. ex. Laws) to poorly stocked stands of tree species less susceptible to oxidants. Photochemical oxidant air pollution, chiefly O_3, was first identified as the agent responsible for the slow decline and death of ponderosa pine trees in southern California by Miller et al., 1963. Miller (1973) and the 1978 oxidant criteria document (U.S. Environmental Protection Agency, 1978) provided a thorough discussion of this oxidant-induced forest change. Ponderosa pine is one of five major species of the mixed-conifer forest that covers wide areas of the western Sierra Nevada Mountains and mountain ranges from 1000 to 2000 m (3000 to 6000 ft) elevation, including the San Bernardino Mountains in southern California. Above 200 m, Jeffrey pine (Pinus jeffreyi Grev and Balf) replaces ponderosa pine. Other species are sugar pine (Pinus lambertiana Dougl.), white fir (Abies concolor Lindl.), incense cedar (Libocedrus decurrens Torr.), and California black oak (Quercus kelloggii Newb.). The response of these five major tree species to oxidant air contaminants in the San Bernardino National Forest has varied. Ponderosa pine exhibited the most severe visible foliar response to elevated levels of ambient O_3 (0.05 - 0.06 for 24 hr). A 1969 aerial survey conducted by the U.S. Department of Agriculture, Forest Service, indicated some degree of stress in 1.3 million ponderosa or Jeffrey pines over an area of more than 405

km^2 (155 mi^2). Mortality of ponderosa pine has been extensive. Death has been typically attributed to bark beetle infestation of trees weakened by air pollution. White fir has generally suffered slight damage, but scattered individual trees have exhibited severe symptoms. Sugar pine, incense cedar, and black oak have exhibited only slight foliar injury from oxidant exposure. A 233-ha (575-acre) study block was delineated in the southwest section of the San Bernardino National Forest to conduct an intensive inventory of vegetation by various size classes and to evaluate the health of the forest. There were more ponderosa pines 30 cm (12 in) in diameter or larger than any other species of comparable size in the study area. These pines were most abundant on the more exposed ridge crest sites of the area. Mortality of ponderosa pine ranged from 8 to 10 percent during 1968 to 1972. Clearly, the loss of a dominant species in a forest ecosystem produces profound change in that system. Miller (1973) concluded that a shift to a greater proportion of white fir will probably occur in the lower two-thirds of the study area. It was judged that incense cedar would probably remain secondary to white fir. Sugar pine was thought to be restricted by its lesser competitive ability and by dwarf mistletoe (Arceuthobium) infection. The rate of compositional change was deemed to depend on the rate of mortality of ponderosa pine, as its selective death directly affects other conifer species. The upper one-third of the study area, characterized as being more environmentally severe because of the additional climatic and edaphic stress, supported less vigorous growth of white fir. Thus, following the loss of ponderosa pine in this area, sugar pine and incense cedar may assume greater importance. Miller (1973) suggests, however, that natural regeneration of these latter species may be restricted in the more barren, drier sites characteristic of the upper ridge area, so that California black oak and shrub species may become more abundant there.

Additional research on forest composition in the San Bernardino National Forest has been reported (Miller and Elderman, 1977; Miller et al., 1982). Tree population dynamics were examined on 18 permanent plots, established in 1972 and 1973, and on 83 temporary plots, established in 1974, to investigate forest development as a function of time since the most recent fire. Generally, the data continue to support the hypothesis that forest succession toward species more tolerant of O_3, such as white fir and incense cedar, occurs in the absence of fire. In the presence of fire, pine may be favored by seedbed preparation and elimination of competing species. These recent

studies suggest that 5 forest subtypes exist. These are (1) ponderosa pine, (2) ponderosa pine-white fir, (3) ponderosa pine - Jeffrey pine, (4) Jeffrey pine - white fir, and (5) Jeffrey pine. Destruction of the pine forest canopy by fire and O_3 leads to a dominance of self-perpetuating, fire-adapted, O_3-tolerant mixtures of shrub and oak species that have lower commercial and amenity values than the former pine forest. Forest stand age and species structure are variables that have the most relevance and direct effect on human welfare in both recreational and commercial forests. The interplay of insects and diseases, drought, ozone injury, and forest fires shapes stand age and species structure (Miller et al., 1982).

From 1973 to 1978, during the period of interdisciplinary study of oxidant impact on the San Bernardino National Forest, the average May through September 24-hr O_3 concentrations ranged from a background of 0.03 to 0.04 ppm up to a maximum of 0.1 to 0.12 ppm (Miller et al., 1982). Because this southern California forest is used intensively for recreation and because the loss of ponderosa pine has reduced its aesthetic qualities, the species changes in forest composition caused by oxidants is a management concern.

In southern California, the predominant native shrubland vegetation consists of chaparral and coastal sage scrub. Chaparral occupies upper elevations of the coastal mountains and extends into the North Coast ranges, east to central Arizona, and south to Baja California. Coastal sage scrub occupies lower elevations of the coastal and interior sides of the coast ranges from San Francisco to Baja California. Westman (1979) applied standard plant ordination techniques used to determine species composition to these shrub communities to examine the influence of air pollution. The reduced cover of native species of coastal sage scrub documented on some sites was statistically correlated with elevated levels of atmospheric oxidants, with a mean annual average concentration of 0.18 ppm on the 11 most polluted sites. Sites of high ambient oxidant levels were also characterized by declining species richness. Further, Stolte (1982) concluded that seedlings of pioneer species in recently burned chaparral stands were vulnerable to oxidant stress.

Oxidant-induced injury to vegetation has also been observed in the eastern United States for many years. Needle blight of eastern white pine was first reported in the early 1900's; however, it was not until 1963 that it was shown to be the result of acute and chronic O_3 exposure until 1963 (Berry and Ripperton, 1963). Hayes and Skelly (1977) monitored total oxidants and recorded associated oxidant injury on eastern white pine in three rural Virginia

sites between April 1975 and March 1976. Injury was associated with total oxidant peaks of 0.08 ppm or higher. Ozone peak concentrations of 0.17 ppm have been measured in the Blue Ridge Mountains (Skelly, 1980). Increased injury symptoms were observed on pine trees previously categorized as sensitive or intermediately sensitive following the O_3 exposures. No injury was observed on trees categorized as insensitive. Hayes and Skelly (1977) suggested that continued exposure of sensitive and intermediately sensitive white pine to acute and chronic oxidant concentrations resulted in the trees being placed under stress that could ultimately influence their vegetative vigor and reproductive ability. Inability to reproduce could result in the pines being replaced by another species. Injury to herbaceous vegetation growing in the Virginia mountains was also observed (Duchelle et al., 1983). Ambient O_3 concentrations were shown to reduce growth and productivity of graminoid and forb vegetation in the Shenandoah National Park. For each year of the study, biomass production was greatest in the filtered air chambers. The total 3-year cumulative dry weight for the filtered chambers was significantly ($P < 0.05$) different from non-filtered and open air plots. Common milkweed (Ascelepias syrica L.) and common blackberry (Rubus allegheniensis Porter) were the only two native species to develop visible injury. Milkweed has been previously shown to be very sensitive to O_3 (Duchelle and Skelly, 1981). Ozone episodes occurred several times each year during the period of the study. Peak hourly concentrations ranged from 0.08 to 0.10 ppm; however, O_3 concentrations exceeding 0.06 ppm were recorded for 1218, 790, and 390 hours during 1979, 1980, and 1981, respectively. The effects of O_3 in altering the natural vegetation of the Virginia mountains was not assessed. Lower biomass production could result in selection for vegetation better able to cope with the O_3 stress. As in California, O_3 is transported from distant sources. In the Blue Ridge and Appalachian Mountains, these sources include the industrial midwest, eastern Virginia, and the Washington, D.C. area.

McClenahen (1978) has provided quantitative data on the impact of polluted air on the various strata of a forest ecosystem. Forest vegetation was measured in seven stands on similar sites in a 50 km^2 (19 mi^2) area of the upper Ohio River Valley. The stands, some of which have been exposed to air pollution for nearly 40 years, were situated along a gradient of polluted air containing elevated concentrations of chloride, sulfur dioxide (SO_2), fluoride, and photochemical oxidants, although the latter were not monitored. Overstory,

subcanopy, shrub, and herb strata were analyzed for pollution effects. Increasing exposure to air pollutants reduced the density of woody stands in the overstory and herb layers, but density in other strata tended to increase along the same gradient. A shift occurred in the species composition of forests on the sites investigated. The relative abundance of sugar maple (Acer saccharum Marsh.), the most abundant species in the overstory of low-exposure stands, was greatly reduced in all strata as pollutant dose increased; but yellow buckeye (Aesculus octandra Marsh.) increased in canopy dominance, and spice bush (Lindera benzoin (L.) Blume) became a codominant with paw paw (Asimina triloba (L.) Dunal) in the subcanopy of high-exposure areas. In the herb layer, there was an increase in light-tolerant species, an indirect effect of air pollution resulting from the reduced overstory density. Light-tolerant species composed 68 percent of the total in areas of high pollution compared to 34 percent in areas of low pollutant exposure. Concentrations of O_3 in the area of the study were not reported; however, results of the study illustrate how pollutant mixtures typical of ambient conditions can change the species composition of forested areas. Pollutant stress on forest communities tends to decrease diversity and simplify structure as the vegetative layers are stripped away from the overstory downward (Woodwell, 1970).

Treshow and Stewart (1973) conducted one of the few studies concerned with the impact of air pollution on natural plant communities. The aim of the study was to determine the concentration of O_3 necessary to injure the most prevalent species in some of the vegetation associations in the intermountain grassland, oak, aspen, and conifer communities. Seventy common plant species indigenous to those communities were fumigated with O_3 to establish vegetational sensitivity. Injury was generally evident at concentrations above 0.15 ppm for 2 hr. Species found to be most sensitive to O_3 in the grassland and aspen communities included some dominant species considered key to community integrity. Bromus tectorum L. (cheatgrass), the most prevalent species in the grassland community, was also the most sensitive. Severe injury to this introduced annual resulted from a single 2-hr exposure to 0.15 ppm of O_3. Cheatgrass is a species that is widely distributed in the intermountain western United States. Removal of this dominant species from plant communities could result in a shift in dominance to another species. The significance of such a change would depend on the species replacing cheatgrass. The other grasses studied were not as sensitive to O_3, nor were the forbs (Table 8-1); however the production of carbohydrates in visibly injured grasses was significantly reduced.

TABLE 8-1. INJURY THRESHOLDS FOR 2-HOUR EXPOSURES TO OZONE

Species	Injury threshold ($ppm\ O_3$ for 2 hr)
Grassland-oak community species:	
Trees and shrubs:	
Acer grandidentatum Nutt.	over 0.40
Acer negundo L.	over 0.25
Artemesia tridentata Nutt.	0.40
Mahonia repens G. Don	over 0.40
Potentilla fruticosa L.	0.30
Quercus gambelii Nutt.	0.25
Toxicodendron radicans (L.) Kuntze	over 0.30
Perennial forbs:	
Achillea millefolium L.	over 0.30
Ambrosia psilostachya DC.	over 0.40
Calochortus nuttallii Torr.	over 0.40
Cirsium arvense (L.) Scop.	0.40
Conium maculatum L.	over 0.25
Hedysarum boreale Nutt.	0.15
Helianthus anuus L.	over 0.30
Medocagp satova L.	0.25
Rumex crispus L.	0.25
Urtica gracilis Ait.	0.30
Vicia americana Muhl.	over 0.40
Grasses:	
Bromus brizaeformis Fish. & Mey.	0.30
Bromus tectorum L.	0.15
Poa pratensis L.	0.25
Aspen and conifer community species:	
Trees and shrubs:	
Abies concolor (Gord. & Glend.) Lindl.	0.25
Amelanchier alnifolia Nutt.	0.20
Pachystima myrsinites (Pursh) Raf.	over 0.30
Populus tremuloides Michx.	0.15
Ribes hudsonianum Richards.	0.30
Rosa woodsii Lindl.	over 0.30
Sambucus melanocarpa A. Gray	over 0.25
Symphoricarpos vaccinioiders Rydb.	0.30
Perennial forbs:	
Actaeu arguta Nutt.	0.25
Agastache urticifolia (Benth.) Kuntze	0.20
Perennial forbs:	
Allium acuminatum Hook	0.25
Angelica pinnata S. Wats.	under 0.25
Aster engelmanni (Eat.) A. Gray	0.15
Carex siccata Dewey	0.30
Cichorium intybus L.	0.25
Cirsium arvense (L.) Scop.	under 0.40
Epilobium angustifolium L.	0.30
Epilobium watsoni Barbey	0.30
Eriogonum heraclioides Nutt.	0.30
Fragaria ovalis (Lehm.) Rydb.	0.30
Gentiana amarella L.	over 0.15
Geranium fremontii Torr.	under 0.40
Geranium richardsonii Fisch. & Traut.	0.15
Juncus sp.	over 0.25
Lathyrus lanzwertii Kell.	over 0.25
Lathyrus pauciflorus Fern.	0.25
Mertensia arizonica Greene	0.30
Mimulus guttatus DC.	over 0.25
Mimulus moschatus Dougl.	under 0.40
Mitella stenopetala Piper	over 0.30
Osmorhiza occidentalis Torr.	0.25
Phacelia heterophylla Pursh	under 0.25
Polemonium foliosissimum A. Gray	0.30
Rudbeckia occidentalis Nutt.	0.30
Saxifraga arguta D. Don	under 0.30
Senecio serra Hook.	0.15
Taraxacum officinale Wiggers	over 0.25
Thalictrum fendleri Engelm.	over 0.25
Veronica anagallis-aquatica L.	0.25
Vicia americana Muhl.	over 0.25
Viola adunca Sm.	over 0.30
Annual forbs:	
Chenopodium fremontii Wats.	under 0.25
Callomia linearis Nutt.	under 0.25
Descurainia californica (Gray) O.E. Schulz	0.25
Galium bifolium Wats.	over 0.30
Gayophytum racemosum T. & G.	0.30
Polygonum douglasii Greene	over 0.25
Grasses:	
Agropyron caninum (L.) Beauv.	over 0.25
Bromus carinatus Hook. & Arn.	under 0.25

Source: Treshow and Stewart (1973).

In the aspen community the most dramatic example was aspen (Populus tremuloides Michx.) itself. A single 2-hr exposure to 0.15 ppm O_3 caused severe symptoms on 30 percent of the foliage. Because white fir seedlings require aspen shade for optimal juvenile growth, the authors suggested that significant losses in aspen populations might restrict white fir development and later forest succession; conversion to grasslands could occur. In a companion study, Harward and Treshow (1975) evaluated the growth and reproductive response of 14 understory species to O_3. Plants were fumigated in greenhouse chambers 3 hr/day, 5 days per week throughout their growing seasons (roughly June to September). Exposure was to ambient air peaks of O_3 ranging from 0.05 to 0.07 ppm and to concentrations of 0.15 and 0.3 ppm for 2 hr each day. Symptoms were observed on the most sensitive species (Chenopodium fremontii, Descurainia pinnata, and Polygonum aviculare) after 3 to 4 weeks of exposure to ambient air peaks of O_3. All species were injured at 0.15 ppm and 0.30 ppm. The most resistant species were injury-free until nearly mature. The most sensitive species produced fewer seeds. Reduction in root and top growth also occurred. It was apparent that in a natural community exposed to O_3, the tolerant species would soon become the dominants. The authors concluded that O_3 must be considered a significant environmental parameter that influences the composition, diversity, and stability of natural plant communities and "may ultimately play a major role in plant succession and dominance."

The foregoing studies indicate that the impact of O_3 changes the composition and succession patterns of plant communities. The more mature stages of ecosystems use nutrients and energy more efficiently. Mature systems are tight; disturbances cause leakage. The leakage may be large enough under certain circumstances to in time reduce the potential of the site to support life (Woodwell, 1974). Changes that cause reductions in biotic structure are destabilizing and retrogressive. The entire array of plants is changed by disturbance from one in which large-bodied, long-lived species occur to one in which small-bodied, short-lived, rapidly reproducing plants predominate (Woodwell, 1974). This pattern is exemplified by the San Bernardino National Forest, where the mixed conifer forest is being replaced by low-growing shrubs and annual herbs. It is also occurring in the eastern United States, where the degradation of the Appalachian forests from North Carolina to Maine is currently taking place as the red spruce (Picea rubens Sarg.) and other large, long-lived species are being removed by at present unknown forces (Johnson and Siccama, 1983). Also associated with the loss of stable ecosystems is the

maintenance of normal water and climatic conditions, protection from wind and erosion, and protection from noise pollution (Guderian, R., 1977).

8.3.3 Effects on Tree Growth

Plant growth and yield is the culmination of a variety of biochemical and physiological processes (Chapter 7). Impairment of any of these processes places stress on the plant. Response of plants to stress is mediated by biological, physical, and chemical variables. Tree responses, unless they are the result of a specific biotic disease or an acute pollutant exposure, are cumulative and frequently the culmination of a number of chronic stresses. The term decline has been used by forest pathologists to describe responses of this type that are not the result of a single causative agent (Figure 8-3; Manion, 1981). Forest declines involve three or more sets of factors: predisposing, incitants, and contributing (Figure 8-4). Predisposing factors weaken a plant. Incitants are of short duration and may be physical or biological in nature. They usually produce drastic injury. Contributing factors are indicators of a weakened host. They appear over time (Manion, 1981).

Decline in vigor is a response commonly observed in trees sensitive to O_3 stress (Miller et al., 1982; McLaughlin et al., 1982; Skelly, 1980). Symptoms of chronic decline include the following sequence of events and conditions: (1) premature senescence and loss of older needles at the end of the growing season, (2) reduced storage capacity in the fall and resupply capacity in the spring to support new needle growth, (3) increased reliance of new needles on self-support during growth, (4) shorter new needles resulting in lower gross photosynthetic productivity, (5) higher retention of current photosynthate by foliage resulting in reduced availability of photosynthate for external usage (including repair of chronically stressed tissues of older needles), and (6) premature casting of older needles (McLaughlin et al., 1982).

Ozone-associated stress on the mixed coniferous forest ecosystem of the San Bernardino Mountains of southern California decreased photosynthesis, affected directly or indirectly translocation of carbon, mineral nutrients, and water, and reduced trunk diameter, tree height, and seed production in ponderosa and Jeffrey pine (Miller et al., 1982). White fir, black oak, incense cedar, and sugar pine were less sensitive. Average 24-hr O_3 concentrations ranged from a background of 0.03 to 0.04 ppm to maxima of 0.10 to 0.12 ppm. Foliar injury, needle abscission, and premature senescence were

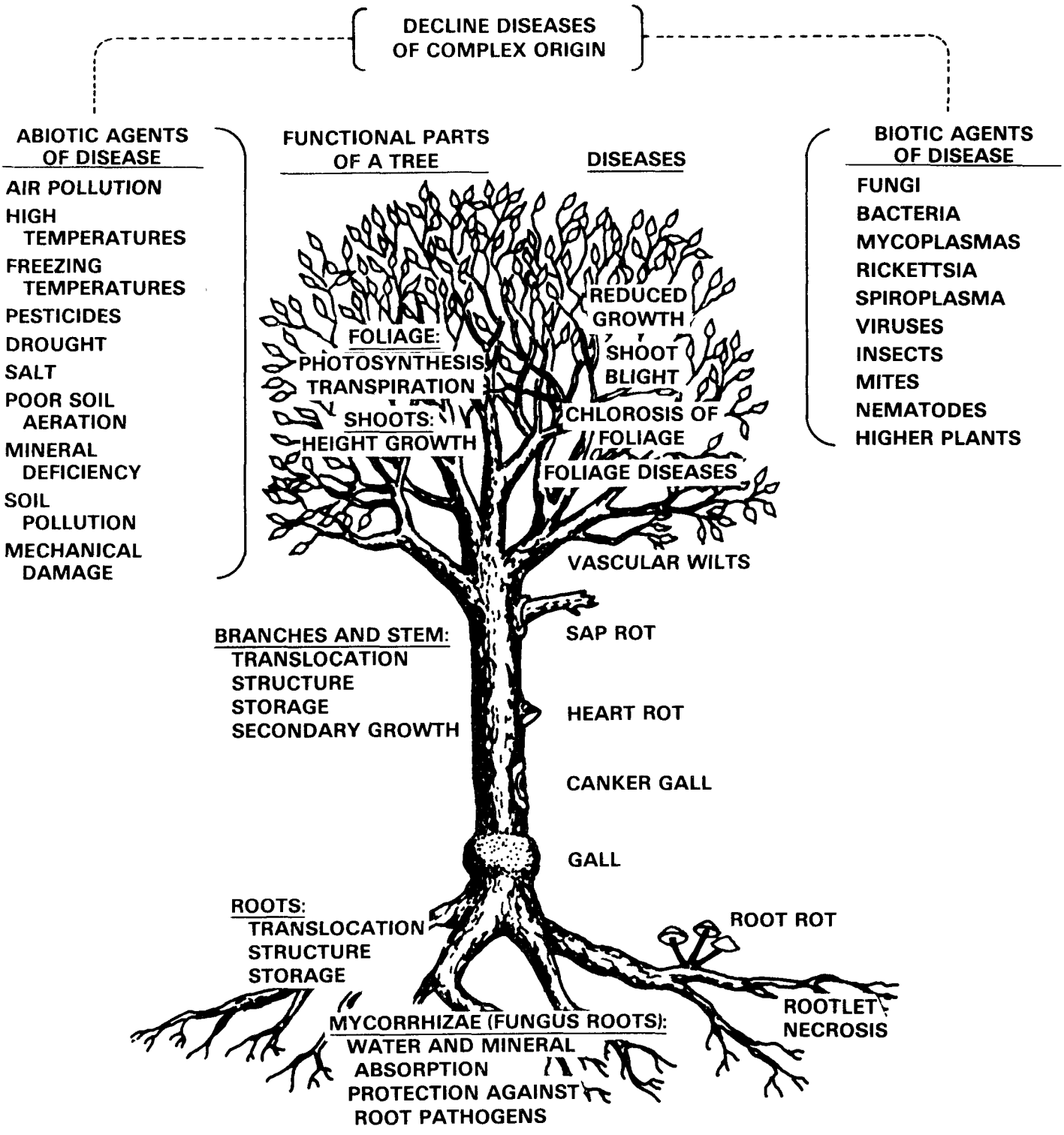

Figure 8-3. Summation of abiotic and biotic agents involved in diseases of trees, given by types of diseases and functional parts of the tree. Decline diseases are caused by a combination of biotic and abiotic agents.
Source: Manion (1981).

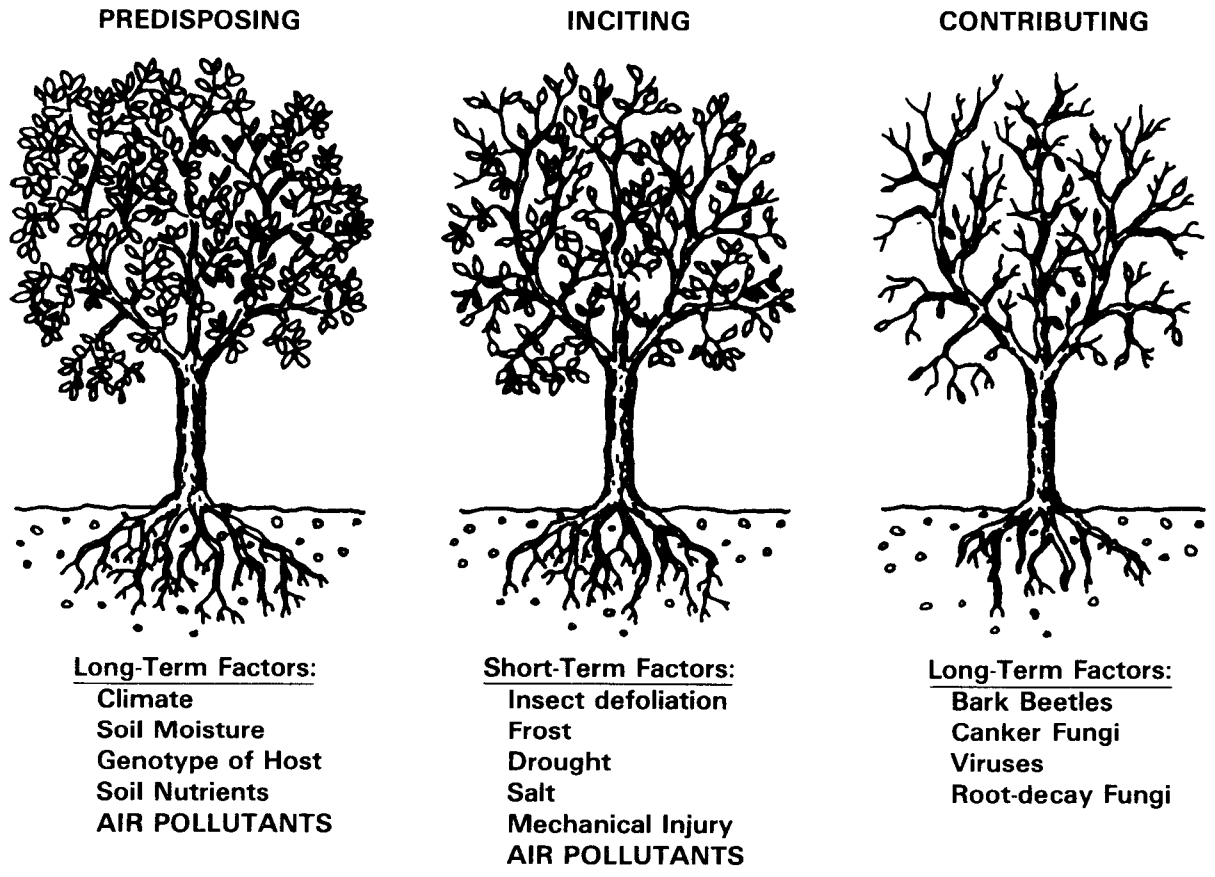

Figure 8-4. Categories of factors influencing declines.
Source: Manion (1981).

noted on the affected trees. Injury to ponderosa pine occurred at concentrations of 0.05 to 0.06 ppm for 24 hr. PAN has not been associated with injury to trees.

