Air Resources Board

State of California

Governor Arnold Schwarzenegger

October 2005 Revision

Review of the California Ambient Air Quality Standard For Ozone

Volume II of IV
Chapters 3-8

Staff Report
Initial Statement of Reasons for Proposed Rulemaking

October 27, 2005

California Environmental Protection Agency

Air Resources Board

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: http://www.arb.ca.gov.

California Environmental Protection Agency

Alan C. Lloyd, Ph.D., Secretary

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Abbreviations and Definitions

abscission	the normal separation, involving a layer of specialized cells, of flowers, fruits and leaves of plants
AOT40	accumulated exposure over threshold of 40 ppb ozone
AQDA	air quality data action
ARB	Air Resources Board
AVG	aminoethoxyvinyl glycine
BSA	Broader Sacramento Area
Ca^{2+}	calcium ion
canopy	a cover of foliage that forms when the leaves on the branches trees in a forest overlap during the growing season
CEC	controlled environment chamber
CFR	Code of Federal Regulations
CO_2	carbon dioxide
COPD	chronic obstructive pulmonary disease
d	day
edaphic	the physical, chemical, and biological characteristics of soil
ESPACE	European Stress Physiology and Climate Experiment
FACE	Free Air Carbon Enrichment system, a chamber-free, open-air fumigation design
FEF25-75%	forced expiratory flow rate between 25 and 75% of forced vital capacity
FEM	federal equivalent method (for air monitoring)
FEV1	forced expiratory volume in one second
fine roots	roots with a diameter between 0.5 to 3 mm
foliar	of or referring to a plant leaf
FRM	federal reference method (for air monitoring)
full-sib	seedlings that have the same parents, but not necessarily from seed produced in the same year
FVC	forced vital capacity
g	gram
GBVAB	Great Basin Valleys Air Basin
gdw	gram dry weight
GIS	geographic information system

gfw	gram fresh weight
hr	hour
ha	hectare (= 10,000 m^2; an area that is 100 m x 100 m)
half-sib	seedlings that have one parent in common
hm	hourly mean
HNO_3	nitric acid
homeostasis	the tendency toward maintaining physiological stability within an organism (plant or animal)
H&SC	Health and Safety Code
IPM	Integrated Pest Management.
Jeffrey pine	*Pinus jeffreyi* Grev. and Balf.
k	allometric growth coefficient describing the distribution of dry weight gain between competing plant parts, defined as the ratio of the relative growth rates of the competing plant parts
K^+	potassium ion
kg	kilogram (= 1,000 g = 2.205 pounds)
km	kilometer (= 1,000 m = 0.6214 miles)
L	liter
LCAB	Lake County Air Basin
LST	local standard time
LTAB	Lake Tahoe Air Basin
m	meter (= 3.28 feet)
m^2	square meter, an area that is 1 m x 1 m
MCAB	Mountain Counties Air Basin
MDAB	Mojave Desert Air Basin
mesophyll cells	the internal cells of a leaf, distinct from cells at the leaf surface or from cell layers immediately adjacent to the leaf surface
mixed conifer	forests with a tree-layer dominated by a mixture of conifer species
montane	of or relating to a mountain or mountainous area
mRNA	messenger RNA (ribonucleic acid)
mycorrhizae	a biological association of a fungus (e.g., *Pisolithus tinctorius*) with the root cells of a plant (e.g., ponderosa pine tree)
mycorrhizal trees	trees with roots associated a mycorrhizae fungus

n	sample size
NARSTO	a public/private partnership to coordinate research in Canada, Mexico and the United States on tropospheric air pollution (formerly the North American Research Strategy for Tropospheric Ozone)
NCAB	North Coast Air Basin
NCCAB	North Central Coast Air Basin
NCLAN	National Crop Loss Assessment Network, a national study of ozone impacts on crops, undertaken during the 1980s
NEPAB	Northeast Plateau Air Basin
ng	nanogram (= 0.000000001 g = 10^{-9} g)
NH_4N_3	ammonium nitrate
nL	nanoliter (10^{-9} L)
nm	nanometer, or one billionth of a meter
NO	nitric oxide, the primary nitrogen-containing by-product of combustion
NO_2	nitrogen dioxide
NO_X	nitrogen oxides (or oxides of nitrogen)
ns	not statistically significant at p =0.05
O_3	ozone; triatomic oxygen
OII	ozone injury index
OTC	open top field exposure chamber
PAR	photosynthetically active radiation (400 – 700 nm)
phloem	the plant tissue through which sugars and other organic materials are transferred to different parts of the plant
photosynthesis	the production by green plants of organic compounds from water and carbon dioxide using energy absorbed from sunlight
Pisolithus tinctorius	a mycorrhizae-forming fungus that forms root-associations with a wide variety of pine and other tree species
ppb	parts per billion by volume
ppb-hr	parts per billion hours (i.e., sum of concentration times duration), a measure of exposure to ozone
ppm	parts per million by volume
ppm-hr	parts per million hours (i.e., sum of concentration times duration), a measure of exposure to ozone

process rates	the degree or amount at which specific actions or activities occur (e.g., water vapor loss from leaves of plants)
QAS	Quality Assurance Section (of ARB)
R:S	ratio of root biomass (dry weight) to shoot biomass
RGR	relative growth rate, defined as the difference in the dry weight of a plant or plant part over a time period, divided by the initial dry weight and the length of the time period
RH	relative humidity
RuBisCO	ribulose bisphosphate carboxylase-oxygenase
RuBP	ribulose bisphosphate
SCCAB	South Central Coast Air Basin
SCOIAS	Sierra Cooperative Ozone Impact Assessment Study
SDAB	San Diego Air Basin
senescence	the onset of aging -- a phase in plant development from maturity to the complete loss of organization and function in plants
SFBAAB	San Francisco Bay Area Air Basin
shoot	the aboveground portion of the plant (e.g., leaves, stems, flowers, and fruits)
sieve cells	the primary type of cell found in the phloem of plants
SIP	State Implementation Plan
SJVAB	San Joaquin Valley Air Basin
SoCAB	South Coast Air Basin
SSAB	Salton Sea Air Basin
sucrose	a disaccharide (with 12 carbon atoms) commonly found in plants
(sucrose) translocation	the movement of sucrose (or other soluble organic food materials) through plant tissues – most commonly from leaves to stems/roots
SUM06	an ozone exposure metric involving concentration weighting, defined as the sum of all hourly mean ozone concentrations equal to or greater than 70 ppb
terrain-effect winds	air currents influenced by the geographic features of the land that it passes over
TREEGRO	a physiologically based computer simulation model of tree growth and development

Ulmus americana	the scientific name for “American Elm”
UN-ECE	United Nations Economic Commission for Europe
USD	United States dollars
USDA	United States Department of Agriculture
USDI	United States Department of the Interior
USEPA	United States Environmental Protection Agency
USV	Upper Sacramento Valley
V_d	deposition velocity, defined as deposition flux of ozone divided by its concentration in air (usually in cm/s or m/s)
VPD	vapor pressure deficit, a measure of evaporative demand of air
whorl	the arrangement of leaves, petals, etc., at about the same place on a stem
wk	week
yr	year
ZAP	zonal application system, a chamber-free, open-air exposure system
µg	microgram (= 0.000001 g = 10^{-6} g)
µm	micrometer or micron (= 0.000001 m = 10^{-6} m)

3 Physics and Chemistry of Ozone Air Pollution

3.1 Introduction

The ozone molecule consists of three oxygen atoms that are bound together (triatomic oxygen, or ozone), and for the purposes of this report, is measured and reported as parts per million (ppm) by volume. Ozone is a powerful oxidizing agent. It can react with gases (such as nitric oxide or NO), and with surfaces (such as dust particles). Ozone can also react with biological materials, such as leaves and cell membranes. These reactions can damage living cells, such as those present in the linings of the human lungs. Exposure has been associated with several adverse health effects, such as aggravation of asthma and decreased lung function.

Ozone was first observed in the Los Angeles area in the 1940s, but not identified as such until the early 1950s. The ozone that the ARB regulates as an air pollutant is mainly produced close to ground (tropospheric ozone), where people live, exercise, and breathe. This should not be confused with the layer of ozone high up in the atmosphere, called stratospheric ozone, that reduces the amount of ultraviolet light entering the earth's atmosphere. Without the protection of the stratospheric ozone layer, plant and animal life would be seriously harmed. In this document, 'ozone' refers to tropospheric ozone unless otherwise specified.

Most of the ozone in California's air results from reactions between substances emitted from vehicles, power plants, industrial plants, consumer products, and vegetation. These reactions involve volatile organic compounds (VOCs, which the ARB also refers to as reactive organic gases or ROG) and oxides of nitrogen (NO_X) in the presence of sunlight. As a photochemical pollutant, ozone is formed only during daylight hours under appropriate conditions, but is destroyed throughout the day and night. Thus, ozone concentrations vary depending upon both the time of day and the location. Ozone concentrations are higher on hot, sunny, calm days. In metropolitan and downwind areas of California, ozone concentrations frequently exceed regulatory standards during the summer.

From the 1950s into the 1970s, California had the highest ozone concentrations in the world, with hourly average concentrations in Los Angeles peaking over 0.5 ppm and triggering frequent "smog alerts". The smog alert system was designed in 1955 to prevent a possible air pollution disaster in Los Angeles County. In the early 1970s, the ARB initiated emission control strategies that provided for concurrent and continuing reductions of both NO_X and VOC from mobile sources and, in conjunction with the local air districts, stationary and area sources. Since then, peak ozone concentrations have decreased by more than 60 percent and smog alerts rarely occur in the Los Angeles area, despite more than a 35 percent increase in population and almost a doubling in vehicle miles traveled. However, most Californians still live in areas that do not attain the State's health-based standard (0.09 ppm for one hour) for ozone in ambient air. Section 7.2.8 of this review includes ozone trends by air basin since 1982.

This chapter discusses the processes by which ozone is formed and removed, background ozone, the role of weather, and spatial and temporal variations in ozone concentrations. In addition, this chapter includes discussions of research that the ARB has been conducting in the following areas that affect ozone concentrations: reactivity, weekend/weekday effect, and biogenic emissions. Subsequent sections of this chapter include ARB websites for more information. The ARB also conducts more general research in atmospheric processes that affect air pollution; information is available at

http://www.arb.ca.gov/research/apr/past/atmospheric.htm#Projects. For more extensive general information on the physics and chemistry of ozone, the reader is referred to Finlayson-Pitts and Pitts (2000), Seinfeld and Pandis (1998), and Whitten (1993).

3.2 Formation and Removal of Tropospheric Ozone

The formation of ozone in the troposphere is a complex process involving the reactions of hundreds of precursors.

3.2.1 Nitrogen Cycle and the Photostationary-State Relationship for Ozone

The formation of ozone in the troposphere results from only one known reaction: addition of atomic oxygen (O) to molecular oxygen (O_2) in the presence of a third "body" (M). [M is any "body" with mass, primarily nitrogen or oxygen molecules, but also particles, trace gas molecules, and surfaces of large objects. M absorbs energy from the reaction as heat; without this absorption, the combining of O and O_2 into ozone cannot be completed.]

$$O + O_2 + M \rightarrow O_3 + M \qquad (1)$$

The oxygen atoms are produced from photolysis of NO_2 by the ultraviolet portion (wavelength = 290 - 430 nm) of solar radiation ($h\nu$).

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

Reaction 3 converts ozone back to oxygen and NO back to NO_2, completing the "nitrogen cycle."

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (3)$$

Reactions 1 and 3 are comparatively fast. Therefore, the slower photolysis reaction 2 is usually the rate-limiting reaction for the nitrogen cycle and the reason why ozone is not formed appreciably at night. It is also one of the reasons why ozone concentrations are high during the summer months, when temperatures are high and solar radiation is intense. The cycle time for the three reactions described above is only a few minutes. Ozone accumulates over several hours, depending on emission rates and meteorological conditions. Therefore, the nitrogen cycle operates fast enough to maintain a close approximation to the following photostationary-state equation derived from the above reactions.

$$[O_3]_{photostationary\text{-}state} = (k_2/k_3) \times [NO_2]/[NO]$$

(the brackets denote concentration)

The ratio of the rate constants for reactions 2 and 3, (k_2/k_3), is about 1:100. Assuming equilibrium could be reached in the ambient air and assuming typical urban pollution concentrations, a NO_2 to NO ratio of 10:1 would be needed to generate about 0.1 ppm of ozone (a violation of the state one-hour ozone standard [0.09 ppm]). In contrast, the NO_2 to NO emission ratio is approximately 1:10; therefore, the nitrogen cycle by itself does not generate the high ozone concentrations observed in urban areas. The net effect of the nitrogen cycle is neither to generate nor destroy ozone molecules. Therefore, for ozone to accumulate according to the photostationary-state equation, an additional pathway is needed to convert NO to NO_2; one that will not destroy ozone. The photochemical oxidation of VOCs, such as hydrocarbons and aldehydes, provides that pathway.

3.2.2 The VOC Oxidation Cycle

Hydrocarbons and other VOCs are oxidized in the atmosphere by a series of reactions, to ultimately form carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O). Intermediate steps in this overall oxidation process typically involve cyclic stages driven by hydroxyl radical (OH) attack on the parent hydrocarbon, on partially oxidized intermediate compounds, and on other VOCs. Hydroxyl radical is ubiquitous in the ambient air; it is formed by photolysis from ozone in the presence of water vapor, and also from nitrous acid, hydrogen peroxide, and other sources. In the sequence shown below, R can be hydrogen or virtually any organic fragment. The oxidation process usually starts with reaction 4, from OH attack on a hydrocarbon or other VOC:

$$RH + OH \rightarrow H_2O + R \qquad (4)$$

This is followed by reaction with oxygen in the air to generate the peroxy radical (RO_2).

$$R + O_2 + M \rightarrow RO_2 + M \qquad (5)$$

The key reaction in the VOC oxidation cycle is the conversion of NO to NO_2. This takes place through the fast radical transfer reaction with NO.

$$RO_2 + NO \rightarrow NO_2 + RO \qquad (6)$$

R can also be generated by photolysis, which usually involves only VOCs with molecules containing the carbonyl (C=O) bond. The simplest VOC molecule that contains the carbonyl bond is formaldehyde (HCHO). Because formaldehyde enters into several types of reactions of importance for understanding ozone formation and removal, we will use it to help illustrate these reactions. The oxidation cycle for formaldehyde can be written in the following sequence of reactions.

$$OH + HCHO \rightarrow H_2O + HCO \qquad (7)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (8)$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (9)$$

Hydroperoxyl radical (HO_2) is generated by reaction 8, and the hydroxyl radical (consumed in reaction 7) returns in reaction 9 to complete the cycle. In addition, reaction 9 produces the NO_2 required for ozone formation, as described above. Also, the carbon monoxide (CO) generated by reaction 7 can react like an organic molecule to yield another hydroperoxyl radical.

$$OH + CO \rightarrow H + CO_2 \qquad (10)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (11)$$

Another component that formaldehyde provides for smog formation is a source of hydrogen radicals.

$$HCHO + h\nu \rightarrow H + HCO \qquad (12)$$

The hydrogen atom (H) and formyl radical (HCO) produced by this photolysis reaction yield two hydroperoxyl radicals via reaction with oxygen, as shown in reactions 8 and 11.

The reactions above comprise the simplest VOC oxidation cycle. Actually, hundreds of VOC species participate in thousands of similar reactions.

3.2.3 The Nitrogen Dioxide and Radical Sink Reaction

Another reaction is central to a basic understanding of ozone formation: the NO_2 plus radical sink reaction that forms nitric acid.

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (13)$$

The previous discussion can be used to explain the typical pattern of ozone concentrations found in the urban atmosphere. Nitric oxide concentrations are relatively high in the early morning because the free radicals needed to convert the NO_X emissions (which are primarily NO) to NO_2 are not yet present in sufficient quantities. After sunrise, photolysis of formaldehyde (reaction 12) and other compounds starts the VOC oxidation cycle for the hundreds of organic gases present in the atmosphere. Subsequent NO to NO_2 conversion by the peroxy radical reaction 6 results in NO_2 becoming the dominant NO_X species. When the NO_2 to NO ratio becomes large enough, ozone builds up. In the South Coast Air Basin (Los Angeles area), the highest ozone concentrations are observed in the San Bernardino Mountains, many miles downwind from the highest concentration of emission sources (freeways, power generating facilities, and oil refineries along the coast), because the reactions involving the organic gases are relatively slow. Meanwhile, NO_2 concentrations decrease via the sink reaction 13.

Winds disperse and dilute both NO_X and ozone. During the day, NO_X is also diluted by the diurnal rising of the inversion layer, allowing for more mixing (see Section 3.5 for further discussion). For ozone, however, the deepening mixing layer may cause its concentration to decrease on some days and increase on others. Although increased mixing almost always dilutes NO_X, the effect of increased mixing on ozone concentrations depends upon whether higher concentrations of ozone are present aloft. Ozone that is trapped above the

inversion layer overnight is available to increase the concentrations of ozone generated by the following day's emissions.

During the night, NO and ozone combine to form NO_2 and oxygen via reaction 3 until either the NO or ozone is consumed. Nitrous acid or HONO is also present at night in polluted ambient air in California. Nitrous acid is produced from NO_2 and water, and is also emitted from various combustion sources. Its levels are low during the day because sunlight breaks it down rapidly. At sunrise, sunlight causes gas-phase HONO to react rapidly to provide NO and OH, two key reactants in the formation of ozone. In this way, they help initiate ozone formation in the morning by being available to react with VOCs as soon as their emissions increase due to an increase in human activity.

Nitric acid (HNO_3) was once thought to be a permanent sink for NO_X and for radicals. However, nitric acid on surfaces may react with NO to regenerate NO_2, which would increase the ozone-forming potential of NO_X emissions.

3.2.4 Ratio of Volatile Organic Compounds to Nitrogen Oxides in Ambient Air

Although VOCs are necessary to generate high concentrations of ozone, NO_X emissions can be the determining factor in the peak ozone concentrations observed in many locations (Chameides, 1992; National Research Council, 1991). VOCs are emitted from both natural and anthropogenic sources. Statewide, natural VOC sources dominate, primarily from vegetation. However, in urban and suburban areas, anthropogenic VOC emissions dominate and, in conjunction with anthropogenic NO_X emissions, lead to the peak concentrations of ozone observed in urban areas and areas downwind of major urban areas.

The relative balance of VOCs and NO_X at a particular location helps to determine whether the NO_X behaves as a net ozone generator or a net ozone inhibitor. When the VOC/NO_X ratio in the ambient air is low (NO_X is plentiful relative to VOC), NO_X tends to inhibit ozone formation. In such cases, the amount of VOCs tends to limit the amount of ozone formed, and the ozone formation is called "VOC-limited". When the VOC/NO_X ratio is high (VOC is plentiful relative to NO_X), NO_X tends to generate ozone. In such cases, the amount of NO_X tends to limit the amount of ozone formed, and ozone formation is called " NO_X -limited". The VOC/NO_X ratio can differ substantially by location and time-of-day within a geographic area. Furthermore, the VOC/NO_X ratio measured near the ground might not represent the ratio that prevails in the air above the ground where most of the tropospheric ozone is generated.

3.2.5 Reactivity

Photochemical reactivity, or reactivity, is a term used in the context of air quality management to describe a VOC's ability to react (participate in photochemical reactions) to form ozone in the atmosphere. Different VOCs react at different rates. The more reactive a VOC, the greater potential it has to form ozone. Examples of the more reactive VOCs in California’s atmosphere include propene, *m*-xylene, ethene, and formaldehyde. The ARB has helped to pioneer

an approach to ozone control that considers the reactivity of each VOC constituent. In California's urban areas, ozone formation tends to be limited by the availability of VOCs. Therefore, the reactivity-based regulatory approach has been applied in conjunction with reduction of NO_X emissions. Reactivity-based regulations promote the control of those VOCs that form ozone most effectively, thereby guiding the affected industries (such as manufacturers of motor vehicle and consumer product formulators that use solvents) to choose the most cost-effective processes and designs to reduce VOC emissions.

A complete table of reactivity values is available at the ARB website, http://www.arb.ca.gov/regact/mir2003/appa.pdf. Further information on photochemical reactivity is available from the ARB website, http://www.arb.ca.gov/research/reactivity/reactivityresearch.htm.

3.3 Background Ozone Concentrations in California

Contributions to background ground-level ozone concentrations include downward mixing of ozone from the stratosphere, and ozone formation due to photochemical reactions of locally emitted natural precursors. Lightning, wildfires, and transport are additional factors. This topic, "background ozone concentrations" is discussed in detail in Chapter 4.

Although little mixing occurs between the troposphere and stratosphere, stratospheric ozone intrusion occasionally causes localized ozone increases, especially at high mountain locations. Most of this intrusion is due to "tropopause folding", which results from strong storms that draw stratospheric air down into the troposphere. In California, this tends to occur in spring. Because stable, stagnant conditions are necessary to support high ozone concentrations in urban California, this process generally does not contribute significantly to peak ozone concentrations. Stratospheric ozone intrusion is also due to general stratospheric subsidence. On a global basis, California is particularly prone to springtime stratospheric ozone intrusion from this process. However, this process is a relatively minor contributor to surface ozone concentrations in California, especially in the summer when ozone concentrations tend to be highest.

Another process leading to ground-level ozone arises from photochemical reactions involving natural precursors. Plants emit VOCs (see Section 3.4), and soil microbes produce NO_X that is vented into the air. (Small amounts of NO_X are also emitted from crops, apparently related to fertilizer application.) Natural precursors may react with anthropogenic precursors to produce ozone concentrations that are of ambiguous origin. Where vegetation produces large amounts of VOCs, if anthropogenic NO_X is also present, significant amounts of ozone can be produced.

Lightning contributes to the formation of ozone by heating and ionizing the air along the path of the discharge, thus forming the ozone precursor NO_X. However, lightning tends to occur when meteorological conditions are not conducive to high ozone concentrations. Wildfires also contribute to ozone formation by producing NO_X from combustion, and by distilling VOCs from vegetation. However, wildfires in California are not a major contributor to ozone pollution.

Finally, transport from outside of California contributes to in-state ozone concentrations. Cities in neighboring states and Mexico emit ozone precursors that impact California. In addition, urban plumes can be lofted high enough into the atmosphere to be entrained in global circulation and transported thousands of miles. In particular, ozone due to emissions in Asia reaches California in springtime. However, this transport is not a major contributor to peak ozone concentrations in California because downward mixing of Asian ozone to the surface is precluded by the strong surface inversion usually present during high ozone episodes. Also, periods of effective long-range transport are generally restricted to spring, while high ozone concentrations due to local sources in California tend to occur in late summer and fall.

3.4 Effect of Vegetation on Ozone Concentrations

California's varied ecosystems interact with emissions related to human activity to influence ozone concentrations. Certain desert species, oaks, and pines emit substantial amounts of highly reactive VOCs, called biogenic emissions. Vegetation can either increase or decrease the ambient ozone concentration as the result of complex processes briefly described below.

Vegetation can reduce ozone concentrations by providing cooling and by removing pollutants. The shade provided by trees lowers ozone concentrations in several ways. It reduces the pollutant emissions from many sources (such as less evaporation of fuel from cooler parked vehicles). By cooling homes and offices, tree shade lowers emissions associated with electricity generation because less power is needed for air conditioning. In addition, cooling reduces the speed of chemical reactions in ambient air that lead to the formation of ozone.

Vegetation can also enhance the removal of ozone through deposition on plant surfaces. The surfaces of leaves and pine needles allow for deposition of ozone and NO_2. Several different factors affect pollutant removal, such as how long a parcel of air is in contact with the leaf, and the total leaf area available for deposition. Also, rain tends to reduce ambient ozone concentrations by washing out atmospheric gases as well as gases deposited on leaves and needles.

Other processes involving vegetation can lead to higher concentrations of ozone. For example, trees and other types of vegetation emit biogenic VOCs, such as isoprene, pinenes, and terpenoid compounds. These biogenic VOCs can react with NO_X emitted from sources such as cars and power plants to form ozone. Many biogenic VOCs are highly reactive (i.e., especially efficient in reacting to form ozone); some VOCs are even more efficient in forming ozone than those emitted from cars and power plants. In addition, VOCs can be emitted from decomposing leaves.

To help understand the complex mechanisms by which vegetation influences ambient ozone concentrations, the ARB established a “Biogenic Working Group” (BWG). The BWG has developed vegetation maps, leaf biomass databases, emission factors, and a California-specific “biogenic emissions inventory through geographic information systems” (BEIGIS) that has satisfactorily accounted for

observed ambient ozone concentrations. The information developed by the BWG will help the ARB to better model ozone formation, and to better determine the relative importance of VOC and NO_X control. Additional information is available from the ARB website,
http://www.arb.ca.gov/research/ecosys/biogenic/biogenic.htm.

3.5 Role of Weather in Ozone Air Quality

In the troposphere, the air is usually warmest near the ground. Warm air has a tendency to rise and cold air to sink, causing the air to mix, which disperses ground-level pollutants. However, if cooler air gets layered beneath warm air, no mixing occurs -- the air is stable or stagnant. The region in which temperature is so inverted is called an inversion layer. One type of inversion occurs frequently several thousand feet above the ground and limits the vertical dispersion of pollutants during the daytime. Another type of inversion occurs on most evenings very near the ground and limits the vertical dispersion of pollutants to a few hundred feet during the night. Pollutants released within an inversion tend to get trapped there. When the top of the daytime inversion is especially low, people can be exposed to high ozone concentrations. Mountain chains, such as those downwind of California's coastal cities and the Central Valley, help to trap air and enhance the air quality impact of inversions. Cooler air draining into the state's valleys and 'air basins' also enhances inversion formation.

The direction and strength of the wind also affect ozone concentrations. Based on worldwide climate patterns, western coasts at California's latitude tend to have high-pressure areas over them, especially in summer. By preventing the formation of storms, and by promoting the sinking of very warm air, these high-pressure areas are associated with light winds and temperature inversions, both of which limit dispersion of pollutants.

On a daily basis, the highest ozone concentrations tend to occur in the afternoon. This is because ozone forms as a result of photochemical reactions involving other pollutants; these reactions generally require a few hours (see Section 3.2) after the emissions of substantial amounts of VOCs. Also, these photochemical reactions are most effective when sunlight is intense and air temperatures are warm. Therefore, ozone concentrations in California are usually highest in the summer, although the ozone season in some areas of the State can include spring and fall. The prevailing daytime winds in summer are on-shore, bringing relatively clean air from over the ocean to the immediate coastal areas, but carrying emissions of ozone precursors further inland. With the climatically favored clear skies and temperature inversions that limit the vertical dispersion of pollutants, these emissions are converted into ozone, with the highest concentrations tending to occur at distances a few tens of miles downwind of urban centers (ARB 2002).

During the periods of the year when the sunlight is most intense, much of California experiences a high frequency of inversions, relatively low inversion heights, and low wind and rainfall. As a result, no other State has more days per

year with such a high meteorological potential for unhealthy ozone concentrations.

Additional information on the effects of weather on air pollution is available from the following textbooks:

Ahrens, C.D. (1994), *Meteorology Today*, West Publishing Co., St. Paul, MN.

Neiburger, M., Edinger, J.G., and Bonner, W.D. (1982), *Understanding our Atmospheric Environment*, W.H. Freeman & Co., San Francisco, CA.

3.6 Spatial and Temporal Variations of Ozone Concentrations

3.6.1 Spatial Variations of Ozone Concentrations

Ambient ozone concentrations can vary from non-detectable near combustion sources, where nitric oxide (NO) is emitted into the air, to several hundred parts per billion (ppb) in areas downwind of VOC and NO_X emissions. In continental areas far removed from direct anthropogenic effects, ozone concentrations are generally 20-40 ppb. In rural areas downwind of urban centers, ozone concentrations are higher, typically 50-80 ppb, but occasionally 100-200 ppb. In urban and suburban areas, ozone concentrations can be high (well over 100 ppb), but peak for at most a few hours before deposition and reaction with NO emissions cause ozone concentrations to decline (Finlayson-Pitts and Pitts 2000, Chameides et al. 1992, Smith et al. 1997).

Ozone concentrations vary in complex ways due to its photochemical formation, its rapid destruction by NO, and the effects of differing VOC/NO_X ratios in air. A high ratio of NO_X emissions to VOC emissions usually causes peak ozone concentrations to be higher and minimum concentrations to be lower, compared to background conditions. Peak ozone concentrations are usually highest downwind from urban centers. Light winds carry ozone from urban centers, and photochemical reactions create ozone from urban emissions of VOC and NO_X Also, away from sources of NO_X emissions, less NO is available to destroy ozone. Due to the time needed for transport, these peak ozone concentrations in downwind areas tend to occur later in the day compared to peak ozone concentrations in urban areas.

Due to the lack of ozone-destroying NO, ozone in rural areas tends to persist at night, rather than declining to the low concentrations (<30 ppb) typical in urban areas and areas downwind of major urban areas, that have plenty of fresh NO emissions. Ratios of peak ozone to average ozone concentrations are typically highest in urban areas and lowest in remote areas (ARB 2002). Within the ground-based inversions that usually persist through the night, ozone concentrations can be very low. In urban areas, emissions of NO near the ground commonly reduce ozone below 30 ppb. In rural areas, however, NO emissions are less prevalent and nighttime ozone may persist well above 30 ppb.

3.6.2 Temporal Variations in Ozone Concentrations

Ambient ozone concentrations tend to vary temporally in phase with human activity patterns, magnifying the resulting adverse health and welfare effects.

Ambient ozone concentrations increase during the day when formation rates exceed destruction rates, and decline at night when formation processes are inactive. This diurnal variation in ozone depends on location, with the peaks being very high for relatively brief periods of time (an hour or two duration) in urban areas, and being low with relatively little diurnal variation in remote regions. In urban areas, peak ozone concentrations typically occur in the early afternoon, shortly after solar noon when the sun's rays are most intense, but persist into the later afternoon, particularly where transport is involved. Thus, the peak urban ozone period of the day can correspond with the time of day when people, especially children, tend to be active outdoors.

In addition to varying during the day, ozone concentrations vary during the week. In the 1960s, the highest ozone concentrations at many urban monitoring sites tended to occur on Thursdays. This pattern was believed to be due to the carryover of ozone and ozone precursors from one day to the next, resulting in an accumulation of ozone during the workweek. In the 1980s, the highest ozone concentrations at many sites tended to occur on Saturdays and the "ozone weekend effect" became a topic of discussion. Since then, the weekend effect has become prevalent at more urban monitoring locations and the peak ozone day of the week has shifted to Sunday. Although ozone concentrations have declined on all days of the week in response to emission controls, they have declined faster on weekdays than on weekends. Thus, the peak ozone period of the week now tends to coincide with the weekend, when more people tend to be outdoors and active than during the week.

The causes of the ozone weekend effect and its implications regarding ozone control strategies have not yet been resolved. Almost all of the available data represent conditions at ground level, where the destruction of ozone by fresh emissions of NO is a major factor controlling ozone concentrations. However, most ozone is formed aloft, and the air quality models used to analyze ozone formation have not demonstrated the ability to represent the ozone-forming system aloft with sufficient realism. In addition, several potentially significant photochemical processes are yet to be fully incorporated in simulation models. These deficiencies leave unresolved this fundamental question: does the ozone weekend effect occur because more ozone is formed (aloft) on weekend, because more ozone is destroyed (at the surface) on weekdays, or because ozone formation is more efficient on weekends? More information may be obtained from the ARB website, http://www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm, and from a review article in EM magazine (Croes et al., 2003)

Ozone concentrations also vary seasonally. Ozone concentrations tend to be highest during the summer and early fall months. In areas where the coastal marine layer (cool, moist air) is prevalent during summer, the peak ozone season tends to be in the early fall. Additionally, as air pollution controls have reduced the emissions of ozone precursors and the reactivity of VOCs, ozone concentrations have declined faster during times of the year when temperatures and the amount of sunlight are less than during the summer. Thus, the peak

ozone season corresponds with the period of the year when people tend to be most active outdoors.

Also, ozone concentrations can vary from year to year in response to meteorological conditions such as El Niño and other variations in global pressure systems that promote more or less dispersion of emissions than typical. Although peak ozone concentrations vary on a year-to-year basis, peak ozone concentrations in southern California have been declining on a long-term basis, as anthropogenic emissions of VOC and NO_X have declined. However, since the advent of the industrial revolution, global background concentrations of ozone appear to be increasing (Finlayson-Pitts and Pitts, 2000). This increase has implications regarding the oxidative capability of the atmosphere and potentially global warming processes (ozone is a strong greenhouse gas but is present at relatively low concentrations). Further discussion of these topics is beyond the scope of this document.

3.7 References

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4 “Policy-Relevant Background” Ozone in California

Many “pollutant” chemicals do not originate solely from controllable sources such as industrial emissions or automobile tailpipes. The fractions of the ambient concentrations of pollutant species that are not due to regulated emissions are commonly referred to as “background;” and, sometimes erroneously, as “natural background.” The notion of “background” pollutant concentrations derives from laboratory parlance in which “background” in controlled experiments (or modeling exercises) is a constant value used to keep track of material distinct from that being studied or manipulated. In the open environment, even under “natural” conditions, ambient concentrations of most pollutant species vary with location, time of day, and weather, making it impossible to specify a single “background” level, and rendering the usage of the term “background” confusing at best.

Earth’s “natural” ozone regime prevailed prior to the industrial revolution, but there is little direct evidence of actual ozone concentrations at that time. Bojkov (1986) resurrected a smattering of historical measurements from Europe and the American Midwest taken in the period 1870 through the 1900, and Lisac and Grubisic (1991) report ozone data from Zagreb, Yugoslavia for the period 1888 to 1900. There are no known measurement records for other regions. Bojkov's data show a strong seasonal trend, peaking in spring, and typical daily maxima in the range of 30 to 50 ppb. The Zagreb data show a similar but narrower range of monthly mean values (30-35 ppb, peaking in April and May). “Preindustrial” ozone concentrations reconstructed through modeling (Lelieveld and Dentener, 2000; Hauglustaine and Brasseur, 2001) are in rough agreement, and show that ozone concentrations were highly variable under “pre-industrial” conditions.

Ozone in the modern world has multiple origins and concentrations may change for many reasons: ozone produced by “natural” causes may be raised or lowered by reaction with anthropogenic emissions; natural ozone precursors may react with anthropogenic precursors to produce ozone concentrations that are of ambiguous origin; and ozone may be transported from one region to another.

From a regulatory perspective, the important distinction is not between “natural” and “anthropogenic” ozone, but between ozone produced by controllable emissions and ozone due to emissions beyond the reach of regulation. In a policy context, anthropogenic ozone produced outside the jurisdiction of an agency and transported into a control region is functionally indistinguishable from that due to natural processes. Within the range of concentrations due to such external or uncontrollable sources, those concentrations that may impact determinations of compliance with air quality standards or limit the potential air quality improvements due to control programs are the “policy-relevant background.”

The following sections present a brief overview of atmospheric ozone creation and summarize current understanding of “policy-relevant background” ozone concentrations impacting California. A full treatment of ozone chemistry and

atmospheric transport far exceeds the scope of this discussion; the reader needing such information is directed to the section of this report dealing with ozone chemistry and the references cited in both sections.

4.1 "Natural" Ozone

Under preindustrial conditions, ozone at ground level is largely the result of three processes: meteorologically regulated downward mixing of ozone from the stratosphere, local boundary layer ozone formation due to photochemical reactions of natural precursors, and regional to continental scale impacts of large biomass fires producing episodic releases of large volumes of ozone precursors (VOCs and NO_X). Since there are only a few ozone measurements available from preindustrial times, global distributions of "natural" concentrations must be inferred from chemical kinetics and atmospheric modeling (Lelieveld and Dentener, 2000). In this regard, ARB staff disagrees with the assumption embedded in many published papers on "background" ozone, that observed elevated ozone in non-urban, non-industrial sites can be presumed to be due to natural causes (*e.g.* Lefohn et al., 2001). ARB staff believe that such observations need to be supported by chemical and meteorological data that preclude anthropogenic influences if the measurements are to be accepted as "natural."

4.1.1 Stratospheric Ozone

Earth's atmosphere is layered and ozone is not uniformly distributed vertically or horizontally. The energy that drives atmospheric processes comes from the sun, and most sunlight penetrates the atmosphere to the ground or ocean where solar energy goes into surface heating and evaporation of water. Air in contact with the heated planetary surface becomes warmer than the overlying air and then rises, carrying heat and water vapor into the atmosphere. Rising air expands and cools with decreasing pressure, thus air temperature in the lower atmosphere tends to be cooler with increasing altitude. The bottom 85 percent of the atmosphere, where circulation is driven by surface heating and energy stored and released by evaporation and condensation of water, is termed the troposphere (Levine, 1985).

Conversely, the upper layers of the atmosphere are heated from above by the small amount of sunlight that is absorbed. At altitudes above about 100km the atmosphere is highly modified by intense extreme ultraviolet (EUV) radiation, X-rays, and cosmic rays from the sun and outer space; this flux ionizes and heats the outer layers (collectively termed the ionosphere). Radiation absorption by the ionosphere shades the lower layers from the effects of interplanetary radiation, such that the common atmospheric molecules (N_2, O_2, CO_2, etc.) can survive (Levine, 1985).

Below about 90km the solar UV flux is still strong enough to heat the air from above; this temperature gradient suppresses convective mixing, hence this zone is termed the stratosphere. The base of the stratosphere, at the level of equilibrium between the influence of convective surface heating from below and direct solar heating from above, is the tropopause; its height varies with location

and season – highest in the tropics, lowest over the poles, higher in summer than in winter. Over California, the tropopause ranges from 10 to 20 km above the surface (Levine, 1985).

The presence of ozone in the stratosphere was determined by Hartley using sun spectrometry in the 1880s; a photochemical mechanism of ozone formation was first proposed by Chapman in the 1930s, and modified by Turco, Crutzen, and others in the 1970s (Turco, 1985): Intense solar ultraviolet (UV) radiation causes oxygen molecules to split into free oxygen atoms (photolysis); the singlet oxygen atoms quickly bond with diatomic oxygen, forming ozone; ozone is recycled back into diatomic oxygen by UV photolysis and reaction with hydroxyl radical, oxides of nitrogen, and various trace constituents in the air. Thus stratospheric ozone concentrations represent a dynamic equilibrium between ozone creation and destruction, and ozone concentration varies seasonally and geographically with changes in UV radiation intensity and concentrations of reactive trace chemicals (Turco, 1985).

Since ozone itself absorbs ultraviolet light, it shades the lower atmosphere in UV bands and weakens ozone production lower in the atmosphere, resulting in an equilibrium ozone concentration appearing as a distinct layer near 20 km altitude. The stratospheric ozone layer contains about 90 percent of total atmospheric ozone (Turco, 1985).

Of course, ozone in the stratosphere, isolated far above the ground, is only "policy relevant" if it can be transported to lower altitudes where it may impact terrestrial organisms (especially humans).

4.1.2 Ozone Exchange Across the Tropopause

Because ozone concentrations in the lower atmosphere are high near the tropopause, it was long believed that downward diffusion of ozone from the troposphere was the major source of tropospheric ozone. More recently, new three-dimensional chemical modeling and better understanding of tropospheric chemistry indicates that much of the ozone in the troposphere, even in nonindustrial regions, is generated in situ (Lelieveld and Dentener, 2000). Nonetheless, stratospheric ozone intrusions do cause localized ozone increases.

Under stable meteorological conditions, the troposphere and stratosphere do not mix, so stratospheric ozone generally remains isolated far above the ground. Strong storms in the troposphere can occasionally cause stratospheric air to be drawn downward into the lower atmosphere. Such stratospheric intrusions or "tropopause folding events" can bring high concentrations of ozone far down into the troposphere. In the midlatitudes of the northern hemisphere these events tend to occur in spring accompanying deep pressure "troughs." When present, stratospheric ozone will be greatest at high mountain locations; effects near sea level are usually small (Lelieveld and Dentener, 2000).

The dynamics of stratospheric ozone intrusion are not fully understood, and are still a focus of active research, but there are two general aspects of the phenomenon that are not in dispute. First, stratospheric ozone transport requires

strong, deep tropospheric circulation to draw ozone-laden air downward, such that ozone intrusions are associated with strong midlatitude cyclonic storms and general midlatitude subsidence. Second, warmer temperatures and strong sunlight promote both tropospheric and stratospheric ozone formation processes. Taken together, these factors make stratospheric ozone intrusions greatest in late winter and spring, when strong latitudinal temperature gradients promote strong circulation and high solar zenith angles promote abundant ozone formation (Lelieveld and Dentener, 2000).

Ozone intrusion has recently been the subject of intensive investigation and model development (STACCATO, 2003). There are two mechanisms of stratospheric ozone intrusion: tropopause folding events (TFEs), which are rapid (a day or two) and somewhat localized (a few hundred km in extent), and general stratospheric subsidence (SS), which is more or less continuous and of continental or larger scope.

4.1.2.1 Tropopause Folding Events

A two year ozone lidar study of tropopause folding over Europe provides a picture of "typical" conditions (Galani et al., 2003). Meteorological modeling was used to anticipate potential folding events for study – 45 potential events were noted during the two years. About half (24) were successfully probed with lidar, and of those about 1/3 actually produced the expected elevated ozone concentrations, generally at altitudes greater than 3km. Only one of the 45 events produced a clear ozone pulse at a low altitude surface measurement site (850m elevation); on that occasion (in March 2001) surface ozone reached 75 ppb. Most events produced elevated (5-6 km) ozone layers with concentrations in the range of 50-75 ppb, and ozone pulses around 50 to 60 ppb at mountain monitoring sites (above 3km elevation). ARB staff believes that the European observations are representative processes acting throughout the northern hemisphere. This is reinforced by the global assessments of Lelieveld and Dentener (2000), Lawrence et al. (2003), and the record of ozonesonde observations reported by Newchurch et al. (2003).

From a regulatory perspective, TFEs are likely to be easily recognized as such because they do not replicate "typical" anthropogenic ozone events. Seasonally, TFEs tend to occur in winter and early spring, outside the anthropogenic ozone season. Geographically, TFEs will manifest themselves with higher concentrations at elevated sites than lowland sites, and will not be constrained by "air basin" distribution patterns. Meteorologically, TFEs will exhibit very low relative humidity, since stratospheric air is dry to begin with, and will be warmed by significant adiabatic heating in the descent from the tropopause to the surface. Chemically, TFEs will exhibit high ozone without the accompanying markers for anthropogenic emissions such as volatile organic compounds (VOCs), carbon monoxide (CO), and oxides of nitrogen (NO_X). Since California has a fairly large network of ozone monitoring sites, many of which also collect other gas data such as CO and NO_X, suspect ozone events should be amenable to retrospective analysis using archived meteorological data and data from surrounding monitoring stations.

4.1.2.2 Stratospheric Subsidence

Globally there is a slow turnover between the troposphere and the stratosphere. Very strong convective lofting in the intertropical convergence zone, the warmest areas of the western Pacific, and the poleward ends of major warm ocean currents (Japan Current, Gulf Stream, etc.) injects tropospheric air into the stratosphere where it is globally dispersed. The upward flux into the stratosphere is balanced by persistent subsidence in the midlatitudes. Together these processes comprise the Brewer-Chapman circulation (Turco, 1985).

Recent global circulation modeling exercises (Wernli and Bourqui, 2002; Lelieveld and Dentener, 2000) indicate that global-scale stratospheric down-mixing is concentrated near the polar jet stream, such that ozone intrusion is strongest and most frequent in bands between 30 and 50 degrees latitude in both hemispheres. In the Northern Hemisphere there are zones of stronger stratospheric ozone intrusion in the eastern and western North Pacific, the western North Atlantic, and the Mediterranean Sea. California is particularly prone to springtime stratospheric ozone intrusion (Wernli and Borqui, 2002; Seo and Bowman, 2002; Fiore et al., 2002). The mean stratospheric contribution to the middle troposphere (5km altitude) varies from about 20 ppb in march to about 5 ppb in August (Lelieveld and Dentener, 2000). Surface concentrations due to the Brewer-Chapman circulation would be somewhat lower.

From a regulatory perspective, long term contributions of stratospheric subsidence to observed high surface concentrations are small in winter and trivial in summer. Fiore et al. (2002) calculated that, in summer, no more than 2-ppb ozone at the surface could be ascribed to stratospheric origin.

Direct evidence of stratospheric subsidence would be seen in routine ozonesonde observations. Newchurch et al., (2003) reported analysis of weekly ozonesonde releases from 1997 through 2002 at Trinidad Head in northwestern California. They observed seasonal variation in ozone consistent with the general pattern described above, but noted that surface ozone at Trinidad Head was consistently low, especially in summer. This pattern is due to the prevention of mixing of air from aloft to the surface due to the persistent cool, stable marine layer along the California coast. The authors contrast this with the stronger mixing seen at continental sites or on the east coast of the United States. It is reasonable to extrapolate from the Trinidad Head data that, since all of coastal California experiences the effects of the cool California current and the associated marine layer, stratospheric down-mixing is suppressed throughout coastal California.

The data and models discussed here reflect the peculiar dynamics of the California climate. Average “natural background” ozone near sea level in the coastal zone is in the range of 15 – 35 ppb, with a maximum monthly mean of about 40 ppb at low altitude inland sites. At altitudes above 2 km stratospheric intrusions can infrequently push peak “natural background” concentrations to 45 –50 ppb. Extreme downmixing of stratospheric ozone as in “tropopause folding events” (TFEs) can raise ozone well above these levels, but such events

only very rarely reach the surface (there has been one documented case in California since ozone monitoring began) and ARB has in place an "exceptional events" policy to exempt such events from regulatory consideration as exceedances of air quality standards.

4.1.3 Natural Tropospheric Ozone

4.1.3.1 Lightning

Lightning heats and ionizes air along the path of the discharge, forming NO_X which reacts with biogenic VOCs (including CO) to form ozone (Lelieveld and Dentener, 2000). This process accounts for 10 to 40 percent of present day tropospheric ozone (20 – 42 percent under preindustrial conditions), depending on local humidity, precursor emissions, and sunlight. Recent work suggests that lightning is the source of much of the vertical increase in ozone in the troposphere (Lelieveld and Dentener, 2000; STACCATO, 2003).

4.1.3.2 Photochemistry of Biogenic Emissions

Natural volatile organic compounds (VOCs) are emitted by plants and NO_X is emitted by soil microbiota. Emission rates are highly variable across plant species and ecosystems. VOC emissions are generally greater during the growing season, but instantaneous emission rates are governed less by season than specific conditions such as sunlight and air temperature. Biogenic NO_X is produced by microbial processes in soils and vented to the atmosphere by diffusion. Just as in urban areas, the combination of sunlight, VOCs, and NO_X works to produce ozone. The strength of natural VOC emissions is usually limited by type and density of vegetation, and total ozone formation is usually constrained by low natural NO_X flux (Lelieveld and Dentener, 2000).

Surface ozone production in areas remote from anthropogenic precursor sources has been observed to be uniformly limited to concentrations well below the level of the proposed standard. Data on 19th century ozone concentrations measured in Europe and the U.S. (Bojkov, 1986; Lisac and Grubisic, 1991) show that spring peak ozone partial pressures were about 4 ± 1 mPa (30-50 ppb) in the Midwestern U.S. and ranged from 2-3 mPa (20-30 ppb) in Europe. Although the 19th century data are somewhat uncertain, these values are supported by a report by Derognat et al. (2003) that model computations of the modern biogenic fraction of ground level ozone in central France peak at 40 ppb.

A detailed modeling study of summertime ozone formation over the United States mainland (Fiore et al., 2002) estimates that natural precursors in the local troposphere react to produce about 50 percent of observed ozone (15 – 25 ppb), and the balance is advected from other regions.

In locations where vegetation produces large amounts of VOCs, ozone may be enhanced or diminished. Fiore et al. (2002) estimate that 10-20 percent of ozone destruction in rural areas in the eastern U.S. is due to reaction with biogenic hydrocarbons.

Conversely, when anthropogenic NO_X is available (e.g. downwind of an urban area), reaction with biogenic VOCs can create significant amounts of ozone.

Excellent demonstrations of this process have been reported in both NO_X- and VOC- limited cases. In a NO_X-limited case, St. John, Chameides and Saylor (1998) reported total ozone was similar in a VOC-poor powerplant plume to that in the VOC-rich Nashville urban plume. In a VOC-limited case reported by Dreyfus, Schade, and Goldstein (2002) the Sacramento CA urban plume's encounter with oak forests enhanced ozone by 20 to 70 ppb (40 to 100 percent) through reaction of urban NO_X emissions with biogenic isoprene.

The regulatory policy implications of ozone formed by reactions involving biogenic precursors hinge on a definitional dilemma: some is clearly "natural", but some exists by virtue of reaction with anthropogenic precursors. This can be resolved by revisiting the definition of "policy relevance:" concentrations beyond regulatory control. Viewed in this perspective, truly "natural" ozone - for which the precursors are themselves beyond regulatory control (e.g. the 15-25 ppb identified by Fiore et al. (2002) – are part of the uncontrollable background. Enhanced ozone such as that observed east of Sacramento (e.g. as reported by Dreyfus, Schade, and Goldstein, 2002) is controllable since the NO_X input to the reaction is anthropogenic and thus potentially amenable to regulatory action. In other words, ozone produced by reaction of natural and anthropogenic precursors may be an unwelcome complication in ozone control, but it is not "background."

4.1.3.3 Biomass Burning

The processes discussed above tend to operate whenever the sun shines, with modulation of ozone concentration due to meteorological conditions, change of season, etc. Some ozone production is much more sporadic, depending on infrequent precursor emissions.

Biomass fires accelerate natural ozone formation by distilling large amounts of VOCs out of plant material and producing CO and NO_X as products of combustion. Ozone photochemistry in smoke plumes is somewhat different from that under clear-sky conditions. The large amount of carbonaceous aerosol reduces solar UV flux, slowing photochemical processes near the fire, but the very high concentrations of combustion gases and long lifetimes of very large smoke plumes cause ozone formation far downwind by oxidation of CO and methane (Crutzen, 1995). Very large fires observed by satellite have been shown to have high ozone concentrations accompanying their smoke plumes far downwind (Jenkins and Ryu, 2003). Ozone concentrations associated with fires are highly variable, but large tropical fire plumes have been observed to commonly have 70-ppb ozone or more in the middle troposphere, but ground level impacts are much less, typically in the range of 15-25 ppb (Jenkins and Ryu, 2003).

Although less studied than tropical fires, boreal forest fires in northern Canada and Siberia have recently been identified as strong but highly variable sources of very large biomass smoke plumes that have the potential to reach the western United States. Modeling by Fiore et al. (2002) found limited biomass fire ozone impact in North America, with the summer average ozone impact of biomass fires

over Canada in the range of 4-8 ppb for 1995. Modeling supported by surface and aircraft measurements reported by Jaegle et al. (2003) looked at springtime (March-May, 2001) transport of pollutants due to Asian sources. The model showed less than 1 ppb ozone due to Asian biomass burning (SE Asia in this season) arriving at the surface in the Pacific Northwest.

Global modeling by Galanter, Levy and Carmichael (2000) indicates that biomass burning contributes half or more of surface and about a quarter of mid-troposphere ozone in the tropics and over the southern oceans. Conversely, the limited burn season and irregular nature of boreal fires limits their average impact to about ¼ of surface ozone in Alaska, western Canada and Siberia in summer and near zero the rest of the year.

Despite the limited long-term mean impact of biomass fires, occasional strong fire impacts are possible. New reports based on ground, aircraft, and transport modeling (Jaffe, et al., 2003a, 2004; Bertschi, et al., 2004; Weiss-Penzias, et al., 2003) indicate that ground level CO, ozone, and particulate pollution in the Puget sound region is occasionally enhanced by smoke plumes from very large Siberian fires. Preliminary data on the impact of one event (June 2-4, 2003) show peak ozone concentration aloft (up to 6km) reached 100 ppb; surface monitoring data showed possible enhancement of suburban ozone by about 10 – 20 ppb. Such events appear to be rare (once in an entire summer of observations in a year of unusually large Siberian fire activity). If further study demonstrates that this phenomenon occurs with some regularity (i.e. more than once in three years) it would be prudent for regulators to develop a methodology for recognizing such an event (e.g. merging back trajectories, satellite fire data, and observed atmospheric chemistry) to assure recognition as an “unusual event”.

In California, the potential for Siberian fire ozone impacts enhancing urban ozone appears to be significantly lower than that for the Pacific Northwest. This is due to a combination of reduced potential transport at the lower latitudes of California’s major urban areas and stronger local inversions during ozone episodes. This view is supported by the modeling of Galanter, Levy, and Carmichael (2000) which shows a strong decreasing gradient of boreal biomass fire ozone along the coast of North America, from a peak in interior Alaska to no impact in southern California.

Although much of California’s natural vegetation is prone to frequent burning, there is little evidence that local fires significantly impact measured ozone in the state. Small fires produce much the same mix of ozone precursors as do large ones, however plumes from small fires tend to disperse more readily, and thus precursor concentrations are lower and there is less time for ozone to form. Although there has been little scientific research on the ozone effects of California fires, the general nature of burning in California suggests it is not large. California’s aggressive fire suppression policies sharply restrict the frequency of very large fires, and keep most small fires from spreading or lasting more than a few hours. The degree of fire suppression is evident in statistics compiled by the California Department of Forestry and Fire Protection (CDFFP, 2004a,b). The year 2003 was a very bad fire year, with enormous damage due to an

unprecedented group of fires in southern California in October – despite that, annual statistics for 2003 show that, of over 7600 fires reported, only about 120 exceeded 300 acres (121 hectares). Air Pollution measurements influenced by large fires are generally recognized as exceptional events and excluded from consideration for standards compliance, and regulators should be aware of major fires in proximity to monitoring sites. Large fires are inherently low frequency events in any particular area, since it takes many years for fuel to accumulate after a major fire. Taken together, these considerations keep local biomass burning from being considered a significant contributor to California's ozone pollution.

4.2 Transported Anthropogenic Ozone

Because ozone is highly chemically reactive it was long believed that its influence on downwind air quality was limited to local transport of concentrated urban plumes. In California, ozone due to precursor emissions outside the State's jurisdiction were thought to be limited to border cities such as Tijuana, Mexico. Although technically exogenous to California, ozone from such sources is well-understood and subject to indirect control through international agreements and bi-national control programs.

Research during the last decade has changed perception of the spatial scale of impact for urban/industrial ozone. Urban plumes lofted high enough into the atmosphere to be entrained in global circulation can maintain considerable chemical integrity and effectively transport ozone thousands of kilometers. Individual pollution plumes from urban / industrial areas have recently been traced from the eastern United States across the Atlantic Ocean to Europe (Trickl et al., 2003), from Europe to Asia (Pochanart et al., 2003), Asia to the north Pacific Ocean (Thouret, et al., 2001), from Asia to North America (Jaffe, McKendry, Anderson, and Price, 2003), and from all the industrialized regions of the Northern Hemisphere to the Arctic (Browell et al., 2003).

Globally, injection of anthropogenic ozone precursors (especially NO_X) into the free troposphere has been estimated to enhance tropospheric ozone by 12 percent (Lawrence, et al., 2003).

Ozone due to urban and industrial emissions in east Asian megacities (Beijing, Tokyo, Hong Kong, Taipei, Shanghai, *etc.*) has been observed to reach western North America in springtime (Jaffe et al., 1999; Jaffe et al., 2003b; Jaffe, McKendry, Anderson, and Price, 2003). Modeling exercises aimed at determining the Asian air pollution contribution in western North America have consistently shown frequent enhancement of carbon monoxide and aerosols, but ozone effects have been harder to discern. This may be, in part, due to recent shifts in the balance of ozone chemistry over the Pacific Ocean. Pacific basin and global ozone chemical dynamics modeling (Jaegle et al., 2003; Lawrence et al., 2003) indicates that increasing anthropogenic NO_X emissions are pushing tropospheric chemistry over the northeastern Pacific Ocean from net ozone destruction to net ozone formation. Jaegle et al. (2003) show that about half of CO observed at Cheeka Peak, WA is Asian, while only 10-20 percent of ozone is Asian. This

implies that the Asian CO signal would be expected to be detected earlier in the growth of Asian emissions, with positive ozone impacts delayed until Asian NO_X emissions shift the balance for eastern Pacific ozone formation. Jacob, Logan and Murti (1999) presented model results that are consistent with this hypothesis, indicating mean Asian ozone impact in western North America would increase from around 1 ppb in 1985 to as much as 7 ppb in 2010 if Asian NO_X emissions continue to grow at late 20th century rates (4-5 percent/year). Berntsen, Karlsdottir and Jaffe (1999) modeled transPacific transport to Cheeka Peak, WA, with model validation based on aircraft and ground measurements; they reported a mean springtime Asian ozone increment of 4 ppb, with peak events (48 hours) reaching 7.5 ppb. Jaffe et al. (2003b) report statistical analyses of ozone records from rural sites from northern California to the Olympic Peninsula from the mid-1980s to 2002 that show a broad regional increase in "background" ozone. All sites show a statistically significant increase in springtime ozone (about 4 ppb/decade) for days selected for oceanic influence, with stronger gradients for higher elevation sites. This is consistent with the vertical gradient pattern of Asian aerosol impacts (VanCuren and Cahill, 2002), ozonesonde observations (Newchurch, et al., 2003), and increased transport exposure above the marine boundary layer shown in transport modeling (Jaegle et al., 2003).

4.3 Exogenous Impacts on California Ozone Air Quality

4.3.1 Present Conditions

The exogenous ozone sources discussed above are generally not major contributors to observed peak ozone concentrations in California. This is due to the meteorology of the processes that transport ozone on continental and hemispheric scales, and to a seasonal mismatch between peak transport and local ozone maxima.

Stratospheric ozone intrusions generally occur as a result of large scale atmospheric disturbances – conditions that are inimical to the stable, stagnant conditions necessary to support buildup of pollutants in an urban area, thus the probability of stratospheric ozone adding to a high ozone concentration due to anthropogenic emissions is low. In addition, stratospheric ozone events can be recognized by unique atmospheric chemistry – very dry air, low aerosol concentrations, a general lack of anthropogenic precursor gases (VOCs and NO_X), and very low carbon monoxide (CO) concentrations compared to typical urban plumes. This chemical signature should make it possible to recognize stratospheric intrusion and to classify associated ozone concentrations as "exceptional events".

Long-range transport of anthropogenic ozone is similarly restricted to particular meteorological conditions. Jacob, Logan and Murti (1999) report that, although the lofting of Asian precursors is associated with unstable air along frontal boundaries, the movement of ozone downward to impact the surface in North America is dominated by subsidence in the middle and lower troposphere, sometimes assisted by dry convection in the lower layers of the atmosphere. In California, weak subsidence is associated with strong surface inversions in the

heavily populated coastal zone and Central Valley, while strong subsidence is associated with “Santa Ana” conditions. Downward mixing of Asian ozone to the surface is not possible when a strong surface inversion is present, thus locally generated high ozone concentrations are unlikely to be enhanced by long range transport. Conversely, Santa Ana conditions are generally associated with low ozone concentrations in the coastal zone as locally generated ozone precursors are swept out to sea; under such conditions transported ozone would tend to replace, rather than supplement locally generated ozone.

There is also a seasonal mismatch between the peak of long range transport and California’s ozone seasons. Periods of effective long range transport are generally restricted to late winter and spring (Berntsen, Karlsdottir and Jaffe, 1999), while high ozone due to local sources in California tend to occur in late summer and fall.

4.3.2 Past and Future Trends

Ozone delivered by long range transport may be contributing to a small increase in ozone concentration on days that would otherwise have low ozone. Statistical analyses of U.S. ozone data (Lin et al., 2000) indicate that “background” effects appear to be driving an increase in minimum ozone concentrations at rural locations in the U.S. at the some time as peak ozone concentrations are declining due to U.S. emission controls. They estimate a mean increase in U.S. “background” ozone of 3 – 5 ppb between 1980 and 1998.

Model studies indicate that long-range transport of ozone to the western U. S. may increase as global energy use increases, especially as it drives NO_X emissions in Asia. Jacob, Logan and Murti explored the change in Asian ozone impact in the United States for a base case of Asian NO_X emissions for 1985 and a tripling of the 1985 level projected to occur around 2010. The growth scenario caused Asian ozone contributions along the U.S. west coast to develop a spring “bubble” rising from 3-4 ppb in March to a peak between 5 and 6 ppb in May, then dropping gradually through the summer to return to about 2-3 ppb in August.

4.4 Total “Background” Ozone in California.

Fiore et al*.,* (2002) modeled summer ozone over the United States using a global air quality model and retrieved from the results separate signals for “natural” ozone from all sources, total ozone due to non-U.S. sources (natural + Asia, Europe), and total ozone including all sources.

“Natural” ozone is highly sensitive to insolation, thus the desert southwest showed the highest values, 20- 25 ppb mean afternoon maxima for the season (June-August). The model identified a gradient along the coast, ranging from 15 ppb over the ocean to about 20 ppb in interior California. Transported ozone from outside the U.S. follows a similar pattern. Due to the combination of strong sunlight and atmospheric subsidence, the desert southwest again is the “hot spot” with mean seasonal afternoon ozone in the range of 30 – 35 ppb, and there is there is a gradient from the ocean inland, ranging from 20-25 ppb over the ocean to about 30 ppb in interior California.

The difference between these two cases gives an estimate of the transported anthropogenic increment of background. The peak summer afternoon impact of 7 ppb falls in the northern Great Basin (eastern Oregon, southern Idaho, northern Nevada). The entire intermountain west and interior California lie in the area receiving 5 or more ppb, while the Pacific coast shows a weak gradient from about 4 ppb near the Mexican border to about 5 near the Canadian border.

However, it does provide a basis for exploring the relationship between background and peak ozone concentrations in general. Statistics from the model runs show that the mean enhancement to summer ozone levels is low (about 2 ppb) when total ambient ozone is low (<30 ppb) or high (>80 ppb). Exogenous enhancement rises to about 5 (range 1-10) ppb when ambient ozone concentrations are moderate (40-65 ppb). This result is consistent with the observations of Lin et al. (2000), supporting the view that exogenous ozone impacts are not driving peak concentrations, but probably are increasing long term averages by a few ppb.

4.5 Summary - Estimating the "Policy Relevant " Background

Overall, it appears that "background" ozone in California is dominated by natural tropospheric and stratospheric processes. The effects of occasional very large biomass fires and anthropogenic emissions are secondary factors. The foregoing discussion indicates that average "natural background" ozone near sea level is in the range of 15 – 35 ppb, with a maximum of about 40.

Exogenous enhancements to "natural" levels generally are small (about 5 ppb), and are unlikely to alter peak concentrations.

At altitudes above 2km stratospheric intrusions can push peak ambient concentrations to 45 – 50 ppb. The timing, spatial extent, and chemical characteristics of stratospheric air mass intrusions makes these events recognizable in air quality records, providing that the affected region has a fairly extensive monitoring network and that multiple air quality parameters (CO, VOC, PM, RH) were being measured as well.

Intermittent episodes of "natural" ozone from very large biomass fires in boreal forests (Alaska, Canada, Siberia) can produce short-lived pulses of ozone up to 20 ppb that may arrive during the North American ozone season. Present understanding suggests that these are infrequent events at latitudes below about 50N. There are no data documenting such an event in California.

Long range transport of anthropogenic ozone may grow as Asian energy consumption increases the continent's NO_X emissions. Model studies indicate that the Asian ozone increment in North America could double over the next few decades. Assuming the temporal pattern of transport remains unchanged, such an impact could increase mean ozone concentrations by 2-6 ppb. The potential effect on peak transport events is unknown at this time.

4.6 References

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5 Ozone Precursor Sources and Emissions

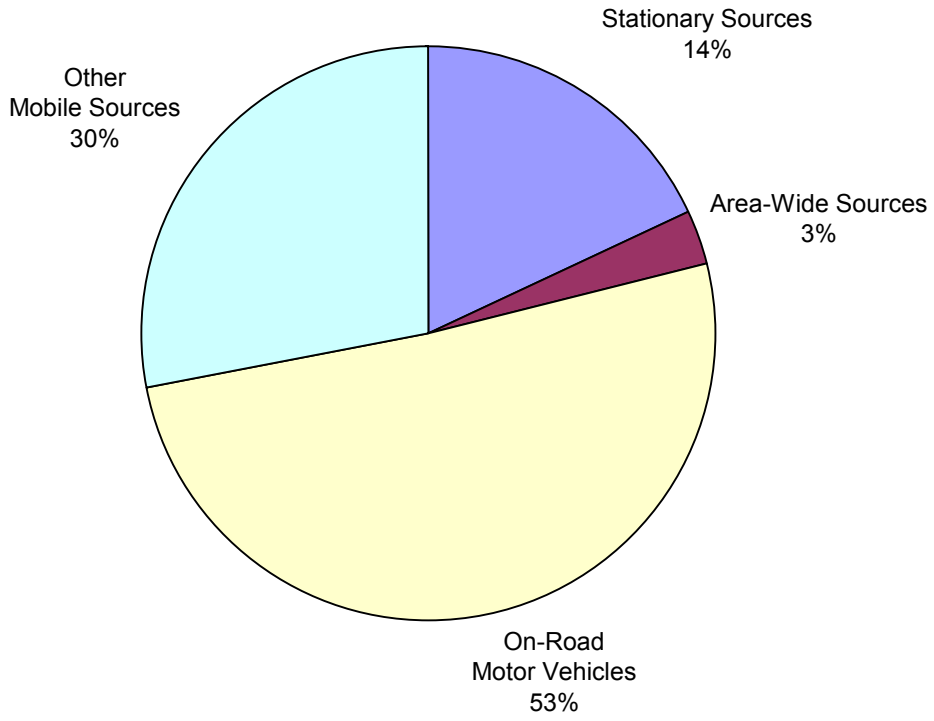
5.1 Ozone Precursor Sources

Ozone is an oxidant gas that forms photochemically in the atmosphere when nitrogen oxides (NO_X) and reactive organic gases (ROG) are present under appropriate atmospheric conditions (see Chapter 3). Carbon monoxide (CO) is also an ozone precursor. Both ROG and NO_X are emitted from mobile sources, point sources, and area-wide sources. ROG emissions from anthropogenic sources result primarily from incomplete fuel combustion, and from the evaporation of solvents and fuels, while NO_X emissions result almost entirely from combustion processes.

5.2 Sources of NO_X Emissions

NO_y is defined as a group of gaseous compounds of nitrogen and oxygen, many of which contribute to the formation of ozone. For example, NO_X includes nitric oxide (NO) and nitrogen dioxide (NO_2), which result from the combustion of fuels. Mobile sources (including on-road and others) made up about 83 percent of the total statewide NO_X emissions in 2003. The category of other mobile sources includes emissions from aircraft, trains, ships, recreational boats, industrial and

NOx emissions (tons/day, annual average)



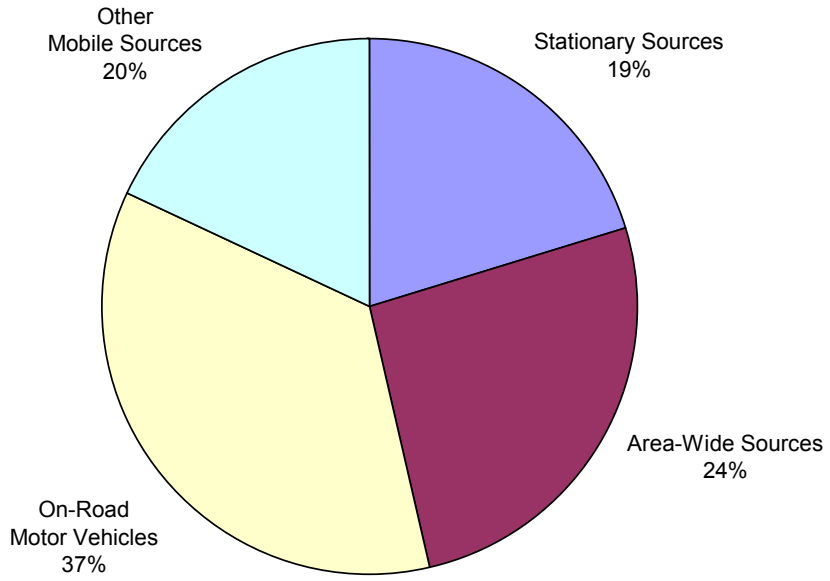
construction equipment, farm equipment, off-road recreational vehicles, and other equipment. Stationary sources of NO_X include both internal and external combustion processes in industries such as electric utilities, which contribute approximately 2% of Statewide NO_X emissions, manufacturing, food processing, and petroleum refining. Area-wide sources, which include residential fuel combustion, waste burning, and fires, contribute only a small percent of the total NO_X emissions.

5.3 Sources of ROG Emissions

ROG consists of volatile organic compounds that are photochemically reactive and contribute to the formation of ozone. These emissions result primarily from incomplete fuel combustion and the evaporation of chemical solvents and fuels. Mobile sources (including on-road and others) made up approximately 57 percent of total statewide ROG emissions in 2003. This category includes emissions from cars, trucks, and motorcycles powered by gasoline and diesel fuels. Stationary sources of ROG emissions include processes that use solvents (such as dry cleaning, degreasing, and coating operation) and petroleum-related processes (such as petroleum refining and marketing and oil and gas extraction). Electricity generation is estimated to contribute about 1% of Statewide ROG emissions. Area-wide ROG sources include consumer products, pesticides, aerosol and architectural coatings, asphalt paving and roofing, and other evaporative emissions.

To determine the amount of ROG in the emissions, speciation profiles are used. These profiles provide estimates of the chemical composition of emissions, and are used in the emission inventory and air quality models. The ARB maintains and updates estimates of the chemical composition and reactive fractions of total organic gases (TOG), for a variety of emission source categories.

ROG emissions (tons/day, annual average)



5.4 Regional Differences in Ozone Precursor Emissions

Emissions from different types of sources vary regionally in California. The following table shows 2003 ozone precursor emissions from mobile sources statewide and regionally for selected areas. The emissions are expressed as a percentage of total emissions for each area.

Percentage of Ozone Precursor Emissions From Mobile Sources

Area	*NO_X (%)*	*ROG (%)*
Statewide	*83*	*57*
Sacramento Valley	84	49
San Diego	95	56
San Francisco Bay Area	85	61
San Joaquin Valley	75	44
South Coast	90	64

5.5 Temporal Differences in Ozone Precursor Emissions

Generally speaking, emissions of ozone precursors will be higher in warmer months than in cooler ones. However, the emissions for individual source categories may further vary with time, season and place. For example, ROG emissions from on-road motor vehicles are significantly higher in warmer months because of the effect of higher ambient temperatures on evaporative emissions. Stationary source emissions of ROG and NO_X may vary based on the nature of the source. Power plants typically have higher emissions of ROG and NO_X in the summer because of widespread use of air conditioning in homes and workplaces, while emissions associated with oil extraction will fluctuate based on the price of crude oil and other factors. Emissions from manufacturing facilities are subject to great variation. They may be consistent year-round for one business or may vary seasonally for another business because of the product being manufactured. Area-wide source emissions may likewise vary. For example, ROG emissions associated with the application of exterior paint increase in the summer because it is more practical to apply paint in warm and dry weather.

5.6 Natural Source Emissions

Natural source emissions include a variety of compounds and occur as a result of geologic or meteorological activity (such as petroleum seeps or wildfires), or living processes by flora and fauna (such as vegetation foliage or soil microbes). Natural source emissions are strongly affected by seasonal influences on factors such as temperature and moisture conditions, or wind regimes. Estimates of

natural source emissions are calculated and used as inputs to climate research and photochemical modeling.

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6 Measurement of Ozone

6.1 Introduction

Ozone is a highly reactive, colorless gas. Any method used to measure ozone in an atmosphere must consider these properties. Ozone must be measured at the sampling location, as samples cannot be taken back to a laboratory for analysis.

Two measurement methods for ozone are approved for use in the U.S. by the USEPA: one is based on the chemiluminescence that occurs when ozone and ethylene react, and the other on the attenuation of ultraviolet (UV) radiation by ozone. The method based on UV spectrometry is almost universally used in practice. Specifications and criteria for both methods exist in federal regulation. The UV photometry-based method is approved for use in California for state air quality standards. Both state and federal requirements are applied directly by the ARB and the air districts in the ozone monitoring network in California.

6.2 Existing Monitoring Methods

The USEPA has developed design and performance criteria for methods used to measure tropospheric ozone. The federal reference method (FRM) is based on gas-phase chemiluminescence (40 CFR Part 50, Appendix D), and the federal equivalent methods (FEMs) are based on UV photometry (40 CFR Part 53, and McElroy et al., 1997), with the exception of one method based on gas-solid chemiluminescence (USEPA, 1996).

The state ambient air quality standard for ozone (California Code of Regulations, Title 17, section 70200) stipulates that ultraviolet photometry is the method to be used to measure ozone. The standard also allows an equivalent method to be used, as described in the first footnote to the “Table of Standards” in section 70200:

“Any equivalent procedure which can be shown to the satisfaction of the ARB to give equivalent results at or near the level of the air quality standard may be used.”

To implement the general requirement of a UV photometry-based measurement method, ARB and air district staff employ specific UV photometry-based methods and procedures as prescribed by the USEPA. These UV methods must be operated in accordance with the manufacturers’ instructions and instrument-specific ARB standard operating procedures, both of which are consistent with the requirements.

Below are general descriptions of the chemiluminescence and UV methods for ozone measurement.

6.2.1 Gas-Phase Chemiluminescence Methods

The most common chemiluminescence method for ozone is direct gas phase reaction of ozone with olefin to produce electronically excited products, which decay with the emission of light. When ozone reacts with ethylene gas, an olefin,

electronically excited formaldehyde is produced. As this excited species returns to the ground state, it gives off light in a band centered at 430 nanometers (nm) in proportion to the amount of ozone present. This chemiluminescence can be measured using a photomultiplier tube, and the concentration of ozone is calculated (ARB, 1987, and USEPA, 1996).

The USEPA has identified specific monitoring instruments based on gas-phase chemiluminescence as FRMs for ozone measurement. Any other measurement method or instrument must be compared against the reference method, and must perform on a par with the reference method to be deemed equivalent. A detailed discussion of the measurement method principle and the calibration procedures for chemiluminescence-based instruments is given in the Code of Federal Regulations (CFR) 40 CFR, Part 50, Appendix D, and USEPA, 1996.

Humidity causes a positive bias in chemiluminescence methods. This can be compensated for by using humidified air for instrument calibration.

Because the reference method uses a potentially flammable gas as a reactant, and because there is an equivalent method for directly measuring ozone, chemiluminescence-based monitors are seldom used for routine air monitoring. In areas of high humidity, the interference has been problematic and the debate continues as to the instrument's complete reliability for such an important purpose.