The best documented correlation of growth variables of large trees growing under field conditions with ambient O_3 levels is the comprehensive oxidant study conducted in the San Bernardino National Forest in California (Miller and Elderman, 1977; Miller et al., 1982). Radial growth of ponderosa pine during periods of low pollution (1910 to 1940) was compared to periods of high pollution (1941 to 1971) (Table 8-2). The average annual rainfall for these periods was 111 and 117 cm/yr (43 and 46 in/yr), respectively. It was postulated that 30-year-old trees grown in the two periods would have diameters of 30.5 cm and 19.0 cm. The difference in these diameters is attributed to air pollution during the 1941 to 1971 period. Oxidant air pollution reduced the average annual growth in diameter of ponderosa pine by approximately 40 percent and height by 25 percent in trees less than 30 years of age. Marketable volume growth of trees of this age was reduced by 83 percent in zones with the highest O_3 concentrations. The San Bernardino study documented reduced seed production of Jeffrey pine (Miller et al., 1980).

In the east, reduced growth of eastern white pine under ambient conditions caused by O_3 exposure has been documented (Benoit et al., 1982). A study of radial increment growth of native eastern white pines of reproducing age evaluated the possible effects of oxidant (primarily O_3) air pollution on long-term growth of forest species in a region of the Blue Ridge Mountains of Virginia extending from the northern end of Skyline Drive in Shenandoah National Park to the southernmost end of the Blue Ridge Parkway in Virginia. White pines in the study plots were classified as sensitive, intermediate, and tolerant, based on a foliar rating scale that incorporated needle length, needle retention by number of years, and the presence of typical O_3 symptoms on needles. The mean ages of tolerant, intermediate, and sensitive tree classes were 53, 52, and 56 years, respectively. Growth in mean annual increment for sensitive trees was significantly less ($P = 0.01$) than that of the tolerant trees for the period 1955 to 1978 (Table 8-3). Growth for sensitive trees was 25 percent less, and for intermediate trees, 15 percent less than tolerant trees. Smaller mean increments in the last ten years when compared to the previous 24-year period indicated a decline in overall growth rates in all classes of trees. A comparison of growth during the 1974 to 1978 period with that during 1955 to 1959 showed a decrease of 26, 37, and 51 percent for

TABLE 8-2. AVERAGE ANNUAL RADIAL GROWTH OF 19 PONDEROSA PINE TREES IN TWO LEVELS OF OXIDANT AIR POLLUTANTS IN THE SAN BERNARDINO NATIONAL FOREST, CALIFORNIA.

High Pollution (0.03-0.12 ppm)		Low Pollution (<0.03 ppm)	
Age[a] (yr)	Average radial growth (cm) 1941-1971	Age[a] (yr)	Average annual radial growth (cm) 1910-1940
20	0.20	60	0.52
21	0.33	55	0.49
29	0.22	55	0.61
22	0.33	57	0.34
25	0.30	64	0.40
35	0.23	63	0.55
27	0.29	60	0.44
28	0.31	65	0.46
35	0.26	60	0.75
22	0.43	71	0.67
39	0.21	63	0.71
35	0.34	71	0.65
29	0.37	66	0.78
33	0.37	63	0.53
35	0.34	60	0.33
35	0.37	70	0.38
36	0.35	61	0.32
36	0.33	62	0.37
34	0.36	59	0.37

Source: Miller and Elderman, 1977.

[a]Age at 1.4 m above ground in 1971.

TABLE 8-3. ANNUAL MEAN RADIAL GROWTH INCREMENT (MM) BASED ON THE 24-YEAR PERIOD (1955 to 1978)[a] FOR TREE OZONE SENSITIVITY CLASSES OF NATIVE EASTERN WHITE PINES (*PINUS STROBUS* L.) GROWING IN TEN PLOTS OF THREE TREES EACH ALONG THE BLUE RIDGE MOUNTAINS IN VIRGINIA

Plot	Tolerant trees*	Intermediate trees	Sensitive trees
1	4.59	2.13	3.08
2	3.52	2.12	2.86
3	8.19	6.34	6.89
4	4.80	3.75	2.62
5	5.94	6.53	5.73
6	4.64	3.76	2.62
7	2.85	2.75	1.51
8	3.91	4.52	1.96
9	3.32	2.04	2.61
10	1.67	2.98	1.46
Mean	4.34 A[b]	3.69 AB	3.10 B

Source: Benoit et al. (1982).

[a]White pines rated tolerant, intermediate, or sensitive to O_3 based on foliar symptoms.

[b]Sensitivity classes with the same letter are not significantly different at P = 0.01 based on Duncan's multiple range test.

tolerant, intermediate, and sensitive trees, respectively. The significant reduction in radial growth of O_3-sensitive white pines was associated with cumulative stress resulting from reduced photosynthetic capacity of oxidant-injured trees. Developing first-year needles utilize photosynthate from needles of previous years (Benoit et al., 1982). Extensive oxidant injury to needles, senescence, or premature abscission of needles could decrease the amount of photosynthate available for growth. The monitoring of O_3 in the study area indicates the presence of concentrations of 0.05 to 0.07 ppm on a recurring basis, with episodic peaks frequently in excess of 0.12 ppm. Concentrations during the peak episodes ranged from 0.10 to 0.20 ppm.

The effects of chronic O_3 stress on the growth of white pine trees has also been reported by McLaughlin et al. (1982), who studied the decline of white pines in the Cumberland Plateau area of east Tennessee. A steady decline in annual ring increment of sensitive white pines was observed during the years 1962 to 1979 (Figure 8-5). Reductions of 70 percent in average annual growth (Figure 8-5A) and 90 percent in average bole growth (Figure 8-5B) of sensitive trees, compared to the growth of tolerant and intermediate trees, were noted. Tolerant trees showed a consistently higher growth rate of 5 to 15 percent ($P > F \leq 0.05$) than intermediate trees for the 1960 to 1968 interval. The cause of decline is attributed primarily to chronic O_3 exposure, which frequently occurs at phytotoxic concentrations ($0.08\geq$) in the area (Table 8-4). Though the pollutants SO_2 and fluoride have been measured in the area, the premature loss of needles and occasional tip necrosis of needles of the current year are manifestations associated with O_3, which occurs in high concentrations during the occurrence of stable air masses. Needles of sensitive trees were 15 to 45 percent shorter than those of either of the other classes. The decline in vigor and reduced annual growth of sensitive trees have taken place during the past 25 years. In addition to the reduced growth above ground, less available carbohydrate reduces the vigor of root systems and enhances susceptibility of trees to root diseases (McLaughlin et al., 1982). The loss in vigor of the trees has been accompanied by reduced annual radial growth and a loss in the capacity to respond in years when conditions are favorable for growth. The primary cause of decline appears to be exposure to elevated concentrations of O_3 and the sequence of events and conditions that lead to premature senescence and loss of older needles, lower gross photosynthetic productivity, and reduced photosynthate availability for growth and maintenance of trees (McLaughlin et al., 1982).

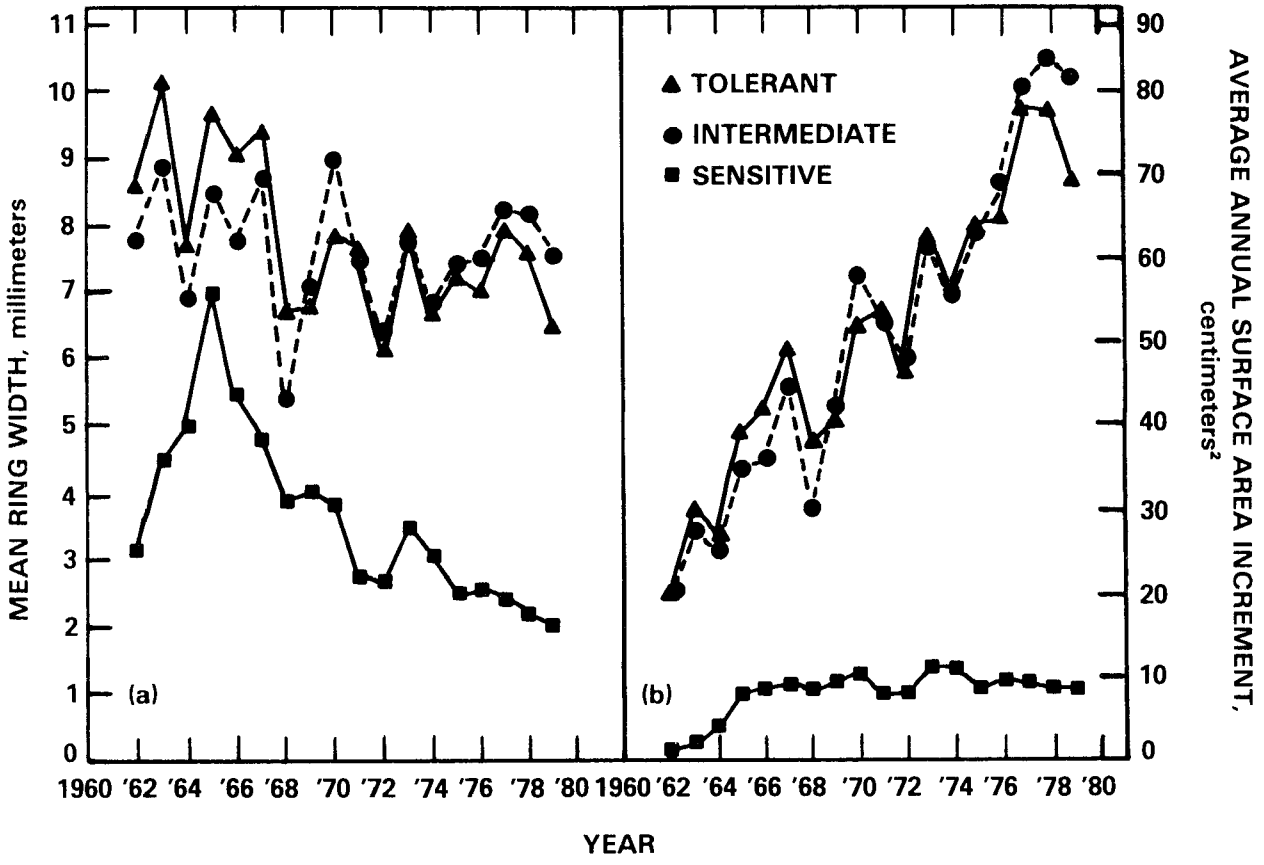

Figure 8-5. Average annual growth of white pine trees in each of three sensitivity classes expressed as increment in ring width (a) and cross-sectional area (b). Data are averages of three trees in each sensitivity class.
Source: McLaughlin et al. (1982).

TABLE 8-4. ANNUAL OCCURRENCES OF OZONE AT HOURLY CONCENTRATIONS $\geq$ 0.08 PPM IN THE KNOXVILLE, TENNESSEE AREA

Month	Number of hours with $O_3 \geq 0.08$ ppm			
	1976	1977	1978	1979
March	0	0	0	3
April	0	35	15	10
May	0	89	28	40
June	35	105	28	44
July	40	110	33	4
August	75	(a)	27	24
September	40	(a)	34	0
October	0	(a)	13	0
November	0	(a)	12	0
Total	190	>339	190	125
Maximum level (ppm)	0.130	0.200	0.124	0.134

Source: McLaughlin et al. (1982).

[a]Data missing.

Documentation of foliar symptoms on western conifers in the southern Sierra Nevada mountain range in central California (Williams et al., 1977; Williams, 1980, 1983) and on eastern white pine in Indiana and Wisconsin (Usher and Williams, 1982) may suggest growth impacts by oxidants in these regions also.

Studies by Krause (1984) and others in West Germany associate O_3 with the dieback of fir (Abies alba Mill.) and spruce (Picea alba (L.) Karst.). Ozone damages the cell membranes in the needles of conifers and the leaves of certain hardwoods (beech, Fagus sylvatica L.) and leads to uncontrolled loss of nutrients. Fog and/or rain, depending on ionic strength and pH, readily leach the nutrients from the needles or leaves. Leaching is enhanced by high light intensity and low nutrient soils. Membrane damage may occur without visible injury.

Forest decline began in the early 1970's in West Germany. Dieback of fir was the first indication that the Black Forest and the forests in the mountainous areas of Bavaria were under stress. Acid rain was first blamed for forest decline, but studies did not confirm this hypothesis. Injury affects spruce and fir of virtually all ages. Ozone was first postulated as the cause of forest decline (Krause, 1984) in 1982. Field observations and laboratory experiments have confirmed this hypothesis. Loss of nutrients and reductions in photosynthesis, carbohydrate production, and root growth due to O_3 injury leads to a mobilization by trees of nutrient reserves from older needles and their translocation to the sites of greatest metabolic activity. Dieback occurs because the growing tips of tree branches do not receive the nutrients and carbohydrates necessary for growth.

Trees are the controller organisms, those that determine structure (species composition and trophic relationships) of forest ecosystems (Ehrlich and Mooney, 1983). Injury to or disturbance of these species begins the retrogressive successional processes that may ultimately lead to the loss of the ecosystem.

Replacement or reforestation of one tree species by another is not necessarily a valid solution. Substitution of Monterey pine (Pinus radiata D. Don) for native Australian tree species resulted in reduced energy flow and a lower rate of mineral cycling in the ecosystem and a loss of soil nutrients. Substitution of a different trees species can require large energy subsidies to produce growth, and the new species are almost totally unable to supply the genetic pool of the forest ecosystem they replaced (Ehrlich and Mooney, 1983).

8.3.4 Effects on Food Webs

Autotrophs are organisms that manufacture their own food and are, therefore, in the first trophic level. They are the producers. Biomass accumulation at this trophic level is termed primary production. In a forest ecosystem, this is the addition of new organic matter in trees, shrubs, and herbs. Producers, as discussed previously, are the primary sources of the energy transferred within ecosystems. Energy from the sun is harnessed through photosynthesis for the production of food by plants, and it is subsequently available to consumers and decomposers (heterotrophs) along food webs. Any mature natural community transfers 10 to 20 percent of the energy fixed by plants to herbivores (Woodwell, 1974). Previous sections have discussed the impact of O_3 on photosynthesis. Disruption of photosynthesis and subsequent carbon allocation for vegetative and reproductive growth can decrease the amount of food available to other trophic levels in the food web and thus slow the movement of energy and nutrients through an entire system. Disturbance causes leaks and losses of nutrients from the system. The indirect effects of O_3 on food web components are discussed in the following sections.

8.3.4.1 Heterotrophs (Consumers). Heterotrophs are organisms that feed on other organisms and constitute all trophic levels above the first. Production (energy storage) of heterotrophs is termed secondary production. Heterotrophs are extremely diverse, and only a limited amount of information on their response to pollutants is available (Newman, 1979). The influence of oxidants on these organisms is assumed to be chiefly through the food web. At this time, studies have not indicated a direct impact of O_3 on the organisms themselves. However, disruption of photosynthesis, reproduction, or a structural change among the producers within ecosystems can affect heterotrophs (consumers) by removing their shelter and food sources.

Small vertebrates, for example, unable to migrate to relatively unpolluted areas, may receive a direct effect from O_3 exposure, as well as an indirect effect, through alterations in food abundance from plants that provide an important segment of their diet. In the San Bernardino Mountains of California, a trapping program at vegetation plots differentially impacted by chronic oxidant dose indicated that the same species were present as compared to results from trappings made 70 years ago (Kolb and White, 1974). Population numbers, however, appeared to be lower in comparison with other similar forest systems. There is some evidence to suggest that the size and frequency of acorn crops from California black oak may be smaller in areas receiving the

greatest seasonal oxidant exposure (Miller et al., 1980). Reduced acorn availability could have an impact on small mammal populations.

The San Bernardino National Forest study has also provided evidence for the impact of O_3 stress on other mammals (Newman, 1980). Fruit and seeds make up the largest part of the diet of most of the small mammals in this mixed conifer forest. This is particularly true for the deer mouse (Peromyscus sp.), harvest mouse (Reithrodontormys sp.), chipmunk (Eutamias sp.), ground squirrel (Callospermophilus sp.), and western gray squirrel (Sciurus griseus anthonyi). Alterations in availability of seeds and fruits can alter the habitats and reproduction of these rodents (Taylor, 1973). Certain bird species are known to prefer coniferous forests (Smith, R. L., 1980). No studies appear to have been made concerning changes in bird populations due to the death of tree species. It is not clear what other specific effects oxidants may have on ambient wildlife, nor are exposure-response levels available.

8.3.4.2 Phytophagous Insects. Invertebrate consumer populations (e.g., arthropods) may be subject to the influence of oxidant impact on their habitat or host. Insects are among the most important heterotrophic groups in ecosystems. The literature addressing the relationship between O_3 and insects in temperate forests is meager and extremely disproportionate to the importance of arthropods in forest ecosystems. Generally speaking, the killing or injury of leaves by injured air pollution would most adversely affect insect defoliators.

Bark beetles are the most damaging and economically significant insect pests of commercially important conifers in the United States. Beetle outbreaks in western forests are associated with several predisposing factors. These include host weakening caused by photochemical oxidants; microbial infection, such as root disease initiated by fungi, Heterobasidion annosum (Fomes annosus) or Verticicladiella wagenerii (Stark and Cobb, 1969); by insect defoliation, such as pine looper stripping of ponderosa pine (Dewey et al., 1974); or by various climatic stresses, such as drought and windthrow (uprooting and breakage by strong winds) (Rudinsky, 1962). Photochemical oxidant injury of ponderosa pines results in reduced oleoresin yield, rate of flow and exudation pressure, moisture of phloem and sapwood, and phloem thickness. All of these are believed to be important in the defense of the tree against bark beetles (Stark and Cobb, 1969).

Studies at the University of California Blodgett Research Forest indicate that a disease-insect relationship exists between root-infecting fungi and

bark beetles. Approximately 80 percent of the ponderosa pines infested with bark beetles had been infected by root-disease fungi prior to beetle infestation (Stark and Cobb, 1969). Verticicladiella wagenerii was the major fungus attacking the roots. The fungus moves from tree to tree via the roots. Skelly (1980) reported oxidant injury of eastern white pines in Virginia increased the incidence of root disease caused by Verticicladiella procera. Heterobasidion annosum was likewise found to have infected conifer roots prior to beetle attack. Heterobasidion usually does not become a serious problem in California forest until disturbances by humans, such as logging, have occurred (Stark and Cobb, 1969).

During the summer of 1966, a survey of ponderosa pines was carried out in the San Bernardino Mountains of California. These forests are subject to elevated levels of atmospheric oxidants from the Los Angeles urban complex to the west. Over 1000 trees were examined for amount of O_3 injury, for infestation from the western pine beetle (Dendroctonus brevicomis) and/or the mountain pine beetle (D. monteola), and for tree mortality. Trees with the greatest pollution injury were most commonly found to be supporting populations of one or both bark beetle species. As the degree of oxidant injury increased, live crown ratio decreased, and the occurrence of bark beetle infestation increased (Stark et al., 1968). This is perhaps the most completely documented example of enhancement of insect damage by air pollution in North America (Miller, 1973).

Dahlsten and Rowney (1980) investigated the interaction between ponderosa pine weakened by photochemical oxidants and the western pine beetle. It was found that an initial attack by a smaller number of bark beetles in oxidant-damaged trees produced approximately the same total brood as a large number in healthier trees. Therefore, in stands with a higher proportion of injured trees, beetles can spread through the stands faster and a given population of bark beetles could kill more trees and propagate at a greater rate than in a stand with a lower proportion of damaged trees.

8.3.4.3 Pathogens. By weakening the trees, O_3 makes the trees of the forest ecosystem more susceptible to attack by certain parasites and can thus hasten structural changes within an ecosystem. There is some indication that O_3 may enhance the development of disease caused by pathogens that normally infect stressed or senescent plant parts or invade nonliving woody plant tissues. Lophodermium pinastri and Aureobasidium pullulans were the fungi more commonly collected from eastern white pine foliage showing O_3 injury. When inoculated

in conjunction with tree exposure to 0.06 to 0.10 ppm O_3 for 4.5 hr, however, no evidence of additive or interactive effects were found (Costonis and Sinclair, 1972).

Weidensaul and Darling (1979) inoculated Scots pine (Pinus sylvestris L.) seedlings with the fungus, Scirrhia acicola 5 days before or 30 min following fumigation for 6 hr with 0.20 ppm SO_2, 0.20 ppm O_3, or both gases combined. Significantly more brown spot lesions were formed on seedlings fumigated with SO_2 alone or SO_2 combined with O_3 than on controls, when inoculation was done 5 days before fumigation. When inoculation was done 30 min after gas exposure, seedlings exposed to SO_2 alone had more lesions than those exposed to O_3 alone or O_3 combined with SO_2, but no significant differences were noted between fumigated seedlings and controls. The authors judged that O_3-induced stomatal closure may have been responsible for the latter observation.

Heterobasidion annosum (syn Fomes annosus) is a basidiomycete fungus capable of causing significant root decay in a variety of coniferous hosts throughout temperate forests. A comprehensive examination of oxidant stress on California forest ecosystems has included a study of the influence of O_3 on this fungus and the disease it causes in ponderosa and Jeffrey pines (Miller and Elderman, 1977). Root inoculations were made on trees exhibiting varying degrees of oxidant stress. Pine seedlings were also artificially inoculated following fumigation with O_3. Because of the importance of freshly cut stump surfaces in the spread of this fungus, trees exhibiting different levels of susceptibility to O_3 were cut, and their stumps were inoculated with H. annosum. There was no correlation between the amount of disease development in roots of field-inoculated ponderosa and Jeffrey pines and the degree of oxidant damage of the two. Results of stump inoculation tests, however, did suggest that air pollution injury may have increased the susceptibility of pine stumps to colonization by H. annosum (James et al., 1980). The percentage of infection of fumigated seedlings was also greater than that of nonfumigated seedlings. Pollutant-plant-pest and pollutant-plant-pathogen interactions are discussed in greater detail in section 7.3.2 of Chapter 7.

8.3.4.4 Other Microorganisms, Symbionts, and Decomposers. The dose of O_3 required for direct impact on microbial metabolism may be quite high. The data of Hibben and Stotsky (1969) are illustrative. These investigators examined the response of detached spores of 14 fungi to 0.1 to 1.0 ppm of O_3 for 1, 2, and 6 hr. The large pigmented spores of Chaetomium sp., Stemphylium sarcinaeforme, S. loti, and Alternaria sp. were not influenced by 1.0 ppm

(1960 $\mu g/m^3$) of O_3. Germination of Trichoderma viride, Aspergillus terreus, A. niger, Penicillium egyptiacum, Botrytis allii, and Rhizopus stolonifera spores were reduced by O_3 exposure, but only in concentrations above 0.5 ppm and occasionally by doses of 0.25 ppm of O_3 for 4 to 6 hr; lower doses stimulated spore germination in some cases.

Symbiotic microbes play important roles in nutrient relations in forest ecosystems. Trees have evolved critically important symbiotic relationships with soil fungi and bacteria that enhance nutrient supply and uptake. This relationship is particularly important in trees growing on nutrient-poor soils. The feeder rootlet systems of ponderosa pines in the San Bernardino Mountains have shown marked deterioration; this involves a decrease in the number of mycorrhizal rootlets and their replacement by saprophytic fungi in the small rootlets on stressed trees (Parmeter et al., 1962). Mycorrhizae are very sensitive to the photosynthetic capacity of the host and the host capacity to translocate carbon compounds to the roots (Hacskaylo, 1973). When seedlings of Virginia pine (Pinus virginiana Mill.) inoculated with the mycorrhizal fungus Thelephora terrestris and growing under a 16-hr photoperiod, were switched to 8-hr photoperiods, the seedlings became dormant within 4 weeks. No further infection of rootlets by the fungus occurred even though root growth continued. Fungal sporophores were formed on the seedlings that remained under the 16-hr photoperiod. Studies have shown that simple sugars provided by plant roots are readily utilized by mycorrhizae and enhance infection (Hacskaylo, 1973).

McCool et al. (1979) observed that O_3 exposure reduced mycorrhizal infection of the host plant. Both infection and chlamydospore production by the mycorrhizal fungus Glomus fasciculatus were reduced when Troyer citrange, a hybrid between Trifoliate and Sweet Orange [Ponicirus trifoliata (L.) Raf x Citrus sinesis (L.) Asbeck], were exposed to O_3 concentrations of 0.09 ppm for 6 hr once a week for 19 weeks. In mycorrhizal plants, dry weight was reduced 42 percent, but in non-mycorrhizal plants there was only 19 percent reduction. Exposure to O_3 (0.45 ppm, 3 hr/day, 2 days/week for 19 weeks) decreased mycorrhizal spore production.

Ozone exposure changed cation levels in citrange leaf tissue. Possibly this change reflected reduced cation absorption by the roots (McCool et al., 1979). Reductions in availability of photosynthates for the fungus could affect the degree of mycorrhizal infection.

Mycorrhizae are known to assist in protecting conifer roots from pathogens such as Heterobasidion annosum (Krupa and Fries, 1971). Injury to the mycorrhizae can remove this protection. Non-mycorrhizal and mycorrhizal root systems contain essentially the same major volatile compounds; however, studies using Scots pine (Pinus sylvestris L.) indicate that the concentrations of primarily monoterpenes and sesquiterpenes increase twofold to eightfold in the roots infected by mycorrhizae. Many of the monoterpenes identified in mycorrhizal root systems are constituents of the oleoresins commonly found in conifers. Oleoresins play an important role in the resistance of wood to decay fungi (Rishbeth, 1951). Volatile oleoresin components from ponderosa pine inhibit the growth of Heterobasidion annosum and four Ceratocystis species (Cobb et al., 1968), and are believed to aid in defense of trees from bark beetles (Stark and Cobb, 1969).

Properly functioning mycorrhizal systems are necessary for the growth of healthy trees. Mycorrhizae absorb nutrients from the soil and protect tree roots from certain pathogens. Ozone, by inhibiting photosynthesis and reducing the photosynthate available for transfer to the tree roots, disrupts the relationship between the mycorrhizal fungus and the host tree. Bark beetles attack the weakened trees usually after the mycorrhizal relationship has been destroyed, and hasten their demise.

Ozone also influences bacterial symbiosis. Reduced root growth and nodulation of soybeans (Glycine max (L.) Merr.) cv Dare, by the bacterium Rhizobium japonicum occurred when plant tops were exposed to O_3. No growth reductions occurred when the plant tops were protected from exposure to O_3 (Blum and Tingey, 1977). In an earlier study (Tingey and Blum, 1973), nodule number, nodule weight per plant, root growth, and leghemoglobin content per plant were all reduced by a 1-hr exposure to 0.075 ppm O_3. The reductions were associated with reduced photosynthetic capacity and less photosynthate for translocation to the roots. The rate of nitrogen fixation is also dependent on the rate of photosynthesis. Symbiotic nitrogen fixation is the major biological source of fixed nitrogen (Tingey and Blum, 1973). Ladino clover (Trifolium repens L. cv. Tillman) was treated with filtered air, 0.3 ppm (588 $\mu g/m^3$) of O_3, or 0.6 ppm (1176 $\mu g/m^3$) of O_3 for two 2-hr exposures, one week apart in controlled environment chambers (Letchworth and Blum, 1977). Plants of various ages were treated. Ozone reduced the growth and nodulation of test plants. The influence of O_3 varied with gas concentration and plant age. Mahoney (1982) has presented evidence that indicates that the mycorrhizal association of loblolly pine

seedlings was not impaired by exposure to 0.07 ppm of O_3 plus 0.06 ppm of SO_2 for 6 hr/day for 35 days.

A comparison of lichen species found on conifers in the San Bernardino Mountains of southern California during the years 1976 to 1979 with collections from the early 1900's was made to determine the effects of oxidant air pollution. Fifty percent fewer lichen species were found. Marked morphological deterioration of the common species Hypogymnia enteromorpha was documented in areas of high oxidant concentrations (Sigal and Nash, 1983).

Generally, one third or more of the energy and carbon fixed annually in the forests is contributed to the forest floor as litter (mostly leaves) (Ovington, 1957). The reservoir of energy and mineral nutrients represented by litter is a very important resource in natural ecosystems. The growth of new green plants depends on the slow release of nutrients by decomposer organisms. In agroecosystems, litter is often removed or burned. Fertilizer is added to the soil to replace the nutrients lost. In a conifer forest, litter production and decomposition release approximately 80 percent of the total minerals in the biomass of the stand; the remainder is retained in the living parts of the tree (Millar, 1974). Decomposer organisms are essential components of ecosystems, because they release bound nutrients from litter and provide elements essential for the continued growth and development of living organisms by recycling them. Numerous small animals, arthropods, fungi, and bacteria occupy the mantle on the surface layers of the soil where they degrade dead plant and animal material and release essential elements such as calcium, phosphorus, and magnesium to growing plants. Much of this decomposition occurs in the forest floor; however, pine needles are infected by fungal microflora several months before needles are shed (Stark, 1972). Although rapid fluxes of O_3 to soil surfaces and the forest floor can occur (Smith, 1981), it is not yet clear what effect this may have on decomposer organisms in natural environments.

Bruhn (1980) has investigated the effects of oxidants on needle microflora population dynamics of pine in the San Bernardino National Forest. The decomposition of litter comprised of O_3-stressed needles was concluded to be more rapid. However, the taxonomic diversity and population density of fungi that colonized living needles and later participated in decomposition were both reduced by O_3 injury as the normal increase with age was blocked by premature needle senescence and abscission. The author concluded that this alteration in microflora could weaken the stability of the decomposer community.

Laurence and Weinstein (1981) have emphasized the critical importance of examining multiple pollutant effects and the interactive effects of air pollutants with pathogens and insects in determinations of growth impacts. Ecosystem responses will always be the integration of multiple stresses acting over time and space on diverse populations.

8.3.5 Oxidant-Induced Effects on a Western Coniferous Forest Ecosystem: The San Bernardino Study

8.3.5.1 Introduction. The interdisciplinary study of the pine and mixed conifer forests of the San Bernardino Mountains of southern California is the most comprehensive and best documented report on the effects of oxidants on an ecosystem (Miller et al., 1982). The mixed conifer forests in the San Gabriel and San Bernardino mountain ranges east of Los Angeles have been exposed to oxidant air pollution since the early 1950's (Miller, 1973). Extensive visible injury and concern about possible adverse effects of chronic O_3 exposure on an important ecosystem led to the inderdisciplinary study from 1973 to 1978. The study was designed to answer two questions: (1) How do the organisms and biological processes of the conifer forest respond to different levels of chronic oxidant exposure; and (2) how can these responses be interpreted within an ecosystem context (Miller et al., 1982)?

The major physical (abiotic) components studied were water (precipitation), temperature, light, mineral nutrients (soil substrate), and O_3 air pollution. Biological components included producers (an assortment of tree species and lichens), consumers (wildlife, insects, disease organisms), and decomposers. The decomposer populations were composed of the populations of saprophytic fungi responsible for the decay of leaf and woody litter.

The ecosystem processes analyzed were (1) carbon flow (the movement of carbon dioxide into the plant; its incorporation into green plant organic matter; and then its partitioning among consumers, litter and decomposers, the soil and return to the atmosphere); (2) the movement of water in the soil-plant-atmosphere continuum; (3) mineral nutrient flow through the green plant litter and soil-water compartments; and 4) the shift in diversity patterns in time and space as represented by changes in composition of tree species in stands, age, structure, and density.

8.3.5.2 Effects Observed. In previous sections of this chapter the effects of O_3 on a variety of ecosystem components have been discussed. The San Bernardino

study illustrates the response of a whole ecosystem to the stresses placed on its components. The effects of chronic O_3 stress observed were associated with average 24-hr O_3 concentrations in the San Bernardino Mountains during the months of May through September. They ranged from a background of 0.03 to 0.04 ppm to maxima of 0.10 to 0.12 ppm. Foliar injury of ponderosa pine, a very sensitive species, occurred at 24-hr concentrations of 0.05 to 0.06 ppm. Other trees, in decreasing order of sensitivity, were Jeffrey pine, white fir, black oak, incense cedar, and sugar pine. Decreased photosynthetic capacity due to foliar injury and premature leaf fall decreased radial growth and height of stem, reduced nutrient retention, and caused the weakening of trees. Pines became more susceptible to root rot (Heterobasidion annosum) and pine beetle (Dendroctonus brevicomis) due to host weakening by photochemical oxidants. Stressed trees showed a decrease in the number of mycorrhizal rootlets (Parmeter et al., 1962). Mortality rate of the trees reached 2 to 3 percent in some years. Injured ponderosa and Jeffrey pines older than 130 years produced significantly fewer cones per tree than uninjured trees of the same age (Luck, 1980). Ecosystem components most directly affected by O_3 were tree species, the fungal microflora of needles, and foliose lichens occupying tree bark. Heavy litter accumulation occurred in stands with the most severe needle injury and defoliation. Pine seed establishment was hindered by litter depth, but the growth of oxidant-tolerant understory species was encouraged. Buildup of litter and the presence of easily ignited foliage on smaller trees could lead to destructive fires. Removal by fires and by O_3 of the pine forest overstory has resulted in a shift in dominance to self-perpetuating, fire-adapted, O_3-tolerant shrub and oak species mixtures that provide fewer commodity and amenity values than the former pine forest.

The most important ecosystem processes affected either directly or indirectly were flows of carbon, mineral nutrients, and water. Changes in vegetation cover diversity patterns over time and space also occurred. Diminished flow of carbon in the tree layer resulted from a decrease in the amount of foliage conducting photosynthesis and the decreased photosynthetic capacity of the remaining foliage. Stressed trees also retained a smaller amount of assimilated carbon after respiration losses. The store of carbon and mineral nutrients that accumulated in the thick needle litter layer understands of O_3-injured trees influenced nutrient availability due to losses by volatilization during fires and in subsequent surface runoff. In the absence of the

pine-dominated forest, a cover of shrub and oak species emerges as a self-perpetuating community of species capable of sprouting after fire, quickly obtaining crown closure and inhibiting the natural reestablishment of pines and other conifers. Chronic O_3 stress can be seen to have had a severe effect on this coniferous forest ecosystem.

8.4 INTERRELATED ECOSYSTEMS

8.4.1 Aquatic Ecosystems

Because evidence for assessing the influence of ambient O_3 on aquatic ecosystems is not available, it is not possible to judge accurately this relationship.

Nevertheless, it is extremely important to consider that an adverse impact on a forest ecosystem may in turn adversely affect adjacent aquatic systems. A variety of linkages for energy and nutrient exchange exist. Disruptions induced by air pollution stress on terrestrial ecosystems often trigger dysfunctions in neighboring aquatic ecosystems, such as streams, lakes, and reservoirs. Sediments resulting from erosion can change the physical character of stream channels, causing changes in bottom deposits, erosion of channel banks, obstruction of flow, and increased flooding. They can fill in natural ponds and reservoirs. Finer sediments can reduce water quality, affecting public and industrial water supplies and recreational areas. Turbidity caused by increased erosion can also reduce the penetration of light into natural waters. This, in turn, can reduce plant photosynthesis and lower supplies of dissolved oxygen, leading to changes in the natural flora and fauna (Bormann and Smith 1980). Significant forest alterations, therefore, may have a regional impact on nutrient cycling, soil stabilization, sedimentation, and eutrophication of adjacent or nearby aquatic systems. Interfacing areas, such as wetlands and bogs, may be especially vulnerable to impact.

As noted in the San Bernardino study, forest biomass reduction results in a corresponding reduction in the total inventory of nutrient elements held within a system, and loss of the dominant vegetation destroys cycling pathways and mechanisms of nutrient conservation. Research on the northern hardwood forest has clearly established that retention of nutrients within a forest ecosystem depends on constant and efficient cycling between the various components of the intrasystem cycle and that deforestation impairs this retention

(Likens et al., 1977). Extensive nutrient loss can pollute downstream aquatic resources; this can result in enrichment or eutrophication of a site, with long-term consequences for potential plant growth.

8.4.2 Agricultural Ecosystems

Agricultural ecosystems are artificial systems created by humans for efficient food and forage productivity. Such systems generally have a single, dominant autotrophic plant species. If this component is very sensitive to O_3, its market value may be destroyed. If this occurs, efforts are made to find a resistant cultivar (e.g., with tobacco) or to convert the site to a crop less sensitive to O_3 stress. If the plant is not severely injured by exposure to ambient O_3, it may be influenced in one of the many ways described in Chapter 7. In such a case, the primary concern is oxidant impact on production, growth, and yield. This topic is thoroughly treated in Chapter 7. In structure, agroecosystems resemble primary successional stages of natural ecosystems. Unlike natural ecosystems, their maintenance requires large investments of human and fossil fuel energy and the addition of nutrients.

8.5 ECOSYSTEM MODELING

Systems ecology is a useful tool for addressing the complexity of the impact of O_3 on ecosystems. Forest models provide a mechanism for integrating forest growth and development data with indicators of air pollution stress. Shugart et al. (1980) have provided a comprehensive review of forest growth models, including tree, stand, and gap models. Although lack of critical information limits model completeness, these approaches have already yielded valuable information. The importance of competition in modifying the responses of individual species to air contamination in a forest stand has been indicated (Shugart and West, 1977; West et al., 1980). Kickert and Gemmill (1980) modeled O_3 effects on the San Bernardino National Forest. They concluded that the exclusion of natural fires and exposure to O_3 pollution can induce sudden qualitative changes in conifer forest composition.

8.6 VALUING ECOSYSTEMS

Natural ecosystems provide free public and private goods and services to humans. The free services are provided only if the integrity of the ecosystems is maintained. One of the greatest obstacles to the conservation, wise use, and sound management of natural ecosystems is that humans do not recognize, or else grossly undervalue, the functions and services provided by these systems (Farnworth et al., 1981).

A major barrier to communication between ecologists and economists is the ambiguity surrounding the concept and usage of the word value. Most definitions contain a monetary interpretation; a few definitions characterize value in relative terms without assignment or intrinsic worth. Definitions of value are relativistic in that they compare one item against another or against money (Farnworth et al., 1981). Value in each of these definitions is established as ordinal (ranked) or cardinal (related to a standard) measure. Both ordinal and cardinal measures are relativistic means of valuation, i.e., values exist only in comparison with other things, and value exists only on the basis of human judgment or preferences. Any sense of immaterial, intrinsic, or absolute value is not included except to the extent that these factors are relevant to individual judgment (Farnworth et al., 1981).

To incorporate the subtle and indirect meanings associated with the concept of value, Farnworth et al. (1981) presented a framework that integrated economic and ecological thought to separate value into (a) market values of private goods and (b) non-market values of public goods and services (though admittedly, many public goods and services have many market values). Non-market values are separated into attributable or assignable values and intangible or non-assignable values. Value I is defined as market price and is based on the functioning of the marketplace and on how accurately the marketplace reflects a theoretical concept, the market model. Frequently, but not always, market value reflects accurately society's evaluation of an item. Farnworth et al. (1981) use tropical moist forests as an example of how a natural resource provides market and non-market values. Conversion of tropical moist forests has provided marketable goods that have brought increased wealth to certain individuals and political groups, but has also resulted in the severe alteration or destruction of the systems that produce the goods (Myers, 1979, 1980).

Lumber, plywood and veneer, and fiber used for paper are some of the marketable products. In addition, forests are being converted to agriculture,

tree plantations, and pasture. Beef cattle have become a major commodity in the tropics. Cattle-ranching produces an exportable commodity that has created a great incentive to cut and clear forests for this alternative use. The forest is viewed as an exploitable resource from which foreign exchange or personal wealth can be realized. The value of the forest products in the long term is likened to the value of the system. The integrated system also produces other goods and services that are not included in the market price of the commodities obtained from the forests (Farnworth et al., 1981).

In the area of common property resources the marketplace is irrelevant even though the language of the market model is used to discuss common property and public goods. Political mechanisms are used to assign a price or value to Value II items because society believes that the value assigned by the marketplace mechanisms are inadequate. If an item is improperly handled by the marketplace, the item is placed before the political process which seeks to judge values and allocate resources more efficiently. The political process strives through negotiations to achieve agreement. Free services and goods provided to humans by natural ecosystems are services for which no marketplace values exist. These services have been or can be incorporated into a political system (Farnworth et al., 1981). Among the free services provided to humans by forests, both temperate and tropical, are the maintenance of global air and water quality, aesthetic and recreational benefits and genetic stocks. Type II values are inherent in the integrated functioning of the forest. The free services provided by the forest are reduced or eliminated when marketable goods are extracted and the forests disrupted or destroyed (Farnworth et al., 1981).

Values I and II, comprising market values and non-market attributable or assignable values, respectively, are established by institutional mechanisms, the market and the political system. Value III items, unlike those in the two previous values, have not been incorporated into any agreement system because the intangible or non-assignable non-market goods and services are difficult to evaluate. These absolutely non-market values are seen as individual or societal (public) benefits. Often they conflict with the private benefits of natural systems. Farnworth et al. (1981) state, "At present, private market economics cannot efficiently price these mainly ecological benefits, but non-market valuation theory to determine these intangibles is now emerging."

Assignable values that currently are not incorporated into any valuation system are natural life-support systems that provide free service and the inherent value of natural systems. Examples of these are maintenance of the global carbon balance; maintenance of atmospheric stability; habitats for native people; intrinsic value of species, culture, and ecosystems; a natural laboratory for the study of evolution, natural selection, and nutrient cycling (Farnworth et al., 1981). A majority of these attributes apply to all of the world's forest ecosystems. At the present no agreement system exists, and thus the total value of the system can only be approximated.

High-technology societies are coupled to the natural system only through extensive outside subsidies of materials and energy. Natural ecosystems are regarded as exploitable entities rather than human/nature compatible systems. Frequently, the natural system is exploited for short-term gain. The decision to alter irreversibly a natural resource implicitly assumes that future generations will not value the unaltered resources as highly as present generations do the development of the resource (Farnworth et al., 1981).

Westman (1977) also points out certain corollaries that accompany the decisions to utilize natural ecosystems for present day benefits:

> (1) The human species has the exclusive right to use and manipulate nature for its own purposes. (2) Monetary units are socially acceptable as means to equate the value of natural resources destroyed and those developed. (3) The value of services lost during the interval before the replacement or substitution of the usurped resource has occurred is included in the cost of the damaged resource. (4) The amount of compensation in monetary units accurately reflects the full value of the loss to each loser in the transaction. (5) The value of the item to future generations has been judged and included in an accurate way in the total value. (6) The benefits of development accrue to the same sectors of society, and in the same proportions, as the sectors on whom the costs are levied, or acceptable compensation has been transferred.

Each of these assumptions, and others not listed, can and have been challenged.

Humans receive from natural ecosystems free public and private goods. The free work and provision is inherent in the integrity of the system, and its value is related to this integrity. Only if the integrity of the systems is maintained will the natural life-support ecosystems continue to provide free services to humans. Functional systems provide not only public goods and services but in addition yield private goods. Only through the maintenance of an integrated, functional system will both public and private goods (values) be assured (Farnworth et al., 1981). Natural systems have an integrity which

is embodied in the totality of structure and functioning of the system. It is this integrity that is valued as having inherent worth, as without it the goods and services they provide would not be available.

Although markets for pricing environmental services usually are lacking, analysts have developed--and are continuing to test and compare--a variety of techniques to value such services indirectly.

8.7 SUMMARY

Temperate forest ecosystems within the United States currently are experiencing perturbation by O_3. Decline of ponderosa and Jeffrey pine in the San Bernardino Mountains of southern California, and of eastern white pine along the Blue Ridge Parkway in Virginia and on the Cumberland Plateau of East Tennessee has been attributed to O_3 stress. Decline in vigor is a commonly observed response in trees sensitive to O_3 exposure. The decline in vigor and reduced annual growth of sensitive trees have resulted from the following sequence of events and conditions: 1) premature senescence and the loss of older needles at the end of the growing season, 2) reduction in storage capacity in the fall and resupply capacity of photosynthate in spring to support new needle growth, 3) increased reliance of new needles on self-support for growth, 4) shorter new needles resulting in lower gross photosynthetic productivity, 5) higher retention of currently formed photosynthate by needles so that the photosynthate available for translocation, as well as repair of chronically stressed tissues of older needles, is reduced, and 6) premature dropping of older needles. These events and conditions, when coupled with a higher respiratory to photosynthetic ratio as indicated by gas exchange measurements, lead to a reduction in photosynthesizing tissue and availability of carbohydrates for growth and maintenance of trees.

Ecosystems, because of their complexity, respond to stress in a manner different from individuals. Trees are a single, highly, visible component of these multifaceted, highly structured organizations. Their decline is an indication that the whole system is under stress. Ecosystems respond to perturbations through the populations of organisms that comprise the system. There are three main levels of interaction: between the individual and its environment, the population and its environment, and the ecosystem (the community and its environment). These ecological systems are involved in the processes of energy transfer and nutrient cycling so that the ecosystem develops a

specific structure. Perturbation disrupts energy transfer and nutrient cycling. The ecosystem reverts to a simpler structure when the functioning of its components is impaired or altered.

The most thoroughly studied ecosystem is that in the San Bernardino Mountains of southern California. The mixed conifer forests of the San Gabriel and San Bernardino mountain ranges east of Los Angeles have been exposed to oxidant air pollution since the early 1940's. From 1973-1978 an interdisciplinary study was made of the impact of O_3 on the pine and mixed conifer forests in the San Bernardino Mountains. Both biotic and abiotic components were studied. The biotic components were the producers (an assortment of tree species and lichens), the consumers (wildlife, insects, disease organisms), and decomposers (mainly fungi); abiotic components included water (precipitation), temperature, light, mineral nutrients (soil substrate) and the air pollutant, ozone. Changes in the ecosystem processes of energy flow (carbon), water movement, mineral nutrient cycling and the shift in diversity patterns were noted. Ecosystem components most directly affected by exposure to ozone were various tree species, the fungal microflora of needles, and the foliose lichens occupying the bark of trees. Ozone inhibits photosynthesis, decreases the products formed in photosynthesis, and alters the transport and allocation of these products from the leaf to other parts of the plant (Chapter 7). Foliar injury to sensitive ponderosa and Jeffrey pine was observed when O_3 concentrations ranged from 0.05 to 0.06 ppm. During the period of study, average 24-hr O_3 concentrations during the months May through September ranged from a background of 0.03 to 0.04 ppm to a maximum of 0.10 to 0.12 ppm. Less sensitive trees in decreasing order of sensitivity were white fir, black oak, incense cedar and sugar pine. Associated with foliar injury were a decrease in photosynthesis, a reduction in tree growth in both height and diameter and in seed production in ponderosa and Jeffrey pine. Reduced tree growth and seed production is an indication that the important ecosystem processes of energy (carbon), mineral nutrients and water flow were affected either directly or indirectly by O_3 exposure. A comparison of the radial growth of ponderosa pine during years of low pollution (1910 to 1940) with years of high pollution (1941 to 1971) indicate that O_3 exposure reduced the average annual radial growth by approximately 40 percent, height by 25 percent, and wood volume by 84 percent in trees less than 30 years of age.

Studies made along the Blue Ridge Parkway and on the Cumberland Plateau of east Tennessee support the view that exposure to O_3 reduces growth in sensitive trees (Benoit et al., 1982). Eastern white pine of reproducing age located in experimental plots situated along the Blue Ridge Parkway from the Shenandoah National Park in the north to the southernmost end of the Parkway in Virginia were studied to determine the radial increment during 1955-1978 period. Growth of trees classified as sensitive was 25 percent less, and of trees classified as intermediate in sensitivity was 15 percent less than tolerant trees. Mean radial increments for all trees during the last 10 years of the study were smaller than for the previous 24 years. Comparison of growth during 1974-1978 with radial growth during 1955-1959 indicated a decrease in growth of 26, 37, and 51 percent for tolerant, intermediate, and sensitive trees. During the period of the study, concentrations of 0.05 to 0.07 ppm of O_3 were recorded on a recurring basis with episodic peaks of 0.12 ppm or higher (Benoit et al., 1982). Steady decline in annual ring increments of sensitive white pine was also observed on the Cumberland Plateau during the years 1962-1979. A reduction of 70 percent in average annual growth and 90 percent in average bole growth was observed in sensitive white pine when compared to both tolerant trees and trees of intermediate sensitivity. Annual occurrences of O_3 at hourly concentrations of 0.08 ppm or greater were associated with the growth reductions. Reduction in growth of sensitive white pine on the Blue Ridge Parkway and on the Cumberland Plateau, as in the case of the San Bernardino Mountains, was correlated with extensive oxidant injury to pine needles, senescence or premature abscission of needles, decrease in photosynthesis, reduction in stored photosynthate and impairment of its transfer and allocation; weakened trees result. Weakened trees are predisposed to attack by root rot fungi such as Heterobasidion annosum and Verticicladella wagenerii, to defoliation by insects and to attack by the pine beetle, Dendroctonus brevicomis. In the San Bernardino Mountains several bark beetles attacked the weakened ponderosa pines. Weakened trees are also subject to attack by various pathogens that infect stressed or senescent plant parts or invade nonliving woody tissue. Mortality in the San Bernardino forest reached 2 to 3 percent in some years.