6.2.2 Ultraviolet Photometry Methods

Ozone exhibits a strong absorption band in the ultraviolet region at 254 nm. This feature is the basis of the photometric measurement method for ozone. Many commercially-available UV instruments meet U.S. EPA equivalency criteria as set forth in 40 CFR Part 53, § 53.32. A discussion of the principle of the UV spectrometric method for ozone is given in ARB (1987), McElroy et al. (1997), and U.S. EPA (1996). Calibration techniques and other quality control and quality assurance methods and practices for the state method are described in the ARB Air Monitoring Quality Assurance Manual Volume II (Appendix A, 1995); see the on-line copy of the manual at:
http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.html

Other species present in the atmosphere such as aromatic hydrocarbons also absorb at or near 254 nm, and so represent potential interferences to the method. The commercially-available instruments compensate for this possible interference by comparing the absorbance of the sample with the absorbance of air in which the ozone has been catalytically reduced to molecular oxygen (O_2); consequently attenuation of the UV light due to non-ozone species is taken into account. However, negative interference due to high humidity and positive interference due to high hydrocarbon concentrations have been reported. For details on this, the reader is referred to McElroy et al. (1997).

6.3 Precision and Significant Figures

It is important to consider the number of significant figures when reporting ambient air quality data to avoid overstating, or understating; the preciseness of

measured concentrations. By definition, significant figures are those digits in a number that are known with certainty, *plus* the first uncertain digit. In other words, the last digit (rightmost digit) is an estimated digit.

The precision of a measurement method refers to measurement repeatability, or variability, and is expressed as the sample variance, or standard deviation. A simple evaluation of method precision determines the number of appropriate significant figures that should be used to record and report measurement data for that method.

For a grouping of monitors, such as a network, one way to evaluate *method* precision is to look at the performance of all monitors in the group or *network*. In effect, you are determining the *network precision*. For purposes of this report, the evaluation of network precision was made by examination of ozone performance audit data. Performance audits are conducted by testing an ozone monitor with know concentrations of ozone. Each audit consists of testing the monitor at the high, mid and low range of the monitor. Since the level of interest for this report (0.070 ppm) is closest to the low audit level, only low concentration audit data (from 0.030 to 0.080 ppm) were evaluated to get the best estimate of precision at this level (USEPA 1983, 1984).

Performance audits are primarily used to assess the accuracy (or systematic bias) of *individual* ozone monitors. However, when the individual biases of many monitors are combined, and looked at as a group, the variability of average bias can appear random, and therefore be used to assess the *precision of the network*.

For 2003, the most recent year of finalized audit data, ARB staff conducted performance audits for 137 ozone monitors. The average bias of all 137 audits was –2.0%, with a standard deviation of 4.3%. To express standard deviation in units of ppm, we multiply 4.3% by the concentration of interest, in this case, 0.070 ppm. The result is 0.0030 ppm. By convention, this means that ozone measurements are uncertain in the third decimal place, to the degree of plus or minus 0.003 ppm. (This result is consistent with audit data going back to 1999 and preliminary audit data from 2004.)

Since significant figures include all certain digits, *plus the first uncertain digit*, the precision of California's ozone network (as determined above) indicates that ozone measurements should be recorded and reported to the third decimal place ppm.

6.4 Monitor Calibration Methods

Ozone instruments are calibrated by comparing the responses of an ambient monitoring station ozone analyzer to a certified ozone transfer standard. The response to ozone gas is compared at 4 levels and regressed using the "least squares" method. The four levels are approximately 0.400 ppm , 0.300 ppm, 0.200 ppm, and 0.090 ppm. Calibration gas at each of these levels is introduced into the ozone analyzer until a steady and unchanging analyzer response is achieved. Typically, a steady reading of 10 minutes is taken as the calibration

data point. The regression results are not used to correct data; they are used to determine the instrument's linearity and deviation from the true based on the regression slope. An instrument is not adjusted to match the transfer standard unless it is beyond 2% from true (slope of 0.98 to 1.02). We would not expect any difference in accuracy/precision for the 8-hour concentration, since the standard is an average of eight 1-hour concentrations. Precision is not increased or decreased by arithmetic operations.

6.5 Recommendations

Staff recommends that the Board continue to endorse the UV method as the approved method in California for determining compliance with the state Ambient Air Quality Standard for ozone. By reference, therefore, staff recommends all federally approved UV methods be incorporated as California Approved Samplers for ozone. This will result in no change in air monitoring practices, but will align state monitoring requirements with federal requirements. Specifically, we recommend that a new part be added to the California Administrative Code 70100.1, to read, in part:

Ozone Methods. The method for determining compliance with the ozone ambient air quality standard shall be the Federal Equivalent Method for the Determination of Ozone in the Atmosphere (40 CFR, part 53). California Approved Samplers for ozone are set forth in Air Monitoring Quality Assurance Manual Volume IV, Part C: Monitoring Methods for Ozone.

The list of UV methods (USEPA/ORD, 2002) is given at
http://www.epa.gov/ttn/amtic/criteria.html"

The following methods and instruments are *California Approved Samplers for Ozone* for the purposes of determining compliance with the state ambient air quality standard:

Ultraviolet Method for the Determination of Ozone in the Atmosphere, 40 CFR, Chapter 1, Part 50, Appendix D as published in FR 62, 38895, July 18, 1977. The specific instruments approved are:

a. Dasibi Models 1003-AH, 1003-PC, or 1003-RS Ozone Analyzers, USEPA Automated Equivalent Method EQOA-0577-019, as published in FR 42, 28571, June 03, 1977.

b. Dasibi Models 1008-AH, 1008-PC, or 1008-RS Ozone Analyzers, USEPA Automated Equivalent Method EQOA-0383-056, as published in FR 48, 10126, March 10, 1983.

c. DKK-TOA Corp. Model GUX-113E Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0200-134, as published in FR 65, 11308, March 02, 2000.

d. Environics Series 300 Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0990-078, as published in FR 55, 38386, September 18, 1990.

e. Environment S.A. Model ozone41M UV Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0895-105, as published in FR 60, 39382, August 02, 1995.

f. Environment S.A. Model ozone42M UV Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0206-148, as published in FR 67, 42557, June 24, 2002.

g. Environment S.A. SANOA Multigas Longpath Monitoring System, USEPA Automated Equivalent Method EQOA-0400-137, as published in FR 65, 26603, May 08, 2000.

h. Horiba Instruments Models APOA-360 and APOA-360-CE Ozone Monitor, USEPA Automated Equivalent Method EQOA-0196-112, as published in FR 61, 11404, March 20, 1996.

i. Monitor Labs/Lear Siegler Model 8810 Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0881-053, as published in FR 46, 52224, October 26, 1981.

j. Monitor Labs/Lear Siegler Models ML9810, ML9811, or ML9812, Monitors Labs Model ML9810B, or Wedding & Associates Model 1010 Ozone Analyzers, USEPA Automated Equivalent Method EQOA-0193-091, as published in FR 58, 6964, February 03, 1993.

k. Opsis Model AR 500 and System 300 Open Path Ambient Air Monitoring Systems for Ozone, USEPA Automated Equivalent Method EQOA-0495-103, as published in FR 60, 21518, May 02, 1995.

l. PCI Ozone Corporation Model LC-12 Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0382-055, as published in FR 47, 13572, March 31, 1982.

m. Philips PW9771 03 Analyzer, USEPA Automated Equivalent Method EQOA-0777-023, as published in FR 42, 38931, August 01, 1977; FR 42, 57156, November 01, 1977.

n. Teledyne-Advanced Pollution Instrumentation, Inc. Model 400E Ozone Analyzer, Advanced Pollution Instrumentation, Inc. Model 400/400A Ozone Analyzer, USEPA Automated Equivalent Method EQOA-0992-087, as published in FR 57, 44565, September 28; 1992, FR 63, 31992, June 11, 1998; FR 67, 57811, September 12, 2002.

o. Thermo Electron/Thermo Environmental Instruments Models 49, 49C, USEPA Automated Equivalent Method EQOA-0880-047, as published in FR 45, 57168, August 27, 1980.

6.6 Estimated Costs and Impacts

Because the recommended change reflects the existing practice in air monitoring for ozone, approval of the recommendation will result in no costs or savings to any public agency, or to any private business.

6.7 References

Air Resources Board. September, 1987. Effects of ozone on health, technical support document, pages 5-13.

Code of Federal Regulations. Title 40, Part 50, Appendix D, Measurement principles and calibration procedure for the measurement of ozone in the atmosphere.

Code of Federal Regulation. Title 40, Part 53, Revised requirements for designation of reference and equivalent methods for PM2.5 and ambient air quality surveillance for particulate matter. Pgs 1-28.

McElroy F, Dennis M, Monica N. 1997. Determination of ozone by ultraviolet analysis. A new method for Volume II, Ambient air specific methods, quality assurance handbook for air pollution measurement systems.

USEPA. 1996. Air Quality Criteria for ozone and related photochemical oxidants, EPA/600/P-93/004q-cF, pages 3-90 to 3-102.
http://cfpub.epa.gov/ncea/cfm/ozone.cfm

Title 17, Barclay California Code of Regulation, section 70200.
USEPA/ORD (2002). List of designated reference and equivalent methods. http://www.epa.gov/ttn/amtic/criteria.html

Appendix A (1995). Dasibi model 1003 AH ozone analyzer. Volume II: standard operating procedures for air monitoring, air monitoring quality assurance, California Air Resources Board.
http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm

USEPA, 1984. Special Report, Issues Concerning the Use of Precision and Accuracy Data, EPA-450/4-84-006, pages 2 – 23.
http://www.epa.gov/ttn/amtic/cpreldoc.html

USEPA, 1983. Guideline on the Meaning and Use of Precision and Accuracy Data Required By 40 CFR Part 58, Appendices A and B, EPA-600/4-83-023, pages 6-33. http://www.epa.gov/ttn/amtic/cpreldoc.html

7 Exposure to Ozone

The purpose of this chapter is to provide a characterization of current air quality with respect to ozone. The chapter describes ambient ozone concentrations throughout California, with a focus on the current State 1-hour standard (0.09 ppm) and the proposed State 8-hour standard (0.070 ppm), as well as the federal 1-hour (0.12 ppm) and 8-hour ozone standards (0.08 ppm). The federal one-hour ozone standard is scheduled to be phased out in June 2005. Much of the information relates to current air quality, in particular, ozone data collected during 2001 through 2003. In addition, the chapter provides information about the State and federal area designation processes and data rounding conventions.

Section 7.1 describes the current area designations for the State and federal 1-hour ozone standards, as well as the United States Environmental Protection Agency's (USEPA) recent area designations for the federal 8-hour standard. The area designations indicate which areas of the State attain the health-based standards. Included in the State area designation discussion is information related to the identification of *highly irregular or infrequent events*. Data affected by these types of events are excluded from the State designation process. Section 7.2 gives a characterization of ambient ozone air quality. Information in this section includes discussions of current air quality and the frequency of maximum daily concentrations, as well as information about the ozone season, diurnal patterns of ambient ozone concentration, and historical trend data for each air basin or planning area. Finally, Section 7.3 gives a characterization of exposure to peak 1-hour and 8-hour ozone indicator values throughout the State.

It is important to note that some of the tables and graphs in Sections 7.2 and 7.3 do not include information for the Great Basin Valleys and Northeast Plateau Air Basins because, at the time this Staff Report was prepared, 2001 data for these two areas either were not reliable or not complete. In particular, reliable third quarter 2001 data were not available for the Mammoth Lakes monitoring site in the Great Basin Valleys Air Basin, and data for the Yreka monitoring site in the Northeast Plateau Air Basin were not complete during the 2001 summer months, when high concentrations are expected to occur. Where 2001 data do not impact the air quality statistics, data for these two areas are included (for example, maximum 1-hour and 8-hour concentrations for 2002 and 2003 are included).

7.1 Area Designations for the State and Federal Ozone Standards

7.1.1 Background

The California Health & Safety Code (H&SC) section 39607(e) requires the Air Resources Board (ARB) to establish and periodically review criteria for designating areas as attainment or nonattainment with respect to the State ambient air quality standards. Areas are designated separately for each pollutant for which there is an ambient air quality standard specified in section 70200 of Title 17, California Code of Regulations. The ARB originally adopted State designation criteria in June 1989. The ARB subsequently amended the designation criteria in June 1990, May 1992, December 1992, November 1993, November 1995, September 1998, and January 2004. H&SC section 39608

requires the ARB to use the designation criteria in assessing the designation status of areas in California (ARB 2003).

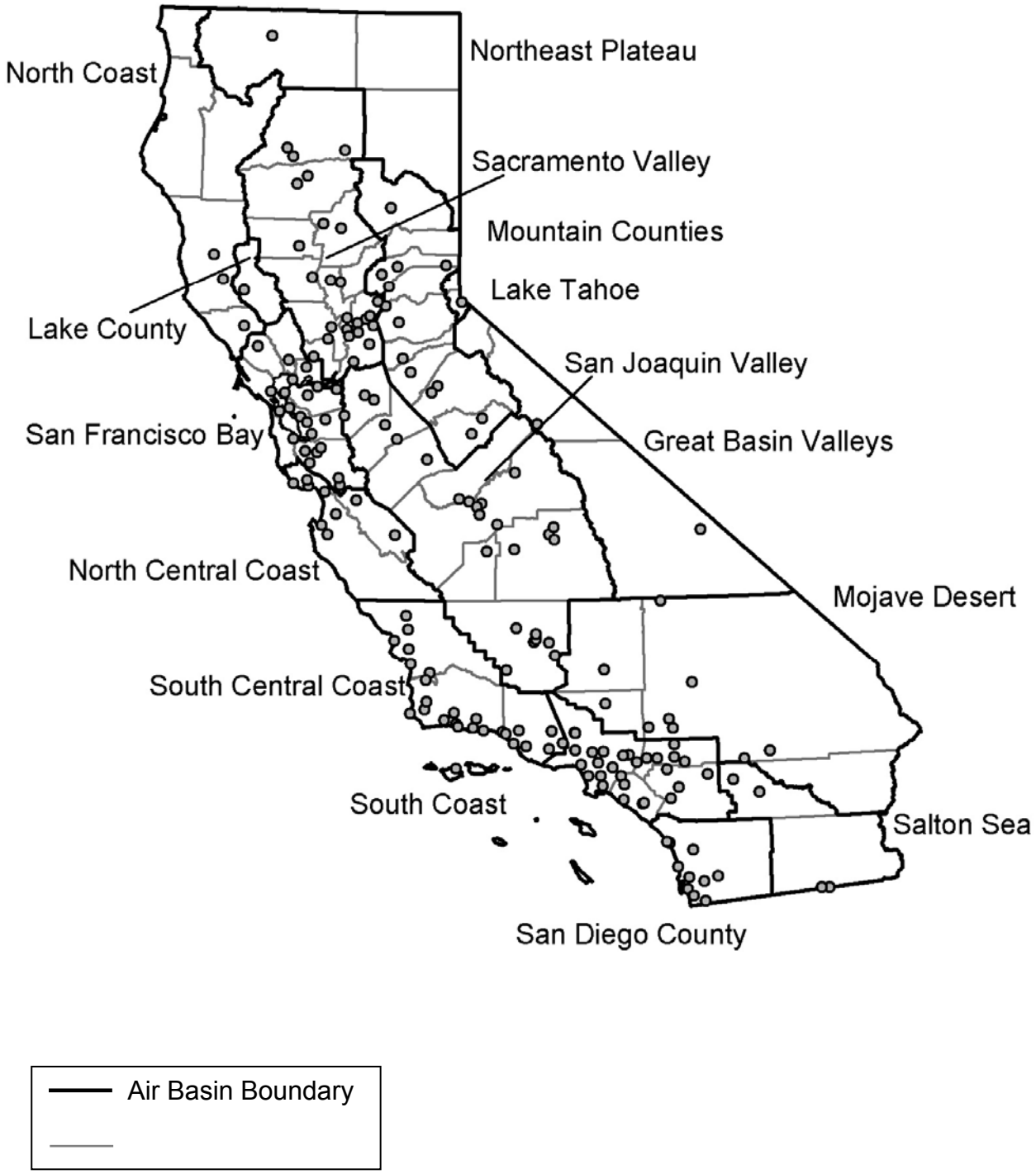
State area designations indicate whether an area meets the health-based State ambient air quality standards. There are three basic designation categories: *nonattainment, attainment,* and *unclassified*. A *nonattainment designation* indicates that the air quality violates a State standard. There is a subcategory of the nonattainment designation called nonattainment-transitional. This designation is given to areas that still violate the State standard, but are making progress and are close to attainment. In contrast to nonattainment, an *attainment designation* indicates that the air quality does not violate the State standard. Finally, an *unclassified designation* indicates that there are insufficient data for determining attainment or nonattainment.

Under State law (H&SC section 40921 and section 40921.5(a) and (c)), areas designated as nonattainment for the State 1-hour ozone standard are also assigned a classification that is commensurate with the severity of their air quality problem and the degree of emission control required to achieve attainment. For example, take two ozone nonattainment areas, with the first area having a measured maximum concentration of 0.10 ppm and the second area having a measured maximum concentration of 0.19 ppm. While both areas are designated as nonattainment, the second area has a more severe ozone problem and will need to implement a more stringent emission control strategy to achieve attainment. Therefore, although these two areas would have the same designation, they would not have the same classification. Under State law (H&SC section 40921 and section 40921.5(a) and (c)), areas are classified as moderate, serious, severe, and extreme with respect to the State 1-hour ozone standard, based on data for calendar years 1989 through 1991.

The USEPA has a similar process for designating and classifying areas with respect to the federal ozone standards. However, the USEPA uses only two designation categories. Similar to the State designations, areas with air quality that violates the federal standard are designated as *nonattainment*. However, areas with air quality that does not violate the standard and areas with insufficient data for determining nonattainment are generally combined in a category called *unclassified/attainment*. Similar to State requirements, the USEPA also classifies ozone nonattainment areas according to the severity of their ozone air quality problem.

Both the ARB and the USEPA designate areas based on recent ambient air quality data. As shown in Figure 7-1, California has an ozone monitoring network with approximately 175 monitors located throughout the State. These monitors are generally operated by the ARB or by local air pollution control or air quality management districts (districts). However, a few sites are operated by other organizations, such as the National Park Service. At each site, a monitor provides continuous hourly averages of ambient ozone concentrations. These hourly measurements can be aggregated into longer-term measurements, such

Figure 7-1 Ozone Monitoring Sites in California (as of December 31, 2002)



as 8-hour averages. Because they are used for regulatory purposes, these measured data must satisfy specific siting and quality assurance procedures established by the ARB and USEPA (additional information about air quality monitoring can be found in Chapter 6). In general, area designations for both the State and federal standards are based on data collected during the previous three years.

7.1.2 Exclusion of Data

The State area designation process has several provisions for excluding high values that are not reasonable to control through the regulatory process. These excluded values are identified as concentrations affected by *highly irregular or infrequent events*. While a concentration identified as a highly irregular or infrequent event "exceeds" the level of the State standard, such an exceedance is not considered a "violation" of the standard. This is important because only a "violation" can trigger a nonattainment designation. As a result, although the State ozone standard is expressed as a concentration that is "not to be exceeded," the designation criteria allow some leeway for excluding exceedances that are not reasonable to control. Under State law, there are three types of highly irregular or infrequent events: extreme concentration events, exceptional events, and unusual concentration events.

An *extreme concentration event* is identified by a statistical procedure (ARB 1993) and is the most frequently used method for excluding values from the State area designation process. This type of event is not necessarily tied to any specific, identifiable event. However, adverse meteorology is one potential cause of an extreme concentration event. Because meteorology is a potential cause of an extreme concentration event and meteorology varies from year-to-year, an area may have several values excluded during years with adverse meteorology and no values excluded during years with more normal meteorology.

In identifying extreme concentration events, a statistical procedure is used to calculate a site-specific and pollutant-specific value representing the concentration that is expected to be exceeded once per year, on average, based on the distribution of data for the site. The site-specific, statistically derived value, commonly referred to as the peak indicator value or the Expected Peak Day Concentration (EPDC), is rounded to the precision of the State standard before being used. The measured or averaged (for example, 8-hour averages) pollutant concentrations are also rounded before being compared with the rounded EPDC. Any rounded concentration that is higher than the rounded EPDC value is identified as an extreme concentration eventand is excluded from the State designation process. Furthermore, these extreme concentrations are not considered violations of the State standard.

In contrast to an extreme concentration event, an *exceptional event* is a specific, identifiable event that causes an exceedance of a standard, but is considered unreasonable to control through the regulatory process. Exceptional events may be identified for both State and federal designation purposes, and are evaluated on a case-by-case basis. An example of an ozone exceptional event is stratospheric ozone intrusion.

Federal guidelines (which are also used in the State designation process) define stratospheric ozone intrusion as occurring when a parcel of air originating in the stratosphere (average height 20 kilometers or about 12.4 miles) is entrained directly to the surface of the earth. Stratospheric ozone intrusions are typically associated with strong frontal passages or severe thunderstorms, and such conditions occur primarily during springtime (USEPA 1986).

Generally, the district identifies questionable data and gathers relevant information to document the cause and effect relationship. For stratospheric ozone intrusion, these data may include the intensity and location of low pressure zones, the relative amount of carbon monoxide present in the air, the relative humidity of the air, and in rare cases, the presence of trace elements characteristic of stratospheric air. The district then submits their request to the ARB for evaluation and potential identification. As stated in the area designation criteria, the ARB will evaluate potential exceptional events only if they have the potential to affect an area's designation status.

Finally, an *unusual concentration event* is an anomalous exceedance of a State standard that cannot be identified as an extreme concentration event or an exceptional event. Unusual concentration events can be identified only for areas designated as attainment or unclassified at the time the exceedance occurs. Furthermore, this type of event is usually identified in areas with limited monitoring data, where we do not have a long-term record for determining what is "characteristic" for the area. In identifying such events, the ARB's Executive Officer must make specific findings based on relevant information. An area may retain its attainment or unclassified designation by excluding an exceedance affected by an unusual concentration event for up to three consecutive years. However, if an exceedance occurs during the fourth year, the area is redesignated as nonattainment, unless the exceedance can be excluded as an extreme concentration event or an exceptional event.

For both State and federal area designations, the size of an area designated for ozone is generally an air basin. However, for the State standards, the ARB may designate a smaller area if it finds (based on air quality data, meteorology, topography, or the distribution of population and emissions) there are areas within an air basin with distinctly different air quality that can be attributed to sources and conditions that do not affect the entire air basin. In this case, the ARB may designate an area smaller than an air basin, using political boundary lines to the extent possible. The smaller designated area must include those sources whose emissions contribute to a violation of the standard. Furthermore, contiguous areas within an air basin that have the same designation, are designated as a single area.

7.1.3 State Area Designations

The State ozone standard is 0.09 ppm for one hour, not to be exceeded. The State area designations are based on a site-by-site comparison of the 1-hour State ozone standard with the maximum measured 1-hour concentration (that is not excluded as a highly irregular or infrequent event) during a three-year period . As described previously, highly irregular or infrequent exceedances may be

excluded as extreme concentration events, exceptional events, or unusual concentration events.

Figure 7-2 shows the area designations for the State 1-hour ozone standard. In addition to San Luis Obispo County and the North Coast Air Basin, which were designated as attainment in January 2004, the Lake County, Lake Tahoe, and Northeast Plateau Air Basins are also designated as attainment (ARB 2003). In contrast, however, most of the rest of the State, including all of the major urban areas, have ozone concentrations that violate the State standard. These areas are designated as nonattainment.

The method used for determining area designation values is generally consistent across all pollutants. First, if there is a valid EPDC, the EPDC is rounded to the given number of decimal places for the applicable State standard (for example, 2 decimal places for the State 1-hour ozone standard). Next, all measured values for the three-year period used in area designations are rounded to the given number of decimal places. All values that are higher than the valid rounded EPDC are excluded as extreme concentration events and therefore, not considered in the area designation process. The value used to designate an area (the designation value) is the highest rounded value for the previous three-year period that is less than or equal to the rounded EPDC. However, if this value is identified as affected by an exceptional event or unusual concentration event, it is excluded from the area designation process and the next highest value becomes the designation value.

7.1.4 Data Rounding Conventions

As noted above, before ozone measurements are used in designating areas for the State standard, they are rounded to the precision of the standard. In addition, the Expected Peak Day Concentration or EPDC is also rounded to the precision of the State standard before it is used to identify and exclude measurements affected by extreme concentration events.

All raw air quality data are stored in the Board's Aerometric Data Analysis and Management (ADAM) database, as they are reported. However, the reported values and the stored values can and do differ very slightly, because ADAM stores numbers in a floating-point format. For example, a number reported as 0.123 might actually be stored as 0.1229999998 or as 0.12300000001. Nonetheless, great care is taken to ensure that these "slight" differences have no impact on calculated values used for area designations.

The precision or given number of decimal places varies for each State standard and depends on how the level of the standard is specified. For example, the current 1-hour ozone standard is 0.09 ppm, which is given to 2 decimal places. In contrast, a proposed 8-hour standard of 0.070 ppm is given to 3 decimal places. Individual measurements and statistics are generally rounded up or down (to the precision of the standard) using the digit just beyond the given number of decimal places and according to standard rounding conventions. Values that are below 5 round down, while those that are equal to or greater than 5 round up. For example, the State 1-hour ozone standard is given to 2 decimal places. Therefore, a measured value of 0.123 ppm rounds to 0.12 ppm because 0.003 is less than 0.005. In contrast, a measured value of 0.127 ppm rounds to 0.13 ppm

because 0.007 is greater than 0.005. Similarly, a measured value of 0.125 ppm rounds to 0.13 ppm because 0.005 exactly equals 0.005.

7.1.5 Federal Area Designations

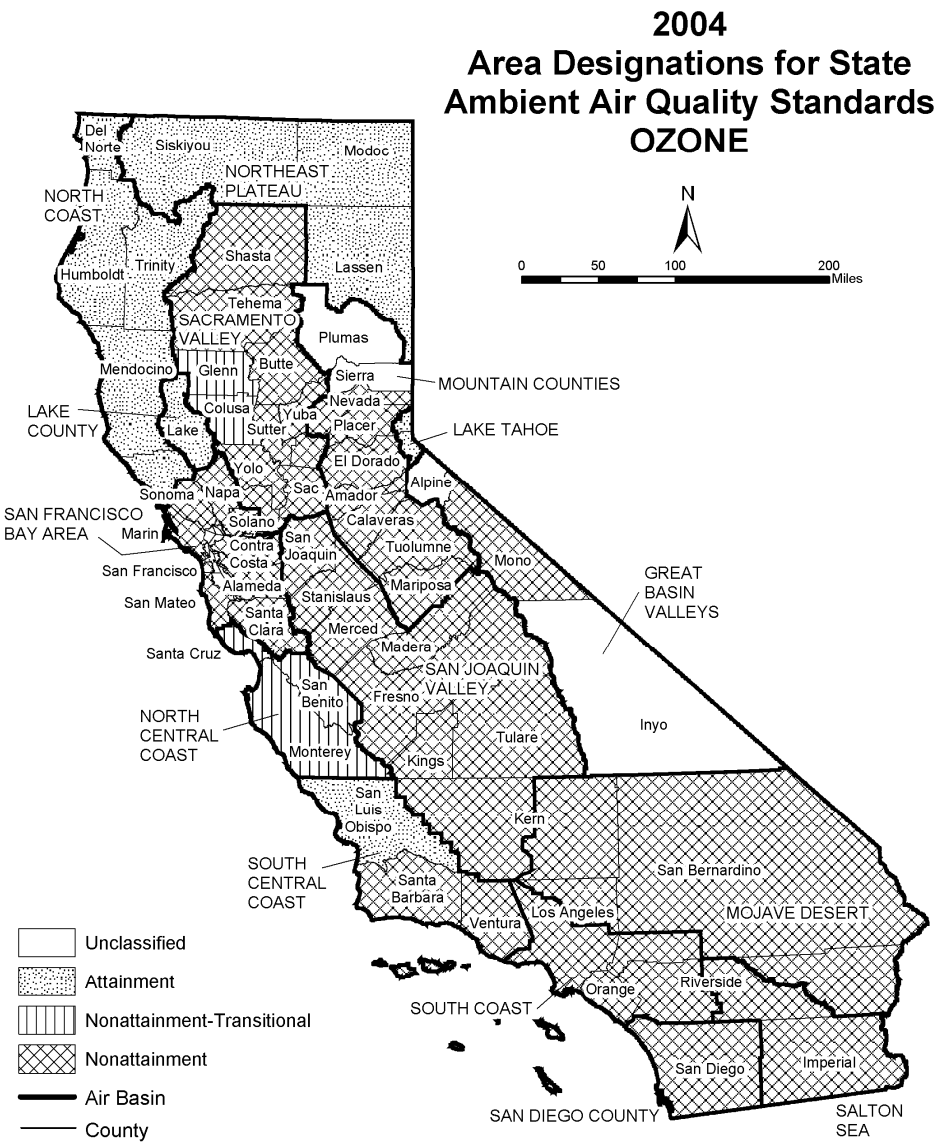
There are two federal standards for ozone: a 1-hour standard and an 8-hour standard. The federal 1-hour ozone standard is 0.12 ppm. For an area to be designated as attainment for the federal 1-hour standard, there may not be more than three violations of the standard at any site in the area during a three-year period. Compliance with the federal 1-hour standard is generally based on comparing the federal standard of 0.12 ppm with the 4th high 1-hour ozone concentration measured at each site in the area during a three-year period. If the 4th high concentration at any site in the area violates the standard, the area is designated as nonattainment. As mentioned earlier, areas that either do not violate the standard or do not have sufficient data to determine compliance with the standard are combined together in a designation category called unclassified/attainment.

Figure 7-3 shows the current area designations for the federal 1-hour ozone standard. Similar to the State designations, Figure 7-3 shows that most of the major urban areas in California are designated as nonattainment for the federal 1-hour standard. Over the last several years, ozone air quality in Butte County, northern Sutter County, Yuba County, Santa Barbara County, Ventura County, San Diego County, eastern Kern County, and the San Francisco Bay Area Air Basin has improved, and air quality in these areas now attains the federal 1-hour ozone standard. Recognizing these improvements, USEPA recently redesignated San Diego County and Santa Barbara County as attainment for the federal 1-hour ozone standard. However, the other four areas have not yet been officially redesignated, and they are shown as nonattainment areas in Figure 7-3.

Although some areas of California no longer violate the federal 1-hour standard, a number of these same areas do violate the new federal 8-hour ozone standard of 0.08 ppm, not to be exceeded. Compliance with the 8-hour standard is based on the annual 4th highest concentration at each site, averaged over three years. Although the federal 8-hour ozone standard is relatively new, long-term data are available for assessing attainment and trends because the 8-hour concentrations are based on an average of 1-hour ozone observations, which have been monitored for many years.

As with the federal 1-hour standard, all monitoring sites within an area must be in compliance with the 8-hour standard for the area to be designated as attainment. The ARB developed recommendations for the federal 8-hour designations and transmitted them to USEPA during early 2004. Figure 7-4 shows the final designations as made by USEPA on April 15, 2004. The final designations are based on air quality data collected during 2001 through 2003. As shown in Figure 7-4, the 8-hour nonattainment areas mirror those for the federal 1-hour standard, with the addition of much of the Mountain Counties Air Basin area. The remainder of the State is included in the unclassified/attainment category.

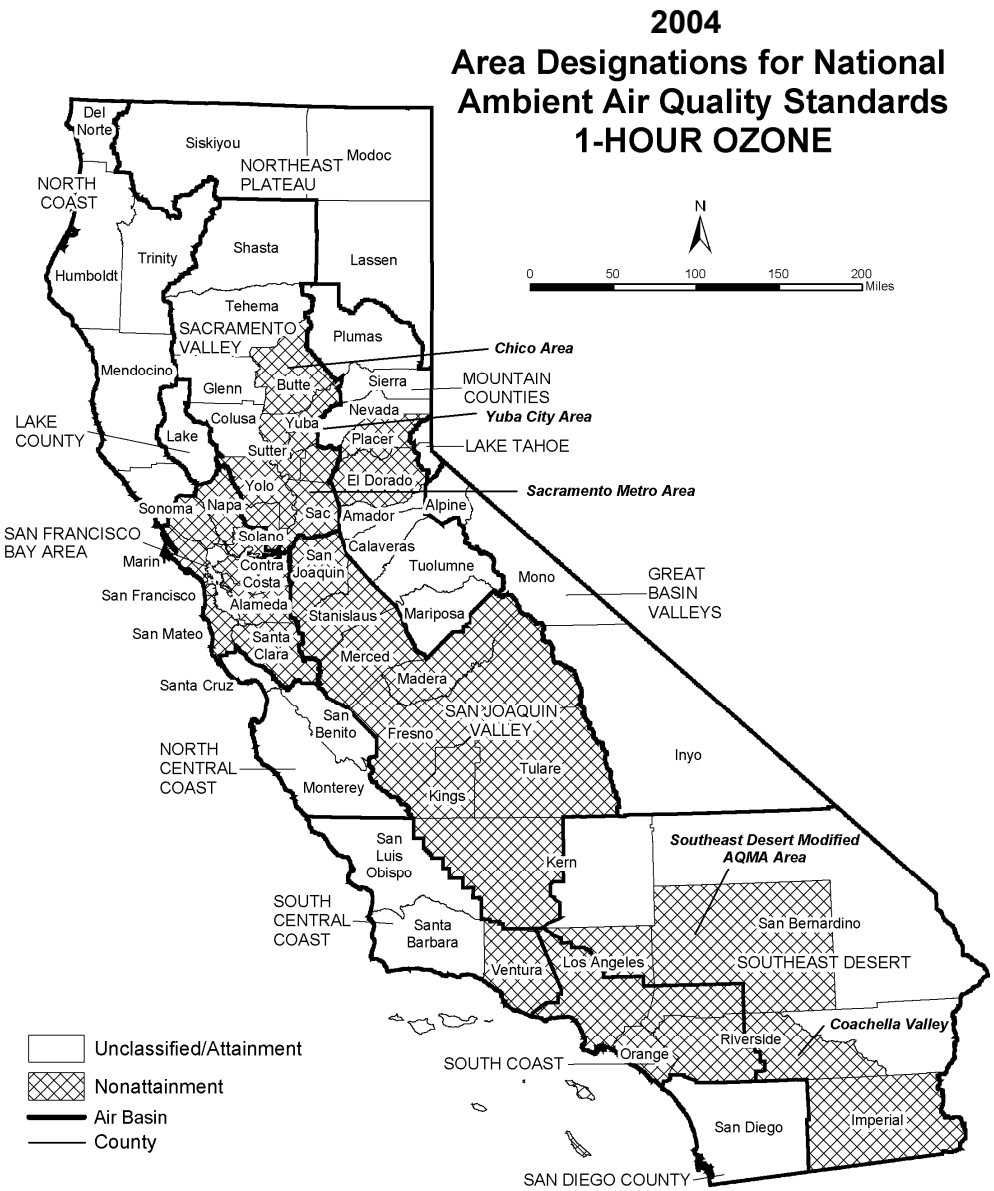
Figure 7-2 2004 Area Designations for the State 1-Hour Ozone Standard



Source Date:
October 2003
Emission Inventory Branch, PTSD

October 18, 2004

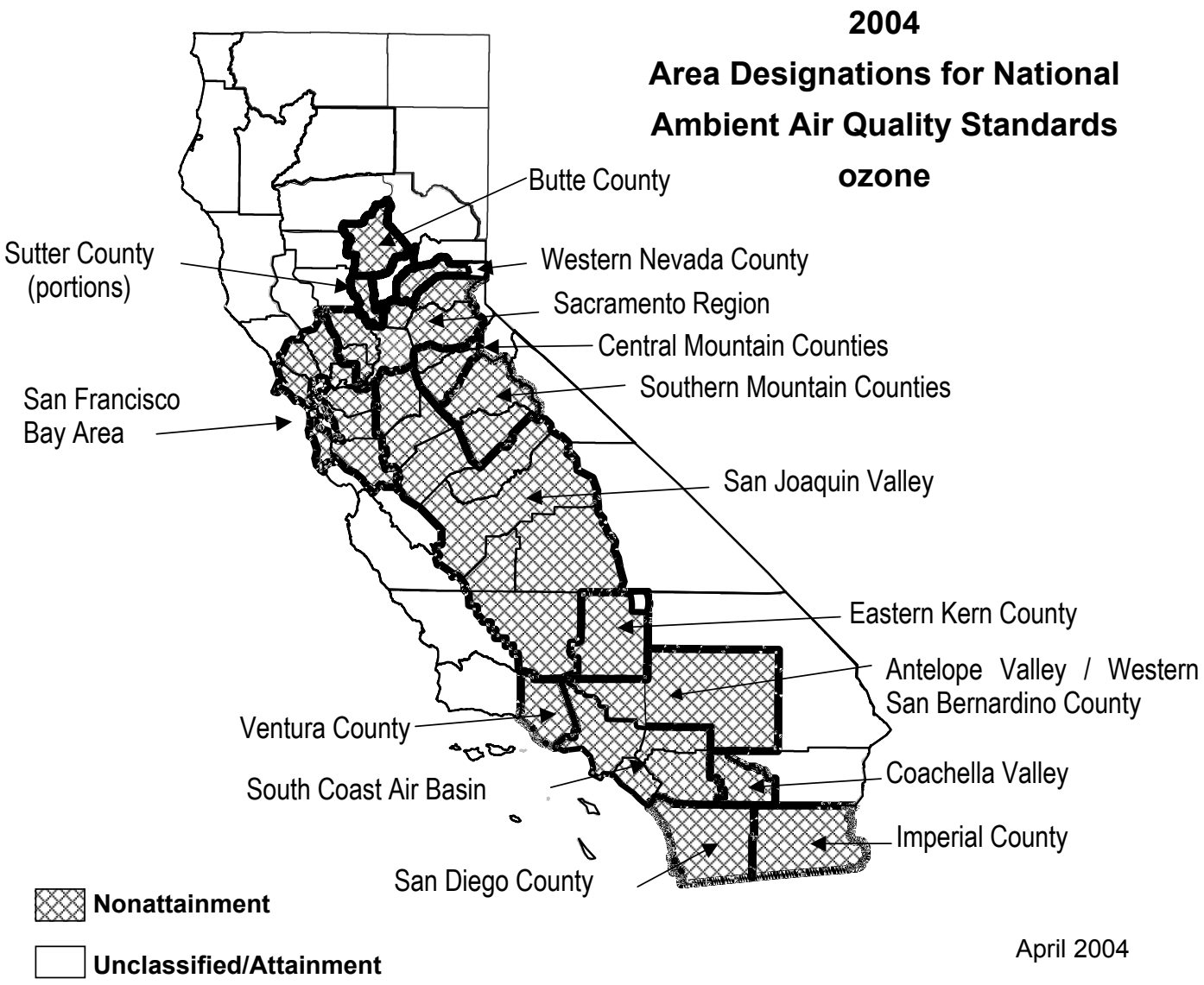
Figure 7-3 2004 Area Designations for the Federal 1-Hour Ozone Standard



Source Date:
October 2003
Emission Inventory Branch, PTSD

October 19, 2004

Figure 7-4 2004 Area Designations for the Federal 8-Hour Ozone Standard



7.2 Characterization of Ambient Ozone Air Quality

7.2.1 Overview

This section discusses air quality with reference to ambient ozone in each of California's air basins and/or planning areas, based on measured and statistically derived values. The information includes summary information about the magnitude and frequency of monitored concentrations for both the 1-hour and 8-hour averaging times. In addition, there is information about the seasonal and diurnal variations and a characterization of ozone concentrations in each area. These discussions include current ozone statistics, as well as historical trends.

Ozone is monitored continuously at approximately 175 sites in California. The data for each monitoring site are reported as 1-hour average concentrations. These 1-hour data can be aggregated into 8-hour average ozone concentrations, and can be summarized as daily, seasonal, or annual maximum 1-hour and 8-hour concentrations. In addition, these data are used in determining the number of days during which measured concentrations exceed the State and federal ozone standards.

For purposes of evaluating long-term ozone air quality trends and population exposures, the maximum concentration usually is not the best measure, because maximum concentrations can be highly influenced by year-to-year variations in meteorology. In contrast to the maximum values, two calculated statistics that provide more stable measures of long-term trends are the *peak indicator value*, or EPDC, and the *moving 3-year mean*. The peak indicator represents the maximum concentration expected to be exceeded once per year, on average. This indicator is based on a statistical calculation using three years of ambient monitoring data and is calculated for each monitoring site in an area. The highest peak indicator value among all sites in an area is generally used when evaluating area-wide air quality. A moving 3-year mean of the annual maximum measured concentrations also tends to be a more stable trend indicator, when compared to the measured maximum concentration. Although the moving 3-year mean is not as robust as the peak indicator, the 3-year mean does tend to dampen some of the year-to-year variation caused by meteorology. This yields data that are more suitable for trend analysis, when compared with data for individual years.

The statistics presented in the following sections represent an air basin, except for the two Sacramento Valley areas and the Mountain Counties area. The Sacramento Valley Air Basin (SVAB) is divided between the Sacramento Metropolitan (Metro) Area and the Upper Sacramento Valley to be consistent with the areas used for federal area designations and air quality planning activities. The Sacramento Metro Area includes the southern urbanized portion of the Sacramento Valley Air Basin (Sacramento, SVAB portion of Solano, and Yolo counties), the southern one-third of Sutter County, the SVAB portion of Placer County, and the portions of El Dorado and Placer counties that lie within the Mountain Counties Air Basin. The remaining portion of the Sacramento Valley Air Basin is included in the Upper Sacramento Valley. Because the Mountain Counties Air Basin portions of El Dorado and Placer counties are included in the Sacramento Metro Area, sites in these areas are not included in the Mountain Counties summary statistics included in this Report.

Data presented in this subsection are evaluated using the maximum measured concentrations, as well as the peak indicator and the number of days the State and federal standards were exceeded. In most cases, the data used reflect data for record extracted from the ARB ADAM (Aerometric Data Analysis and Measurement) or USEPA AIRS (Aerometric Information Retrieval System) databases.

7.2.2 Ambient 1-Hour Ozone Concentrations

Table 7-1 shows the maximum measured 1-hour ozone concentration, the number of days with measured 1-hour concentrations exceeding the State 1-hour standard of 0.09 ppm, and the number of days with measured 1-hour concentrations exceeding the federal 1-hour standard of 0.12 ppm. The table includes statistics for the years 2001 through 2003 and were extracted from the ARB ADAM database during March 2004. It is important to note that the counts of exceedance days reflect area-wide totals. In other words, each day with an exceedance is counted as one day, regardless of the number of individual sites, with concentrations exceeding the standard.

In contrast to Table 7-1, Table 7-2 lists several calculated ozone statistics for each air basin or planning area. The calculated statistics include the 3-year mean of the number of days over the State standard, the peak 1-hour indicator or EPDC, and the 3-year mean of the number of days over the federal 1-hour standard. In addition, Table 7-2 lists the highest 4th high 1-hour ozone concentration, which is an indicator of compliance with the federal 1-hour standard. This statistic represents the maximum of the 4th highest 1-hour ozone concentration measured at any site in each air basin or planning area during the three-year period. Furthermore, the maximum 4th high reflects the federal 1-hour design value, as long as it meets data completeness requirements.

During 2001 through 2003, neither the State nor federal 1-hour standard was exceeded in the Lake County Air Basin, North Coast Air Basin, or Northeast Plateau Air Basin. Data for four additional areas, Great Basin Valleys Air Basin, Lake Tahoe Air Basin, North Central Coast Air Basin, and the Upper Sacramento Valley show exceedances of the State standard, but not the federal 1-hour standard (as described earlier, representative data for the Northeast Plateau Air Basin and Great Basin Valleys Air Basin are available for 2002 and 2003 only). Both the State and federal 1-hour standards were exceeded during at least two of the three years in all other areas.

The highest number of exceedance days for both the State and federal 1-hour standards occurred in the San Joaquin Valley Air Basin and the South Coast Air Basin. Both areas had more than 115 State standard exceedance days and 31 or more federal standard exceedance days during each of the three years. The Sacramento Metro Area, Mojave Desert Air Basin, and Salton Sea Air Basin all averaged more than 50 State standard exceedance days and averaged 6 or more federal standard exceedance days during 2001 through 2003. The remaining five areas (Mountain Counties Air Basin, San Diego Air Basin, San Francisco Bay Area Air Basin, South Central Coast Air Basin, and the Upper Sacramento Valley) averaged from 12 to 45 State standard exceedance days. The Upper Sacramento Valley area had no exceedances of the federal standard

while the Mountain Counties Air Basin, San Diego Air Basin, San Francisco Bay Area Air Basin, and South Central Coast Air Basin each averaged 1 to 2 federal standard exceedance days for the three-year period.

The range of the measured maximum 1-hour concentrations tends to follow a similar pattern. The South Coast Air Basin showed the highest values, with measured concentrations of 0.169 ppm or higher during all three years. The next highest 1-hour ozone concentrations occurred in the Salton Sea Air Basin and San Joaquin Valley Air Basin, which had concentrations of 0.149 ppm or higher during 2001 through 2003. The Sacramento Metro Area, Mojave Desert Air Basin, and San Francisco Bay Area Air Basin had maximum measured concentrations ranging from 0.128 ppm to 0.163 ppm during each of the three years. Maximum 1-hour concentrations in the Mountain Counties Air Basin, San Diego Air Basin, and South Central Coast Air Basin had maximum 1-hour concentrations of 0.120 ppm or higher during each year. Three areas (North Central Coast Air Basin, Upper Sacramento Valley, and Lake Tahoe Air Basin) had maximum 1-hour concentrations above 0.100 ppm during at least two of the three years. The remaining areas (Great Basin Valleys Air Basin, Lake County Air Basin, North Coast Air Basin, and Northeast Plateau Air Basin) had maximum 1-hour ozone concentrations of 0.100 ppm or less during each of the years.

The values for the peak 1-hour indicator and the highest 4th high 1-hour ozone concentration, shown in Table 7-2, reflect similar patterns. The highest values are found in the South Coast and San Joaquin Valley air basins, followed by the Sacramento Metro Area, Salton Sea Air Basin, and Mojave Desert Air Basin. The highest 4th high 1-hour ozone concentration, used as an indicator of compliance with the federal 1-hour standard, is above the level of the standard in each of these five areas.

Table 7-1 Measured Ozone Statistics for 2001-2003 for California Air Basins or Planning Areas

Basin	Year	Maximum 1-Hour Concentration	Days Exceeding State 1-Hour Std	Days Exceeding Federal 1-Hour Std
Great Basin Valleys	2001	Representative data not available		
	2002	0.100	8	0
	2003	0.089	0	0
Lake County	2001	0.070	0	0
	2002	0.090	0	0
	2003	0.070	0	0
Lake Tahoe	2001	0.095	1	0
	2002	0.102	1	0
	2003	0.112	3	0
Mojave Desert	2001	0.146	72	6
	2002	0.157	75	16
	2003	0.163	93	13
Mountain Counties[1]	2001	0.120	29	0
	2002	0.132	41	2
	2003	0.135	45	2
North Central Coast	2001	0.108	3	0
	2002	0.115	8	0
	2003	0.111	3	0
North Coast	2001	0.090	0	0
	2002	0.092	0	0
	2003	0.090	0	0
Northeast Plateau	2001	Representative data not available		
	2002	0.087	0	0
	2003	0.089	0	0
Sacramento Metro Area[2]	2001	0.148	52	3
	2002	0.156	59	10
	2003	0.145	53	6

San Diego	2001	0.141	29	2
	2002	0.121	15	0
	2003	0.125	23	1
San Francisco Bay Area	2001	0.134	15	1
	2002	0.160	16	2
	2003	0.128	19	1
San Joaquin Valley	2001	0.149	123	32
	2002	0.164	127	31
	2003	0.156	137	37
Salton Sea	2001	0.167	81	15
	2002	0.156	68	5
	2003	0.187	69	9
South Central Coast	2001	0.129	34	2
	2002	0.132	24	1
	2003	0.130	45	2
South Coast	2001	0.190	121	36
	2002	0.169	116	45
	2003	0.194	125	64
Upper Sacramento Valley	2001	0.104	12	0
	2002	0.117	17	0
	2003	0.117	19	0

Data Source: ADAM – 03/08/04 and 03/16/04

[1] Mountain Counties Air Basin excludes Cool-Highway 193, Placerville-Gold Nugget Way, and Colfax sites.

[2] Sacramento Metro Area includes the following sites: Cool-Highway 193, Placerville-Gold Nugget Way, and Colfax from Mountain Counties Air Basin and Auburn-Dewitt-C Avenue, Davis-UCD Campus, Elk Grove-Bruceville Road, Folsom-City Corporation Yard, Folsom-Natoma Street, North Highlands-Blackfoot Way, Pleasant Grove-4 miles SW, Rocklin-Rocklin Road, Rocklin-Sierra College, Roseville-N Sunrise Blvd, Sacramento-3801 Airport Road, Sacramento-Del Paso Manor, Sacramento-T Street, Sloughhouse, Vacaville-Elmira Road, Woodland-Gibson Road, and Woodland-Sutter Street from Sacramento Valley Air Basin.

Notes: Days exceeding State and federal 1-hour standards are distinct areawide days, meaning the exceedance day is counted only once, even if multiple sites experienced an exceedance on the same day. The State ozone standard is exceeded when the concentration is equal to or greater than 0.095 ppm. The federal 1-hour ozone standard is exceeded when the concentration is equal to or greater than 0.125 ppm.

Table 7-2 Calculated Ozone Statistics for 2001-2003 for California Air Basins or Planning Areas

Basin	3-Year Mean # Days over State 1-Hr Std	Peak 1-Hour Indicator	3-Year Mean # Days over Federal 1-Hr Std	Highest 4th High 1-Hr Ozone Conc
Great Basin Valleys	Representative data not available			
Lake County	0	0.082	0	0.080
Lake Tahoe	2	0.103	0	0.094
Mojave Desert	80	0.138	12	0.138
Mountain Counties	38	0.117	1	0.117
North Central Coast	5	0.105	0	0.106
North Coast	0	0.082	0	0.083
Northeast Plateau	Representative data not available			
Sacramento Metro Area	55	0.146	6	0.143
Salton Sea	73	0.135	10	0.142
San Diego	22	0.117	1	0.118
San Francisco Bay Area	17	0.130	1	0.123
San Joaquin Valley	129	0.152	33	0.151
South Central Coast	34	0.124	2	0.124
South Coast	121	0.178	48	0.180
Upper Sacramento Valley	16	0.121	0	0.113

Note:
The peak 1-hour indicator and highest 4th high 1-hour ozone concentration reflect data from the high site in the air basin or planning area.

7.2.3 Ambient 8-Hour Ozone Concentrations

The federal ozone standard, promulgated by the USEPA in 1997, is 0.08 ppm for 8 hours. As discussed earlier, ozone is measured continuously, and running 8-hour averages are computed from hourly ozone concentrations. Each of the 8-hour averages is assigned to the first hour of the 8-hour period. For example, an 8-hour average calculated from data collected during the 8-hour period starting at 12 p.m. is assigned to 12 p.m. With complete data, there are twenty-four 8-hour average concentrations calculated for each day. The highest of these daily 8-hour averages is identified as the maximum 8-hour concentration for the day (USEPA 1998).

The federal 8-hour ozone standard is not to be exceeded, based on the fourth highest concentration each year, averaged over three years. In other words, take the fourth highest concentration recorded at a site during each of three years, average these three values together, and then compare the average value to the standard. This comparison is made for each site in an area, and if the value for any site exceeds the standard, the area is nonattainment.

Table 7-3 shows both measured and calculated ozone statistics related to an 8-hour averaging time. The statistics include the maximum 8-hour concentration, the peak 8-hour indicator or EPDC value, the fourth highest 8-hour concentration, the 3-year mean of the fourth highest 8-hour concentration, the number of days on which the federal 8-hour standard was exceeded, and the 3-year mean of the number of days on which the federal 8-hour standard was exceeded. These six statistics are given for each air basin or planning area, for each of the years 2001, 2002, and 2003. These statistics were extracted from the ARB ADAM database during March 2004.

As mentioned earlier, the form of the federal 8-hour standard used for determining attainment is the average of the fourth highest daily concentration during each year of a three-year period. However, this analysis focuses on the peak 8-hour indicator, the maximum 8-hour concentrations, and the number of days on which the maximum concentration exceeded the level of the federal standard. These statistics are used to assess ambient concentrations.

As with the 1-hour statistics, the highest 8-hour values are again found in the South Coast Air Basin and San Joaquin Valley Air Basin. Maximum 8-hour concentrations in the South Coast Air Basin ranged from 0.144 ppm to 0.153 ppm during 2001 through 2003, while maximum 8-hour concentrations in the San Joaquin Valley ranged from 0.120 ppm to 0.132 ppm during the same three-year period. Three other areas, the Mojave Desert Air Basin, the Sacramento Metro Area, and the Salton Sea Air Basin also had a maximum 8-hour concentration above 0.120 ppm during at least one of the three years.

With respect to the federal 8-hour ozone standard, Lake County Air Basin and North Coast Air Basin showed no exceedance days during 2001 through 2003. One area, the Lake Tahoe Air Basin, averaged only one exceedance day for the three-year period, while the North Central Coast Air Basin averaged three 8-hour exceedance days. In contrast, the San Joaquin Valley Air Basin showed the highest average number of exceedance days (123), followed by the South Coast Air Basin (99). The Sacramento Metro Area, Mojave Desert Air Basin, Mountain

Table 7-3 Measured and Calculated Ozone Statistics for Ambient 8-Hour Concentrations 2001 through 2003

Basin	Year	Maximum 8-Hour Conc	Peak 8-Hour Indicator	4th High 8-Hour Conc	3-Year Mean of 4th High Conc	# of Days Fed Std Exceeded	3-Year Mean of # of Days Fed Std Exceeded
Great Basin Valleys	2001	Representative data not available					
	2002	0.088	0.090	0.084	0.081	3	
	2003	0.084	0.084	0.080	0.081	0	
Lake County	2001	0.065	0.071	0.060	0.063	0	
	2002	0.077	0.073	0.072	0.064	0	
	2003	0.061	0.074	0.058	0.063	0	0
Lake Tahoe	2001	0.084	0.079	0.076	0.075	0	
	2002	0.079	0.080	0.077	0.075	0	
	2003	0.103	0.093	0.084	0.084	3	1
Mojave Desert	2001	0.117	0.114	0.106	0.102	65	
	2002	0.123	0.116	0.118	0.106	66	
	2003	0.130	0.118	0.119	0.106	74	68
Mountain Counties	2001	0.106	0.103	0.095	0.097	29	
	2002	0.113	0.106	0.099	0.098	47	42
	2003	0.103	0.107	0.101	0.098	49	
North Central Coast	2001	0.088	0.085	0.079	0.079	2	
	2002	0.094	0.088	0.086	0.081	5	
	2003	0.088	0.089	0.081	0.081	2	3
North Coast	2001	0.073	0.078	0.065	0.069	0	
	2002	0.072	0.069	0.067	0.063	0	
	2003	0.080	0.068	0.062	0.062	0	0
Northeast Plateau	2001	Representative data not available					
	2002	0.075	0.071	0.066	0.055	0	
	2003	0.074	0.073	0.068	0.057	0	
Sacramento Metro Area	2001	0.109	0.113	0.105	0.104	41	
	2002	0.137	0.119	0.111	0.106	47	
	2003	0.122	0.122	0.106	0.107	43	44

Salton Sea	2001	0.113	0.110	0.111	0.100	54	
	2002	0.124	0.118	0.109	0.105	55	
	2003	0.110	0.119	0.105	0.108	47	52
San Diego	2001	0.116	0.101	0.098	0.094	17	
	2002	0.100	0.103	0.096	0.095	13	
	2003	0.103	0.101	0.089	0.093	6	12
San Francisco Bay Area	2001	0.102	0.094	0.094	0.082	7	
	2002	0.106	0.096	0.096	0.082	7	
	2003	0.101	0.098	0.092	0.086	7	7
San Joaquin Valley	2001	0.120	0.119	0.115	0.109	109	
	2002	0.132	0.120	0.125	0.115	125	
	2003	0.127	0.122	0.119	0.115	134	123
South Central Coast	2001	0.113	0.107	0.103	0.101	25	
	2002	0.109	0.106	0.100	0.097	16	
	2003	0.114	0.104	0.100	0.095	35	25
South Coast	2001	0.144	0.144	0.138	0.129	92	
	2002	0.144	0.144	0.138	0.128	96	
	2003	0.153	0.146	0.146	0.131	109	99
Upper Sacramento Valley	2001	0.089	0.102	0.088	0.087	8	
	2002	0.103	0.100	0.099	0.089	16	
	2003	0.099	0.104	0.094	0.089	19	14

Notes: Days exceeding federal 8-hour standard are distinct areawide days, meaning the exceedance day is counted only once, even if multiple sites experienced an exceedance on the same day. The federal 8-hour ozone standard is exceeded when the three-year average of the 4th highest 8-hour concentrations is equal to or greater than 0.085 ppm.

Data Source: ADAM - 3/10/04 and 03/16/04

Counties Air Basin, and Salton Sea Air Basin each averaged between 42 and 68 exceedance days during 2001 through 2003. The remaining four areas averaged between 7 and 25 federal 8-hour exceedance days during the three-year period.

7.2.4 Available 2004 Ozone Data

Although ozone concentrations are monitored continuously at air quality monitoring sites, there is a delay between the time the concentrations are measured and the time they have been quality assured and approved for final use. Because 2003 is the last year for which complete, quality assured data are available, this is the last year used in the trends analyses in this chapter. However, preliminary 2004 data are available for some sites. Table 7-4 lists the available 1-hour and 8-hour ozone statistics for 2004 (note that although the 2004 data for these areas are complete, they are still preliminary and therefore, subject to further review and possible revision). The statistics include the maximum 1-hour concentration, the number of days exceeding the State and the federal 1-hour standards, the maximum 8-hour concentration, and the number of days exceeding the federal 8-hour standard. Statistics are listed for six urban areas in California. These statistics represent the data available in the ARB's AQMIS 2 (Air Quality and Meteorological Information System) database on January 28, 2005.

For all six areas, the values for 2004 are comparable or lower than those for 2003. This is because meteorological conditions during 2003 in many areas of the State were adverse – meaning the meteorological conditions were conducive to ozone formation. Therefore, the ozone concentrations in many areas during 2003 were higher than normal. Overall, during 2004, all six areas had values above one or more of the State and federal standards. Again, the highest values occurred in the South Coast and San Joaquin Valley Air Basins.

Table 7-4 Preliminary 2004 measured Ozone Statistics for Six Urban Areas

Area	Maximum 1-Hour Conc	Days Exceeding State 1-Hour Standard	Days Exceeding Federal 1-Hour Standard	Maximum 8-Hour Conc	Days Exceeding Federal 8-Hour Standard
Sacramento Metro Area	0.12	27	0	0.10	19
San Diego Air Basin	0.13	9	1	0.10	7
San Francisco Bay Area	0.11	7	0	0.08	0
San Joaquin Valley	0.16	103	9	0.13	109
South Coast	0.16	111	27	0.13	87
Ventura County	0.12	22	0	0.10	17

Note: Days exceeding State and federal standards are distinct, areawide days. data are complete, but still preliminary and therefore, subject to further review.

Data Source: AQMIS – 1/28/05

7.2.5 Ozone Season

Ozone is not directly emitted as a pollutant, but is formed in the atmosphere when precursor emissions, namely VOCs and oxides of nitrogen, react in the presence of sunlight. Because of the reaction time involved, the highest ozone concentrations often occur far downwind of the precursor emissions. As a result, ozone is a regional pollutant that often impacts large areas.

Meteorology and terrain play major roles in ozone formation. Generally, low wind speeds or stagnant air, coupled with warm temperatures and cloudless skies, provide the optimum conditions for ozone formation. Therefore, the highest ozone concentrations tend to occur during the summer season. In most urban areas, the ozone season for the current standards runs from May through September. However, the data show that the San Joaquin Valley Air Basin and South Coast Air Basin can record high ozone levels throughout the year. In general, the length or duration of the ozone season reflects the stringency of the standard. In other words, a more stringent standard will have a longer ozone season.

Figures 7.5 and 7.6 and Tables 7.5 and 7.6 show the total number of days each month with exceedances of the State 1-hour and federal 8-hour ozone standards, respectively, during 1990 through 2003. The graphs and tables include information for each of California's largest air basins or planning areas. Although the highest ozone concentrations for both standards tend to occur during the summertime, meteorological conditions can vary from year-to-year and can be a significant factor in the year-to-year variation in ambient ozone. In general, inland areas (such as the San Joaquin Valley, Sacramento Valley, and inland portions of the South Coast Air Basin) tend to experience hotter temperatures and more stagnant conditions than coastal areas. This combination of meteorological conditions can lead to multi-day episodes of elevated ozone concentrations.

To highlight the similarity in the distributions for both the 1-hour and 8-hour standards, Figures 7.5 and 7.6 both are plotted with the same x-axis scale. The trend lines are almost identical for both standards. However, in all areas, the total number of exceedance days for the federal 8-hour standard is the same or lower than the total number of exceedance days for the State 1-hour standard.

Figure 7-4 Seasonal Distribution of the Number of Days Exceeding the State 1-Hour Ozone Standard

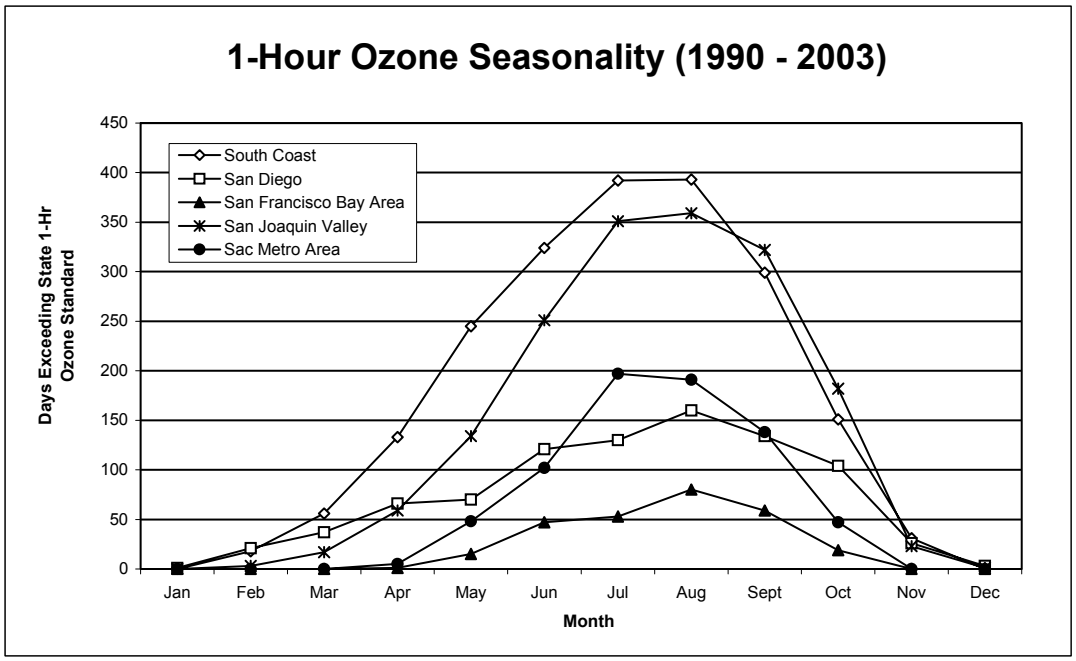


Table 7-5 Total Number of Days with Exceedances of the State 1-Hour Ozone Standard During 1990 to 2003

MONTH	AIR BASIN				
	Sacramento Metropolitan Area	San Diego	San Francisco Bay Area	San Joaquin Valley	South Coast
January	0	1	0	0	0
February	0	21	0	3	18
March	0	37	0	17	56
April	5	66	1	59	133
May	48	70	15	134	245
Jun	102	121	46	251	324
July	196	130	53	351	392
August	191	160	80	359	393
September	138	134	59	322	299
October	47	104	19	182	151
November	0	26	0	23	31
December	0	3	0	1	0

Note: The seasonality is represented by the monthly count of exceedance days that were measured at one or more monitoring sites in an air basin or planning area for the years1990 to 2003.
Data Source: ADAM - 3/18/04

Figure 7-5 Seasonal Distribution of the Number of Days Exceeding the Federal 8-Hour Ozone Standard

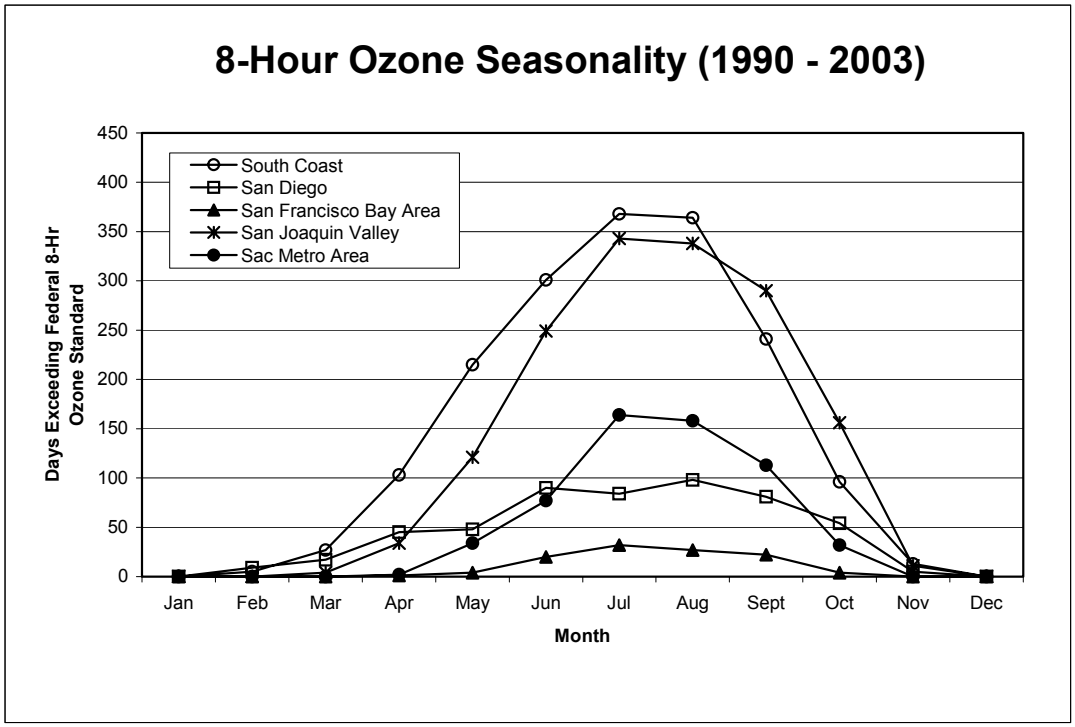


Table 7-6 Total Number of Days with Exceedances of the Federal 8-Hour Ozone Standard During 1990 to 2003

MONTH	AIR BASIN				
	Sacramento Metropolitan Area	San Diego	San Francisco Bay Area	San Joaquin Valley	South Coast
January	0	0	0	0	0
February	0	9	0	0	5
March	0	17	0	4	27
April	2	45	1	34	103
May	34	48	4	121	215
June	77	90	20	249	301
July	164	84	32	343	368
August	158	98	27	338	364
September	113	81	22	290	241
October	32	54	4	156	96
November	0	5	0	11	13
December	0	0	0	0	0

Note: The seasonality is represented by the monthly count of exceedance days that were measured at one or more monitoring sites in an air basin or planning area for the years 1990 to 2003.

Data Source: ADAM - 3/19/04

7.2.6 Frequency of Measured 1-Hour and 8-Hour Ozone Concentrations

The following graphs and tables present frequency distributions of both 1-hour and 8-hour ozone concentrations for each of the years 2001, 2002, and 2003. The frequency distributions represent a summary of the maximum daily ozone concentrations measured at all the sites within each air basin or planning area, as well as for all sites within the State. Maximum ozone concentration levels are aggregated into bins or concentration ranges of 0.01 ppm in size (for example, daily maximum concentrations in the range of 0.00 ppm to 0.01 ppm, 0.01 ppm to 0.02 ppm, 0.02 ppm to 0.03 ppm, etc.). The original input data were taken from the ARB air quality CD (ARB 2004).

It is interesting to note that in many cases, there are a higher number (frequency) of 8-hour observations than 1-hour observations. For example, during 2003, there were a total of 60,138 1-hour observations for California, compared with 60,145 8-hour observations. The higher number of 8-hour observations is a function of how the 8-hour average is calculated. Because the 8-hour average can span hours in two separate days, it is possible to have a valid 8-hour value, but not a valid 1-hour value. As a result, the total number of 8-hour observations can be higher.

Figures 7.7 through 7.12 show frequency information on a statewide basis. In contrast, Tables 7.7 through 7.12 present information for each area of California, as well as for the State as a whole. Each figure and table provides information for an individual year: 2001, 2002, or 2003. The tabular information includes the frequency of the various ranges of maximum daily 1-hour and 8-hour concentrations measured in each area, expressed both as a count and as a percentage of the total. In addition, the tables show the cumulative frequency (again, expressed as a count and as a percentage), from the lowest range to the highest range. The frequency graphs and tables provide information on the frequency of high concentrations for each area, as well as the most frequent, or predominant concentrations levels. This information provides insight about the impact of setting the standards at various levels.

As shown in Figures 7.7 through 7.9, the majority of maximum daily 1-hour ozone concentrations during 2001 to 2003 were below the level of both the State and federal 1-hour standards. Statewide, an average of 44.6 percent of the daily maximums were in the range of 0.03 ppm to 0.05 ppm. During all three years, an average of 97.1 percent of the daily maximum concentrations were at or below 0.10 ppm, the level of the State 1-hour standard. As shown in Figures 7.10 through 7.12, an average of 45.8 percent of the daily maximum 8-hour concentrations were in the range of 0.03 ppm to 0.05 ppm, during the three-year period. An average of 95.2 percent of the maximum concentrations were at or below 0.08 ppm, the level of the federal 8-hour standard.

When looking at the data for individual air basins or planning areas, the results are similar. We do, however, see some variation in the ranges of concentrations represented. For example, the maximum concentrations represented in the South Coast Air Basin range from 0.00 ppm to 0.20 ppm for the 1-hour concentrations and 0.00 ppm to 0.16 ppm for the 8-hour concentrations. In contrast, the concentrations represented in the North Coast Air Basin range from

0.00 ppm to 0.10 ppm for the 1-hour values and 0.00 ppm to 0.08 ppm for the 8-hour values. However, all individual air basins and planning areas show relatively large percentages of concentrations in the 0.03 ppm to 0.05 ppm range, and all areas had at least 37 percent of their maximum 1-hour and 8-hour concentrations at or below 0.05 ppm during 2001 through 2003. Furthermore, more than 50 percent of the 1-hour and 8-hour maximums were at or below 0.06 ppm for all areas during all three years.