Studies indicate that a disease-insect relationship exists between root-infecting fungi and bark beetles. In the majority of the cases studied root disease fungi infected ponderosa pine trees before they became infested with

bark beetles. Both Verticicladiella Wagnerii and Heterobasidion annosum were found to have entered tree roots prior to beetle attack. In eastern white pine, oxidant injury increased the incidence of Verticicladiella precera. Heterobasidion annosum usually becomes a serious problem in California only after forest disturbances by humans such as logging.

The presence of mycorrhizae on the roots of conifers assists in protecting the trees from attack by such root pathogens as Heterobasidion annosum (Krupa and Fries, 1971). The presence of mycorrhizae on conifer roots increases the concentrations of monoterpenes and sesquiterpenes two to eight times. Monoterpenes are constituents of the oleoresins that are commonly found in conifers and play an important role in the resistance of wood to decay fungi (Risbeth, 1951) and also in preventing attack by Heterobasidion annosum and four species of Ceratocystis.

The presence of mycorrhizae, on the other hand, is greatly influenced by the photosynthetic capacity of the host and its capacity to translocate carbohydrates to the roots. Seedlings of Virginia pine inoculated with the mycorrhizal fungus Thelephora terrestris and growing under an 18-hr photoperiod became dormant when transferred to an 8-hr photoperiod. In contrast with the seedlings continuing to grow under the 18-hr photoperiod, no further infection of rootlets occurred. Studies indicate that simple sugars found in the tree roots are readily utilized by mycorrhizae and enhance infection. McCool et al. (1979) noted that infection of Troyer citrange by Glomus fasiculatus, a mycorrhizal fungus, was reduced when the host was exposed to O_3 concentrations of 0.09 ppm.

Mycorrhizae on the roots of trees are essential for the growth of healthy trees. Inhibition of photosynthesis in conifer needles by O_3 begins a chain reaction that ultimately disrupts the functioning of mycorrhizae on the tree roots and leads to their being weakened and more readily attacking root rot fungi and bark beetles.

Declines of trees are usually the result of a number of chronic stresses. The predisposing factor in these studies was oxidant air pollution, accompanied by reduced photosynthesis, carbohydrate, moisture flow, and soil nutrients. Insects, bark beetle and fungus attack all contribute to the further weakening of trees. Declining trees usually have a serious depletion of stored carbohydrates, reserves necessary for starting growth in the spring or in regenerating tissues attacked by fungi or insects as well as infection by mycorrhizae. Depletion of its stored carbohydrate reserves by excessive continuous demands

limits a tree's ability to respond to stresses. Death eventually results after continued stress. The process usually takes a number of years for completion, and mature trees are the ones involved.

Forest ecosystems are not the only ecosystems impacted by oxidant air pollution. The coastal sage scrub vegetational community of California ranges from Baja California to San Francisco. The reduced cover of native species in this shrub community was correlated with high oxidant concentrations on the most polluted sites. A decline in species number was also observed. In recently burned chaparral communities in the same area, seedling pioneer species were vulnerable to oxidant stress. Other ecosystems in which ozone injury has been observed are the grassland, oak, aspen and conifer communities in the Salt Lake Valley and Wasatch Mountains of Utah and the indigenous vegetation communities of the Blue Ridge Mountains of Virginia.

In Utah, some dominant species considered keys to community integrity were found to be sensitive. Bromus tectorum L. (cheatgrass), the most prevalent species in the grassland community was also the most sensitive to O_3. Other grasses and forbs were not as sensitive; however, in those grasses with visible injury, carbohydrate production was significantly reduced. Aspen (Populus tremuloides Michx) was the most sensitive member of the aspen community. In both cases single 2-hr exposures to 0.15 ppm of O_3 caused severe injury. Removal of the dominant species (cheatgrass) from plant communities could result in a shift to another species. Decline in or removal of aspen could affect the growth of white fir because seedlings require the shade provided by aspen for optimal juvenile growth. Loss of aspen populations could influence forest succession by restricting white fir development, causing a shift from a forest to a grassland or forb vegetation community. In a companion study conducted in chambers in the greenhouse, O_3 exposures of 0.15 to 0.3 ppm for 2-hr per day reduced root- and top growth and fewer seeds were produced. A reduction in biomass production was also observed in the study conducted in the Shenandoah National Park and the Blue Ridge Mountains of Virginia. Native forbs, grasses and sedges in a high meadow community were exposed to monthly hourly average O_3 concentrations ranging from 0.035 to 0.06 ppm. Peaks ranged from 0.08 to 0.12 ppm. The studies discussed above illustrate that O_3 inhibits photosynthesis, decreases formation of organic compounds needed for plant growth and can alter transport and allocation of the decreased products of photosynthesis so that sugar storage and root growth are affected (Duchelle et al., 1983).

Changes in diversity in plant communities occurring with time and space result as those plant species sensitive to O_3 decrease in numbers and O_3-tolerant species take their place. The shift in species has been particularly obvious in the San Bernardino Forest where shrub and oak species have emerged as dominants after removal of ponderosa and Jeffrey pine. The breakdown in the processes of energy flow and nutrient cycling has also had its impact on other components of the forest ecosystem. The change in dominant producers influenced the small mammal population by changing its habitat and upsetting its food web. Fruits and seeds comprise the major portion of the small mammal diet. Removal of their food source directly impacts them. Decomposition also was affected as the species composition and density of fungi which colonize living needles and later participate in decomposition were prevented from developing due to the premature needle senescence and abscission.

The impact of O_3 on ecosystems depends on the response of the producer community. Producers as well as decomposers are critical to the maintenance of ecosystems. The solar energy and mineral nutrients necessary for the proper functioning of ecosystems enters through the producers. Interference of O_3 with the proper functioning of the process of photosynthesis results in a perturbation felt throughout the ecosystem.

Natural and agricultural ecosystems possess the same basic functional components. They require energy flow and mineral nutrient cycling for maintenance and are subject to the dominating influences of climate and substrate. Agroecosystems, however, are highly manipulated monocultures, usually similar in genetic composition and age. Manipulation of the monocultures is to maximize the yield of a particular species. If the species grown does not produce, it is replaced. Cost alone would prevent the replacement of the variety of species in a natural ecosystem. The complexity of natural ecosystems makes it much more difficult to quantify their benefits. No one knows what all of the benefits are and in many cases the benefits may not have dollar value. Some of the unpriced benefits to society are soil stabilization, enhanced water quality, climate amelioration, nutrient and energy conservation, gene preservation and amenity and aesthetic function. It is extremely important to recognize that societal benefits derived from natural ecosystems are obtained without appreciable direct dollar expenditures or extensive management.

8.8 REFERENCES

Barbour, M. G.; Burk, J. H.; Pitts, W. D. (1980) Terrestrial plant ecology. Menlo Park, CA: Benjamin Cummings Pub. Co.

Bennett, J. P.; Runeckles, V. C. (1977) Effects of low levels of ozone on plant competition. J. Appl. Ecol. 14: 877-880.

Benoit, L. F.; Skelly, J. M.; Moore, L. D.; Dochinger, L. S. (1982) Radial growth reductions of Pinus strobus L. correlated with foliar ozone sensitivity as an indicator of ozone-induced losses in eastern forests. Can. J. For. Res. 12: 673-678.

Berry, C. R.; Ripperton, L. A. (1963) Ozone, a possible cause of white pine emergence tipburn. Phytopathology 53: 552-557.

Billings, W. D. (1978) Plants and the ecosystem. 3rd Edition. Belmont, CA: Wadsworth Publishing Company, Inc.; pp. 1-62.

Bormann, F. H. (1976) An inseparable linkage: conservation of natural ecosystems and the conservation of fossil energy. BioScience 26: 754-760.

Bormann, F. H.; Likens, G. E. (1979) Catastrophic disturbance and the steady state in northern hardwood forests. Am. Sci. 67: 660-669.

Bormann, F. H.; Smith, W. H. (1980) Effects of air pollution on forest ecosystems. In: Energy and the fate of ecosystems. Washington, DC: National Academy of Sciences; pp. 308-318.

Botkin, D. B.; Keller, E. A. (1982) Environmental studies: the earth as a living planet. Columbus, OH: Charles E. Merrill Publishing Co.; pp. 93-122.

Bruhn, J. N. (1980) Effect of oxidant air pollution on ponderosa and Jeffrey pine foliage decomposition. Berkeley, CA: University of California. Ph.D. Thesis.

Cairns, J. Jr., ed. (1980) The recovery process in damaged ecosystems. Woburn, MA: Ann Arbor Science; p. 167.

Cobb, F. W., Jr.; Stark, R. W. (1970) Decline and mortality of smog-injured ponderosa pine. J. For. 68: 147-149.

Cobb, F. W., Jr.; Kinstic, M.; Zavarin, E.; Barber, H. W., Jr. (1968) Inhibitory effects of volatile oleoresin components on Fomes annosus and four Ceratocystis species. Phytopathology 58: 1327-1337.

Costonis, A. C.; Sinclair, W. A. (1972) Susceptibility of healthy and ozone injured needles of Pinus strobus to invasion by Lophodermium pinastri and Aureobasidium pullulans. Eur. J. For. Pathol. 2: 65-73.

Cox, G. W.; Atkins, M. D. (1979) Agricultural ecology: an analysis of world food production systems. San Francisco, CA: W.H. Freeman and Co.; pp. 35-38.

Coyne, P. E.; Bingham, G. E. (1981) Comparative ozone response of gas exchange in a ponderosa pine stand exposed to long-term fumigations. J. Air Pollut. Control Assoc. 31: 38-41.

Curtis, J. T. (1956) The modification of mid-latitude grasslands and forests by man. In: Thomas, W. L., ed. Man's role in changing the face of the earth. Chicago, IL: University of Chicago Press; pp. 721-736.

Dahlsten, D. L.; Rowney, D. L. (1980) Influence of air pollution on population dynamics of forest insects and on tree mortality. In: Miller, P. R., ed. Proceedings of the symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture Forest Service; pp. 125-130; genl. tech. report no. PSW-43.

Dewey, J. E.; Ciesla, W. M.; Meyer, H. E. (1974) Insect defoliation as a predisposing agent to bark beetle outbreak in eastern Montana. Environ. Entomol. 3: 722.

Duchelle, S. F.; Skelly, J. M.; Chevone, B. I. (1982) Oxidant effects on forest tree seedling growth in the Appalachian Mountains. Water Air Soil Pollut. 18: 363-373.

Duchelle, S. F.; Skelly, J. M. (1981) Response of common milkweed to oxidant air pollution in the Shenandoah National Park in Virginia. Plant Disease 65: 661-662.

Duchelle, S. F.; Skelly, J. M.; Sharick, T. L.; Chevone, B. I.; Yang, Y. S.; Nellessen, J. E. (1983) Effects of ozone on the productivity of natural vegetation in a high meadow of the Shenandoah National Park of Virginia. J. Environ. Manage. 17:299-308.

Ehrlich, P. R.; Mooney, H. A. (1983) Extinction, substitution and ecosystem services. BioScience 33:248-254.

Flagler, R. B.; Youngner, V. B. (1982) Ozone and sulfur dioxide effects on three tall fescue cultivars. J. Environ. Qual. 11: 413-416.

Gemmill, B. (1980) Radial growth of California black oak in the San Bernardino Mountains. In: Proc. Symposium on the Ecology, Management and Utilization of California Oaks. U.S. Department of Agriculture, Forest Service, Gen. Tech. Rep. PSW-44; pp. 128-135.

Gorham, E.; Vitousek, P. M.; Reiners, W. A. (1979) The regulation of chemical budgets over the course of terrestrial ecosystem succession. Annu. Rev. Ecol. System. 10: 53-84.

Hacskaylo, E. (1973) The Torrey symposium on current aspects of fungal development. IV. Dependence of mycorrhizal fungi on hosts. Bull. Torrey Bot. Club 100: 217-223.

Harward, M. R. (1971) The impact of ozone on understory plants of the aspen zone. Salt Lake City, UT: University of Utah. Available from: University Microfilms, Ann Arbor, MI; publication no. 72-509. Dissertation.

Harward, M. R.; Treshow, M. (1975) Impact of ozone on the growth and reproduction of understory plants in the aspen zone of western U.S.A. Environ. Conserv. 2: 17-23.

Hayes, E. M.; Skelly, J. M. (1977) Transport of ozone from the northeast U.S. into Virginia and its effect on eastern white pines. Plant Dis. Rep. 61: 778-782.

Heck, W. W. (1973) Air pollution and the future of agriculture. In: Naegele, J. A., ed. Air pollution damage to vegetation. Washington, D.C: American Chemical Society (Advances in Chemistry Series No. 122); pp. 118-129.

Holling, C. C. (1973) Resilience and stability of ecological systems. Annu. Rev. Ecol. Syst. 4: 1-23.

Hibben, C. R.; Stotsky, G. (1969) Effects of ozone on the germination of fungus spores. Can. J. Microbiol. 15: 1187-1196.

Hibben, C. R.; Taylor, M. P. (1975) Ozone and sulphur dioxide effects on the lilac powdery mildew fungus. Environ. Pollut. 9: 107-114.

Hutchinson, B. A.; Taylor, F. G.; Wendt, R. L. (1982) Use of vegetation to ameliorate building microclimates: an assessment of energy conservation potentials. Oak Ridge, TN: Oak Ridge National Laboratory; publication no. ORNL/CON-87; 86 pp.

James, R. L.; Cobb, F. W., Jr.; Wilcox, W. W.; Rowney, D. L. (1980) Effects of photochemical oxidant injury of ponderosa and Jeffrey pines on susceptibility of sapwood and freshly cut stumps to Fomes annosus. Phytopathology 70: 704-408.

Johnson, A. H.; Siccama, T. G. (1983) Acid deposition and forest decline. Environ. Sci. Technol. 17: 294A-305A.

Jordan, C. F.; Medina, E. (1977) Ecosystem research in the tropics. Ann. Mo. Bot. Garden 64: 737-745.

Kickert, R. N.; Gemmill, B. (1980) Data-based ecological modeling of ozone air pollution effects in a southern California mixed conifer ecosystem. In: Miller, P.R., ed. Proceedings of the symposium on effects of air pollutants on Mediterranean and temperature forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture Forest Service; genl. tech. report no. PSW-43; pp. 203-214.

Kolb, J. A.; White, M. (1974) Small mammals of the San Bernardino Mountains. Calif. Southwest National 19: 112-113.

Krause, G. H. M. (1974) Forest effects in West Germany. In: Symposium on Air Pollution and the Productivity of the Forest; October 1983; Washington, DC. Arlington, VA: Izaak Walton League of America; in press.

Kress, L. W.; Skelly, J. M. (1982) Responses of several eastern forest tree species to chronic doses of ozone and nitrogen dioxide. Plant Dis. 66: 1149-1152.

Krupa, S.; Fries, N. (1971) Studies on mycorrhizae of pine. I. Production of volatile organic compounds. Can. J. Bot. 49: 1425-1431.

Laurence, J. A.; Weinstein, L. H. (1981) Effects of air pollutants on plant productivity. Annu. Rev. Phytopathol. 19: 257-71.

Letchworth, M. B.; Blum, V. (1977) Effects of acute ozone exposure on growth, nodulation and nitrogen content of ladino clover. Environ. Pollut. 14: 303-312.

Luck, R. F. (1980) Impact of oxidant air pollution on ponderosa and Jeffrey pine cone production. In: Miller, P.R., ed. Proceedings of the symposium on the effects of air pollutants on Mediterranean and temperate forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture, Forest Service; genl. tech. report no. PSW-43; p. 256.

Mahoney, M. J. (1982) An analysis of the potential effects of air pollutants emitted during coal combustion on yellow poplar and loblolly pine and influences on mycorrhizal associations of loblolly pine. Unpublished. Blacksburg, VA: Virginia Polytechnical Institute; Ph.D. Thesis.

Manion, P. (1981) Tree disease concepts. Englewood Cliffs, NJ: Prentice-Hall, Inc.; pp. 12-16, 325-339.

Mann, L. K.; McLaughlin, S. B.; Shriner, D. S. (1980) Seasonal physiological responses of white pine under chronic air pollution stress. Environ. Exp. Bot. 20: 99-105.

McBride, J. R.; Semion, V.; Miller, P. R. (1975) Impact of air pollution on the growth of ponderosa pine. Calif. Agric. 29 (12): 8-10.

McClenahen, J. R. (1978) Community changes in a deciduous forest exposed to air pollution. Can. J. For. Res. 8: 432-438.

McCool, P. M.; Menge, J. A.; Taylor, O. C. (1979) Effects of ozone and HCl gas on the development of the mycorrhizal fungus Glomus faciculatus and growth of 'Troyer' citrange. J. Am. Soc. Hort. Sci. 104: 151-154.

McLaughlin, S. B.; McConathy, R. K.; Duvick, D.; Mann, L. K. (1982) Effects of chronic air pollution stress on photosynthesis, carbon allocation and growth of white pine trees. For. Sci. 28: 60-70.

Millar, C. S. (1974) Decomposition of coniferous leaf litter. In: Dickinson, C. H.; Pugh, G. J. F., eds. Biology of Plant Litter Decomposition. Volume I. New York, NY: Academic Press, Inc.; pp. 105-128.

Miller, P. R. (1973) Oxidant-induced community change in a mixed conifer forest. In: Naegele, J.A., ed. Air pollution damage to vegetation. Washington, DC: American Chemical Society, (Advances in chemistry series: no. 122); pp. 101-117.

Miller, P. R.; Elderman, M. J., eds. (1977) Photochemical oxidant air pollutant effects on a mixed conifer forest ecosystem: a progress report, 1976. Corvallis, OR: U.S. Environmental Protection Agency; EPA report no. EPA-600/3-77-104. Available from: NTIS, Springfield, VA; PB-274531.

Miller, P. R.; McBride, J. R. (1975) Effects of air pollutants on forests. In: Mudd, J.B.; Kozlowski, T.T., eds. Responses of plants to air pollution. New York, NY: Academic Press, Inc.; pp. 195-235.

Miller, P. R.; Parmeter, J. R., Jr.; Flick, R. B.; Martinze, C. W. (1969) Ozone dosage response of ponderosa pine seedlings. J. Air Pollut. Control Assoc. 19: 435-438.

Miller, P. R.; Longbotham, G. J.; Van Doren, R. E.; Thomas, M. A. (1980) Effect of chronic oxidant air pollution exposure on California black oak in the San Bernardino Mountains. In: Proceedings of the symposium on the ecology, management and utilization of California oaks. U.S. Department of Agriculture, Forest Service, gen. tech. rept. PSW-44; pp. 220-229.

Miller, P. R.; Parmeter, J. R., Jr.; Taylor, O. C.; Cardiff, E. A. (1963) Ozone injury to the foliage of Pinus ponderosa. Phytopathology 53: 1072-1076.

Miller, P. R.; Taylor, O. C.; Wilhour, R. G. (1982) Oxidant air pollution effects on a western coniferous forest ecosystem. Corvallis, OR: U.S. Environmental Protection Agency; EPA-600/D-82/276; 10 pp.

Myers, N. (1979) The Sinking Ark: A New Look at the Problem of Disappearing Species. Oxford, England: Pergamon Press; xi + 307 pp.

Myers, N. (1980) The present status and future prospects of tropical moist forests. Environ. Conserv. 7: 101-114.

National Research Council. (1977) Ozone and other photochemical oxidants. Washington, DC: National Academy of Sciences; pp. 437-642.

National Research Council, Committee on Nuclear and Alternative Energy Systems. (1980) Energy and the fate of ecosystems. Washington, DC: National Academy Press; supporting paper no. 8; pp. 1-31.

Newman, J. R. (1979) Effects of industrial air pollution on wildlife. Biol. Conserv. 15: 181-190.

Newman, J. R. (1980) Air pollutants and their effects on wildlife with particular reference to the house wren (Delichon urbica). In: Miller, P.R., ed. Proceedings of the symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture Forest Service; genl. tech. report no. PSW-43; pp. 131-135.

Odum, E. P. (1969) The strategy of ecosystem development. Science (Washington, DC) 164: 262-270.

Odum, E. P. (1971a) Fundamentals of ecology, third edition. Philadelphia, PA: W. B. Saunders; pp. 1-38.

Odum, E. P. (1971b) Ecosystem theory in relation to man. In: Wiens, J.A., ed. Ecosystem structure and function: proceedings of the 31st annual biology colloquium; 1971; Corvallis, OR. Corvallis, OR: Oregon State University Press; pp. 11-24.

Ovington, J. D. (1957) Dry-matter production by Pinus sylvestris L. Ann. Bot. (London) 21: 87-314.

Parmeter, J. R., Jr.; Bega, R. V.; Neff, T. (1962) A chlorotic decline of ponderosa pine in southern California. Plant Dis. Rep. 46: 269-273.

Rae, D. A. (1982) The value to visitors of improving visibility at Mesa Verde and Great Smoky National Parks. In: Rowe, R; Chestnut, L., eds. Managing air quality and visual resources at national parks and wilderness areas. Boulder, CO: Westview Press.

Research Foundation, State University of New York. (1980) Actual and potential effects of acid precipitation on a forest ecosystem in the Adirondack Mountains. Albany, NY: New York State Energy Research and Development Authority; report no. ERDA 80-28.

Risbeth, J. (1951) Observations on the biology of Fomes annosus with particular reference to East Anglian pine plantations. III. Natural and experimental infection of pines and some factors affecting severity of the disease. Ann. Bot. (London) (N.S.) 15: 221-246.

Roose, M. L.; Bradshaw, A. D.; Roberts, T. M. (1982) Evolution of resistance to gaseous air pollutants. In: Unsworth, M. H.; Ormrod, D. P., eds. Effects of gaseous air pollution in agriculture and horticulture. London: Butterworth Scientific; pp. 379-409.

Rudinsky, J. A. (1962) Ecology of Scolytidae. Annu. Rev. Entomol. 7: 327-348.

Shugart, H. H.; West, D. C. (1977) Development of an Appalachian deciduous forest succession model and its application to assessment of the impact of the chestnut blight. J. Environ. Manage. 5: 161-179.

Shugart, H. H.; McLaughlin, S. B.; West, D. C. (1980) Forest models: their development and potential applications for air pollution effects research. In: Miller, P.R., ed. Proceedings of the symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture, Forest Service; genl. tech. report no. PSW-43; pp. 203-214.

Sigal, L. L.; Nash, T. H. (1983) Lichen communities on conifers in southern California mountains: an ecological survey relative to oxidant air pollution. Ecology 64: 1343-54.

Skelly, J. M. (1980) Photochemical oxidant impact on Mediterranean and temperate forest ecosystems: real and potential effects. In: Miller, P.R., ed. Proceedings of the symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture Forest Service; genl. tech. report no. PSW-43; pp. 38-50.

Smith, D. F.; Hill, D. M. (1975) Natural and agricultural ecosystems. J. Environ. Qual. 4: 143-145.

Smith, R. L. (1980) Ecology and field biology, 3rd ed. New York, NY: Harper and Row; pp. 11-199.

Smith, W. H. (1970) Technical review: trees in the city. J. Am. Inst. Planners 36: 429-435.

Smith, W. H. (1980) Air pollution--a 20th century allogenic influence on forest ecosystems. In: Miller, P.R., ed. Proceedings of the symposium on effects of air pollutants on Mediterranean and temperate forest ecosystems; June; Riverside, CA. Berkeley, CA: U.S. Department of Agriculture, Forest Service; genl. tech. report no. PSW-43; pp. 79-87.

Smith, W. H. (1981) Air pollution and forests: interactions between air contaminants and forest ecosystems. New York, NY: Springer-Verlag.

Stark, N. (1972) Nutrient cycling pathways and litter fungi. BioScience 22: 355-360.

Stark, R. W.; Cobb, F. W., Jr. (1969) Smog injury, root diseases and bark beetle damage in ponderosa pine. Calif. Agric. 23: 13-15.

Stark, R. W.; Miller, P. R.; Cobb, F. W., Jr.; Wood, D. L.; Parmeter, J. R., Jr. (1968) I. Incidence of bark beetle infestation in injured trees. Hilgardia 39: 121-126.

Stolte, K. W. (1982) The effects of ozone on chaparral plants in the California South Coast Air Basin. Riverside, CA: University of California; Master's Thesis.

Taylor, O. C., ed. (1973) Oxidant air pollutant effects on a western coniferous forest ecosystem. Task c: study site selection and on-site collection of background information. Riverside, CA: University of California, Statewide Air Pollution Research Center; EPA report no. EPA-R3-73-043B.

Treshow, M.; Stewart, D. (1973) Ozone sensitivity of plants in natural communities. Biol. Conserv. 5: 205-214.

U.S. Environmental Protection Agency. (1978) Air quality criteria for ozone and other photochemical oxidants. Research Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office; EPA report no. EPA-600/8-78-004. Available from: NTIS, Springfield, VA; PB83-163337.

Usher, R. W.; Williams, W. T. (1982) Air pollution toxicity to eastern white pine in Indiana and Wisconsin. Plant Dis. 66: 199-204.

Vogl, R. J. (1980) The ecological factors that produce perturbation-dependent ecosystems. In: Cairns, J. Jr., ed. The recovery of damaged ecosystems. Ann Arbor, MI: Ann Arbor Science Publishers; pp. 63-112.

Weidensaul, T. C.; Darling, S. L. (1979) Effects of ozone and sulfur dioxide on the host-pathogen relationship of Scotch pine and Scirrhia acicola. Phytopathology 69: 939-941.

West, D. C.; McLaughlin, S. B.; Shugart, H. H. (1980) Simulated forest response to chronic air pollution stress. J. Environ. Qual. 9: 43-49.

Westman, W. E. (1977) How much are nature's services worth? Science (Washington, D.C.) 197: 960-964.

Westman, W. E. (1978) Measuring the inertia and resilience of ecosystems. BioScience 28: 705-710.

Westman, W. E. (1979) Oxidant effects on Californian coastal sage scrub. Science (Washington, D.C.) 205: 1001-1003.

Whittaker, R. H. (1965) Dominance and diversity in land plant communities. Science (Washington, D.C.) 147: 250-260.

Whittaker, R. H. (1975) Communities and ecosystems; second edition. New York, NY: MacMillan.

Whittaker, R. H.; Woodwell, G. M. (1978) Retrogression and coenocline distance. In: Whittaker, R.H. ed. Ordination of plant communities. The Hague, The Netherlands: Dr. W. Junk B.V.; pp. 51-70.

Williams, W. T. (1980) Air pollution disease in the Californian forests: a base line for smog disease on ponderosa and Jeffrey pines in the Sequoia and Los Padres National Forests, California. Environ. Sci. Technol. 14: 179-182.

Williams, W. T. (1983) Tree growth and smog disease in the forests of California: Case history, ponderosa pine in the southern Sierra Nevada. Environ. Pollut. (in press).

Williams, W. T.; Brady, M.; Willison, S. C. (1977) Air pollution damage to the forests of the Sierra Nevada Mountains of California. Air Pollut. Control Assoc. 27: 230-234.

Woodwell, G. M. (1962) Effects of ionizing radiation on terrestrial ecosystems. Science (Washington, DC) 138: 574-577.

Woodwell, G. M. (1970) Effects of pollution on the structure and physiology of ecosystems. Science (Washington, D.C.) 168: 429-433.

Woodwell, G. M. (1974) Success, succession, and Adam Smith. BioScience 24: 81-87.

Young, Y. S.; Skelly, J. M.; Chevone, B. I.; Birch, J. B. (1983) Effects of long-term ozone exposure on photosynthesis and dark respiration of eastern white pine. Environ. Sci. Technol. 17: 371-373.

9. OTHER WELFARE EFFECTS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

9.1 INTRODUCTION

Photochemical oxidants comprise various chemical species capable of reacting with a number of nonbiological materials. The nature and amount of damage to these materials can be approximated from oxidant concentrations (Chapter 6) and the rate constants of individual species. Unfortunately, there is virtually no information on the rates of reaction of photochemical oxidants other than ozone (O_3) on specific materials. Although ozone has been the primary photochemical oxidant studied, its prominence in the research literature does not necessarily indicate that it is the only important oxidant responsible for damaging materials. Under experimental conditions with certain chemical groups, OH radicals, which are far less abundant than ozone, have rates of reactivity much higher than those of ozone.

Nearly all 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. It has been shown that oxidants harden and embrittle elastomers, causing a loss in physical integrity and cracking. Damage, specifically by ozone, occurs mainly on the surface of these materials and is accelerated by mechanical stress. In the absence of ozone, oxidation by atmospheric oxygen still occurs, but at a slower rate and more in the bulk of the material. These effects have been known for years, and various antioxidants and other protective measures have been formulated to reduce the rates of attack. 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. Like elastomeric products, fibers and dyes particularly sensitive to ozone may be partly protected with resistant coatings or replaced with more durable formulations. Ultimately, these protective measures add to the cost of products. 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 sulfur dioxide, tends to overshadow the role of ambient ozone in estimating paint damage.

To determine the actual damage to in-use materials, exposure must be estimated. As an example of the variables that must be taken into account, the ozone exposure of textile fibers and dyes used for clothing depends on the activity patterns of the wearer (i.e., time at home, at work, or outdoors), but the exposure of the same materials used for carpets and drapes involves only indoor air. Accordingly, a knowledge of product use and indoor/outdoor ozone gradients is essential when evaluating estimates of materials damage.

The literature selected for review in this section includes research previously reported in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) and a limited number of references published before and after 1978. Of the twelve recent post-1978 references in this review, eight involve laboratory/field research, and four involve analyses that use previously published material. Because little recent work has been reported on the effects on nonbiological materials, reference to older studies is necessary for unity and coherence, for determining dose-response relationships, and for assessing economic impact. Technical areas considered in evaluating the cited studies include the type of study and exposure methods used (field versus laboratory; ambient conditions versus accelerated, artificial environments), the pollutant-monitoring and analytical methods used, the design and conditions of the experiment (e.g., inclusion of variables such as relative humidity and temperature), the statistical methods and level of significance, and the importance of the specific material studied. The absence of this type of information is noted in the text, when applicable.

This assessment of the effects on nonbiological 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.

9.2 MECHANISMS OF OZONE ATTACK AND ANTIOZONANT PROTECTION

9.2.1 Elastomers

Most elastomeric materials found in the marketplace are composed of unsaturated, long-chain organic molecules. That is, the molecules contain carbon-carbon double bonds. Natural rubber and synthetic polymers/copolymers of butadiene, isoprene, and styrene account for the bulk of elastomer production for products such as automobile tires and protective electrical coverings used in outdoor environments (Mueller and Stickney, 1970). These types of compounds

are susceptible to oxidation and are particularly susceptible to 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 O_3 damage (Mueller and Stickney, 1970), but higher cost and limiting physical and chemical properties have constrained their use in outdoor environments.

The differences and similarities between simple oxidation (reaction with oxygen) and O_3 attack are described by Mueller and Stickney (1970). In the elastomer molecule, simple oxidation is postulated to proceed through the removal of a hydrogen atom from a carbon atom adjacent to a double bond; this is followed by the formation of a peroxy radical and subsequent radical reactions, which leads to chain scission and/or cross-linking (see Figure 9-1). Ozone is thought to attack by adding atoms directly across the double bond, forming a five-membered ring structure. This structure quickly rearranges (via Criegee ozonolysis) to form a zwitterion and an aldehyde (see Figure 9-2). Subsequent reactions of the zwitterion lead to a permanently oxidized elastomer.

Ozone damage, usually in the form of cracking, tends to be more of a surface phenomenon than simple oxidation. It is greatly accelerated by mechanical stress, which produces fresh surface area at crack boundaries. Simple oxidation, on the other hand, is slower; it occurs more in the bulk of a material, and it is less affected by the degree of stress.

At very high concentrations and high mechanical stress, O_3 damage can result in a large number of surface microcracks that produce a frosted appearance and mechanical weakening (Crabtree and Malm, 1956). However, because both simple oxidation and O_3 reactions lead to chain scission and chain cross-linking, the end result of both types of damage can be very similar in appearance. At pollutant concentrations and stress levels normally encountered outdoors (and in many indoor environments), the elastomer hardens or becomes brittle and cracked, which results in a loss of physical integrity. The influence of O_3 is evidenced primarily by the increased rate at which damage accumulates and by the degree of protection provided by various antioxidants and antiozonants.

According to Fisher (1957), work at the Rock Island Arsenal by R. F. Shaw, Z. T. Ossefa and W. J. Tonkey in 1954 lead to the development of effective antioxidant additives to protect elastomers from O_3 degradation. Subsequently, antiozonants were generally incorporated into elastomeric formulations

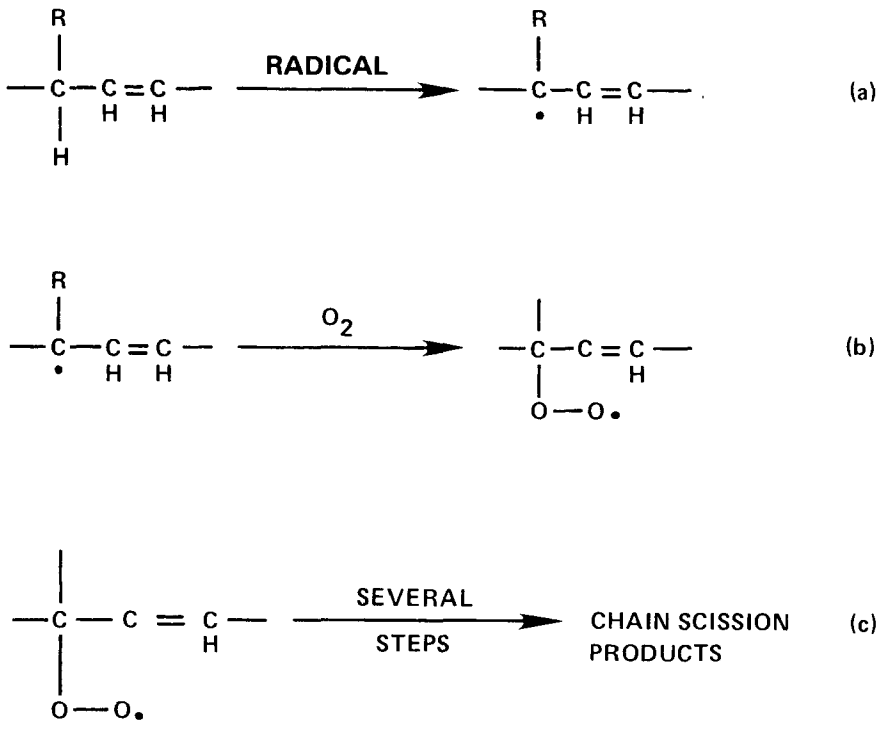

Figure 9-1. Postulated mechanism for damage to elastomers by oxygen.
Source: Adapted from Mueller and Stickney (1970).

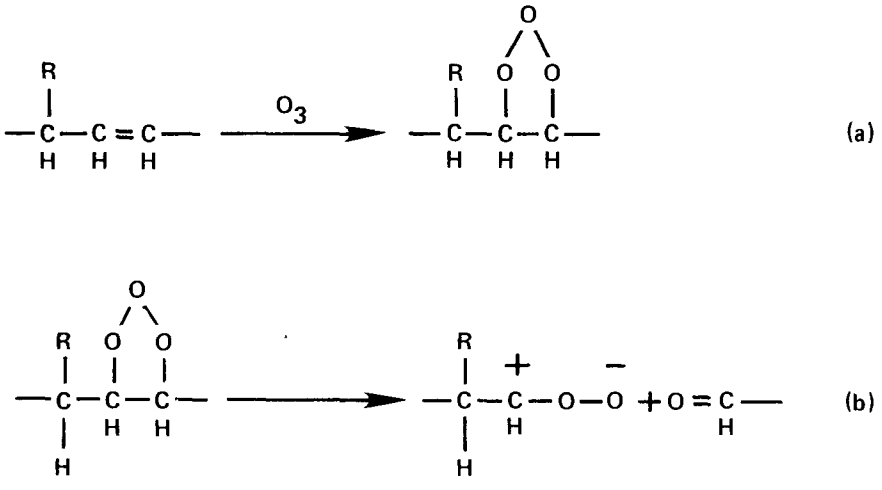

Figure 9-2. Postulated mechanism for damage to elastomers by ozone.
Source: Mueller and Stickney (1970).

during mixing, and their protection was effective even when elastomers were stretched or flexed (Fisher, 1957; Mueller and Stickney, 1970).

Several theories have been advanced to explain the mechanism of antiozonant protection. As summarized by Andries and Diem (1974), these are the scavenger theory, the protective film theory, the recombination theory, and the self-healing film theory.

The scavenger theory suggests that the antiozonant diffuses to the surface, where it reacts with the O_3 at a faster rate than with the carbon-carbon double bonds of the rubber, thereby protecting it sacrificially. The protective film theory also includes diffusion to the surface, but assumes that the resulting layer is less reactive with O_3 than is the rubber and thus constitutes a protective layer. The recombination theory proposes that the antiozonant prevents the propagation of the radical chain reactions initiated by O_3 attack. The self-healing film theory assumes that reaction products form on the surface and resist further degradation.

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 O_3 reacts preferentially with PIPP at a ratio of three O_3 molecules per one PIPP molecule.

Andries et al. (1979), by using carbon-black-loaded natural rubber (NR) compounds with and without antiozonants, attempted to distinguish between 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 and 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.

In addition to reactive antiozonants, paraffinic and microcrystalline waxes are used to protect the elastomers in rubber products such as tires. Typically, the wax migrates to the surface of the rubber and forms a barrier against O_3 attack. The wax's ability to protect the rubber depends on how well the wax migrates to the surface. This phenomenon, known as blooming, depends on a number of factors besides the characteristics of the wax. Dimauro et al. (1979) studied the ability of 18 waxes to protect rubber against degradation due to 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. However, it was found 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.

9.2.2 Textile Fibers and Dyes

Damage to textile fibers from O_3 is difficult to distinguish from that caused by oxidation by oxygen. Reduction in breaking strength and an increased rate of wear are the types of damage most commonly observed. Cellulose-based fibers, acrylic fibers, and nylon fibers are affected by O_3, and modacrylic and polyester fibers have been shown to be relatively unaffected by the levels of O_3 normally experienced in the ambient atmosphere (Zeronian et al., 1971). However, as stated by Bogaty et al. (1952), for most uses of textile fibers, the action of O_3 or oxygen is less important in product lifetime than physical abrasion, biological degradation, soiling, fashion, and other factors. 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. Nevertheless, an important property of textile products is appearance or color; O_3 reacts with a number of dyes to cause fading or changes in color.

Oxidation is the fundamental chemical reaction leading to color change in dyed fibers exposed to O_3. Compared with other oxidizing pollutants such as nitrogen oxides, O_3 often leads to a higher degree of oxidation and thus to different types of color changes. Terms such as O-fading and Gulf Coast fading have been given to some of the unique color changes attributed to reactions with O_3.

Figure 9-3 illustrates the reaction of Disperse Blue #3 with O_3 and with nitrogen oxides (Haylock and Rush, 1976). Although the nitrogen oxides removed an alkylamine side chain, O_3 attacked the quinoid portion of the molecule, completely rupturing the ring system chromophore and oxidizing the dye to phthalic acid, which is colorless.

The reactions between various chemical categories of dyestuffs and O_3 is influenced not only by the properties of the dye but also by the chemical

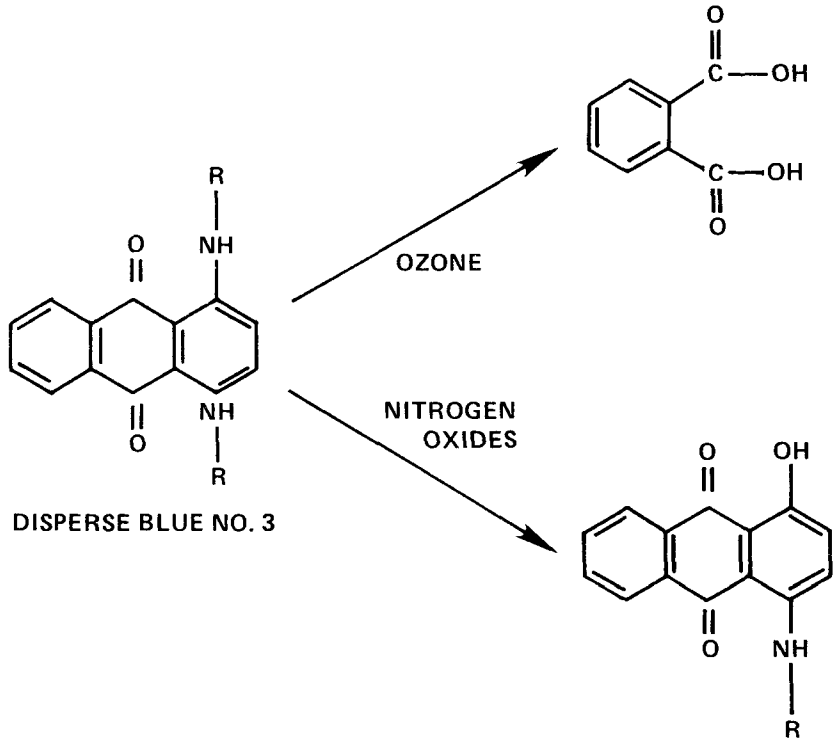

Figure 9-3. Reaction of anthraquinone dyes with ozone and with nitrogen oxides.
Source: Haylock and Rush (1976).

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; synergistic or additive effects of temperature, air moisture, and other pollutants; and even the degree of strain of the base fiber caused by folding or creasing.

For example, in a study of O_3 fading of anthraquinone dyes on nylon, Haylock and 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. Given this complexity and sensitivity, it is not practical to relate a specific mechanism of damage to a broad class of damage situations. Furthermore, it may not be necessary to do so. In most cases, some combination of dye, fibers, and protective treatments can eliminate major problems due to O_3 exposure and still provide the range of colors desired in the final products.

9.2.3 Paint

The mechanisms of paint damage due to O_3 have not been defined well: 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 due to chain scission and cross-linking. However, the data available on O_3 damage to paints come primarily from studies of surface erosion caused by gaseous pollutants. 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.

9.2.4 Other Materials

Although the effects of oxidants on other materials have been examined by several investigators, most of the limited information is qualitative and centers on mechanisms of effects. Sanderson (1975), in a review of the effects of photochemical smog on materials, included possible effects on plastic and asphalt. However, because these effects were recorded in a laboratory environment at extremely high O_3 levels, the indicated impacts have little direct applicability.

Haynie and Upham (1971) reported a possible beneficial effect of photochemical oxidants on the corrosion behavior of steel on the basis of field

study data. However, laboratory studies did not show any statistically significant effect of O_3 on steel corrosion.

Polyethylene, commonly used as electrical insulating material, may be adversely affected by ambient O_3 concentrations. Laboratory studies (National Research Council, 1977) have demonstrated by means of infrared and other techniques that terminal double bonds in polyethylene end groups are attacked by "ozonized" oxygen to form carboxylic acid groups and, through ruptures in the polymer chain, to produce short-chain dicarboxylic acids.

It is also known that atomic oxygen reacts with polyethylene at room temperature to produce a loss in weight and some morphologic changes. The work of Trozzolo and Winslow (1968) and Kaplan and Kelleher (1970) suggests that singlet oxygen also interacts with polyethylene to form hydroperoxides. Laboratory studies suggest that hydroperoxides may be the dominant oxidants that attack polyethylene or other materials in ambient air.

Despite the known interactions of oxidants with polyethylene and other polyolefins to form intermediate peroxy radicals, there is no evidence that the chemical reactions go far beyond the surface. It is believed that the effects of atmospheric O_3 on polyethylene insulation and other polyethylene products are negligible in comparison with the embrittlement caused by a combination of oxygen and sunlight. The mechanisms by which this embrittlement occurs probably involve sensitization to oxidation by absorption of ultraviolet (UV) radiation, by residual hydroperoxy and carbonyl groups in the polymer, and by surface deposits of aromatic sensitizers from polluted air. Deterioration of the electrical insulating properties of polyethylene by oxidation in some environments cannot be attributed to ambient O_3.

9.3 DOSE-RESPONSE DATA

Most dose-response studies are criticized for their reliance on artificial environments (laboratory settings) 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.

9.3.1 Elastomer Cracking

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 (Table 9-1): indoor and outdoor belt flex, indoor and outdoor wheel, and stress relaxation. They found that the behavior of rubber exposed to O_3 under laboratory conditions correlated well with the service behavior of tires in localities where atmospheric O_3 concentrations were high. The relative susceptibilities of different formulations of white sidewall rubber were generally similar, whether exposed under laboratory conditions to as much as 0.5 ppm (980 $\mu g/m^3$) of O_3 or exposed in the ambient air of the Los Angeles area, which had annual average O_3 concentrations near 0.04 ppm (80 $\mu g/m^3$) (U.S. Department of Health, Education, and Welfare, 1970). The exact exposure times, pollutant measurement methods, and statistical analyses were not reported.

Bradley and Haagen-Smit (1951) evaluated a natural rubber (NR) formulation for susceptibility to O_3 cracking. Strips were strained approximately 100 percent by bending and then exposed in a small chamber to 40,000 mg/m^3 (20,000 ppm) of O_3; these specimens cracked almost instantaneously and broke completely within 1 s. When these NR formulations were exposed to lower concentrations of O_3, different time periods were required for cracks to develop as shown in Figure 9-4, and this action increased with increasing temperature. Humidity and sunlight had little influence on cracking rate. According to the data in this figure, the initiation of cracks and subsequent deepening are controlled by the dose of O_3 (concentration x time).

Meyer and Sommer (1957) exposed thin polybutadiene specimens to constant load, ambient room air, and O_3. Specimens exposed in the summer to average O_3 concentrations of about 0.048 ppm (94 $\mu g/m^3$) broke after 150 to 250 hr. In the fall, at average O_3 concentrations of 0.042 ppm (82 $\mu g/m^3$), specimens failed after exposures of 400 to 500 hr. In the winter, at average O_3 concentrations of 0.024 ppm ($\sim$47 $\mu g/m^3$), failures occurred between 500 and 700 hr. Like the Bradley and Haagen-Smit study, these data also show the strong dependence of breakage on O_3 dose over the average time of exposure where failure occurred (average concentrations x time), but not in the same linear fashion. Dose-response levels in this study are noted parenthetically for the following concentrations: 0.048 ppm (9.6 ppm/hr); 0.042 ppm (18.9 ppm/hr); 0.024 ppm (14.4 ppm/hr).

TABLE 9-1. TIRE INDUSTRY EXPOSURE TESTS[a]

Test	Strain	Conditions	Reasons for Use
Belt flexing	dynamic at 4500 to 7500 flexures per hour	ozone chamber at 0.35 to 0.50 ppm, or outdoors for several days	rapid evaluation, variable conditions for screening sidewall compounds
Stress relaxation	dynamic or static; 25 percent extension at 90 cpm	ozone cabinet at 0.25 to 0.50 ppm for 16-hr increments	rapid evaluation, variable conditions for screening sidewall compounds
Outdoor wheel	dynamic and static; variable loads, inflation, and speed	Los Angeles area, high ozone for several weeks	quicker and cheaper than tire testing on autos in actual service
Indoor wheel	dynamic and static; variable loads, inflation, and speed	large ozone chamber at 0.01 to 0.35 ppm and -20 to 100° F, for days to weeks	strain most similar to actual service, quicker and cheaper than outdoor wheel
Tire tests on vehicles	dynamic and static; variable loads, inflation, and speed	extreme and typical service areas for 1/2 to 2 years	ultimate test of product life

[a]Adapted from Hofmann and Miller, 1964.

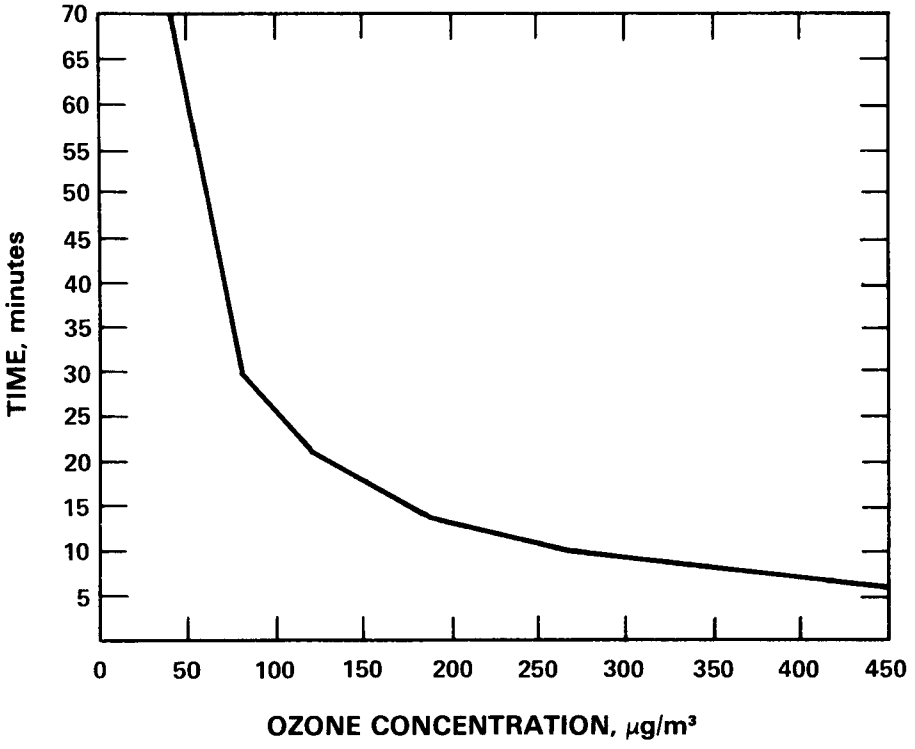

Figure 9-4. Relationship of cracking in rubber and ozone concentration: time to first sign of cracking at 4x magnification in natural rubber samples stressed at 100%.
Source: Bradley and Haagen-Smit (1951).