Figure 7-6

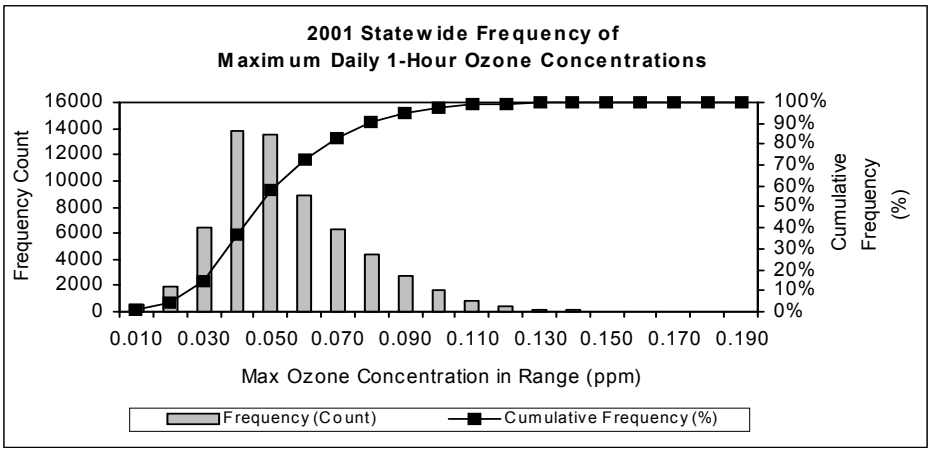


Figure 7-7

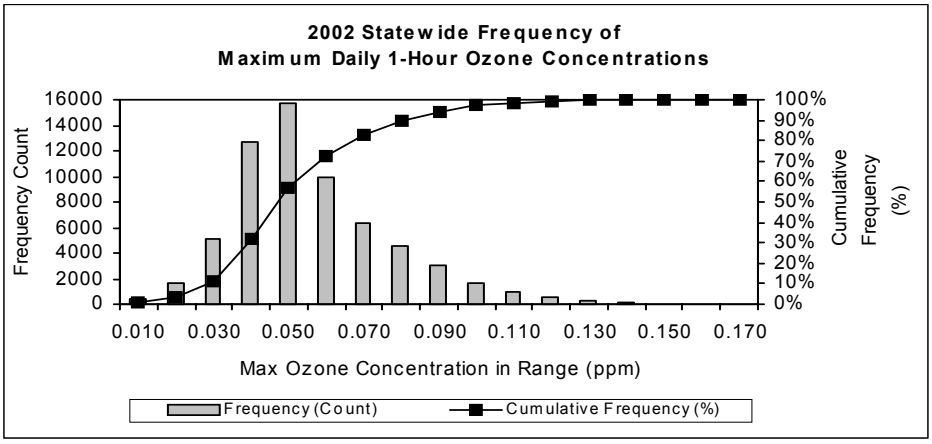


Figure 7-8

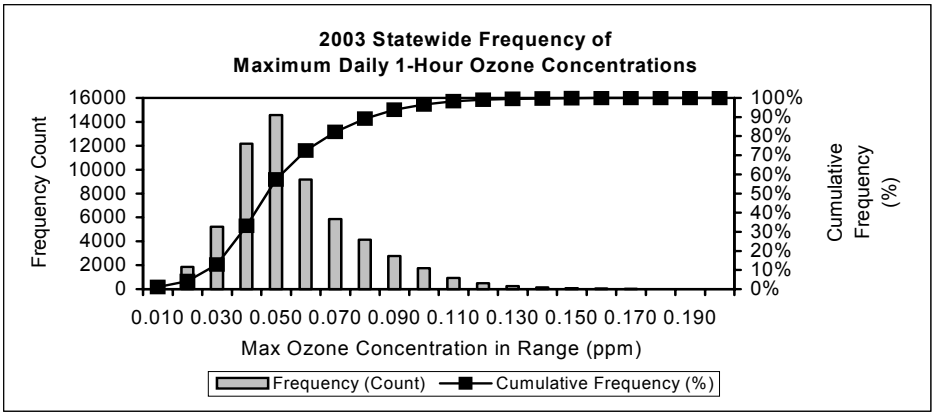


Figure 7-9

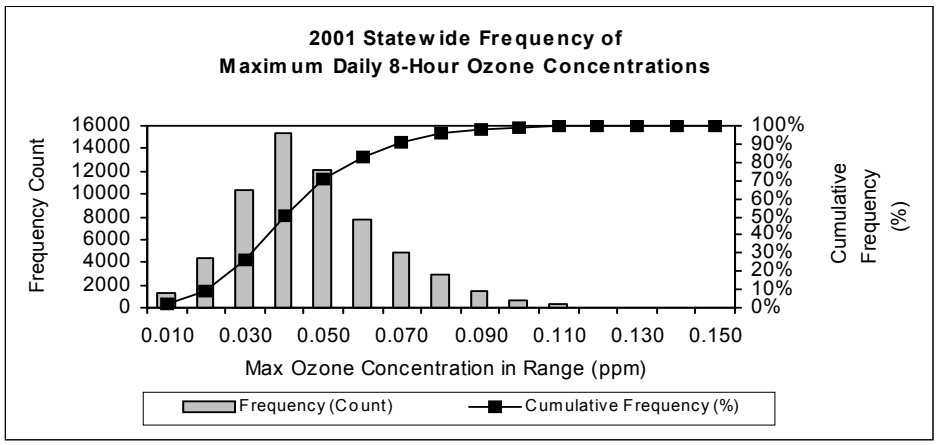


Figure 7-10

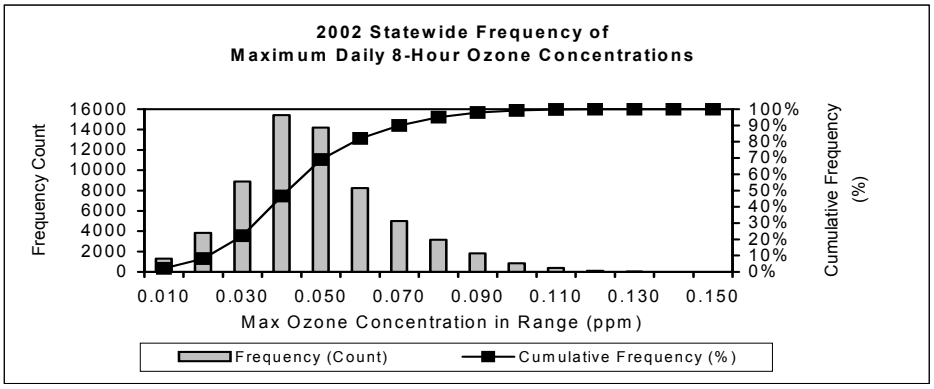


Figure 7-11

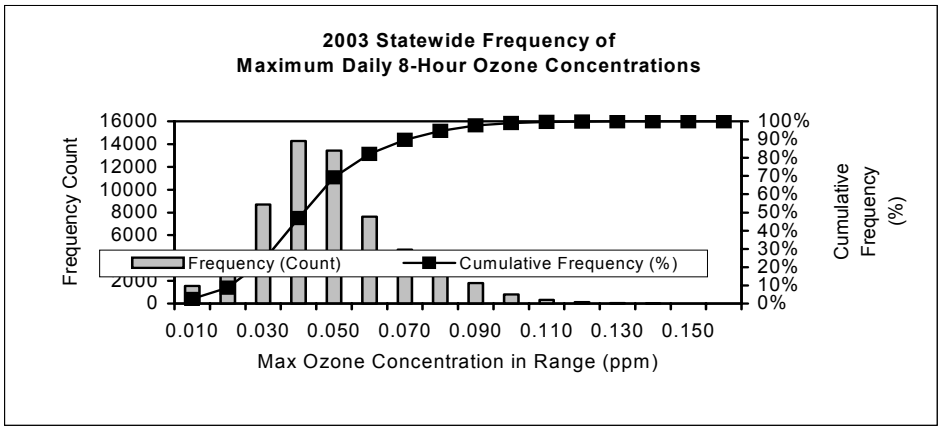


Table 7-7 Frequency of 1-Hour Ozone Concentrations Measured During 2001

Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Great Basin Valleys	Representative data not available					
Lake County	0.01	0.02	6	1.6%	6	1.6%
	0.02	0.03	56	15.3%	62	17.0%
	0.03	0.04	138	37.8%	200	54.8%
	0.04	0.05	111	30.4%	311	85.2%
	0.05	0.06	39	10.7%	350	95.9%
	0.06	0.07	15	4.1%	365	100.0%
Lake Tahoe	0.02	0.03	4	0.6%	4	0.6%
	0.03	0.04	69	9.8%	73	10.3%
	0.04	0.05	220	31.2%	293	41.5%
	0.05	0.06	215	30.5%	508	72.0%
	0.06	0.07	124	17.6%	632	89.5%
	0.07	0.08	55	7.8%	687	97.3%
	0.08	0.09	18	2.5%	705	99.9%
	0.09	0.10	1	0.1%	706	100.0%
Mojave Desert	0.00	0.01	3	0.1%	3	0.1%
	0.01	0.02	21	0.7%	24	0.7%
	0.02	0.03	110	3.4%	134	4.2%
	0.03	0.04	585	18.2%	719	22.3%
	0.04	0.05	630	19.6%	1349	41.9%
	0.05	0.06	526	16.3%	1875	58.3%
	0.06	0.07	471	14.6%	2346	72.9%
	0.07	0.08	384	11.9%	2730	84.8%
	0.08	0.09	245	7.6%	2975	92.4%
	0.09	0.10	129	4.0%	3104	96.5%
	0.10	0.11	73	2.3%	3177	98.7%
	0.11	0.12	28	0.9%	3205	99.6%
	0.12	0.13	10	0.3%	3215	99.9%
	0.13	0.14	1	0.0%	3216	99.9%
	0.14	0.15	2	0.1%	3218	100.0%

Table 7-7 (continued)

Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Mountain Counties	0.00	0.01	6	0.2%	6	0.2%
	0.01	0.02	19	0.6%	25	0.8%
	0.02	0.03	181	5.9%	206	6.7%
	0.03	0.04	458	15.0%	664	21.7%
	0.04	0.05	657	21.5%	1321	43.2%
	0.05	0.06	561	18.3%	1882	61.5%
	0.06	0.07	517	16.9%	2399	78.4%
	0.07	0.08	396	12.9%	2795	91.3%
	0.08	0.09	188	6.1%	2983	97.5%
	0.09	0.10	47	1.5%	3030	99.0%
	0.10	0.11	24	0.8%	3054	99.8%
	0.11	0.12	7	0.2%	3061	100.0%
North Central Coast	0.00	0.01	3	0.1%	3	0.1%
	0.01	0.02	36	1.0%	39	1.1%
	0.02	0.03	507	14.0%	546	15.1%
	0.03	0.04	1525	42.2%	2071	57.2%
	0.04	0.05	988	27.3%	3059	84.5%
	0.05	0.06	337	9.3%	3396	93.9%
	0.06	0.07	130	3.6%	3526	97.5%
	0.07	0.08	63	1.7%	3589	99.2%
	0.08	0.09	22	0.6%	3611	99.8%
	0.09	0.10	6	0.2%	3617	100.0%
	0.10	0.11	1	0.0%	3618	100.0%
North Coast	0.00	0.01	3	0.3%	3	0.3%
	0.01	0.02	74	6.9%	77	7.2%
	0.02	0.03	266	24.7%	343	31.9%
	0.03	0.04	413	38.4%	756	70.3%
	0.04	0.05	230	21.4%	986	91.7%
	0.05	0.06	65	6.0%	1051	97.8%
	0.06	0.07	20	1.9%	1071	99.6%
	0.07	0.08	3	0.3%	1074	99.9%
	0.08	0.09	1	0.1%	1075	100.0%
Northeast Plateau	Representative data not available					

Table 7-7 (continued)

Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Sacra-mento Metro Area	0.00	0.01	55	1.0%	55	1.0%
	0.01	0.02	150	2.8%	205	3.8%
	0.02	0.03	533	9.8%	738	13.6%
	0.03	0.04	1103	20.3%	1841	33.9%
	0.04	0.05	1021	18.8%	2862	52.7%
	0.05	0.06	887	16.3%	3749	69.1%
	0.06	0.07	663	12.2%	4412	81.3%
	0.07	0.08	439	8.1%	4851	89.4%
	0.08	0.09	292	5.4%	5143	94.8%
	0.09	0.10	160	2.9%	5303	97.7%
	0.10	0.11	85	1.6%	5388	99.3%
	0.11	0.12	29	0.5%	5417	99.8%
	0.12	0.13	6	0.1%	5423	99.9%
	0.13	0.14	2	0.0%	5425	100.0%
	0.14	0.15	2	0.0%	5427	100.0%
Salton Sea	0.00	0.01	16	0.7%	16	0.7%
	0.01	0.02	22	1.0%	38	1.7%
	0.02	0.03	89	3.9%	127	5.5%
	0.03	0.04	335	14.6%	462	20.1%
	0.04	0.05	460	20.0%	922	40.1%
	0.05	0.06	467	20.3%	1389	60.4%
	0.06	0.07	355	15.4%	1744	75.9%
	0.07	0.08	228	9.9%	1972	85.8%
	0.08	0.09	138	6.0%	2110	91.8%
	0.09	0.10	98	4.3%	2208	96.0%
	0.10	0.11	47	2.0%	2255	98.1%
	0.11	0.12	18	0.8%	2273	98.9%
	0.12	0.13	15	0.7%	2288	99.5%
	0.13	0.14	7	0.3%	2295	99.8%
	0.14	0.15	3	0.1%	2298	100.0%
	0.16	0.17	1	0.0%	2299	100.0%

Table 7-7 (continued)

Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Diego	0.00	0.01	4	0.1%	4	0.1%
	0.01	0.02	54	1.5%	58	1.6%
	0.02	0.03	221	6.0%	279	7.6%
	0.03	0.04	767	20.9%	1046	28.5%
	0.04	0.05	1161	31.6%	2207	60.1%
	0.05	0.06	739	20.1%	2946	80.2%
	0.06	0.07	385	10.5%	3331	90.7%
	0.07	0.08	196	5.3%	3527	96.1%
	0.08	0.09	79	2.2%	3606	98.2%
	0.09	0.10	40	1.1%	3646	99.3%
	0.10	0.11	16	0.4%	3662	99.7%
	0.11	0.12	6	0.2%	3668	99.9%
	0.12	0.13	1	0.0%	3669	99.9%
	0.13	0.14	2	0.1%	3671	100.0%
	0.14	0.15	1	0.0%	3672	100.0%
San Francisco Bay Area	0.00	0.01	90	1.2%	90	1.2%
	0.01	0.02	522	7.2%	612	8.5%
	0.02	0.03	1829	25.3%	2441	33.8%
	0.03	0.04	2327	32.2%	4768	66.1%
	0.04	0.05	1398	19.4%	6166	85.4%
	0.05	0.06	517	7.2%	6683	92.6%
	0.06	0.07	231	3.2%	6914	95.8%
	0.07	0.08	154	2.1%	7068	97.9%
	0.08	0.09	85	1.2%	7153	99.1%
	0.09	0.10	38	0.5%	7191	99.6%
	0.10	0.11	15	0.2%	7206	99.8%
	0.11	0.12	9	0.1%	7215	100.0%
	0.12	0.13	2	0.0%	7217	100.0%
	0.13	0.14	1	0.0%	7218	100.0%
San Joaquin Valley	0.00	0.01	35	0.4%	35	0.4%
	0.01	0.02	219	2.6%	254	3.0%
	0.02	0.03	557	6.5%	811	9.5%
	0.03	0.04	1189	14.0%	2000	23.5%
	0.04	0.05	1243	14.6%	3243	38.1%
	0.05	0.06	1080	12.7%	4323	50.8%
	0.06	0.07	1108	13.0%	5431	63.8%
	0.07	0.08	1035	12.2%	6466	76.0%
	0.08	0.09	861	10.1%	7327	86.1%
	0.09	0.10	610	7.2%	7937	93.3%
	0.10	0.11	337	4.0%	8274	97.3%
	0.11	0.12	146	1.7%	8420	99.0%
	0.12	0.13	56	0.7%	8476	99.6%
	0.13	0.14	26	0.3%	8502	100.0%
	0.14	0.15	4	0.0%	8506	100.0%

Table 7-7 (continued)

Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
South Central Coast	0.00	0.01	14	0.2%	14	0.2%
	0.01	0.02	47	0.5%	61	0.7%
	0.02	0.03	527	5.8%	588	6.5%
	0.03	0.04	2442	26.9%	3030	33.4%
	0.04	0.05	2914	32.1%	5944	65.5%
	0.05	0.06	1585	17.5%	7529	83.0%
	0.06	0.07	789	8.7%	8318	91.7%
	0.07	0.08	429	4.7%	8747	96.4%
	0.08	0.09	190	2.1%	8937	98.5%
	0.09	0.10	83	0.9%	9020	99.4%
	0.10	0.11	31	0.3%	9051	99.8%
	0.11	0.12	16	0.2%	9067	100.0%
	0.12	0.13	4	0.0%	9071	100.0%
South Coast	0.00	0.01	197	2.0%	197	2.0%
	0.01	0.02	543	5.5%	740	7.5%
	0.02	0.03	1130	11.4%	1870	18.9%
	0.03	0.04	1825	18.5%	3695	37.4%
	0.04	0.05	1779	18.0%	5474	55.5%
	0.05	0.06	1298	13.2%	6772	68.6%
	0.06	0.07	957	9.7%	7729	78.3%
	0.07	0.08	659	6.7%	8388	85.0%
	0.08	0.09	518	5.2%	8906	90.2%
	0.09	0.10	371	3.8%	9277	94.0%
	0.10	0.11	212	2.1%	9489	96.1%
	0.11	0.12	149	1.5%	9638	97.6%
	0.12	0.13	98	1.0%	9736	98.6%
	0.13	0.14	63	0.6%	9799	99.3%
	0.14	0.15	32	0.3%	9831	99.6%
	0.15	0.16	25	0.3%	9856	99.9%
	0.16	0.17	8	0.1%	9864	99.9%
	0.17	0.18	2	0.0%	9866	100.0%
	0.18	0.19	4	0.0%	9870	100.0%

Table 7-7 (continued)

Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Upper Sacra-mento Valley	0.00	0.01	54	1.6%	54	1.6%
	0.01	0.02	179	5.2%	233	6.8%
	0.02	0.03	365	10.6%	598	17.4%
	0.03	0.04	597	17.3%	1195	34.7%
	0.04	0.05	689	20.0%	1884	54.7%
	0.05	0.06	610	17.7%	2494	72.4%
	0.06	0.07	478	13.9%	2972	86.3%
	0.07	0.08	304	8.8%	3276	95.1%
	0.08	0.09	135	3.9%	3411	99.0%
	0.09	0.10	29	0.8%	3440	99.9%
	0.10	0.11	4	0.1%	3444	100.0%
California	0.00	0.01	480	0.8%	480	0.8%
	0.01	0.02	1892	3.1%	2372	3.9%
	0.02	0.03	6375	10.4%	8747	14.2%
	0.03	0.04	13773	22.4%	22520	36.6%
	0.04	0.05	13501	21.9%	36021	58.5%
	0.05	0.06	8926	14.5%	44947	73.0%
	0.06	0.07	6243	10.1%	51190	83.2%
	0.07	0.08	4345	7.1%	55535	90.2%
	0.08	0.09	2772	4.5%	58307	94.7%
	0.09	0.10	1612	2.6%	59919	97.4%
	0.10	0.11	845	1.4%	60764	98.7%
	0.11	0.12	408	0.7%	61172	99.4%
	0.12	0.13	192	0.3%	61364	99.7%
	0.13	0.14	102	0.2%	61466	99.9%
	0.14	0.15	44	0.1%	61510	99.9%
	0.15	0.16	25	0.0%	61535	100.0%
	0.16	0.17	9	0.0%	61544	100.0%
	0.17	0.18	2	0.0%	61546	100.0%
	0.18	0.19	4	0.0%	61550	100.0%

Table 7-8 Frequency of 1-Hour Ozone Concentrations Measured During 2002

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Great Basin Valleys	0.02	0.03	7	1.4%	7	1.4%
	0.03	0.04	59	12.0%	66	13.4%
	0.04	0.05	154	31.3%	220	44.7%
	0.05	0.06	101	20.5%	321	65.2%
	0.06	0.07	90	18.3%	411	83.5%
	0.07	0.08	43	8.7%	454	92.3%
	0.08	0.09	21	4.3%	475	96.5%
	0.09	0.10	17	3.5%	492	100.0%
Lake County	0.01	0.02	8	2.2%	8	2.2%
	0.02	0.03	45	12.5%	53	14.7%
	0.03	0.04	133	36.8%	186	51.5%
	0.04	0.05	79	21.9%	265	73.4%
	0.05	0.06	53	14.7%	318	88.1%
	0.06	0.07	33	9.1%	351	97.2%
	0.07	0.08	9	2.5%	360	99.7%
	0.08	0.09	1	0.3%	361	100.0%
Lake Tahoe	0.02	0.03	8	1.1%	8	1.1%
	0.03	0.04	72	10.0%	80	11.1%
	0.04	0.05	245	34.0%	325	45.1%
	0.05	0.06	219	30.4%	544	75.5%
	0.06	0.07	111	15.4%	655	90.8%
	0.07	0.08	50	6.9%	705	97.8%
	0.08	0.09	15	2.1%	720	99.9%
	0.10	0.11	1	0.1%	721	100.0%
Mojave Desert	0.00	0.01	2	0.1%	2	0.1%
	0.01	0.02	12	0.4%	14	0.4%
	0.02	0.03	84	2.6%	98	3.0%
	0.03	0.04	396	12.1%	494	15.2%
	0.04	0.05	774	23.7%	1268	38.9%
	0.05	0.06	533	16.3%	1801	55.2%
	0.06	0.07	438	13.4%	2239	68.7%
	0.07	0.08	405	12.4%	2644	81.1%
	0.08	0.09	294	9.0%	2938	90.1%
	0.09	0.10	162	5.0%	3100	95.1%
	0.10	0.11	86	2.6%	3186	97.7%
	0.11	0.12	39	1.2%	3225	98.9%
	0.12	0.13	26	0.8%	3251	99.7%
	0.13	0.14	5	0.2%	3256	99.9%
	0.14	0.15	3	0.1%	3259	100.0%
	0.15	0.16	1	0.0%	3260	100.0%

Table 7-8 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Mountain Counties	0.00	0.01	7	0.2%	7	0.2%
	0.01	0.02	38	1.2%	45	1.4%
	0.02	0.03	136	4.3%	181	5.8%
	0.03	0.04	392	12.5%	573	18.2%
	0.04	0.05	596	19.0%	1169	37.2%
	0.05	0.06	524	16.7%	1693	53.9%
	0.06	0.07	491	15.6%	2184	69.5%
	0.07	0.08	504	16.0%	2688	85.5%
	0.08	0.09	290	9.2%	2978	94.8%
	0.09	0.10	120	3.8%	3098	98.6%
	0.10	0.11	35	1.1%	3133	99.7%
	0.11	0.12	7	0.2%	3140	99.9%
	0.12	0.13	1	0.0%	3141	99.9%
	0.13	0.14	2	0.1%	3143	100.0%
North Central Coast	0.00	0.01	4	0.1%	4	0.1%
	0.01	0.02	48	1.3%	52	1.4%
	0.02	0.03	412	11.3%	464	12.7%
	0.03	0.04	1377	37.8%	1841	50.5%
	0.04	0.05	1181	32.4%	3022	83.0%
	0.05	0.06	349	9.6%	3371	92.5%
	0.06	0.07	160	4.4%	3531	96.9%
	0.07	0.08	68	1.9%	3599	98.8%
	0.08	0.09	29	0.8%	3628	99.6%
	0.09	0.10	11	0.3%	3639	99.9%
	0.10	0.11	3	0.1%	3642	100.0%
	0.11	0.12	1	0.0%	3643	100.0%
North Coast	0.00	0.01	15	1.4%	15	1.4%
	0.01	0.02	46	4.2%	61	5.6%
	0.02	0.03	203	18.5%	264	24.1%
	0.03	0.04	444	40.5%	708	64.7%
	0.04	0.05	245	22.4%	953	87.0%
	0.05	0.06	95	8.7%	1048	95.7%
	0.06	0.07	35	3.2%	1083	98.9%
	0.07	0.08	7	0.6%	1090	99.5%
	0.08	0.09	2	0.2%	1092	99.7%
	0.09	0.10	3	0.3%	1095	100.0%

Table 7-8 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Northeast Plateau	0.00	0.01	6	1.7%	6	1.7%
	0.01	0.02	25	7.2%	31	8.9%
	0.02	0.03	56	16.1%	87	25.0%
	0.03	0.04	70	20.1%	157	45.1%
	0.04	0.05	73	21.0%	230	66.1%
	0.05	0.06	64	18.4%	294	84.5%
	0.06	0.07	40	11.5%	334	96.0%
	0.07	0.08	13	3.7%	347	99.7%
	0.08	0.09	1	0.3%	348	100.0%
Sacra-mento Metro Area	0.00	0.01	53	1.0%	53	1.0%
	0.01	0.02	152	2.9%	205	3.9%
	0.02	0.03	403	7.8%	608	11.7%
	0.03	0.04	931	17.9%	1539	29.6%
	0.04	0.05	1004	19.3%	2543	49.0%
	0.05	0.06	833	16.0%	3376	65.0%
	0.06	0.07	645	12.4%	4021	77.4%
	0.07	0.08	488	9.4%	4509	86.8%
	0.08	0.09	341	6.6%	4850	93.4%
	0.09	0.10	163	3.1%	5013	96.6%
	0.10	0.11	104	2.0%	5117	98.6%
	0.11	0.12	46	0.9%	5163	99.4%
	0.12	0.13	15	0.3%	5178	99.7%
	0.13	0.14	9	0.2%	5187	99.9%
	0.14	0.15	4	0.1%	5191	100.0%
	0.15	0.16	1	0.0%	5192	100.0%
Salton Sea	0.01	0.02	15	0.5%	15	0.5%
	0.02	0.03	130	4.5%	145	5.0%
	0.03	0.04	420	14.6%	565	19.7%
	0.04	0.05	634	22.1%	1199	41.7%
	0.05	0.06	573	20.0%	1772	61.7%
	0.06	0.07	464	16.2%	2236	77.9%
	0.07	0.08	296	10.3%	2532	88.2%
	0.08	0.09	178	6.2%	2710	94.4%
	0.09	0.10	80	2.8%	2790	97.1%
	0.10	0.11	47	1.6%	2837	98.8%
	0.11	0.12	23	0.8%	2860	99.6%
	0.12	0.13	7	0.2%	2867	99.8%
	0.13	0.14	4	0.1%	2871	100.0%
	0.15	0.16	1	0.0%	2872	100.0%

Table 7-8 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Diego	0.00	0.01	2	0.1%	2	0.1%
	0.01	0.02	24	0.7%	26	0.8%
	0.02	0.03	159	4.9%	185	5.7%
	0.03	0.04	557	17.0%	742	22.7%
	0.04	0.05	1108	33.9%	1850	56.5%
	0.05	0.06	813	24.8%	2663	81.4%
	0.06	0.07	361	11.0%	3024	92.4%
	0.07	0.08	145	4.4%	3169	96.8%
	0.08	0.09	64	2.0%	3233	98.8%
	0.09	0.10	29	0.9%	3262	99.7%
	0.10	0.11	5	0.2%	3267	99.8%
	0.11	0.12	5	0.2%	3272	100.0%
	0.12	0.13	1	0.0%	3273	100.0%
San Francisco Bay Area	0.00	0.01	128	1.7%	128	1.7%
	0.01	0.02	447	5.9%	575	7.6%
	0.02	0.03	1323	17.6%	1898	25.2%
	0.03	0.04	2518	33.5%	4416	58.7%
	0.04	0.05	1832	24.4%	6248	83.1%
	0.05	0.06	651	8.7%	6899	91.7%
	0.06	0.07	301	4.0%	7200	95.7%
	0.07	0.08	156	2.1%	7356	97.8%
	0.08	0.09	100	1.3%	7456	99.1%
	0.09	0.10	36	0.5%	7492	99.6%
	0.10	0.11	15	0.2%	7507	99.8%
	0.11	0.12	10	0.1%	7517	99.9%
	0.12	0.13	2	0.0%	7519	100.0%
	0.13	0.14	1	0.0%	7520	100.0%
	0.15	0.16	1	0.0%	7521	100.0%

Table 7-8 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Joaquin Valley	0.00	0.01	83	1.0%	83	1.0%
	0.01	0.02	274	3.2%	357	4.1%
	0.02	0.03	570	6.6%	927	10.7%
	0.03	0.04	1096	12.7%	2023	23.4%
	0.04	0.05	1448	16.8%	3471	40.2%
	0.05	0.06	1074	12.4%	4545	52.6%
	0.06	0.07	907	10.5%	5452	63.1%
	0.07	0.08	1002	11.6%	6454	74.7%
	0.08	0.09	848	9.8%	7302	84.5%
	0.09	0.10	656	7.6%	7958	92.1%
	0.10	0.11	359	4.2%	8317	96.2%
	0.11	0.12	180	2.1%	8497	98.3%
	0.12	0.13	95	1.1%	8592	99.4%
	0.13	0.14	31	0.4%	8623	99.8%
	0.14	0.15	13	0.2%	8636	99.9%
	0.15	0.16	5	0.1%	8641	100.0%
	0.16	0.17	1	0.0%	8642	100.0%
South Central Coast	0.00	0.01	8	0.1%	8	0.1%
	0.01	0.02	53	0.6%	61	0.7%
	0.02	0.03	392	4.3%	453	4.9%
	0.03	0.04	1977	21.4%	2430	26.4%
	0.04	0.05	3308	35.9%	5738	62.3%
	0.05	0.06	2023	21.9%	7761	84.2%
	0.06	0.07	845	9.2%	8606	93.4%
	0.07	0.08	374	4.1%	8980	97.4%
	0.08	0.09	154	1.7%	9134	99.1%
	0.09	0.10	52	0.6%	9186	99.7%
	0.10	0.11	22	0.2%	9208	99.9%
	0.11	0.12	6	0.1%	9214	100.0%
	0.12	0.13	2	0.0%	9216	100.0%
	0.13	0.14	1	0.0%	9217	100.0%

Table 7-8 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
South Coast	0.00	0.01	79	0.8%	79	0.8%
	0.01	0.02	381	3.9%	460	4.7%
	0.02	0.03	854	8.8%	1314	13.5%
	0.03	0.04	1633	16.8%	2947	30.3%
	0.04	0.05	2215	22.7%	5162	53.0%
	0.05	0.06	1470	15.1%	6632	68.1%
	0.06	0.07	950	9.8%	7582	77.9%
	0.07	0.08	722	7.4%	8304	85.3%
	0.08	0.09	494	5.1%	8798	90.3%
	0.09	0.10	336	3.5%	9134	93.8%
	0.10	0.11	226	2.3%	9360	96.1%
	0.11	0.12	164	1.7%	9524	97.8%
	0.12	0.13	104	1.1%	9628	98.9%
	0.13	0.14	71	0.7%	9699	99.6%
	0.14	0.15	21	0.2%	9720	99.8%
	0.15	0.16	15	0.2%	9735	100.0%
	0.16	0.17	4	0.0%	9739	100.0%
Upper Sacra-mento Valley	0.00	0.01	69	1.9%	69	1.9%
	0.01	0.02	184	5.1%	253	7.0%
	0.02	0.03	284	7.8%	537	14.8%
	0.03	0.04	629	17.3%	1166	32.1%
	0.04	0.05	846	23.3%	2012	55.5%
	0.05	0.06	605	16.7%	2617	72.2%
	0.06	0.07	475	13.1%	3092	85.2%
	0.07	0.08	324	8.9%	3416	94.2%
	0.08	0.09	143	3.9%	3559	98.1%
	0.09	0.10	43	1.2%	3602	99.3%
	0.10	0.11	21	0.6%	3623	99.9%
	0.11	0.12	4	0.1%	3627	100.0%

Table 7-8 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
California	0.00	0.01	456	0.7%	456	0.7%
	0.01	0.02	1707	2.7%	2163	3.4%
	0.02	0.03	5066	8.0%	7229	11.4%
	0.03	0.04	12704	20.1%	19933	31.6%
	0.04	0.05	15742	24.9%	35675	56.5%
	0.05	0.06	9980	15.8%	45655	72.3%
	0.06	0.07	6346	10.0%	52001	82.4%
	0.07	0.08	4606	7.3%	56607	89.6%
	0.08	0.09	2975	4.7%	59582	94.4%
	0.09	0.10	1708	2.7%	61290	97.1%
	0.10	0.11	924	1.5%	62214	98.5%
	0.11	0.12	485	0.8%	62699	99.3%
	0.12	0.13	253	0.4%	62952	99.7%
	0.13	0.14	124	0.2%	63076	99.9%
	0.14	0.15	41	0.1%	63117	100.0%
	0.15	0.16	24	0.0%	63141	100.0%
	0.16	0.17	5	0.0%	63146	100.0%

Table 7-9 Frequency of 1-Hour Ozone Concentrations Measured During 2003

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Great Basin Valleys	0.02	0.03	3	0.8%	3	0.8%
	0.03	0.04	64	17.7%	67	18.6%
	0.04	0.05	76	21.1%	143	39.6%
	0.05	0.06	103	28.5%	246	68.1%
	0.06	0.07	61	16.9%	307	85.0%
	0.07	0.08	42	11.6%	349	96.7%
	0.08	0.09	12	3.3%	361	100.0%
Lake County	0.00	0.01	1	0.3%	1	0.3%
	0.01	0.02	14	3.8%	15	4.1%
	0.02	0.03	53	14.6%	68	18.7%
	0.03	0.04	129	35.4%	197	54.1%
	0.04	0.05	109	29.9%	306	84.1%
	0.05	0.06	43	11.8%	349	95.9%
	0.06	0.07	14	3.8%	363	99.7%
	0.07	0.08	1	0.3%	364	100.0%
Lake Tahoe	0.02	0.03	8	0.6%	8	0.6%
	0.03	0.04	93	7.2%	101	7.8%
	0.04	0.05	406	31.5%	507	39.4%
	0.05	0.06	415	32.2%	922	71.6%
	0.06	0.07	253	19.7%	1175	91.3%
	0.07	0.08	77	6.0%	1252	97.3%
	0.08	0.09	25	1.9%	1277	99.2%
	0.09	0.10	9	0.7%	1286	99.9%
	0.11	0.12	1	0.1%	1287	100.0%
Mojave Desert	0.00	0.01	1	0.0%	1	0.0%
	0.01	0.02	18	0.5%	19	0.5%
	0.02	0.03	138	4.0%	157	4.5%
	0.03	0.04	525	15.1%	682	19.6%
	0.04	0.05	820	23.6%	1502	43.2%
	0.05	0.06	562	16.2%	2064	59.4%
	0.06	0.07	446	12.8%	2510	72.3%
	0.07	0.08	378	10.9%	2888	83.1%
	0.08	0.09	264	7.6%	3152	90.7%
	0.09	0.10	173	5.0%	3325	95.7%
	0.10	0.11	90	2.6%	3415	98.3%
	0.11	0.12	32	0.9%	3447	99.2%
	0.12	0.13	17	0.5%	3464	99.7%
	0.13	0.14	7	0.2%	3471	99.9%
	0.14	0.15	1	0.0%	3472	99.9%
	0.15	0.16	1	0.0%	3473	100.0%
	0.16	0.17	1	0.0%	3474	100.0%

Table 7-9 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Mountain Counties	0.00	0.01	20	0.7%	20	0.7%
	0.01	0.02	78	2.7%	98	3.4%
	0.02	0.03	188	6.5%	286	10.0%
	0.03	0.04	337	11.7%	623	21.7%
	0.04	0.05	670	23.3%	1293	45.0%
	0.05	0.06	470	16.4%	1763	61.4%
	0.06	0.07	393	13.7%	2156	75.0%
	0.07	0.08	365	12.7%	2521	87.7%
	0.08	0.09	209	7.3%	2730	95.0%
	0.09	0.10	89	3.1%	2819	98.1%
	0.10	0.11	38	1.3%	2857	99.4%
	0.11	0.12	14	0.5%	2871	99.9%
	0.12	0.13	1	0.0%	2872	100.0%
	0.13	0.14	1	0.0%	2873	100.0%
North Central Coast	0.00	0.01	2	0.1%	2	0.1%
	0.01	0.02	53	1.5%	55	1.5%
	0.02	0.03	428	11.8%	483	13.3%
	0.03	0.04	1309	36.0%	1792	49.2%
	0.04	0.05	1162	31.9%	2954	81.2%
	0.05	0.06	397	10.9%	3351	92.1%
	0.06	0.07	166	4.6%	3517	96.6%
	0.07	0.08	82	2.3%	3599	98.9%
	0.08	0.09	32	0.9%	3631	99.8%
	0.09	0.10	6	0.2%	3637	99.9%
	0.10	0.11	1	0.0%	3638	100.0%
	0.11	0.12	1	0.0%	3639	100.0%
North Coast	0.00	0.01	72	6.6%	72	6.6%
	0.01	0.02	85	7.8%	157	14.4%
	0.02	0.03	207	18.9%	364	33.3%
	0.03	0.04	351	32.1%	715	65.4%
	0.04	0.05	265	24.2%	980	89.6%
	0.05	0.06	75	6.9%	1055	96.4%
	0.06	0.07	34	3.1%	1089	99.5%
	0.07	0.08	3	0.3%	1092	99.8%
	0.08	0.09	2	0.2%	1094	100.0%

Table 7-9 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Northeast Plateau	0.00	0.01	2	0.8%	2	0.8%
	0.01	0.02	9	3.4%	11	4.2%
	0.02	0.03	21	8.0%	32	12.2%
	0.03	0.04	38	14.5%	70	26.7%
	0.04	0.05	66	25.2%	136	51.9%
	0.05	0.06	67	25.6%	203	77.5%
	0.06	0.07	45	17.2%	248	94.7%
	0.07	0.08	12	4.6%	260	99.2%
	0.08	0.09	2	0.8%	262	100.0%
Sacra-mento Metro Area	0.00	0.01	91	2.1%	91	2.1%
	0.01	0.02	222	5.1%	313	7.3%
	0.02	0.03	383	8.9%	696	16.1%
	0.03	0.04	727	16.8%	1423	33.0%
	0.04	0.05	802	18.6%	2225	51.6%
	0.05	0.06	632	14.6%	2857	66.2%
	0.06	0.07	557	12.9%	3414	79.1%
	0.07	0.08	391	9.1%	3805	88.2%
	0.08	0.09	248	5.7%	4053	93.9%
	0.09	0.10	154	3.6%	4207	97.5%
	0.10	0.11	56	1.3%	4263	98.8%
	0.11	0.12	30	0.7%	4293	99.5%
	0.12	0.13	10	0.2%	4303	99.7%
	0.13	0.14	11	0.3%	4314	100.0%
	0.14	0.15	1	0.0%	4315	100.0%
Salton Sea	0.00	0.01	7	0.2%	7	0.2%
	0.01	0.02	70	2.5%	77	2.7%
	0.02	0.03	261	9.3%	338	12.0%
	0.03	0.04	460	16.4%	798	28.4%
	0.04	0.05	667	23.8%	1465	52.2%
	0.05	0.06	530	18.9%	1995	71.1%
	0.06	0.07	353	12.6%	2348	83.7%
	0.07	0.08	203	7.2%	2551	90.9%
	0.08	0.09	116	4.1%	2667	95.0%
	0.09	0.10	64	2.3%	2731	97.3%
	0.10	0.11	36	1.3%	2767	98.6%
	0.11	0.12	27	1.0%	2794	99.6%
	0.12	0.13	9	0.3%	2803	99.9%
	0.13	0.14	1	0.0%	2804	99.9%
	0.14	0.15	2	0.1%	2806	100.0%

Table 7-9 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Diego	0.00	0.01	10	0.3%	10	0.3%
	0.01	0.02	66	2.0%	76	2.3%
	0.02	0.03	276	8.5%	352	10.9%
	0.03	0.04	733	22.6%	1085	33.5%
	0.04	0.05	977	30.1%	2062	63.6%
	0.05	0.06	575	17.7%	2637	81.4%
	0.06	0.07	325	10.0%	2962	91.4%
	0.07	0.08	164	5.1%	3126	96.5%
	0.08	0.09	65	2.0%	3191	98.5%
	0.09	0.10	39	1.2%	3230	99.7%
	0.10	0.11	9	0.3%	3239	99.9%
	0.11	0.12	1	0.0%	3240	100.0%
	0.12	0.13	1	0.0%	3241	100.0%
San Francisco Bay Area	0.00	0.01	157	2.3%	157	2.3%
	0.01	0.02	399	5.8%	556	8.0%
	0.02	0.03	1194	17.2%	1750	25.3%
	0.03	0.04	2047	29.5%	3797	54.8%
	0.04	0.05	1748	25.2%	5545	80.0%
	0.05	0.06	715	10.3%	6260	90.3%
	0.06	0.07	331	4.8%	6591	95.1%
	0.07	0.08	166	2.4%	6757	97.5%
	0.08	0.09	88	1.3%	6845	98.8%
	0.09	0.10	51	0.7%	6896	99.5%
	0.10	0.11	22	0.3%	6918	99.8%
	0.11	0.12	8	0.1%	6926	100.0%
	0.12	0.13	3	0.0%	6929	100.0%
San Joaquin Valley	0.00	0.01	154	1.8%	154	1.8%
	0.01	0.02	384	4.6%	538	6.4%
	0.02	0.03	558	6.6%	1096	13.0%
	0.03	0.04	1116	13.3%	2212	26.3%
	0.04	0.05	1197	14.2%	3409	40.6%
	0.05	0.06	1105	13.1%	4514	53.7%
	0.06	0.07	855	10.2%	5369	63.9%
	0.07	0.08	906	10.8%	6275	74.7%
	0.08	0.09	833	9.9%	7108	84.6%
	0.09	0.10	662	7.9%	7770	92.5%
	0.10	0.11	362	4.3%	8132	96.8%
	0.11	0.12	168	2.0%	8300	98.8%
	0.12	0.13	77	0.9%	8377	99.7%
	0.13	0.14	20	0.2%	8397	99.9%
	0.14	0.15	4	0.0%	8401	100.0%
	0.15	0.16	3	0.0%	8404	100.0%

Table 7-9 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
South Central Coast	0.00	0.01	3	0.0%	3	0.0%
	0.01	0.02	46	0.5%	49	0.5%
	0.02	0.03	547	6.1%	596	6.7%
	0.03	0.04	2265	25.3%	2861	31.9%
	0.04	0.05	3032	33.9%	5893	65.8%
	0.05	0.06	1578	17.6%	7471	83.4%
	0.06	0.07	691	7.7%	8162	91.1%
	0.07	0.08	423	4.7%	8585	95.9%
	0.08	0.09	214	2.4%	8799	98.3%
	0.09	0.10	107	1.2%	8906	99.5%
	0.10	0.11	37	0.4%	8943	99.9%
	0.11	0.12	10	0.1%	8953	100.0%
	0.12	0.13	2	0.0%	8955	100.0%
South Coast	0.00	0.01	59	0.7%	59	0.7%
	0.01	0.02	238	2.8%	297	3.5%
	0.02	0.03	592	6.9%	889	10.4%
	0.03	0.04	1283	14.9%	2172	25.3%
	0.04	0.05	1781	20.7%	3953	46.0%
	0.05	0.06	1319	15.4%	5272	61.4%
	0.06	0.07	876	10.2%	6148	71.6%
	0.07	0.08	676	7.9%	6824	79.5%
	0.08	0.09	520	6.1%	7344	85.5%
	0.09	0.10	369	4.3%	7713	89.8%
	0.10	0.11	291	3.4%	8004	93.2%
	0.11	0.12	209	2.4%	8213	95.7%
	0.12	0.13	139	1.6%	8352	97.3%
	0.13	0.14	106	1.2%	8458	98.5%
	0.14	0.15	57	0.7%	8515	99.2%
	0.15	0.16	43	0.5%	8558	99.7%
	0.16	0.17	19	0.2%	8577	99.9%
	0.17	0.18	6	0.1%	8583	100.0%
	0.18	0.19	1	0.0%	8584	100.0%
	0.19	0.20	1	0.0%	8585	100.0%

Table 7-9 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Upper Sacra-mento Valley	0.00	0.01	79	2.2%	79	2.2%
	0.01	0.02	161	4.5%	240	6.8%
	0.02	0.03	359	10.1%	599	16.9%
	0.03	0.04	698	19.7%	1297	36.5%
	0.04	0.05	780	22.0%	2077	58.5%
	0.05	0.06	582	16.4%	2659	74.9%
	0.06	0.07	453	12.8%	3112	87.7%
	0.07	0.08	253	7.1%	3365	94.8%
	0.08	0.09	135	3.8%	3500	98.6%
	0.09	0.10	36	1.0%	3536	99.6%
	0.10	0.11	10	0.3%	3546	99.9%
	0.11	0.12	3	0.1%	3549	100.0%
California	0.00	0.01	658	1.1%	658	1.1%
	0.01	0.02	1843	3.1%	2501	4.2%
	0.02	0.03	5216	8.7%	7717	12.8%
	0.03	0.04	12175	20.2%	19892	33.1%
	0.04	0.05	14558	24.2%	34450	57.3%
	0.05	0.06	9168	15.2%	43618	72.5%
	0.06	0.07	5853	9.7%	49471	82.3%
	0.07	0.08	4142	6.9%	53613	89.1%
	0.08	0.09	2765	4.6%	56378	93.7%
	0.09	0.10	1759	2.9%	58137	96.7%
	0.10	0.11	952	1.6%	59089	98.3%
	0.11	0.12	504	0.8%	59593	99.1%
	0.12	0.13	259	0.4%	59852	99.5%
	0.13	0.14	146	0.2%	59998	99.8%
	0.14	0.15	65	0.1%	60063	99.9%
	0.15	0.16	47	0.1%	60110	100.0%
	0.16	0.17	20	0.0%	60130	100.0%
	0.17	0.18	6	0.0%	60136	100.0%
	0.18	0.19	1	0.0%	60137	100.0%
	0.19	0.20	1	0.0%	60138	100.0%

Table 7-10 Frequency of 8-Hour Ozone Concentrations Measured During 2001

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Great Basin Valleys	Representative data not available					
Lake County	0.01	0.02	12	3.3%	12	3.3%
	0.02	0.03	60	16.4%	72	19.7%
	0.03	0.04	145	39.7%	217	59.5%
	0.04	0.05	103	28.2%	320	87.7%
	0.05	0.06	42	11.5%	362	99.2%
	0.06	0.07	3	0.8%	365	100.0%
Lake Tahoe	0.01	0.02	4	0.6%	4	0.6%
	0.02	0.03	18	2.5%	22	3.1%
	0.03	0.04	115	16.3%	137	19.4%
	0.04	0.05	255	36.1%	392	55.5%
	0.05	0.06	197	27.9%	589	83.4%
	0.06	0.07	93	13.2%	682	96.6%
	0.07	0.08	23	3.3%	705	99.9%
	0.08	0.09	1	0.1%	706	100.0%
Mojave Desert	0.00	0.01	12	0.4%	12	0.4%
	0.01	0.02	69	2.1%	81	2.5%
	0.02	0.03	261	8.1%	342	10.6%
	0.03	0.04	717	22.3%	1059	32.9%
	0.04	0.05	582	18.1%	1641	51.0%
	0.05	0.06	606	18.8%	2247	69.8%
	0.06	0.07	466	14.5%	2713	84.3%
	0.07	0.08	303	9.4%	3016	93.7%
	0.08	0.09	139	4.3%	3155	98.0%
	0.09	0.10	50	1.6%	3205	99.5%
	0.10	0.11	13	0.4%	3218	99.9%
	0.11	0.12	2	0.1%	3220	100.0%

Table 7-10 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Mountain Counties	0.00	0.01	8	0.3%	8	0.3%
	0.01	0.02	82	2.7%	90	2.9%
	0.02	0.03	311	10.2%	401	13.1%
	0.03	0.04	506	16.5%	907	29.6%
	0.04	0.05	701	22.9%	1608	52.5%
	0.05	0.06	591	19.3%	2199	71.9%
	0.06	0.07	488	15.9%	2687	87.8%
	0.07	0.08	273	8.9%	2960	96.7%
	0.08	0.09	79	2.6%	3039	99.3%
	0.09	0.10	20	0.7%	3059	100.0%
	0.10	0.11	1	0.0%	3060	100.0%
North Central Coast	0.00	0.01	15	0.4%	15	0.4%
	0.01	0.02	173	4.8%	188	5.2%
	0.02	0.03	1072	29.6%	1260	34.8%
	0.03	0.04	1430	39.5%	2690	74.4%
	0.04	0.05	645	17.8%	3335	92.2%
	0.05	0.06	189	5.2%	3524	97.5%
	0.06	0.07	64	1.8%	3588	99.2%
	0.07	0.08	26	0.7%	3614	99.9%
	0.08	0.09	2	0.1%	3616	100.0%
North Coast	0.00	0.01	15	1.4%	15	1.4%
	0.01	0.02	140	13.0%	155	14.4%
	0.02	0.03	333	31.0%	488	45.4%
	0.03	0.04	409	38.1%	897	83.5%
	0.04	0.05	146	13.6%	1043	97.1%
	0.05	0.06	25	2.3%	1068	99.4%
	0.06	0.07	5	0.5%	1073	99.9%
	0.07	0.08	1	0.1%	1074	100.0%
Northeast Plateau	Representative data not available					

Table 7-10 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Sacra-mento Metro Area	0.00	0.01	107	2.0%	107	2.0%
	0.01	0.02	390	7.2%	497	9.2%
	0.02	0.03	860	15.9%	1357	25.0%
	0.03	0.04	1243	22.9%	2600	48.0%
	0.04	0.05	1082	20.0%	3682	67.9%
	0.05	0.06	778	14.4%	4460	82.3%
	0.06	0.07	481	8.9%	4941	91.2%
	0.07	0.08	262	4.8%	5203	96.0%
	0.08	0.09	146	2.7%	5349	98.7%
	0.09	0.10	57	1.1%	5406	99.7%
	0.10	0.11	14	0.3%	5420	100.0%
Salton Sea	0.00	0.01	25	1.1%	25	1.1%
	0.01	0.02	77	3.3%	102	4.4%
	0.02	0.03	244	10.6%	346	15.0%
	0.03	0.04	502	21.8%	848	36.8%
	0.04	0.05	476	20.7%	1324	57.5%
	0.05	0.06	463	20.1%	1787	77.6%
	0.06	0.07	254	11.0%	2041	88.7%
	0.07	0.08	138	6.0%	2179	94.7%
	0.08	0.09	77	3.3%	2256	98.0%
	0.09	0.10	32	1.4%	2288	99.4%
	0.10	0.11	9	0.4%	2297	99.8%
	0.11	0.12	5	0.2%	2302	100.0%
San Diego	0.00	0.01	36	1.0%	36	1.0%
	0.01	0.02	170	4.6%	206	5.6%
	0.02	0.03	515	14.0%	721	19.6%
	0.03	0.04	1118	30.4%	1839	50.1%
	0.04	0.05	988	26.9%	2827	77.0%
	0.05	0.06	529	14.4%	3356	91.4%
	0.06	0.07	216	5.9%	3572	97.3%
	0.07	0.08	66	1.8%	3638	99.0%
	0.08	0.09	27	0.7%	3665	99.8%
	0.09	0.10	7	0.2%	3672	100.0%
	0.11	0.12	1	0.0%	3673	100.0%

Table 7-10 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Francisco Bay Area	0.00	0.01	272	3.8%	272	3.8%
	0.01	0.02	1218	16.9%	1490	20.6%
	0.02	0.03	2385	33.0%	3875	53.6%
	0.03	0.04	2014	27.9%	5889	81.5%
	0.04	0.05	861	11.9%	6750	93.5%
	0.05	0.06	285	3.9%	7035	97.4%
	0.06	0.07	118	1.6%	7153	99.0%
	0.07	0.08	49	0.7%	7202	99.7%
	0.08	0.09	15	0.2%	7217	99.9%
	0.09	0.10	5	0.1%	7222	100.0%
	0.10	0.11	1	0.0%	7223	100.0%
San Joaquin Valley	0.00	0.01	124	1.5%	124	1.5%
	0.01	0.02	510	6.0%	634	7.5%
	0.02	0.03	974	11.5%	1608	18.9%
	0.03	0.04	1276	15.0%	2884	33.9%
	0.04	0.05	1282	15.1%	4166	49.0%
	0.05	0.06	1141	13.4%	5307	62.4%
	0.06	0.07	1069	12.6%	6376	75.0%
	0.07	0.08	971	11.4%	7347	86.5%
	0.08	0.09	678	8.0%	8025	94.4%
	0.09	0.10	347	4.1%	8372	98.5%
	0.10	0.11	110	1.3%	8482	99.8%
	0.11	0.12	16	0.2%	8498	100.0%
South Central Coast	0.00	0.01	34	0.4%	34	0.4%
	0.01	0.02	190	2.1%	224	2.5%
	0.02	0.03	1207	13.3%	1431	15.8%
	0.03	0.04	3139	34.6%	4570	50.4%
	0.04	0.05	2540	28.0%	7110	78.5%
	0.05	0.06	1156	12.8%	8266	91.2%
	0.06	0.07	520	5.7%	8786	96.9%
	0.07	0.08	188	2.1%	8974	99.0%
	0.08	0.09	67	0.7%	9041	99.8%
	0.09	0.10	16	0.2%	9057	99.9%
	0.10	0.11	4	0.0%	9061	100.0%
	0.11	0.12	2	0.0%	9063	100.0%

Table 7-10 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
South Coast	0.00	0.01	557	5.6%	557	5.6%
	0.01	0.02	1064	10.8%	1621	16.4%
	0.02	0.03	1659	16.8%	3280	33.2%
	0.03	0.04	1958	19.8%	5238	53.0%
	0.04	0.05	1719	17.4%	6957	70.4%
	0.05	0.06	1136	11.5%	8093	81.9%
	0.06	0.07	715	7.2%	8808	89.1%
	0.07	0.08	437	4.4%	9245	93.6%
	0.08	0.09	266	2.7%	9511	96.3%
	0.09	0.10	173	1.8%	9684	98.0%
	0.10	0.11	108	1.1%	9792	99.1%
	0.11	0.12	46	0.5%	9838	99.6%
	0.12	0.13	25	0.3%	9863	99.8%
	0.13	0.14	15	0.2%	9878	100.0%
	0.14	0.15	3	0.0%	9881	100.0%
Upper Sacra-mento Valley	0.00	0.01	118	3.4%	118	3.4%
	0.01	0.02	309	9.0%	427	12.4%
	0.02	0.03	441	12.8%	868	25.2%
	0.03	0.04	744	21.6%	1612	46.8%
	0.04	0.05	701	20.3%	2313	67.1%
	0.05	0.06	588	17.1%	2901	84.2%
	0.06	0.07	362	10.5%	3263	94.7%
	0.07	0.08	155	4.5%	3418	99.2%
	0.08	0.09	29	0.8%	3447	100.0%
California	0.00	0.01	1323	2.1%	1323	2.1%
	0.01	0.02	4408	7.2%	5731	9.3%
	0.02	0.03	10340	16.8%	16071	26.1%
	0.03	0.04	15316	24.9%	31387	51.0%
	0.04	0.05	12081	19.6%	43468	70.6%
	0.05	0.06	7726	12.6%	51194	83.2%
	0.06	0.07	4854	7.9%	56048	91.1%
	0.07	0.08	2892	4.7%	58940	95.8%
	0.08	0.09	1526	2.5%	60466	98.2%
	0.09	0.10	707	1.1%	61173	99.4%
	0.10	0.11	260	0.4%	61433	99.8%
	0.11	0.12	72	0.1%	61505	99.9%
	0.12	0.13	25	0.0%	61530	100.0%
	0.13	0.14	15	0.0%	61545	100.0%
	0.14	0.15	3	0.0%	61548	100.0%

Table 7-11 Frequency of 8-Hour Ozone Concentrations Measured During 2002.

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Great Basin Valleys	0.02	0.03	17	3.5%	17	3.5%
	0.03	0.04	91	18.5%	108	22.0%
	0.04	0.05	153	31.1%	261	53.0%
	0.05	0.06	113	23.0%	374	76.0%
	0.06	0.07	78	15.9%	452	91.9%
	0.07	0.08	32	6.5%	484	98.4%
	0.08	0.09	8	1.6%	492	100.0%
Lake County	0.01	0.02	13	3.6%	13	3.6%
	0.02	0.03	50	13.9%	63	17.5%
	0.03	0.04	131	36.4%	194	53.9%
	0.04	0.05	90	25.0%	284	78.9%
	0.05	0.06	51	14.2%	335	93.1%
	0.06	0.07	20	5.6%	355	98.6%
	0.07	0.08	5	1.4%	360	100.0%
Lake Tahoe	0.01	0.02	3	0.4%	3	0.4%
	0.02	0.03	31	4.3%	34	4.7%
	0.03	0.04	115	16.0%	149	20.7%
	0.04	0.05	269	37.3%	418	58.0%
	0.05	0.06	201	27.9%	619	85.9%
	0.06	0.07	78	10.8%	697	96.7%
	0.07	0.08	24	3.3%	721	100.0%
Mojave Desert	0.00	0.01	8	0.2%	8	0.2%
	0.01	0.02	72	2.2%	80	2.5%
	0.02	0.03	205	6.3%	285	8.7%
	0.03	0.04	545	16.7%	830	25.5%
	0.04	0.05	737	22.6%	1567	48.1%
	0.05	0.06	539	16.5%	2106	64.6%
	0.06	0.07	456	14.0%	2562	78.6%
	0.07	0.08	375	11.5%	2937	90.1%
	0.08	0.09	197	6.0%	3134	96.2%
	0.09	0.10	83	2.5%	3217	98.7%
	0.10	0.11	28	0.9%	3245	99.6%
	0.11	0.12	12	0.4%	3257	100.0%
	0.12	0.13	1	0.0%	3258	100.0%

Table 7-11 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Mountain Counties	0.00	0.01	19	0.6%	19	0.6%
	0.01	0.02	88	2.8%	107	3.4%
	0.02	0.03	252	8.0%	359	11.4%
	0.03	0.04	468	14.9%	827	26.3%
	0.04	0.05	629	20.0%	1456	46.3%
	0.05	0.06	520	16.5%	1976	62.8%
	0.06	0.07	533	17.0%	2509	79.8%
	0.07	0.08	397	12.6%	2906	92.4%
	0.08	0.09	189	6.0%	3095	98.4%
	0.09	0.10	43	1.4%	3138	99.8%
	0.10	0.11	5	0.2%	3143	100.0%
	0.11	0.12	1	0.0%	3144	100.0%
North Central Coast	0.00	0.01	17	0.5%	17	0.5%
	0.01	0.02	170	4.7%	187	5.1%
	0.02	0.03	862	23.7%	1049	28.8%
	0.03	0.04	1509	41.4%	2558	70.2%
	0.04	0.05	768	21.1%	3326	91.3%
	0.05	0.06	188	5.2%	3514	96.5%
	0.06	0.07	86	2.4%	3600	98.8%
	0.07	0.08	31	0.9%	3631	99.7%
	0.08	0.09	11	0.3%	3642	100.0%
	0.09	0.10	1	0.0%	3643	100.0%
North Coast	0.00	0.01	25	2.3%	25	2.3%
	0.01	0.02	106	9.7%	131	12.0%
	0.02	0.03	300	27.4%	431	39.4%
	0.03	0.04	418	38.2%	849	77.5%
	0.04	0.05	176	16.1%	1025	93.6%
	0.05	0.06	58	5.3%	1083	98.9%
	0.06	0.07	10	0.9%	1093	99.8%
	0.07	0.08	2	0.2%	1095	100.0%
Northeast Plateau	0.00	0.01	20	5.7%	20	5.7%
	0.01	0.02	53	15.2%	73	21.0%
	0.02	0.03	64	18.4%	137	39.4%
	0.03	0.04	64	18.4%	201	57.8%
	0.04	0.05	63	18.1%	264	75.9%
	0.05	0.06	64	18.4%	328	94.3%
	0.06	0.07	19	5.5%	347	99.7%
	0.07	0.08	1	0.3%	348	100.0%

Table 7-11 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Sacra-mento Metro Area	0.00	0.01	147	2.8%	147	2.8%
	0.01	0.02	298	5.7%	445	8.6%
	0.02	0.03	703	13.5%	1148	22.1%
	0.03	0.04	1061	20.4%	2209	42.5%
	0.04	0.05	1042	20.1%	3251	62.6%
	0.05	0.06	788	15.2%	4039	77.8%
	0.06	0.07	533	10.3%	4572	88.1%
	0.07	0.08	331	6.4%	4903	94.4%
	0.08	0.09	169	3.3%	5072	97.7%
	0.09	0.10	78	1.5%	5150	99.2%
	0.10	0.11	30	0.6%	5180	99.8%
	0.11	0.12	10	0.2%	5190	100.0%
	0.12	0.13	1	0.0%	5191	100.0%
	0.13	0.14	1	0.0%	5192	100.0%
Salton Sea	0.00	0.01	3	0.1%	3	0.1%
	0.01	0.02	108	3.8%	111	3.9%
	0.02	0.03	333	11.6%	444	15.5%
	0.03	0.04	614	21.4%	1058	36.9%
	0.04	0.05	646	22.5%	1704	59.4%
	0.05	0.06	572	19.9%	2276	79.3%
	0.06	0.07	314	10.9%	2590	90.2%
	0.07	0.08	155	5.4%	2745	95.6%
	0.08	0.09	78	2.7%	2823	98.3%
	0.09	0.10	29	1.0%	2852	99.3%
	0.10	0.11	17	0.6%	2869	99.9%
	0.11	0.12	1	0.0%	2870	100.0%
	0.12	0.13	1	0.0%	2871	100.0%
San Diego	0.00	0.01	12	0.4%	12	0.4%
	0.01	0.02	139	4.2%	151	4.6%
	0.02	0.03	389	11.9%	540	16.5%
	0.03	0.04	877	26.8%	1417	43.3%
	0.04	0.05	1107	33.8%	2524	77.1%
	0.05	0.06	526	16.1%	3050	93.2%
	0.06	0.07	143	4.4%	3193	97.6%
	0.07	0.08	58	1.8%	3251	99.3%
	0.08	0.09	16	0.5%	3267	99.8%
	0.09	0.10	6	0.2%	3273	100.0%

Table 7-11 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Francisco Bay Area	0.00	0.01	326	4.3%	326	4.3%
	0.01	0.02	906	12.0%	1232	16.4%
	0.02	0.03	2071	27.5%	3303	43.9%
	0.03	0.04	2521	33.5%	5824	77.4%
	0.04	0.05	1173	15.6%	6997	92.9%
	0.05	0.06	320	4.3%	7317	97.2%
	0.06	0.07	125	1.7%	7442	98.9%
	0.07	0.08	54	0.7%	7496	99.6%
	0.08	0.09	22	0.3%	7518	99.9%
	0.09	0.10	9	0.1%	7527	100.0%
	0.10	0.11	1	0.0%	7528	100.0%
San Joaquin Valley	0.00	0.01	217	2.5%	217	2.5%
	0.01	0.02	569	6.6%	786	9.1%
	0.02	0.03	868	10.0%	1654	19.1%
	0.03	0.04	1340	15.5%	2994	34.6%
	0.04	0.05	1292	15.0%	4286	49.6%
	0.05	0.06	1082	12.5%	5368	62.1%
	0.06	0.07	998	11.5%	6366	73.7%
	0.07	0.08	915	10.6%	7281	84.3%
	0.08	0.09	755	8.7%	8036	93.0%
	0.09	0.10	379	4.4%	8415	97.4%
	0.10	0.11	187	2.2%	8602	99.5%
	0.11	0.12	35	0.4%	8637	99.9%
	0.12	0.13	4	0.0%	8641	100.0%
	0.13	0.14	1	0.0%	8642	100.0%
South Central Coast	0.00	0.01	23	0.2%	23	0.2%
	0.01	0.02	178	1.9%	201	2.2%
	0.02	0.03	946	10.3%	1147	12.5%
	0.03	0.04	2845	30.9%	3992	43.4%
	0.04	0.05	3143	34.1%	7135	77.5%
	0.05	0.06	1382	15.0%	8517	92.5%
	0.06	0.07	472	5.1%	8989	97.6%
	0.07	0.08	164	1.8%	9153	99.4%
	0.08	0.09	42	0.5%	9195	99.9%
	0.09	0.10	10	0.1%	9205	100.0%
	0.10	0.11	3	0.0%	9208	100.0%

Table 7-11 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
South Coast	0.00	0.01	340	3.5%	340	3.5%
	0.01	0.02	855	8.8%	1195	12.3%
	0.02	0.03	1385	14.2%	2580	26.5%
	0.03	0.04	2012	20.6%	4592	47.1%
	0.04	0.05	2049	21.0%	6641	68.1%
	0.05	0.06	1261	12.9%	7902	81.1%
	0.06	0.07	761	7.8%	8663	88.9%
	0.07	0.08	445	4.6%	9108	93.5%
	0.08	0.09	286	2.9%	9394	96.4%
	0.09	0.10	180	1.8%	9574	98.2%
	0.10	0.11	102	1.0%	9676	99.3%
	0.11	0.12	53	0.5%	9729	99.8%
	0.12	0.13	9	0.1%	9738	99.9%
	0.13	0.14	6	0.1%	9744	100.0%
	0.14	0.15	2	0.0%	9746	100.0%
Upper Sacra-mento Valley	0.00	0.01	147	4.1%	147	4.1%
	0.01	0.02	269	7.4%	416	11.5%
	0.02	0.03	394	10.9%	810	22.3%
	0.03	0.04	796	21.9%	1606	44.3%
	0.04	0.05	840	23.2%	2446	67.4%
	0.05	0.06	567	15.6%	3013	83.0%
	0.06	0.07	377	10.4%	3390	93.4%
	0.07	0.08	168	4.6%	3558	98.1%
	0.08	0.09	48	1.3%	3606	99.4%
	0.09	0.10	20	0.6%	3626	99.9%
	0.10	0.11	2	0.1%	3628	100.0%
California	0.00	0.01	1304	2.1%	1304	2.1%
	0.01	0.02	3827	6.1%	5131	8.1%
	0.02	0.03	8870	14.0%	14001	22.2%
	0.03	0.04	15407	24.4%	29408	46.6%
	0.04	0.05	14177	22.5%	43585	69.0%
	0.05	0.06	8232	13.0%	51817	82.1%
	0.06	0.07	5003	7.9%	56820	90.0%
	0.07	0.08	3157	5.0%	59977	95.0%
	0.08	0.09	1821	2.9%	61798	97.9%
	0.09	0.10	838	1.3%	62636	99.2%
	0.10	0.11	375	0.6%	63011	99.8%
	0.11	0.12	112	0.2%	63123	100.0%
	0.12	0.13	16	0.0%	63139	100.0%
	0.13	0.14	8	0.0%	63147	100.0%
	0.14	0.15	2	0.0%	63149	100.0%

Table 7-12 Frequency of 8-Hour Ozone Concentrations Measured During 2003.

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Great Basin Valleys	0.02	0.03	6	1.7%	6	1.7%
	0.03	0.04	74	20.5%	80	22.2%
	0.04	0.05	81	22.4%	161	44.6%
	0.05	0.06	110	30.5%	271	75.1%
	0.06	0.07	60	16.6%	331	91.7%
	0.07	0.08	28	7.8%	359	99.4%
	0.08	0.09	2	0.6%	361	100.0%
Lake County	0.00	0.01	1	0.3%	1	0.3%
	0.01	0.02	19	5.2%	20	5.5%
	0.02	0.03	55	15.1%	75	20.5%
	0.03	0.04	130	35.6%	205	56.2%
	0.04	0.05	116	31.8%	321	87.9%
	0.05	0.06	37	10.1%	358	98.1%
	0.06	0.07	7	1.9%	365	100.0%
Lake Tahoe	0.01	0.02	3	0.2%	3	0.2%
	0.02	0.03	33	2.6%	36	2.8%
	0.03	0.04	179	13.9%	215	16.7%
	0.04	0.05	456	35.4%	671	52.1%
	0.05	0.06	413	32.1%	1084	84.2%
	0.06	0.07	154	12.0%	1238	96.2%
	0.07	0.08	37	2.9%	1275	99.1%
	0.08	0.09	10	0.8%	1285	99.8%
	0.09	0.10	1	0.1%	1286	99.9%
	0.10	0.11	1	0.1%	1287	100.0%
Mojave Desert	0.00	0.01	10	0.3%	10	0.3%
	0.01	0.02	84	2.4%	94	2.7%
	0.02	0.03	317	9.1%	411	11.8%
	0.03	0.04	639	18.4%	1050	30.2%
	0.04	0.05	753	21.7%	1803	51.9%
	0.05	0.06	579	16.7%	2382	68.6%
	0.06	0.07	471	13.6%	2853	82.1%
	0.07	0.08	335	9.6%	3188	91.8%
	0.08	0.09	174	5.0%	3362	96.8%
	0.09	0.10	77	2.2%	3439	99.0%
	0.10	0.11	24	0.7%	3463	99.7%
	0.11	0.12	8	0.2%	3471	99.9%
	0.12	0.13	3	0.1%	3474	100.0%

Table 7-12 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Mountain Counties	0.00	0.01	55	1.9%	55	1.9%
	0.01	0.02	147	5.1%	202	7.0%
	0.02	0.03	248	8.6%	450	15.6%
	0.03	0.04	409	14.2%	859	29.9%
	0.04	0.05	700	24.3%	1559	54.2%
	0.05	0.06	439	15.3%	1998	69.5%
	0.06	0.07	413	14.4%	2411	83.8%
	0.07	0.08	308	10.7%	2719	94.5%
	0.08	0.09	126	4.4%	2845	98.9%
	0.09	0.10	25	0.9%	2870	99.8%
	0.10	0.11	6	0.2%	2876	100.0%
North Central Coast	0.00	0.01	17	0.5%	17	0.5%
	0.01	0.02	186	5.1%	203	5.6%
	0.02	0.03	823	22.6%	1026	28.2%
	0.03	0.04	1431	39.3%	2457	67.5%
	0.04	0.05	835	23.0%	3292	90.5%
	0.05	0.06	217	6.0%	3509	96.5%
	0.06	0.07	99	2.7%	3608	99.2%
	0.07	0.08	26	0.7%	3634	99.9%
	0.08	0.09	4	0.1%	3638	100.0%
North Coast	0.00	0.01	102	9.3%	102	9.3%
	0.01	0.02	132	12.1%	234	21.4%
	0.02	0.03	262	24.0%	496	45.4%
	0.03	0.04	341	31.2%	837	76.6%
	0.04	0.05	203	18.6%	1040	95.2%
	0.05	0.06	46	4.2%	1086	99.5%
	0.06	0.07	5	0.5%	1091	99.9%
	0.07	0.08	1	0.1%	1092	100.0%
Northeast Plateau	0.00	0.01	8	3.1%	8	3.1%
	0.01	0.02	20	7.6%	28	10.7%
	0.02	0.03	32	12.2%	60	22.9%
	0.03	0.04	45	17.2%	105	40.1%
	0.04	0.05	75	28.6%	180	68.7%
	0.05	0.06	61	23.3%	241	92.0%
	0.06	0.07	18	6.9%	259	98.9%
	0.07	0.08	3	1.1%	262	100.0%

Table 7-12 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
Sacra-mento Metro Area	0.00	0.01	190	4.4%	190	4.4%
	0.01	0.02	322	7.5%	512	11.9%
	0.02	0.03	565	13.1%	1077	25.0%
	0.03	0.04	840	19.5%	1917	44.4%
	0.04	0.05	849	19.7%	2766	64.1%
	0.05	0.06	666	15.4%	3432	79.6%
	0.06	0.07	427	9.9%	3859	89.5%
	0.07	0.08	252	5.8%	4111	95.3%
	0.08	0.09	136	3.2%	4247	98.5%
	0.09	0.10	48	1.1%	4295	99.6%
	0.10	0.11	11	0.3%	4306	99.8%
	0.11	0.12	6	0.1%	4312	100.0%
	0.12	0.13	1	0.0%	4313	100.0%
Salton Sea	0.00	0.01	29	1.0%	29	1.0%
	0.01	0.02	210	7.5%	239	8.5%
	0.02	0.03	453	16.1%	692	24.7%
	0.03	0.04	616	21.9%	1308	46.6%
	0.04	0.05	648	23.1%	1956	69.7%
	0.05	0.06	413	14.7%	2369	84.4%
	0.06	0.07	234	8.3%	2603	92.7%
	0.07	0.08	106	3.8%	2709	96.5%
	0.08	0.09	58	2.1%	2767	98.6%
	0.09	0.10	29	1.0%	2796	99.6%
	0.10	0.11	11	0.4%	2807	100.0%
San Diego	0.00	0.01	48	1.5%	48	1.5%
	0.01	0.02	224	6.9%	272	8.3%
	0.02	0.03	453	13.9%	725	22.2%
	0.03	0.04	1019	31.2%	1744	53.4%
	0.04	0.05	844	25.8%	2588	79.3%
	0.05	0.06	445	13.6%	3033	92.9%
	0.06	0.07	153	4.7%	3186	97.6%
	0.07	0.08	52	1.6%	3238	99.2%
	0.08	0.09	24	0.7%	3262	99.9%
	0.09	0.10	1	0.0%	3263	99.9%
	0.10	0.11	2	0.1%	3265	100.0%

Table 7-12 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
San Francisco Bay Area	0.00	0.01	336	4.8%	336	4.8%
	0.01	0.02	712	10.3%	1048	15.1%
	0.02	0.03	1851	26.7%	2899	41.8%
	0.03	0.04	2086	30.1%	4985	71.9%
	0.04	0.05	1352	19.5%	6337	91.4%
	0.05	0.06	365	5.3%	6702	96.6%
	0.06	0.07	138	2.0%	6840	98.6%
	0.07	0.08	62	0.9%	6902	99.5%
	0.08	0.09	30	0.4%	6932	99.9%
	0.09	0.10	4	0.1%	6936	100.0%
	0.10	0.11	1	0.0%	6937	100.0%
San Joaquin Valley	0.00	0.01	356	4.2%	356	4.2%
	0.01	0.02	594	7.1%	950	11.3%
	0.02	0.03	837	10.0%	1787	21.3%
	0.03	0.04	1207	14.4%	2994	35.7%
	0.04	0.05	1197	14.3%	4191	49.9%
	0.05	0.06	1061	12.6%	5252	62.5%
	0.06	0.07	991	11.8%	6243	74.3%
	0.07	0.08	899	10.7%	7142	85.1%
	0.08	0.09	750	8.9%	7892	94.0%
	0.09	0.10	360	4.3%	8252	98.3%
	0.10	0.11	120	1.4%	8372	99.7%
	0.11	0.12	24	0.3%	8396	100.0%
	0.12	0.13	1	0.0%	8397	100.0%
South Central Coast	0.00	0.01	13	0.1%	13	0.1%
	0.01	0.02	222	2.5%	235	2.6%
	0.02	0.03	1208	13.5%	1443	16.1%
	0.03	0.04	2930	32.7%	4373	48.9%
	0.04	0.05	2688	30.0%	7061	78.9%
	0.05	0.06	1058	11.8%	8119	90.7%
	0.06	0.07	492	5.5%	8611	96.2%
	0.07	0.08	218	2.4%	8829	98.7%
	0.08	0.09	95	1.1%	8924	99.7%
	0.09	0.10	21	0.2%	8945	100.0%
	0.10	0.11	3	0.0%	8948	100.0%
	0.11	0.12	1	0.0%	8949	100.0%

Table 7-12 (continued)

Air Basin / Planning Area	Lower Limit Conc (ppm)	Upper Limit Conc (ppm)	Frequency (Count)	Frequency (%)	Cumulative Frequency	Cumulative Frequency (%)
South Coast	0.00	0.01	222	2.6%	222	2.6%
	0.01	0.02	579	6.7%	801	9.3%
	0.02	0.03	1048	12.2%	1849	21.5%
	0.03	0.04	1565	18.2%	3414	39.7%
	0.04	0.05	1866	21.7%	5280	61.5%
	0.05	0.06	1181	13.7%	6461	75.2%
	0.06	0.07	759	8.8%	7220	84.0%
	0.07	0.08	476	5.5%	7696	89.6%
	0.08	0.09	370	4.3%	8066	93.9%
	0.09	0.10	224	2.6%	8290	96.5%
	0.10	0.11	144	1.7%	8434	98.2%
	0.11	0.12	85	1.0%	8519	99.2%
	0.12	0.13	44	0.5%	8563	99.7%
	0.13	0.14	20	0.2%	8583	99.9%
	0.14	0.15	7	0.1%	8590	100.0%
	0.15	0.16	2	0.0%	8592	100.0%
Upper Sacra-mento Valley	0.00	0.01	155	4.4%	155	4.4%
	0.01	0.02	272	7.7%	427	12.1%
	0.02	0.03	516	14.6%	943	26.7%
	0.03	0.04	755	21.4%	1698	48.1%
	0.04	0.05	780	22.1%	2478	70.2%
	0.05	0.06	552	15.6%	3030	85.8%
	0.06	0.07	312	8.8%	3342	94.7%
	0.07	0.08	145	4.1%	3487	98.8%
	0.08	0.09	32	0.9%	3519	99.7%
	0.09	0.10	11	0.3%	3530	100.0%
California	0.00	0.01	1542	2.6%	1542	2.6%
	0.01	0.02	3726	6.2%	5268	8.8%
	0.02	0.03	8707	14.5%	13975	23.2%
	0.03	0.04	14266	23.7%	28241	47.0%
	0.04	0.05	13443	22.4%	41684	69.3%
	0.05	0.06	7643	12.7%	49327	82.0%
	0.06	0.07	4733	7.9%	54060	89.9%
	0.07	0.08	2948	4.9%	57008	94.8%
	0.08	0.09	1811	3.0%	58819	97.8%
	0.09	0.10	801	1.3%	59620	99.1%
	0.10	0.11	323	0.5%	59943	99.7%
	0.11	0.12	124	0.2%	60067	99.9%
	0.12	0.13	49	0.1%	60116	100.0%
	0.13	0.14	20	0.0%	60136	100.0%
	0.14	0.15	7	0.0%	60143	100.0%
	0.15	0.16	2	0.0%	60145	100.0%

7.2.7 Diurnal Variations

Ozone is formed by the reaction of nitrogen oxides and VOCs in the presence of sunlight (see Chapter 3 for further discussion). Because the intensity of sunlight and the strength of the emissions of nitrogen oxides and VOCs that produce ozone vary throughout the day, the concentration of ozone varies throughout the day, as well. In urban areas, the diurnal variation of 1-hour ozone concentrations traces a wave-like pattern throughout the 24-hour day with the highest concentration occurring near 12-noon and the lowest concentration occurring in the early morning, around 6 a.m., Local Standard Time. The 1-hour ozone peak near the 12-noon hour is usually caused by the photochemistry of local emissions.