In describing a new test method for evaluating the O_3 sensitivity of elastomers, Edwards and Storey (1959) presented data demonstrating the O_3 resistance of two styrene-butadiene rubber (SBR) compounds (Polysar S and Polysar Krylene). Both compounds were exposed without and with different levels of antiozonant protection to 0.25 ± 0.05 ppm of O_3 (490 ± 98 $\mu g/m^3$) at 120°F (49°C) under 100 percent strain twice the original sample length. The results are presented in Table 9-2. Without antiozonants, a linear relationship is indicated between O_3 dose (ppm/hr) and cracking depth. The coefficient of determination for the linear regression for both materials was 0.98 compared with 0.92 for the exponential fit. Note that the Polysar S compound displays much greater resistance to the effects of O_3 than does the Polysar Krylene compound. Nevertheless, increasing the amount of antiozonants significantly reduced the rate of cracking for both 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 percent) for 250, 500, and 1000 hr to O_3 concentrations of 160 $\mu g/m^3$ and 1000 $\mu g/m^3$. The O_3 level was found to be statistically significant in the rate of cracking of this rubber. However, cracking rates are not directly proportional to O_3 concentrations for these two levels. The average results with respect to strain and O_3 level are given in Table 9-3.

Using the mean cracking rate calculated after long-term (1000 hr) exposure to conditions representative of the primary air quality standard for O_3 and the annual average standard for nitrogen dioxide (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. Additional time would be necessary to attack the cords. For this particular premium tire, therefore, sidewall failure from O_3 damage does not appear to be the cause of reduced tire life. However, the casing might have questionable value for retreading. Tread wear, rather than sidewall failure, probably determines the life of a typical rubber tire, and the rubber used in tire treads is generally more resistant to O_3 than that in the sidewalls.

Veith and Evans (1980) investigated the effect of atmospheric pressure on the cracking rate of rubber as tested in O_3 chambers. It was found that a change in barometric pressure alters the rate of cracking. Interlaboratory

TABLE 9-2. EFFECTS OF OZONE ON DIFFERENT SBR POLYMERS CONTAINING VARIOUS ANTIOZONANT CONCENTRATIONS

Polymer	Antiozonant (pph)	Crack depth (10^{-3} in.), length of exposure (hr) 19	27	43	51	Cracking depth rate (10^{-4} in./hr)	(μm/hr)
Polysar S ("Hot" SBR)	0.0	1.37	2.42	4.20	4.65	0.92	2.34
	0.5	0.95	1.90	3.10	3.52	0.69	1.75
	1.0	0.50	0.75	1.47	1.95	0.35	0.89
	2.0	0.25	0.25	0.45	0.78	0.13	0.33
Polysar Krylene ("Cold" SBR)	0.0	2.17	4.52	7.25	7.90	1.58	4.01
	0.5	1.25	2.02	3.75	4.50	0.85	2.16
	1.0	1.05	1.50	2.24	2.90	0.57	1.45
	2.0	0.50	0.75	1.00	1.18	0.24	0.61

Source: Edwards and Storey, 1959.

TABLE 9-3. CRACKING RATES OF WHITE SIDEWALL TIRE SPECIMENS

Ozone concentration μg/m³ (ppm)	Strain percent	Mean cracking rate ± standard deviation mm/yr	μm/hr
160 (0.08)	10	11.66 ± 7.32	1.33
	20	17.00 ± 10.45	1.94
1000 (0.5)	10	15.38 ± 5.38	1.76
	20	25.74 ± 8.23	2.94

Source: Haynie et al., 1976.

comparisons were made among facilities at different geographic elevations and thus significantly different atmospheric pressures. It was found that a 16-percent difference in cracking rate or in the extent of cracking at a fixed O_3 concentration could occur. In an effort to correct the problem and standardize the testing techniques, Veith and Evans (1980) recommended that O_3 content in accelerated chamber testing be expressed in terms of O_3 partial pressure (in Pa units) rather than simply in terms of concentrations.

Gandslandt and Svensson (1980) evaluated the stress test methodology used to estimate the O_3 resistance of rubber compounds. This test measures the decrease in the isoelastic force of stressed rubber exposed to O_3. The authors suggested that materials should be prestressed in an O_3-free atmosphere for at least 72 hr before testing, because the complicating effects of the natural relaxation of the material's isoelastic force constant decreases exponentially with time. The effects of this natural relaxation mechanism become insignificant after 2 to 3 days of prestressing compared to the effects caused by O_3 cracking.

Ten different mixtures of three rubber compounds, NR, SBR, and CR (a compound not defined by the authors) were tested with the isoelastic force method (Gandslandt and Svensson, 1980). The O_3 protection afforded each rubber formulation is summarized in Table 9-4. After a relaxation time of 70 hr in an O_3-free atmosphere (two hours less than their prescribed criteria for sample exposure), the samples at 50-percent elongation were exposed to O_3 concentrations of 0.5 ppm (980 $\mu g/m^3$) at 30°C. The time to 10-percent and 20-percent 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 203, 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 9-5. Compounds SS 202 B (Figure 9-5a) and SS 200 C (Figure 9-5b), both protected with wax and antiozonant, showed fairly good resistance when gauged by the

TABLE 9-4. PROTECTION OF TESTED RUBBER MATERIALS

Rubber formulation		Unprotected	Protected	
			Wax	Antiozonant
GL 2073	B, C		X	X
	G		X	
	D	X		
SS 200	A, C		X	X
	B	X		
SS 202	A	X		
	B		X	X
SS 203		X		

Source: Gandslandt and Svensson, 1980.

10-percent and 20-percent stress relaxation tests but failed after approximately 50 hr and 58 hr of exposure, respectively. On the other hand, compounds SS 203 and SS 200 A, 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 9-5b.

Davies (1979) reported on the effects of ozone 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 product will be inadequate. Ozone attack on synthetic polyisoprene 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_3 concentrations of 0.15 ppm (294 $\mu g/m^3$), but the adhesion of the NR/SBR blend decreases by approximately 30 percent. Large reductions (on the order of 70 percent) 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

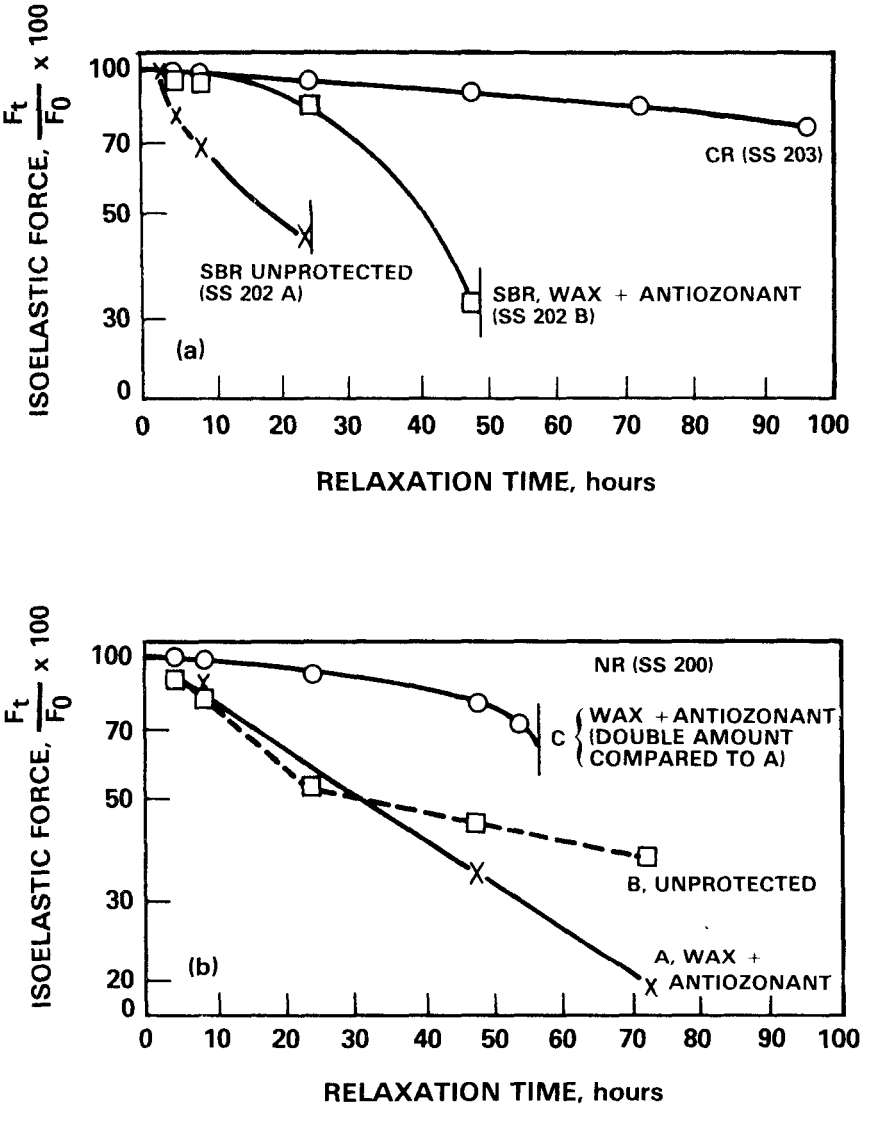

Figure 9-5. Relaxation of rubber compounds in O_3 is affected by the combination of rubber formulation and type of O_3 protection. Compounds were tested at O_3 concentration, 0.5 ppm (980 $\mu g/m^3$); temperature, 30° C; elongation, 50%. Vertical line at the end of a curve means total failure, and vertical axis represents relaxation where F_0 is the initial force; F_t is the force after time, t.
Source: Gandslandt and Svenson, 1980.

levels of O_3 and humidity are summarized in Table 9-5. The adhesion of the SBR compound is superior to that of the other two compounds, which were greatly affected by increased RH.

TABLE 9-5. EFFECT OF OZONE AND HUMIDITY ON INTERPLY ADHESION[a]

Compound	Initial adhesion	Final adhesion: 0.15 ppm O_3 (294 µg/m^3) 30% RH	Final adhesion: 0.25 ppm O_3 (490 µg/m^3) 30% RH	Final adhesion: 0.15 ppm O_3 (294 µg/m^3) 60% RH
NR	5	2-3	1	1
IR	5	4-5	2-1	1
SBR	5	4-5	3-4	3-4

Source: Adapted from Davies, 1979.

[a]Adhesion is rated from 1 (bad) to 5 (excellent), based on a visual scale standardized by the authors.

[c]All exposures were 16 hr in duration.

Davies examined antiozonants, antioxidants, and fast-blooming waxes as means of protecting NR compounds from sunlight and O_3 attack and the subsequent development of the films that lead to poor adhesion between plies. The results of these evaluations are presented in Table 9-6. Of the samples exposed after 16 hr at O_3 concentrations of 0.15 ppm (294 µg/m^3), only those protected by the fast-blooming waxes were found to resist O_3 and have excellent adhesion between plies (Table 9-6). Antiozonants and antioxidants in the NR did not aid interply adhesion (Tables 9-6). Davies (1979) theorized that antiozonants and antioxidants react with ozonized rubber and form a protective film against further attack by O_3. However, this film also apparently acts as a barrier to proper adhesion between plies. Davies noted that after exposure to sunlight alone, the antioxidants generally maintained good adhesions, but the waxes gave only fair protection. He concluded that the combination of a fast-blooming wax and an effective antioxidant or antiozonant is necessary to protect NR from O_3 attack and sunlight.

TABLE 9-6. EFFECT OF ANTIOZONANTS, ANTIOXIDANTS, AND FAST-BLOOMING WAXES ON INTERPLY ADHESION IN NATURAL RUBBER[a]

Antiozonant[b,d]	Rating[c]
Untreated	1
ETMQ	1
6 PPD	1
1 PPD	1
77 PPD	1
TBMP	2
TMQ	2
Wax 1	5
Wax 2	5

Source: Davies, 1979.

[a]Ozone resistance rated from 1 (bad) to 5 (excellent), based on a visual scale standardized by the author.

[b]All substances were given an initial rating of 5.

[c]Rating assigned after 16-hr exposure to 0.15 ppm (294 $\mu g/m^3$) of O_3.

[d]See appendix for explanation of abbreviations.

Wenghoefer (1974) studied the effects of O_3 on adhesion and the climatic sensitivity of tire cords dipped in resorcinal-formaldehyde latex (RFL). Climatic sensitivity was described as summer sickness, a problem affecting cords primarily during hot, humid weather. Many fibers and dip formulations were studied to determine their sensitivity to O_3, humidity, nitrogen dioxide (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 (2940 $\mu g/m^3$) and to relative humidity (RH) levels ranging from 20 to 90 percent. Adhesion deteriorated due to 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 due to O_3 and the combined effects of O_3 and humidity were most notable in the first 6 hr of exposure. The detrimental effects of heat, NO_2, and the synergistic interaction of NO_2 and humidity were much less pronounced. Table 9-7 summarizes the elastomer dose-response studies.

9.3.2 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

TABLE 9-7 DOSE-RESPONSE STUDIES ON EFFECTS OF OZONE ON ELASTOMERS

Conditions	Material/Product	Pollutant	Concentration, ppm	Measurement method	Environmental exposure	Variables	Dose, ppm-hr	Effects	Comment	Reference
Laboratory/ Field	Automotive tires	Ozone	0.25 to 0.5	NA	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.	Hoffman and Miller, 1969
		Ambient air	0.04 O_3 (annual average)	NA	>1 yr	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	NA	3 to 65 min	Physical stress	~0.02 to 0.03	Surface cracking	Test was designed to establish dose/response curves on O_3-sensitive rubber for use as an analytical method.	Bradley and Haagen-Smit, 1951
Controlled field	Rubber tires and various polymers	Ambient air	0.023 to 0.048 O_3	NA	150 to 700 hr	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 Plysar Krylene with and without antiozonants	Ozone	0.25	NA	19 to 51 hr	120°F, 100% strain	4.75 to 12.75	Percent antiozonant was related to cracking depth rate	Demonstrated dose/response linear relationship for ozone on unprotected rubber.	Edwards and Storey, 1959

TABLE 9-7 (cont'd). DOSE-RESPONSE STUDIES ON EFFECTS OF OZONE ON ELASTOMERS

Conditions	Material/Product	Pollutant	Concentration, ppm	Measurement method	Environmental exposure	Variables	Dose, ppm-hr	Effects	Comment	Reference
Laboratory	White sidewall tire specimens	Ozone	0.08 to 0.5	NA	250 to 1000 hrs	10 and 20% strain	20 to 500	Mean cracking rates were determined for different stress and ozone levels.	Detailed data not available to verify author's statement that 2-1/2 years of ambient conditions were required for ozone cracks to penetrate cord depth.	Haynie et al., 1976
Laboratory	Ten different NR, SBR, CR formulations with and without protection	Ozone	0.5	NA	Up to 300 hr	30°C	Up to 50	Time to 10 to 20% relaxation	Both formulation and protection affected relaxation.	Glandslandt and Svensson, 1980
Laboratory	Several NR/SBR blends with and without protection	Ozone	0.05 to 0.15	NA	~3 to 16 hr	Sunlight, humidity	~0.15-2.4	Interply adhesion affected at 0.05 ppm and above	Both waxes and antiozonants needed for protection against sunlight plus ozone.	Davies, 1979
Laboratory	Tire cords (66 nylon; Dacron polyester; Kevlar aramid)	Ozone	0 to 1 5	NA	0 to 48 hr	UV light; heat (100°C); RH (20-90%); NO_2	up to 72	RFL adhesion loss occurred primarily during 6-hr exposure to high RH and 0.2 ppm O_3.	Synergism between O_3 and RH; RFL deterioration occurred at surface.	Wenghoefer, 1974
		Nitrogen dioxide	0 to 20	NA						

important to color fading, the effects of O_3 were noted by Salvin and Walker (1955) nearly three decades ago. The phenomenon was termed O-fading. The primary products affected were permanent press garments (polyester and cotton) and nylon carpeting. In permanent press garments, dye fading occurs primarily at the creases and folds. The fading of nylon carpeting occurs in the presence of high RH and depends on the dyes used. Ozone fading most affected the blue and red disperse dyes of the anthraquinone series but not the azo series of dyes.

Salvin and Walker (1955) tested disperse dyes that were resistant to the effects of nitrogen oxides. They exposed a series of drapery products to confirm their resistance to the dye fading that was thought to be attributable to NO_2. Different types of dyes ranging in vulnerability to nitrogen oxides were exposed in Pittsburgh, Pennsylvania (an urban region of high NO_2 concentrations), and Ames, Iowa (a suburban area with low NO_2 concentrations). After 6 months of exposure, the investigators found that NO_2-resistant dyes had performed well in Pittsburgh but poorly in Ames, indicating the influence of another fading agent. By using a combination of laboratory chamber studies and outdoor exposure, Salvin and Walker (1955) demonstrated that O_3 was the pollutant responsible for the change. Blue anthraquinone dyes and certain red anthraquinone dyes were markedly bleached after exposure to just 0.1 ppm (196 $\mu g/m^3$) 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 diphenylethylenediamine 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.

To explain much of the fading of certain dyed fabrics during lightfastness testing and service exposure trials, Schmitt (1960, 1962) also invoked the concept of O_3 fading. In studies to demonstrate colorfastness of certain dyes when exposed to sunlight, Schmitt exposed 38 color specimens for 12 months at Phoenix, Arizona, and Sarasota, Florida, and for 7 months in Chicago, Illinois. Specimens exposed included direct dyes on cotton, acid dyes on nylon, acid dyes on wool, disperse dyes on acetate, disperse dyes on acrilan, disperse dyes on dynel, acid dyes on dynel, cationic dyes on orlon, and disperse dyes on dacron.

Each specimen was exposed to a predetermined amount of direct sunlight, measured by a pyroheliometer, and then examined in the laboratory to measure the amount of fading. Schmitt found that samples given equal amounts of sun exposure tended to fade more in Florida than in Arizona. He concluded that the higher RH was a contributory factor and that atmospheric contaminants were the principal factor in accelerated fading. Schmitt also exposed certain dyed fabrics in covered test frames where the effect of sunlight would be eliminated. After 24 days of exposure in Florida, Schmitt found that even in covered frames, fading was of the same magnitude as noted with samples exposed to sunlight. His work also demonstrated the importance of RH in the dye-fading mechanism by suggesting that the increased moisture content of the fibers promoted and accelerated the absorption and reaction of pollutants with vulnerable dyes.

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, Florida; Phoenix, Arizona; Cincinnati, Ohio; and four urban-rural combinations: Chicago and Argonne, Illinois; Washington, D.C. and Poolesville, Maryland; Los Angeles and Santa Paula, California; and Tacoma and Purdy, Washington. Among those fabrics exhibiting a high degree of fading at both urban and rural sites in the first 6 months, fading was much greater at the urban sites than 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 rate occurred in samples exposed in Los Angeles, Chicago, and Washington, D.C. 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. However, editorial problems between the text and tabular material tend to confuse the authors' discussion.

Ajax and co-workers also exposed the fabrics to irradiated and nonirradiated auto exhaust with and without sulfur dioxide (SO_2) for 9 hr/day for six consecutive days. From the results of this chamber study, they 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." Although their conclusions are easily substantiated in the research literature, the O_3 levels measured in their chamber are

questionable. The daily 9-hr average O_3 concentrations (measured by neutral KI, Mast instrument) were identical for irradiated (UV) and nonirradiated exhaust (0.02 ppm); irradiated exhaust plus SO_2 produced 0.55 ppm of O_3.

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 and four rural sites used in the Ajax studies. The study was carried out over a 2-year period, in eight consecutive 3-month 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, and the amount of fading varied among metropolitan areas and seasons. Samples exposed in Chicago and Los Angeles demonstrated the greatest degree of fading, and those exposed in Purdy, Washington, and Phoenix showed the least amount. The small amount of fading evidenced by the samples exposed at extreme temperature and/or humidity indicated that these factors by themselves have no effect on fading. The sample 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_2 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, which examined fading as a function of six independent variables (NO_2, SO_2, O_3, nitrogen oxide, temperature, and humidity). After eliminating those fabrics that developed only trace fading and those for which the regression was not significant, the analysis focused on 25 fabric dye samples, 23 of which showed SO_2 to be a significant variable. Ozone was also a significant contributor to fading of eight dyed fabrics and NO_2 to fading of seven dyed fabrics. The dominance of SO_2 as a factor in fading may have been complicated by soiling.

The 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_3: 0.05 ppm (98 $\mu g/m^3$) and 0.50 ppm (980 $\mu g/m^3$). The laboratory studies demonstrated that high O_3 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 exposed to O_3 concentrations of 0.05 ppm (98 $\mu g/m^3$). These levels are similar to those frequently found in metropolitan areas. The laboratory study also demonstrated that high RH (90 percent) is a significant factor in promoting and accelerating O_3-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_3 concentration (980 and 196 $\mu g/m^3$; 0.5 and 0.1 ppm, respectively), high and low RH (90 percent and 50 percent), and high and low concentrations of NO_2 and SO_2. The three fabrics selected for this study were a royal blue rayon-acetate, a red rayon-acetate, and a plum cotton duck. The samples were exposed in the chamber for periods of 250, 500, and 1000 hr; the degree of fading was measured with a color difference meter. The fading of the plum-colored material was statistically related to the RH and NO_2 concentration. For the red and blue fabrics, only RH appeared to be a significant factor. The effects of concentrations of ozone on the amount of fading of these dyes were not statistically significant, even after exposure for 1000 hr to 980 $\mu g/m^3$ (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 and Olive II was exposed to varying levels of temperature, RH, and O_3. Material dyed with Olive I and exposed at 70 percent RH, 40°C (104°F), and 0.2 ppm (392 $\mu g/m^3$) of O_3 showed visible fading after 16 hr of exposure. At 90 percent RH, similar fading occurred in less than 4 hr. Under the same RH and temperature conditions, increasing the O_3 concentration from 0.2 ppm to 0.9 ppm (392 to 1760 $\mu g/m^3$) resulted in a parallel increase in fading. Samples in knitted sleeve form demonstrated much greater susceptibility to O_3 attack than samples exposed in skein form.

Using Disperse Blue 3 and Disperse Blue 7 dyes exposed to constant conditions of 40°C (104°F), 90 percent RH, and 0.2 ppm (392 $\mu g/m^3$) of O_3, 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 necessity of high temperature and high humidity for O_3 fading to occur in nylon was further confirmed by the additional work of Haylock and Rush (1978). Their studies showed a good correlation between accelerated O_3 fading in the laboratory and in outdoor, in-service exposure, during which temperature and humidity extremes were common. However, control samples exposed indoors, where temperatures and humidities were lower, did not exhibit nearly the same magnitude of fading as the laboratory samples.

Heuvel et al. (1978) investigated the importance of the physical nature of Nylon 6 yarns on the O_3 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 (980 $\mu g/m^3$) of O_3 at 40°C and an RH of 85 percent. Heuvel et al. found that the microfibril diameter and specific surface area of the fiber were the fiber characteristics most closely related with O_3 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 atmospheric contaminant fading by O_3 of carpets in a home versus the American Association of Textile Chemists and Colorists (AATCC) Standard Test Method 129, Colorfastness to Ozone in the Atmosphere Under High Humidities. (Measurements were also taken to compare the fading due to oxides of nitrogen.) 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 months 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.

Attempts were made to relate the color change for each exposure period to outside temperature and RH, but the statistical analyses of the data showed no correlation between outside weather conditions and in-home fading by either contaminant. Geographical location appeared to have a significant effect on fading. Test samples from sites in the southeast and northeast showed far more O_3 fading than 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_3 during July, August, and September than in January, February, and March.

Typically, O_3 levels indoors are higher during the summer, when doors and windows tend 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, as shown in Table 9-8. In a sample that performs satisfactorily through 1.08 cycles of exposure in AATCC Test 129, there is a 98-percent probability against in-service fading over a 1-year period. A sample that performs satisfactorily through only 0.6 test cycles of fade has only a 90-percent probability of satisfactory performance after 1 year of in-service exposure.