In certain areas, the diurnal 1-hour ozone profile has more than one peak. Urban areas that lie downwind of larger urban areas can have an ozone diurnal profile with a double peak, one around 12-noon and the other during the mid- to late-afternoon. The ozone peak near the 12-noon hour reflects local emissions, while the later peak results from ozone transported from an upwind area.

Small towns and rural locations, especially in the foothills and higher elevations of the Sierra Nevada Mountains, that are downwind of large urban areas usually have their maximum daily 1-hour ozone concentration anywhere from early afternoon to late evening depending on the distance downwind of the urban area(s). One location on the eastern side of the Sierra Nevada Mountains has observed a daily maximum 1-hour ozone concentration at midnight or in the very early morning. For these types of locations, the early afternoon to nighttime occurrence of the daily maximum ozone concentration is the result of ozone transported from upwind areas.

Under some circumstances, the maximum daily 1-hour ozone concentration can occur during the late morning hours. These late morning maximums are typically caused either by the carryover of ozone aloft from the previous day or from overnight transport of ozone aloft. Ozone aloft reaches the surface when the early morning low-level inversion disappears, as a result of convective mixing.

In contrast to the 1-hour concentrations, which reflect a single measurement, the 8-hour concentrations reflect an average of eight hourly values. As such, the 8-hour concentrations generally span the period during which the highest 1-hour concentrations occur. Based on air quality data for 2001 through 2003, the most common starting time for 8-hour concentrations that exceed the federal standard is 10 a.m. or 11 a.m. These high 8-hour periods then extend on through the 5 p.m. or 6 p.m. observation. 8-hour concentrations that exceed the level of the federal ozone standard can begin at other hours, but the rate is less than half of those beginning at 10 a.m. to 11 a.m.

7.2.8 Characterization of Ozone by Air Basin or Planning Area

Ozone air quality has improved substantially over the last two decades in most areas of California, despite significant population and economic growth. On a statewide basis (using the site with the highest value for each year), the peak 1-hour indicator decreased 54 percent and the peak 8-hour indicator decreased 47 percent from 1982 to 2003. In contrast, the statewide population increased 45 percent, and the average number of vehicle miles traveled each day statewide

increased 104 percent during the same time period. Even though there has been substantial improvement in ozone air quality, current levels still represent a significant concern in many areas. The following subsections describe the trends in both 1-hour and 8-hour average ozone concentrations for each air basin or planning area of California.

7.2.8.1 Great Basin Valleys Air Basin

The Great Basin Valleys Air Basin (GBVAB) includes all of Alpine, Inyo, and Mono counties, located along the eastern border of California. Much of the area is sparsely populated, and the air basin as a whole, is home to less than 1 percent of California's population. As previously discussed, at the time this Staff Report was prepared, representative data were not available for the Great Basin Valleys Air Basin during 2001. Therefore, air quality statistics using 2001 data are not included in the following discussion.

Similar to many other areas of the State, ozone concentrations in the GBVAB tend to be highest during the summer months. Ozone levels, as indicated by the peak 1-hour indicator, changed little in the GBVAB from 1982 through 2003. The maximum 1-hour concentration shows more variation than the peak indicator, especially during the early 1990s. These variations may have been caused by year-to-year changes in meteorology. Both the peak 1-hour indicator and the maximum 1-hour concentration statistics show similar values during the two end years: 1982 and 2000 for the peak indicator and 1982 and 2003 for the maximum concentration. The 8-hour values show similar trends, however, the 8-hour peak indicator has been a bit more stable than the 1-hour peak indicator. Similar to the 1-hour trend, the 8-hour peak indicator values for the two end years (1982 and 2000) and the maximum 8-hour values for the two end years (1982 and 2003) are nearly identical.

Figures 7.13 and 7.14 both show a slight increase in the maximum 1-hour and 8-hour values for 2002 when compared with 2000 and 2003. During 2002, the maximum 1-hour ozone concentration was 0.10 ppm, which exceeds the State ozone standard. Between 1997 and 2000, there were no exceedances of the State ozone standard. There was also an increase during 2002 in the number of days with concentrations exceeding the State standard (8 days during 2002, compared with 0 days during 1999 and 2003) and the federal 8-hour standard (3 days during 2002, compared with 0 days during 1999 and 2003). These year-to-year variations are probably attributable to variations in meteorology rather than overall changes in emissions.

Figure 7-12

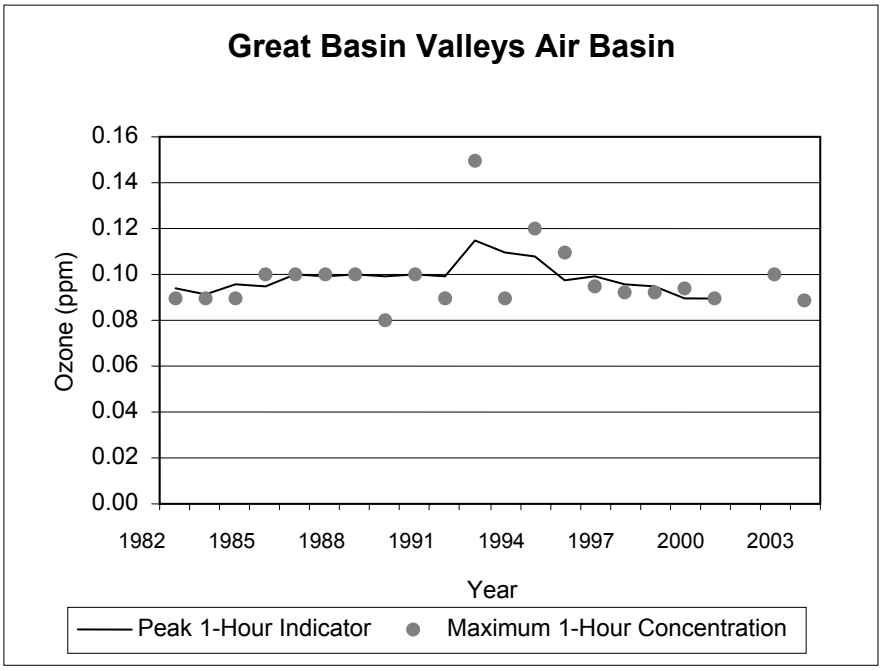
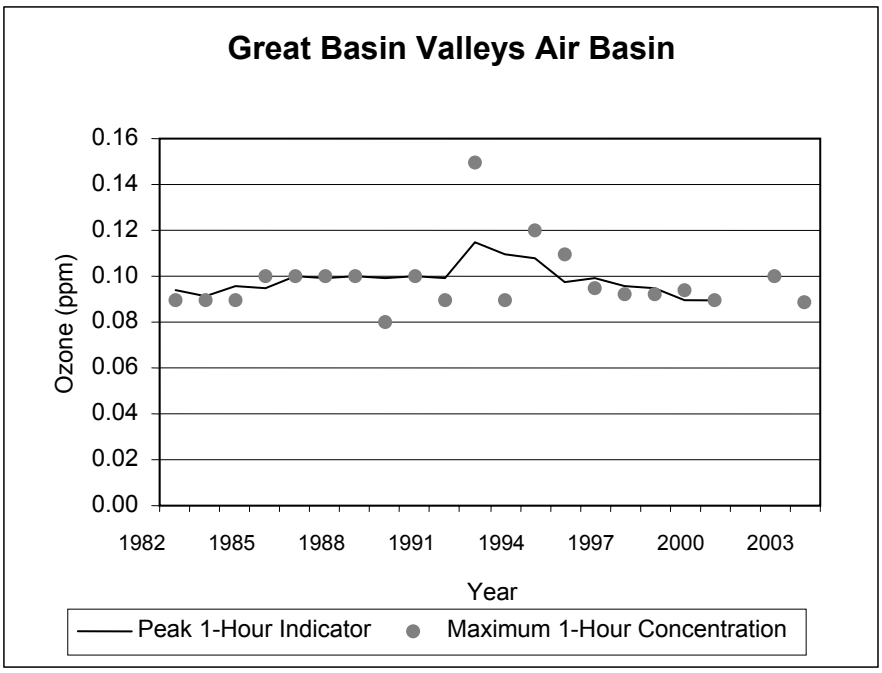


Figure 7-13



7.2.8.2 Lake County Air Basin

The Lake County Air Basin (LCAB) comprises all of Lake County. Less than 1 percent of the State's population lives in the LCAB. This air basin is the only area of California that attains all of the State ambient air quality standards, including the State ozone standard. Air quality in LCAB also does not violate either the 1-hour or 8-hour federal standards.

Ozone levels are relatively low in the LCAB. During 1982 through 2003, the peak 1-hour indicator varied between 0.074 ppm and 0.087 ppm. In contrast, the maximum 1-hour concentration was more variable, ranging between 0.06 ppm and 0.09 ppm. This is not unexpected, since the maximum 1-hour concentration is less stable than the peak indicator and therefore, more affected by year-to-year changes in meteorology. The 8-hour values show a similar trend over the same time period. Again, the maximum 8-hour concentration shows more variation, with concentrations ranging between 0.05 ppm and 0.08 ppm. The 8-hour peak indicator shows less variation, ranging between 0.060 ppm and 0.076 ppm.

Figure 7-14

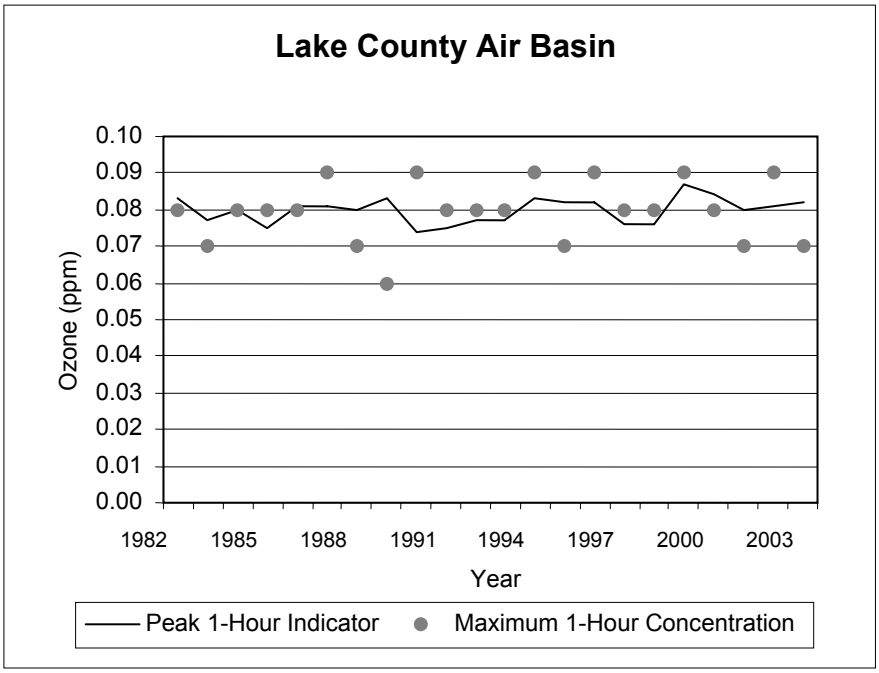
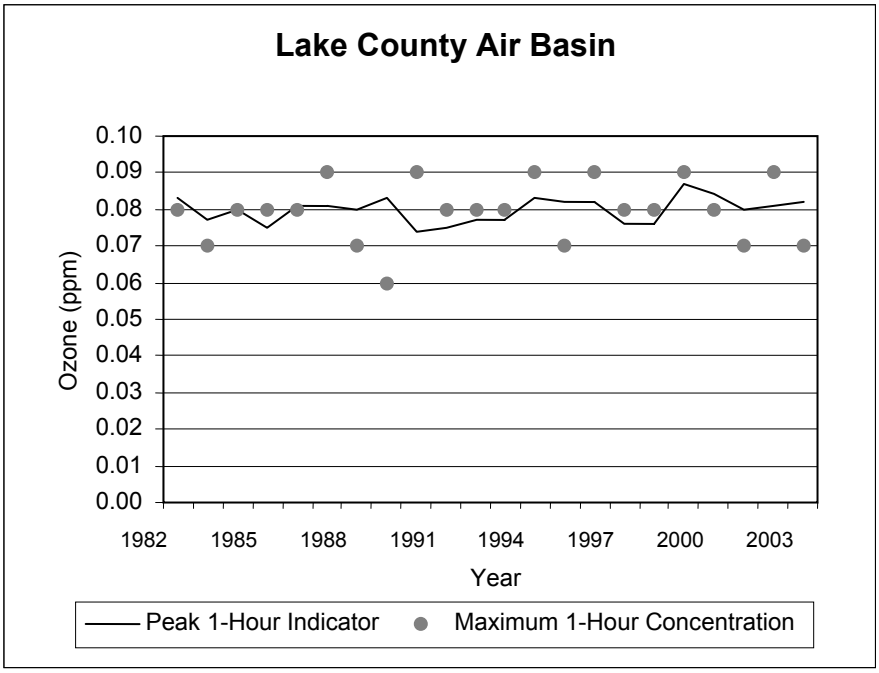


Figure 7-15



7.2.8.3 Lake Tahoe Air Basin

The Lake Tahoe Air Basin (LTAB) consists of the eastern portions of El Dorado and Placer counties. Less than 1 percent of the State's population lives in the LTAB. Ozone concentrations in this air basin tend to be highest during the summer months. However, the highest concentrations in the LTAB are still relatively low, compared to other areas of California.

Similar to the Lake County Air Basin, ozone levels in the LTAB do not show a substantial change during the 1982 through 2003 time period. The peak indicators and the maximum measured concentrations for both the 1-hour and 8-hour averaging times were similar for 1982 and 2001. All of the trend lines show a slight upswing during the last year or two. However, several more years of data are needed to determine if the upswing will continue or if it was caused by variations in meteorology.

The number of days with concentrations above the State standard remains low during the last three years (1, 1, and 3 days during 2001, 2002, and 2003, respectively). The number of days with concentrations above the federal 8-hour standard was similarly low (0, 0, and 3 days during 2001, 2002, and 2003, respectively). At this time, the LTAB remains designated as attainment for the State ozone standard and unclassified/attainment for the federal 1-hour ozone standard. The area is also unclassified/attainment for the federal 8-hour ozone standard.

Figure 7-16

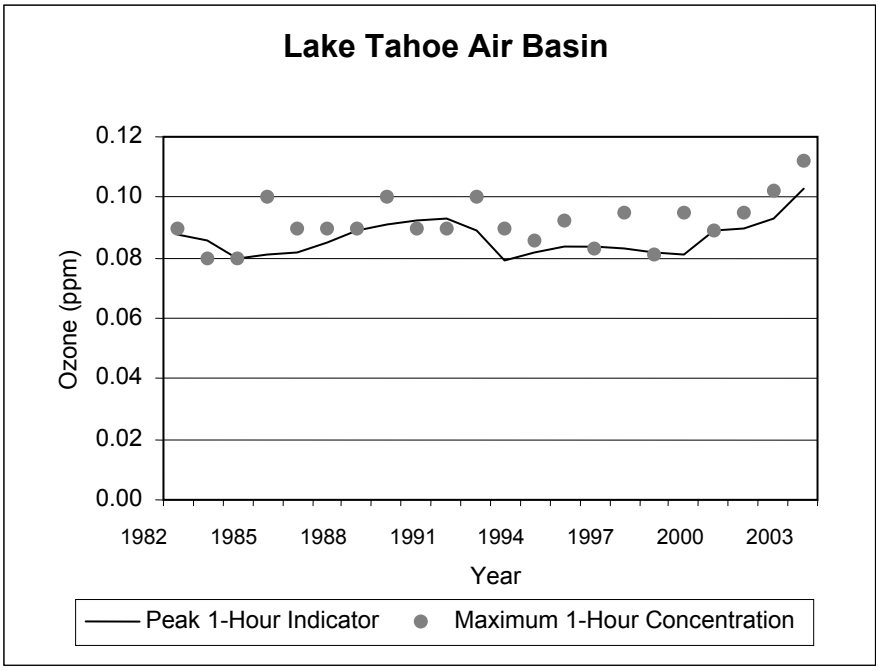
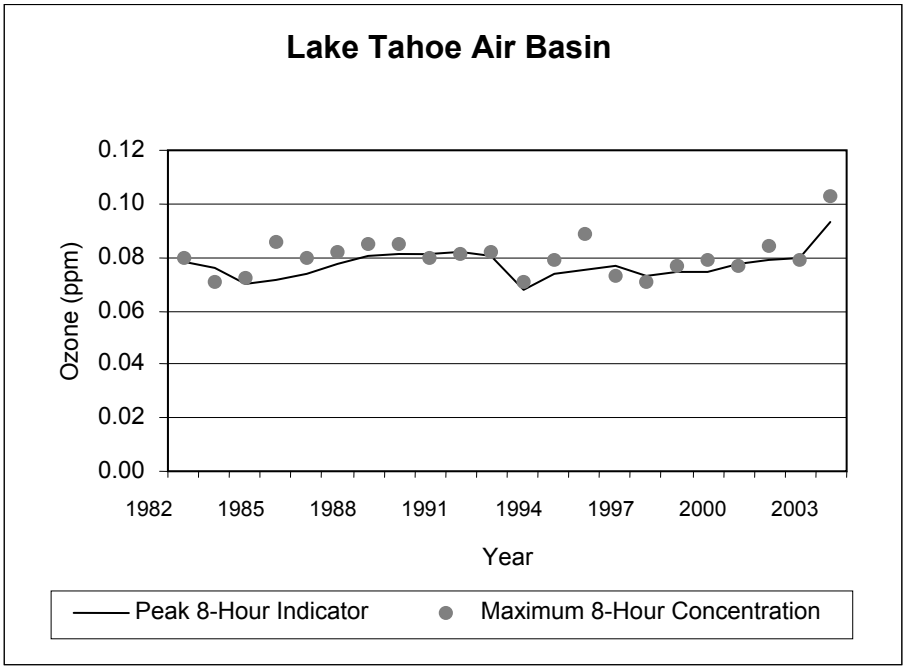


Figure 7-17



7.2.8.4 Mojave Desert Air Basin

The Mojave Desert Air Basin (MDAB) covers a large part of California's high desert. The air basin includes the eastern half of Kern County, the northeastern portion of Los Angeles County, all of San Bernardino County except for the southwestern corner, and the eastern third of Riverside County. Less than 3 percent of California's population resides in the MDAB. Because of the year-round warm temperatures, and therefore, less distinct seasonality, the ozone season in the MDAB can be longer than in other areas of California.

Overall, the peak 1-hour indicator shows a decrease of 37 percent, and the peak 8-hour indicator shows a decrease of 32 percent from 1982 to 2003. During the same time period, the maximum 1-hour concentration declined about 19 percent, and the maximum 8-hour concentration declined about 10 percent. There is a fair amount of year-to-year variation in the values for both averaging times, probably caused by year-to-year variations in meteorology. There has also been a substantial decrease in the number of exceedance days for both the State and federal standards. State standard exceedance days declined from 120 days in 1982 to 93 days in 2003. During this same time period, the number of federal 1-hour exceedance days was 38 in 1982 compared with only 13 in 2003. With respect to the federal 8-hour concentrations, there were 104 exceedance days in 1982 compared with 74 exceedance days in 2003.

Figure 7-18

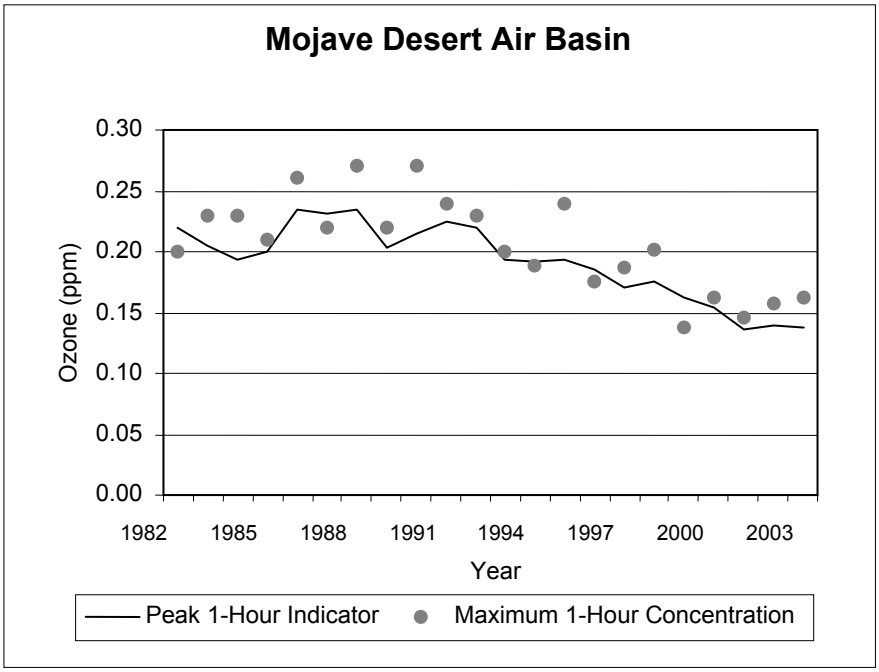
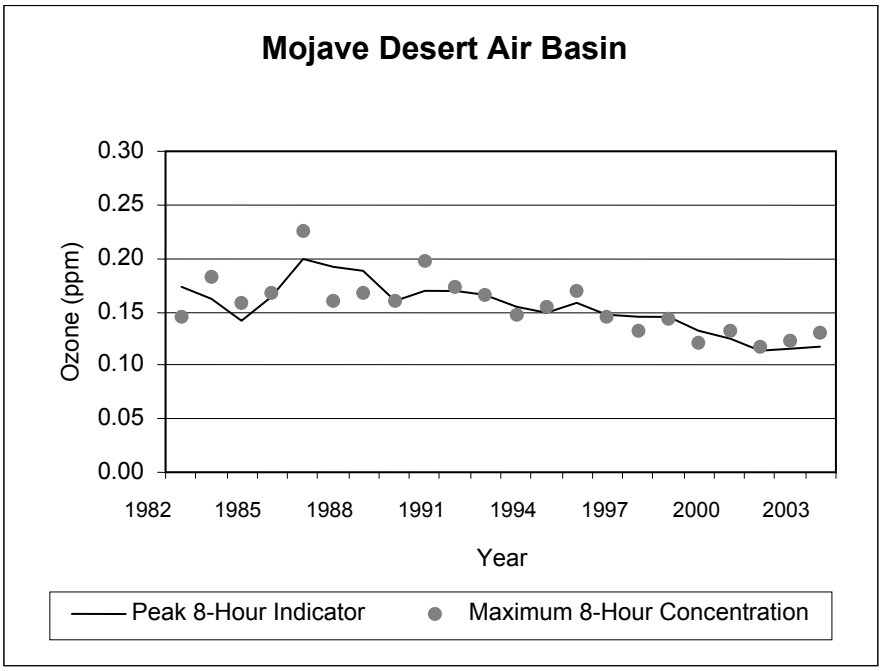


Figure 7-19



7.2.8.5 Mountain Counties Air Basin

For the purposes of this document, the Mountain Counties Air Basin (MCAB) comprises the central and northern portions of the Sierra Nevada mountain region, including Amador, Calaveras, Mariposa, Nevada, Plumas, Sierra, and Tuolumne counties (the MCAB portions of Placer and El Dorado counties are included in the Sacramento Metropolitan Area). The MCAB is thinly populated, its communities separated from one another by the region's complex terrain. A little less than 1 percent of the State's population lives in the MCAB.

Unlike the rest of California, ozone data are available for a representative number of sites in the Mountain Counties Air Basin only since 1987. Between 1987 and 2003, the maximum 1-hour ozone concentrations show a fair amount of year-to-year variation. The trend line for the peak 1-hour indicator is much more stable. This indicator has decreased since 1998, but shows little change during the last three years. During 2001 through 2003, the State ozone standard was exceeded an average of 38 days per year, while the federal 1-hour standard was exceeded an average of only once per year.

Compared with the 1-hour trend lines, the 8-hour trend lines show little change over the 22-year time period. Both the maximum 8-hour concentrations and the peak 8-hour indicator values are relatively stable. While the maximum 8-hour concentrations for 1982 and 2003 show a difference of only 0.008 ppm, there is essentially no difference in the peak 8-hour indicator values for the two end years (0.106 ppm for 1982 versus 0.107 ppm for 2003). During 2001 through 2003, the federal 8-hour ozone standard was exceeded an average of 43 times per year.

Figure 7-20

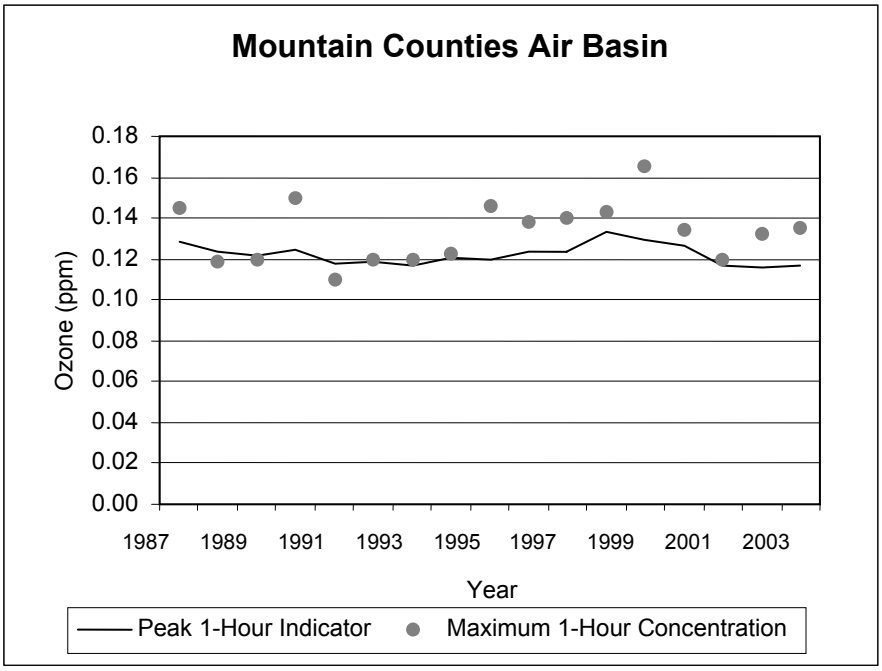
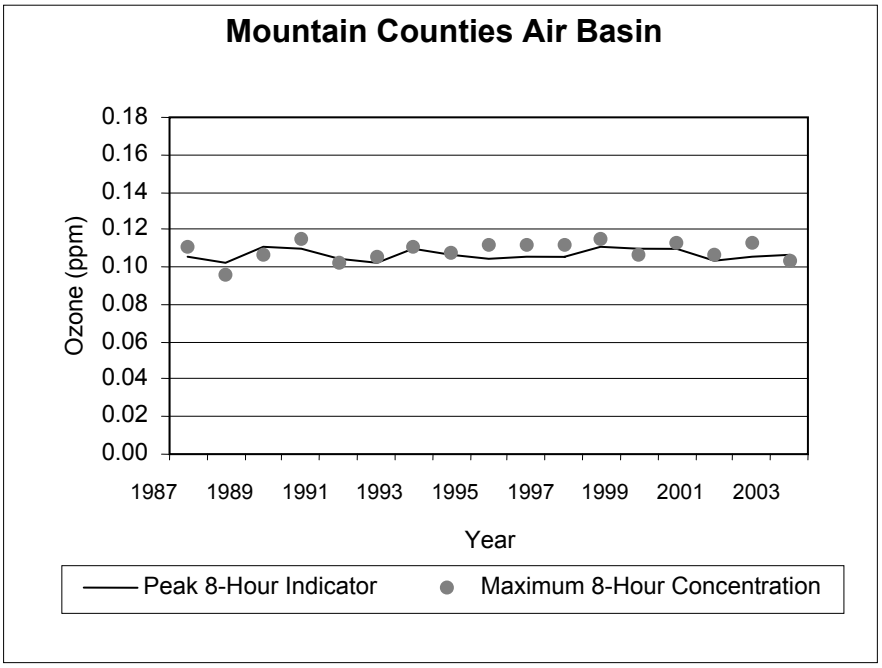


Figure 7-21



7.2.8.6 North Central Coast Air Basin

The North Central Coast Air Basin (NCCAB) is located on the coast of California and includes all of Monterey, San Benito and Santa Cruz counties. About 2 percent of the State's population live in the NCCAB.

The NCCAB enjoys relatively clean air, with only a few exceedances of the State ozone standard each year. The NCCAB trend lines for both the 1-hour values and the 8-hour values are relatively flat from 1982 through 1986, with substantial increases in 1987. During 1987, a new monitoring site was established at the Pinnacles National Monument in San Benito County, and ozone concentrations at this site were higher than those measured at the other existing monitoring sites in the NCCAB. Since 1987, the peak 1-hour indicator declined 28 percent, and the maximum 1-hour concentration declined 24 percent. The 8-hour trend lines show similar reductions, with the peak 8-hour indicator declining 23 percent and the maximum 8-hour concentration declining 21 percent since 1987.

During 2001 through 2003, there was an average of only 4 days with concentrations above the State standard during each year. While ozone concentrations in the NCCAB did not exceed the federal 1-hour standard during this time period, 8-hour concentrations exceeded the federal standard an average of 3 days per year during 2001 through 2003.

Figure 7-22

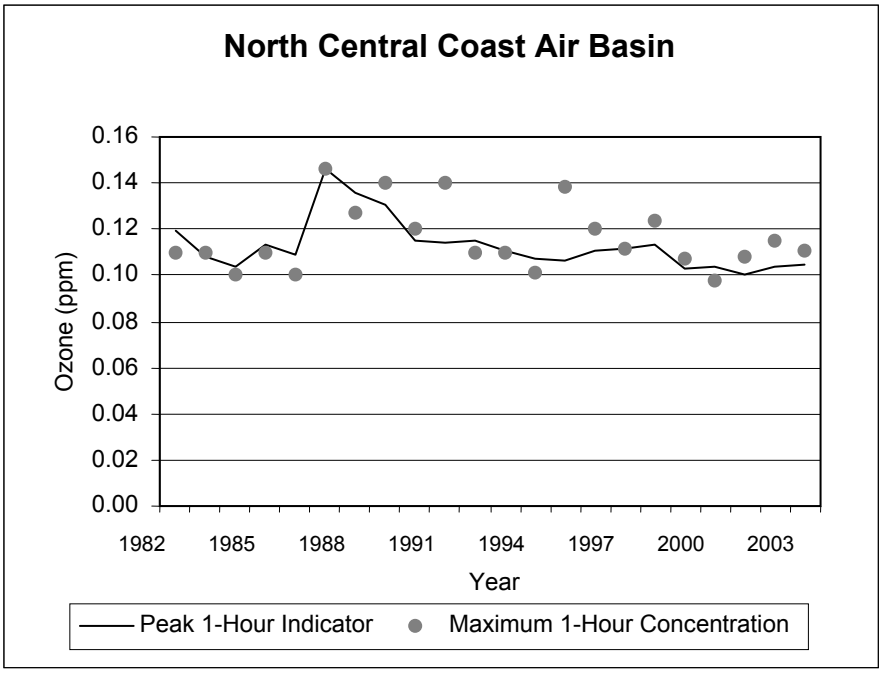
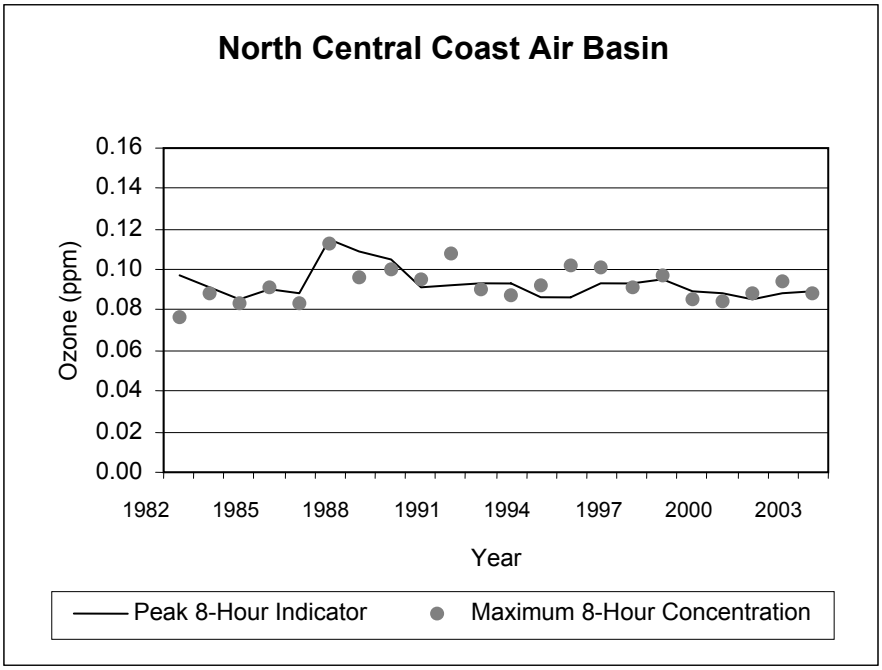


Figure 7-23



7.2.8.7 North Coast Air Basin

The North Coast Air Basin (NCAB) includes all of Del Norte, Humboldt, Mendocino, and Trinity counties, as well as the northern portion of Sonoma County. Slightly less than 1 percent of the State's population lives in the NCAB.

Ozone air quality in the NCAB does not exceed any of the State or federal ozone standards. However, both the 1-hour and the 8-hour ozone statistics for the NCAB show a general increase in 1992, coinciding with the establishment of a new ozone monitoring site at the Healdsburg Municipal Airport in Sonoma County. Since that time, the Healdsburg site has consistently recorded the highest ozone concentrations in the NCAB. The values for both averaging times during 1992 through 2003 show considerable variation, probably caused by year-to-year changes in meteorology. However, the values for all variables show a general overall decline since 1999. Recognizing the progress made in the NCAB, the ARB redesignated the NCAB as attainment for the State ozone standard in January 2004. In addition, the entire NCAB is designated as unclassified/attainment for both the federal 1-hour standard and the federal 8-hour standard.

Figure 7-24

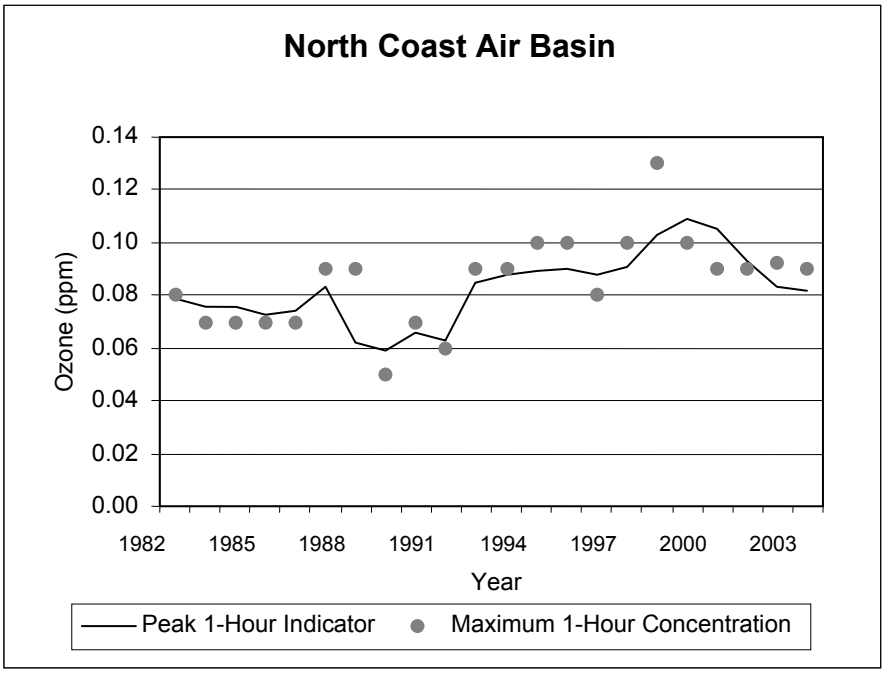
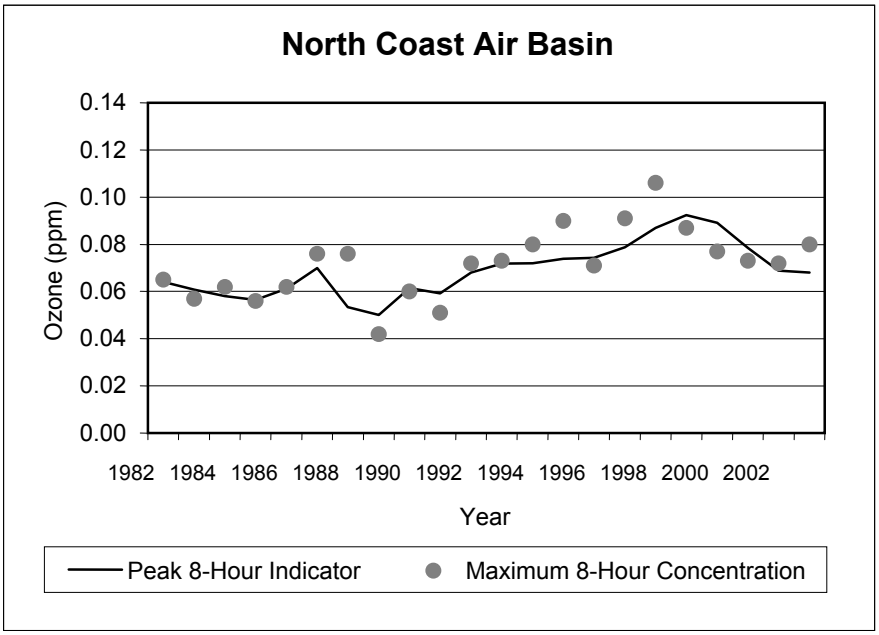


Figure 7-25



7.2.8.8 Northeast Plateau Air Basin

The Northeast Plateau Air Basin (NEPAB) is located in the northeast corner of California and includes Lassen, Modoc, and Siskiyou counties. The area is sparsely populated, housing less than 1 percent of California's population. As previously discussed, representative data are not available for the Northeast Plateau Air Basin during 2001. Therefore, air quality statistics using 2001 data are not included in the following discussion.

Ozone concentrations in this air basin tend to be relatively low, and neither the State nor federal 1-hour ozone standards were exceeded during the past 22 years. Trend lines for both the 1-hour and 8-hour statistics follow the same general pattern, and are relatively flat throughout the entire time period. However, there is some variability, caused by year-to-year variations in meteorology. Maximum concentrations for both averaging times show a slight upswing during the last several years, but the values remain below both the State and federal ozone standards. Additional years of data are needed to determine if an upward trend will continue.

Figure 7-26

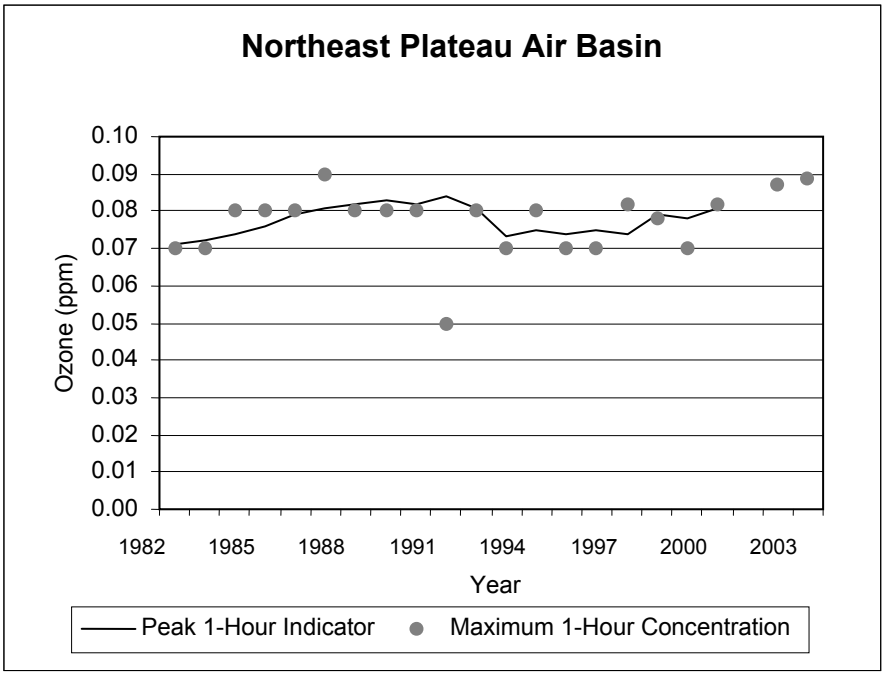
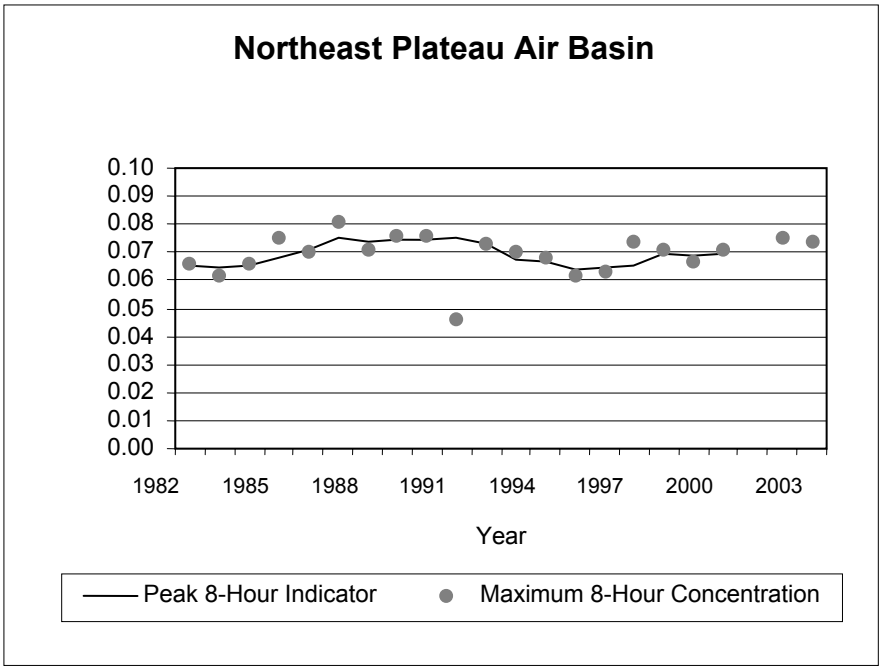


Figure 7-27



7.2.8.9 Sacramento Metro Area

The Sacramento Metro Area includes all of the urbanized southern portion of the Sacramento Valley Air Basin or SVAB (all of Sacramento and Yolo counties, the SVAB portion of Solano County, the southern one-third of Sutter County, and the SVAB portion of Placer County), as well as the portions of El Dorado and Placer counties that are located within the Mountain Counties Air Basin. The Sacramento Metro Area is consistent with the area used for federal 1-hour ozone area designations and air quality planning. In terms of population, the Sacramento Metro Area is home to about 6 percent of California's citizens.

Similar to many other areas of the State, ozone concentrations tend to be highest during the summer months, with the ozone season running from May through October. Peak 1-hour ozone levels in the Sacramento Metro Area have not declined as quickly over the last several years as they have in some other urban areas. The maximum peak 1-hour indicator remained fairly constant during the 1980s. Since then, the peak 1-hour indicator has decreased slightly, and the overall decline during the 22-year period is about 16 percent. The maximum measured 1-hour concentrations have also decreased, but with more year-to-year variation. During 2001 through 2003, the Sacramento Metro Area had an average of 55 State standard exceedance days and 6 federal 1-hour exceedance days per year.

The 8-hour statistics show less variation than the 1-hour statistics and again, little change over the 22-year time period. From 1982 to 2003, the peak 8-hour indicator decreased about 10 percent and the maximum 8-hour concentration decreased only 8 percent. During 2001 through 2003, ozone concentrations in the Sacramento Metro Area exceeded the federal 8-hour standard an average of 44 days per year.

Figure 7-28

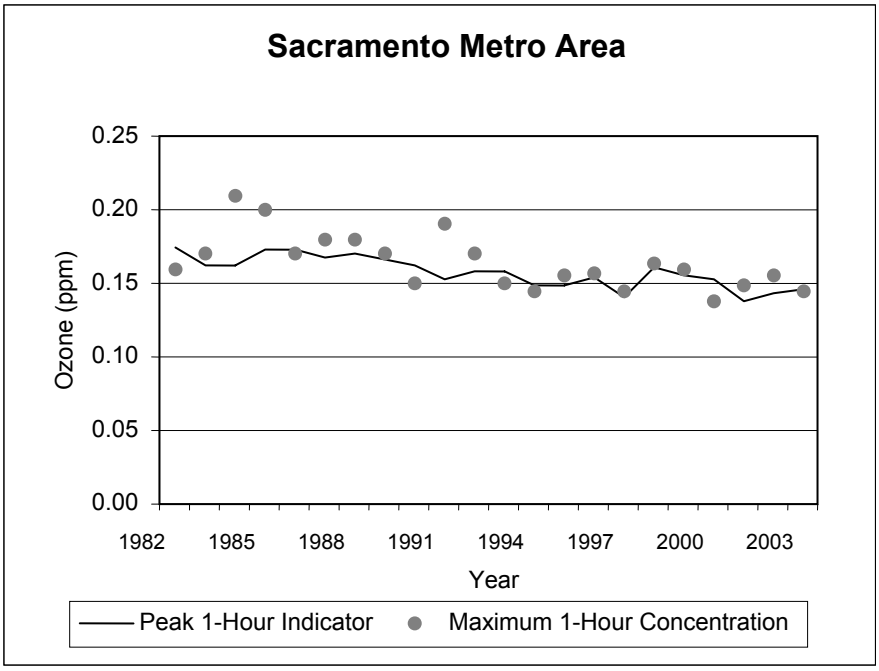
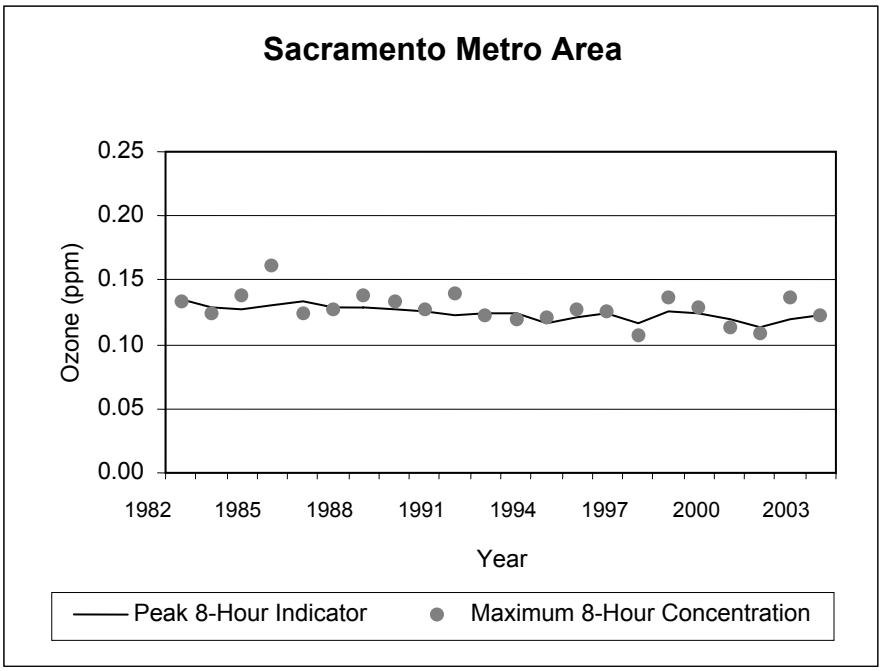


Figure 7-29



7.2.8.10 Salton Sea Air Basin

The Salton Sea Air Basin (SSAB) occupies the southeast corner of California and includes all of Imperial County, as well as the central portion of Riverside County. Less than 2 percent of the State's population lives in this air basin.

Ozone concentrations in the SSAB have exceeded the State standard and both federal ozone standards on multiple occasions. The maximum 1-hour ozone concentrations for 1982 through 2003 show substantial variation between years, with much of this variation probably caused by year-to-year changes in meteorology. However, the trend line for the peak 1-hour indicator is more stable across the 22-year period, showing a steady decline. The overall decline in the peak 1-hour indicator is 35 percent from 1982 to 2003. During each of the years 2001 through 2003, the number of exceedance days for the State ozone standard ranged between 68 and 81, and between 5 and 15 for the federal 1-hour standard.

Although much less variable, the peak 8-hour indicator and maximum 8-hour concentrations also show a steady decline over the entire time period. The peak 8-hour indicator declined 26 percent, while the maximum 8-hour concentration showed a drop of 23 percent. During the most recent three years, 2001 through 2003, ozone concentrations in the Salton Sea Air Basin exceeded the federal 8-hour standard an average of 52 days per year.

Figure 7-30

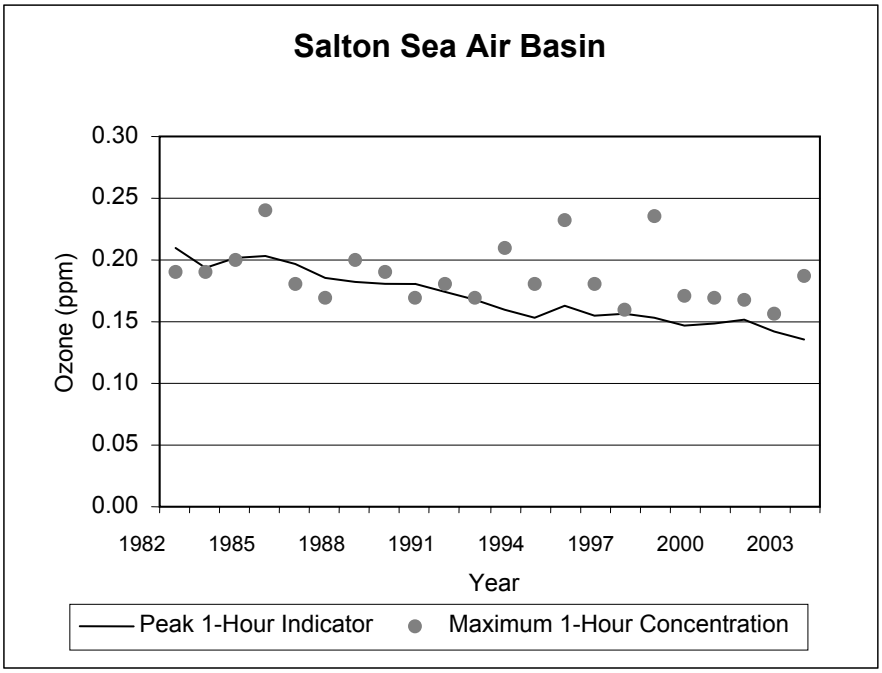
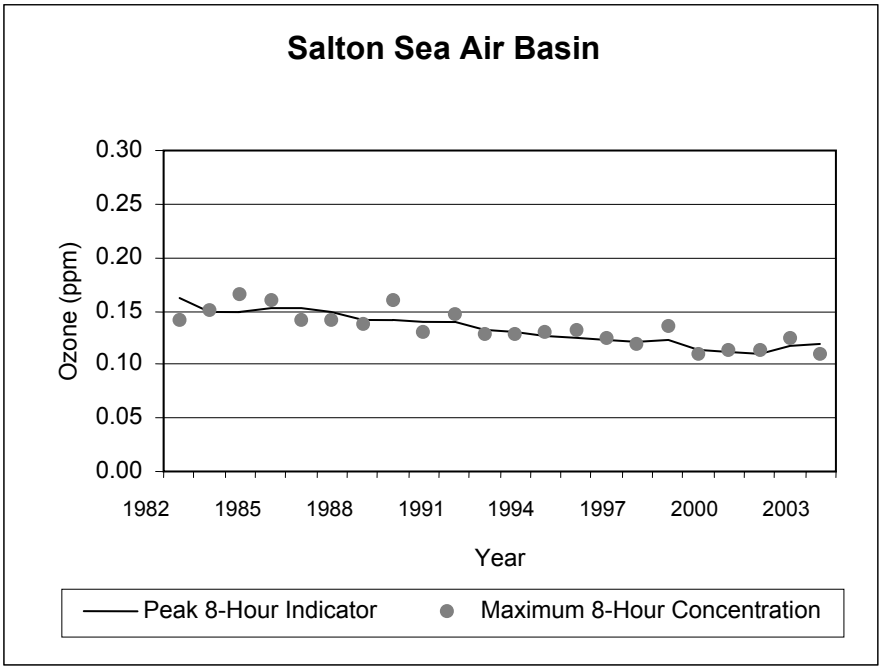


Figure 7-31



7.2.8.11 San Diego Air Basin

The San Diego Air Basin (SDAB) lies in the southwest corner of California and includes all of San Diego County. About 8 percent of California's population live in the SDAB. However, the population and emissions are concentrated mainly in the western portion of the air basin. Because of its southerly location and proximity to the ocean, much of the SDAB has a relatively mild climate, without marked seasonality.

Both the 1-hour and 8-hour ozone statistics for the SDAB indicate a substantial improvement in ozone air quality since 1982. The peak 1-hour indicator shows an overall decline of 42 percent – from 0.203 ppm in 1982 to 0.117 ppm in 2003. The measured maximum 1-hour concentration shows a similar reduction – 46 percent from 1982 to 2003. The peak 8-hour indicator also shows a similar overall decline, 38 percent, from 0.1616 ppm in 1982 to 0.1008 ppm in 2003. The measured maximum 8-hour concentration shows a 46 percent decline from 1982 to 2003.

The number of exceedance days in the SDAB has also dropped substantially over the 22-year period. There were 120 State standard exceedance days and 47 federal 1-hour exceedance days in 1982. These numbers compare with 23 State standard exceedance days and only 1 federal 1-hour exceedance day during 2003. Based on the improvements in this area, the USEPA recently redesignated the San Diego Air Basin as attainment for the federal 1-hour ozone standard. However, although the SDAB now attains the federal 1-hour ozone standard, the federal 8-hour standard continues to pose a more substantial problem, with an average of 12 exceedance days per year during 2001 through 2003.

Figure 7-32

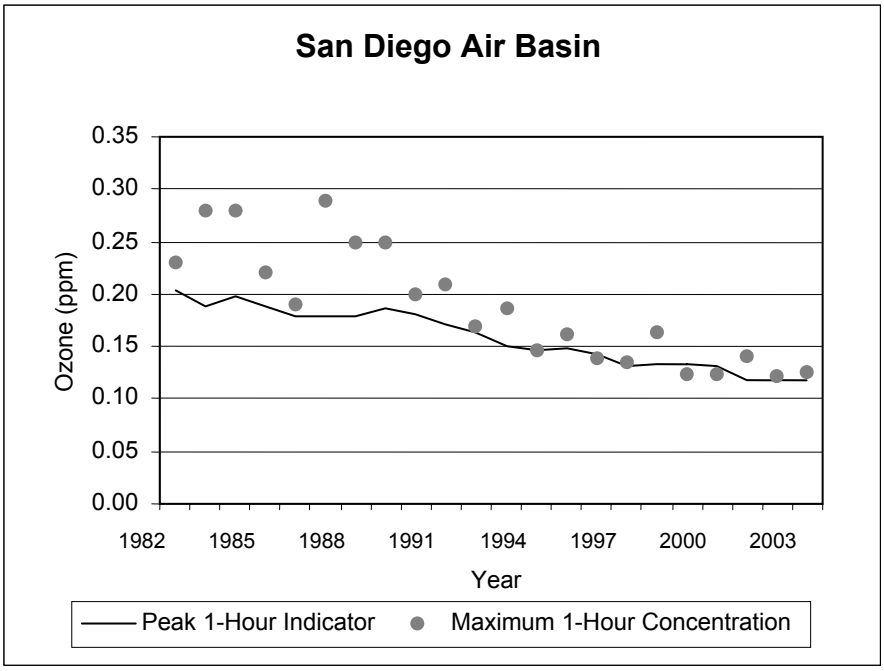
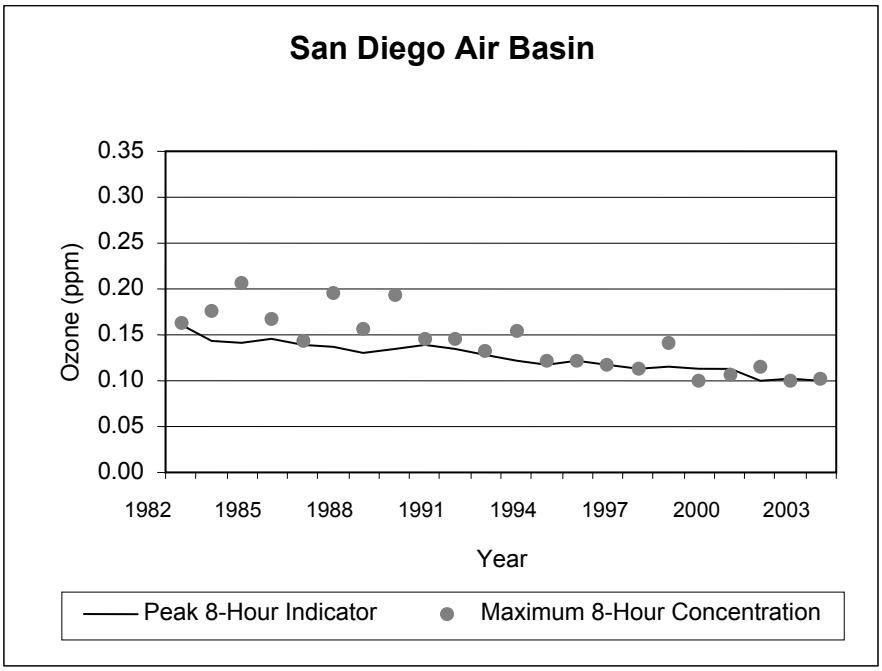


Figure 7-33



7.2.8.12 San Francisco Bay Area Air Basin

The nine-county San Francisco Bay Area Air Basin (SFBAAB) includes all of Alameda, Contra Costa, Marin, Napa, San Francisco, San Mateo, and Santa Clara counties, the southern half of Sonoma County, and the southwestern portion of Solano County. The SFBAAB is California's second largest urban area and is home to about 19 percent of California's citizens. Because of the SFBAAB's more favorable climate, with cooler temperatures and better ventilation, ozone concentrations in the SFBAAB are much lower than they are in the South Coast Air Basin and San Joaquin Valley Air Basin.

Although ozone air quality trends for the SFBAAB do not show a consistent downward trend, there have been overall improvements during the 22-year trend period. Furthermore, much of the year-to-year variation in the trends is probably attributable to variations in meteorology. The peak 1-hour indicator declined about 16 percent from 1982 to 2003, and the maximum 1-hour concentration declined about 15 percent. There is a much greater difference in the percentage changes of the two 8-hour statistics. The peak 8-hour indicator declined about 19 percent from 1982 to 2003, while the maximum 8-hour concentration declined only about 6 percent. However, it is important to keep in mind that changes in meteorology have a much greater influence on maximum concentrations than on peak indicator values. In contrast to previous years, values for 2001 through 2003 are lower and relatively stable compared with values during the prior few years, for both the 1-hour and 8-hour statistics.

The decreases in exceedance days have been more impressive than the decreases in concentrations and peak indicator values. During 1982, there were 36 State and 5 federal 1-hour exceedance days, compared with 19 State and 1 federal 1-hour exceedance days during 2003. This represents a reduction of nearly 50 percent in the number of State exceedance days and 80 percent in the number of federal 1-hour exceedance days. With respect to the federal 8-hour standard, there were 13 exceedance days in 1982 compared with 7 exceedance days during 2003. This represents a 46 percent decrease.

Figure 7-34

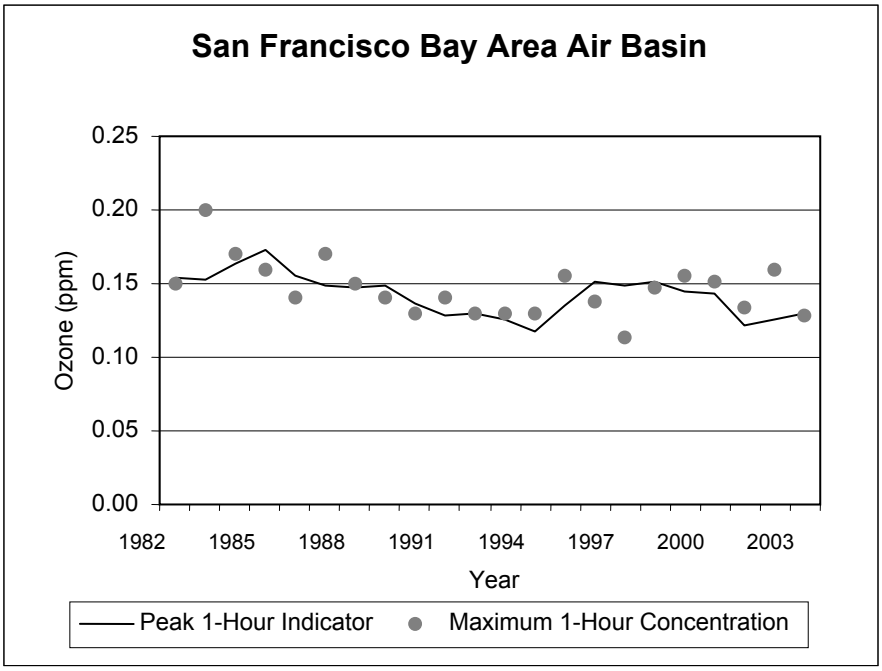
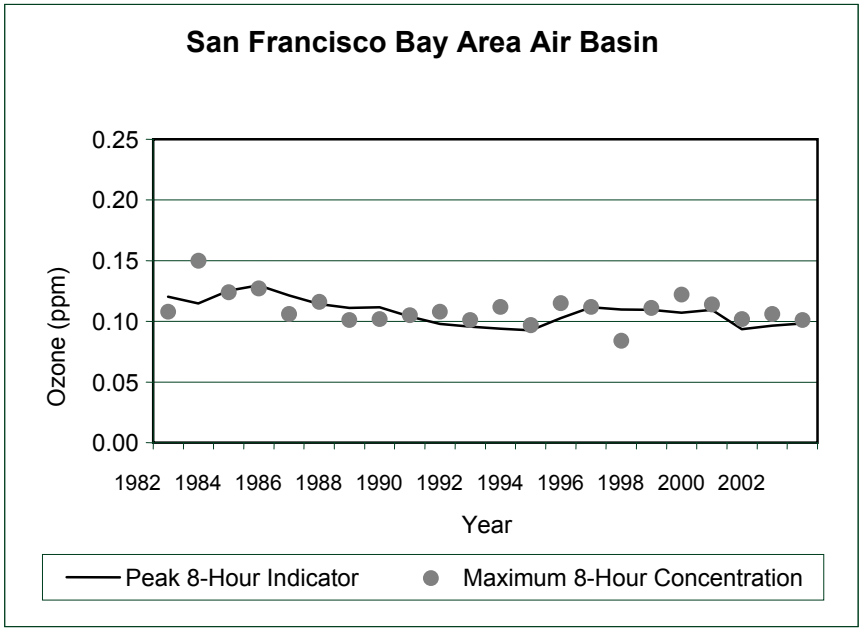


Figure 7-35



7.2.8.13 San Joaquin Valley Air Basin

The San Joaquin Valley Air Basin (SJVAB) occupies the southern two-thirds of California's Central Valley. The eight-county area includes Fresno, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare counties, as well as the western portion of Kern County. Close to 10 percent of the State's population resides in the SJVAB. Similar to other inland areas, the San Joaquin Valley has hot dry summers. Generally, the ozone season extends from April through October. Currently, the SJVAB is designated as nonattainment for both the State and federal 1-hour ozone standards. The SJVAB is also nonattainment for the federal 8-hour standard.

The ozone problem in the SJVAB ranks among the most severe in the State. While the average maximum 1-hour and 8-hour concentrations in the SJVAB during 2001 through 2003 were not vastly different from those in the Sacramento Metro Area, the number of exceedance days was substantially higher. During these three years, the SJVAB had an annual average of 129 State and 33 federal 1-hour exceedance days compared with 55 State and 6 federal 1-hour exceedance days in the Sacramento Metro Area. For the federal 8-hour standard, the SJVAB had an annual average of 123 exceedance days during 2001 through 2003, compared with 44 exceedance days in the Sacramento Metro Area.

In contrast to these comparisons, during 2001 through 2003, the SJVAB had a lower average maximum 1-hour concentration than the South Coast Air Basin (0.156 ppm compared with 0.184 ppm), but a slightly higher 3-year average of State standard exceedance days (129 days compared with 121 days). The same pattern holds true for the 8-hour statistics. During 2001 through 2003, the average maximum 8-hour concentration for the SJVAB was 0.126 ppm compared with 0.147 ppm for the South Coast Air Basin. However, during the same three years, the average number of federal 8-hour exceedances days was 123 for the SJVAB compared with 99 for the South Coast Air Basin.

Despite the severity of the SJVAB ozone problem, the area has made some progress in reducing ambient ozone. From 1982 to 2003, the peak 1-hour indicator decreased 19 percent, and the maximum 1-hour ozone concentration decreased 13 percent. In comparison to these modest declines, the decrease in the number of exceedance days is more substantial. Since the late 1980s, the number of federal 1-hour exceedance days has declined 50 percent. However, the decrease in the number of State exceedance days has not been as great (only 12 percent since the late 1980s).

With respect to the federal 8-hour standard, the pattern is similar, but the declines are smaller. From 1982 to 2003, the peak 8-hour indicator decreased about 12 percent, while the maximum 8-hour concentration decreased only about 5 percent. The decrease in the number of federal 8-hour exceedance days is much smaller than the decrease in federal 1-hour exceedance days. Since the late 1980s, the number of federal 8-hour exceedance days decreased only about 12 percent. This smaller decrease in 8-hour exceedances may stem from the fact that although the peak concentrations have been reduced, there are still a

substantial number of hours with concentrations above the level of the 8-hour standard, and these hours contribute to exceedances of the 8-hour standard.

Although the San Joaquin Valley has seen an overall improvement in ozone air quality, this region remains a challenge. High concentration areas still remain, especially in the major urban areas of Fresno and Bakersfield. The geography and climate pose a significant challenge to air quality progress, as high summer temperatures coupled with poor ventilation in the valley area contribute to high ozone levels.

Figure 7-36

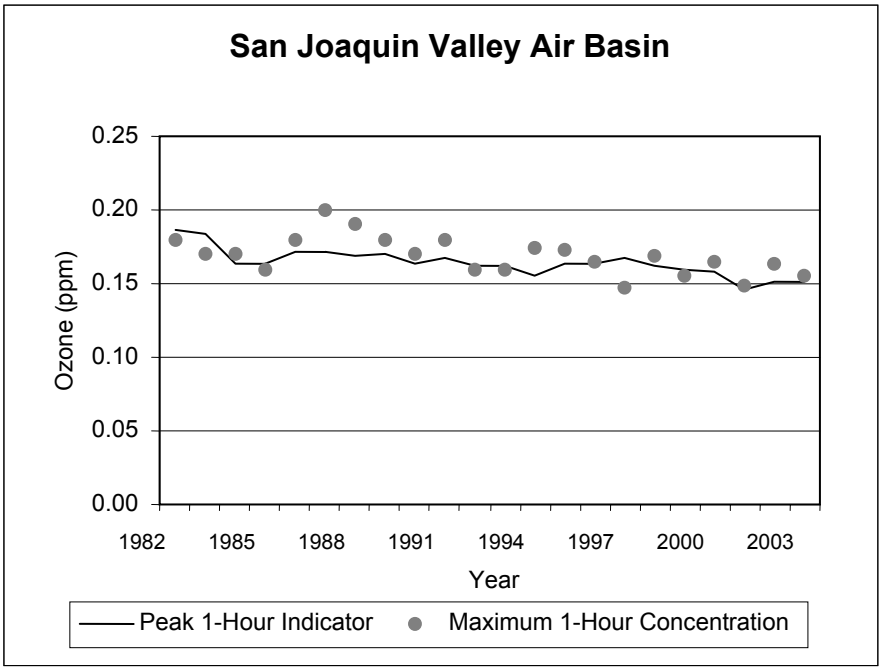
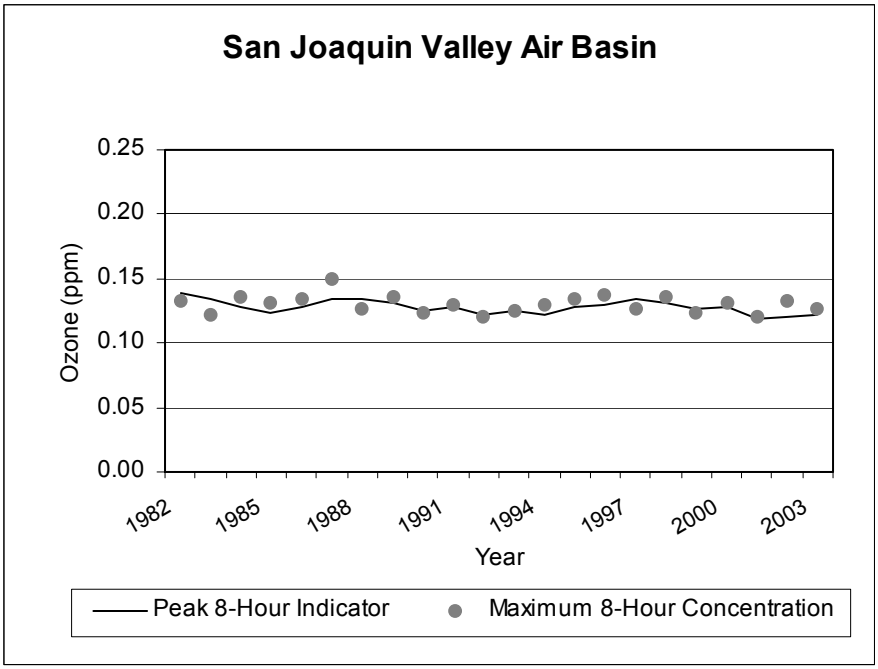


Figure 7-37



7.2.8.14 South Central Coast Air Basin

The South Central Coast Air Basin (SCCAB) includes all of San Luis Obispo, Santa Barbara, and Ventura counties. About 4 percent of the State's total population live in the SCCAB.

During January 2004, the Board designated San Luis Obispo as attainment for the State ozone standard. The remainder of the SCCAB is designated as nonattainment for the State ozone standard. For the federal 1-hour standard, both San Luis Obispo County and Santa Barbara County are designated as unclassified/attainment while Ventura County remains designated as nonattainment. However, Ventura County has made considerable progress and now qualifies as attainment for the federal 1-hour standard.

Ozone statistics for both the 1-hour and 8-hour averaging times show similar trends, with a consistent decline over the 22-year trend period. The peak 1-hour and 8-hour indicators show overall drops of 37 percent and 36 percent, respectively, from 1982 to 2003. The maximum 1-hour and 8-hour concentrations show a substantial amount of variation from one year to the next, probably caused by year-to-year differences in meteorology. However, between 1982 and 2003, the maximum 1-hour concentration shows an overall decline of 43 percent and the maximum 8-hour concentration shows an overall decline of 32 percent.

The number of exceedance days declined by an even larger percentage. The number of State standard exceedance days decreased from 145 in 1982 to 45 in 2003 (an overall decrease of about 69 percent). During this same time period, the number of federal 1-hour exceedance days decreased from 72 to only 2 (an overall reduction of 97 percent). The number of 8-hour exceedance days also shows a substantial decrease, a 72 percent reduction from 1982 to 2003. As mentioned above, the entire SCCAB has now either attained or is close to attaining the federal 1-hour ozone standard. With respect to the federal 8-hour standard, Ventura County is nonattainment, whereas San Luis Obispo and Santa Barbara counties are attainment for the federal 8-hour standard.