Kamath et al. (1982) 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. studied the diffusion and destruction of C.I. Disperse Blue Dye 3 on Nylon 6 continuous filament yarn measuring about 45 μm in diameter. With this method, they 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 (392 $\mu g/m^3$) for 2 to 120 hr at a temperature of 40°C and RH levels of 90 percent, 85 percent, and 65 percent. 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. As shown in Figure 9-6, the dependence of fading rates on humidity was substantial. Even slight rises in humidity from 85 percent to 90 percent caused a significant increase in the extent of fading. At 65 percent 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.

Kamath et al. (1982) used a surface reaction model to attempt to explain the amount of fading (dye loss) due to O_3 exposure. However, they found that this approach could explain only a very small portion of the loss. They concluded that the dye distribution profile across the fiber resulted from

TABLE 9-8. COLORFASTNESS OF TEST SAMPLES COMPARED WITH COLORFASTNESS OF IN-USE CARPETING

Probability of acceptable colorfastness of in-use carpeting	Number of test cycles equivalent to 1 year of in-use service	Number of test cycles equivalent to 5 years of in-use service
99	1.36	6.80
98	1.08	5.40
95	0.80	4.00
90	0.60	3.00
80	0.42	2.10
75	0.37	1.85
70	0.33	1.65
60	0.27	1.35
50	0.22	1.10

Source: Adapted from Nipe, 1981.

penetration of O_3 into the fiber itself. Subsequent reaction of this O_3 with dye diffusing toward the surface of the fiber was therefore considered to be an important mechanism in O_3 fading of anthraquinone dyes in nylon.

Salvin (1969) reported that O_3 and (to a lesser extent) NO_2 caused dye fading of cotton/permanent press fabrics. As summarized by Dorset (1975), O_3 was found to be the major fading agent, with nitrogen oxides also capable of causing fading, though to a lesser extent. The fading mechanism occurs as a result of the curing operation and involves the disperse dyes on the polyester fibers rather than the vat dyes on cotton. During curing, some disperse dyes partially migrate to the permanent press finish, which is a combination of reactant resin, catalysts, softeners, and nonionic wetting agents. This migration occurs preferentially along the folds and creases, causing fading to predominate in these areas. The disperse dyes migrate to the solubilizing agents in the finish, a medium in which fading by air contaminants can easily occur. 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 catalyst in the permanent press process, and using different surfactants and softeners. The use of magnesium chloride as a catalyst makes O_3-sensitive dyes more sensitive to O_3 and less fast to washing (Dorset, 1975). When the catalyst is zinc nitrate, dyes are more washfast and resistant to O_3 fading. Thus, the amount of dye fading might not be a function only of O_3 concentration but also of the number of times the garment is washed. The present use

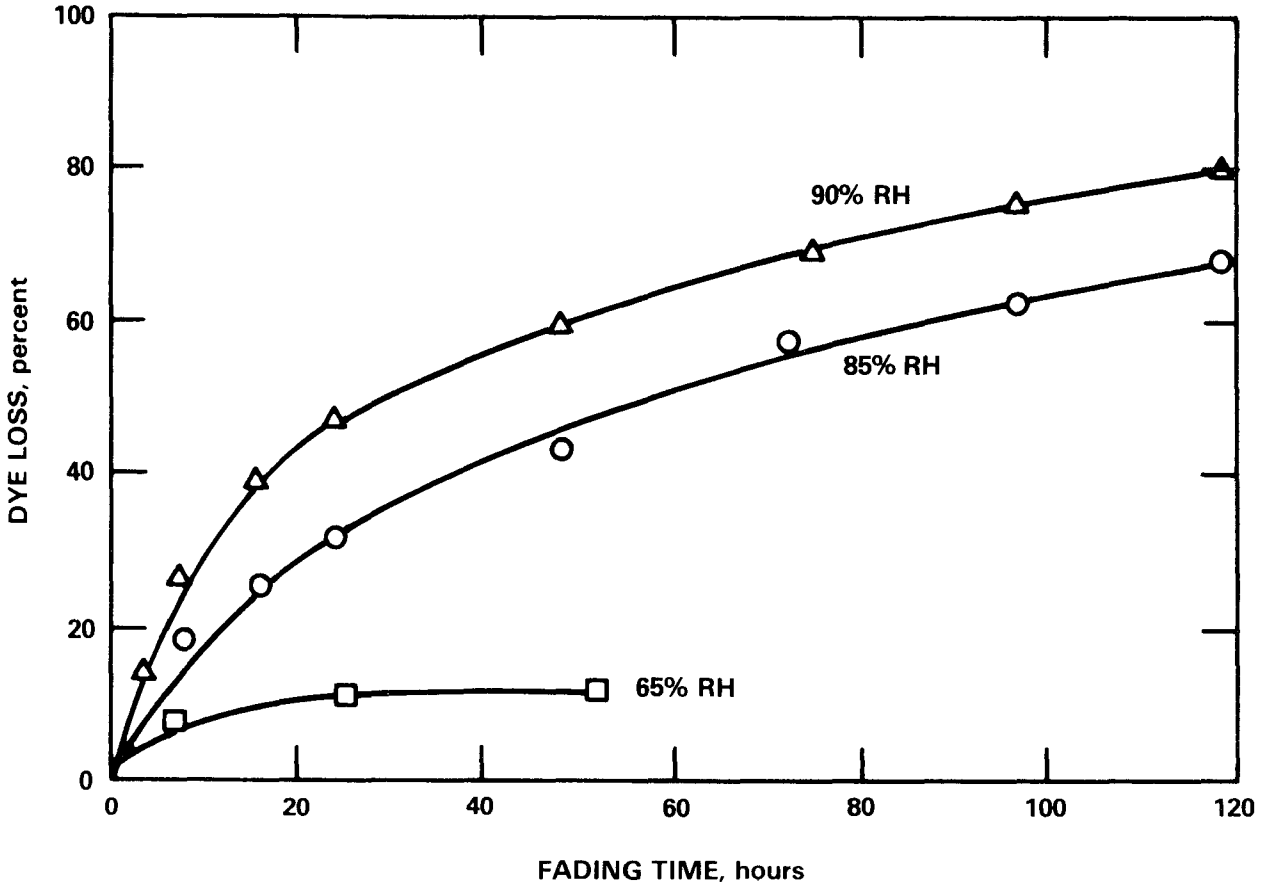

Figure 9-6. Effects of relative humidity (RH) on fading of C.I. Disperse Blue 3 (CIDB-3) in Nylon 6 after exposure to 0.2 ppm ozone. Source: Adapted from Kamath et al., (1982).

of a zinc nitrate catalyst appears to have generally eliminated the problem of the prefading of dyes in permanent press fabrics due to the effects of O_3. A summary of the dye fading studies is presented in Table 9-9.

9.3.3 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_3 at normal ambient levels is generally small by comparison.

In a review of the effects of weather and atmospheric pollutants on textiles, Warty (1977) outlined a number of damage mechanisms, the complexity of the mechanisms, and their effects on manmade and natural fibers. The damage mechanisms reviewed included those involving soiling, O_3, sunlight, microbial attack, humidity, and SO_2. Natural fibers such as jute, flax, hemp, sisal, and coconut, which have a multicellular structure and contain lignin, are much more resistant to the effects of weathering than is cotton, a natural fiber with no lignin. However, even in amounts as small as 0.2 percent, lignin will cause yellowing or browning of the material when exposed to light. Compounds added to increase resistance to one weathering agent may actually accelerate the damage caused by others. For example, phenolic compounds used as antimicrobial agents accelerate fabric degradation due to the effects of light.

Cellulose fibers, whether natural or manmade, are very sensitive to sunlight in the UV portion of the spectrum. Ultraviolet light causes disruption of the chemical bonds within the fiber itself. Even in protected fabrics, a secondary photochemical reaction can occur with certain dyes and pigments. Bleached fabrics, which are much more resistant to microbial attack, tend to be much more sensitive to the action of sunlight. The bleaching weakens molecular linkages, making the carbon-carbon and carbon-oxygen bonds much easier to break when exposed to sunlight.

Synthetic fibers, though highly resistant to microbial attack, are still adversely affected by UV light. Degradation can be minimized or avoided by use of UV-absorbing additives applied as coatings or in the manufacturing process. Warty (1977) concluded that, because the weathering process is a very complex interaction of several variables, it is difficult to rely on a single test method to define performance.

TABLE 9-9. SUMMARY OF DYE FADING STUDIES

Dye and fabric	Dose and test conditions	Effects	Reference
Disperse dyes on drapery material	Six-month field study in suburban area	Fading related to ozone concentrations	Salvin and Walker (1955)
Anthraquinone dyes	Ozone concentration of 0.1 ppm (196 $\mu g/m^3$) in the laboratory	Marked bleaching	Salvin and Walker (1955)
Sixty-nine dye/fabric combinations	Outdoor exposure in light-free cabinets at 11 sites	Fading generally corresponding to seasonal variations in ozone levels	Ajax et al. (1967)
Various dyed fabrics	Eight 3-month exposure periods in the field in urban and rural sites	Ozone a contributor to fading of 8 of 25 samples	Beloin (1972, 1973)
Thirty dyed fabric samples	Ozone levels of 0.05 ppm (98 $\mu g/m^3$) and 0.50 ppm (980 $\mu g/m^3$) in the laboratory	More fading at higher ozone level. Fading in about one-third of sensitive fabrics at lower level. High RH a significant factor	Beloin (1972, 1973)
Drapery fabrics: royal blue rayon-acetate, red rayon-acetate, and plum cotton duck	Ozone levels of 0.1 ppm (196 $\mu g/m^3$) and 0.5 ppm (980 $\mu g/m^3$) and RH of 50 and 90 percent for 250, 500, and 1000 hr in the laboratory	No fading at any dose	Haynie et al. (1976), Upham et al. (1976)
Anthraquinone dyes on nylon fibers	Various levels of RH and ozone (0.2-0.9 ppm, 392-1760 $\mu g/m^3$) in the laboratory	Fading varying markedly with RH and ozone concentration at 40°C. Surface area of fibers also important. Findings correlated with field study results	Haylock and Rush (1976, 1978)

TABLE 9-9. SUMMARY OF DYE FADING STUDIES (continued)

Dye and fabric	Dose and test conditions	Effects	Reference
Disperse blue dyes on Nylon 6 yarns	Ozone level of 0.5 ppm (980 μg/m^3) at 40°C and RH of 85 percent in the laboratory	Microfibril diameter and specific surface area of fibers related to ozone fading	Hueval et al. (1978)
Disperse and acid dye formulas on Nylon 6 and 66 carpet samples	Samples exposed in homes in various locations tested every 3 months for 3 years.	More ozone fading of samples in southeast and northeast than in west and far west. More ozone fading in summer than in winter	Nipe (1981)
C.I. Disperse Blue Dye 3 on Nylon 6 yarn	Ozone concentration of 0.2 ppm (392 μg/m^3) for 2-120 hr at 40°C and RH levels of 65, 85, and 90 percent in the laboratory	Initial fading occurred near surface of fiber. Ozone penetration an important mechanism in fading. Rate of fading greatly affected by RH	Kamath et al. (1982)

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_3 in the deterioration of cotton textiles. These investigators exposed samples of duck and print cloth to air containing 0.02 and 0.06 ppm (39 and 118 $\mu g/m^3$) of O_3. 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 percent. Similar fabric samples were exposed to similar O_3 concentrations with no moisture added, and another control group was similarly wetted but exposed to clean (O_3-free) air. After exposure to O_3, the wetted samples showed a loss in breaking strength of approximately 20 percent. The wet print control cloth showed a loss in breaking strength of only half this amount. The study showed that low levels of O_3 degrade cotton fabrics if they are sufficiently moist. Bogaty et al. surmised that an estimated 500 to 600 days of natural exposure might be required to reach a similar stage of degradation due to a 50-day exposure to O_3 alone. Because unprotected fabrics typically reach a much more advanced state of decay after such long exposures to weathering, Bogaty et al. concluded that the effect of O_3 is slighter than that of other agents. Although not noted by Bogaty et al., the O_3 and increased moisture may have caused the formation of hydrogen peroxide (H_2O_2), which could account for the loss in breaking strength.

Morris (1966) also studied the effects of O_3 on cotton. Samples were exposed in the absence of light to 0.5 ppm (980 $\mu g/m^3$) of O_3 [compared to a National Ambient Air Quality Stadard (NAAQS) of 235 $\mu g/m^3$ or 0.12 ppm] for 50 days in a chamber maintained at 70°F (21°C) and 72 percent 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_3 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_3 and the amount of fading and degradation of moist, dyed fabrics exposed to O_3. They exposed samples of print cloth, dyed with CI Vat Blue 29, in a chamber to a continuous supply of purified air containing O_3 concentration levels of 1 ± 0.1 ppm (1960 ± 196 $\mu g/m^3$). The samples were exposed at room temperature (25°C) in the 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 percent, and that of the soaked fabrics, 9 percent. 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 the 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 charcoal-filtered air contaminated with 0.2 ppm (392 $\mu g/m^3$) of O_3 at 48°C (118°F) and 39 percent RH. During exposure, the fabric samples were sprayed with water for 18 min every 2 hr. 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 et al. 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. But the degree of difference in the change of fabric properties between those exposed to light and air and those exposed to light and air containing 0.2 ppm (392 $\mu g/m^3$) of O_3 was not significant.

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 like H_2O_2. 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. A similar view was proposed by the National Academy of Sciences (National Research Council, 1977) in a review of the effects of O_3 and other photochemical oxidants on nonbiological materials.

9.3.4 Paint Damage

A paint surface may suffer several types of damage that affect its usefulness, including cracking, peeling, erosion, and discoloration. 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. Studies of paint cracking and peeling have focused on the effects of moisture and have not dealt with the possible influence of ambient pollutants.

Several damage functions for O_3-induced erosion of paint have been reported in the literature. Such reports are based on either accelerated chamber studies or long-term outdoor exposure studies. Unfortunately, all studies to date have significant flaws that render their results highly questionable. 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 outdoor exposure study to date has been able to match all factors exactly to separate the impact of O_3 from the other factors.

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_2, NO_2, and O_3 in various combinations. Statistically significant effects of O_3-caused damage were observed on the vinyl coil coating and the acrylic coil coating. There was a positive interaction between O_3 and RH on the vinyl coil coating and a positive direct O_3 effect on the erosion rate of the acrylic coil coating. However, the rate of erosion was low, and both vinyl and acrylic coil coatings were shown to be very durable. Coatings as thin as 20 μm should last more than 20 years before requiring replacement because of the effects of O_3. A linear regression for the acrylic coil coating data gives:

$$\text{Erosion rate} = 0.159 + 0.000714\ O_3 \qquad (9\text{-}1)$$

where erosion rate is in μm/yr and O_3 is $\mu g/m^3$.

Although the O_3 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 (235 $\mu g/m^3$) of O_3, the erosion rate is 0.33 μm/yr. At an average annual O_3 level of 100 $\mu g/m^3$, 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_3 and SO_2. After exposure, the panels were examined by measuring erosion, gloss, surface roughness, tensile strength, attenuated total reflectance (ATR), and the surface effects revealed by scanning electron microscopy and infrared examination. The panels were examined after 0, 400, 700, and 1000 hr of chamber exposure (considered as equivalent to 0, 200, 350, and 500 days, respectively, of exposure).

The relative sensitivity of a coating to pollutant damage depended on the particular test used to define the damage. For example, when comparing oil-based house paint with automotive paint, the former showed the greatest ATR change but no change in gloss, but the latter exhibited little ATR change and the largest change in gloss. In general, exposures to 1 ppm (1960 $\mu g/m^3$) of O_3 produced greater increases in erosion rates than did clean air. However, concentrations of this magnitude do not represent typical ambient exposure levels of O_3. At the more representative level of 0.1 ppm (196 $\mu g/m^3$), O_3 did not produce statistically significant increases in erosion rates.

In conjunction with the 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, North Dakota); a moderately polluted atmosphere (Valparaiso, Indiana); a heavily polluted (SO_2) atmosphere (Chicago, Illinois); and a high-oxidant, moderately polluted atmosphere (Los Angeles, California). 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. Since 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_2 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 are likely reacting with the organic binder of the coil coating and oil house paints. However, a mechanism for this reaction was not developed from this exposure study.

In an outdoor exposure test of the effects of air pollutants on material, 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, Missouri. In conjunction with the material exposure, measurements of meteorological parameters, O_3, oxides of nitrogen, total hydrocarbons, total sulfur, SO_2, and hydrogen sulfide were made. The investigator used a regression model to relate the corrosion rates (i.e., rate of change of damage) to the meteorological parameters, air quality parameters, and length of exposure. There is some uncertainty in the results of the analysis because the independent variables show a degree of correlation with each other. Nevertheless, the results of several of the material pollutant relationships are worth noting. For the latex house paint, concentrations of atmospheric O_3 were found to contribute significantly more to the accelerated erosion of the painted surface than the length or direction (north, south) of the sample's exposure. The length of exposure and sulfate were the most important factors in explaining the erosion of oil-based paint. Mansfeld suggested that these effects indicate the different responses and behaviors of the two types of paint.

Some of the color pigments used in commercial paints and dyes are also used in artists' paints. Shaver et al. (1983) studied the colorfastness of several of these pigments exposed to 0.40 ppm of O_3 for 95 days under controlled temperature and humidity conditions. Several of the 1,2-dihydroxyanthraquinone-type pigments faded considerably, but no dose-response curves could be determined. Furthermore, the effects on pigments combined with the various binders used in actual applications has not been investigated. Nevertheless, because works of art have an indefinite service life compared with, for example, the short service life for textiles, further research is needed before estimates of the type and amount of damage to paintings and prints are possible.

The effects of O_3 on paint are still being studied. The preliminary results of Mansfeld's work indicate that there may be a statistically significant relationship between the erosion of latex paint, RH, and O_3. However, further studies are necessary before a cause-and-effect relationship can be conclusively established.

9.4 ECONOMICS

9.4.1 Introduction

Damage to nonbiological materials from ozone is usually expressed in terms one or both of the following two general classes of costs to producers and consumers: (1) ozone accelerated replacement and repair costs, as when the service life and/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 would otherwise 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 existing empirical estimates of ozone damage to materials are far from reliable for the following reasons:

1. In some studies, coverage is limited to one or two classes of materials, and to restricted geographical regions.

2. Other studies are entirely too aggregative, suffering deficiencies because of (1) broad and vague notions of materials exposure and ozone concentrations; (2) little or no data on the spatial and temporal distributions of the exposed materials; (3) unverified guesses regarding the incidence and level of cost increases and production adjustments incurred by ozone-affected industries; and (4) inadequate attention to economic trade-offs among different industries and different regions, and between producers versus consumers.

3. The engineering/economic estimates are not well related to the scientific literature in this area, and tend to be far too simplistic to meet the concerns of the scientist.

4. Most of the cost assessments were conducted in the early 1970s. Few recent studies exist. Moreover, these earlier studies cite extensively from each other and there are few independent analyses that do not merely rework old data.

5. As a consequence of the fourth item above, many of the ozone-related costs reported in the early 1970s for research and development, product substitution, etc., are no longer appropriate. Some of these were presumably once-only costs that are no longer charged against current production. Because the literature is dated, there may also be some current research and development, substitution attempts, and so on, not at all reflected in the studies cited in this section. In sum, the cost estimates largely reflect technologies and ozone concentrations prevailing some 10 to 20 years ago.

6. Most of the so-called economic studies of ozone damage to materials have been conducted using an engineering approach. That approach focuses on the classification and quantification of the various kinds of costs incurred by the producers and users of the ozone-sensitive materials. Economic theory would argue, however, that this is merely the first step in the assessment process, and that supply-demand relationships are then needed in order to proceed with the calculation of social net benefits (i.e., changes in producer and consumer surpluses). In practice, however, it appears that almost all of the damage assessments conducted to date stop short of obtaining an econometric measure of economic surplus. As such, the studies reported in this section must be interpreted accordingly.

9.4.2 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 of 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 ozone 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 ozone concentration.

A number of factors complicate the use of both the replacement and the avoidance methodologies. Data on key variables are generally missing or merely assumed. Lessening the reliability of the final cost estimates are deficiencies in knowledge of (1) the physical damage functions; (2) the quantities and types of materials exposed to ozone indoors, outdoors, and in respective regions of the country; (3) the actual expenditures incurred for increased replacement,

maintenance, and avoidance that can be directly attributed to ozone; (4) the threshold ozone damage levels that prompt mitigating action; and (5) the range of substitution strategies that can be used to ameliorate degradation. On this latter point, few attempts have been made to identify current technology practices and possibilities. 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 ozone exposure.

An additional complication is that repair, replacement, and substitution are frequently dominated by factors unrelated to ozone 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 ozone levels associated with automotive exhaust. Alternatively, it 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.

Another illustration is the substitution of dyes. New dyes that replace ozone-sensitive dyes may also be more colorfast and able to survive more washings than the dyes they replace. In this case, apportionment of the costs of the new dyes between ozone resistance and the other improved characteristics embodied in the new formulations is an extremely arbitrary and perhaps meaningless exercise.

9.4.3 Aggregate Cost Estimates

The important caveats identified in the preceding discussion qualify the empirical data presented in this and following sections. Table 9-10 summarizes reports of highly aggregated estimates of oxidant damage to 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, the figures are expressed in 1984 currency equivalents alongside 1970 currency equivalents, the base data for the reference studies. They do not, however, represent 1984 supply-demand relationships, production technologies, or ozone concentrations. It must be emphasized that the costs cited in 1984 currency equivalents therefore cannot be considered true 1984 costs.

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

TABLE 9-10. SUMMARY OF DAMAGE COSTS TO MATERIALS BY OXIDANTS
(in millions of 1970 and 1984 dollars)

Study	Materials costs		
	Elastomers/plastics	Fabric/dye	All
Barrett and Waddell (1973)	ND[a]	(260)	(3878)
Mueller and Stickney (1970)	500.0 (1500)[b]	ND	ND
Salmon (1970)	295.2 (915)	358.4 (1111)	653.6 (2026)
Salvin (1970)	ND	83.5 (259)	ND
Waddell (1974)	ND	ND	900.0 (2790)
Yocum and Grappone (1976)	ND	ND	572.0 (1773)
Freeman (1979)	ND	ND	505.0 (1566)

[a]ND=No data. Investigator(s) did not develop estimates in this category.
[b]1984 dollars are listed parenthetically next to 1970 dollars.

material included in his study, a weighted average factor for the percentage of the material exposed to air pollution, and a 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 ozone affected all of the fibers, plastics, and rubber in the study by Salmon, then annual damage costs attributed to ozone would have been $2026 million (1984$). Salmon did not consider ozone-related damage to paint, since the dominant paint-damaging mechanisms are soiling and gaseous sulfur dioxide. 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 $3,878 million (1984$).

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 oxides of nitrogen were $2,031 million (1984$). Of this total, roughly 46 percent was damage to textiles and dyes (from Salvin 1970), while the remaining 54 percent was damage to elastomers (from Mueller and Stickney, 1970). Freeman then assumed a 20 percent reduction in oxidant levels since 1970, and went on to conclude that the monetary benefits of controlling oxidants, oxidant precursors, and oxides of nitrogen were between $170 and $510 million (1984$). Freeman computed the savings due to oxidant controls alone as $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 $6,820 million (1984$) as the total gross annual damage for materials losses in 1970 resulting from air pollution. The component attributable to ozone and oxidants alone was $2,790 million (1984$), within a wide range of $1,550 to $4,030 million (1984$).

Yocom and Grappone (1976), in work for the Electric Power Research Institute, estimated that the cost of air pollution damage to materials was about $6,820 million (1984$) in 1970. Of this total, ozone was responsible for $1,773 million (1984$), or some 26 percent 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. The empirical estimates of materials damage at the aggregate level are typified by a paucity of original research, primary data, and fresh insights. Rather, successive

layers of estimates have been generated upon essentially the same weak foundations. No recent research (e.g., post-1979) is available to improve upon this circumstance.

9.4.4 Damage to Elastomers

The damage to rubber and other elastomers by ozone can be significant in terms of the kinds and quantities of materials that are susceptible. For example, damage to rubber seals, hoses, belts, cables, pharmaceutical goods, and vehicle tires has been mentioned as economically important (Mueller and Stickney, 1970).

If damage induced by pollutants is to be considered economically important, however, the effective useful life of the product must be significantly affected by pollutant exposure. The life of many rubber products is determined more by the wear and tear of normal use than by pollutant damage. For example, the rubber in surgical gloves can be shown to be sensitive to ozone exposure. Because these gloves are used indoors, however, and because they also are usually discarded after one use, the outdoor ozone concentration has no influence on their useful lifetime.

Vehicle tires represent the major use of rubber that is subject to significant economic costs from the effects of ozone (McCarthy et al., 1983). The amount of antiozonants added to a tire formulation depends on two factors: ozone concentrations and expected tire life. Previously, tire manufacturers varied the amount of antiozonants regionally, depending on ozone concentrations. Now, however, most companies produce for a national market from each plant, and consequently formulate their compounds for worst-case conditions with an appropriate margin for safety.