Figure 7-38

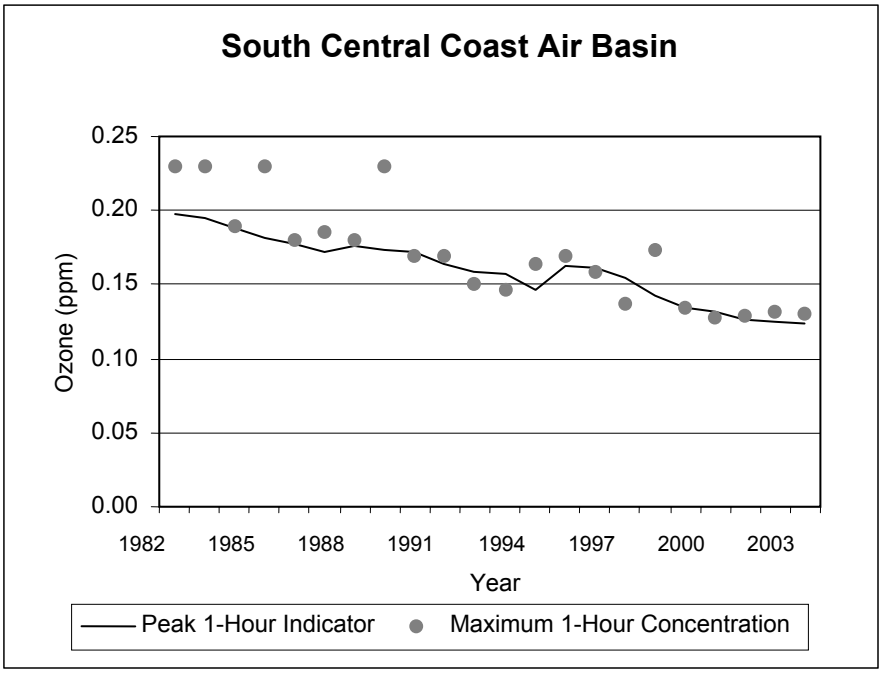
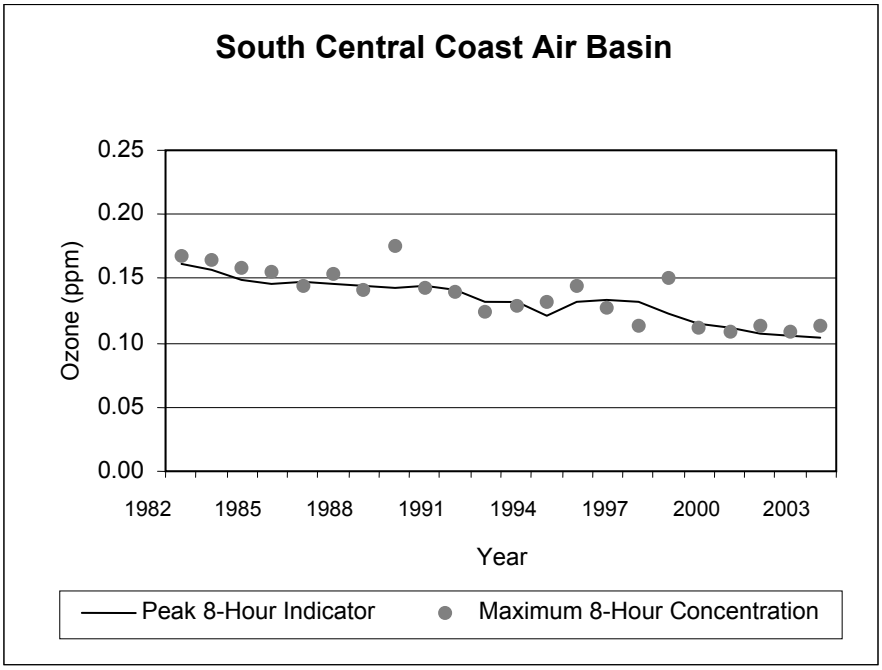


Figure 7-39



7.2.8.15 South Coast Air Basin

The South Coast Air Basin (SoCAB) includes California's largest metropolitan region, and 43 percent of the State's population lives within its boundaries. The area includes the southern two-thirds of Los Angeles County, all of Orange County, and the western urbanized portions of Riverside and San Bernardino counties. The area's warm sunny weather, associated with a persistent high-pressure system, is conducive to the formation of ozone. The ozone problem is further aggravated by surrounding mountains, frequent low inversion heights, and stagnant air conditions. These factors all act together to trap pollutants within the SoCAB.

The ozone problem in the SoCAB is one of the most severe in the State, in terms of maximum concentrations and number of days with exceedances of the standards. However, there has been considerable improvement over the years. The long tradition of emission control programs in the SoCAB has had a continuing impact on the area's ozone air quality. The long-term trends show substantial improvements in ozone air quality, despite substantial increases in population and the number of vehicle miles traveled each day.

Overall, the peak 1-hour indicator declined 54 percent from 1982 to 2003, and the peak 8-hour indicator declined 47 percent. The maximum measured concentrations show similar rates of decline during the same time period, with the maximum 1-hour concentration decreasing 52 percent and the maximum 8-hour concentration decreasing 42 percent. From 1982 to 2003, the number of State standard exceedance days decreased about 37 percent. During this same 22-year period, the number of days with concentrations above the federal 1-hour standard decreased 58 percent and the number of days with concentrations above the federal 8-hour standard decreased 34 percent.

The 2003 ozone season in the South Coast Air Basin was worse than any ozone season during the previous five years. Furthermore, there were more days with concentrations above the ozone standards than during any year since 1998. The region also recorded its first Stage 1 smog alert since 1998. A Stage 1 alert occurs when the 1-hour ozone concentration reaches 0.20 ppm. Because the 2003 Stage 1 smog alert occurred at a special study site (Rim of the World High School), it is not included as part of the data reflected in Figures 7.41 and 7.42. ARB staff analyses indicate that 2003 had more days with meteorological conditions that are conducive to higher ozone than in the last 24 years. Therefore, the higher values were substantially influenced by meteorology rather than overall changes in emissions.

Figure 7-40*

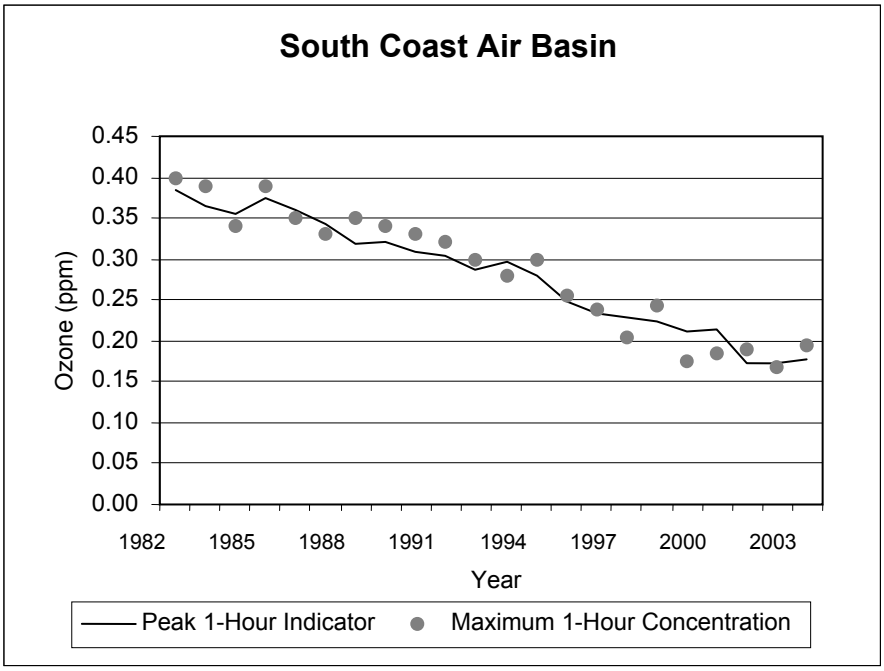
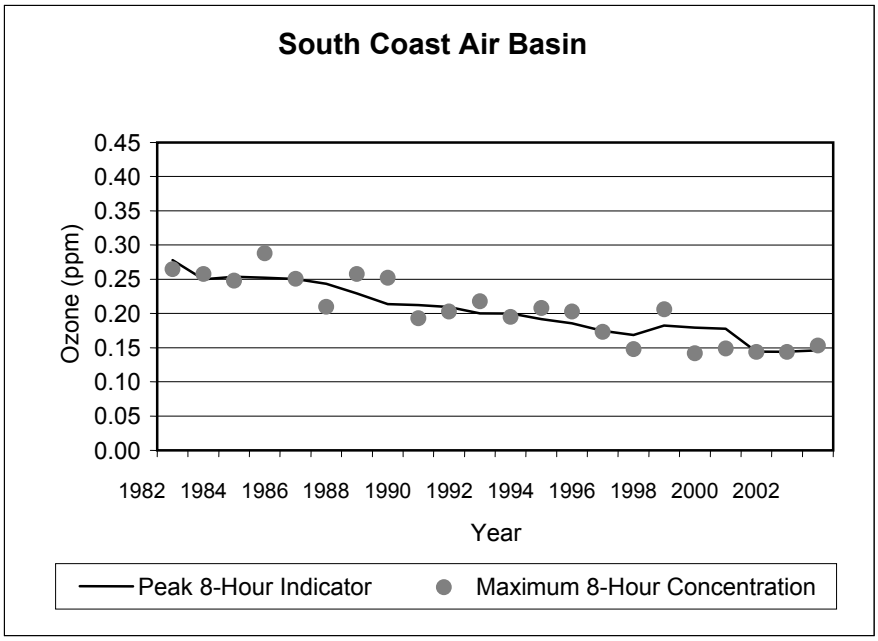


Figure 7-41*



*Values for the South Coast Air Basin do not include data for the Rim of the World High School site.

7.2.8.16 Upper Sacramento Valley Area

The Upper Sacramento Valley (USV) generally comprises the northern two-thirds of the Sacramento Valley Air Basin. The USV includes the northern two-thirds of Sutter County and all of Butte, Colusa, Glenn, Shasta, Tehama, and Yuba counties. Less than 2 percent of the State's population live in the USV.

Although the USV attains the federal 1-hour ozone standard, ambient concentrations continue to exceed the State standard. Furthermore, portions of the USV are nonattainment for the federal 8-hour ozone standard. Overall, the 1-hour and 8-hour ozone statistics for the USV show little change over the 22-year period. During 1982 through 2003, the maximum 1-hour concentrations ranged from 0.10 ppm to 0.14 ppm, with a difference of only 6 percent in the values for 1982 and 2003. Maximum 8-hour concentrations ranged from 0.89 ppm to 0.126 ppm during the same time period, with almost no difference between the end-year values (0.096 ppm in 1982 versus 0.099 ppm in 2003). The peak 1-hour and 8-hour indicator values also show little change across the entire trend period, and the values for the end-years are very close, for both averaging times. During 2001 through 2003, the USV experienced an average of 16 days each year with concentrations exceeding the State 1-hour ozone standard and 14 days each year with concentrations exceeding the federal 8-hour standard. There were no exceedances of the federal 1-hour ozone standard during this same time period.

Figure 7-42

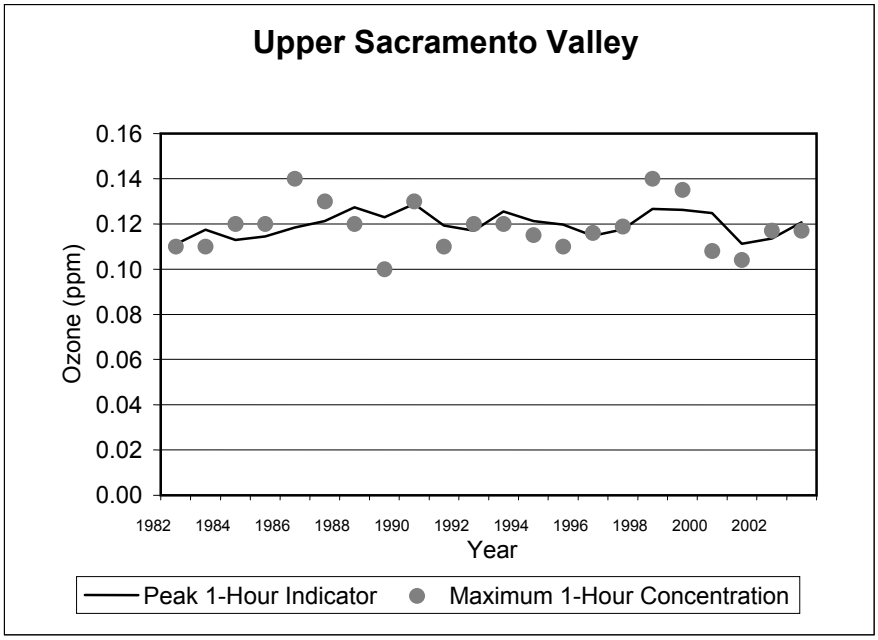
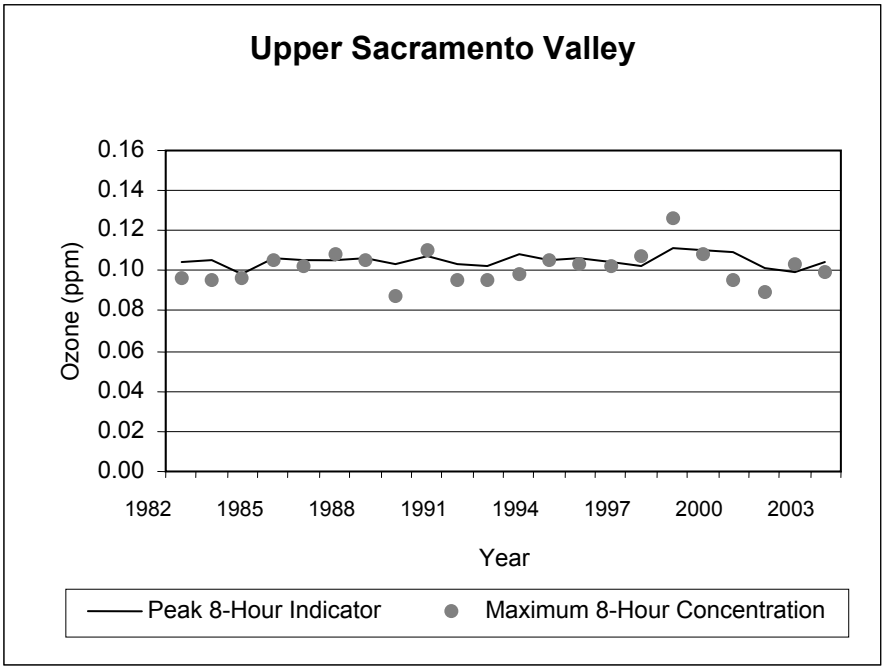


Figure 7-43



7.3 Analysis of Peak Ozone Exposure in California

7.3.1 Introduction

This section provides information on the ranges of peak outdoor 1-hour and 8-hour ozone concentrations to which people in different parts of California are potentially exposed. The term “potentially” is used because we realize that daily activity patterns influence a person’s exposure. For example, being inside a building will decrease a person’s exposure to outdoor ozone concentrations in their vicinity. However, any person who is outdoors during the peak concentration period will be exposed to the peak concentration. Furthermore, the exposures presented here provide an integrated regional perspective rather than an indication of exposure at any individual location.

This exposure analysis is based solely on “outdoor” ozone data, as measured by the statewide network of ambient ozone monitoring sites. The following tables and graphs present information on the population that could be exposed to different peak ozone concentrations within each air basin or planning area in California, as well as for the State as a whole. It is important to note that no exposure information is included for the Great Basin Valleys and Northeast Plateau air basins. As described in Section 7.4.2, below, the exposure indicator is based on three years of data (2001 through 2003). At the time this Staff Report was prepared, the third quarter 2001 ozone data for the Great Basin Valleys were under investigation by the local district and ARB. These data appeared to be low, by a factor of 10, and therefore, could not be used to calculate a reliable peak value. In contrast, the 2001 ozone data for the Northeast Plateau are missing for key summer months, when ozone is expected to be highest. Therefore, these data are not sufficient for calculating a realiable peak value.

7.3.2 Calculation of Peak Outdoor Ozone Exposures

This analysis is based on the Inverse Distance Weighting method from the Geostatistical Analyst 8.2 software. For this discussion, ozone peak indicator values and population counts were associated by census tract and merged to assemble a distribution of exposures across a range of peak ozone concentrations.

Concentrations of many air pollutants, including ozone, may change substantially from place to place. Accordingly, population exposure estimates tend to be more accurate when the population data and air quality data on which they are based are highly resolved, geographically. Population counts by census tract provide a convenient source of highly resolved population data. A typical census tract contains several thousand people. As a result, densely populated areas have many census tracts, while sparsely populated areas have very few.

Air quality data from the statewide network of monitors were also resolved to each census tract. The concentration assigned to a census tract was a weighted-average of the concentrations measured at the monitors. The weight assigned to each monitor was a function of its distance from the centroid or center of mass of the census tract, using an inverse distance weighting function (1/distance to a power). In this way, close monitors are more influential than are distant monitors. Using a weighting factor of 1/distance squared is a common

practice. However, the Geostatistical Analyst 8.2 software was able to modify the power used, in order to improve the estimations. In addition to the weighting factor, a search radius of 50 kilometers was specified. However, each census tract interpolation was based on observations for at least three neighboring sites, even if those sites were beyond the 50 kilometer search radius. Geographical barriers such as mountain ranges that may impede the movement of emissions and pollutants were not considered in the exposure calculations, but this omission had little impact on the results since monitors typically collect data in populated areas on both sides of such barriers.

Ambient ozone data used in this exposure analysis were extracted from the ARB air quality data CD (ARB 2004) and from the ARB ADAM database, and they represent the annual 1-hour and 8-hour peak indicator values for each site during the 2001 through 2003 time period. The peak indicator, sometimes referred to as the Expected Peak Day Concentration or EPDC, is a highly precise estimate of the 99.73 percentile (364/365 percentile) of the 1-hour or 8-hour ozone concentrations measured at a monitoring site. An exponential-tail model is used to calculate the peak indicator, making use of the highest twenty percent of all daily maximum values during a 3-year period (ARB 1993). Because the peak indicator represents the highest concentration expected to occur once per year, on average, the exposure results provide an assessment of the highest expected 1-hour and 8-hour exposures for each monitor.

Distributions for peak exposures were prepared for both a 1-hour and an 8-hour averaging time, using year 2000 census data. On a statewide basis, about 84 percent of California's population is exposed to peak 1-hour values above the State standard (0.09 ppm) and about 67 percent are exposed to peak 8-hour values above the federal 8-hour ozone standard (0.08 ppm).

Complete results of the exposure analyses for both the 1-hour and 8-hour averaging times are given in the following tables and figures. For each averaging time, there are results for each of the air basins or planning areas, as well as for the State as a whole. For each area, the population is allocated to different peak ozone in 0.005 ppm concentration ranges. The cumulative percent of the population exposed to each range of values above the level of the relevant standard is also included.

Table 7-13 and Figures 7-45 through 7-59 show the distribution of exposure estimates based on the peak 1-hour indicator. All areas of the State except Lake County Air Basin show some percentage of their population exposed to peak 1-hour ozone levels above 0.09 ppm. Furthermore, six areas, Mojave Desert, Sacramento Metro Area, Salton Sea, San Joaquin Valley, South Coast, and Upper Sacramento Valley, have 98 to 100 percent of their population exposed to peak 1-hour ozone levels above 0.09 ppm.

The highest 1-hour exposures occur in the Mojave Desert, Salton Sea, San Joaquin Valley, and South Coast areas. In these four areas, 23 percent or more of the population was exposed to peak 1-hour ozone levels above 0.130 ppm. People in the Mojave Desert and South Coast areas were exposed to the highest 1-hour peak ozone values – in the range of 0.155 to 0.160 ppm in the Mojave Desert and 0.170 to 0.175 ppm in the South Coast. In comparison, the

maximum exposure levels were somewhat lower in the San Joaquin Valley (0.150 ppm to 0.155 ppm) and Salton Sea (0.145 ppm to 0.150 ppm). Regardless of how they compare, the peak exposure values for all four of these areas are still well above the level of the current State 1-hour ozone standard.

Table 7-14 and Figures 7.60 through 7.74 show the distribution of exposure estimates based on the peak 8-hour indicator. All areas of the State except the Lake County Air Basin show some exposure to peak 8-hour ozone levels above 0.08 ppm. In contrast, Salton Sea and San Joaquin Valley both show 100 percent of their population exposed to peak 8-hour ozone levels above 0.080 ppm. For the Mojave Desert, Sacramento Metro Area, and Upper Sacramento Valley, more than 98 percent of the population is exposed to peak 8-hour ozone levels above 0.080 ppm. However, the severity of these exposures varies greatly among all these areas.

To assess the level of outdoor exposure, one must look not only at the percent of population exposed, but also the range of concentrations reflected by the percentage value. For example, in the Upper Sacramento Valley, nearly 100 percent of the population is exposed to peak 8-hour ozone levels above 0.080 ppm. However, the highest peak indicator value is between 0.100 ppm and 0.105 ppm. In contrast, only about 86 percent of the population in the South Coast Air Basin is exposed to peak 8-hour ozone levels above 0.080 ppm. However, 34 percent of these exposures occur at levels above 0.105 ppm. Furthermore, the population in the South Coast Air Basin is much larger than the population in the Upper Sacramento Valley. As a result, the peak 8-hour ozone exposures in the South Coast Air Basin have a greater impact on public health compared to exposures in the Upper Sacramento Valley. These factors are very important to consider when interpreting the peak exposure data.

Table 7-13 Summary of Ozone Peak 1-Hour Indicator Population-Weighted Exposure

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.09 ppm
Great Basin Valleys	Representative data not available				
Lake County	0.075	0.08	1451	2.5%	
	0.080	0.085	54346	93.2%	
	0.085	0.090	2512	4.3%	
		LC Total:	**58309**	**Total >0.09**	**0.0%**
Lake Tahoe	0.080	0.085	11253	24.4%	
	0.085	0.090	3310	7.2%	
	0.090	0.095	1364	3.0%	3.0%
	0.095	0.100	3909	8.5%	11.4%
	0.100	0.105	7990	17.3%	28.7%
	0.105	0.110	6072	13.1%	41.9%
	0.110	0.115	4857	10.5%	52.4%
	0.115	0.120	7445	16.1%	68.5%
		LT Total:	**46200**	**Total >0.09**	**68.5%**
Mojave Desert	0.075	0.080	14619	1.8%	
	0.080	0.085	1858	0.2%	
	0.085	0.090	0	0.0%	
	0.090	0.095	2115	0.3%	0.3%
	0.095	0.100	13003	1.6%	1.9%
	0.100	0.105	43493	5.3%	7.2%
	0.105	0.110	49988	6.1%	13.3%
	0.110	0.115	7048	0.9%	14.2%
	0.115	0.120	34908	4.3%	18.4%
	0.120	0.125	3575	0.4%	18.9%
	0.125	0.130	97684	12.0%	30.8%
	0.130	0.135	124785	15.3%	46.1%
	0.135	0.140	266115	32.6%	78.7%
	0.140	0.145	146078	17.9%	96.6%
	0.145	0.150	8483	1.0%	97.6%
	0.150	0.155	2381	0.3%	97.9%
	0.155	0.160	609	0.1%	98.0%
		MD Total:	**816742**	**Total >0.09**	**98.0%**

Table 7-13 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.09 ppm
Mountain Counties	0.085	0.090	26088	9.9%	
	0.090	0.095	7393	2.8%	2.8%
	0.095	0.100	9935	3.8%	6.6%
	0.100	0.105	4993	1.9%	8.5%
	0.105	0.110	54037	20.5%	29.0%
	0.110	0.115	73533	27.9%	56.8%
	0.115	0.120	58102	22.0%	78.9%
	0.120	0.125	24067	9.1%	88.0%
	0.125	0.130	5549	2.1%	90.1%
		MC Total:	**263697**	**Total >0.09**	**90.1%**
North Central Coast	0.070	0.075	6025	0.8%	
	0.075	0.080	209446	29.5%	
	0.080	0.085	201570	28.4%	
	0.085	0.090	179902	25.3%	
	0.090	0.095	42330	6.0%	6.0%
	0.095	0.100	63684	9.0%	14.9%
	0.100	0.105	7641	1.1%	16.0%
		NCC Total:	**710598**	**Total >0.09**	**16.0%**
North Coast	0.065	0.070	24886	8.0%	
	0.070	0.075	22103	7.1%	
	0.075	0.080	48516	15.6%	
	0.080	0.085	57361	18.5%	
	0.085	0.090	47285	15.2%	
	0.090	0.095	96345	31.1%	31.1%
	0.095	0.100	13572	4.4%	35.4%
		NC Total:	**310068**	**Total >0.09**	**35.4%**
Northeast Plateau	Representative data not available				
Sacramento Metro Area	0.085	0.090	2703	0.2%	
	0.090	0.095	0	0.0%	0.0%
	0.095	0.100	734	0.0%	0.0%
	0.100	0.105	30024	1.7%	1.8%
	0.105	0.110	157159	9.0%	10.7%
	0.110	0.115	324179	18.5%	29.2%
	0.115	0.120	358081	20.4%	49.6%
	0.120	0.125	387246	22.1%	71.7%
	0.125	0.130	343817	19.6%	91.3%
	0.130	0.135	145127	8.3%	99.6%
	0.135	0.140	4941	0.3%	99.8%
		SMA	**1754011**	**Total >0.09**	**99.8%**

Table 7-13 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.09 ppm
Salton Sea	0.095	0.100	1139	0.2%	0.2%
	0.100	0.105	13406	2.9%	3.1%
	0.105	0.110	16123	3.5%	6.6%
	0.110	0.115	28677	6.2%	12.7%
	0.115	0.120	120808	25.9%	38.7%
	0.120	0.125	71786	15.4%	54.1%
	0.125	0.130	85422	18.3%	72.4%
	0.130	0.135	81352	17.5%	89.9%
	0.135	0.140	37889	8.1%	98.0%
	0.140	0.145	6448	1.4%	99.4%
	0.145	0.150	2836	0.6%	100.0%
		SS Total:	**465886**	**Total >0.09**	**100.0%**
San Diego	0.075	0.080	10139	0.4%	
	0.080	0.085	60883	2.2%	
	0.085	0.090	287031	10.2%	
	0.090	0.095	618435	22.0%	22.0%
	0.095	0.100	1081023	38.4%	60.4%
	0.100	0.105	579186	20.6%	81.0%
	0.105	0.110	108618	3.9%	84.8%
	0.110	0.115	60378	2.1%	87.0%
	0.115	0.120	7066	0.3%	87.2%
	0.120	0.125	1011	0.0%	87.3%
		SD Total:	**2813770**	**Total >0.09**	**87.3%**
San Francisco Bay Area	0.060	0.065	182456	2.7%	
	0.065	0.070	707493	10.6%	
	0.070	0.075	602682	9.0%	
	0.075	0.080	801287	12.0%	
	0.080	0.085	411973	6.2%	
	0.085	0.090	329285	4.9%	
	0.090	0.095	436796	6.6%	6.6%
	0.095	0.100	500334	7.5%	14.1%
	0.100	0.105	1309795	19.7%	33.7%
	0.105	0.110	1139535	17.1%	50.8%
	0.110	0.115	155743	2.3%	53.2%
	0.115	0.120	19512	0.3%	53.5%
	0.120	0.125	64229	1.0%	54.4%
		SFBA	**6661120**	**Total >0.09**	**54.4%**

Table 7-13 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.09 ppm
San Vallev	0.095	0.100	9814	0.3%	
	0.100	0.105	322715	10.1%	10.1%
	0.105	0.110	165526	5.2%	15.3%
	0.110	0.115	228875	7.2%	22.5%
	0.115	0.120	689818	21.6%	44.1%
	0.120	0.125	658731	20.7%	64.8%
	0.125	0.130	360413	11.3%	76.1%
	0.130	0.135	244276	7.7%	83.7%
	0.135	0.140	362643	11.4%	95.1%
	0.140	0.145	96589	3.0%	98.1%
	0.145	0.150	41823	1.3%	99.4%
	0.150	0.155	8162	0.3%	99.7%
		SJV Total:	**3189385**	**Total >0.09**	**99.7%**
South Coast	0.065	0.070	96532	6.9%	
	0.070	0.075	156513	11.2%	
	0.075	0.080	82498	5.9%	
	0.080	0.085	84029	6.0%	
	0.085	0.090	334320	23.9%	
	0.090	0.095	135552	9.7%	9.7%
	0.095	0.100	118109	8.4%	18.1%
	0.100	0.105	80854	5.8%	23.9%
	0.105	0.110	88803	6.3%	30.3%
	0.110	0.115	64995	4.6%	34.9%
	0.115	0.120	60142	4.3%	39.2%
	0.120	0.125	45428	3.2%	42.5%
	0.125	0.130	26760	1.9%	44.4%
	0.130	0.135	19269	1.4%	45.8%
	0.135	0.140	4692	0.3%	46.1%
		SCC	**1398496**	**Total >0.09**	**46.1%**

Table 7-13 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.09 ppm
South Coast	0.080	0.085	13235	0.1%	
	0.085	0.090	265666	1.8%	
	0.090	0.095	852643	5.8%	5.8%
	0.095	0.100	994109	6.8%	12.7%
	0.100	0.105	1400457	9.6%	22.3%
	0.105	0.110	1536657	10.5%	32.8%
	0.110	0.115	1027585	7.0%	39.8%
	0.115	0.120	1223463	8.4%	48.2%
	0.120	0.125	960987	6.6%	54.8%
	0.125	0.130	672583	4.6%	59.4%
	0.130	0.135	672383	4.6%	64.0%
	0.135	0.140	720309	4.9%	69.0%
	0.140	0.145	665763	4.6%	73.5%
	0.145	0.150	618711	4.2%	77.8%
	0.150	0.155	710721	4.9%	82.6%
	0.155	0.160	1061720	7.3%	89.9%
	0.160	0.165	686129	4.7%	94.6%
	0.165	0.170	499248	3.4%	98.0%
	0.170	0.175	8513	0.1%	98.1%
		SC Total:	**14590882**	**Total**	**98.1%**
Upper Sacramento Valley	0.085	0.090	1450	0.2%	
	0.090	0.095	35840	5.9%	5.9%
	0.095	0.100	261253	43.3%	49.2%
	0.100	0.105	148057	24.5%	73.8%
	0.105	0.110	129396	21.4%	95.2%
	0.110	0.115	20956	3.5%	98.7%
	0.115	0.120	6566	1.1%	99.8%
		USV Total:	**603518**	**Total**	**99.8%**

Table 7- 13 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.09 ppm
California	0.060	0.065	182456	0.5%	
	0.065	0.070	845294	2.5%	
	0.070	0.075	829558	2.5%	
	0.075	0.080	1167956	3.5%	
	0.080	0.085	896508	2.7%	
	0.085	0.090	1481723	4.4%	
	0.090	0.095	2230408	6.6%	6.6%
	0.095	0.100	3071868	9.1%	15.7%
	0.100	0.105	3948611	11.7%	27.4%
	0.105	0.110	3457662	10.2%	37.7%
	0.110	0.115	1996826	5.9%	43.6%
	0.115	0.120	2585911	7.7%	51.2%
	0.120	0.125	2217060	6.6%	57.8%
	0.125	0.130	1592228	4.7%	62.5%
	0.130	0.135	1287192	3.8%	66.3%
	0.135	0.140	1396589	4.1%	70.5%
	0.140	0.145	914878	2.7%	73.2%
	0.145	0.150	671853	2.0%	75.2%
	0.150	0.155	721264	2.1%	77.3%
	0.155	0.160	1062329	3.1%	80.5%
	0.160	0.165	686129	2.0%	82.5%
	0.165	0.170	499248	1.5%	84.0%
	0.170	0.175	8513	0.0%	84.0%
		State	**33752064**	**Total >0.09**	**84.0%**

Figure 7-44

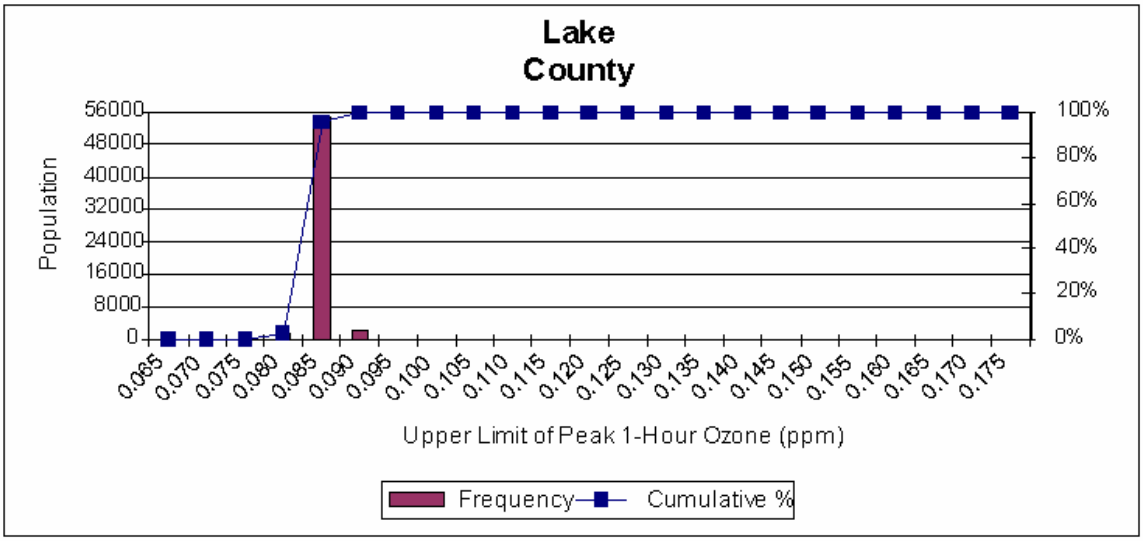


Figure 7-45

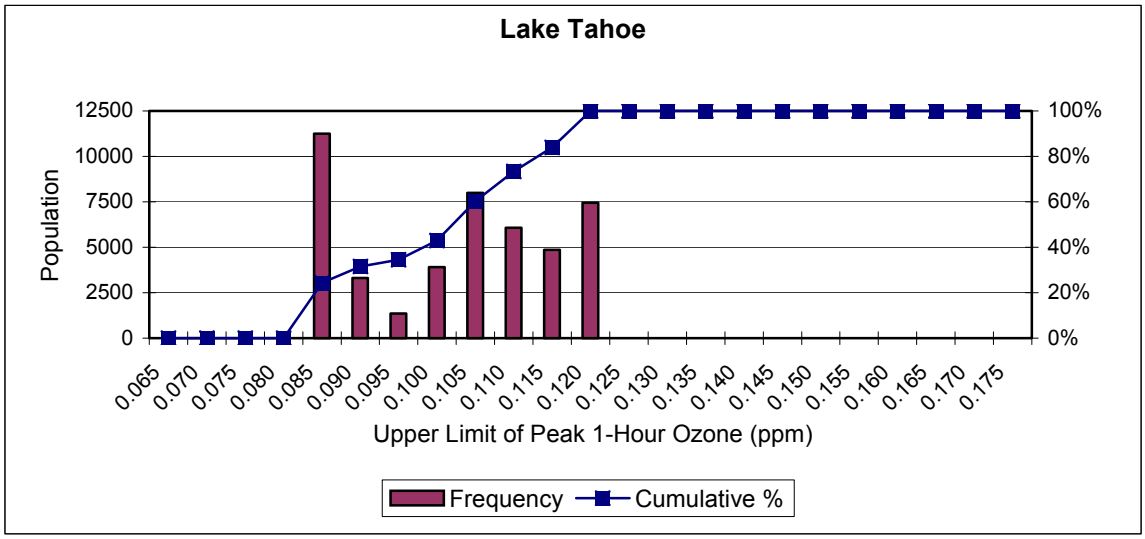


Figure 7-46

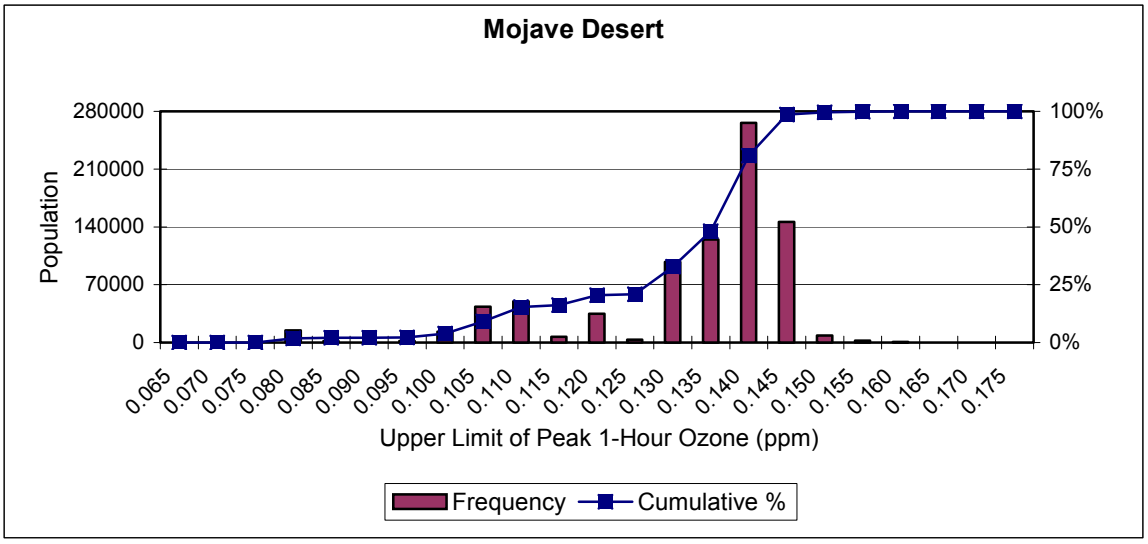


Figure 7-47

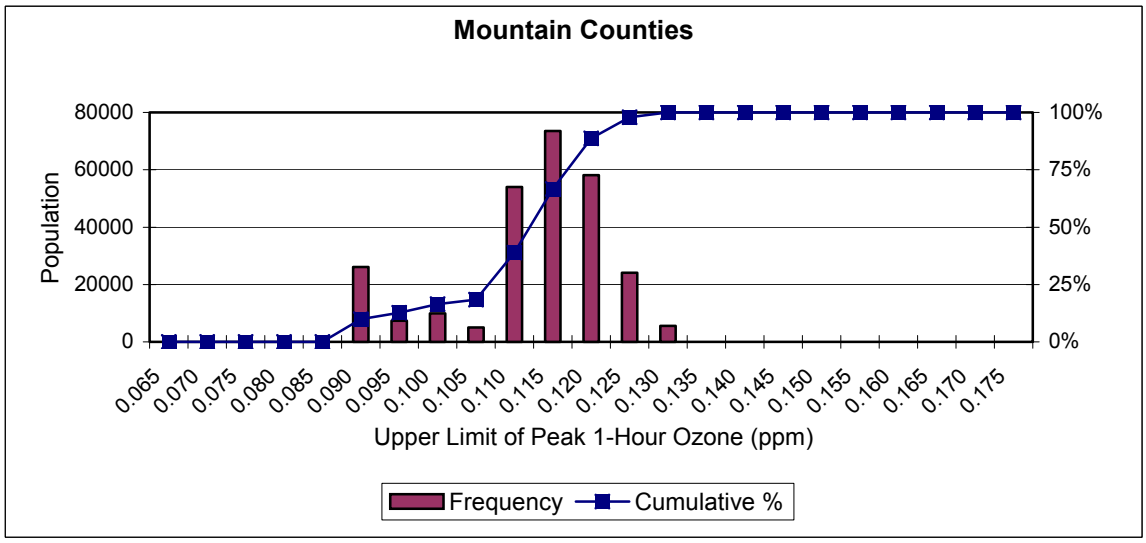
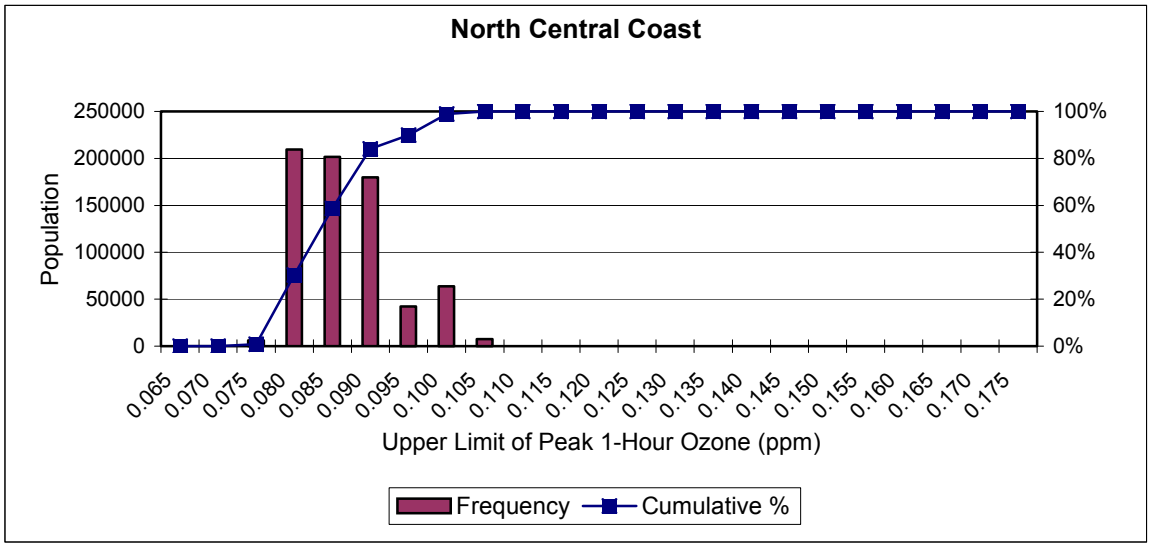


Figure 7-48



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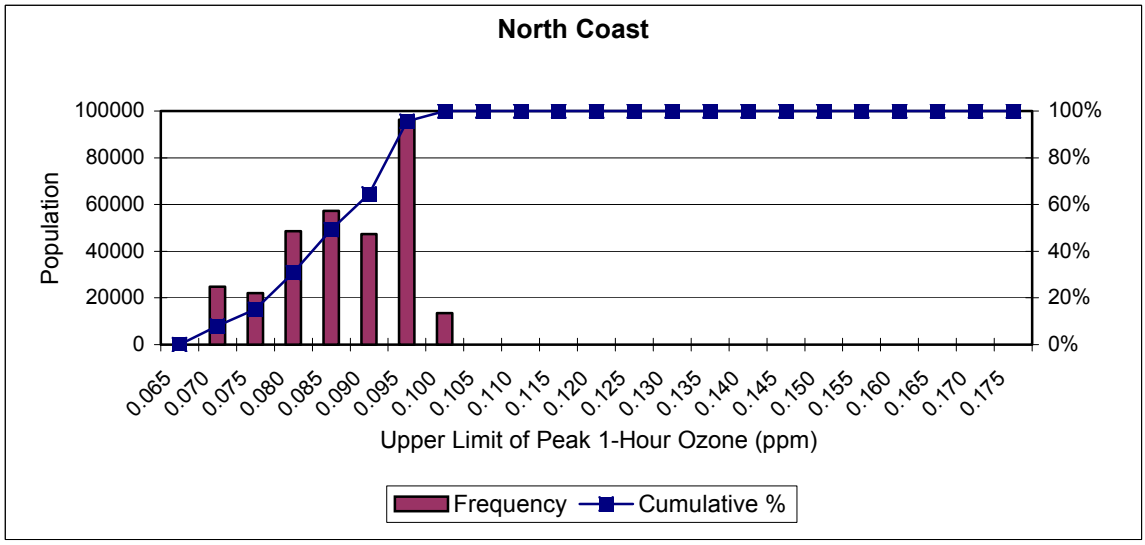
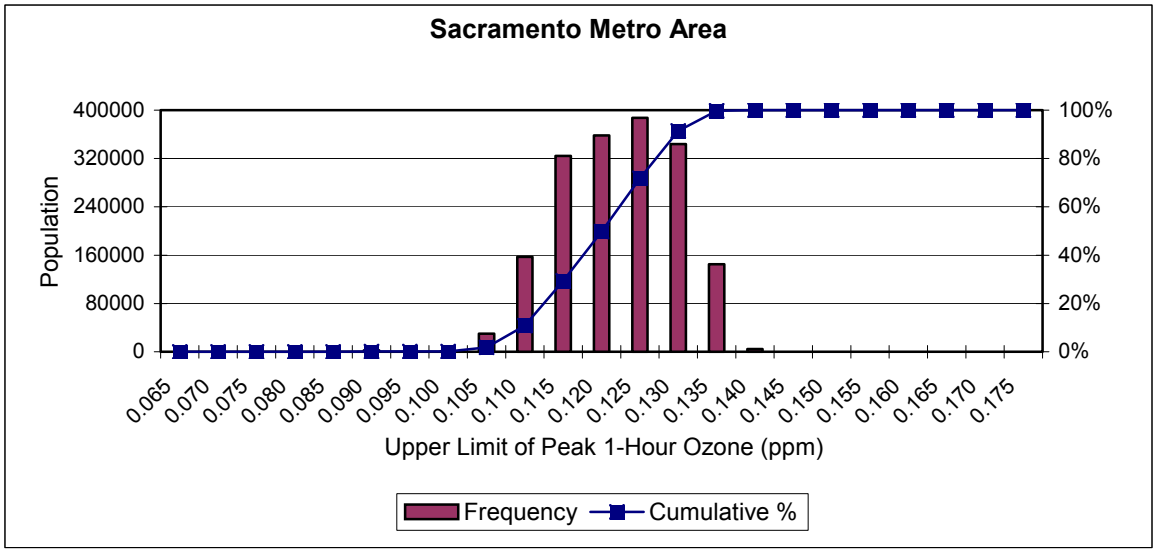


Figure 7-50



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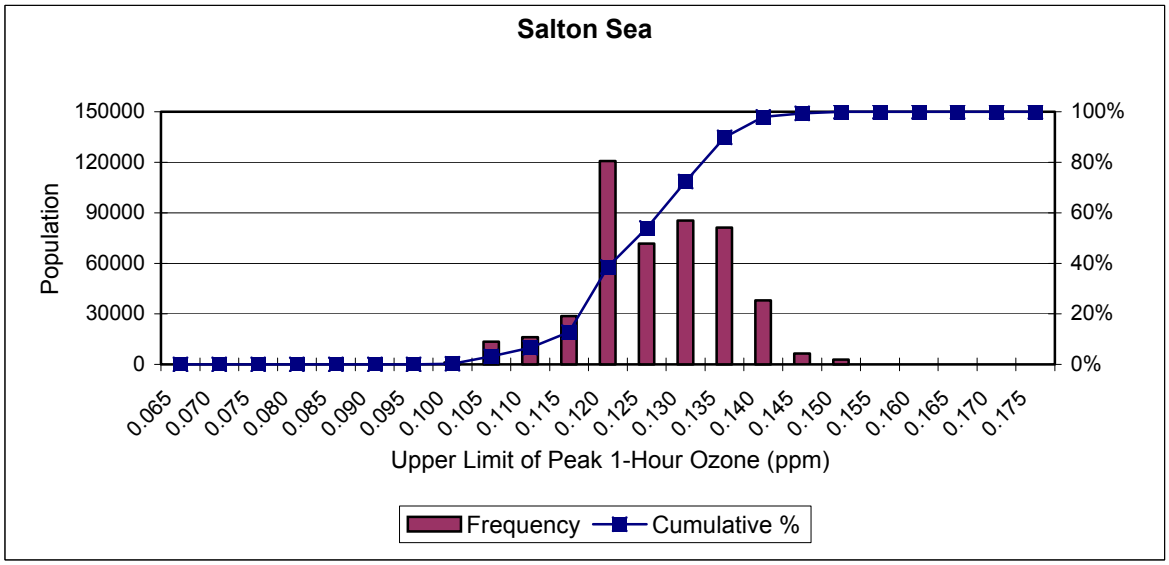

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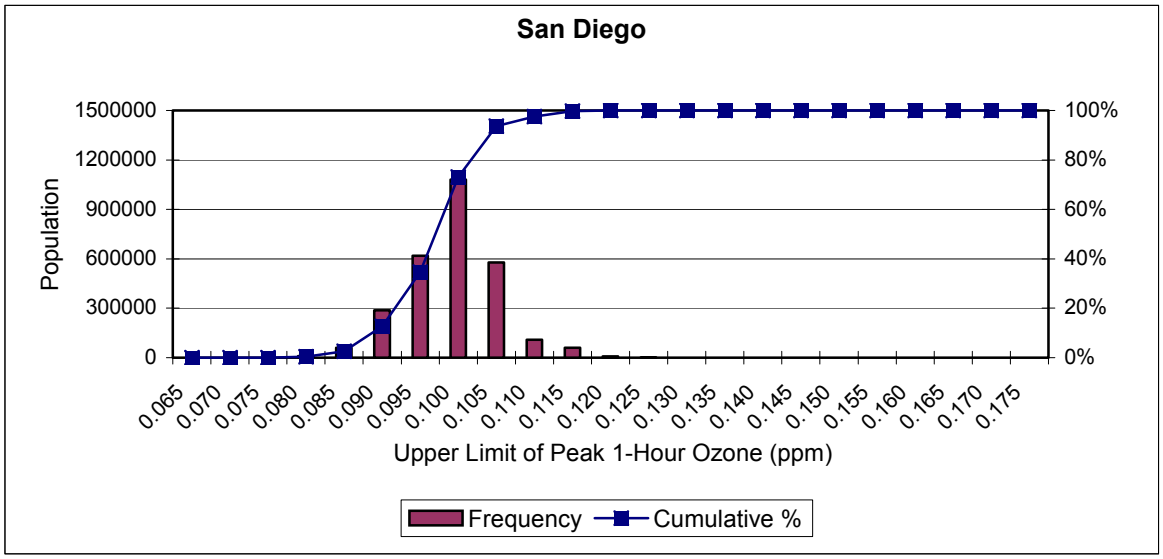

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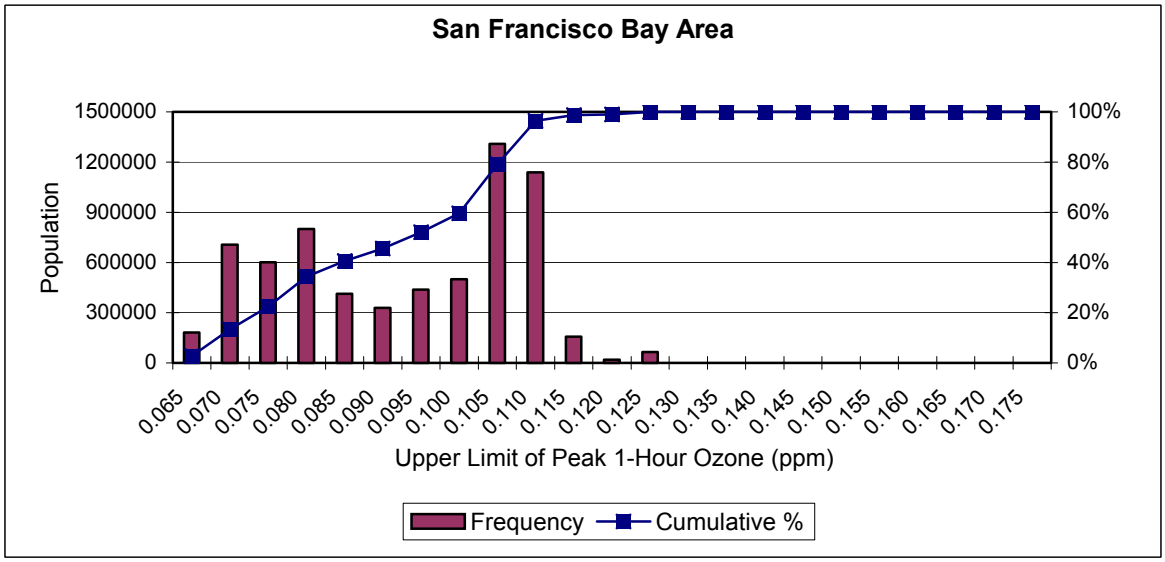

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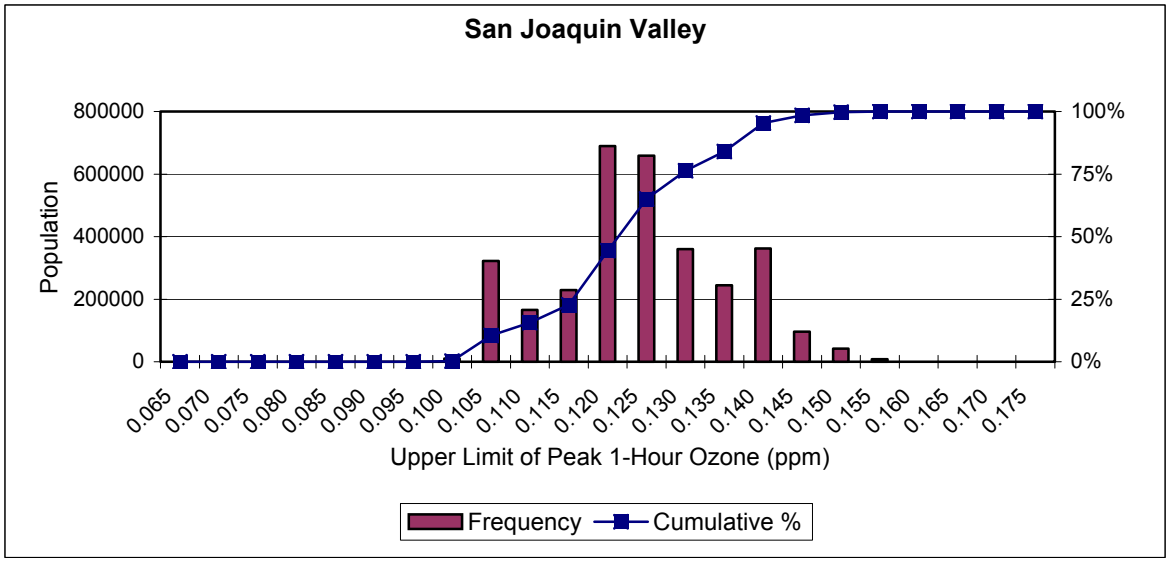

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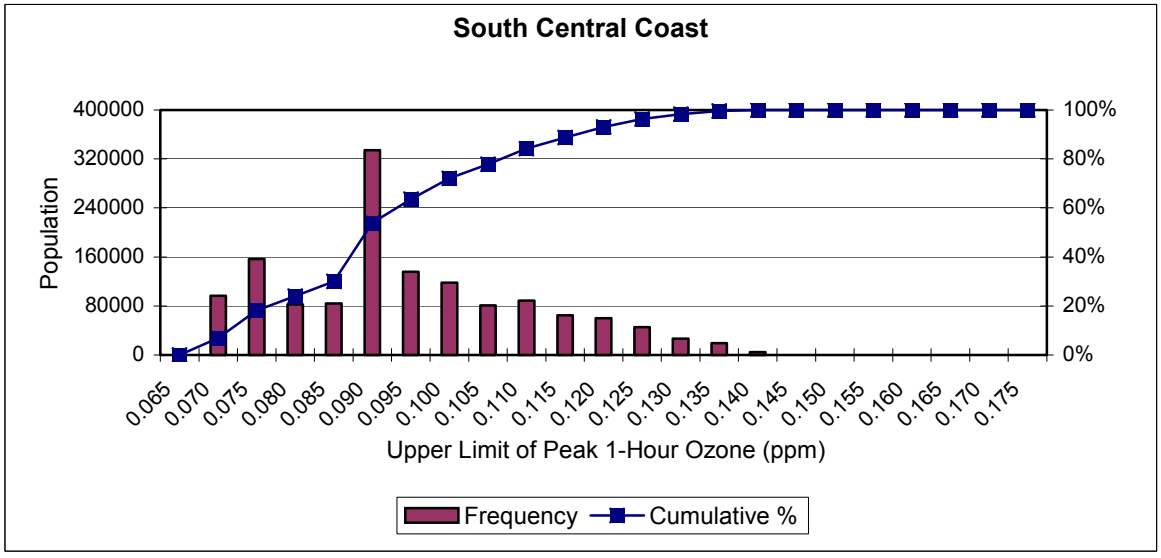


Figure 7-56

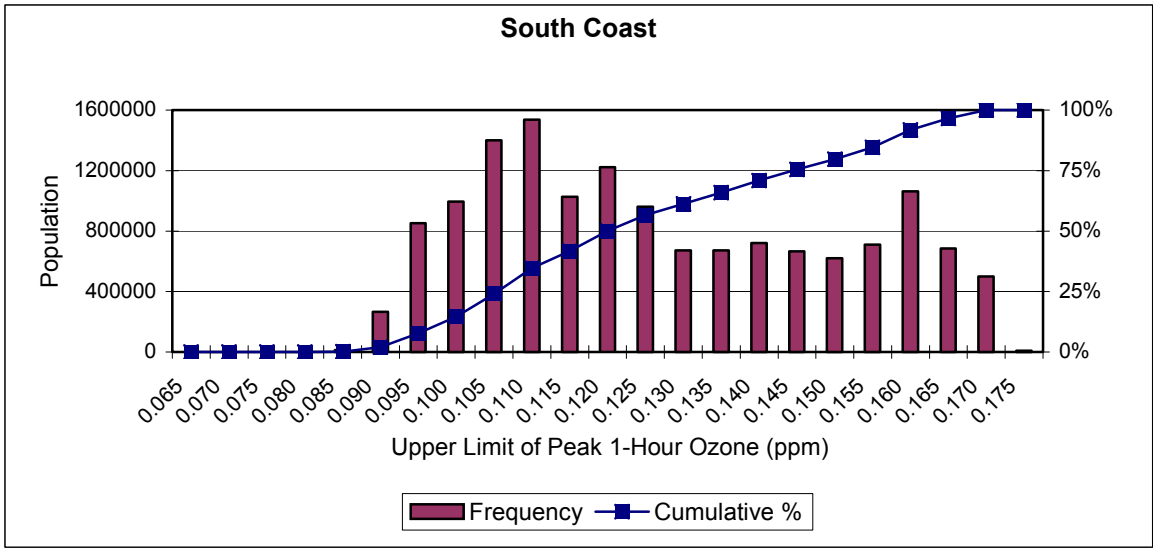


Figure 7-57

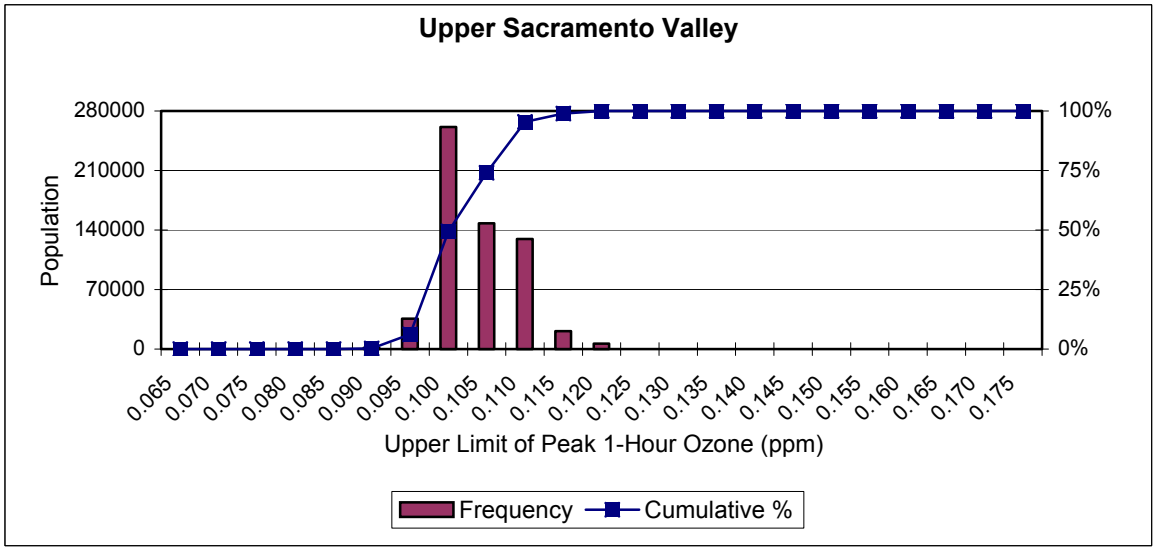


Figure 7-58

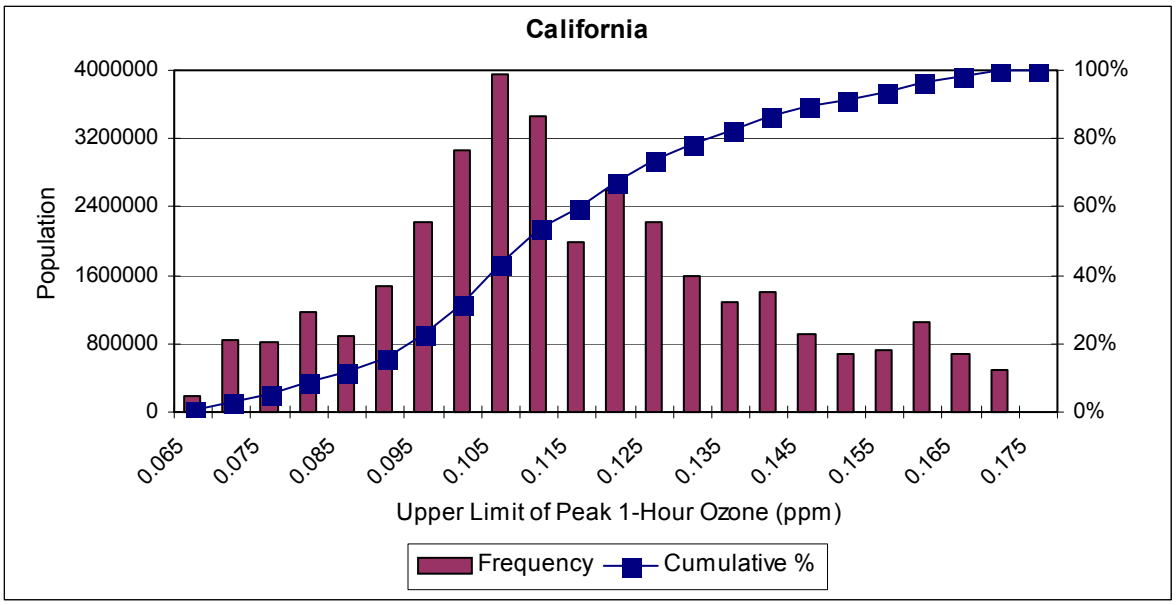

California
4000000
3200000
2400000
1600000
800000
0
Population
100%
80%
60%
40%
20%
0%
0.065
0.075
0.085
0.095
0.105
0.115
0.125
0.135
0.145
0.155
0.165
0.175
Upper Limit of Peak 1-Hour Ozone (ppm)
Frequency
Cumulative %

Table 7-14 Summary of Ozone Peak 8-Hour Indicator Population-Weighted Exposure

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.08 ppm
Great Basin Valleys	Representative data not available				
Lake County	0.065	0.070	10253	17.6%	
	0.070	0.075	45544	78.1%	
	0.075	0.080	2512	4.3%	
		LC Total:	**58309**	**Total >0.08**	**0.0%**
Lake Tahoe	0.070	0.075	1441	3.1%	
	0.075	0.080	13122	28.4%	
	0.080	0.085	4269	9.2%	9.2%
	0.085	0.090	2910	6.3%	15.5%
	0.090	0.095	9921	21.5%	37.0%
	0.095	0.100	6825	14.8%	51.8%
	0.100	0.105	7712	16.7%	68.5%
		LT Total:	**46200**	**Total >0.08**	**68.5%**
Mojave Desert	0.070	0.075	14619	1.8%	
	0.075	0.080	1858	0.2%	
	0.080	0.085	10423	1.3%	1.3%
	0.085	0.090	630	0.1%	1.4%
	0.090	0.095	51709	6.3%	7.7%
	0.095	0.100	49749	6.1%	13.8%
	0.100	0.105	24299	3.0%	16.8%
	0.105	0.110	32243	3.9%	20.7%
	0.110	0.115	167985	20.6%	41.3%
	0.115	0.120	411271	50.4%	91.6%
	0.120	0.125	45229	5.5%	97.2%
	0.125	0.130	5686	0.7%	97.9%
	0.130	0.135	1041	0.1%	98.0%
		MD Total:	**816742**	**Total >0.08**	**98.0%**

Table 7-14 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.08 ppm
Mountain Counties	0.070	0.075	9811	3.7%	
	0.075	0.080	6365	2.4%	
	0.080	0.085	18906	7.2%	7.2%
	0.085	0.090	11747	4.5%	11.6%
	0.090	0.095	63407	24.0%	35.7%
	0.095	0.100	72750	27.6%	63.3%
	0.100	0.105	9852	3.7%	67.0%
	0.105	0.110	70859	26.9%	93.9%
		MC Total:	**263697**	**Total >0.08**	**93.9%**
North Central Coast	0.060	0.065	50075	7.0%	
	0.065	0.070	302175	42.5%	
	0.070	0.075	244556	34.4%	
	0.075	0.080	47454	6.7%	
	0.080	0.085	66338	9.3%	9.3%
		NCC Total:	**710598**	**Total >0.08**	**9.3%**
North Coast	0.05	0.055	10409	3.4%	
	0.055	0.060	27178	8.8%	
	0.060	0.065	37665	12.1%	
	0.065	0.070	75408	24.3%	
	0.070	0.075	7855	2.5%	
	0.075	0.080	50707	16.4%	
	0.080	0.085	91266	29.4%	29.4%
	0.085	0.090	9580	3.1%	32.5%
		NC Total:	**310068**	**Total >0.08**	**32.5%**
Northeast Plateau	Representative data not available				
Sacramento Metro Area	0.075	0.080	3343	0.2%	
	0.080	0.085	6737	0.4%	0.4%
	0.085	0.090	127056	7.2%	7.6%
	0.090	0.095	330397	18.8%	26.5%
	0.095	0.100	387534	22.1%	48.6%
	0.100	0.105	522121	29.8%	78.3%
	0.105	0.110	317033	18.1%	96.4%
	0.110	0.115	59790	3.4%	99.8%
		SMA	**1754011**	**Total >0.08**	**99.8%**

Table 7-14 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.08 ppm
Salton Sea	0.080	0.085	11054	2.4%	2.4%
	0.085	0.090	33027	7.1%	9.5%
	0.090	0.095	77733	16.7%	26.1%
	0.095	0.100	35919	7.7%	33.9%
	0.100	0.105	81231	17.4%	51.3%
	0.105	0.110	60682	13.0%	64.3%
	0.110	0.115	41624	8.9%	73.3%
	0.115	0.120	111986	24.0%	97.3%
	0.120	0.125	12104	2.6%	99.9%
	0.125	0.130	526	0.1%	100.0%
		SS Total:	**465886**	**Total >0.08**	**100.0%**
San Diego	0.065	0.070	50101	1.8%	
	0.070	0.075	427672	15.2%	
	0.075	0.080	1051093	37.4%	
	0.080	0.085	1098796	39.1%	39.1%
	0.085	0.090	75922	2.7%	41.7%
	0.090	0.095	99909	3.6%	45.3%
	0.095	0.100	9266	0.3%	45.6%
	0.100	0.105	1011	0.0%	45.7%
		SD Total:	**2813770**	**Total >0.08**	**45.7%**
San Francisco Bay Area	0.05	0.055	763096	11.5%	
	0.055	0.060	957772	14.4%	
	0.060	0.065	1020174	15.3%	
	0.065	0.070	668135	10.0%	
	0.070	0.075	991820	14.9%	
	0.075	0.080	1384142	20.8%	
	0.080	0.085	431659	6.5%	6.5%
	0.085	0.090	361776	5.4%	11.9%
	0.090	0.095	82546	1.2%	13.2%
		SFBA	**6661120**	**Total >0.08**	**13.2%**
San Joaquin Valley	0.080	0.085	8579	0.3%	0.3%
	0.085	0.090	353061	11.1%	11.3%
	0.090	0.095	277622	8.7%	20.0%
	0.095	0.100	317234	9.9%	30.0%
	0.100	0.105	656639	20.6%	50.6%
	0.105	0.110	820218	25.7%	76.3%
	0.110	0.115	723099	22.7%	99.0%
	0.115	0.120	32933	1.0%	100.0%
		SJV Total:	**3189385**	**Total >0.08**	**100.0%**

Table 7-14 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.08 ppm
South Central Coast	0.060	0.065	204918	14.7%	
	0.065	0.070	134775	9.6%	
	0.070	0.075	141945	10.1%	
	0.075	0.080	362448	25.9%	
	0.080	0.085	135523	9.7%	9.7%
	0.085	0.090	125914	9.0%	18.7%
	0.090	0.095	118145	8.4%	27.1%
	0.095	0.100	68312	4.9%	32.0%
	0.100	0.105	62936	4.5%	36.5%
	0.105	0.110	28774	2.1%	38.6%
	0.110	0.115	14806	1.1%	39.6%
		SCC	**1398496**	**Total >0.08**	**39.6%**
South Coast	0.065	0.070	984	0.0%	
	0.070	0.075	827859	5.7%	
	0.075	0.080	1262909	8.7%	
	0.080	0.085	1973784	13.5%	13.5%
	0.085	0.090	2017916	13.8%	27.4%
	0.090	0.095	1643198	11.3%	38.6%
	0.095	0.100	1067479	7.3%	45.9%
	0.100	0.105	854422	5.9%	51.8%
	0.105	0.110	732178	5.0%	56.8%
	0.110	0.115	502485	3.4%	60.3%
	0.115	0.120	884039	6.1%	66.3%
	0.120	0.125	679312	4.7%	71.0%
	0.125	0.130	799747	5.5%	76.4%
	0.130	0.135	829078	5.7%	82.1%
	0.135	0.140	490458	3.4%	85.5%
	0.140	0.145	25034	0.2%	85.7%
		SC Total:	**14590882**	**Total >0.08**	**85.7%**
Upper Sacramento Valley	0.070	0.075	654	0.1%	
	0.075	0.080	796	0.1%	
	0.080	0.085	76960	12.8%	12.8%
	0.085	0.090	272315	45.1%	57.9%
	0.090	0.095	212207	35.2%	93.0%
	0.095	0.100	28913	4.8%	97.8%
	0.100	0.105	11673	1.9%	99.8%
		USV	**603518**	**Total >0.08**	**99.8%**

Table 7-14 (continued)

Air Basin	Lower Conc Limit (ppm)	Upper Conc Limit (ppm)	Census 2000 Pop Affected	% of Pop Exposed	Cumulative % Pop >0.08 ppm
California	0.050	0.055	773505	2.3%	
	0.055	0.060	1043568	3.1%	
	0.060	0.065	1312832	3.9%	
	0.065	0.070	1241980	3.7%	
	0.070	0.075	2716684	8.0%	
	0.075	0.080	4188708	12.4%	
	0.080	0.085	3934294	11.7%	11.7%
	0.085	0.090	3397602	10.1%	21.7%
	0.090	0.095	2966794	8.8%	30.5%
	0.095	0.100	2043981	6.1%	36.6%
	0.100	0.105	2231896	6.6%	43.2%
	0.105	0.110	2061987	6.1%	49.3%
	0.110	0.115	1509789	4.5%	53.8%
	0.115	0.120	1440229	4.3%	58.0%
	0.120	0.125	736645	2.2%	60.2%
	0.125	0.130	805959	2.4%	62.6%
	0.130	0.135	830119	2.5%	65.1%
	0.135	0.140	490458	1.5%	66.5%
	0.140	0.145	25034	0.1%	66.6%
		State	**33752064**	**Total >0.08**	**66.6%**

Figure 7-59

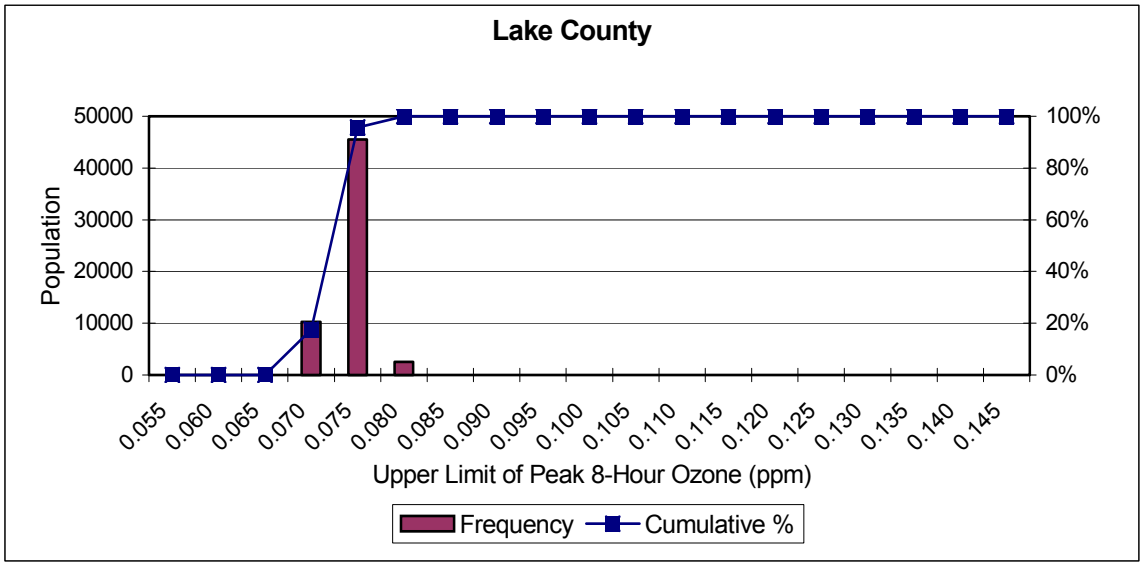


Figure 7-60

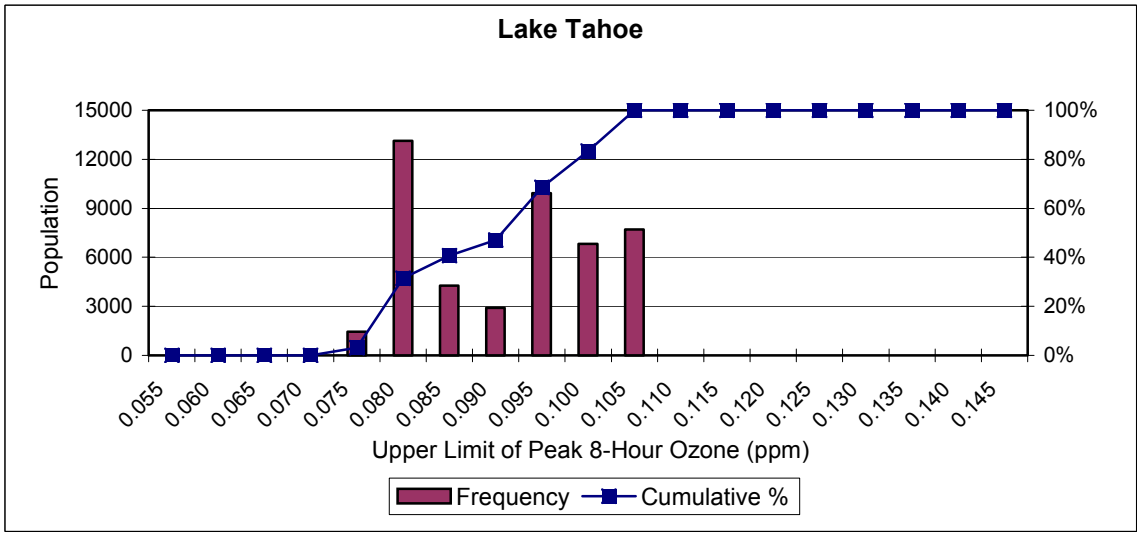


Figure 7-61

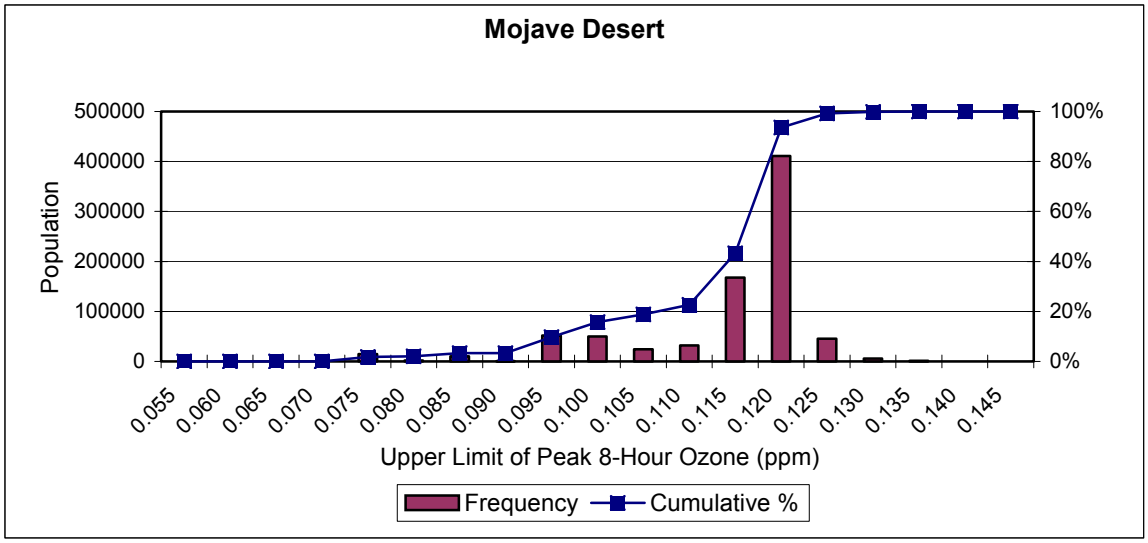


Figure 7-62

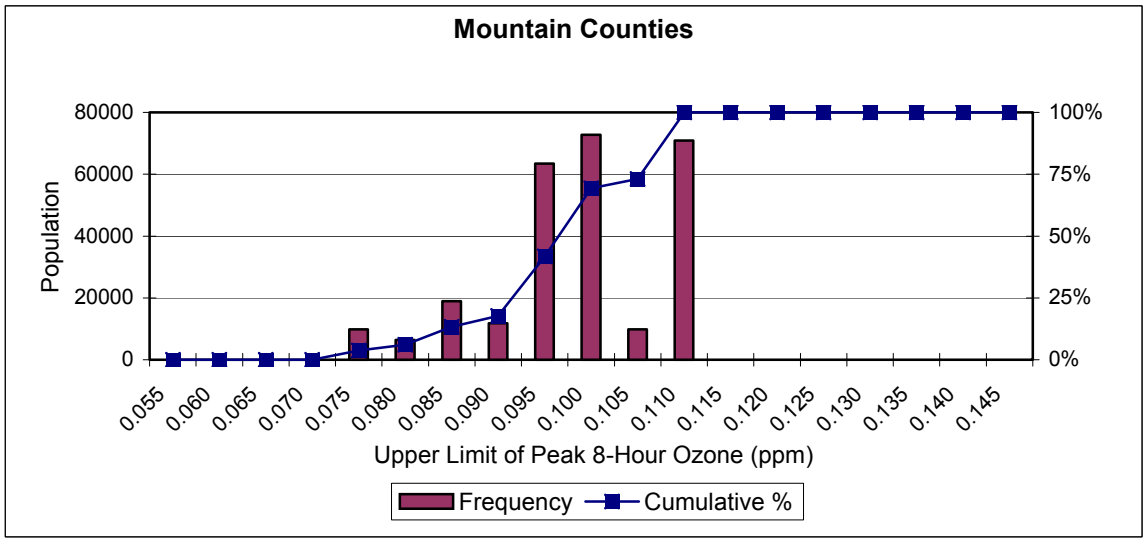


Figure 7-63

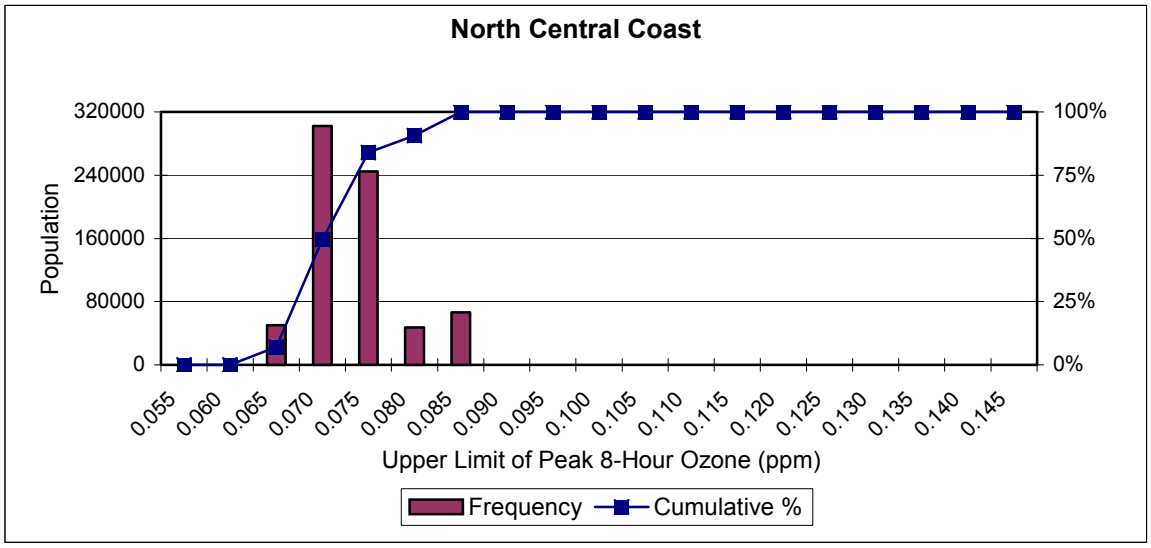


Figure 7-64

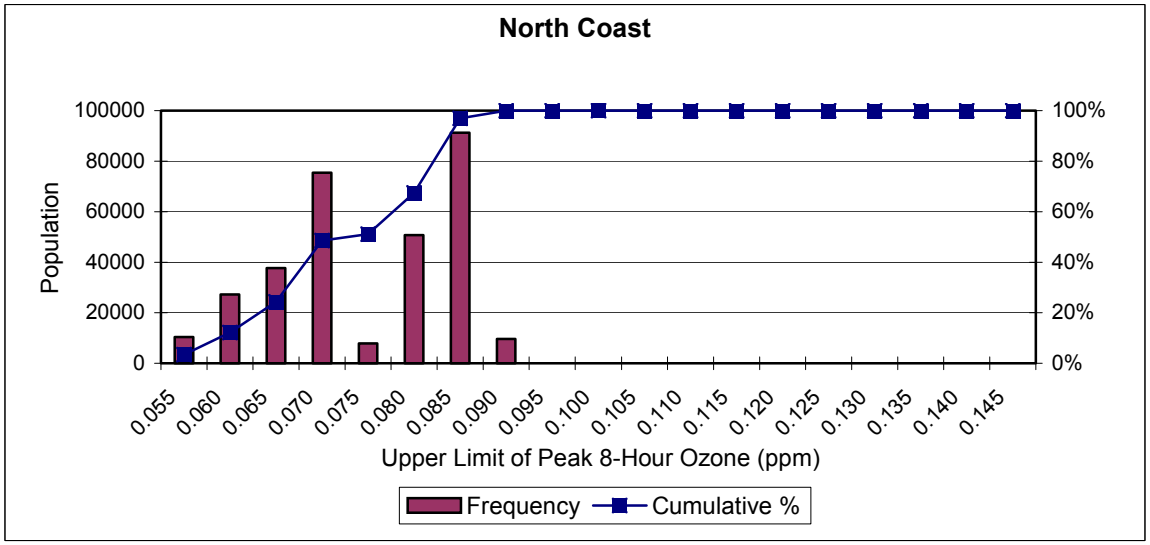


Figure 7-65

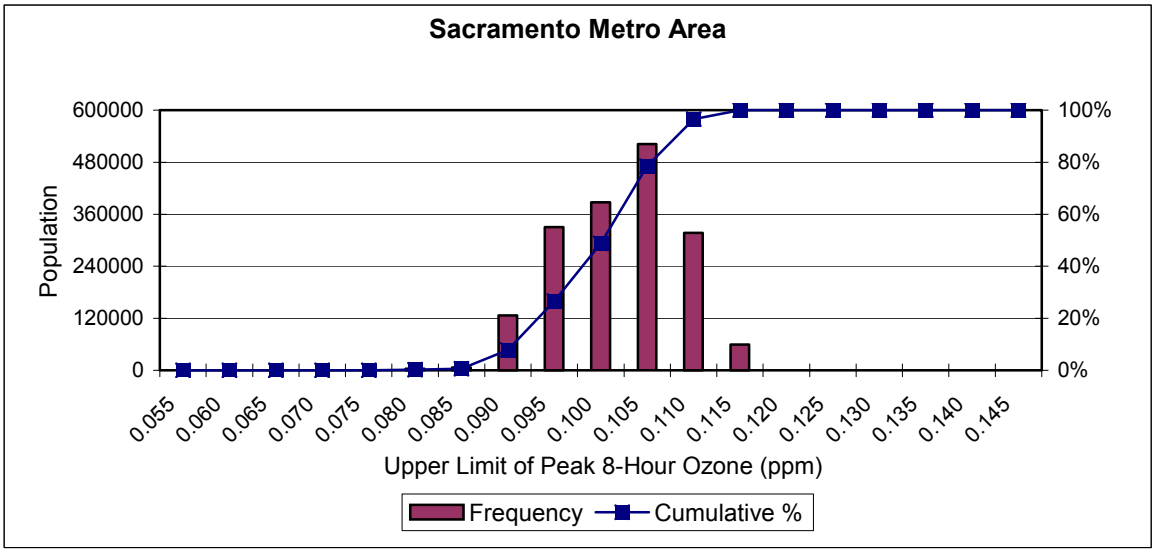


Figure 7-66

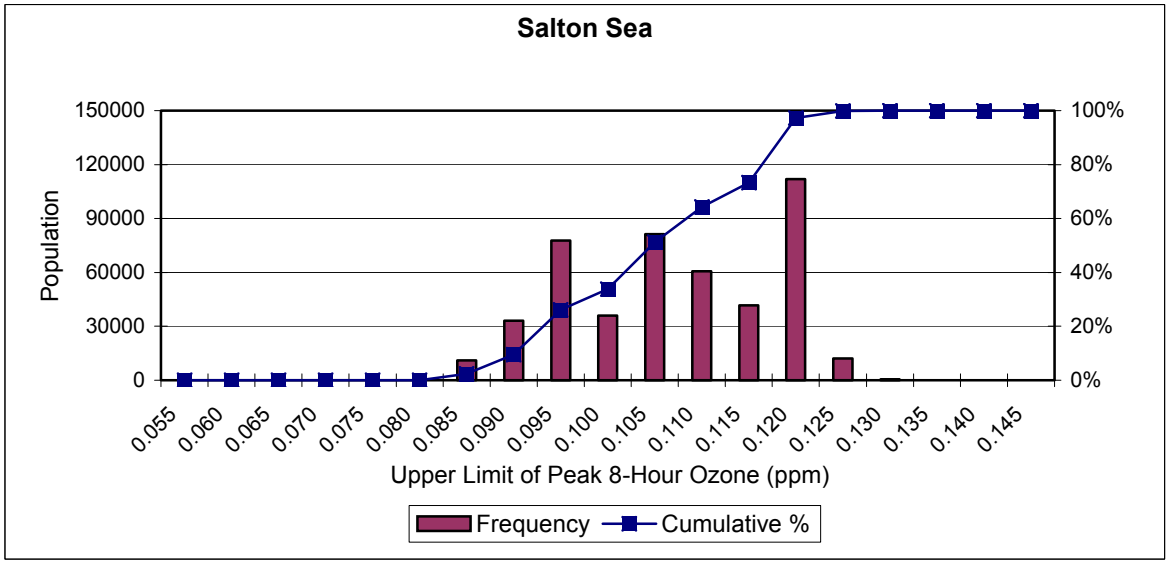


Figure 7-67

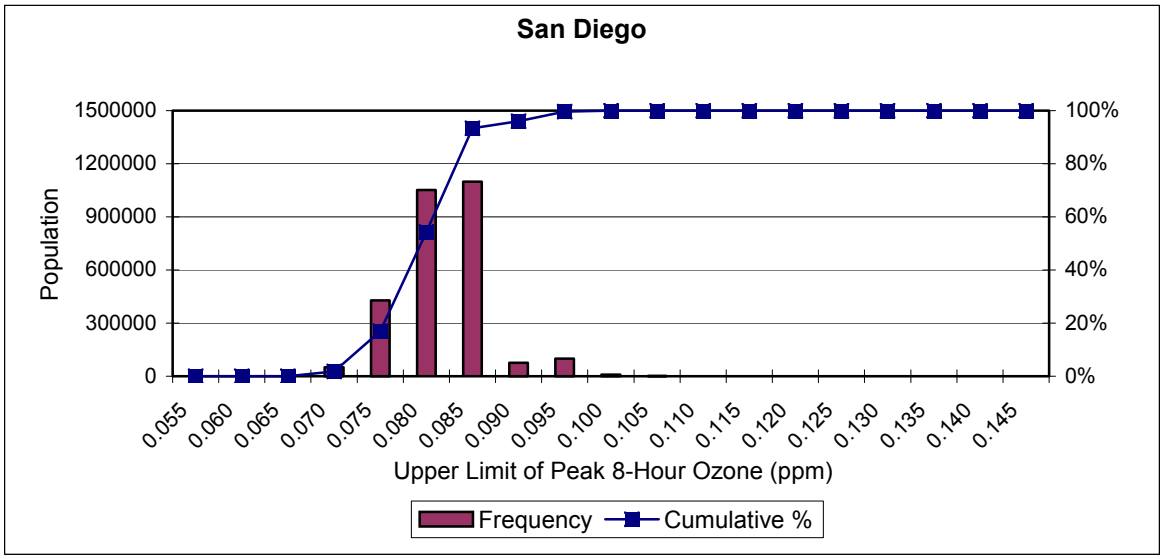


Figure 7-68

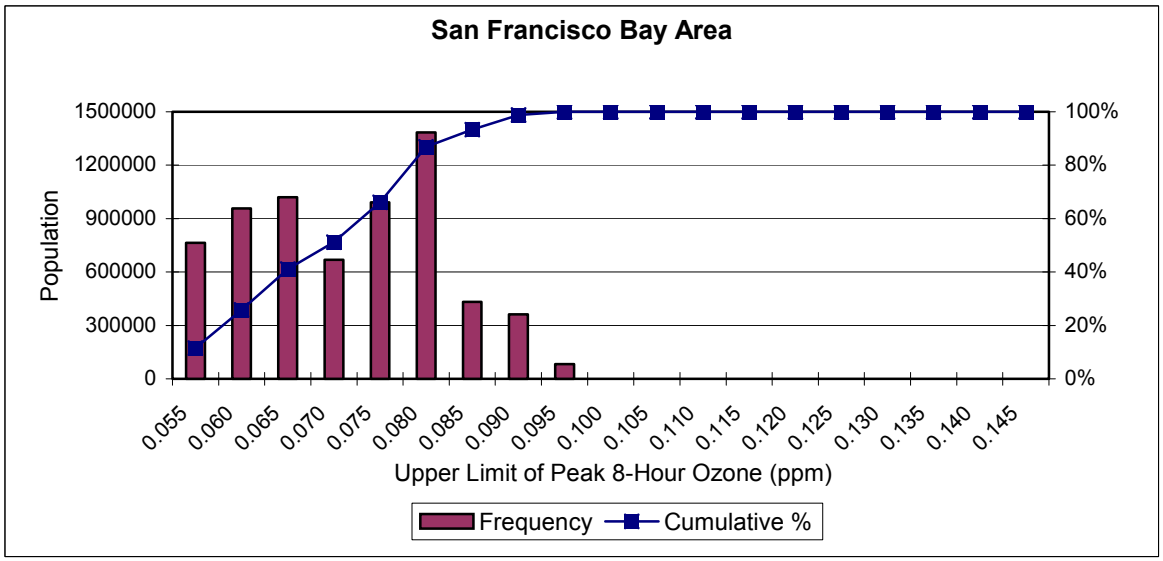


Figure 7-69

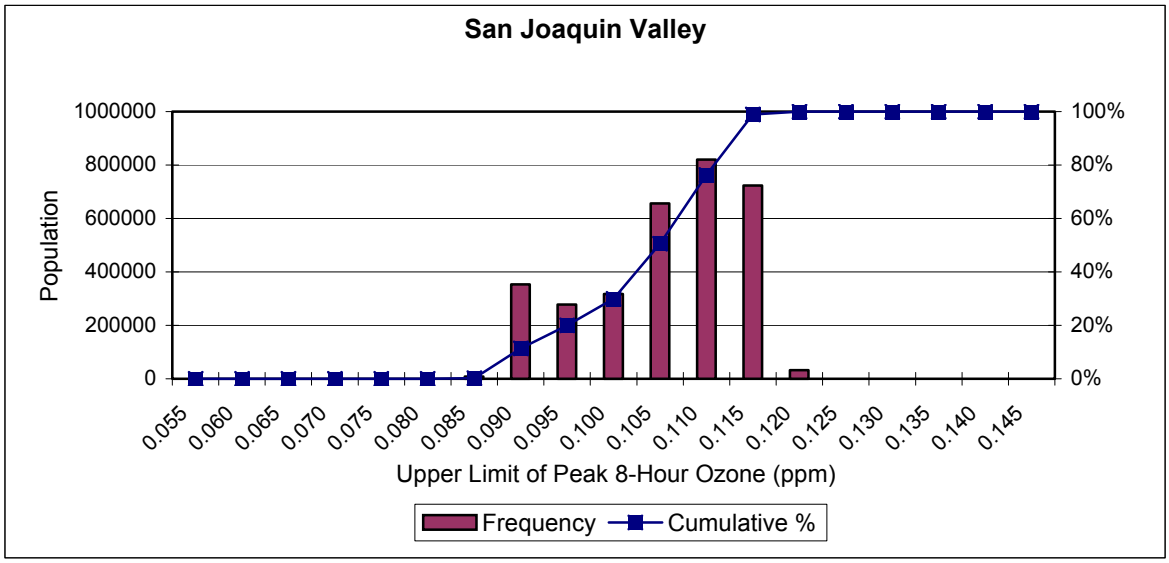


Figure 7-70

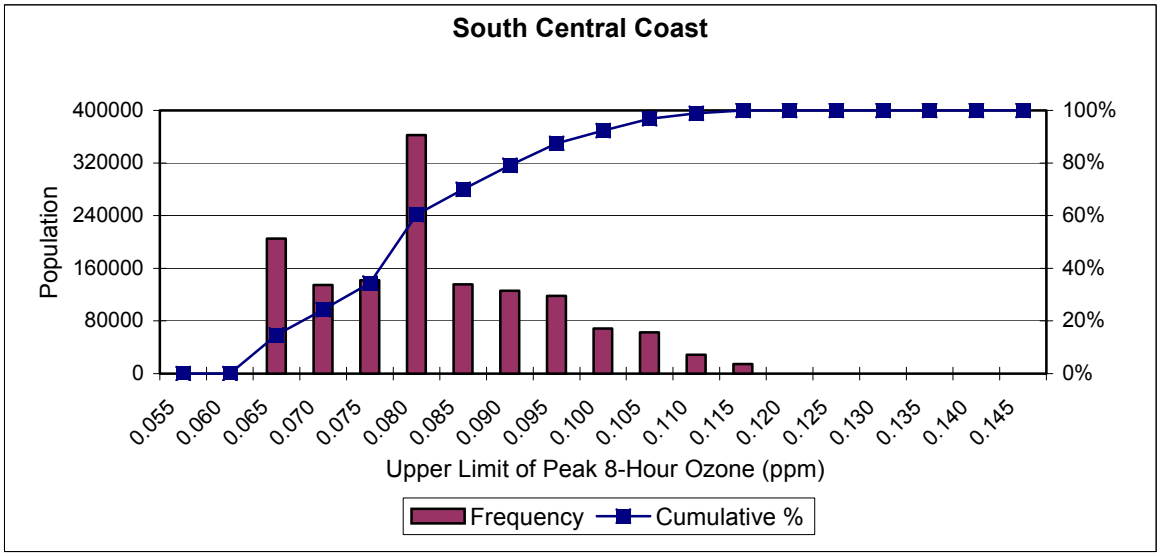


Figure 7-71

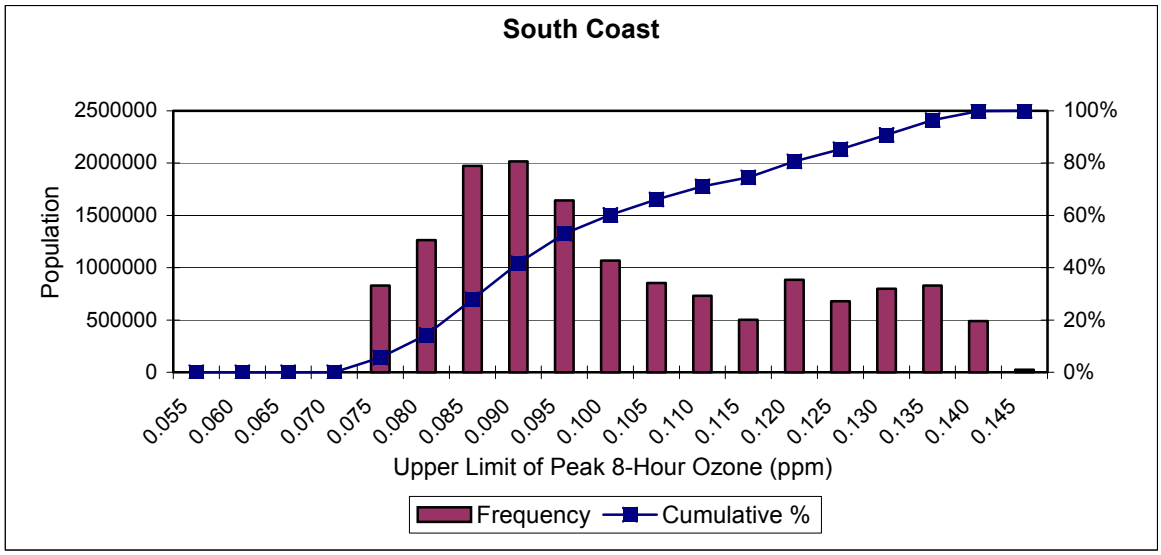


Figure 7-72

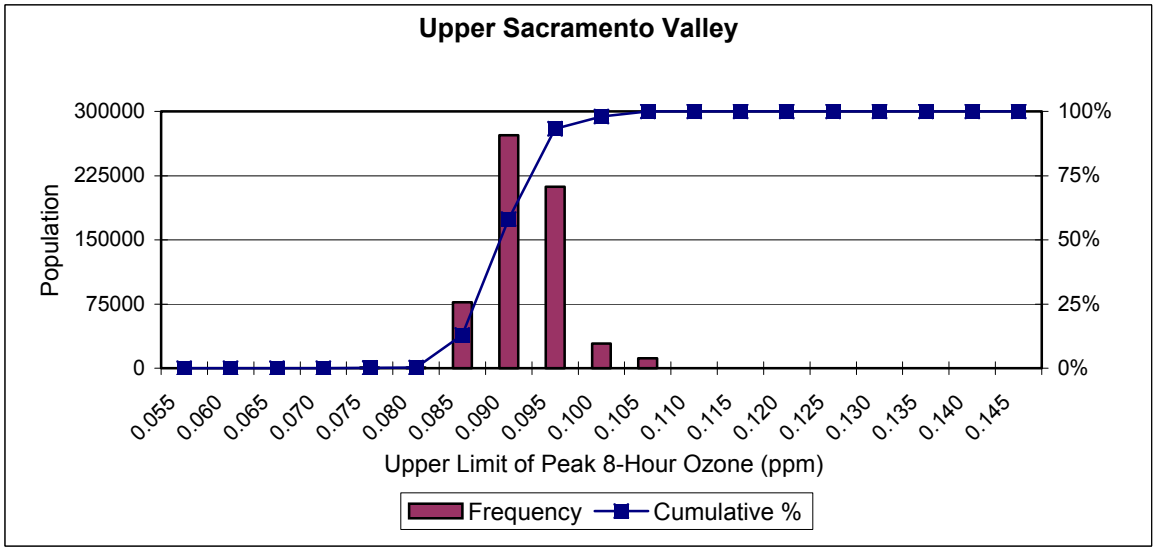
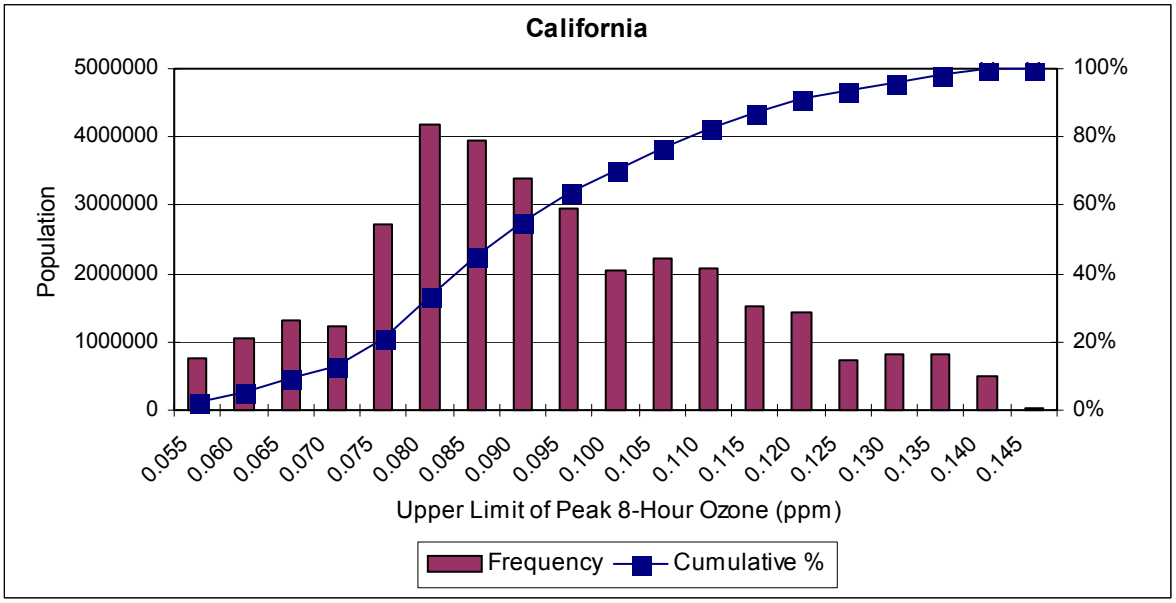


Figure 7-73



7.4 Indoor and Personal Exposures to Ozone

Californians' indoor and personal exposures to ozone are largely determined by the outdoor ozone concentrations in their community. Nonetheless, some Californians experience a substantial exposure to ozone indoors, due to the increasing use of certain types of appliances and equipment that emit ozone. Others, such as many children and those who are employed in outdoor occupations, may experience substantially greater exposures to ozone than the rest of the population, because they spend time outdoors during peak ozone periods.

This section discusses indoor ozone concentrations and sources of ozone, and briefly describes some of the chemical reactions know to occur in indoor environments when ozone is present. Information is also presented on Californians' personal exposures to ozone.

7.5 Indoor Ozone Concentrations

Indoor ozone concentrations are influenced by the outdoor ozone concentration, the rate of exchange between outdoor and indoor air (air exchange rate), the emission rates of indoor sources of ozone, removal by indoor surfaces, and reactions between ozone and other chemicals in the air (Weschler 2000). Temperature and relative humidity also affect indoor ozone concentrations, but to a lesser extent. As a result of these multiple interacting factors, indoor ozone levels tend to be highly variable across time, climate, location, and season, and may vary from building to building due to differences in building characteristics and emissions from indoor sources when they are present.

7.5.1 California Studies

Robust indoor data for California are limited. Measured average indoor levels have ranged from less than 10 ppb to greater than 25 ppb in studies where concurrent average outdoor levels ranged from 37 ppb to over 60 ppb (Avol et al. 1998; Geyh et al. 2000; Lee et al. 2002).

7.5.1.1 Homes

Several studies have examined indoor ozone concentrations in homes in California. Avol et al. (1998) studied indoor and outdoor ozone concentrations for 126 southern Californian homes. Indoor ozone levels (13 ± 12 ppb) were lower than outdoor levels (37 ± 19 ppb). Investigators with the Harvard Southern California Chronic Ozone Exposure Study measured indoor and outdoor ozone concentrations and personal ozone exposures over a 1-year period for 169 elementary school children and their homes in Upland and several towns in the San Bernardino mountains (Geyh et al. 2000). During the ozone season, average indoor concentrations were higher overall than during the non-ozone season, and were 3-17 ppb higher in the mountain homes than in the Upland homes due to natural ventilation and higher ambient concentrations in the mountain communities. The mean indoor and outdoor ozone levels in the Upland communities for the ozone season were 11.8 ± 9.2 ppb and 48.2 ± 12.2 ppb, respectively, vs. 21.4 ± 14.8 ppb and 60.1 ± 17.1 ppb for the mountain communities. Indoor and outdoor means in the non-ozone season were 3.2 ± 3.9 ppb and 21.1 ± 10.7 ppb for Upland, and 2.8 ± 4.2 ppb and 35.7 ± 9.3 ppb for the mountain communities. In 119 homes recruited from the Harvard Southern California Chronic Ozone Exposure Study, Lee et al. (2002) also found that average indoor ozone levels were higher in the mountain sites (16.3 ± 17.0 ppb) than the Upland sites (13.4 ± 8.5 ppb). Additionally, average outdoor concentrations (56.5 ± 22.3 ppb) were higher than indoor levels (14.9 ± 13.3 ppb).

7.5.1.2 Offices

One study in California has examined indoor ozone concentrations in an office setting. Indoor and outdoor concentrations of ozone, NO, and NO_2 were measured in real time for 14 months at a telecommunications office in Burbank, CA (Weschler et al. 1994). During the course of the study, the damper setting for the office ventilation system changed with fluctuations in outdoor and indoor air temperatures, resulting in a varying air exchange rate of 0.3 – 1.9 air changes per hour (ach). Consistent with previous work in California homes, indoor levels were higher during the ozone season (March through October) than during the non-ozone season (November through December), and were lower than outdoor levels. Findings from the Burbank site are presented in Table 7-15.

Table 7-15 95th Percentile and Median Ranges (ppb) for Indoor and Outdoor ozone at an Office in Burbank, CA.

Months	95% Indoor	Median Indoor	95% Outdoor	Median Outdoor
Mar – Oct	**24.6 – 55.7**	**0.4 – 8**	**53.3 – 106.2**	**3.4 – 21.1**
Nov – Feb	**7.3 – 18.9**	**0.2 – 1.2**	**21.6 – 32.8**	**1 – 4.5**

7.5.2 Other Studies

Studies in other areas of the country are illustrative of indoor concentrations that might also occur in parts of California. Liu et al. (1993) measured indoor, outdoor, and personal ozone concentrations for 23 children and their homes in State College, PA. As expected, the homes experienced significantly higher mean indoor concentrations during the day (19.2 ppb) than at night (10.5 ppb). The mean estimated outdoor daytime concentration (45.9 ppb) was much higher than the corresponding indoor level. As part of the Canadian Research on Exposure Assessment Modeling (CREAM) study, Liu et al. (1995) measured personal, indoor and outdoor ozone concentrations for 50 Toronto homes and offices in the winter and summer of 1992. For both homes and offices, mean indoor ozone concentrations were lower in the winter (home indoor: 1.6 ppb; workplace: 0.7 ppb) than in the summer (home indoor: 7.1 ppb; workplace: 10.0 ppb). The same seasonal effect was observed for home outdoor levels (summer: 19.1 ppb; winter: 15.4 ppb). Outdoor levels for homes were also higher overall than indoor levels, with greater concentrations during the day than at night.

7.5.3 Factors that Influence Indoor Ozone Concentrations

7.5.3.1 Outdoor Air

Studies have shown that indoor ozone levels generally follow the diurnal and seasonal patterns of outdoor ozone, with higher levels in the daytime and summer months (see above). Most indoor ozone originates from the outdoors (Weschler et al. 1989). Like outdoor concentrations, indoor ozone levels can remain elevated for long periods of time, generally eight hours or more, and display peak variations throughout the day.

7.5.3.1.1 Indoor/Outdoor Ozone Ratios

Researchers sometimes have characterized the relationship of indoor ozone concentrations to ambient concentrations with an I/O (indoor-outdoor) ozone ratio. Typically, indoor ozone concentrations range from 20% to 80% of outdoor values (Weschler et al. 1989), but vary substantially due to a number of factors, such as season, building ventilation rate, and microenvironment.

7.5.3.1.2 Season

Avol et al. (1998) measured seasonal variations in the indoor-outdoor ozone relationships for southern Californian homes. The I/O ratios were 0.43 ± 0.29 during the summer and 0.32 ± 0.21 for the non-summer months. In the CREAM study, I/O ratios also varied by season (Liu et al. 1995). A higher air exchange rate in the summer (1.04 ± 1.28 ach, mean) corresponded with a higher summer I/O ratio (0.40 ± 0.29).

7.5.3.2 Ventilation

For buildings with negligible indoor sources of ozone, the indoor-outdoor ozone relationship is largely dependent on the building ventilation rate. In general, studies show that open windows and doors allow outdoor ozone to enter, while closed windows and doors greatly reduce infiltration. In their study of a telecommunications office in Burbank, CA, Weschler et al. (1994) explained: “For

species originating outdoors, the air exchange rate is a major factor determining indoor concentrations (appearing in both source and sink terms); it influences the lag time between changes in indoor concentrations; it determines the amount of time available (residence time) for indoor chemical reactions."

Buildings with higher ventilation rates will yield the strongest indoor-outdoor ozone relationships (Weschler et al. 1989). During July, 1992, a commercial building in Burbank, CA, with an average air exchange rate of 0.4 ach had an I/O ratio of 0.31 (Weschler et al. 1994). A year later, when the air exchange rate was higher (0.7 ach, average), the I/O ratio was also higher (0.42). In a study of southern California homes, the I/O ratio was 0.10 in homes operating an air conditioner and 0.68 ± 0.18 in homes not using AC with windows open (Lee et al. 1999). In New Jersey homes without indoor gas combustion studied under different ventilation conditions, naturally ventilated homes also had higher I/O ratios than air-conditioned homes – 0.59 ± 0.16 and 0.28 ± 0.12, respectively (Zhang et al. 1994a). Gold et al. (1996) compared the relationship of indoor ozone concentrations with ambient concentrations for a school in Mexico City under three different ventilation conditions. With classroom windows/doors open, indoor ozone concentrations were 75% of outdoor concentrations, and with windows/doors closed, only 15% to 18% of outdoor concentrations. The third condition, which evaluated the use of an air cleaner with windows/doors closed, did not provide a significant reduction in indoor ozone levels. The air cleaner was a small portable floor unit, equipped with a charcoal filter for removing reactive gases and particles. When indoor sources of ozone are present, the air exchange rate has a smaller influence on the indoor-outdoor ozone relationship. After controlling for the air exchange rate, a significant association between the use of an electrostatic air cleaner—a potential source of ozone—and an increase in the I/O ratio was identified in 50 Toronto homes and offices (Liu et al. 1995).

7.5.3.3 Microenvironment

Building type and configuration can also impact I/O ratios. Jakobi et al. (1997) took measurements for different microenvironments—a classroom, a gym, offices, homes, and a car. The I/O ozone ratios for each microenvironment were as follows: office (0.40-0.90); classroom (0.54-0.77); gym (0.49-0.92); home (0.47-1.00); car (0.40-0.60). Hayes (1991) found similar peak indoor-outdoor ratios by using an indoor air quality model (IAQM) and making certain assumptions for different microenvironments and ventilation conditions.

7.5.3.4 Indoor Sources

Ozone emissions from a variety of sources have been measured in several studies. Some measured emission rates are surprisingly high, and would result in unhealthful air concentrations in most indoor environments. Within the last 10 to 15 years, the number of indoor sources of directly-emitted ozone has increased. Ozone generating "air cleaners," ionizing air cleaners, electrostatic precipitators, and several types of office equipment, including photocopiers and laser printers, are known to produce ozone. Computer terminals, ink/bubble jet printers, and fax machines also produce ozone, but limited emissions data exist for this type of equipment. Other electronic equipment and activities such as welding can also produce ozone emissions.

7.5.3.4.1 Ozone Generators

Appliances that purposely emit ozone to purportedly clean the air, also called ozone generators, appear to pose the greatest risk to human health relative to other indoor sources of ozone. Many government agencies recommend against the use of ozone generators (ARB, 2005; DHS 1997; Health Canada 1999). Ozone generators deliberately introduce ozone into the indoor environment, as opposed to ionizers and electrostatic precipitators, which are electronic air-cleaning devices that generate ozone as a by-product of the technology they use to remove particles from the air. Two tabletop models of ozone generators tested by Consumers Union (1992) were deemed unacceptable for occupied spaces. They had no effect on particulates in indoor air, they produced ozone at levels exceeding the FDA standard of 50 ppb ozone for medical devices, and they did not control or measure ozone output. Another investigator estimated that individuals within the immediate vicinity of an ozone generator can be exposed to peak exposure levels exceeding the FDA standard of 50 ppb (Kissel 1993). In a more recent study by US EPA, Mason et al (2000) tested ozone generators in a test home and found that ozone emissions in the test home resulted in indoor air concentrations that exceeded health-based ambient air quality standards. Despite their low emission rates relative to some other indoor sources such as large copiers, portable ozone generators can contribute largely to indoor concentrations and personal exposures, because they are often operated for long periods, and they are located in close proximity to people in their homes. Additionally, tests have shown that users of some small “personal air purifiers” intended for use in a person’s immediate breathing zone (near the nose and mouth) would also be exposed to levels well above health-based guidelines (Phillips et al., 1999).

Experimental investigations of ozone generator use reveal that ozone does not successfully remove contaminants or odor from indoor air, except perhaps at levels not safely tolerated by humans (Boeniger 1995; Kissel 1993; Chen and Zhang, 2004). Ozone generators produce ozone at rates faster than ozone can decay; compounds that react with ozone at an effective rate are largely alkenes (Boeniger 1995), and comprise less than 10% of gas phase pollutants (Weschler 2000). The exact number of people exposed to ozone from the residential use of ozone-generating devices is not known, but is estimated to be large due to the increased advertising and sales of air cleaners. In a recent report by Freedonia (2004), a business research organization, sales of air cleaning devices were found to have increased by an average of 5.4% per year for the last five years, and were predicted to continue to increase at that rate for the next five years.

7.5.3.4.2 Office Equipment

Studies have shown that the ozone produced by photocopiers is dependent on copy rates, light intensity, and the maintenance status of the equipment (USEPA 1995; Wolkoff et al. 1992). As a result, photocopiers have highly variable ozone emission rates – averaging 40 µg/copy with peak concentrations of 131 µg/copy, but with emissions as low as 4 µg/copy for advanced, recently serviced photocopying machines (USEPA 1995). A test method developed by Leovic et al. (1996) measured emission rates for four copiers in full operation mode ranging

from 1,300 to 7,900 µg/h. However, one dry-process copier tested extensively by Brown (1999) showed lower ozone emissions, averaging an estimated 0.4 ± 0.1 µg/copy, or 440 µg/h.

Older studies indicate earlier models likely had higher emission rates (Allen et al. 1978). The ozone emissions from 69 photocopiers were in the range of 0-1,350 µg/min with a mean of 259 µg/min, and the ozone concentration in the breathing zone of 19 operators was between ≤0.001 to 0.15 ppm (1 to 150 ppb) at its maximum (Hansen et al. 1986). Ten photocopiers emitted ozone at rates of <1 to 54 µg/copy, resulting in concentrations of < 4 to 300 µg/m^3 (2 to 153 ppb) (Selway et al. 1980).

Laser printers can also be an important source of indoor ozone. Tuomi et al. (2000) tested 4 laser printers for ozone and VOC emissions. Three laser printers equipped with the corona discharge technology had emission rates of 0 to 3,700 µg/h ozone, with resulting air concentrations of 0 to 360 µg/m^3 (0 to 180 ppb). The laser printer without corona discharge rods, representing the newest technological advances, emitted negligible amounts of ozone.

Ozone concentrations resulting from use of laser printers, photocopiers, and other office equipment have been estimated to exceed health standards, especially under low ventilation conditions (Allen et al. 1978; Selway et al. 1980; USEPA 1995). The emission rates as well as the duration of ozone production, location of office equipment within the building, and environmental factors, such as temperature and lighting, influence the amount of indoor ozone found within occupants' breathing zones (USEPA 1995). In an early study, investigators concluded that the use of photocopiers under conditions of poor ventilation or naturally ventilated areas in the summer where outdoor values exceed 50 ppb can pose a health hazard indoors (Allen et al. 1978). Office equipment can be modified to significantly reduce ozone emissions. For photocopiers, using charging rollers in place of corona wires can decrease ozone levels during charge and transfer processes. Ozone filters, which catalytically convert ozone to oxygen, but do not remove ozone from the air, also reduce ozone emissions. Laser printers without a filter showed average ozone emissions of 440 µg/min as opposed to laser printers with a filter, which averaged 100 µg/min (USEPA 1995). The efficiency of ozone filters is relative to filter thickness, air velocity across the filter, beginning ozone concentration, and the cleanliness of the filter. Activated carbon filters tend to be the most effective.

7.5.3.5 Indoor Chemistry

7.5.3.5.1 <u>Heterogeneous Reactions</u>

Ozone that has been deposited onto indoor surfaces can react with chemicals that constitute, or are adsorbed onto, surface materials; these reactions are referred to as heterogeneous reactions (Weschler, 2000). Deposition onto surfaces may be the most important removal process for indoor ozone (Jakobi et al. 1997; Weschler et al. 1994). The removal rate is dependent on the surface-to-volume ratio, airflow, relative humidity, surface composition, and exposure history of the indoor environment (Lee et al., 1999; Reiss et al., 1994; Weschler 2000). In general, smaller rooms and rooms with fleecy surfaces have faster rates of

indoor ozone removal. Ozone decay also occurs at a faster rate when temperature and humidity levels are high, because the deposition velocities of ozone to different surfaces increase with higher temperature and relative humidity (Weschler 2000).

In addition to removing ozone from indoor air, ozone deposition can also influence the emissions of potentially harmful chemicals from building products (Kleno et al., 2001). Natural rubbers and neoprene, compounds associated with latex paint, linoleum and carpet, unsaturated components of waxes and polishes, and unsaturated semi-volatile organics adsorbed on indoor surfaces react with ozone to produce highly volatile chemicals harmful to human health and damaging to materials such as rubbers, dyes, film, and books (Weschler 2000). Reiss et al. (1995a) studied the heterogeneous reaction of ozone with latex paint in an environmental chamber. Significant amounts of formaldehyde and lesser concentrations of acetone and acetaldehyde were produced with the exposure of latex paint surfaces to ozone. In the presence of indoor ozone, the unsaturated fatty acids from paints using linseed oil as a drying agent reacted readily with ozone to produce aldehydes and organic acids (Weschler 2000). Olefins or other chemicals contained in surface materials such as plywood and plaster also react with ozone to produce formaldehyde (Moriske et al., 1998). Ozone was also shown to impact indoor levels of VOCs in a carpeted environmental chamber (Weschler et al., 1992). Nonvolatile substances in the carpet fibers reacted with ozone to produce the higher molecular weight aldehydes. Carpet can act as a reservoir for the aldehydes, adsorbing them once they have formed and releasing them long after the ozone exposure ends (Weschler, 2000).

7.5.3.5.2 <u>Homogeneous (Gas-phase) Reactions.</u>

In contrast to heterogeneous reactions, homogeneous reactions occur in the gas phase when ozone reacts with other airborne chemicals (Weschler, 2000). Ozone reaction rates for inorganic gases commonly found in indoor air (i.e., formaldehyde, acetaldehyde, ammonia, sulfur dioxide and carbon monoxide) are too slow to effectively compete with air exchange rates for removal of indoor ozone. However, some volatile organic chemicals (VOCs) with unsaturated carbon-carbon bonds react with ozone equal to or faster than the rate of air exchange. Most notably, these chemicals include the terpenes: d-limonene, α-pinene, isoprene, and styrene. Terpenes are used in a variety of cleaning products and other consumer products to impart a scent to the product, or to contribute desirable solvent properties. The reaction of terpenes with ozone leads to the production of irritant chemicals such as formaldehyde and ultrafine particles (Wilkins et al., 2001; Weschler and Shields, 1999; Atkinson and Arey, 2003). Studies examining the effects of ozone on VOCs emitted by carpet and in environmental tobacco smoke (ETS) showed similar results (Shaughnessy et al. 2001; Weschler et al. 1992).

Reiss et al. (1995b) used a model to examine the homogeneous removal of ozone in several studies. They found that the homogeneous reaction of ozone with d-limonene, α-pinene, and styrene in residential environments accounted for 85%, 14%, and 1% of the ozone removal, respectively. Additionally, Reiss et al.

(1995b) noted that homogeneous chemistry comprised 20% of the total ozone removal in another study of homes.

Ozone-terpene reactions can also be a significant source of sub-micron particles. Weschler and Shields (1999) examined particle formation and indoor ozone concentrations in an office setting. In the first experiment, ozone from an ozone generator and a selected terpene were deliberately introduced into one office, while a second office served as a control. Particles ranging from 0.10-0.20 µm in aerodynamic diameter were 20 times more prevalent in the first office than in the control environment. In the second experiment, d-limonene was intentionally added to an office where outdoor air was the main source of ozone. Particles closely tracked indoor ozone concentrations, and formed at a rate 10 times greater in the presence of d-limonene. Wainman et al. (2000) also demonstrated that limonene can influence indoor particle concentrations. In a series of experiments conducted in a dynamic chamber system, ozone was reacted with limonene at 30%, 50% and 70% relative humidity. Particle formation with aerodynamic diameters from 0.1 to 0.3 µm was measured for all experiments, and was shown to increase with larger surface areas and smaller air exchange rates.

Another important reaction in indoor air chemistry is the ozone-nitric oxide reaction. The reaction does not require photochemical initiation, and occurs when both precursors are present in indoor air (Zhang et al. 1994b). When gas appliances are operating, ozone will react with the NO produced, leading to a decrease in ozone concentration (Weschler 2000). In an office setting in Burbank, California, the reaction rate for the ozone-nitric acid reaction varied with time, and was most apparent in the late morning and early evening (Weschler et al. 1994). In a southern Californian home, the operation of a gas stove decreased the ratio of indoor-outdoor ozone from 0.82 to 0.15 within 7 minutes (Lee et al. 1999). However, gas combustion is not a recommended means for removing ozone from indoor air, and is not as effective as removal by surfaces (Zhang et al. 1994a).

The product of the ozone-nitric oxide reaction – nitrogen dioxide – also reacts with ozone, forming the nitrate radical. The nitrate radical is highly reactive, and converts quickly to nitric acid, a strong oxidizing agent that can contribute to numerous respiratory ailments. The nitrate radical may also initialize another pathway leading to the formation of formic acid from formaldehyde (Zhang et al. 1994b). Formic acid can also be formed indoors through the reaction of ozone with unsaturated VOCs (Zhang et al. 1994a).

7.5.4 Personal Exposures to Ozone

People's personal exposures to ozone vary directly by their personal locations and activities throughout the day, especially the time they spend outdoors. As shown in Table 7-16, California adults spend about 87 percent of their time indoors, on average, and about 6 percent of their time outdoors, and 7 percent of their time inside vehicles (Jenkins et al, 1992). California children, on the other hand, spend an average of 10% of their time outdoors. However, older children spend more time outdoors: children 6-11 years of age spend 13 percent of their

time outdoors, on average, and some children spend even more time outdoors (Phillips et al., 1991).

Table 7-16 Average Percent of Time Californians Spend in Major Locations

AGE	AVERAGE PERCENT OF TIME[1,2]			
	Inside the Home	Other Indoors	Outdoors	Inside a Vehicle
7.5.4.1.1 Children 0 - 2	85	4	7	4
3 - 5	76	9	10	5
6 - 11	71	12	13	4
All Children (0 - 11)	76	10	10	4
Adults and Teens	62	25	6	7

[1]From: *Study of Children's Activity Patterns* (Wiley et al., 1991a, ARB Contract no. A733-149; Phillips et al., 1991).

[2]From: *Activity Patterns of California Residents* (Wiley et al., 1991b, ARB Contract no. A6-177-33; Jenkins et al., 1992a).

Most importantly, children are often outdoors during the time of day when ozone levels tend to be highest. In the California Children's Activity Pattern Study (Phillips et al., 1991), 82.8 percent of the children ages 0 -11 spent time outdoors during their diary day, and those children spent, on average, 70 percent of their time outdoors during the hours of 12 noon to 8 p.m. Ozone concentrations peak anytime from noon to late evening – the time when children are most likely to be outdoors. Research indicates that the pulmonary function of children is affected by their peak ozone exposure each day and total ozone exposure (Lioy et al. 1989).

7.5.4.2 California Personal Exposure Studies

Information on personal ozone exposures comes from the use of passive samplers, such as the Harvard ozone monitor, and from predictive results obtained from microenvironmental models. Models have been developed to explain up to 72% of the variability in personal ozone exposures (Liu et al. 1995). Liu et al. (1995) concluded that: "With a sufficient number of ambient monitoring sites and time-activity information, the weighted mean ambient measurements may be suitable for predicting personal exposures."

In the Harvard Southern California Chronic Ozone Exposure Study, Geyh et al. (2000) found that personal exposures were more closely associated with indoor levels than outdoor levels (Table 7-17), and were significantly influenced by

Table 7-17 Personnal Ozone Exposure Studies

Reference	Location and population	No. of subjects	Study period	Age	Averaging time	Concentration: arithmetic mean; all in ppb			r[b]
						Personal[a]	Indoor[a]	Outdoor[a]	
California Studies									
Geyh et al. 2000	Upland, CA	84 children 61 homes	06-09/95, 05/96	6-12	6 days (144 h)	18.8 ± 10.1	11.8 ± 9.2	48.2 ± 12.2	NA[c]
			10/95-04/96			6.2 ± 5.4	3.2 ± 3.9	21.1 ± 10.7	NA
	Mountain towns	85 children 54 homes	06-09/95, 05/96	6-12	6 days (144 h)	25.4 ± 13.4	21.4 ± 14.8	60.1 ± 17.1	NA
			10/95-04/96			5.7 ± 5.1	2.8 ± 4.2	35.7 ± 9.3	NA
Liu et al. 1997	San Diego, CA	22	05-07/94	10-47	12-h day	13.6	NA	63.1 (APCD)	NA
		18	09-10/94	9-38		10.5	NA	54.5 (APCD); 45.1 (p[e]); 44.0	NA

								(a[f])	
Delfino et al. 1996	San Diego, CA	12	09-10/93	9-16	12-h day	11.5 ± 11.2	NA	43 ± 17 (APCD[d])	0.5
Other Studies									
Liu et al. 1995	Toronto, Canada; CREAM	34 people, 50 homes and offices	01-03/92	NA	weekly	1.3 ± 2.9	1.6 ± 4.1 (home); 0.7 ± 0.7 (work)	15.4 ± 6.0 (home); 11.4 ± 3.0 (p[g]); 9.3 ± 4.2 (c[h])	NA
		89 people, 50 homes and offices	06-08/92	NA	12-h day	8.2 ± 8.7	7.1 ± 12.6 (home); 10.0 ± 11.6 (work)	19.1 ± 10.8 (home); 18.5 ± 9.6 (p); 18.4 ± 12.6 (c)	0.2
					12-h night	NA	6.2 ± 9.5 (home)	9.4 ± 10.2	NA
					24-h	NA	NA	15.6 ± 8.5 (p); 15.5 ± 9.2 (c)	NA
					weekly	NA	NA	13.2 ± 4.0 (p); 13.0 ± 2.7 (c)	NA

Liu et al. 1993	State College, PA	23 children and their homes	07-08/91	10-11	12-h day	23.9 ± 16.2	19.2 ± 11.3	45.9 ± 21.3 (home); 56.4 ± 16.2 (p[g]); 55.3 ± 14.7 (c[h])	0.4
					12-h night	NA	10.5 ± 7.2	19.1 ± 8.9 (p); 20.1 ± 10.1 (c)	NA
					24-hr	NA	NA	29.8 ± 14.3 (home); 37.8 ± 10.7 (c)	NA
a-All personal, indoor, and outdoor samples were taken with the Harvard passive sampler unless otherwise noted.									
b-Correlation of personal ozone exposures to the stationary ambient monitoring (SAM) site									
c-Information not available									
d-continuous measurement made at the San Diego County Air Pollution Control District (APCD) monitoring site(s)									
e-passive (collocated with 4 active monitors)									
f-active (used at 12 outdoor locations)									
g-passive (collocated with continuous monitor at SAM site)									
h-continuous measurement taken with a UV photometric ozone analyzer and/or chemiluminescence monitor at SAM site									

community and gender. Study participants in the mountain communities were exposed to 35% more ozone on average than the Upland community. In particular, boys, who averaged more time outside than girls, had higher personal exposures than girls did – a difference that was more pronounced during the summer months. In the spring and fall of 1994, Liu et al. (1997) conducted personal and outdoor ozone monitoring for cohorts of 22 and 18 subjects over an 8-week period in San Diego, California, using the Harvard passive and active samplers. As shown in Table 7-17, Liu et al. (1997) found that outdoor concentrations were four to five times higher than personal exposure levels for both seasons.

Delfino et al. (1996) measured outdoor and personal ozone concentrations during peak exposure hours for 12 asthmatic subjects from 9 to 16 years of age in San Diego, California. Results showed little correlation between personal and outdoor ozone; personal ozone was 27% of outdoor ozone (see Table 7-17).

7.5.4.2.1 Indoor Activity

While the source of indoor ozone is mostly outdoor air, indoor ozone exposures (concentration x time) tend to be larger than outdoor exposures, because most people spend nearly 90% of their time indoors (Weschler et al. 1989). In the study of 23 children and their homes in State College, PA, Liu et al. (1993) identified indoor ozone concentrations (19.2 ppb, mean) as the most important predictors of personal exposures (23.9 ppb, mean). Zhang et al. (1994a) estimated that exposure in indoor residential environments in New Jersey accounted for 67% of the estimated potential dose of ozone (Table 7-18). The potential dose is equal to the concentration multiplied by the contact rate and time.

Table 7-18 Potential Dose from New Jersey Homes.

Exposure Factor	Outdoor Mean	Indoor Mean
Concentration (mg/m^3)	0.19 (95 ppb)	0.035 (18 ppb)
Contact Rate (m^3/hr)	1.4	0.83
Time (hr/day)	0.88	15.37
Potential Dose (mg/day)	0.22	0.45

7.5.4.2.2 Outdoor Activity

In addition to indoor concentrations, research indicates that the amount of time spent outdoors is also an important variable in predicting ozone exposure. Brauer et al. (1995) conducted personal exposure monitoring for three groups of healthy adults with specified activity patterns – 25 office workers, 25 camp counselors, and 15 farmworkers. Because camp counselors and farmworkers spent more time outdoors than office workers did, their personal exposure levels were closer to the ambient concentration. The mean differences between ambient and

personal concentrations were 12 ppb, 8.5 ppb, and 2.5 ppb for office workers, camp counselors, and farm workers, respectively. During episodes of high ozone in Philadelphia and Los Angeles, children and retired adults were estimated to experience higher personal-to-outdoor ratios under the assumption that they spent more time outdoors than other population groups (Hayes et al. 1989). Individuals accustomed to spending more time outdoors on the weekends will likely experience higher personal exposures to ozone (Liu et al. 1997). In their study of San Diego residents, Liu et al. (1997) found that the mean personal exposure was 22.6 ppb on Saturday, and 17.3 ppb on weekdays.

7.5.4.3 Role of Outdoor Ozone

Although it may be a useful indicator of peak exposure, the outdoor ozone concentration by itself is not a reliable indicator of personal ozone exposures. Outdoor measurements tend to overestimate personal measurements. Delfino et al. (1996) found that personal levels for 12 children were less than one-third the outdoor levels measured at the Air Pollution Control District (APCD) monitoring sites in San Diego, CA (Table 7-17). In the study of 50 Toronto homes and offices, Liu et al. (1995) also measured personal levels that were significantly lower than outdoor levels. There was also very little correlation between personal ozone exposures and measurements taken from the stationary ambient monitoring (SAM) site in a study of Pennsylvanian children and their homes (Liu et al. 1993). Table 7-17 shows the Pearson correlation coefficients (r), which range from 0.22 to 0.45, for personal-ambient levels for three recent personal ozone exposure studies.

7.5.5 Summary

Indoor ozone concentrations are highly variable, and typically range from about 20% to 80% of outdoor values. The relationship of indoor air to outdoor air is largely dependent on the building air exchange rate, except when indoor sources are present. Indoor sources of ozone include air cleaners, such as ozone generators and ionizers, and office equipment, such as copiers and laser printers. The ozone emitted from these sources can react with indoor surfaces and compounds in indoor air, and produce harmful chemicals, such as aldehydes, organic acids, and fine aerosols.

Time-activity patterns are key determinants of personal ozone exposures. Those who spend substantial time outdoors, such as children who play outdoors and workers in outdoor occupations, experience substantially greater exposures than most of the population. Although indoor ozone concentrations are typically much lower than outdoor levels, the greatest exposure to ozone for most individuals occurs indoors, because of the amount of time spent indoors. However, outdoor ozone exposures are generally more reflective of peak exposures, which may be more relevant in determining health impacts.

7.6 Conclusions

The State area designation process has several provisions for excluding high values that are not reasonable to control through the regulatory process. Under State law, there are three types of highly irregular or infrequent events: extreme concentration events, exceptional events, and unusual concentration events.

While a concentration identified as a highly irregular or infrequent event "exceeds" the level of the State standard, such an exceedance is not considered a "violation" of the standard. This is important because only a "violation" can trigger a nonattainment designation. Although the State ozone standard is expressed as a concentration that is "not to be exceeded," the designation criteria allow some leeway for excluding exceedances that are not reasonable to control.

Both the California 1-hour ozone standard of 0.09 ppm, and the proposed California 8-hour standard of 0.070 ppm are more stringent than the federal 1-hour standard of 0.12 ppm, and the federal 8-hour standard of 0.08 ppm. In addition, attainment designation criteria for California standards add stringency in that they are based on one exceedance per year, on average, compared to federal area designation processes, which are based on the fourth highest ozone concentration over three years, which allows four exceedences per year.

Indoor ozone concentrations are highly variable, and typically range from about 20% to 80% of outdoor values. The relationship of indoor air to outdoor air is largely dependent on the building air exchange rate, except when indoor sources are present. Indoor sources of ozone include air cleaners, such as ozone generators and ionizers, and office equipment, such as copiers and laser printers. The ozone emitted from these sources can react with indoor surfaces and compounds in indoor air, and produce harmful chemicals, such as aldehydes, organic acids, and fine aerosols.

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8 Welfare Effects

8.1 Agricultural Effects – Introduction

The Health & Safety Code (§39014) defines an "ambient air quality standard" as:

> … specified concentrations and durations of air pollutants which reflect the relationship between the intensity and composition of air pollution to undesirable effects established by the state board or, where applicable, by the federal government.

In establishing state ambient air quality standards, the Air Resources Board is called upon to divide the state into air basins (i.e., regions of similar meteorological and geographical conditions), and to adopt standards in consideration of public health and welfare (Health & Safety Code §39606). While the primary purpose of establishing an ambient air quality standard for ozone is public health protection , studies have also shown that impacts to vegetation often occur at exposures below those that would result from the concentrations and durations specified by the existing health-based ambient air quality standards (e.g., Peterson et al., 1987). Despite the volume of published reports documenting ozone impacts to plants, a previous effort in California to establish a secondary standard to protect vegetation from the adverse effects of ozone was not successful (ARB, 1987).

In the following three subsections, the impacts of ozone on agricultural crops, forest trees, and materials are reviewed, respectively. In broad terms, impacts to crops are generally more severe than for forest trees owing to their inherently more vigorous rates of physiological activity and growth. In the subsection on crops, methods used to expose plants to ozone are first examined to clarify various issues and concerns that have arisen with respect to the validity of data collected using experimental systems that allow for controlling aerometric conditions and ozone concentrations to plants. This is followed by a critical examination of the physiological basis of ozone damage to plants, with special emphasis on carbon metabolism and the resulting impacts on crop growth and yield. The subsection on effects to forests focuses on data collected since the 1950s on mixed conifer forests in the San Bernardino Mountains and the Sierra Nevada. These data, collected over a multi-decade time frame, indicate that increasing numbers of ponderosa and Jeffrey pines exhibit ozone-specific needle damage due to the pollutant's cumulative effects. The third subsection discusses the impacts of ozone on materials, including building materials, rubber, paint, and fabrics. It should be noted that the material presented in this chapter is intended to give a brief overview of ozone-related effects other than those related to human health. Since the ambient air quality standard for ozone is based on

human health endpoints, we have not estimated potential welfare benefits that may be associated with attainment of the proposed standards.

8.2 Ozone Impacts on Crop Production In California

8.2.1 Introduction and Summary

The previous Technical Support Document dealing with the effects of tropospheric ozone on crop productivity in California, entitled “Effects of Ozone on Vegetation and Possible Alternative Ambient Air Quality Standards, was issued by ARB in March, 1987 (ARB, 1987).

Considerable new research has been conducted and published in the peer reviewed literature in the intervening period (Heagle, 1989). This material includes two Air Quality Criteria Documents for Ozone and Related Photochemical Oxidants (USEPA 1986, 1996a) and an interim document (USEPA 1992), which are mandated by the federal Clean Air Act to be developed by the U.S. Environmental Protection Agency at prescribed intervals. A series of ARB-initiated research programs and resulting ARB reports have also been generated during this period that generalize ozone-induced crop yield losses across California. A review of ozone-induced crop loss focused mainly on the National Crop Loss Assessment Network (NCLAN) studies (Heagle, 1989). Another provided a multidisciplinary evaluation of the NCLAN program (Heck et al., 1988a). While advances have been made in mechanistic studies, the conclusions from the early efforts to quantify the economic damage caused by ambient ozone (ozone) remain largely valid.

The regional distribution of ozone makes it the most damaging air pollutant for agricultural productivity, both globally and in California (Heagle, 1989). Current impacts of ozone (ozone) on crop production, including alteration of basic physiological processes, functional aspects of native ecosystems, and suppression of crop yield and quality, are significant under current ambient conditions. Despite substantial investment in regulatory initiatives and mitigation technologies, ozone concentrations in rural crop production areas of California continue to exceed phytotoxic levels. These concentrations are increasing in many rural areas driven by growing population and associated emissions of ozone precursors from industrial and transportation sources (NARSTO, 2000; Taylor et al., 1994). For background information see Heck et al. (1982, 1988a), Davison and Barnes (1998), Heggestad et al. (1988), Miller (1988), Heggestad and Lee (1990), Temple et al. (1993), Skelly et al. (1983), Materna (1984), Miller and McBryde (1999), USEPA (1996a,b), Schulze et al. (1989).

The following review considers the mechanisms of ozone phytotoxicity, the physiological injury to plant function, and quantifiable damage to agronomic and horticultural yields. It is important to demonstrate plausible mechanisms of yield reduction, in order to attribute confidence to available yield loss data. These data are necessarily variable, as they arise from a hugely diverse range of [genotype x environment x ozone exposure conditions]. Only a few of the potential combinations can ever be investigated. Process modeling will extend this to somewhat more cases in which suitable mechanistic information is available.

Yield losses for most possible combinations of local relevance, particularly in California's diverse agricultural economy, will inevitably be predicted in only semi-quantitative terms from available exposure-response relationships combined with incomplete knowledge of response mechanisms. Demonstration and communication of plausible mechanisms, and of non-monetary injury to plant systems, is essential in the absence of precise estimates of yield loss in specific production situations.

The conclusions of this review do not differ appreciably from those of previous similar documents (e.g., ARB, 1987; USEPA 1986, 1996a). It is clear from available evidence that ozone at ambient concentrations damages crop yield under many situations. It is also clear that the extent of damage depends on a variety of environmental, exposure, and genetic parameters that are poorly understood for a few crops and completely unknown for many others. The uncertainty in exposure vs. yield loss relationships is larger than the uncertainty in ambient ozone concentration data. The post-NCLAN conclusions of Adams et al. (1988), i.e., that further research to improve the precision of yield loss functions does not proportionally reduce the uncertainty in economic loss forecasts, may be more accurate for large-scale aggregate analyses, such as for the eight major crops over the entire U.S. than for the highly diverse California agricultural production system. Lack of information on individual species and genotypes, some of high production value in California, remains a serious limitation in California ozone exposure-yield loss assessment.

Much of the available information has been determined using field exposure chambers, particularly in the U.S., the NCLAN-type open top chamber (OTC; Heagle et al., 1973). This technology, largely because of the enormous role it has played in producing the available data sets, has come under intense recent scrutiny (e.g., Manning and Krupa, 1992; Krupa and Kickert, 1997; Grunhage et al., 2001). It is therefore important to evaluate the reliability of exposure-response data obtained in OTCs, and its relevance to crop loss estimation under ambient conditions. As such considerations underpin currently available conclusions, this review first considers the range of available exposure technologies.

Given the wide range of known crop sensitivities to ozone, and the narrow range of crops that have been investigated, some uncertainty will remain in any regulatory threshold, due to the inherent compromises and averages over many crops and conditions. The precision of estimates of ozone impacts on yield are also subject to the limitation that ozone, itself, is rarely the dominant yield suppressing factor under ambient conditions. It is one of many such factors, albeit potentially a significant one. The multiple areas of focus in the following review are intended to address the common argument that scientific uncertainty in assigning specific yield loss valuations implies any uncertainty regarding the reality of crop damage due to current ambient concentrations of ozone. These impacts ultimately affect both producers and consumers of agricultural produce.

8.3 Methods Of Exposing Plants To Ozone

8.3.1 Exposure Technologies.

The previous document (ARB, 1987) reviewed the types of exposure technologies then available for crop loss assessment. Four classes of exposure technologies were considered, with some variation within the major categories: controlled systems, managed systems, seminatural systems, and natural systems. These technologies are also considered by USEPA (1996a), Hogsett et al., (1988), Grunhage and Jager (1994), and Manning and Krupa (1992). This list of available technologies remains adequate today, though considerable refinements in methodology have taken place. Characteristics of these systems, drawn from many of these sources, are presented in Table 1.

An important, if implicit, conclusion of the earlier document (ARB, 1987) was that results obtained from most of the available exposure technologies could be integrated with results obtained using other technologies. Results were considered to differ quantitatively, rather than qualitatively, and a unified body of conclusions could be drawn with respect to ozone impacts on crop yield.

In contrast, literature published since 1987 has questioned this conclusion. As most quantitative exposure-response functions have been developed using Open Top Chambers (OTCs), these techniques have come under particularly critical re-evaluation. An evaluation of the limitations and assessment of the reliability of relationships derived using OTC techniques is central to current understanding of ozone impacts on crops.

Many of the exposure technologies in Table 2 are no longer considered appropriate for crop yield assessment. The currently most acceptable technologies are open top field exposure chambers (OTCs) in the field and a variety of chamberless field designs. Chemical exclusion (principally EDU; Manning and Krupa, 1992) has been considered for crop loss assessment. On balance, however, this remains a technique for the future. The effects of such compounds on plant physiological processes, both in the presence and absence of ozone exposure, remain to be more fully elucidated. This conclusion regarding chemical exclusion confirms that of the previous document (ARB, 1987).

8.3.1.1 Free Air Exposure Systems

Recent literature has called for greater attention to non-chamber designs, partly in response to perceived limitations of OTC-derived response relationships. Such designs are attractive in many ways, but they are not new (Table 1). Zonal Air Pollution (ZAP) exposure and air exclusion systems allowed exposures to sub-ambient and elevated concentrations of ozone, both in their original (Jones et al., 1977; Olszyk et al., 1986b; Olszyk et al., 1986b) and more recent (Runeckles et al., 1990) designs. The recent innovations largely incorporate modernized computer control and more realistic ozone exposure dynamics.

A circular free air system for chamberless ozone exposure, similar to the now familiar Free Air Carbon Dioxide Enrichment (FACE) systems for CO_2 enrichment, has been deployed in several countries (McLeod et al., 1992; Shaw,

1986). Uniform average concentrations are imposed on the circular area at the center of each chamberless plot. A similar system is now operational in the U.S. incorporating exposures to both CO_2 and ozone (Karnosky et al., 1999).

Theoretical rationales and experimental difficulties associated with such studies have been reviewed by Oren et al. (1989) and were considered in the summary publications of NCLAN (McLeod and Baker, 1988; Ormrod et al. 1988). These chamberless designs do not allow strict replication over time, as wind speed direction and turbulence determine the actual exposure. With zonal systems multiple treatments may be imposed with increasing distance from the emitting manifold. With sufficient treatments within a locality, a statistical regression analysis may be used to relate damage to exposure.

8.3.1.2 Field gradient studies

Planned gradient studies utilize plants of uniform genotype planted across a naturally occurring gradient of ozone concentration. Optimally the ozone gradient can be isolated from gradients in other parameters. Such a protocol was considered promising in the previous document (ARB, 1987). More recent evaluations suggest that this technique may be nearly ideal in theory (e.g., Manning and Krupa, 1992), but limited in practice to the southern California experience (e.g., Oshima et al., 1976, 1977a,b; Grulke, 1999). There is a general lack of other demonstrated gradients of sufficient magnitude. A gradient study was conducted downwind of the London metropolitan area (Ashmore et al., 1988). In this case it proved impossible to isolate the effect of ozone among the multiple covarying pollutants and environmental factors. A study using uniform potting medium and two clones of white clover was performed across the U.S.A. (Heagle et al., 1995). Although climate differed considerably a relationship with ozone exposure was discernable.

In addition to co-occuring gradients in other anthropogenic air pollutants, ambient gradient studies are also frequently confounded by covariation in microclimate, soil type, and exposure dynamics (i.e., diurnal and seasonal timing of peak concentrations), along with the planned gradient in ozone concentration. Analysis in these cases must ultimately rely upon multifactor regression analyses (Oshima et al., 1976, 1977b). The utility of experiments conducted along ambient gradients will be facilitated by further development of process models that adequately reflect physiological interactions of microenvironmental and pollution variables. Despite these limitations, the utility and past successes of gradient studies, and their unique applicability to remote areas including those in developing countries, has led to their recent favorable review (Bell and Marshall, 2000).

Field survey methods represent a subset of ambient gradient studies, in which unplanned epidemiological or natural history studies are conducted (Oren et al., 1989) using available distributions of crops and ozone exposures. Correlations may become apparent between measures of damage such as crop loss and metrics of ambient ozone concentration. These studies suffer from the same limitations as planned field gradient experiments, in addition to problems of

unplanned spacing of observations along the gradient, and possibly inadequate levels of (pseudo)replication at similar points along the gradient.

The shortcomings of chamberless experiments of all types differ from those of OTC experiments. In some cases they may be equally severe.

8.3.1.3 Open Top Chambers

Development of the OTC allowed exposure to a range of ozone concentrations at, above, and below ambient levels. OTCs exclude intrusion of ambient pollutants by maintaining positive pressure of filtered air. The pollutant of interest may be added to clean air in varying concentrations.

The cylindrical NCLAN chamber was three meters in diameter by 2.4 meters tall. In some cases a conical frustrum was installed to minimize wind intrusion and in some cases a rain cover was installed. The design and micro-environmental impact of the NCLAN OTC (Heagle et al., 1973) was evaluated at the time of publication of the original NCLAN results (Heck, 1989; Heagle et al., 1988), and in detail in USEPA (1986). An overview of the microenvironmental impacts of the OTC is provided in Table 2.

Use of small, partially enclosed chambers, such as OTCs, required some experimental compromises. Some of the potential limitations of exposure-crop loss relationships obtained using OTC techniques are considered below. These OTC technologies were considered a major technological advance at the time of their adoption, over the conventional closed top chambers then in use for air pollution exposure studies (Bell and Marshall, 2000).

8.3.2 Altered Environmental Interactions

The NCLAN study (1980-1988) established protocols and exposure technologies to ensure compatible response data were obtained at a variety of locations with different crops. At the time of final summarization of the NCLAN results, the limitations of the study were recognized and the needs for further study using the same techniques with more comprehensive measurements or different techniques as they became available was acknowledged (Holt, 1988). Concerns were raised in the NCLAN summary (Heck et al., 1988a) regarding the unknown implications of the demonstrably altered plant microclimate.

These microclimate impacts of OTCs have been detailed and evaluated by Heagle et al. (1973, 1979b, 1988a), McLeod and Baker (1988), Unsworth et al. (1984a,b), USEPA (1986, 1996), and Hogsett et al. (1988). They were also considered in the previous document (ARB, 1987). In the intervening years, these altered microclimatic parameters caused by enclosure of plants in OTCs have been raised as serious objections to extrapolation of yield loss relationships developed in them to ambient field conditions (e.g., Manning and Krupa, 1992). These are reviewed below. It appears that plant growth may differ between OTCs and adjacent ambient plots outside, but that sensitivity of yield loss to ozone may be less affected.

A succinct statement of the goals of experimental ozone fumigation has been provided by Colls and Baker (1988): "…all parameters are fixed, one variable is

controlled at a particular value, and a response is observed…appropriate if the variable (which could be the pollutant concentration) is large enough in value for the effects due to it alone to be much greater than any other effects due, for example, to unnatural lighting or soil conditions."

These authors note that there is no *a priori* justification for assuming that changes (e.g., in yield) under unnatural conditions will be observed under ambient conditions. However, in discussing the potential advantages and pitfalls of open field fumigation systems, they further consider the role of OTCs in plant exposure experiments (Colls and Baker, 1988): "The principle of open top chambers is to control only the air supply… This is hard to put into practice [i.e., various micrometeorological parameters are altered]. All these factors affect the growth of plants to some degree; it has not yet been shown whether such unavoidable environmental modifications make a quantitative difference to pollutant sensitivity. "

8.3.2.1 Ozone Concentration

Ozone concentrations are typically monitored and recorded within each OTC. Thus actual exposures are known but may differ from the nominal (planned) exposure, and may differ from ambient values outside the OTCs. Differences between actual and nominal ozone concentrations are due to measurement noise, incursion of ambient ozone and to ozone degradation in the delivery system or against the surfaces inside the OTC. A study reviewed extensively by ARB (1987) found that between 65-81% of ambient ozone concentrations were excluded from the OTC over two years of measurement (Thompson, 1985).