The second factor that determines the amount of antiozonants in tire formulations is expected tire life. Antiozonants are added in sufficient quantities to resist ozone damage for 5 or 6 years in radial tires, and 3 or 4 years in bias-ply and bias-belted tires.

The cost of antiozonants is about $0.80 (1984$) per passenger car tire and about $1.66 (1984$) per truck tire. Given a yearly national production of 100 million passenger tires and 50 million truck tires, the total annual cost of antiozonants is $163 million (1984$). If ozone should be reduced, it is uncertain to what extent tire manufacturers would find it possible and profitable to reduce the level of antiozonants.

Mueller and Stickney (1970) contend that if ozone concentrations were reduced, but the amount of antiozonant per tire was not reduced, more retreadable tire casings would be available for passenger cars. (Truck tires have a comparatively shorter useful economic life and ozone damage is not a significant factor in truck tire retreading). In 1980, nearly 17 million tires were rejected for retreading because of weatherchecking, at least some of which was attributable to ozone. Hence, a reduction in ozone levels cold conceivably make available a greater supply of retreadable tire casings, lowering costs in the retread industry. As qualified previously, however, this depends on the extent to which tire manufacturers find it economical to adjust their levels of antiozonant.

Mueller and Stickney (1970) estimated the damage costs to elastomeric compounds caused by air pollutants, mainly ozone, totaled $1550 million (1984$). Their estimates are presented in Table 9-11. Protection against the effects of ozone (i.e., avoidance costs) represents the added cost of antiozonants, antioxidants, and special rubber blends formulated for their oxidant-resistant and ozone-resistant properties. The second cost element is early replacement because of shortened service life, a cost borne directly by consumers. The heading "indeterminate" refers to the costs of protective wrappings and coatings and research to formulate resistant compounds, and "other" includes labor costs for repair and replacement. To the contrary, the authors note that these two columns cannot be estimated. All of the costs presented in the table refer to the year 1969, and have uncertain reliability and relevance in the context of 1984.

9.4.5 Damage to Fibers and Dyes

Ozone has a significant impact on certain sensitive dyes. Barrett and Waddell (1973) reported that the national cost of dye fading caused by ozone was $260 million (1984$) per year. Of this amount, 30 percent was dye fading in acetate and triacetate, 50 percent was dye fading in nylon carpets, and 20 percent was dye fading of permanent press garments. Barrett and Waddell assumed that avoidance costs included preventive measures to minimize damage, such as use of more expensive dyes as well as additional research and testing. Replacement costs took account of the assumed reduced life of the dyed materials.

No research has been conducted since 1973 to verify or update these estimates. A problem with them is that a proportion of fading and physical wear

TABLE 9-11. SUMMARY OF DAMAGE COSTS TO RUBBER BY OZONE
(in millions of 1920 and 1984 dollars)[a]

	Protection[b]		Early replacement		Indeterminate	Other	All Factors
Total cost	170(527)		225.7(700)		78(242)	~25(78)	~500(1550)
Cost breakdown	Special polymer	20.6 (64)	Tires	37.0(115)			
	Antiozonant	34.1(106)	Mechanical	29.7(90)			
	Wax	5.0(16)	Medical	100.0(312)			
			Belting	22.5(70)			
			Hose	36.0(112)			

Source: Mueller and Stickney, 1970.

[a]1984 dollars are given parenthetically next to 1970 dollars.

[b]Retail costs approximately three times the costs of manufacturing.

[c]"Ballpark estimates" by authors for costs of research and developing, wrapping, coating. (Authors' Table 9 notes that these factors cannot be estimated).

[d]"Labor cost in connection with early replacement." Authors note that this amount <u>again</u> "represents the area in which detailed estimates cannot be made."

was arbitrarily assigned to ozone rather than to other factors. As noted previously, the use of magnesium chloride as a catalyst in the permanent-press process led to dyes that were more sensitive to ozone and also less washfast. Thus, the rate of fading is caused not only by the interaction between the dye and ozone, but also by the frequency of washing.

Salvin (1970) conducted a study on how ozone and the oxides of nitrogen increase the costs of fading of dyed fabrics. Costs in the work of Salvin included those for more resistant dyes, inhibitors, research and development, and reduced service life. Of the total cost of dye fading, that part caused by ozone was $259 million (1984$) per year. Salvin contacted manufacturers to obtain costs of dyes, processes, and preventive measures. The costs of reduced service life were based, however, on estimates rather than observations. Salvin's study does not seem to take account of the differences between indoor and outdoor ozone concentrations and the significance of this for textile exposure; thus, the result must be viewed cautiously for that reason.

9.4.6 Damage to Paint

Ozone levels typically occurring in the ambient air (chapter 6) have not been shown to cause damage to paint. Campbell et al. (1974) were unable to demonstrate a relationship between ozone and paint damage either in a carefully controlled chamber study or in outside exposure tests. Haynie and Upham (1971) showed that the only statistically significant effects of ozone on paint were damage to vinyl and acrylic coil coatings; however, the effects of ozone were insignificant in shortening coating lifetimes. McCarthy et al. (1981) found that the costs associated with premature replacement of acrylic and vinyl coil coatings were minimal and could not be attributed to pollutants alone.

Aesthetics tend to be a decisive factor in the use of acrylic and vinyl coatings. Although the coating retains its primary function of providing a protective surface, changes in gloss and sheen, as well as degradation of color, can be problems. The causative agents for these aesthetic effects are environmental factors (primarily sunlight), as well as the qualities of the pigment, formulation and mixing, and application. No data are available to suggest the role of ozone (possibly in conjunction with other pollutants) in this fading. Hence, the costs of diminished aesthetics attributable to ozone are largely undetermined.

9.5 SUMMARY AND CONCLUSIONS

Over two decades of research show that ozone damages certain nonbiological materials; the amount of damage to actual in-use materials, however, is poorly characterized. Knowledge of indoor/outdoor ozone gradients, for example, has expanded considerably in recent years, and this type of exposure information has not been incorporated in materials damage studies. Moreover, virtually all materials research on photochemical oxidants has focused on ozone. Theoretically, a number of the less abundant oxidants may equal or surpass ozone in reactivity with certain materials, but this possibility has not been tested empirically. In the absence of photochemical pollution, oxidative damage to certain materials still occurs from atmospheric oxygen, but at a much reduced rate and through different chemical mechanisms. Generally, ozone damages elastomers by cracking along the line of physical stress, whereas oxygen causes internal damage to the material.

The materials most studied in ozone research are elastomers and textile fibers and dyes. 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 ozone 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-cracking rate is reduced considerably, although the extent of reduction differs widely according to the material and the type and amount of protective measures used.

The formation of cracks and the depth of cracking in elastomers are related to ozone dose and are influenced greatly by humidity and mechanical stress. Dose is defined as the product of concentration and time of exposure. The importance of ozone dose was demonstrated by Bradley and Haagen-Smit (1951), who used a specially formulated ozone-sensitive natural rubber. Samples exposed to ozone at a concentration of 20,000 ppm cracked almost instantaneously, and those exposed to lower concentrations took a proportionately longer time to crack. At concentrations of 0.02 to 0.46 ppm, and

under 100-percent strain, the cracking rate was directly proportional to the time of exposure, from 3 to 65 min. Cracking occurred at a rate of 0.02 to 0.03 ppm/hr over the entire range of concentrations.

Similar findings were reported by Edwards and Storey (1959), who exposed two SBR elastomers to ozone at a concentration of 0.25 ppm for 19 to 51 hr under 100-percent strain. With ozone doses of 4.75 ppm-hr to 12.75 ppm-hr, a proportional rate in cracking depth was observed, averaging 2.34 μm/hr for cold SBR and 4.01 μm/hr for hot SBR. When antiozonants were added to the compounds, the reduction in cracking depth rate was proportional to the amount added. Haynie et al. (1976) exposed samples of a tire sidewall to ozone at concentrations of 0.08 and 0.5 ppm for 250 to 1000 hr under 10 and 20 percent-strain. Under 20-percent strain, the mean cracking rate for 0.08 ppm was 1.94 μm/hr. From these and other data, they estimated that at the ozone standard of the time (0.08 ppm, 1-hr average), and at the annual NO_x standard of 0.05 ppm, it would take 2.5 years for a crack to penetrate cord depth.

In addition to stress, factors affecting the cracking rate include atmospheric pressure, humidity, sunlight, and other atmospheric pollutants. Veith and Evans (1980) found a 16-percent difference in cracking rates reported from laboratories located at various geographic elevations.

Ozone has been found to affect the adhesion of plies (rubber-layered strips) in tire manufacturing. Exposure to ozone concentrations of 0.05 to 0.15 ppm for a few hours significantly decreased adhesion in an NR/SBR blend, causing a 30-percent decrease at the highest ozone level. This adhesion problem worsened at higher relative humidities. When fast-blooming waxes and antiozonants or other antioxidants were added, only the combination of protective measures allowed good adhesion and afforded protection from ozone and sunlight attack. Wenghoefer (1974) showed that ozone (up to 0.15 ppm), especially in combination with high relative humidity (up to 90 percent), caused greater adhesion losses than did heat and NO_2 with or without high relative humidity.

The effects of ozone on dyes have been known for nearly three decades. In 1955, Salvin and Walker exposed certain red and blue anthraquinone dyes to a 0.1 ppm concentration of ozone and noted fading, which until that time, was thought to be caused by NO_2. Subsequent work by Schmitt (1960, 1962) confirmed the fading action of ozone and the importance of relative humidity in the absorption and reaction of ozone in vulnerable dyes. The acceleration in fading

of certain dyes by high relative humidity was noted later by Beloin (1972, 1973) at an ozone concentration of 0.05 ppm and relative humidity of 90 percent. Kamath et al. (1982) also found that a slight rise in relative humidity (85 to 90 percent) caused a 20-percent dye loss in nylon fibers.

Both the type of dye and the material in which it is incorporated are important factors in a fabric's resistance to ozone. Haynie et al. (1976) and Upham et al. (1976) found no effects from ozone concentrations of 0.1 to 0.5 ppm for 250 to 1000 hr under high and low relative humidity (90 vs. 50 percent) on royal blue rayon-acetate, red rayon-acetate, or plum cotton. On the other hand, Haylock and Rush (1976, 1978) showed that anthraquinone dyes on nylon fibers were sensitive to fading from ozone at a concentration of 0.2 ppm at 70 percent relative humidity and 40°C for 16 hr. Moreover, the same degree of fading occurred in only 4 hr at 90 percent relative humidity. At higher concentrations, there was a parallel increase in fading. Along with Huevel et al. (1978) and Salvin (1969), Haylock and Rush (1976, 1978) noted the importance of surface area in relation to the degree of fading. In explaining this relationship, Kamath et al. (1982) found that ozone penetrated into the fiber itself and caused most of the fading through subsequent diffusion to the surface.

Field studies by Nipe (1981) and laboratory work by Kamath et al. (1982) showed a positive association between ozone levels and dye fading of nylon materials at an ozone concentration of 0.2 ppm and various relative humidities. In summary, dye fading is a complex function of ozone concentration, relative humidity, and the presence of other gaseous pollutants. At present, the available research is insufficient to quantify the amount of damaged material attributable to ozone alone. Anthraquinone dyes incorporated into cotton and nylon fibers appear to be the most sensitive to ozone damage.

The degradation of fibers from exposure to ozone 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. Under laboratory conditions, Bogaty et al. (1952) found a 20 percent loss in breaking strength in cotton textiles under high-moisture conditions after exposure to a 0.06 ppm concentration of ozone for 50 days; they equated these conditions to a 500-to 600-day exposure under natural conditions. Kerr et al. (1969) found a net

loss of 9 percent in breaking strength of moist cotton fibers exposed to ozone at a concentration of 1.0 ppm for 60 days. The limited research in this area indicates that ozone in ambient air may have a minimal effect on textile fibers, but additional research is needed to verify this conclusion.

The effects of ozone on paint are small in comparison with those of other factors. Past studies have shown that, of various 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 ozone and relative humidity on latex house paint, but the final results of those studies are needed before conclusions can be drawn.

For a number of important reasons, the estimates of economic damage to materials are far from reliable. Most of the available studies are now outdated in terms of the ozone concentrations, technologies, and supply-demand relationships that prevailed when the studies were conducted. 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 ozone. Assumptions about exposure to ozone generally ignored the difference between outdoor and indoor concentrations. Also, analysts have had difficulty separating ozone damage from other factors affecting materials maintenance and replacement schedules. For the most part, the studies of economic cost have not marshalled factual observations on how materials manufacturers have altered their technologies, materials, and methods in response to ozone. Rather, the analysts have merely made bold assumptions in this regard, most of which remain unverified through the present time.

Even more seriously, the studies followed engineering approaches that do not conform with acceptable methodologies for measuring economic welfare. Almost without exception, the studies reported one or more types of estimated or assumed cost increases borne by materials producers, consumers, or both. The recognition of cost increase is only a preliminary step, however, towards evaluating economic gains and losses. The analysis should then use these cost data to proceed with supply and demand estimation that will show how materials prices and production levels are shifted. Because the available studies fail to do this, there is a serious question as to what they indeed measure.

Increased ozone levels increase sales for some industries even as they decrease welfare for others. For example, manufacturers of antiozonants for automobile tires conceivably stand to increase sales as ozone increases, while purchasers of tires stand to pay higher prices. This is only one illustration of a fundamental analytical deficiency in the various studies of materials damage: the absence of a framework for identifying gainers and losers, and the respective amounts they gain and lose.

Among the various materials studies, research has narrowed the type of materials most likely to affect the economy from increased ozone exposure. These include elastomers and textile fibers and dyes. Among these, natural rubber used for tires is probably the most important economically for the following reasons: (1) significant ambient air exposure and long use life; (2) significant unit cost; and (3) large quantities and widespread distribution.

The study by McCarthy et al. (1983) calculated the cost of antiozonants in tires for protection against ozone along with the economic loss to the retread industry. While limitations in this study preclude the reliable estimation of damage costs, the figures indicate the magnitude of potential damage from exposure to ozone in ambient air.

Research has shown that certain textile fibers and dyes and house paint are also damaged by ozone, but the absence of reliable damage functions make accurate economic assessments impossible. Thus, while damage to these materials is undoubtedly occurring, the actual damage costs cannot be estimated confidently.

9.6 REFERENCES

Ajax, R. L.; Conlee, C. J.; Upham, J. B. (1967) The effects of air pollution on the fading of dyed fabrics. J. Air Pollut. Control Assoc. 17(4): 220-224.

Andries, J. C.; Diem, H. E. (1974) Letter in J. Polym. Sci., Polym. Lett. Ed. 12: 281. Cited in Davies (1979).

Andries, J. C.; Rhee, C. K.; Smith, R. W.; Ross, D. B.; Diem, H. E. (1979) A surface study of ozone attack and antiozonant protection of carbon black loaded natural rubber compounds. Rubber Chem. Technol. 52(4): 823-837.

Barrett, L. B.; Waddell, T. E. (1973) Cost of air pollution damage--a status report. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA report no. AP-85.

Beloin, N. J. (1972) A field study: fading of dyed fabrics by air pollution. Text. Chem. Color. 4: 77-78.

Beloin, N. J. (1973) Fading of dyed fabrics by air pollutants: a chamber study. Text. Chem. Color. 5: 128-133.

Bogaty, H.; Campbell, K. S.; Appel, W. D. (1952) The oxidation of cellulose by ozone in small concentrations. Text. Res. J. 22: 81-83.

Bradley, C. E.; Haagen-Smit, A. J. (1951) The application of rubber in the quantitative determination of ozone. Rubber Chem. Technol. 24: 750-775.

Campbell, G. G.; Schurr, G. G.; Slawikowski, D. E.; Spence, J. W. (1974) Assessing air pollution damage to coatings. J. Paint Technol. 46: 59-71.

Crabtree, J.; Malm, F. S. (1956) Deterioration of rubber from use and with age. In: McPherson, A. T.; Klemin, A., eds. Engineering uses of rubber. New York, NY: Reinhold Publishing Corp.; pp. 140-170.

Davies, K. M. (1979) Influence of environmental factors on interply adhesion. In: Proceedings of the International Rubber Conference; pp. 80-89.

Dimauro, P. J.; Paris, H. L.; Foth, M. A. (1979) Wax protection. Rubber Chem. Technol. 52(5): 973-984.

Dorset, B. C. M. (1975) Pollution and fading fabrics. Text. Manuf. 99: 27-29, 31.

Edwards, D. C.; Storey, E. B. (1959) A quantitative ozone test for small specimens. Chem. Can. 11: 34-38.

Fisher, H. L. (1957) Antioxidation and antiozonation. In: Chemistry of natural and synthetic rubbers. New York, NY: Reinhold Publishing Corp.; pp. 49-55.

Freeman, A. M. (1979) The benefit of air and water pollution control: a review and synthesis of recent estimates. Council on Environmental Quality; Contract No. EQ9E59. Available from: NTIS, Springfield, VA; PB80-178759.

Gandslandt, E.; Svensson, S. (1980) Stress relaxation tests for determination of ozone attack on rubber. Polym. Testing 1: 81-89.

Gillette, D. C. (1975) SO_2 and material damage. J. Air Pollut. Control Assoc. 25: 1238-1243.

Haylock, J. C.; Rush, J. L. (1976) Studies on the ozone fading of anthraquinone dyes on nylon fibers. Text. Res. J. 46: 1-8.

Haylock, J. C.; Rush, J. L. (1978) Studies on the ozone fading of anthraquinone dyes on nylon fibers. Part II: in-service performance. Text. Res. J. 48: 143-149.

Haynie, F. H.; Upham, J. B. (1971) Effects of atmospheric pollutants on corrosion behavior of steels. Mater. Prot. Perform. 10: 18-21.

Haynie, F. H.; Spence, J. W.; Upham, J. B. (1976) Effects of gaseous pollutants on materials: a chamber study. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA Report No. EPA-600/3-76-015.

Hershaft, A.; Freeman, A. M., III; Crocker, T. D.; Stevens, J. B. (1978) Critical review of estimating benefits of air and water pollution control. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development; EPA report no. EPA-600/5-78-014.

Hofmann, C. M.; Miller, R. L. (1969) Resistance of passenger tires to atmospheric exposure. J. Mater. 4: 31-43.

Huevel, H. M.; Huisman, R.; Schmidt, J. M. (1978) Ozone fading of disperse blue 3 on nylon 6 fibers. In: The influence of physical fiber properties. Text. Res. J. 48: 376-384.

Kamath, Y. K.; Ruetsch, S. B.; Weigmann, H. D. (1982) Micro-spectrophotometric study of ozone fading of disperse dyes in nylon. Text. Res. J.: in press.

Kaplan, M. L.; Kelleher, P. G. (1970) Oxidation of a polymer surface with gas phase singlet oxygen. Science 169: 1206-1207.

Kerr, N.; Morris, M. A.; Zeronian, S. H. (1969) The effect of ozone and laundering on a vat-dyed cotton fabric. Am. Dyest. Rep. 58: 34-36.

Mansfeld, F. (1980) Effects of airborne sulfur pollutants on materials. Research Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Science Research Laboratory; EPA report no. EPA-600/4-80-007.

McCarthy, E. F.; Stankunas, A. R.; Yocum, J. E.; Rae, D. (1983) Damage cost models for pollutant effects on material. East Hartford, CT: TRC Environmental Consultants, Inc.; TRC project no. 1574-J80. U.S. Environmental Protection Agency; EPA report no. 600/3-84-012.

Meyer, D. A.; Sommer, J. G. (1957) Final technical report: the development of weather and aging resistant pneumatic tires and mechanical rubber goods. Dayton, OH: Dayton Rubber Co.

Morris, M. A. (1966) Effect of weathering on cotton fabric. Calif. Agric. Exp. Stn. Bull. 823: 1-29.

Mueller, W. J.; Stickney, P. B. (1970) A survey and economic assessment of the effects of air pollution on elastomers. Columbus, OH: Battelle Memorial Institute; NAPCA contract no. CPA-22-69-146.

National Research Council. (1977) Ozone and other photochemical oxidants. Washington, DC: National Academy of Sciences; pp. 643-672.

Nipe, M. R. (1981) Atmospheric contaminant fading. Text. Chem. Color. 13(6): 18-28.

Razumovskii, S. D.; Batashova, L. S. (1970) Mechanism of protection against ozone by N-phenyl-N'-isopropyl-p-phenylenediamine. Rubber Chem. Technol. 43(6): 1340-1348.

Salmon, R. L. (1970) Systems analysis of the effects of air pollution on materials. St. Louis, MO: Midwest Research Institute; Contract No. CPA-22-69-113.

Salvin, V. S. (1969) Ozone fading of dyes. Text. Chem. Color. 1: 245-251.

Salvin, V. S. (1970) Textile pollution loss is in the billions. Raleigh News and Observer. March 28: 4, p. 10.

Salvin, V. S.; Walker, R. A. (1955) Service fading of disperse dyestuffs by chemical agents other than the oxides of nitrogen. Text. Res. J. 24: 571-585.

Sanderson, H. P. (1975) The effect of photochemical smog on materials. In: Associate Committee on Scientific Criteria for Environmental Quality. Photochemical air pollution: formation, transport and effects. Ottawa, Canada: National Research Council of Canada; Environmental Secretariat publication no. NRCC 14096; pp. 71-87.

Schmitt, C. H. A. (1960) Lightfastness of dyestuffs on textiles. Am. Dyest. Rep. 49: 974-980.

Schmitt, C. H. A. (1962) Daylight fastness testing by the Langley System. Am. Dyest. Rep. 51: 664-675.

Shaver, C. L.; Cass, G. R.; Druzik, J. R. (1983) Ozone and the deterioration of works of art. Environ. Sci. Technol. 17: 748-752.

Spence, J. W.; Haynie, F. H. (1972) Paint technology and air pollution: a survey and economic assessment. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA report no. AP-103.

Trozzolo, A. M.; Winslow, F. H. (1968) A mechanism for the oxidative photodegradation of polyethylene. Macromolecules 1: 98-100.

Upham, J. B.; Haynie, F. H.; Spence, J. W. (1976) Fading of selected drapery fabrics by air pollutants. J. Air Pollut. Control Assoc. 26: 790-792.

U.S. Department of Health, Education, and Welfare. (1970) Air Quality Criteria Document for Ozone.

U.S. Environmental Protection Agency. (1978) Air quality criteria for ozone and other photochemical oxidants. Research Triangle Park, NC: U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office; EPA report no. EPA-600/8-78-004. Available from NTIS: Springfield, VA; PB83-239830.

Veith, A. G.; Evans, R. L. (1980) Effect of atmospheric pressure on ozone cracking of rubber. Polym. Testing 1: 27-38.

Waddell, T. E. (1974) The economic damages of air pollution. Washington, DC: U.S. Environmental Protection Agency; EPA Report No. EPA-600/5-74-012.

Warty, S. S. (1977) Effect of weather on textiles. Man-Made Text. India 20(10): 498-501.

Wenghoefer, H. M. (1974) Environmental effects on RFL adhesion. Rubber Chem. Technol. 47(5): 1066-1073.

Yocum, J. E.; Grappone, N. (1976) Effects of power plant emissions on materials. Electric Power Research Institute Report EC-139.

Zeronian, S. H.; Alger, K. W.; Omaye, S. T. (1971) Reaction of fabrics made from synthetic fibers to air contaminated with nitrogen dioxide, ozone, or sulfur dioxide. In: Englund, H. M.; Berry, W. T., eds. Proceedings of the Second International Clean Air Congress. New York, NY: Academic Press, Inc.; pp. 468-476.

APPENDIX

CHEMICAL ABBREVIATIONS USED IN THE TEXT

CBS	N-Cyclohexyl-2-benzothiazole sulphenamide
6PPD	N-phenyl-N'(1,3 dimethylbutyl)-p-phenylenediamine
IPPD	N-Isopropyl-N'-phenyl-p-phenylenediamine
77PD	N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine
DTPD	Di-tolyl-p-phenylenediamine
TMQ	1,2-Dihydro-2,2,4-trimethylquinoline, polymerized
ETMQ	6-Ethoxy-2,2,4-trimethylquinoline
ADPA	Acetone diphenylamine condensate
MBI	2-Mercaptobenzimidazole
TBMP	4,4'-Thiobis (2-tertbutyl-5-methylphenol)

COMPOUND DETAILS

NR	NR, 100; HAF, 65; Oil, 3; Stearic Acid, 1; Zinc Oxide, 5; Sulphur, 2.5; CBS, 0.6
NR/SBR	NR, 50; SBR, 50; HAF, 50; Oil, 8; Stearic Acid, 2; Zinc Oxide, 4; Sulphur, 2.5; CBS, 1
SBR	SBR, 100; HAF, 50; Oil, 8; Stearic Acid, 2; Zinc Oxide, 4; Sulphur, 2.5; CBS, 1.2
IR	IR, 100; HAF, 65; Oil, 3; Stearic Acid, 1; Zinc Oxide, 5; Sulphur, 2.5; CBS, 0.6