The NCLAN style OTC injected air into the chamber at or below canopy height, in contrast to ambient field exposure in which ozone arrives from above. This effectively reverses the normal gradient between ozone concentration and height above and within the canopy. While the gradients in the NCLAN OTCs are statistically significant, they may be of limited biological significance since they are rather small and since light penetration and physiological activity of lower leaves is generally less than of those in the exposed upper canopy. These potential artifacts were reviewed by Heagle et al. (1989a).

Of greater significance than altered within-canopy gradients, is the gradient in the field between the reference height at which ozone is monitored and the canopy top. The OTC technology imposes a known ozone concentration at canopy level. Yield response relationships are thus parameterized with the concentration at the top of the canopy, whereas under ambient conditions the ozone concentration is not monitored at canopy height, but rather at the usually higher concentration at reference height (2 m, 10 m, or other). This inconsistency could overestimate crop loss under ambient conditions. Grungage et al., (2001) have considered the mathematical/micrometeorological transformation of reference height ozone concentrations to canopy height.

The standardization of OTC design (Heagle, 1973, 1979b; Mandl et al., 1973), and formal consideration of the gradients existing under ambient sampling conditions (DeSantis, 1999; Grunhage et al., 1999, 2001) suggests that

correction for these gradients of ozone concentrations could be applied to minimize potential artifacts. The concern in recent literature regarding potential confounding of OTC-derived results may be reduced substantially by further developments in current efforts to quantify ozone exposures in terms of effective ozone flux (Grunhage et al., 2001), incorporating transformation of ozone concentration at reference height to ozone at canopy height.

8.3.2.2 Temperature

Temperature is often slightly higher inside OTCs than outside, generally by about 1-3° C both day and night. It has been suggested that this temperature increase could be exploited experimentally as a surrogate for expected global warming, making studies of ozone responses more relevant to future atmospheres.

Interactions between low temperatures and ozone sensitivity are less significant for crop responses in most of California than in many other areas. Ozonation during winter may reduce chilling resistance (Foot et al. 1996, 1997) and exposure during the growing season may induce winter injury following subsequent sub-freezing temperatures (e.g., Chappelka and Freer-Smith, 1995; USEPA, 1996). ozone in the Mediterranean climate of California is primarily a summer phenomenon, as is most, but not all, crop production.

The importance of allometric relationships among plant component organs affects interactions of ozone with temperature. Growth of *Raphanus sativus* (radish) was inhibited by ozone when roots were chilled to 13° C but not when they were maintained at 18° C (Kleier et al., 2001). Root to shoot biomass ratio (R:S) was reduced by ozone under both root temperatures. ozone increased the sensitivity to root temperature of leaf area (reduced by chilling) and of root to shoot ratio (increased by chilling), though the effects of temperature in these experiments were generally non-significant. Modeling results vary with respect to the importance of [temperature x ozone] interactions. Temperature explained some of the variability, but was rarely a dominant factor, in model treatments of multifactor exposure-response relationships (e.g., Mills et al., 2000; van Oijen and Ewert, 1999). In most cases the combination of temperature and relative humidity (RH) or the closely related evaporative demand (VPD) accounted for a considerable fraction of the observed variability in the ozone-end point relationships. Unfortunately, temperature and both RH and VPD are closely related under many environmental conditions.

8.3.2.3 Humidity

RH will likely be increased in the OTC relative to outside under most conditions (e.g., 3-4% in the study of Thompson, 1985). This will depend on ambient humidity, the transpirational activity and density of plants within the OTC, and prevailing wind speed and humidity outside. Generalizations regarding a consistent OTC effect are not possible.

Humidity, and its alternate expression, evaporative demand (VPD), may directly influence crop sensitivity to ozone by influencing stomatal conductance (Grantz, 1990). In humid air of low VPD, stomata open more widely than in dry air with

higher VPD, thereby increasing the flux of ozone into the leaf interior and increasing potential damage and injury. A multi-site and multi-crop study in Europe led to development of Critical Levels of ozone for short term (5 day) exposures (AOT 40) depending on VPD (500 ppb-hr for dry conditions when VPD > 1.5 kPa; 200 ppb-hr for humid conditions when VPD < 0.15 kPa; Benton et al., 2000).

There is considerable variability among genera, species and cultivars in the significance of the interaction of humidity and ozone sensitivity, with modeling results diverging (Balls et al., 2000; Mills et al., 2000; van Oijen and Ewert, 1999). In the multi-year experiments performed in the Po River Valley in Italy during humid but mild spring growing conditions, an apparent interaction between humidity and ozone sensitivity was identified between years. Other factors, including the phenological timing of ozone dynamics, also differed. This interaction between the progression of growth stages of the plant, which may vary with weather and other conditions, and the timing of peak or sustained moderately elevated concentrations of ozone is increasingly understood to have a large influence on the extent of plant injury.

Assessment of ozone impacts on California agriculture may depend on the relevance of exposure-response relationships determined in humid areas to the summer-dry, Mediterranean climate in California. This issue has parallels with the situation in Europe, where the AOT40 metric was developed using northern European studies, but extrapolated to the Mediterranean climates of the southern European countries (De Santis, 1999, 2000). In the case of Europe, the issue has been addressed using OTC exposures, showing substantial yield losses of a wide variety of crop species in Mediterranean regions (Fumagalli et al., 2001a,b). Nevertheless, the magnitude of damage predicted by the available response equations from Northern Europe was not observed in the south. This is most likely attributed to genotypic differences in cultivars as well as to hardening of plants in response to environmental conditions prevailing in the Mediterranean summer growing season.

A consequence and sometimes correlate of humidity is leaf surface wetness. Leaves in OTC environments are subject to reduced periods of dew formation due to the fan-driven turbulent air. Dew presence on leaves of grape (Grantz et al., 1995) and mixed pasture (Pleijel et al., 1995b) enhanced ozone deposition, though not through the stomatal uptake pathway, but rather through heterogeneous aqueous reactions on the leaf surface. In contrast, in the amphistomatous leaves (i.e., with stomata on both upper and lower surfaces) of cotton, the presence of dew reduced ozone uptake, probably by occlusion of stomatal pores on the underside of the leaves (Grantz et al., 1997). In both cases, and perhaps generally, the impact of leaf wetness on ozone damage and injury, as opposed to deposition, may be minimal.

The conclusion of the previous document (ARB, 1987), and of USEPA (1996a), that increased humidity or reduced VPD is generally associated with greater plant sensitivity to ozone, remains valid. This is due to effects on stomatal conductance rather than to leaf wetness. The general effect of altered humidity

on crop responses to ozone measured in OTCs is unclear. It is probably dominated by irrigation or rainfall, which itself modifies the humidity of the canopy environment, both within and outside of OTCs.

8.3.2.4 Water Status

OTCs reduce effective rainfall that reaches plant roots inside OTCs. This is typically less important in the rain-free, summer growing season for most crops in California and other regions with Mediterranean climates. A tendency to maintain experimental plantings more abundantly irrigated than ambient control plots or reference commercial fields will influence plant growth and could alter sensitivity to ozone. However, effects of soil moisture on growth are much more consistent than on sensitivity to ozone.

The effects of soil moisture deficit on crop response to ozone have remained ambiguous. Drought clearly closes stomata, which reduces flux of ozone into the plant interior. With other factors held constant (e.g., antioxidant defense compounds), this effect will reduce damage caused by ozone. However, drought may induce defense compounds, which increase ozone tolerance. Drought reduces plant growth by inhibiting cell expansion, and also alters development. These impacts on growth and yield may dominate small increases in ozone tolerance.

Soybean exhibited some protection by soil moisture deficit (Vozzo et al., 1995), wheat exhibited only additive effects of ozone and moisture deficit (Fangmaier et al., 1994a,b; Bender et al., 1999; Ommen et al., 1999). Miller et al. (1988) found no [ozone x water deficit] interaction in plant growth of cotton at a moderate level of drought which reduced leaf area and yield but did not affect total biomass production. However, for yield a strong interaction was observed. The water stress reduced yield by 16% at low ozone (20 ppb) but increased yield by 28% at 70 ppb ozone, relative to well-watered plants at the same high ozone concentration. Clearly drought reduced the impact of ozone considerably (Heagle et al., 1988b), though at more moderate levels of ozone the protection afforded by drought did not protect yield nor even restore ozone-exposed yields to control levels in filtered air.

Cotton in California (Temple et al., 1988a) was rendered less sensitive to ozone by both mild and severe water deficits. However, yield was inhibited at even moderate water deficit to such an extent that it fell below well-watered levels at all ozone concentrations at which comparisons were made. Thus the widely cited “protective” effect of water stress was largely illusory, as the impact of water management to protect against ozone was more damaging than the ozone itself. The same was true for total plant biomass productivity in alfalfa (Temple et al., 1988b). Chemical soil drought (i.e., salinity) was mostly additive with ozone in reducing growth of rice (*Oryza sativa*; Welfare et al., 1996).

The conclusion from the multi-site and multi-crop NCLAN study (Heagle et al., 1988a) was that any protective effect of soil drought against ozone damage is inconsistent and dependent in unknown ways on the magnitude and timing of the drought.

An important observational study was conducted in the Ohio River Valley of the Midwestern U.S. (Showman, 1991) in which visual injury was observed on a wide variety of native vegetation. Injury was more substantial in a year of relatively low ozone concentrations but adequate rainfall, than in a subsequent year of higher ozone concentrations but drought. This study is strong evidence for the protective effect of some level of water deficit, though the environmental conditions required to lead to this result remain uncharacterized.

The NCLAN and observational results, above, are supported by modeling results with TREEGRO (Retzlaff et al., 2000). Simulated protection against ozone was found in white fir (*Abies concolor*) at high levels of soil moisture deficit, but additive effects of moisture stress and ozone were predicted at more moderate levels of soil drought. More recent experimental studies support these conclusions, but have not added to the quantitative or mechanistic characterization of the effect (Mills, 2002).

8.3.2.5 Turbulence

Among the most notable microclimate alterations in OTCs is the uniformity of wind speed. A typical constant OTC wind velocity of about 2.5 km h^{-1} is in striking contrast to the diurnal varying wind speed in the ambient environment. Air movement is more constant within the OTC, but may be greater than or less than ambient levels outside the OTC, depending entirely on location. In many environments this may represent a reduction in daytime wind speed, but in the dominant cropping area of California, the San Joaquin Valley, it is often an increase.

Turbulence has three primary impacts on plants. Dew persistence declines as noted above. Thigmotropic (contact or movement sensing) stimulation increases. This may lead to various types of hardening responses that reduce sensitivity to further stimulation, mostly poorly characterized but potentially leading to increased tolerance to ozone exposure. Leaf and canopy boundary layer resistance to penetration of gases present in the mixed atmosphere declines.

In the ambient environment turbulence reduces the gradient between the ozone concentration measured at reference height and that measured at canopy height, and also the gradient between the top of the canopy and the leaf surface. This increases stomatal coupling (Jarvis and McNaughton, 1986) with several consequences. It increases stomatal control of transpirational water loss, increases the CO_2 concentration available at the leaf surface for photosynthesis and that of ozone for uptake. In the turbulent OTC environment, with well mixed, ozonated, air blown directly into the canopy, canopy and leaf boundary layer resistances are minimized. In practical terms, this allows the experimenter to impose a known ozone concentration directly at the leaf surface. It also allows ozone flux into the plant to be calculated from stomatal conductance and ozone concentration.

Another factor of relevance to the OTC is the leaf boundary layer resistance. Fan-generated turbulence in the OTC minimizes this resistance, and stabilizes it throughout the course of the day. In the natural canopy leaf boundary layer

resistance is dependent upon thermal and mechanical (wind-driven) turbulence, which typically varies during the day.

Unsworth (1984a,b) found that boundary layer resistance was reduced by the OTC in soybean canopies, but that fluxes of ozone were similar to measured values in extensive soybean fields.

8.3.2.6 Radiation

The OTC environment is lower in light intensity than the ambient environment. The plastic walls of the OTC generally impose a 10-15% decrease in photosynthetically active photon flux density. This will depend on dust accumulation on the plastic walls, and on the age and weathering of the plastic itself.

Sanders et al., (1991) found a 20% reduction in radiation and a slight (0.8 C) increase in temperature inside OTCs relative to ambient conditions outside. They observed that broad beans (*Vicia faba*) plants yielded more and developed more rapidly under these conditions than outside. There was no indication that impacts of ozone observed inside the OTCs (not reported) would have been substantially altered by the OTC environment (i.e., a significant interaction).

In the northern hemisphere, including California, plants grown on the northern half of OTCs may grow more vigorously and yield more than plants on the southern side (Heagle et al., 1988a). In response to this radiation environment, different quadrants of an OTC may exhibit different yield levels, with significant spatial correlation (within an OTC; across quadrants) between plant performance and microclimate (Heagle et al., 1989a). These obvious differences in plant vigor are not linked to differences in ozone sensitivity (Heagle et al., 1988a) as shown by the lack of spatial correlation (within a quadrant; across chambers) of the relative response of yield to ozone.

[Light x ozone] interactions remain incompletely characterized. Results in multi-layer forest canopy trees (Chappelka and Samuelson, 1998) are complex due to within plant gradients in age and light environments. In many cases ozone sensitivity is greatest near optimal light intensity, varying between shade and sun species or leaves (e.g., Tjoelker et al., 1995b; Fredericksen et al., 1996a,b; Topa et al., 2001; Mortensen, 1990). The previous conclusion of USEPA (1996a), that low light intensities and short photoperiods enhance ozone sensitivity, appears to be an over-generalization, as various contrasting effects have been observed (Tjoelker et al., 1995a; Fredericksen et al., 1996b).

Very high light environments induce photoinhibition (itself a form of oxidant damage). An [ozone x high light] interaction involving both photochemistry and dark biochemistry was apparent in leaves of bean. ozone exposure caused effects largely on dark reactions (Guidi et al., 2000; Dann and Pell, 1989). Some parameters, derived from chlorophyll fluorescence, (e.g., F_o) were significantly affected by light in bean leaves but not by ozone. Others (e.g., $1-q_p$) were affected by ozone but not by light, while still others (e.g., quantum yield for CO_2

fixation) were affected by both to a similar extent, but more than additively when exposed to both ozone and light.

The inconsistent experimental evidence is fully reflected in available modelling treatments. Using two models and the dataset of the European Stress Physiology and Climate Experiment (ESPACE), Bender et al. (1999) found that ozone impact on yield of wheat increased with light intensity. In contrast, the similar modeling study of Ball et al. (1998, 2000) found that the effects of moderate ozone concentrations on clover declined with increasing light intensity. Effects of OTC technologies on light-induced changes in crop sensitivity to ozone exposure are likely to be equally inconsistent.

8.3.2.7 Nutrition

There is considerable interaction between ozone sensitivity and soil fertility. In some cases, ozone sensitivity may be greatest at optimal levels of general soil fertility. However, ozone sensitivity was reduced in *Plantago* and birch by adequately fertile soil (Whitfield et al., 1998; Landolt et al., 1997) and manganese deficiency increased ozone sensitivity of beans.

[Nitrogen x ozone] interactions are the best characterized, and environmentally the most relevant. N may enter plants either via soil deposition or by foliar uptake (Grantz et al., 2003. In long-lived natural communities, N deposition may exacerbate the impacts of ozone on plant health and productivity (Fenn et al., 1996; Takemoto et al., 2001; Grulke, 1999). The complex of tropospheric pollutants in California contains NH_3, derived from dairy and fertilizer emissions, acidic HNO_3 vapor, and NO plus NO_2. This complex leads to formation and deposition of NH_4NO_3 particulate matter, especially in the wintertime in the San Joaquin Valley. HNO_3 vapor exhibits a particularly high rate of deposition in areas in which it is present, particularly the Los Angeles air basin and surrounding mountains (Takemoto et al., 2001).

Ozone sensitivity of a variety of deciduous forest tree species, including aspen, poplar, and birch (Greitner et al., 1994; Bielenberg et al., 2001; Paakkonen and Holopainen, 1995), was minimized at near-optimal levels of N nutrition.

Current rates of ambient N deposition are minor compared with application rates of N containing fertilizers to most crop production systems in California. Increasing nitrogen fertility increased ozone sensitivity of wheat (Cardoso-Vilhena and Barnes, 2001). In cotton, high levels of N fertility protected growth and yield against ozone (Heagle et al., 1999). There was some [N x ozone] interaction in partitioning of carbon within leaves (Booker, 2000). At moderate levels of N fertility ozone exposure increased leaf soluble sugars, but at lower and higher N levels, ozone decreased soluble sugars. The expected protection against ozone by elevated CO_2 (e.g., in leaf starch or soluble sugar concentrations) was reduced at high levels of N fertility.

Natural and managed ecosystems are subject to increasing concentrations of atmospheric CO_2. ozone impacts will be interactive with both increasing temperature and with CO_2 concentration. A retrospective study of [ozone x CO_2]

interactions (on vegetative growth rather than economic yield) concluded that elevated CO_2 would substantially alleviate the ozone-induced reduction in plant growth (Poorter and Perez Soba, 2001). Similar conclusions have generally been drawn from a number of exposure studies of [CO_2 x ozone] effects on crop yield.

There is insufficient evidence at present to predict the impact of nutritional status on plant sensitivity to ozone. Predicted effects of enhanced N nutrition are species dependent. In the case of well-fertilized crop species which are treated with abundant N under commercial agronomic conditions, the typical OTC cultivation regime may have little impact on sensitivity to ozone. Rising CO_2 is likely to reduce the deleterious impacts of ozone on crop yield. However, an equally valid perspective is that any growth and yield enhancement expected due to rising CO_2, will be substantially reduced by ozone.

8.3.2.8 Pest Management

Frequently the intensive cultivation of crops in OTCs leads to finer control of biotic interactions than would be possible commercially in the ambient field environment. The large number of insect, fungal and bacterial species of agronomic and horticultural importance, and the variability in potential ozone exposure dynamics and microenvironmental conditions, renders a complete experimental characterization of all possible interactions unlikely. While generalization from the relatively few experimental treatments will be required, the contrasting conclusions among the few available studies makes even this task uncertain. Further experimental work is required on such [biota x ozone] interactions. This reaffirms previous conclusions (USEPA, 1996a; Docherty et al., 1997; Flukiger et al., 2002).

Insects remain a serious challenge to crop production. Aphid infestation remains the best characterized interaction with ozone exposure. Unfortunately, ozone has been reported to enhance and to inhibit aphid development (Flukiger et al., 2002). In contrast to unambiguous responses of aphids to other air pollutants (SO_2 and NO_2), responses to ozone in the literature are about evenly divided between positive, negative, and null changes (Holopainen, 2002).

ozone impacts on the aphids appear to be indirect, mediated by effects on the host plant. Experimental variability is likely linked to nutritional, genetic and environmental differences in the plant sensitivity to ozone. Relative growth rate of individual Russian wheat aphids (*Diuraphis noxia*) in California increased by over 40% at 12 hm (hourly mean) ozone concentration of 102 ppb (Summers et al., 1994). As with other aspects of plant response to ozone, development of process models that incorporate responses of the various organisms to ozone, and their mutual and environmental interactions will be required to fully generalize the multitude of interactions. A step in this direction, with respect to the aphid interaction, has been the suggestion that aphid performance may be enhanced by ozone when temperatures are near the optimum for the insect, and reduced with both warmer and cooler temperatures (Whittaker, 1994).

Growth of *Lygus rugulipennis* was inhibited by ozone on Scots pine trees. As other *Lygus* species are serious insect pests in cotton, dry beans and other crops

in California, this observation may be of significance to California agriculture. However, as *Lygus* populations evolving in the San Joaquin Valley are doing so under ozone pressure, increased resistance to ozone may be expected in the future.

Spider mite infestation of ozone-sensitive clover and peanut was increased by ozone exposure (Heagle et al., 1994; Hummel et al., 1998). Mites are of concern to California tree crops, particularly citrus, and to cotton, suggesting a potentially deleterious interaction with ozone in California. The possibility of evolving resistance to ozone, as has occurred with miticides in the San Joaquin Valley, cannot be ignored.

Infestation of an ozone-resistant clover by spider mites did not increase following exposure to ozone. This suggests, as above, that the interaction is mediated by the plant response to ozone. This level of mechanistic detail will be required to develop the necessary process models of ozone impact that will allow generalization from limited experimental data to the ambient crop production environment.

California agricultural production systems are now heavily dependent upon low-impact Integrated Pest Management (IPM) techniques. These involve extensive use of beneficial predatory insects and spiders in lieu of synthetic pesticides. ozone has been reported to impede the prey acquisition behavior of at least one parasitoid, *Asobara tabida* (Gate et al., 1995). The widespread use in IPM of pheromone-baited attraction traps, and pheromone-based mating disruption strategies, may also be impacted by ozone. The male pheromone of fruit flies was significantly degraded by ozone (Arndt, 1995) as demonstrated by chemical analysis and by reduced bioactivity as an aggregation stimulus.

While ozone exposure may alter the biology of the insect component of these plant-pest complexes, the reverse may also be true. For example, whitefly has become an important pest in California agriculture. Infestation with the greenhouse whitefly (*Trialeurodes vaporariorum*) increased the sensitivity of common bean (*Phaseolus vulgaris*) to chronic exposure to moderate concentrations of ozone (Rosen and Runeckles, 1976).

Pathogens may exhibit considerable sensitivity to ozone. Postharvest handling of fruit in California has made some use of ozone exposure at higher than ambient concentrations (continuous 300 ppb), as a storage fumigant. This treatment (at 5 ^{o}C and 90% RH) reduced aerial mycelial growth, sporulation, and infection intensity of brown rot (*Monilinia fructicola*) on peaches. Gray mold (*Botrytis cenerea*) was also inhibited on grapes (Palou et al., 2002). A variety of other molds and rots including *Rhizopus stolonifer* (Rhizopus rot) infections were slowed but infection was not reduced. It should be noted that this concentration of ozone, while currently above ambient in California, was not always so, and is not unknown now in urban environments in developing nations.

Infection with facultative pathogens (i.e., those that can feed upon plant material while it is alive or after its death) was increased, or symptoms exacerbated, by prior exposure to realistic ozone concentrations in controlled environment

exposure chambers. Grey mold (*Botrytis cinerea*) infection of bean (*P. vulgaris*) was also increased (Tonneijck, 1994; Tonneijck and Leone, 1993) following inoculation with conidia (asexual spores) but not with mycelia (vegetative tissue) (Tonneijck, 1994) at these moderate concentrations. This contrasts with the effect of 300 ppb, above. Leaf spot (*Marssonina tremulae*) of poplar was enhanced by low concentrations of ozone. Conidial germination was inhibited at higher concentrations of 200 ppb for 8 hours/day over 2 weeks (Beare et al., 1999). White mold of bean (*Sclerotinia sclerotiorum*) was enhanced by ozone (Tonneijck and Leone, 1993), as were tan spot (*Pyrenophora triticirepentis*; Sah et al., 1993) and blotch (*Septoria nodorum)* of wheat (*Triticum aestivum*). The sensitivity of 12 wheat genotypes to ozone was correlated (r^2=0.86) with sensitivity to tan spot, suggesting that similar mechanisms may be involved in response to ozone and to pathogens (e.g., Bahl et al., 1995).

Infection with obligate biotrophic pathogens, (i.e., those that require living plant tissue to feed upon) was similarly variable in their interactions with ozone. Powdery mildew (*Sphaerotheca fulginea*) on cucumber (*Cucumis sativa*) was enhanced at low but decreased at high ozone concentrations (Khan and Khan, 1999). Powdery mildew (*Erysiphe polygoni*) on pea (*Pisum sativum*) was inhibited by ozone exposure (Rusch and Laurence, 1993). However, plant sensitivity to ozone was reduced by the infection, as was the case with cucumber powdery mildew at higher ozone concentrations, and with rust (*Uromyces viciae-fabae*) on broad beans (*Vicia faba*; Lorenzini et al., 1994).

[ozone x nematode] interactions are suggested by the reduced allocation of carbohydrate to roots caused by ozone (Cooley and Manning, 1987). Infection of tomato (*Lycopersicon esculentum*) with root knot nematode (*Meloidogyne incognita*) was exacerbated by ozone exposure, and ozone impacts were enhanced synergistically by nematode infection (Khan and Khan, 1998). This and other nematodes are a substantial factor in California agriculture. The [nematode x ozone] interaction may increase in importance as methyl bromide usage for preplant fumigation is phased out to protect the stratospheric ozone layer.

Weed competition is a leading cause of crop loss, but there is little known about ozone interactions in weed-crop competition. Grass-legume mixtures tend to simplify toward pure grass in response to ozone exposure (USEPA, 1996a). This has been observed in an open air fumigation system (Wilbourne et al., 1995) as well as an OTC exposure system (Nussbaum et al., 1995) with a grass-clover system (*Lolium perenne-Trifolium repens*). Dieback of clover left barren patches that encouraged introduction of weedy species.

Modest alterations of the microenvironment were documented within and above a multi-species pasture inside OTCs, relative to the ambient plots outside (Fuhrer, 1994). Of greatest importance was a reduction in global radiation (22%, averaged over two years) and an increase in temperature (1.3 C in both years). Differences in wind speed, precipitation and vapor pressure deficit were noted, but are extremely site-specific. A significant reduction in the ratio of biomass of clovers to grasses was noted inside relative to outside the OTCs. Weedy species replaced clover, particularly during the second year of the experiment. Clover

decline is often observed in experimental studies of mixed swards, but these were clearly accelerated in this study. It was not demonstrated that responses to ozone were altered (i.e., interaction, which was not considered in this study) though both the OTC environment and ozone reduce the clover contribution to total biomass. Similar effects of both factors on clover were noted by Heagle et al., (1989b), without evidence of interaction.

ozone exposure of an alfalfa-timothy mixture (*Medicago sativa-Phleum pratense*) caused a competitive disadvantage to the alfalfa, probably due largely to the ozone impact on the extensive alfalfa root system (Johnson et al., 1996a). This may be of particular relevance to California production of alfalfa hay and seed, as increased competition from grass weeds is a common cause for retirement of perennial alfalfa fields.

Current capability to predict the interaction between ozone exposure and plant competitive interactions is limited. Outcomes cannot be inferred from the relative ozone sensitivities of the individual species involved (Evans and Ashmore, 1992). For example, an early successional community dominated by sumac (*Rhus copallina*) was replaced during OTC fumigation by a community dominated by blackberry (*Rubus cuneifolius*), even though blackberry is quite ozone sensitive. A potential difficulty in extrapolating ozone exposure-response relationships from OTC to ambient environment may be the greater attention likely given to weed control in OTCs relative to extensive agronomic fields.

8.3.3 Intercomparisons of Available Exposure Technologies.

8.3.3.1 Plant Growth

It is clear that plant growth, and in some cases morphology, may differ between plants grown in OTCs and in ambient plots outside or in nearby commercial fields. This has been documented numerous times (e.g., for winter grown lettuce and wheat; Thompson, 1985; Olszyk et al., 1986a) in southern California. These differences were associated with an increase in temperature ranging from 0.1 to 4.2 C, and a reduction in light intensity of about 25%. More recently, Elagoz and Manning (2002) found that growth of beans (*P. vulgaris*) differed in chambers from plants grown outside under Massachusetts conditions. However, while yield of an ozone tolerant line was suppressed in the OTC relative to the ambient plots outside, there was no effect of ozone on yield in either cultivar (Elagoz and Manning, 2002). Olszyk et al., (1992) found changes in plant growth habit of Valencia oranges in OTCs that had little effect on ozone sensitivity.

Plants of alfalfa exposed to ozone in southern California in a mechanical field exclusion system were shorter than those grown in nearby OTCs. Plants in the OTCs exhibited similar biomass (Olszyk et al., 1986b). Significantly, plants in the field exclusion system were more similar in appearance to plants grown in ambient field plots than to those grown in the OTC. Plant height was one of the few (< 10%) of endpoints that differed across exposure technologies. Height of plants grown inside OTCs and subjected to non-filtered ambient air, were generally taller during the NCLAN experiments than plants grown in ambient plots outside (Olszyk et al., 1980; Heagle et al., 1979b). Plant height was the only

growth parameter that exhibited a consistent difference (Heagle et al., 1988a). A retrospective analysis of multi-location, multi-crop NCLAN studies (Krupa et al., 1994; Legge et al., 1995) found that 39 of 56 yield observations were not significantly different between non-filtered and ambient outside plots.

The altered microenvironment associated with OTC exposure protocols is associated with slight alterations in plant growth. Changes in physiological parameters are less well documented. The increase in humidity (reduction in VPD) under some OTC conditions is predicted to increase stomatal conductance. This would increase ozone flux and plant damage. However these interactions are inconsistent across experiments. Heagle et al. (1988a) reviewed reports of reductions, increases, and unchanged values, in stomatal conductance and carbon assimilation rates in OTC-grown plants of varying species in a variety of NCLAN locations.

The OTC effect on stomatal conductance is important because recent literature suggests that fluxes of ozone to plant internal receptors may be the most closely related exposure parameter to injury or damage. Flux to oat (*Avena sativa*) was compared in OTCs and in an open field (Pleijel et al., 1994b), using a mass balance-resistance analog model and a concentration gradient method, respectively. The results demonstrate clearly that no consistent trend in stomatal conductance was observed that could explain large differences in calculated ozone flux to the plants in the two contrasting conditions. In the case of the oat crop, ozone concentration in the OTC (imposed at canopy height) was 25% lower than in the field (at 2 m reference height). In contrast, flux to the plants plus chamber walls was 40% greater in the OTC. This was not attributed to leaf boundary layer resistance, which was similar under both conditions in the upper canopy, though larger in the OTC at deeper, less active, layers of the canopy. It appears to be (partially) due to the loss of the gradient between 2 m and the outside of the individual leaf boundary layer, and (mostly) to uptake by non-vegetative elements in the OTC such as soil and plastic walls. These data do not seem to cast serious doubt on results obtained using OTC technology. The concerns of Legge et al. (1995) are mostly addressed by a flux based metric as proposed by Grunhage et al. (2001) and particularly if chemical defense mechanisms are included, as proposed by Massman et al. (2000).

8.3.3.2 Sensitivity to Ozone

Several validation tests of the OTC technology have been published. Oshima et al. (1976) used the natural gradient available across southern California with alfalfa in a uniform soil mix and 5 gal pots and found only ozone among a number of microenvironmental parameters, was correlated with yield suppression and leaf abscission (i.e., detachment of the leaf along a biochemically prepared separation zone). In this early study any possible co-occuring gradients of other pollutants were not considered. In the same area of southern California (Olszyk et al., 1986b) a comparison of ambient air plots (unchambered), OTC plots (chambered), closed field chambers, and field exclusion system plots (unchambered) was undertaken, also with alfalfa. Comparisons using each technology were co-located. Comparisons were made using ambient air in

Southern California (high but unspecified ozone concentration) and charcoal filtered air. Yields and plant growth were similar, though plant height was greater in the OTCs. The ozone-induced yield suppression in ambient air in OTCs was similar to that predicted by the chamberless gradient study. This study provides particularly strong evidence that yield responses obtained in OTCs may be reliably extrapolated to field conditions, and with even more confidence, compared with yield responses obtained using other exposure technologies.

Grunhage and Jager (1994) suggest that chamber exposures may overestimate the impact of ozone on crop yield due to invariant deposition velocity. This reflects both atmospheric conductivity (above; Grunhage et al., 2001) and stomatal dynamics which are more constant in an intensively managed OTC than in less optimally managed ambient field settings. Unexpectedly small responses of tobacco to high concentrations of ambient ozone are likely explained by the non-contemporaneous occurrence of stomatal conductance and ozone availablility.

In cool periods of low incident radiation, the increase in temperature but further reduction in light intensity observed inside the OTC may enhance plant sensitivity to ozone. This is not relevant to much of California agriculture, though production of winter vegetables is important in some areas. Microenvironmental effects of OTCs under such conditions were demonstrated in California (Thompson, 1985).

Sensitivity to ozone is not generally affected by growth in OTCs (Heagle et al., 1988a; Olszyk et al., 1986b). The ratio of sensitive to tolerant clover biomass was similar in OTC and ambient plots (Heagle et al., 1996). Comparisons of contrasting ozone exposure technologies have been conducted with clones of trembling aspen. Plants were exposed in OTCs (Karnosky et al., 1996), across an open air exposure gradient in three locations (Karnosky et al., 1999), and in a chamberless FACE system (Karnosky et al., 1999; Isebrands et al., 2000, 2001). In these various comparative studies there was little indication that the relative ranking of ozone sensitivity of these diverse clones (Karnosky et al., 1996, 1999) was altered by the exposure technology. There was similarly no evidence of any systematic increase in ozone sensitivity in those plants exposed in the OTC experiments. Indeed, symptom development may have been more pronounced in the chamberless experiments (Karnosky et al., 1999). Yield of oilseed rape in Britain was reduced by 14% and the number of yield bearing branches by 38% in a free-air (i.e., non-chamber) exposure system. AOT40 levels were 3774 ppb-hr (fall) and 8960 ppb-hr (spring) relative to ambient controls of 239 ppb-hr and 690 ppb-hr, respectively (Ollerenshaw et al., 1999). Peak hourly concentrations were about 77 ppb and 80 ppb relative to control values of 30 ppb and 31 ppb. A similar free-air exposure of winter wheat (Ollerenshaw and Lyons, 1999) to AOT40 = 3472 ppb-hr (fall) and 6178 ppb-hr (spring), with daily mean values of 75 ppb and 81 ppb, reduced yield by 13%, relative to ambient controls of 135 ppb-hr and 469 ppb-hr; 30 ppb and 33 ppb. This is similar to other estimates of the ozone sensititivity of wheat obtained in OTCs (Table 8).

OTCs with raisable side panels were used to reduce the impact of growth environment on plants subjected to ozone (Wiltshire et al., 1992). Apple trees

were grown with the plastic sides raised except when ozone was added, during periods when local ambient atmospheric conditions were conducive to high concentrations of ozone, (high radiation, high temperature and low wind speed) and for only 8 h/day and no more than three consecutive days. Trees exhibited no visible ozone injury and were only intermittently exposed to OTC conditions, yet exhibited substantial ozone-induced leaf abscission and reduced leaf area duration (potential productivity estimated as the product of green leaf area and time of leaf display). Yield was not reported but would be expected to be reduced along with leaf area duration.

The limitations of crop yield loss assessments conducted in OTCs was considered in USEPA (1996a). Concerns included small plot sizes, altered microenvironmental parameters, and effects of charcoal filtration on air quality. The importance of characterizing such factors and their influence on extrapolation and scaling of these controlled exposure experimental data to estimates of regional (e.g., California) crop loss assessment was noted at that time. However, it was concluded that:

"…These uncertainties are not quantified, although there are preliminary data establishing their existence…There is an urgent need to estimate these uncertainties so that the OTC data can be used fully, with little doubt as to how well the data represents (sic) real crop losses."

and that

"…at the current time, OTCs represent the best technology for determination of crop yield responses to ozone; concentration and duration of the gas are well controlled, and the plants are grown under near-field-culture conditions."

These conclusions, similar to those of ARB (1987) and to those explicitly stated by Olszyk et al. (1986b), remain valid today. The definitive studies may not be possible to design, and certainly remain to be reported at this time. There is little scientific justification for the categorical discounting of ozone yield-response relationships obtained using OTC technology.

8.4 Sites and Modes of Ozone Damage to Crops

8.4.1 Ozone Uptake

The previous document (ARB 1987) concluded that ozone present near the plant canopy must overcome physical resistances prior to entry into plant leaves. Entry into the leaf interior was considered prerequisite to injury and damage. Research since 1987 has not invalidated these important conclusions. Possible effects of OTC exposures on these resistances are considered above.

Surface conductance (1/resistance) for deposition of ozone from the atmosphere consists of plant and non-plant components, and depends on interacting physical, physiological and biochemical factors (Baldocchi et al., 1987; Grantz et al., 1997; Hicks et al., 1987). These resistances are associated with a boundary layer of poorly mixed air, and a stomatal resistance that is under physiological control. In contrast to uptake through stomata, external deposition may cause

minor damage to cuticles (the water impermeable leaf coating) and trichomes (leaf hairs) on leaf surfaces, which may increase non-stomatal, cuticular water loss (i.e., through imperfections in the waxy cuticle that covers the epidermis of leaves and other plant parts) (Barnes et al., 1998; Kerstiens, 1989a,b). Heterogeneous reactions leading to ozone destruction occur throughout the canopy (Leuning et al., 1979a,b) and cause little injury but complicate interpretation of ozone fluxes, as the distribution of sinks for ozone within the canopy remains uncertain. In addition, degradation of ozone by bare soil may approach 40% of total deposition under some conditions (Leuning et al., 1979b; Turner et al., 1973). These factors also confound flux measurements in OTCs, as noted above.

The dominant and most damaging route is through stomatal pores of photosynthetically active leaves. Internal leaf sites represent significant regional sinks for ozone, controlled by the physiologically modulated stomatal response (Baldocchi et al., 1987; Grantz et al., 1995; Massman and Grantz, 1995; Roper and Williams, 1989; Thomson et al., 1966; Temple, 1986). In daylight the canopy stomatal conductance is usually smaller than the atmospheric conductance and therefore controls the rate of ozone uptake from the atmosphere, deposition to vegetation, and damage (Grantz et al., 1994, 1995, 1997; Massman and Grantz, 1995; Massman et al.,1994; Wesely et al., 1978). The primacy of stomatal uptake is suggested by a moderate regression, among several highly diverse species, between ozone-induced growth decline and increased stomatal conductance (Volin et al., 1998). Further inclusion of carbon assimilation (as the ratio of assimilation to stomatal conductance) improved this regression substantially.

ozone fluxes between the atmosphere and an extensive cotton canopy in California increased with increasing canopy stomatal conductance, whether the canopy was dew-wetted or dry (Grantz et al., 1997). In isolated leaves, stomatal closure substantially reduced ozone uptake and largely prevented ozone damage to foliage (Butler and Tibbits, 1979). Perennial crops typically exhibit lower gas exchange and stomatal conductance than annual agricultural crop species (Reich 1987). This reduces ozone uptake and damage relative to physiologically more active crop species. These differences were reflected in the eddy covariance determinations of ozone uptake to cotton and grape in California (Grantz et al., 1994). Canopy conductance is thus dominated by stomatal conductance, which constitutes a first line of plant defense (Taylor et al., 1982a; Grantz et al., 1995; Massman and Grantz, 1995).

Normalization of ozone flux, usually measured by micrometeorological techniques, by ambient ozone concentration yields the ozone deposition velocity (V_d = flux/concentration). V_d is typically more strongly related to canopy conductance than is ozone flux (Grantz et al., 1997). This indicates that ambient ozone concentration is not well correlated with stomatal opening. This might be expected both from the inhibitory role of ozone on stomatal opening and from the lack of correspondence between atmospheric conditions that are conducive to stomatal opening (e.g., high humidity) and periods of high ozone concentration and vigorous atmospheric mixing (Grunhage et al., 1997). This means that

neither timecourses of ambient ozone concentration (the current definition of "dose") nor models of stomatal conductance, will yield a general prediction of ozone uptake or plant impacts. The interaction of the two, along with the dynamics of plant sensitivity to ozone (e.g., Massman et al., 2000) may rationalize does-response relationships in OTCs with those obtained in the field.

8.4.2 Metrics for Evaluating Crop Productivity Losses.

Various indices of ozone exposure have been evaluated in the literature, generally using statistical regression techniques that determine how well they relate ozone monitoring data (ambient or experimental) to crop loss. Yield loss indices vary in methods of averaging, weighting peak exposures or discounting sub-threshold concentrations (e.g., SUM06, AOT40) in which higher concentrations receive more mathematical weighting in terms of the response of the vegetation (Lefohn and Runeckles, 1988; Lee et al., 1988), summing concentrations over various periods, and weighting of phenological stages (i.e., time-dependent periods of plant development). None of these various metrics has been linked to mechanistic models. It has not been possible to identify the "best metric" nor to use them to predict interactions of ozone with environmental parameters such as temperature or humidity. Weighting of peak concentrations may predict visible injury indices over short exposures, yet perform less well over over longer, chronic exposures, during which stomatal conductance and ozone uptake may decline. The NCLAN program evaluated four possible ozone exposure statistics. These generally involve long-term means or peak analysis. It remains unresolved whether the average concentration as suggested by the results of Heck et al., (1984) or peak concentrations which were found to be site-specific (and thus exposure dynamics-specific) (Heck et al., 1984) will better predict injury and damage caused by ozone.

Current research suggests that a long-term cumulative metric (i.e., a sum of concentrations over a substantial portion of the growing season) may best predict ozone impacts on agricultural yields (Lee et al., 1994). This is the basis of the AOT40 metric currently identified in Europe and the SUM06 metric frequently used in the U.S. No attempt is made here to resolve these issues. Results of published studies are reported using the original ozone metric. Both recent and older research, as observed previously (e.g., Fuhrer et al., 1992; Massman et al., 2000), indicate that quantitative estimates of effective ozone dose are likely to relate most accurately to resulting injury and damage. Effective ozone dose is appropriate toxicological terminology for the oxidant that reaches the sensitive biochemical receptors within the leaf, following penetration of physical resistances identified above and biochemical resistances associated with extracellular detoxification compounds. Characterization of effective ozone dose remains imprecise, requiring simultaneous quantitative consideration of ambient ozone concentration, atmospheric turbulence, stomatal conductance, and antioxidant metabolic capacity within the leaf (Musselman and Massman, 1999; Massman et al., 2000). It will also require more quantitative treatment of diurnal (Lee and Hogsett, 1999) and phenological (Soja et al., 2000; Tingey et al., 2002)

patterns of ozone tolerance than are currently available. It is not possible at the present time to implement this strategy due to insufficient available data.

8.4.3 Ozone Attack.

ozone injury and its relationship with environmental conditions is poorly characterized. Acute ozone stress is associated with high atmospheric concentrations, even for short periods of time, while chronic stress is associated with exposure over long periods of time, even at low concentration (Koziol and Whatley, 1984; Heath, 1988, 1994a). However, the definition of high and low concentrations differ by genotype, exposure history, and micrometeorological conditions. Exposure leads to initial, or primary, injury which may be followed by secondary injury. The initial site of damage may depend upon plant species, exposure dynamics and the resulting cellular location of oxidant attack. Secondary reactions appear to be similar to those involved in generalized plant stress responses (Pell et al., 1997; Kangasjärvi, 1994; Miller and McBride, 1999).

The biochemical and physiological targets of ozone attack were tabulated in the previous document (ARB, 1987), and are summarized in Table 3. Research since 1987 has not invalidated the conclusions regarding these processes as key targets of ozone impacts. However, considerably greater understanding of the mechanism and characteristics of these impacts has been developed over this period.

The internal concentration of ozone within the intracellular gas phase of the leaf had been considered to be near zero (Laisk et al., 1989). Recent evidence (Moldau and Bichele, 2002) suggests that a substantial concentration of ozone may remain, as expected for sustained damaging exposures. Reactivity of cell wall sites leads to gradients within the substomatal space and the surrounding cell wall space. A Henry's Law equilibrium (i.e., the condition in which the partial pressure of ozone in the gas phase remains proportional to the mole fraction of ozone in the liquid phase) occurs at the interface where the gaseous species dissolves into the aqueous phase. Reductive detoxification by antioxidant metabolites and enzyme systems, including ascorbate, glutathione, and superoxide dismutase, may occur in aqueous solution, often following stimulation of their synthesis in response to ozone exposure. While ozone reacts with unsaturated organic molecules (forming carbonyl and peroxide groups) and with exposed sulfhydryl groups of proteins (forming sulfones and disulfide bridges) (Mudd, 1996), the primary biochemical or physiological target of ozone attack, the mechanism of ensuing ozone phytotoxicity, and the key components of plant resistance to ozone, all remain to be characterized (Heath, 1988).

Ozone is decomposed at internal plant sites at the expense of oxidizing a plant constituent. When this is an antioxidant defense molecule, direct damage may be avoided. However, ozone effects on overall plant productivity include the metabolic costs to synthesize and regenerate such defense compounds. This may be considered a hidden cost of resistance to ozone damage. Rapid entry of oxidant can overwhelm the antioxidant response.

Cell wall and plasma membrane-bound proteins may be early targets of ozone attack, particularly those with exposed cysteine, methionine, or tryptophan. Proteins with enzymatic activity including membrane transport systems (e.g., for cations, sugars) may be physiologically significant early receptors. Inactivation of the K^+-activated ATPase (generally believed to be involved in K^+ transport) by *in vivo* exposure to ozone was linked to a sensitive sulfhydryl group. Altered plasma membrane fluidity, permeability (Elkiey and Ormrod, 1979), K^+-exchange via ATPase reactions (Dominy and Heath, 1985) and Ca^{2+} exclusion (Castillo and Heath, 1990a,b), are among the first detectable responses to ozone exposure. The plasma membrane Ca^{2+} efflux pump was inhibited by ozone exposure and the influx permeability increased (Castillo and Heath, 1990). Fumigation of bean plants inhibited the outward directed, ATP-requiring, Ca^{2+} pump and increased the passive permeability of Ca^{2+} (Dominy and Heath, 1985). The loss of K^+ from the cytoplasm and increase in Ca^{2+} concentration, along with a shift in apoplastic pH could trigger a series of diverse cellular responses in mesophyll cells, leading to photosynthetic disruption, or in phloem companion cells, to disruption of phloem loading. This role of Ca^{2+} as a second messenger with broad impacts on metabolism has been considered a potentially key component of ozone-induced plant damage (Castillo and Heath, 1990).

The similarities between these putative Ca^{2+}-mediated responses to ozone and wounding responses suggest that ozone may trigger wound-regulated genes (Mehlhorn et al., 1991). In many cases ozone attack resembles pathogen challenge followed by a hypersensitive response with localized cell death (Sandermann, 1996). Pathogen attack activates Ca^{2+} channels which triggers the active oxygen defense mechanism which causes localized apoptosis (programmed cell death). Ozone-induced passive inward flow of Ca^{2+} could initiate the same defense system (Castillo and Heath, 1990a,b). Nevertheless, it remains to be demonstrated that Ca^{2+} influx is the first significant event in ozone injury.

8.4.4 Visible Injury Caused By Ozone To Crops

Visible lesions on the leaf surface are the most commonly observed symptom of ozone damage in both native vegetation and crop species. These include a variety of apparently abnormal appearances, depending on species. These may include the appearance of bronze colored lesions or speckling (stippling) on the adaxial (upper) surface of exposed leaves (Flagler, 1998). It may also include the appearance that the leaf tissue is water-filled, with a darkened and faintly wet appearance (often called “waterlogging). The lower surface may also acquire a bronze-colored hue, and the upper surface may develop a silver and slightly shiny coloration. In addition to these highly species-specific discolorations (for pictorial examples see Flagler, 1998), the leaf tissue may become chlorotic (development of a yellow coloration with fading of the dominant green pigmentation of chlorophyll as its concentration declines. With continuing chronic exposure, or acute exposure to very high concentrations of ozone, the tissue may become necrotic (as cells and tissues begin to die). Acute exposure to high concentrations of ozone leads to greater ozone-induced foliar injury symptoms

than chronic exposures to more moderate long-term concentrations. However, damage to crop yield, except for leafy vegetables in which visible injury is economic damage, may be greater over season-long chronic exposures. Chronic exposure even to very low concentrations of ozone accelerates foliar senescence, leading to visible pigment loss and earlier leaf abscission.

The diversity of symptom presentation makes it difficult to attribute foliar injury specifically to ozone. The development of chlorotic mottle and necrotic areas of foliage, and frequently accelerated abscission of leaves following acute episodes or prolonged chronic exposure, represent a loss of photosynthetically active leaf area that may decrease whole-plant carbon assimilation. Chlorosis and necrosis, however, are common responses to a variety of stresses and the various pigmentation reactions may resemble nutrient deficiencies and both microbial and arthropod pest pressure. Nevertheless, these visible injury patterns can be semi-diagnostic to a trained observer (Flagler, 1998).

A trained, international panel was able to identify ozone symptoms in plantings of several uniform genotypes of important crops across the length and breadth of Europe (Benton et al., 2000). This important study demonstrated that ozone is injurious to crops at ambient concentrations across a wide sampling of European crop production areas. Symptoms were observed on beans, tomatoes and watermelon, of particular relevance to California, in one or more sites. Test species were grown in locations only as appropriate, but symptoms were also widely observed in garden vegetation of (presumably) locally adapted crop cultivars.

Unfortunately, even authentic visible ozone injury is not well correlated with physiological, horticultural or ecological endpoints (Davison and Barnes, 1998). In some cases, visible injury indicates an advanced state of metabolic disruption and tissue degradation. Plants may then lack the ability to respond appropriately to environmental cues. In other cases visible symptoms may either precede or follow impacts on physiological processes such as photosynthesis or stomatal response. However, as these physiological indicators require specialized instrumentation to detect, they may go unnoticed in the absence of visible injury.

The mechanism of visible damage appears to involve leakage of cellular electrolytes and production of pigments such as anthocyanins associated with wounding. Ozone and other wounding stimuli induce production of ethylene and a family of polyamine compounds. Inhibition of ethylene synthesis with aminoethoxyvinyl glycine (AVG) inhibited ozone-induced visible injury (Mehlhorn et al., 1991), without reducing effects on damage.

8.4.5 Growth and Photosynthesis

Following a half-century of research, the mechanism of ozone action remains unknown. What remains striking in the available literature is the observation that ozone often causes large impacts on plant growth that cannot be related quantitatively to the relatively small effects on physiological processes such as photosynthetic carbon assimilation. A regulatory system operating at the level of the intact plant must be invoked.

Economic yield in grain, fruit and vegetable crops is only indirectly related to plant growth, linked through the concept of Harvest Index (ratio of marketable to total plant biomass). Thus economic damage due to ozone is mechanistically several steps removed from physiological impacts of ozone.

It is clear that ozone exposure reduces plant biomass production. Uptake of ozone by upland cotton (Oshima et al., 1979; Miller, 1988; Olszyk et al., 1993; Temple et al., 1988a; Temple, 1990a,b) and Pima cotton (Grantz and Yang, 1996), and a variety of diverse plants (Pell et al., 1994). Reductions in biomass occur among all plant components, with root system biomass reduced the most severely (Cooley and Manning, 1987), and occasionally to very low levels (e.g., in Pima cotton exposed in greenhouse chambers; Grantz and Yang, 1996).

A literature search revealed 97 published experimental studies in which ozone effects on growth were considered. Relative Growth Rate (RGR; see List of Abreviations for definition) was reduced in 90% of these observations, with 53 of these statistically significant (Table 4). In contrast, only 5% of observations yielded increases in RGR, and all were non-significant. Reductions in RGR were general among a large array of plants (Appendix Table 1), characterizing 89%, 86%, and 100% of observations with herbaceous (i.e., non-woody) dicotyledonous (generally broad-leaved plant species, with two cotyledons or “seed leaves”), monocotyledonous (generally narrow-leaved or grass-like plant species, with a single cotyledon) and perennial tree (long-lived, woody) species, respectively (Table 4). RGR of herbaceous dicotyledonous species was most sensitive to ozone exposure, with significant declines reported in 63% of experiments and 79% of species. Many crop plants grown in California are herbaceous dicotyledonous species. Averaged over all plants studied (Table 5), RGR was reduced by ozone exposure by 4-17% among the various taxa.

These observations of growth reductions are not limited to experiments conducted in greenhouse chambers and OTCs (Appendix Table 2). Clones of trembling aspen were reduced in stature and stem volume (average 20% reduction), by exposure in a chamberless (FACE) system to a twice-ambient treatment in Wisconsin.

Reduced growth may be caused by ozone inhibition of primary carbon acquisition. ozone is principally deposited to leaves. Visible symptoms occur in leaves. ozone molecules that reach the leaf interior may directly affect photosynthesis in mesophyll cells (Spence et al. 1990).

Carbon assimilation is generally reduced following ozone exposure. Carbon assimilation in seedlings of Pinus taeda was reduced by ozone concentrations up to 95 ppb, 7 hm (Adams et al., 1990a). Carbon assimilation of recently mature leaves of Pima cotton was reduced by up to 20% by brief (45 minute) pulses of high (200 – 800 ppb) ozone concentrations (Grantz and Farrar, 1999). Similar 60 minute pulses of 600 ppb ozone in tomato (Lycopersicon esculentum) reduced photosynthesis by 43%, and in bean (Phaseolus vulgaris) by 29%. 90 minute pulses of 400 ppb ozone reduced assimilation in tobacco (Nicotiana tabacum) by 78% (Hill and Littlefield, 1969).

Early research into the mechanism of ozone impacts demonstrated that plasmalemma and chloroplast membranes were vulnerable to oxidant attack (Heath, 1980). Ozone exposure causes a loss of K^+ and Ca^{2+} from cells (Heath, 1994a; Castillo and Heath, 1990a,b) that could be mediated by membrane-bound signal molecules, and that could indirectly impact chloroplast function. Photosynthetic partial reactions have also been suggested as primary targets of ozone attack (Koziol and Whatley, 1984; Reich and Amundson, 1984; Heath, 1988). Direct effects of ozone on photosynthesis occur over quite short time periods (Farage et al., 1991) and can be severe following both chronic (Wiese and Pell, 1997; Rieling and Davison, 1994) and acute exposures (Darrall, 1989; Forberg et al., 1987; Farage et al., 1991; Farage & Long, 1995; Guidi et al., 1997, 2000; Grantz & Farrar, 1999, Zheng et al., 2000). ozone caused a decline in the activity and quantity of Rubisco (Ribulose bisphosphate carboxylase; E.C. 4.1.1.39), the primary carbon fixation enzyme of photosynthesis (Pell et al., 1992, Farage et al., 1991; Farage and Long, 1995) and a decrease in the regeneration of RuBP (Ribulose bisphosphate, the substrate for carbon fixation) (Farage and Long, 1995). Leaf chlorophyll concentration, carboxylation efficiency and photosystem II activity also declined (Farage et al., 1991; Pell et al., 1994, 1997; Pell and Pearson, 1983; Kangasjarvi et al., 1994; Dann and Pell, 1989; Reich, 1983).

The half-time for the decline in mRNA for the small subunit of Rubisco is a few hours (Krapp et al., 1993), reduced by ozone to about an hour or less by inhibition of transcription and by accelerated degradation. Similar observations hold, over slightly longer time frames, for Rubisco protein and activity. Photoxidation of chlorophyll may occur following ozone exposure as electron transfer from H_2O to NADPH is inhibited with build up of oxidative intermediates or inhibition of the dark reactions that consume small carbohydrate intermediates.

Sakaki et al. (1990) found that chloroplast envelope proteins with potentially oxidant-sensitive sulfhydryl groups were not affected by ozone fumigation, in vivo. The absence of ozone damage to these exposed sulfhydryls suggests that neither ozone nor its oxidizing reaction products penetrate sufficiently to inhibit enzymes located within the envelope. That chloroplastic enzymes, including Rubisco (Pell et al., 1997) are eventually inhibited, suggests transfer of information via a signal cascade, rather than penetration of ozone or its unstable reaction products to the chloroplast.

Photosynthetic responses to ozone are observed in OTC and chamberless exposure settings. In two clones of aspen (tolerant and sensitive to ozone) exposed in a FACE exposure facility, photosynthetic assimilation of carbon declined, particularly in older leaves (Noormets, 2001a). ozone also causes stomatal closure (Farage et al., 1991; Pell et al., 1992; Darrall, 1989; Farage et al., 1991; Farage and Long, 1995; Rieling and Davison, 1994; Minnocci et al., 1999; Torsethaugen et al., 1999; Martin et al., 2000) without affecting calculated intercellular CO_2 concentration or stomatal limitation of photosynthesis (Noormets, 2001a). ozone responses are thus consistent with other

environmental impacts on carbon assimilation. Stomatal closure does not generally limit CO_2 assimilation, due to parallel and apparently coordinated declines in mesophyll photosynthetic capacity and stomatal guard cell function.

Over long term exposures changes in photosynthetic capacity are consistent with the observed acceleration of leaf senescence caused by ozone (Pell et al., 1997; Alscher et al., 1997). Senescence may be accelerated by a primary attack on photosynthesis.

ozone-impacts on photosynthesis are often not large enough to explain effects on growth of plants (e.g., wheat; Meyer et al., 1997). On a whole shoot basis, ozone reduction of source strength in individual leaves may be offset by a compensatory increase in rate of leaf production and higher photosynthetic activity per unit leaf area in young leaves (Pell et al., 1994; Farage and Long, 1995; Pell et al., 1992; McCrady and Anderson, 2000). Despite these compensatory responses ozone often reduces area and longevity of photosynthetically active leaves (Beyers et al., 1992).

8.4.6 Carbohydrate Allocation and Translocation

Recently assimilated carbohydrates must be allocated among plant organs and partitioned among multiple biochemical constituents. Only then can they be integrated into structural and non-structural biomass and enter into metabolism. This is required to sustain plant growth and normal patterns of development (Amthor and Cumming 1988), to mount defense mechanisms (Lechowicz 1987), and to repair wounding (McLaughlin and Shriner 1980; Dickson and Isebrands 1993). These allocation patterns are altered by exposure to ozone. Transport of newly acquired photosynthate to developing sink tissues may be particularly severely reduced by acute or chronic exposure to ozone.

Many reports indicate the general observation that ozone exposure reduces R:S (Cooley & Manning, 1987: Darrall, 1989; Dickson et al., 1997; Reinert & Ho, 1995, Grantz and Yang, 1996; Reinert et al., 1996; Landolt et al., 2000; Landolt et al., 1997; Olszyk and Wise, 1997; Chappelka et al., 1988; Chappelka and Chevone, 1988; Anderson et al., 1991; Bennett et al., 1979; Oshima et al., 1979; Darrall, 1989; Barnes et al., 1998; Laurence et al., 1994; Tingey et al., 1971; Miller, 1988; Kostka-Rick et al., 1993; Taylor and Ferris, 1996). Of 20 diverse plant species surveyed by Cooley and Manning (1987), 17 exhibited a decline in R:S.

Morphological changes in root systems may occur in response to ozone (Warwick and Taylor, 1995) that are not clearly associated with altered biomass allocation (Taylor and Davies, 1990). ozone impacts on biomass allocation to reproductive structures (Oshima et al., 1977b; Bennett et al., 1979; Bergweiler and Manning, 1999) and to stolons (shoot runners that produce roots) (Wilbourn et al., 1995; Barnes et al., 1998) are also observed.

It is not currently known how ozone alters carbohydrate allocation. Root:shoot allometric relationships (R:S) are highly conserved in plants (Hunt, 1990; Gunn et al., 1999), with carbohydrate reserves buffering periods of reduced carbon

assimilation. Resources are diverted to leaves for defense/repair of ozone-induced wounding (Amthor and Cumming, 1988; Barnes, 1972; Barnes et al., 1990a; Skärby et al., 1987; McLaughlin and McConathy, 1983; McLaughlin et al., 1982; Grulke 1999; McLaughlin and Shriner, 1980; Evans and Ting 1973; Ting and Mukerji, 1971) and detoxifying reactive oxygen species produced by the dissolution of ozone (Lee and Bennett 1982, Mehlhorn et al. 1986). This occurs following both experimental exposure to ozone (Cooley and Manning, 1987; Miller, 1988; Oshima et al., 1978; Kasana and Mansfield, 1986; Kostka-Rick and Manning, 1992) and across natural exposure gradients (Grulke and Balduman, 1999; Taylor and Davies, 1990). Resistance to further challenge by biotic or abiotic (e.g., ozone) stressors is probably reduced under these conditions (Laurence et al. 1994; McLaughlin et al., 1982; USEPA, 1986, 1996a; Pell et al., 1993). The energetic costs of ozone-induced repair and resistance have not been quantified.

For annual crops the net effect of reductions in C-allocation to roots may be large, particularly during seedling development. In perennials, such as trees and vines, altered allocation over many years may impose large constraints on growth, even though single year effects observed in many experimental studies may be modest (Retzlaff et al., 1997, 2000). This may be economically significant particularly for almond trees and grape vines that are dominant commodities in California.

In loblolly pine, ozone caused retention of carbon and biomass in shoots, reducing allocation to roots (Kelly et al., 1993; Spence et al., 1990). Ozone reduced allocation of carbohydrate to the fine roots in seedlings of Pinus taeda (Adams et al., 1990a). Ozone reduced allocation to leaves and roots in Populus tremuloides and in two C_3 grasses (Agropyron smithii and Koeleria cristata) but not in Quercus rubra or C_4 grasses (Bouteloua curtipendula and Schizachyrium scoparium). The root biomass ratio (root:plant) and R:S were reduced by ozone in upland cotton (Olszyk et al., 1993; Oshima et al., 1979; Temple, 1990a,c). In Pima cotton allocation of biomass to roots decreased by 40% (Grantz and Yang, 1996, 2000), from 13-14% of plant dry weight in charcoal-filtered air to only about 6-8% at 111 ppb ozone 12 hm. Reduced allocation of biomass to root systems was observed across a wide range of N treatments in poplar (Populus tremuloides) seedlings (Pell et al., 1995). Occasional reports indicate no change or increased allocation to roots has been observed following exposure to ozone (Davison and Barnes, 1998; Reiling and Davison, 1992a; Barnes et al., 1998).

The allometric coefficient (k) is derived from the exponential growth equation (after Troughton, 1955) and relates the relative growth rates of competing plant parts such as root and shoot (Farrar and Gunn, 1998; Gunn et al., 1999). A change in k indicates that the fundamental developmental program of the plant has been altered. While it is common for the rate of plant development to be altered by environmental conditions, with a consequent change in R:S at a given plant age, it is less common for similar changes in k to be observed. In the case of plant response to ozone, the concern is that the highly conserved balance of root system development and shoot development, which enables the shoot to be

physically supported and supplied with sufficient water and nutrients to foster rapid photosynthesis and growth, may be disrupted. The resulting plants with inadequate root systems may exhibit reduced productivity due to physiological disruptions of various types.

A recent literature search revealed 108 experimental exposures of plants to ozone from which k could be derived (Appendix Tables 1, 2). The 108 exposures represented 44 different plant species, of which 50% exhibited significant changes in k (44% of 25 dicotyledonous species) of which 91% exhibited a decrease in k. A number of individual species exhibited both positive and negative effects of ozone on k, reflecting the conserved nature of allometric relationships (Hunt, 1990; Gunn et al., 1999). Most observations yielded negative changes in k, and the majority of significant effects were negative (Table 4). However, many observations of ozone effects on k yielded inconclusive results. Overall, only 29% (24% among herbaceous dicotyledonous species; Table 4) reported a significant effect on k, of which 74% were reductions.

The mean % change in k and RGR, over all observations, trended negatively for all species (Table 5), and was significantly below 0 for the herbaceous dictotyledonous plants. ozone impacts on carbohydrate allocation were not always associated with effects on growth. Several herbaceous dicotyledonous species (*Chenopodium album, Epilobium hirsutum, Rumex acetosa*), five herbaceous monocotyledonous species (*Arrhenatherum elatius; Bromus erectus; Brachypodium pinnatum; Lolium perenne; Triticum aestivum*) and two tree species (*Picea abies; Quercus petraea*) exhibited significant ozone-induced changes in k without exhibiting any response of RGR to ozone.

Reduced biomass allocation to roots by ozone implies a disruption of integrated plant function that could represent a principal effect of ozone exposure (McLaughlin et al., 1982). Differences in the sensitivity of grain yield of cultivars of sweet corn (*Zea mays*) to ozone have been attributed to differential responses of root system development and hydraulic properties (Harris and Heath, 1981). Similarly, cotton plants with restricted root development exhibited reduced productivity (Browning et al., 1975). Sustained reductions in carbon allocation to roots in loblolly pine (Kelly et al., 1993; Spence et al., 1990) were projected to adversely affect water and nutrient acquisition, especially on droughted sites (Kelly et al. 1993).

Lee et al. (1990) demonstrated an increase in root hydraulic conductance per unit root dry weight in seedlings of red spruce (*Picea rubens* Sarg.) exposed to ozone. This reflected ozone-induced reduction of root biomass. There are numerous reports of substantial effects of ozone on fine root development in a number of plant species, including beet (*Beta vulgaris*) and Pima cotton (*Gossypium barbadense*; Grantz and Yang, 1996, 2000). Despite a similar increase in biomass-specific hydraulic conductance, whole root system hydraulic conductance of Pima cotton declined by 94% at 0.111 ppm 12 hm. Hydraulic conductance of Pima cotton declined by 41% on a per unit leaf area basis over this range of ozone exposures, a key measure of root:shoot integration. Hydraulic conductance was also reduced by ozone in upland cotton cultivars

(*Gossypium hirsutum*) selected under ozone pressure in the San Joaquin Valley (Grantz et al., 1999).

The reduction of hydraulic conductance on a leaf area basis could lead to severe water deficits and enhance cavitation in the xylem vessels, induce systemic vascular failure due to embolism, and endanger plant survival under drought conditions (Tyree and Sperry, 1988). ozone increased the impact of water deficit in soybeans (*Glycine max* L.; Heggestad et al., 1985) and red spruce (*Picea rubens* L.; Roberts and Cannon, 1992), inducing a greater loss of biomass productivity and a lower (drier) leaf water potential.

The reverse situation has also been observed, sometimes in the same species. Maintenance of leaf water status despite degraded root hydraulic efficiency reflects a coordinated decline in stomatal conductance (Grantz and Yang, 1996; Meinzer and Grantz, 1989, 1990). ozone causes substantial reductions in stomatal conductance in general, and in Pima (Grantz and McCool, 1992; Grantz and Yang, 1996) and upland (Temple, 1986) cottons, specifically. In the study of Grantz and Yang (1996) stomatal conductance of Pima cotton was reduced by 41%, whereas hydraulic conductance decreased by only about 35% over a range of ozone concentrations from 0 to 0.111 ppm. Leaf water potential of ozone-exposed seedlings of Pima cotton was similar to or greater (wetter) than ozone-free controls (Grantz and Yang, 1996), similar to reports for upland cotton in which stomatal conductance was reduced by about 40% and leaf water potential increased (Temple, 1986, 1990a,b; Temple et al., 1988a). Similar observations have been made in alfalfa (*Medicago sativa* L.; Temple et al., 1988b), and red spruce (Lee et al., 1990). In more variable open field environments the conservation of shoot water status observed in these studies may not prevail. Orange trees exposed to high ozone concentrations exhibited substantially lower leaf water potentials than control trees on some days, but similar leaf water potentials on most days (Olszyk et al., 1991). The characteristics of these contrasting days were not explored.

ozone-inhibited allocation of biomass to roots could thus lead to reduced stomatal conductance and inhibited photosynthesis, a hidden cost of ozone exposure in lost productivity. Hydraulic linkage between edaphic (soil environment) conditions and stomatal response, and chemical communication from roots to shoot (e.g., Dodd et al., 1996) both have integrating roles in whole plant function, as indicated by the model of Grantz et al. (1999).

There is some evidence that ozone may exert direct effects on allocation (e.g., Grantz and Yang, 2000). Direct ozone-inhibition of carbon efflux from source leaves could reduce allocation to roots and indirectly inhibit carbon assimilation in the shoot. Loading of sugars into the phloem (i.e., the specialized, tube-like tissue that carries sugars between different plant organs) was reduced by ozone in several plant systems (McCool and Menge, 1983; McLaughlin and McConathy, 1983; Mortensen and Engvild, 1995; Grantz and Farrar, 1999). While carbon assimilation declines, translocation of carbon is inhibited to a greater extent. This was considered a possible mechanism to reduce R:S in the earliest research on ozone impacts (Tjoelker et al., 1995b). Indirect effects following from a putative

primary lesion in carbon translocation could include feed-back inhibition from accumulation of sugars in leaves, and degraded leaf water relations from constricted root development (Meyer et al., 1997; Grantz et al., 1999). End-product inhibition of photosynthetic carbon metabolism due to accumulation of soluble carbohydrates following ozone exposure alters metabolic activities and could reduce assimilation (Einig et al., 1997).

Exposure of foliage to ozone often results in accumulation of carbohydrate in source leaves due to reduced translocation to distant sinks (e.g., Hanson and Stewart, 1970; Spence et al., 1990; McCool and Menge, 1983; McLaughlin and McConathy, 1983; Gorissen and van Veen, 1988). Translocation of ^{13}C in *Phaseolus vulgaris* was rapidly inhibited by ozone (Okano et al., 1984). Uptake and accumulation of ^{11}C in stem tissues was inhibited by ozone in loblolly pine (*Pinus taeda* L.), with the total amount translocated reduced by about 45% (Spence et al., 1990). A delay in efflux was observed in this species for about 5 h, followed by an apparent acceleration in the loss of ^{14}C, attributed to ozone-enhanced respiratory losses (Friend and Tomlinson, 1992). Exposure to ozone reduced carbohydrate export from source leaves of *Plantago major* (Zheng et al., 2000), reduced the amount of ^{14}C transported to roots of clover (Blum et al., 1983), and at higher concentrations nearly abolished export of recent photosynthate from source leaves of cotton (Grantz and Farrar, 1999).

Rates of export from source needles and velocities of movement down the stem were not significantly affected in loblolly pine or wheat, though both trended downward (Mortensen and Engvild, 1995; Spence et al., 1990). The amount of carbohydrate translocated per unit time declined (Mortensen and Engvild, 1995; Fangmeier et al., 1994b), suggesting that phloem loading was inhibited.

In wheat (Meyer et al., 1997), birch (*Betula pendula*; Einig et al., 1997), and *Plantago major* (Zheng et al., 2002) ozone-impacts on carbon assimilation were attributed by the authors to such feedback inhibition. Photosynthetic capacity was reduced by end product inhibition due to girdling (cutting around the stem to disrupt the phloem) rather than ozone exposure in a variety of plants, particularly those such as cotton and cucurbits (e.g., melons, cucumbers and their relatives), in which carbohydrates are stored as starch (e.g., Goldschmidt and Huber, 1992). Feeding of glucose to a sucrose-storing species (spinach, *Spinacia oleracea*) reduced the activity and content of photosynthetic enzymes and pigments (Krapp et al., 1991).

In tomato (Ho 1976) and upland cotton (Hendrix and Peelen 1987), export of newly assimilated carbon in the light was proportional to leaf sucrose content in the absence of ozone exposure. In tomato, ozone increased retention of ^{14}C in source leaves (McCool and Menge, 1983). In wheat (Balaguer et al., 1995), ozone had no effect on carbon efflux in the light, but virtually abolished export in the subsequent dark period, resulting in enhanced retention of label in the source leaf. This is consistent with the ozone disruption of starch remobilization and carbohydrate translocation observed by Hanson and Stewart (1970). Efflux of label in darkness was generally related to starch content (Hendrix and Grange, 1991; Hendrix and Peelen, 1987), but this correlation was disrupted by exposure

to ozone. Export of label in the light was unrelated to starch content, and little starch was degraded in the light (Hendrix and Grange, 1991). In wheat (Balaguer et al. 1995), efflux and soluble sugar content covaried across a range of treatments in the absence of ozone. This relationship, too, was disrupted by exposure to ozone. Soluble sugars accumulated in Pima cotton subjected to chronic (Grantz and Yang 2000) and acute (Grantz and Farrar, 2000) ozone exposure, while translocation declined. ozone increased foliar concentrations of starch and fructans in wheat (Barnes et al., 1995) and other species. In poplar (*Populus* spp.) prior to visible senescence, soluble sugar contents increased with ozone (Fialho and Bucker, 1996), while starch was unaffected. With the onset of ozone-accelerated senescence, however, total foliar starch concentration declined and concentrated along the minor veins in bundle sheath cells, the sites of phloem loading. In seedlings and mature branches of Douglas fir (Gorissen and Van Veen, 1988; Smeulders et al., 1995) retention of recent photosynthate in a non-soluble fraction increased in needles following chronic exposure to ozone.

In other cases, carbohydrate concentrations declined. In Scots pine and Norway spruce (Peace et al., 1995) activities of sucrose phosphate synthase and sucrose-6-phosphatase, both active in sucrose synthesis, declined along with sugar contents following exposure to ozone. In aspen (Coleman et al., 1995), starch content declined following ozone-treatment. In a number of studies (soybean, Tingey et al., 1973, Miller et al., 1995; *Capsicum* spp., Bennett et al., 1979; upland cotton, Miller et al., 1989, Booker, 2000), sugar and often starch contents declined or were unchanged by ozone. In soybean, levels of soluble sugars and starch were reduced by ozone [65 or 95 parts per million hours (ppm-hr) sum of concentration times duration; Miller et al. 1995], while in cotton and bush bean, ozone-caused reductions in soluble protein were associated with increases in free amino acids (0.5 ppm-hr, Craker and Starbuck 1972, Ting and Mukerji 1971). Exposure to ozone reduced foliar starch and soluble sugar levels in red spruce (~550 ppm-hr, Amundson et al. 1991), starch in primary and secondary needles of loblolly pine (45 ppm-hr, Meier et al. 1990), soluble sugars in white pine and loblolly pine (Wilkinson and Barnes 1973), and total nonstructural carbohydrates and proteins in leaves, stems and roots of *Ulnus americana* (4.5 ppm-hr, Constantinidou and Kozlowski 1979). Carbohydrates in 1 year old needles of *Pinus ponderosa* declined with increasing ozone along a natural pollution gradient (Grulke et al., 2001). Monosaccharide and starch concentrations in fine roots also declined. Over shorter experimental exposures to ozone (9 days) (Smeulders et al., 1995) ozone increased retention of recent photosynthate within needles, though at the highest exposure (400 $\mu g/m^3$) needle starch declined. In these cases translocation could be substrate limited, as in brown rust-infected barley leaves (Tetlow and Farrar, 1993).

Reduced export of carbon from source leaves may be as effective as reduced assimilation in reducing source strength and decreasing carbohydrate allocation to sink tissues such as roots.

8.5 Crop Yield Loss Due to Ozone Damage

In 1987 (ARB 1987) a transition was occurring between evaluating ozone impacts on crops as visible injury (e.g., USEPA 1978), and attempts to assign specific and quantitative measures of damage associated with economic yield reduction (e.g., ARB 1987; USEPA 1986, 1996a). This change coincided with implementation of the studies of the National Crop Loss Assessment Network (NCLAN; summarized by Heck, 1988a) and resulting publications assessing quantitative exposure-yield loss relationships. These studies were conducted in open top field exposure chambers in multiple locations in the U.S., and used commercial cultivars and agronomic techniques appropriate to each location. The details of experimental design and statistical analytical protocols have been considered in detail (USEPA, 1986; Heck et al., 1988a). Crop loss was parameterized using mean ozone concentration (e.g., over 7 or 12 hour daylight periods, 7 hm, 12 hm), or in later studies, a Weibull function (a sigmoidal weighting scheme that emphasizes higher, peak, concentrations). The flexibility of Weibull functions facilitated use of common statistical models across multiple studies during retrospective analyses (Lesser et al., 1990).

The trend toward damage assessment rather than injury description has developed further with additional studies and resulting publications. Because it was concluded in the previous document (ARB, 1987) that many of the NCLAN response relationships may not be directly applicable to California, further studies funded by the ARB were conducted under California conditions.

NCLAN studies were limited to five sites, intended to represent, coarsely, the entire U.S. While one of these sites was in the southern San Joaquin Valley of California, four were in the humid Midwest and East (Heck et al., 1988a). The arid, irrigated, agricultural production practices of California were thus not emphasized in these national studies; composite yield loss equations are weighted toward the humid production areas. Those yield loss equations generated under California conditions, i.e., for alfalfa (*Medicago sativa*), cotton (*Gossypium hirsutum*), barley (*Hordeum vulgare*), lettuce (*Lactuca sativa*) and tomato (*Lycopersicon esculentum*), are representative of only one location with its particular climate, soils, and other undefined production characteristics.

Much of the NCLAN research was devoted to crops not grown in California, particularly soybean (*Glycine max*), or to crops that dominate U.S. agriculture but not that of California, such as maize (corn, *Zea mays*) and wheat (*Triticum aestivium*). The highly diverse, and unique, production of California is necessarily poorly represented by any such national survey. The high value fruit and nut crops of the San Joaquin Valley were not represented at all. The more recent studies, including those reviewed by ARB (1987) attempted to represent yield losses for California agriculture, in a coarse survey fashion, much as the NCLAN studies represented U.S. agricultural losses.

It is clear that humidity and temperature influence plant growth and productivity (Mills et al., 2000; Benton et al., 2000). It is not well established how these impacts on growth scale to impacts on sensitivity orf yield to ozone exposure. As

it is not currently possible to predict ozone sensitivity from environmental conditions, and production conditions even within California are highly variable, there seems to be little scientific justification to exclude studies conducted elsewhere from consideration of yield loss in California. This is particularly so if the plant species, if not cultivar, is relevant to California agriculture. The current (and foreseeable) limitation of exposure studies to a small fraction of those agricultural genotypes grown in California can be expanded with these studies performed elsewhere.

The limited number of specific crops for which ozone-yield loss equations are available should not imply that conclusions cannot be drawn regarding ozone impacts on agricultural production. This was addressed in the context of standard development in Germany (Grunhage et al., 2001) through a meta-analysis of studies using a wide variety of crop species. The data assembled for this section (Tables 6-11) are restricted to crop species of relevance to California, but are drawn from exposure experiments conducted at many locations, generally in the U.S. and Europe.

A major limitation to the available exposure-response data base is its limitation to a very small number of plant species and genotypes. There is considerable genetic diversity among even closely related plants (Warwick and Taylor, 1995; Volin et al., 1998), and even between cultivars of the same domesticated crop species (Benton et al., 2000; Hormaza et al., 1996; Alscher and Wellburn, 1994; Pell et al., 1993; Bell and Treshow, 2002). This contributes to the observed large variation in plant exposure-response relationships, including crop yield loss, following controlled exposures to ozone. A multitude of plant response relationships is to be expected under these conditions, and has been observed. Extrapolation of these limited data, covering a few, largely domesticated, species to the plant kingdom in general has proven contentious. Nevertheless, a complete test of all possible genetic backgrounds in all possible environmental conditions is not feasible (Taylor et al., 1994) and generalization from limited data will be required for the indefinite future (Kickert and Krupa, 1991; Kickert et al., 1999). This is currently hindered by poorly characterized genetic determinants of ozone sensitivity (Pell et al., 1993, 1997). Extrapolation of controlled experiments to the larger ambient environment will be facilitated by greater physiological and genetic understanding, and by development of process models that adequately incorporate interactions between genetic characteristics such as antioxidant defenses, gas exchange behavior, environmental conditions, and ozone exposure dynamics. Unfortunately, existing models require further development to be applied in this way.

Recent efforts to model effective ozone fluxes (Grunhage et al., 2001; Massman et al., 2000) have the capability to integrate response relationships from ambient and a variety of experimental exposure technologies. But appropriate empirical parameterizations must still remain limited to a few genotypes due to experimental constraints of time and resources.

The NCLAN crop loss data judged appropriate to California conditions were summarized in the previous document (ARB, 1987). Some exposures led to

small yield increases, but no increases were statistically significant. It was concluded that ozone reduces crop yield (ARB, 1987) based largely on the studies of Thompson and Olszyk (1986).

Trees and vines (perennial crops) and annual crops each account for about 50% of California's primary agricultural crop production (2001 values). Among the top 50 agricultural commodities in California there are nearly twice the number of annual as perennial crop species. There are hundreds of crops grown commercially in California. From available yield loss vs. ozone relationships determined over prolonged periods under near commercial conditions, it appears that both perennial crops (trees and vines) and annual crops contain both sensitive and tolerant species among those that dominate California agriculture (cf. Tables 6,7,8,9).

In all classes of crops, only a small fraction of those grown in California have been investigated. Of these, yield loss equations vary widely (see Table 6, below; ARB, 1987; USEPA, 1986, 1996a). The interactions considered above suggest that it may never be possible to identify a single threshold ozone concentration that elicits yield reduction, even generalized between closely related species in a single location, or the same genotype grown in different locations.

A concern with all exposure technologies is specification of a control concentration of ozone against which relative loss can be calculated. In many cases charcoal filtered air mixes with incursion of ambient air in open top chambers (OTCs) to yield a concentration suitably near that of pristine sites (about 25 ppb). However, this concentration is not uniform spatially nor temporally, with estimates up to 40 ppb or higher under some conditions (Lefohn et al., 1990). In studies to be analyzed by regression analysis, a very low control concentration may anchor the relationship, and relative yield loss can be calculated between any two concentration points along the regression line.

The material above provides a general framework and rationale for ozone damage to crop plant species at ambient concentrations of ozone. The following considers the specific evidence for yield loss in specific crops grown in California. The studies considered here compute ozone damage to economic yield relative to various control concentrations of ozone. Given the uncertainties inherent in the crop loss functions themselves, this variability is not considered dominant, and is not explicitly considered unless uniform for a set of data (e.g., Tables 6,7).

8.5.1 Annual Crops

Many annual crops are grown for their reproductive parts (fruits, seeds). For example, time to reproductive development was decreased and pollen germination was inhibited in *Brassica campestris* (Stewart et al., 1996). It remains unclear whether ozone directly impacts reproductive development, or whether impacts on yield are secondary effects of primary lesions in the carbohydrate economy. These issues have been reviewed (Black et al., 2000; Stewart et al., 1996).

It has been considered that such crops may be particularly sensitive to ozone exposure during the period in which carbohydrate is actively allocated to fruit expansion or grain filling, whereas biomass crops such as leafy vegetables may be more evenly sensitive over the entire growing period (Lee et al., 1988; Younglove et al., 1994; Soja et al., 2000). However, such simplifying generalizations may be misleading, as biomass crops are vulnerable both in development of a robust root system, which is sensitive to ozone-inhibition throughout the growing period, and to biomass production, particularly during the brief periods between cuttings for multiply harvested crops, such as forages and alfalfa. Similarly, those species grown for reproductive structures may exhibit reduced yield capacity due to season-long exposure, if this results in impaired growth of vegetative portions of the shoot or root that must support (structurally and nutritionally) the yield components.

Using available ozone exposure/crop loss equations, with local ambient ozone concentration data and a GIS-based approach, crop loss due to ozone over a period of several years was estimated for California (Tables 6,7). The important yearly assessments of potential yield losses have been conducted in California by Mutters and colleagues (Mutters et al., 1993; Mutters and Soret, 1995, 1998). These studies have inserted a new ozone concentration data set into the same yield loss equations determined in California and elsewhere. This accounts for the similar estimates of yield loss predicted over the several years of the study (Tables 6,7) as ozone concentrations change only moderately from year to year.

These studies have advanced the science of crop yield reduction estimation by incorporating a geographic information system approach to merging land use (crop cover) with interpolated values of ambient ozone concentration. This finer grid analysis allows the specific crop and the actual ozone exposure to be mated for an accurate calculation of estimated yield loss. The subsequent summation of these calculated values over county or statewide areas improve the regional loss estimation. This improvement led in both annual and perennial crops, to a reduction in estimated yield suppression due to tropospheric ozone (Tables 6,7,8,9).

However, it remains unlikely, as noted by Adams et al. (1988) that either spatial or temporal variation in ambient ozone concentration is the largest contributor to uncertainty in crop yield sensitivity to ozone in the environment. A larger contributor is the actual yield loss equations, themselves, an area in which there has been an unfortunate lack of progress, in the USA and particularly in California, since the last such review of the subject (ARB, 1987). Progress in Europe over this time period has been considerably greater.

Among annual crops these data range from about no loss in grain sorghum to about a 30% loss in cantaloupe. Among perennial crops, alfalfa exhibited under 10% loss, while grapes exhibited about a 25% loss, statewide. The trends for most crops are for increasing losses. These equations, largely generated in OTC experiments, remain adequate at the present time. Thresholds for specific values of loss can be easily derived from the equations assembled by Mutters et al.

(1993) and Mutters and Soret (1995, 1998), from which the values in these tables were taken.

A number of crop loss studies have appeared since the last document (ARB, 1987). Some were considered in Tables 6 and 7. Many were performed in Europe. These studies are listed in comprehensive fashion in Table 8 for annual crops and Table 9 for perennial crops.

In addition to economic damage (yield loss) due to ozone, a variety of quality, aesthetic, or physiological endpoints are also degraded by ozone. These are considered in less comprehensive fashion in Table 10 for annual crops and Table 11 for perennial crops.

Only a few comments follow on several important California crops.

8.5.1.1 Cotton

Yield of upland cotton over two years was reduced in North Carolina by 21 and 22% when exposed season-long to 12 hm ozone concentrations of 71 and 51 ppb (Heagle et al., 1999). In the second year a larger reduction of 49% was induced by 78 ppb (Table 8).

ozone reduces yields of adapted upland cotton (*Gossypium hirsutum* L.) cultivars by up to 20% in the San Joaquin Valley of California (Grantz & McCool 1992; Olszyk et al. 1993; Oshima et al. 1979; Temple et al. 1988a), despite many cycles of yield selection with ozone-pressure. Yield and productivity of Pima (*G. barbadense* L.) cotton cultivars, selected in low-ozone environments and introduced into California, are even more sensitive (Grantz & McCool 1992; Olszyk et al. 1993). More recently developed cultivars of Pima cotton, selected in the San Joaquin Valley, appear to exhibit reduced ozone-sensitivity.

8.5.1.2 Rice

Nouchi et al., (1991) found no impact on yield at 50 ppb, though this was performed in hydroponic culture in growth chambers. Kats et al. (1985) found 12-21% at 200 ppb (5 h/day constant, a particularly high concentration relevant to California production in the San Joaquin Valley in the 1980s, but not relevant to the major production areas in the Sacramento Valley nor to current conditions in the San Joaquin Valley. In contrast, in Japan exposure to 7 hm concentrations of 40 ppb reduced yield by 3-10% (Kobayashi et al., 1994,1995a; Table 8). It is likely but unproven that the California cultivars may exhibit some level of enhanced ozone tolerance due to yield selection under ozone pressure.

8.5.1.3 Wheat

A number of cultivars of wheat have been investigated. All have some relevance to the California situation, though none is directly applicable to a specific production scenario in California. No effort is made here to distinguish between even widely divergent germplasm. Field exposures in OTCs of potted wheat plants (Fangmeier et al., 1994b) found that yield was suppressed by 35% in 7 hm = 71 ppb. Studies in Maryland found 20% reductions with 7 hm = 61-65 ppb (Mulchi et al., 1995; Rudorff et al., 1996a; Table 8). Similar exposures in North

Carolina to 12 hm exposures of 74 and 90 ppb over two years reduced yield but not significantly (Heagle et al., 2000). Combined data from multiple years of investigation in OTCs in Sweden (Danielsson et al., 2003) found a 23% loss in yield of wheat at AOT40 = 15 ppm-hr. These data were also examined for superior predictive performance of an ozone metric involving ozone flux (Emberson et al., 2000). In this case the flux approach improved the exposure (dose)-response relationship, but only slightly (r^2 = 0.34 to 0.39). A similar analysis of multiple experiments conducted under the ESPACE-WHEAT program (e.g., Bender et al., 1999) in Europe found a non-significant 13% reduction in yield at 12 hm = 51 ± 18 ppb and AOT40 = 28.2 ± 23.0 ppm-hr. Bender et al. (1999) did find a significant relationship with 12 hm. Exposure in OTCs in Finland (Ojanpera et al., 1998) reduced yield by 13% at 12 hm = 45 and 61 ppb over two seasons. A study from multiple sites in Europe (Fuhrer et al., 1997 found that an AOT40 = 2.8 ppm-hr caused a 5% yield loss, and AOT40 = 5.7 ppm-hr caused a 10% loss.

A free-air exposure of wheat (Ollerenshaw and Lyons, 1999) to AOT40 = 3.47 ppm-hr in the autumn and 6.18 in spring-summer (winter wheat) reduced yield by 13%.

Grain quality is also affected by exposure to ozone. The major effect seems to be a general inverse relationship between yield (which is suppressed by ozone) and grain protein content (e.g., Gelang et al., 2000).

8.5.2 Perennial Crops

As noted above for annual crops, many perennial crops are grown for their reproductive parts (mostly fruits). Thus the particular sensitivity of reproductive organs to ozone damage is also of considerable potential interest in these crops (e.g., Black et al., 2000). The same caveats apply, enhanced sensitivity to ozone exposure during fruit development may mask the season-long sensitivity as robust vegetative shoot scaffolding and root supporting structures are required for subsequent high yield potential (Lee et al., 1988; Younglove et al., 1994; Soja et al., 2000). Crops grown for biomass such as alfalfa, may be more sensitive to the entire growing season exposure, but the yield of a particular cutting may also respond to exposure during the brief period between cuttings in which currently displayed foliage is exposed to ambient ozone.

As observed in both perennial and annual crop species (Tables 8-11) the variability in ozone sensitivity varies within closely related species and even cultivars as much as it does across distantly related crop species.

8.5.2.1 Alfalfa

Averaged over two years of open top chamber exposures in the San Joaquin Valley, alfalfa yield was suppressed by about 10 % at ambient concentrations of ozone (Temple 1988b). The two years data were consistent despite modest inter-annual differences in ozone concentrations. Water deficit reduced yield in both years. In one year (1985, but not 1984) the sensitivity to ozone was reduced, though at a vastly reduced yield level in the absence of oxidant.

A relatively sensitive northern cultivar of alfalfa was reduced by 31% in a year with many peak exposures above 60 ppb and by 21% in a year with many fewer peak episodes. A more tolerant cultivar was reduced by 14% in the year with many peaks but not significantly in the year with fewer peak exposures (Renaud et al., 1997).

8.5.2.2 Stone Fruit

Stem growth (i.e., production of woody shoot material that does not contribute directly to reproduction or economic yield) of plums was increased by 14% in 12 hm = 91 ppb in Casselman plums grown in the San Joaquin Valley in large rectangular OTCs (Retzlaff et al., 1997). This growth may have come at the expense of the root systems during the 4 year exposure experiment (root biomass was not measured). Fruit yield was reduced by 42%. The ambient treatment of 12 hm = 48 ppb reduced fresh fruit yield by 16%.

Pollen germination was inhibited in a variety of deciduous fruit trees of horticultural importance or their ornamental relatives, including apple (*Malus domoestica*), apricot (*Prunus armeniaca*), almond (*Prunus dulcis=amygdalus*), peach (*Prunus persica*), and pear (*Pyrus communis*) (Hormaza et al., 1996). Ozone-induced changes in pollen tube extension were correlated with responses of photosynthetic carbon assimilation. It is not yet clear whether this indicates an indirect effect of reduced carbohydrate supply on the development of reproductive structures such as pollen tubes, or whether it is evidence of direct oxidant effects of ozone on these delicate structures. In either case, disruption of reproductive processes is likely to have deleterious consequences on economic yield.

8.5.2.3 Strawberry

Strawberry is a perennial plant grown as an annual in California. It has been found repeatedly to be relatively tolerant of ozone, particularly for total fruit yield, both in California and in Britain (Takemoto et al., 1988b; Drogoudi and Ashmore, 2000). Individual berry size, however, has variously been found to increase by 20% (California) and to decrease by 14% (Britain).

8.5.3 Summary and Economic Assessment

The national assessment of ozone-induced crop loss undertaken in USEPA (1996a) concluded that over half (58%) of crop species or cultivars would be expected to sustain a 10% yield reduction at ozone concentrations at or above 50 ppb (7 hm), with 34% between 40 and 50 ppb, and a much smaller fraction (11%) below 35 ppb. Various retrospective analyses of NCLAN data (Lesser et al., 1990; Lee et al., 1994) concluded that about 10% of major crops would exhibit yield suppression by ozone at 12 hm concentrations of 45 ppb, 7 hm of 49 ppb, or SUM06 values of 26.4 ppm-hr. The estimate that 40-50 ppb ambient ozone concentrations are damaging to production of about half of crops investigated has remained relatively conserved from USEPA (1978) through USEPA (1986) and USEPA (1996a). The most recently available data does little to challenge this conclusion. A consensus developed among ozone plant effects

specialists was that ozone concentrations greater than or equal to 0.06 ppm, summed over any 90-day period, during daylight hours (0800-2000 LST) should not exceed 15-20 ppm-hr (SUM06; Heck et al., 1998; Heck and Furiness, 2001) to avoid damage to a wide range of agricultural crops. A similar consensus in Europe led to development of AOT40 (Fuhrer et al. 1997), a similar summation of the amount by which ozone concentrations exceed 40 ppb, also for daylight hours over a 90-day period. Values in excess of 3 ppm-hr were considered damaging to sensitive agricultural crops (Karenlampi and Skarby, 1996).

Extremely sensitive cultivars (11% in the national assessment) would not be expected to be retained in California production areas characterized by high concentrations of ozone. In such areas an informal, ad hoc selection of ozone resistant cultivars has taken place, with those showing ozone symptoms or yielding poorly in polluted environments simply removed from the planting lists of growers and from the advanced breeding lines of cultivar development programs. In contrast, the 58% of crops exhibiting yield reductions below 7 hm concentrations of 50 ppb are unlikely to be removed consistently from California production, but are highly likely to exhibit yield reductions directly attributed to ambient ozone concentrations.

Of particular interest to California agricultural production systems, 18% of those cultivars tested nationwide (USEPA, 1996) were sufficiently resistant to ozone impacts that no yield reduction was likely below 80 ppb (7 hm). Grain crops have typically exhibited less sensitivity to ozone than many other crops, particularly those for which foliage is the marketable commodity.

It was considered by USEPA (1986) and reaffirmed by USEPA (1996a) that tropospheric ozone, at then current ambient concentrations, imposed a substantial economic cost to agricultural production on a national scale. The studies of Kopp et al., (1985) and Adams et al., (1986) and the welfare model studies reviewed by Adams et al. (1988) are considered to have incorporated as many relevant interactions within the economy as feasible. In the previous ARB (1987) document, benefits of reducing ozone concentrations in California to background levels (assumed to be 0.025 ppm) were found to be about 5-6% for both producers and consumers, relative to the economic benefit of the agricultural sector in total. However, this estimate only utilized yield losses on 15 of California's major crops, a small fraction of the total.

The recent review by Spash (1997) confirms the conclusion that current ambient ozone concentrations impose a substantial cost to both producers and consumers of agricultural products. The recent national study of Murphy et al. (1999) specifically of ozone derived from motor vehicle emissions in the U.S. also confirms these conclusions. This study suggested a total economic impact of ambient ozone (in 1990 dollars, relative to background of 0.025 ppm) of $2.8 – 5.8 billion USD. This study applied the same welfare modeling approach as Adams et al. (1986) but also underestimated the true impact, as only 8 major crops nationwide were considered. Various economic assessments have been considered by Mauzerall and Wang (2001).

The recent valuation of ozone reduction benefits in California's heavily agricultural San Joaquin Valley (Kim et al., 1998) found small effects of ozone on health endpoints, due to low population density, but large impacts on agricultural productivity. Costs of ozone control were also considered. A cost benefit analysis, based on the range of crop loss predictions from the previous document (ARB 1987) revealed substantial benefit to the agriculturally dominant central Valley counties of Tulare, Kings, Fresno and Madera. However, in other areas of the northern or southern Valley, which have lower production of crop value and larger production of ozone precursors, there were net costs of meeting any 24 h peak standard below about 150 ppb. This ozone concentration is well above those known to damage crop yield.

Table 8-1. Exposure technologies in increasing order of applicability to field systems and decreasing order of experimental control and reproducibility.

Exposure Technology	Types	Principal Characteristics
Controlled Systems	Controlled Environment Chambers;	High level of environmental and exposure control; Reproducible; Highly suitable for mechanistic studies; Difficult to extrapolate directly to field environment
Managed Systems	Greenhouse Chambers;	Intermediate level of environmental and exposure control; Intermediate reproducibility; Intermediate applicability to field environment
Seminatural Systems--Field Chamber Systems	Closed Top Chambers; Open Top Chambers	
Seminatural Systems--Field Chamberless Systems	Mechanical Field Exclusion; Chemical Exlusion; Open Field Exclusion	
Natural Systems	Gradients; Field surveys	Poor level of environmental and exposure control; Not reproducible; Directly applicable to field environment

Table 8-2 Open-top chamber effects on microclimate (after Heagle et al.,1988)

Variable	Effects in chamber plant-growth area	References
Air temperature	Increases of up to 3.7°C, but usually less than 2.0°C; greatest increase on calm, sunny, and hot days at midday; mean seasonal increase probably less than 1.0°C	Heagle et al., 1973 Heagle et al., 1979*b* Olszyk et al., 1980 Weinstock et al., 1982
Leaf temperature	Slight increase by amounts caused by chamber effects on air temperature.	Weinstock et al., 1982
Light (PAR)	Decreased by as much as 20%; greatest decrease with low sun angle on sunny days; mean seasonal decrease approximately 12%; in northern hemisphere, north chamber positions receive more light than southern positions: Normal vertical gradient (decreased light with increased height) in plant canopy at chamber periphery does not exist if border row plants are not adequate.	Heagle et al., 1979*b* Olszyk et al., 1980
Windspeed	Seasonal mean velocity decreased; but velocity never less than 2-3 km h^{-1}, in chambers; for plants taller than 120 cm, more air movement near base of plant canopy than near top during calm periods.	Heagle et al., 1979*b* Weinstock et al., 1982
Relative humidity	Up to 10% increase or decrease depending on ambient conditions, soil moisture, and type of plant canopy; usually less than 5% difference.	Heagle et al., 1973 Weinstock et al., 1982
Dew point	Up to 2.0°C higher when	Weinstock et al., 1982

	maximum differences in air temperatures occur; less than 0.5°C when cloudy or at night.	
Rainfall	Less direct rainfall at some chamber positions when rain is accompanied by wind; rain intercepted by panels is concentrated at base of chamber walls.	Weinstock et al., 1982

Table 8-3 Physiological and biochemical processes that are believed to be affected directly or indirectly by ozone exposure in crop plants. As the primary target of ozone impact has not yet been determined, these processes are those for which some consensus has emerged based on available data. Other processes, at other levels of biological organization, will likely be found to be affected in the future.

Process	**Impact**
Membrane Permeability	Increased with loss of selectivity
Chloroplast Ultrastructure	Degraded
Photosynthesis	Inhibited
Respiration	Enhanced or Inhibited
Protein Metabolism	Enhanced or Inhibited
Carbohydrate Metabolism	Enhanced or Inhibited
Carbohydrate Translocation	Inhibited
Lipid Metabolism	Degradation and Inhibited Synthesis
Ethylene Production	Increased

Table 8-4 The effect of ozone exposure on growth and allocation among plant groups. Shown are the number of total observations of ozone impacts surveyed in the literature, the number and percent of the total that led to significant results (whether positive or negative), the percentage of significant exposures that yielded negative changes in RGR[1] or k[2], the percentage of total exposures that yielded negative changes in RGR[1] or k[2], and the percentage of total exposures that yielded positive changes in RGR[1] or k[2].

Biological Endpoint	Plant Group	Total Ozone Exposures In Surveyed Literature	Significant Effects of Ozone on RGR or k (% Total Ozone Exposures)	% Significant Effects Yielding a Decrease in RGR or k	% Total Ozone Exposures Yielding a Decrease in RGR or k	% Total Ozone Exposures Yielding an Increase in RGR or k
RGR	Dicotyledonous	75	47 (63)	100	89	5
	Monocotyledonous	14	4 (28)	100	86	8
	Tree	8	0 (0)	na[3]	100	0
	All	97	51 (53)	100	90	5
k	Dicotyledonous	84	20 (24)	80	51	33

	Monocotyledonous	16	9 (56)	56	62	38
	Tree	8	2 (25)	100	75	12
	All	108	31 (29)	74	55	32

[1]RGR, Relative Growth Rate, defined as the difference in the dry weight of a plant or plant part over a time period, divided by the initial dry weight and the length of time.

[2]k, the allometric growth coefficient that describes the distribution of dry weight gain between competing plant parts, defined as the ratio of Relative Growth Rates of different plant parts.

[3]na=not available due to lack of significant effects.

Table 8-5 The effect of elevated ozone on mean whole plant relative growth rate (RGR) and root/shoot allometric coefficient (k). Values are the mean % change ± the standard error calculated from aggregated data without regard for the statistical significance of the individual original observation[a].

	RGR	k
Herbaceous dicotyledons	-7.8 % ± 0.7* n = 75	-2.4 % ± 1.0* n = 75
Herbaceous monocotyledons	-4.2% ± 0.8*** n = 14	-6.4 % ± 5.4 n = 14
Trees	-16.8 % ± 5.0* n = 8	-14.6% ± 16.3 n = 8

[a]From the publications summarized in Appendix Table 1.

*, **, *** = P < .05, .01, .001, respectively.

Table 8-6 An historical view of California statewide loss (%) estimation for selected annual crops, relative to 12 hm of 25 ppb or 7 h mean of 27.2 ppb.

Crop	Experimental Ozone Exposures Considered in ARB 1987[1]		Estimated Losses Sustained under Ambient Conditions					
	Range of Experimental Yield Losses[1]	Maximum Exposure[1]	1984 Yield Loss[2]	1989 Yield Loss[3]	1990 Yield Loss[4]	1991 Yield Loss[5]	1992 Yield Loss[6]	1993 Yield Loss[7]
Bean-Dry	46-100	0.35 ppm x 63 days	27.2	10.3	17.3	9.9	8.8	17.5
Cantaloupe	na[8]	na	na	29.8	30.2	31.5	32.3	32.8
Cotton	5-29	ambient x growing season	19.6	16.9	20.3	19.2	17.4	23.3
Lettuce	na	na	na	0.3	0.4	0.3	0.4	0.5
Maize-Field	<0-40	0.15 ppm x 88 days	1.7	na	na	na	na	1.2
Maize-Silage	na	na	3.5	2.6	1.8	1.8	7.5	na
Maize-Sweet	0-45	0.35 ppm x 71 days	6.1	4.5	4.8	5.7	5.8	na
Onion	na	na	23.2	17.4	10.4	11.3	8.9	10.6
Pepper	19-50	0.20 ppm x 77 days	na	na	na	na	na	na
Potato	25-42	0.20 ppm x 140 days	na	16.4	13.7	na	na	na
Rice	na	na	10.4	4.2	3.3	3.5	4.9	3.9
Sorghum-grain	na	na	na	0.7	0.6	0.6	0.5	na
Tomato	1-45	0.35 ppm x 99 days	na	0.9	0.5	0.5	0.6	0.6

Tomato-Processing	na	0.35 ppm x 99 days	4.5	3.9	6.5	3.0	3.4	6.8
Wheat	1-43	0.13 ppm x 53 days	1.7	5.3	6.9	5.3	5.1	6.7

[1]Table III-3 from ARB (1987) originally from USEPA 1986, describing the full range of experimental observations.

[2]Table III-26 from ARB (1987), based on measured average California ozone concentrations.

[3]Table 5; Mutters et al. (1993); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[4]Table 6; Mutters et al. (1993); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[5]Table 7; Mutters and Soret (1995); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[6]Table 8; Mutters and Soret (1995); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[7]Table 3, Mutters and Soret (1998); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[8]na, not available.

Table 8-7 An historical view of California statewide loss estimation for selected perennial crops.

Crop	Experimental Ozone Exposures Considered in ARB 1987[1]		Estimated Losses Sustained under Ambient Conditions relative to 12 h Mean of 25 ppb or 7 h Mean of 27.2 ppb					
	Range of Experimental Yield Losses[1]	Maximum Exposure[1]	1984 Yield Loss[2]	1989 Yield Loss[3]	1990 Yield Loss[4]	1991 Yield Loss[5]	1992 Yield Loss[6]	1993 Yield Loss[7]
Alfalfa	10-51	0.20 ppm x 70 days	7.6	4.8	7.3	8.5	8.5	9.5
Grape	12-61	0.25 x season	20.8	17.0	23.0	23.2	23.4	25.0
Grape-raisin	na[8]	na	na	20.3	26.1	27.2	26.6	26.2
Grape-table	na	na	na	22.4	27.4	27.2	24.4	29.9
Grape-wine	na	na	na	12.9	19.0	19.0	20.2	22.8
Lemon	32-52	0.1 x season	28.3	8.9	8.9	8.2	9.2	8.4
Orange	na	na	19.3	32.5	15.7	12.6	13.9	14.0

[1]Table III-3 from ARB TSD 1987 originally from USEPA CD (1986), describing the full range of experimental observations.

[2]Table III-26 from ARB TSD 1987, based on measured average California ozone concentrations.

[3]Table 5; Mutters et al. (1993); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[4]Table 6; Mutters et al. (1993); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[5]Table 7; Mutters and Soret (1995); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[6]Table 8; Mutters and Soret (1995); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[7]Table 3, Mutters and Soret (1998); 7 hm and 12 hm exposure models only, based on measured average California ozone concentrations.

[8]na, not available.

Table 8-8 Summary of studies published since publication of ARB (1987) demonstrating, under field conditions, ozone damage to economic yield of annual crops of relevance to California[1].

Crop Species	Exposure Technology	ozone Exposure	Summary of Ozone Impact (% loss)	Original Reference
Barley	OTC	7 hm=29 7 hm=45	No effect	Pleijel et al., 1992
Bean, fresh	OTC	7 hm = 63 ppb	>10	Eason and Reinert, 1991
Bean, fresh	OTC	12 hm = 45 ppb	15.5	Schenone et al., 1992
Bean, fresh	OTC	7 hm = 55-60 ppb	26 (sensitive cv.)	Heck et al., 1988b
Bean, fresh	OTC	8 hm = 80 ppb	20	Bender et al., 1990
Bean, fresh	OTC	9 hm = 44 ppb	29	Tonneijck and van Dijk, 1998
Beans, fresh[2]	OTC	AOT40=1600 AOT40=1700 AOT40=8212 ppb-hr=7 hm=40.4 ppb	5 10 21.4	Fumagalli et al. (2001a)
Bean, fresh[3]	OTC	7 hm = 26 ppb 7 hm = 50 ppb	+48[4] 42	Sanders et al., 1992a
Bean, fresh	OTC	7 hm = 45-50 ppb	18-31	Schenone et al., 1994
Bean, dry	OTC	12 hm = 72 ppb	55-75	Temple, 1991

Bean, dry[5]	OTC	7 hm = 38-39 ppb	10-11	Sanders et al., 1992b
Bean, dry	OTC	7 hm = 58 ppb	51	Sanders et al., 1992b
Beet	Closed Field Chambers	12 hm=25.0 ppb or SUM01=3860 ppb-hr 12 hm=62.6 ppb or SUM01=9650 ppb-hr	10 25	McCool et al., 1987
Celery	OTC	12 hm=66 ppb	12	Takemoto et al., 1988b
Cotton	OTC	12 hm = 44 ppb	19	Heagle et al., 1988b
Cotton	OTC	12 hm = 74 ppb	26.2	Temple et al., 1988a
Cotton	OTC	12 hm = 90 ppb	40-71	Temple, 1990c
Cotton	OTC	12 hm = 71 ppb	22	Heagle et al., 1999
Cotton	OTC	12 hm = 51 ppb 12 hm = 78 ppb	21 49	Heagle et al., 1999
Cotton	OTC multisite	7 hm = 23-53 ppb NF 7 hm = 31-56 ppb AA	0-20	Olszyk et al., 1993
Lettuce	OTC	12 hm=36 12 hm=63	No effect	Temple et al., 1990

Lettuce	Closed Field Chambers	SUM01=1930 ppb-hr SUM01=4820 ppb-hr	10 25	McCool et al., 1987
Maize, field	OTC	7 hm = 70 ppb	13	Mulchi et al., 1995 Rudorff et al., 1996a
Muskmelon	OTC	7 hm=30-40 over 2 years	21.3	Snyder et al., 1988
Onion	OTC	12 hm=36 12 hm=63	5	Temple et al., 1990
Onion	Closed Field Chambers	12 hm=12.6 ppb or SUM01=1680 ppb-hr 12 hm=31.5 ppb or SUM01=4190 ppb-hr	10 25	McCool et al., 1987
Pepper, green		12 hm=66 ppb	12	Takemoto et al., 1988b
Potato	OTC	8 hm 60 ppb	5.2	Craigon et al., 2002
Potato	OTC	8 hm 50 ppb	No effect	Lawson et al., 2001
Rice	OTC	5 hm = 200 ppb	12-21	Kats et al., 1985
Rice	OTC	7hm = 40 ppb	3-10	Kobayashi et al., 1995a
Tomato	OTC	12 hm=109 ppb	17-54	Temple 1990c
Turnip	Closed Field Chambers	12 hm=15.1 12 hm=37.9	10 25	McCool et al., 1987

Turnip	OTC	7 hm=40 ppb 7 hm=60 ppb	7 24	Heagle et al., 1985
Watermelon	OTC	7 hm= 27 ppb	20.8	Snyder et al., 1991
Watermelon[6]	OTC	S06= 295 ppb-hr S06= 4950 ppb-hr	19 39	Gimeno et al., 1999
Wheat	OTC	7 hm=42ppb 7 hm=54 ppb	33 22	Kohut et al., 1987
Wheat	OTC	24 hm = 40 ppb	13	Fuhrer et al., 1989
Wheat	OTC	AOT40=80-93.5 ppm-hr	48-54	Grandjean and Fuhrer, 1989
Wheat	OTC	7 hm=15-22 ppb	7	Pleijel and Skarby, 1991
Wheat	OTC	8 hm=17-23 ppb	10	Adaros et al., 1991
Wheat	OTC	8 hm=38 ppb	5	De Temmerman et al., 1992
Wheat	OTC	7 hm=37-45 ppb	9.5-11.6	Fuhrer et al., 1992
Wheat	OTC	AOT40=15 ppm-hr	23	Danielsson et al., 2003
Wheat	OTC	12 ht=32.6 ppm-hr 12 ht=33.4 ppm-hr 12 ht=34.0 ppm-hr	53 +17 17	Finnan et al. 1996a
Wheat	OTC	7hm=61 7hm=65	20 20	Mulchi et al., 1995 Rudorff et al., 1996c
Wheat	OTC	7h=73	35	Fangmeier et al., 1994b

Wheat	OTC	12h=61/45 ppb AOT40=54.6/40.6 ppm-hr	13/13	Ojanpera et al., 1998
Wheat	Chamberless	AOT40=6.18 ppm-hr Daily mean=80	13	Ollerenshaw and Lyons 1999

[1]Adapted from USEPA (1996a) and later publications.

[2]Mean of 4 cultivars x 2 locations x 3 years; interpolation from Mauzerall and Wang, 2001.

[3]Data indicate an apparent biphasic response, with mostly non-significant yield increases at moderate ozone concentrations, and yield suppression at higher ozone concentrations. Data shown are those concentrations that yield statistically significant differences, relative to CF air (7 hm = 10 ppb).

[4]+ indicates an increase due to ozone exposure.

[5]Similar yield responses were obtained at similar ozone exposures despite different experimental locations and ozone exposure dynamics.

[6]Mean of two years data.

Table 8-9 Summary of studies published since publication of ARB (1987) demonstrating under field conditions ozone damage to economic yield of perennial crops of relevance to California[1].

Crop Species	Exposure Technology	ozone Exposure Averaging Period/Concentration	Summary of Ozone Impact (% loss)	Original Reference
Alfalfa	OTC	12 hm=63 ppb 12 hm=78 ppb	15 19	Temple et al., 1988b
Alfalfa	OTC	12 hm=40 ppb 12 hm=66 ppb	2.4 18.3	Temple et al., 1987
Alfalfa	OTC	12 hm=53 ppb	22	Takemoto et al., 1988b
Alfalfa	OTC	12 hm=36 ppb	22	Takemoto et al., 1988b
Alfalfa	OTC	12 hm=39, 49, 110 ppb 12 hm=34, 42, 94 ppb	31 sens./14 tol.[4] 21 sens./2 ns tol.	Renaud et al., 1997
Alfalfa[2]	OTC	Filtered vs. Ambient (Southern California)	16.1	Olszyk et al., 1986b
Alfalfa[2]	Field Exclusion	Filtered vs. Ambient (Southern California)	14.7	Olszyk et al., 1986b
Alfalfa	Natural Gradient	SUM100=57,000 ppb-hr	31.4	Oshima et al., 1976

Orange, Valencia[3]	OTC	12 hm=75 ppb 12 hm=40 ppb	31 11	Olszyk et al., 1990b
Peach	OTC	AOT60=5398	No effect-yield Quality degraded	Badiani et al., 1996
plum	OTC	12 hm= 117 ppb	29 (fruit no.)	Retzlaff et al., 1992
Strawberry	OTC	12 hm=66 ppb	+20 (fruit weight)[5]	Takemoto et al., 1988b
Strawberry	OTC	8 hm=92 ppb AOT40=24.59 ppm-hr	14 (fruit wt.) ns (yield)	Drogoudi and Ashmore, 2000

[1]Adapted from USEPA (1996a) and later publications.

[2]Mean for shoot dry weight over 7 harvests in 2 consecutive years. Chamberless and OTC comparisons of ambient and charcoal filtered treatments were conducted simultaneously in the same environment.

[3]On year data. In off (non-bearing) year there was no effect.

[4]sens. = sensitive cultivar, tol. = tolerant cultivar. ns = no significant change.

[5]+ indicates an increase due to ozone exposure.

Table 8-10 Summary of studies published since publication of ARB (1987) demonstrating under field conditions injury to non-economic growth and physiology of annual crops of relevance to California[1].

Crop Species	Exposure Technology	ozone Exposure Averaging Period/Concentration	Summary of Ozone Impact (% loss)	Original Reference
Cotton	OTC	12 hm=111 ppb	42% shoot 61% root	Temple et al., 1988a
Potato	OTC	8 hm 60 ppb	9.2 shoot growth	Craigon et al., 2002
Potato	OTC	8 hm=60 ppb	29 (reducing sugars)	Vorne et al., 2002
Potato	OTC	8 hm 50 ppb	8.4 shoot dw	Lawson et al., 2001a
Wheat, spring	OTC	6 hm=125 ppb	35% shoot	Mortensen, 1990

[1]Adapted from USEPA (1996a) and later publications.

Table 8-11 Summary of studies published since publication of ARB (1987) demonstrating under field conditions injury to non-economic growth and physiology of perennial crops of relevance to California[1].

Crop Species	Exposure Technology	ozone Exposure Averaging Period/Concentration	Summary of Ozone Impact (% loss)	Original Reference
Almond	OTC	12 hm=51 ppb 12 hm=117 ppb	6.0 Trunk RGR 28.4 Trunk RGR	Retzlaff et al., 1991
Almond	OTC	12 hm=51 ppb 12 hm=117 ppb	1.7 C Assimilation 49.8 C Assimilation	Retzlaff et al., 1991
Almond	Closed field chambers	250 ppb x 4 h/week	8-36 growth	McCool and Musselman, 1990
Apple	OTC	12 hm=51 ppb 12 hm=117 ppb	20.5 Trunk RGR 33.3 Trunk RGR	Retzlaff et al., 1991
Apple	OTC	12 hm=51 ppb 12 hm=117 ppb	+0.3 C Assimilation[1] 36.5 C Assimilation	Retzlaff et al., 1991
Apricot	OTC	12 hm=51 ppb 12 hm=117 ppb	+25.5 Trunk RGR 52.9 Trunk RGR	Retzlaff et al., 1991
Apricot	OTC	12 hm=51 ppb 12 hm=117 ppb	8.0 C Assimilation 46.7 C Assimilation	Retzlaff et al., 1991
Apricot	Closed field chambers	250 ppb x 4 h/week	growth	McCool and Musselman, 1990
Avocado	OTC/pots	12 hm=86 ppb 12 hm=108 ppb	20 Leaf mass 61 Leaf mass	Eissenstat et al., 1991a

Avocado	OTC/pots	12 hm=86 ppb 12 hm=108 ppb	2° decrease in freeze tolerance (warmer)	Eissenstat et al., 1991a
Cherry	OTC	12 hm=51 ppb 12 hm=117 ppb	20.0 Trunk RGR 24.4 Trunk RGR	Retzlaff et al., 1991
Cherry	OTC	12 hm=51 ppb 12 hm=117 ppb	+4.2 C Assimilation +4.8 C Assimilation	Retzlaff et al., 1991
Grape	OTC		Gas exchange	Roper and Williams, 1989
Grapefruit	OTC/pots	12 hm=86 ppb 12 hm=108 ppb	1° decrease in freeze tolerance (warmer)	Eissenstat et al., 1991a
Grapefruit	OTC/pots	12 hm=86 ppb 12 hm=108 ppb	26 Leaf Mass No effect on Leaf Mass	Eissenstat et al., 1991a
Nectarine	OTC	12 hm=51 ppb 12 hm=117 ppb	+6.0 Trunk RGR +14.4 Trunk RGR	Retzlaff et al., 1991
Nectarine	OTC	12 hm=51 ppb 12 hm=117 ppb	4.2 C Assimilation 4.8 C Assimilation	Retzlaff et al., 1991
Orange	OTC/pots	12 hm=108	No effect leaf mass	Eissenstat et al., 1991a
Peach	Closed field chambers	250 ppb x 4 h/week	growth	McCool and Musselman, 1990
Peach	OTC	AOT60=5398	Shoot growth reduced	Badiani et al., 1996
Peach	OTC	12 hm=51 ppb 12 hm=117 ppb	8.9 Trunk RGR +5.6 Trunk RGR	Retzlaff et al., 1991

Peach	OTC	12 hm=51 ppb 12 hm=117 ppb	7.7 C Assimilation 5.1 C Assimilation	Retzlaff et al., 1991
Pear	OTC	12 hm=51 ppb 12 hm=117 ppb	8.1 Trunk RGR 59.4 Trunk RGR	Retzlaff et al., 1991
Pear	OTC	12 hm=51 ppb 12 hm=117 ppb	15.6 C Assimilation 57.3 C Assimilation	Retzlaff et al., 1991
Plum	OTC	12 hm=51 ppb 12 hm=117 ppb	18.4 Trunk area 42.8 Trunk area	Retzlaff et al., 1991
Plum	OTC	12 hm=51 ppb 12 hm=117 ppb	8.1 Trunk area 46.9 Trunk area	Retzlaff et al., 1991
Plum	OTC	12 hm= ppb	Postharvest water loss increased during storage	Crisosto et al., 1993
Prune	OTC	12 hm=51 ppb 12 hm=117 ppb	25.4 Trunk RGR 4.5 Trunk RGR	Retzlaff et al., 1991
Prune	OTC	12 hm=51 ppb 12 hm=117 ppb	18.4 C Assimilation 41.3 C Assimilation	Retzlaff et al., 1991

[1]+indicates an increase due to ozone exposure.

Table 8-12 Plant species and original references providing data for the growth and allometric analyses. (Data assembled by S. Gunn and D.A. Grantz).

	Binomial	**Reference**
Broadleaf Plants (herbaceous dicotyle-donous species)	*Anthyllis vulneraria*	Warwick & Taylor, 1995
	Brassica napus ssp oleifera	Ollerenshaw et al., 1999
	Chenopodium album	Reiling and Davison, 1992a
	Cirsium acaule	Warwick & Taylor, 1995
	Cerastium fontanum	Reiling and Davison, 1992a
	Citrullus lanatus	Fernandez–Bayon et al., 1993
	Cucumis melo	Fernandez–Bayon et al., 1993
	Calluna vulgaris (summer growth)	Foot et al., 1996
	Deschampsia flexuosa	Reiling and Davison, 1992a
	Epilobium hirsutum	Reiling and Davison, 1992a
	Lotus corniculatus	Warwick & Taylor, 1995
	Medicago sative	[a]Cooley & Manning, 1988
	Nicotiana tabacum Bel–W3	Reiling and Davison, 1992a
	Plantago coronopus	Reiling and Davison, 1992a
	Plantago lanceolata	Reiling and Davison, 1992a

	Plantago major	Reiling and Davison, 1992a [a]Lyons and Barnes, 1998 Reiling & Davison, 1992b Lyons et al., 1997
	Plantago maritima	Reiling and Davison, 1992a
	Plantago media	Reiling and Davison, 1992a
	Pilosella officinarum	Warwick & Taylor, 1995
	Pisum sativum	Reiling and Davison, 1992a
	Rumex acetosa	Reiling and Davison, 1992a
	Rumex acetosella	Reiling and Davison, 1992a
	Rumex obtusifolius	Reiling and Davison, 1992a
	Teucrium scorodonia	Reiling and Davison, 1992a
	Urtica dioica	Reiling and Davison, 1992a
Grass-like Plants (herbaceous monocotyl-	*Arrhenatherum elatius*	Reiling and Davison, 1992a
	Avena fatua	Reiling and Davison, 1992a
	Bromus erectus	Reiling and Davison, 1992a
	Brachypodium pinnatum	Reiling and Davison, 1992a
	Bromus sterilis	Reiling and Davison, 1992a
	Desmazeria rigida	Reiling and Davison, 1992a

edonous species)	*Festuca ovina*	Warwick & Taylor, 1995 Reiling and Davison, 1992a
	Holcus lanatus	Reiling and Davison, 1992a
	Hordeum marinum	Reiling and Davison, 1992a
	Koeleria macrantha	Reiling and Davison, 1992a
	Lolium perenne	Reiling and Davison, 1992a
	Poa annua	Reiling and Davison, 1992a
	Poa trivialis	Reiling and Davison, 1992a
	Triticum aestivum	Barnes et al., 1995 [a]Balaguer et al., 1995
Long-lived, woody Plants (tree species)	*Eucalyptus globules*	Pearson, 1995
	Fraxinus excelsior	Broadmeadow & Jackson, 2000
	Picea abies	[a]Karlsson et al., 1997
	Pinus sylvestris	Broadmeadow & Jackson, 2000
	Quercus petraea	Broadmeadow & Jackson, 2000
	Koeleria macrantha	
	Poa annua	
	Poa trivialis	

[a]Calculated values.

Table 8-13 Ozone Exposure Parameters and References to the Original Studies. (Data assembled by S. Gunn and D.A. Grantz).

Plants	**Stage of growth at initial exposure**	**Growth / exposure conditions**				**Reference**
		[ozone]		Exposure	Length of exposure[a]	
		Control	Elevated			
31 species	Cotyledon / first leaf stage	< 5 nl l^{-1}	70 nl l^{-1}	FC[a]	7 h d^{-1} for 2 weeks	Reiling and Davison, 1992a[b]
5 species	4 weeks	16 nl l^{-1}	71 nl l^{-1}	CEC	7 h d^{-1}, 5 d $week^{-1}$for 21 d	Warwick & Taylor, 1995[b]
Brassica napus ssp oleifera var biennis, (oilseed rape), 5 cv	Seedlings	CF[d]	CF + 75 nmol mol^{-1}	CEC	6.5 h d^{-1} for 16 d	Ollerenshaw et al., 1999[b]
Calluna vulgaris (summer growth)	Cuttings	CF	70 nl l^{-1}	OTC	8 h d^{-1}, 5 d $week^{-1}$ for 24 weeks	Foot et al., 1996[b]
Citrullus lanatus (watermelon) 2 cv *Cucumis melo* (muskmelon), 2 cv	22 d old	< 8 nl l^{-1}	70 nl l^{-1}	FC	6h d^{-1} for 21 d	Fernandez–Bayon et al., 1993[b]
Eucalyptus globulus	Seedlings	4.6 nl l^{-1}	52.3 nl l^{-1}	FC	7 h d^{-1} for 37 d	Pearson 1995[c]

Medicago sative (alfalfa)	4 weeks	CF	0.06 ppm	GH	6 h d^{-1}, 5 d week-1 for 56 d	Cooley & Manning, 1988[c]
Picea abies (Norway spruce), 2 clones	Seedlings	CF	NF	OTC	24 h d^{-1} for 106 d	Karlsson et al., 1997[c]
Plantago major Plants from 22 sites	6 d old seedlings	< 5 nmol mol^{-1}	70 nmol mol^{-1}	CEC	7 h d^{-1}, 14 d	Lyons et al., 1997[b]
Plantago major	6 d old seedlings	< 5 nmol mol^{-1}	70 nmol mol^{-1}	CEC	7 h d^{-1} for 14 d	Lyons and Barnes, 1998[2]
Plantago major, 28 British populations	Cotyledon	< 10 nl l^{-1}	70 nl l^{-1}	CEC	7h d^{-1} for 14 d	Reiling & Davison, 1992b[b]
Quercus petraea *Fraxinus excelsior* *Pinus sylvestris*	Seedlings	55 nl l^{-1}	100 nl l^{-1}	OTC	Max 4 h d^{-1}, 5 months $year^{-1}$ for 3 years	Broadmeadow & Jackson, 2000[b]
Triticum aestivum (spring wheat), 1 cv	8 d after emergence	< 5 nmol mol^{-1}	75 nmol mol^{-1}	CEC	7 h d^{-1}, 30 d	Balaguer et al., 1995[c]
Triticum aestivum 2 cv spring wheat; 3 cv winter wheat	2 leaf stage	< 5 nmol mol^{-1}	75 nmol mol^{-1}	CEC	Max 4 h d^{-1}, 41 d	Barnes et al., 1995[b]

[a]FC, Fumigation cabinets; CEC, Controlled environment cabinets; GH, Greenhouse.

[b]k obtained from tabulated data.

[c]k calculated from data presented.

[d]Charcoal filtered air.

8.6 Agricultural Crops – Summary

In California, forests cover 30-35-million acres of the landscape. Field studies conducted since the 1950s have found widespread damage from ambient ozone in conifer forests, but little, if any, damage in hardwood forests. Mixed conifer forests across California are exposed to elevated levels of ozone. In these forests, 12-hr average ozone levels across the growing season are 0.05-0.06 ppm, and harmful effects are well documented. The adverse effects of ozone culminate at the community-level, as a result of chronic effects on pine needle structure and physiological processes. Alterations in whole-tree biomass occur after several years of exposure due to higher carbon retention in the shoot for ozone detoxification, and lower carbon allocation to roots for maintenance and growth. As such, tree susceptibility to drought, windthrow, and root diseases could be exacerbated due to an imbalance in aboveground:belowground biomass. Changes in the mix of forest tree species may occur after one or more decades of ozone exposure due to the death of ozone-sensitive pines, and their replacement by faster-growing, ozone-tolerant cedar and fir species. It is postulated that ambient ozone will have a deleterious effect on long-term forest health in southern California and the southern Sierra Nevada at current growing season average concentrations.

8.7 Forest Trees – Introduction

Ozone is a gaseous air pollutant that damages plants after it reaches the leaf interior through surface pores called stomata. Within leaves, ozone causes cells to turn yellow or die, resulting in a loss of functional leaf area to carry out photosynthesis, the process by which plants manufacture their food. Depending on the extent of needle injury, the production of carbohydrates for tree growth and homeostasis is reduced. In addition to causing leaf damage, ozone also causes leaves on affected trees to drop off sooner than normal. This acceleration of leaf drop compounds ozone-caused losses in functional leaf area to carry out photosynthesis. After several successive years of exposure, insidious reductions in carbohydrate production lower the amount of resources that trees store to initiate bud break in the spring and to ward off the effects of other stresses (McLaughlin and Shriner 1980). As ozone exposures directly impact the aboveground portion of a tree, greater resources (e.g., energy and carbohydrates) are apportioned to the shoot for detoxification and repair, relative to other parts of the plant. Studies indicate that the increased allocations of carbon to the shoot are offset by reduced allocations to root growth (Grulke et al. 1998), starch storage, winter hardiness, and pest tolerance. On an annual-basis, the net effect of these compensatory reductions in carbon allocation on tree health are expected to be minor, but if they occur over 5-10 consecutive years, the potential for severe, growth-limiting tree damage could be high.

California spans over 100 million acres, of which 23% is occupied by conifer forests (CDF 1988). Of the 12-types of conifer forest in the state, mixed conifer forests cover ~9.3 million acres, and are variously located in the Northern Coast Ranges, Klamath Mountains, Southern Cascades, Sierra Nevada, Central Coast

Ranges, and Southern California Mountains. Reports of oxidant damage to ponderosa or Jeffrey pine in California's mixed conifer forests date back to the 1950s in the San Bernardino Mountains (Richards et al. 1968). Pine tree damage has also been found in the Los Padres National Forest (Williams and Williams 1986), and throughout the Sierra Nevada (Miller and Millecan 1971, Peterson et al. 1987, Peterson and Arbaugh 1988). In the 1990s, a research program by the USDA Forest Service, USDI National Park Service, University of California, Davis, and ARB was conducted to assess injury amounts in six National Forests and three National Parks in the Sierra Nevada and San Bernardino Mountains (Rocchio et al. 1993). The relationships between ozone exposure and injury to pines in the Sierra Nevada and San Bernardino Mountains were recently examined, and a strong relationship between injury scores and 4-yr cumulative summer ozone exposure was reported (Arbaugh et al. 1998). Figure 9.1 shows the locations of forest research sites in California.

In the San Bernardino Mountains, mixed conifer forests at Camp Paivika (1,600 m elevation) are exposed to high levels of ozone (24-hr average concentrations of 0.08-0.09 ppm) (Miller and McBride 1999). In forests of this kind, most of the ozone-sensitive trees are thought to have died as a result of the combined effects of elevated ozone exposure, drought, and insect attack since the 1950s. Of the trees that remain, many are ozone-tolerant, although visible injury is evident throughout forests on the western end of the mountain range. Resistance to drought is likely to have played a role in stand-level selection processes (Dale 1996).

In the San Gabriel Mountains, there are little data on ambient ozone levels in mixed conifer forests, but considerable data have been collected in the chaparral watersheds at Tanbark Flat at lower elevation (Bytnerowicz et al. 1987). At Tanbark Flat (800 m elevation), about 35 km north of Los Angeles, growing season 24-hr average ozone levels are 0.07-0.08 ppm (Bytnerowicz et al. 1989*b*). Relative to the western San Bernardino Mountains, ozone levels are slightly lower, and damage to forests less extensive, due in part to lower soil quality that may limit conifer growth.

Most of California's mixed conifer forest acreage exists on the western slope of the Sierra Nevada (CDF 1988). Cahill et al. (1989) reported that terrain-effect winds were capable of transporting ozone and particulates to 1,800 m elevation during daytime upslope flows, but pollutant transport to elevations at or above 3,000 m would be considerably less. Reports indicate that 24-hr average ozone levels during the growing season on the western slope of the Sierra Nevada are 0.05-0.07 ppm (Van Ooy and Carroll 1995). Currently, the risk posed by ozone in the Sierra Nevada is far less than in the San Bernardino or San Gabriel Mountains in the South Coast Air Basin (SoCAB). While ozone injury to trees has occurred in Sierra Nevada forests, decreases in growth have not been severe to our knowledge.

The principal effect of ozone on mixed conifer forests in California is expected to be reduced growth of ponderosa and Jeffrey pine. Of the western yellow pines, these two species are the most widespread, and documentation of their ozone-

sensitivity is extensive in the open literature. Throughout the state, ambient ozone concentrations are expected to decrease or remain level as a result of proposed control measures in the State Implementation Plan (SIP) (ARB 1994). In selected areas (e.g., San Joaquin Valley), increases in population are expected to be rapid, and ambient ozone levels could remain at current levels if projected emission reductions are offset by increases in emissions due to greater human activity (ARB 2005). While tree health would be impacted to a significant extent by ozone alone, the co-deposition of atmospheric N could exacerbate the deterioration of forest health at ozone-affected sites. This follows from the work of Aber et al. (1989) who advanced the nitrogen saturation hypothesis, in which the mix of tree species in a given forest is altered by excess levels of nitrogen in soil (i.e., above that needed for plant and microbial growth). As exposure to ozone may promote early needle drop and reduced root system growth in pines, a build-up in soil nitrogen levels could be accelerated (e.g., Takemoto et al. 2001). Over time, the leaching of nitrate ions from forest soils may alter nutrient balances and contaminate ground water.

8.7.1 Ambient Ozone Concentrations and Deposition

Relative to air pollution's effect on forest health in North America, ozone is the air pollutant of greatest current concern (Barnard et al. 1991, Shriner et al. 1991). Annual average ozone levels at clean, background sites range from ~0.015 to ~0.04 ppm (Lefohn et al. 1990, Table 1). In comparison, rural forest air quality in the U.S. is impacted by ozone and ozone-precursor transport from upwind urban centers, and an annual mean concentration of 0.030-0.045 ppm is considered to be a representative range for baseline, ambient ozone levels (Lefohn et al. 1990, Taylor and Hanson 1992). Forests that are subject to ozone transport commonly exhibit distinct diurnal profiles in which the difference between daily minima and maxima is 0.04-0.07 ppm (Carroll and Dixon 1993, 1995). Nighttime ozone levels decrease to a minima of 0.02-0.03 ppm at these sites due to the delivery of urban-generated nitric oxide (NO) emissions from roadways in nocturnal downslope air flows. In comparison, forests that receive limited amounts of urban-generated pollutants exhibit flat diurnal profiles, where daily fluctuations in ozone concentration are 0.010-0.015 ppm. Nighttime levels differ only slightly from daytime levels, remaining at 0.04-0.05 ppm, due to the lack of locally emitted NO to scavenge ambient ozone (Böhm et al. 1991, Peterson et al. 1991).

In the Sierra Nevada, growing season daytime 12-hr average ozone levels range from 0.05-0.07 ppm (Carroll 1991, 1992, Carroll and Dixon 1993, 1995). Both flat and distinct diurnal ozone profiles were observed at six mixed conifer forest sites (Figure 1), as well as varying amounts of ozone injury on pine trees growing in the vicinity of the monitoring stations (Arbaugh et al. 1998). Similarly, in the San Bernardino Mountains, growing season average ozone levels at Barton Flats were ~0.06 ppm (Miller et al. 1996a, 1996b), but needle injury amounts were more pronounced than in the Sierra Nevada. The average ozone concentration at Barton Flats in 1991-94 was similar to that reported for the mid-1970s (Miller et al. 1986). Growing season 24-hr average ozone levels of 0.09-0.10 ppm may still

occur at the highly polluted western end of the San Bernardino Mountains (e.g., Camp Paivika, Miller et al. 1986).

Dry deposition is defined as "all processes that deliver gases, vapors, large particles, and aerosols to the canopy in the interval between storms" (Parker 1990). For gaseous air pollutants like ozone, rates of pollutant deposition to the leaf interior are difficult to measure directly, and are commonly calculated by inferential methods, such as the Big Leaf Model (Hicks et al. 1987). Inferential models are used to calculate a deposition velocity (V_d), which is used to estimate pollutant deposition fluxes according to the following equation:

Flux (F) = Concentration (C) * V_d

Where the units of F may be kg/ha/yr, μg/m^3 for C, and cm/s for V_d. For ozone, V_d differs from site-to-site as a function of temporal, meteorological, and vegetation-related factors. For example, sites with elevated wind speeds (which create more turbulent down-mixing of air pollutants into plant canopies), and large amounts of physiologically active leaf area (capable of absorbing pollutants to the leaf interior) are factors that contribute to high values of V_d. Time of day is also important in that V_d tends to be lower at night when atmospheric turbulence is weaker, air temperatures are lower, and stomata are closed (Colbeck and Harrison 1985). A 24-hr average V_d for ozone for a range of vegetated systems (e.g., trees, crops, and grasses) is ~0.5 cm/s.

For a ponderosa pine plantation in the Sierra Nevada, Kurpius et al. (2002) estimated that over the course of a year, summer, fall, winter, and spring contributions to cumulative ozone flux were 37%, 18%, 15%, and 30%, respectively. Ozone flux to the pine plantation was highest 3-4 weeks after bud break, when the mean daytime flux was 70-80 μmol/m^2/hr (Bauer et al. 2000, Goldstein and Panek 2002). In comparison, ozone deposition to conifer forests in Tennessee was estimated to be ~80 μmol/m^2/hr during the day, and ~20 μmol/m^2/hr at night (Taylor and Hanson 1992). Massman et al. (2000) suggested that an ozone flux of 45 μmol/m^2/hr could be a threshold value for injury development in sensitive-crop species.

8.7.1.1 Levels of Ozone Exposure in California's Mixed Conifer Forests

Growing season levels of ambient ozone (24-hr average concentrations in May-October) in selected mixed conifer forests in California range from 0.05-0.06 ppm (Miller et al. 1986), 10-100% higher than the rural baseline level for U.S. forests (Table 9-14). As a consequence, ambient ozone may be causing site-specific phytotoxic effects (e.g., physiological impairment, leaf injury, or reduced growth) across the state. Theoretically, if pine trees growing in unmanaged California forests are exposed to an average ozone concentration of 0.05 ppm for 180-days, they would receive a cumulative growing season ozone exposure in excess of 200 ppm-hr (a.k.a. SUM0 – the sum of all hourly average ozone concentrations).

Controlled chamber studies have shown that ponderosa pine seedlings exposed to acute ozone levels (0.3-0.5 ppm) exhibited injury to current and one-year old

needles after 24-108 ppm-hr over a 2-3 week period (Miller 1969, Miller and Evans 1974, Miller et al. 1969). In field chamber studies conducted over 2- or 3-growing seasons, moderate amounts of ozone injury were observed in ponderosa pine seedlings grown at Whitaker's Forest (0.05-0.06 ppm, Temple et al. 1992), and at Shirley Meadow (~0.06 ppm, Takemoto et al. 1997). While the amount of ozone-caused needle injury is considerably less following chronic vs. acute exposure to ozone, multi-year exposures to ambient ozone in California pose a stress of similar magnitude for native pines to that applied in the two field studies mentioned above (Arbaugh et al. 1998). Physiologically, ozone-caused needle damage reduces the amount of photosynthetically active leaf area (Beyers et al. 1992). It also increases the need for energy and carbohydrates for maintenance respiration (Amthor and Cumming 1988, Barnes 1972, Barnes et al. 1990, Skärby et al. 1987), repairing injured tissues (Evans and Ting 1973, McLaughlin and McConathy 1983, McLaughlin and Shriner 1980, Ting and Mukerji 1971), and detoxifying reactive oxygen species produced by the dissolution of ozone (Lee and Bennett 1982, Mehlhorn et al. 1986).

Currently, the occurrence of acute ozone episodes, comparable to those that occurred in the 1950-60s, are rare, making the impacts from chronic exposures of greater concern. At present concentrations, chronic ozone exposure requires trees to allocate greater amounts of energy and carbohydrates for repair and maintenance, which limits the amount available for growth and storage. Over time, decreased carbohydrate reserves may limit tree resiliency in terms of responding to tree-killing stresses (e.g., drought, insects, and severe winds). As such, chronic ozone stress has a cumulative impact on native pines in that successive years of exposure can increase the amount and severity of needle injury, and rates of starch accumulation that are key to the initiation of bud break in the spring.

8.8 Effects of Ozone on Photosynthesis

Photosynthesis is the process by which plants capture the energy in sunlight, and use the energy to produce carbohydrates (e.g., starch; cf. Wallace et al. 1981). In clean air, photosynthesis occurs at rates that allow plants to produce carbohydrates in amounts sufficient to sustain healthy rates of growth. However, in the presence of ozone, photosynthetic rates in plants may be negatively affected if ozone impedes the plant's ability to absorb sunlight and/or processes involved with carbohydrate production (e.g., Kozlowski et al. 1981).

Concerning the harmful effects of ozone on conifer photosynthesis (e.g., Reich and Amundson 1985), studies have primarily been conducted using ponderosa pine *(Pinus ponderosa)* in the western U.S. (Beyers et al. 1992, Grulke 1999, Takemoto et al. 1997), loblolly pine *(Pinus taeda)* in the southeastern U.S. (Adams et al. 1990, Kelly et al. 1993, Richardson et al. 1992), red spruce *(Picea rubens)* in the northeastern U.S. (Laurence et al. 1989, Rebbeck et al. 1993, Taylor et al. 1986), and Norway spruce *(Picea abies)* and Scots pine (*Pinus sylvestris*) in Europe (Barnes et al. 1990, Benner and Wild 1987, Schulze 1989, Skärby et al. 1987, Zimmerman et al. 1988). As economically important, long-lived conifers that grow in regions with vastly different aerometric and edaphic

(soil-related) characteristics, ambient ozone variously affects photosynthesis in these five-species. In this regard, plant growth is fundamentally linked to rates of photosynthesis, in that nearly all of the carbon used to build cellular components and other biomolecules is a by-product of photosynthesis. To date, ambient ozone has not had a pronounced effect on growth in most cases, but selected studies have found either decreases (Benner and Wild 1987, Richardson et al. 1992, Takemoto et al., 1997) or increases (Kelly et al. 1993) in process rates (Table 2).

Physiologically, conifers exhibit inherently low gas exchange process rates (Larcher 1975), which limits ozone uptake and the magnitude of photosynthetic depression (Reich 1987). As such, it is more difficult to detect statistically significant ozone-caused alterations in conifer photosynthesis than it is for agricultural crop or hardwood species, which have inherently higher gas exchange rates (Reich 1987). While significant decreases in conifer photosynthesis have been observed following acute ozone exposures, adverse effects following exposure to ozone at near-ambient/ambient concentrations have in some cases been observed only after two or more years of exposure. For loblolly pine, however, seedling photosynthesis was significantly decreased by 10% after 100-150 ppm-hr ozone in one-growing season (Table 9-15, Richardson et al. 1992). The lack of consistent impacts on photosynthesis may be due to the relatively low-level of stress imposed by ambient concentrations of ozone (vs. acute), and to the detection limits of existing infrared gas analyzers and the designs of leaf cuvettes (cf. Beyers et al. 1992). With respect to the former, ambient ozone may pose a stress that adversely impacts a subset of genetically related, ozone-sensitive trees, but may not affect those that are tolerant to ozone. In comparison, exposure to a high concentration of ozone would likely damage both sensitive and tolerant trees. As such, studies that used a small number of trees of non-uniform parental stock may yield inconsistent results.

In an acute exposure study, ponderosa pine seedlings were exposed to 81 ppm-hr ozone over a 30- or 60-day period (Table 9-15, Miller et al. 1969). Seedlings exposed to 0.15 ppm ozone for 60-days, exhibited 35% lower rates of photosynthesis than pines grown in charcoal-filtered air, while in pines exposed to 0.30 or 0.45 ppm ozone for 30-days, rates were reduced by 70% or more. The degree of photosynthetic inhibition caused by acute ozone exposure is much greater than that caused by near-ambient/ambient levels of ozone for multi-year periods, where decreases may be ~10% or less. During an acute exposure, large amounts of ozone are deposited to the leaf interior in a short period of time, and the amount of ozone in the leaf interior greatly exceeds plant capacities of ozone detoxification. As such, extensive damage to cellular components occurs before the plant closes its stomata to prevent further ozone uptake. Visible leaf damage may be present as large bands of brown necrotic flecks (Reference). On the other hand, when plants are exposed to ozone at ambient levels, ozone uptake occurs at a much slower rate, and ozone can be metabolized by the plants inherent antioxidant-based defense systems. Visible damage to leaves may be evident as yellow spotting due to the oxidation of chlorophyll. However, under

ambient conditions, plants may not close their stomata to completely prevent ozone uptake (cf. Musselman and Minnick 2000). By keeping their stomata partially open, low-level ozone uptake continues, but concomitant CO_2 uptake serves to maintain photosynthesis at rates that may generate energy and carbon skeletons to mitigate the toxic effects of ozone.

The effect of ambient ozone on photosynthesis in ponderosa pine seedlings was investigated in three field chamber studies. No significant effects were found in two studies, and periodic inhibition was observed during the second growing season in the other. No significant effects were reported after exposure to 140-340 ppm-hr ozone in five- or six-months at Tanbark Flat in the San Gabriel Mountains (Bytnerowicz et al. 1989b, Bytnerowicz and Takemoto 1989), or after 200-600 ppm-hr ozone over three-growing seasons at Whitaker's Forest (Beyers et al. 1992). In comparison, rates in one-year-old needles were inhibited on selected dates after exposure to ~500 ppm-hr ozone in their second growing season at Shirley Meadow in the southern Sierra Nevada (Bytnerowicz and Temple 1993, Takemoto et al. 1997). In many instances, the depression of photosynthesis in ponderosa or Jeffrey pine by ambient ozone has not been strongly correlated with stomatal closure (cf. Weber et al. 1993). Instead, ozone impacts on carboxylation processes (e.g., initial activation of Ribulose Bisphosphate Carboxylase Oxygenase [RuBisCO], regeneration of ribulose bisphosphate [RuBP]) or the light reactions (chlorophyll fluorescence or damage to photosystem II) have been suggested as the site of physiological disruption (Barnes and Davison 1988, Benner and Wild 1987, Coyne and Bingham 1982, Grulke 1999, Patterson and Rundel 1989).

In terms of whole-tree photosynthesis, rates in ozone-stressed trees would be further reduced by decreased levels of foliar chlorophyll (Benner and Wild 1987) and higher rates of needle abscission/senescence (Coyne and Bingham 1981, Richardson et al. 1992). Studies have shown that ozone can oxidize chlorophyll molecules, rendering them unable to trap sunlight to energize the photosynthetic process. Moreover, ozone can oxidize proteins in chloroplast membranes as well as enzymes that catalyze carbohydrate production (Reference). Assuming that trees in central and southern California receive growing-season ozone exposures of 150-250 ppm-hr per year, a cumulative exposure of 600-1,000 ppm-hr would be achieved within 4-years. Upon reaching this level of ozone accumulation, adverse effects on photosynthesis may become evident in needles that are retained for several seasons (Coyne and Bingham 1981), possibly due to the loss of normal stomatal function (Grulke 1999). In highly sensitive ozone-stressed trees, needle retention may be limited to only two or three annual whorls in some cases. For these plants, photosynthetic process rates in two- and three-year-old needles may not be significantly affected during the current year until a threshold level of chlorotic mottle, evident as lower foliar chlorophyll concentration, is achieved (Benner and Wild 1987). If the injury threshold is reached, the needle will likely abscise from the tree during fall or winter, which could result in a net loss in photosynthetic capacity in the following growing season. By dropping ozone-injured needles at the end of the growing season,

some amount of nutrient reabsorption would occur, and fewer resources would be expended in maintenance respiration over winter.

8.8.1 Effects of Ozone on Carbon (C) Allocation and Partitioning

While rates of photosynthesis are a useful indicator of the amount of carbohydrates that can be produced by plants, unless the carbohydrates are distributed and used in the proper proportions, healthy growth may not occur. In clean air, plants typically utilize carbohydrates to avoid or repair injuries caused by insects, disease, and weather-related stresses. In polluted air, plants may also need to utilize carbohydrates to avoid or repair injury caused by ozone, thus reducing the amount that is available for warding off other stresses. Depending on how much injury ozone causes, the amount of carbohydrates available for growth processes may be significantly reduced, thereby limiting the amount of plant growth that can occur during the growing season.

Carbon (C) skeletons produced by photosynthesis (photosynthates) are distributed within plants to sustain growth, homeostasis (Amthor and Cumming 1988), defense (i.e., stress avoidance and/or tolerance, Lechowicz 1987), and repair (i.e., restoration of damaged organs and tissues, McLaughlin and Shriner 1980). The flux of carbon from one plant organ to another, in any chemical form, is referred to as C-allocation (Dickson and Isebrands 1993), which also includes the incorporation of newly produced photosynthates, and carbon mobilized from storage compounds or recycled materials into new leaf tissue. For the most part, carbon is allocated from leaves (photosynthate “sources”) to other plant organs, which are commonly referred to as photosynthate “sinks.” However, sinks may act as storage organs for excess photosynthates produced during periods of high photosynthetic activity, thereby serving as sources to other sinks under certain circumstances. Studies show that when plants are subject to moderate levels of stress, most plants will utilize their carbon reserves in lieu of altering their normal patterns of C-allocation to maintain a balanced [root:shoot] biomass ratio. Changes in C-allocation generally occur only if a stress is severe enough to deplete the stored carbon reserves of a plant (e.g., starch). Under these situations, plant growth may be curtailed due to increased C-allocation to defense and repair, or affected plant parts shed, in order to maintain whole-plant integrity (Laurence et al. 1994).

Numerous workers have postulated that the primary effect of ozone on C-allocation is to reduce the [root:shoot] ratio of a plant: C-allocation to roots is reduced due to greater resource needs in leaves for ozone-related defense and repair (McLaughlin and McConathy 1983). Over time, the change in C-allocation leads to a lower [root:shoot] ratio in ozone-exposed plants relative to control plants (Andersen et al. 2001, Grulke et al. 1998). Since ozone is principally deposited to leaves, ozone molecules that reach the leaf interior may directly affect photosynthesis in mesophyll cells (Spence et al. 1990), and sucrose translocation in phloem sieve cells. In their review of ozone effects on C-allocation and C-partitioning, Cooley and Manning (1987) reported that while ozone often reduces whole plant dry matter content, in most cases, the mass of plant storage organs is most affected by ambient ozone. In loblolly pine, Kelly et

al. (1993) and Spence et al. (1990) both observed greater C-retention in the shoot, and lower C-allocation to roots in seedlings exposed to ozone (Table 2). Sustained reductions in C-allocation to roots were projected to adversely affect water and nutrient acquisition, especially on water-stressed sites (Kelly et al. 1993). Root associations with *Pisolithus tinctorius* could significantly increase root sink strength (Chapin et al. 1987), as mycorrhizal trees are often less sensitive to ozone effects on C-allocation than non-mycorrhizal trees (Cooley and Manning 1987).

In comparison, C-partitioning refers to the transformation of carbon from one chemical form to another within a plant organ (Dickson and Isebrands 1993). With respect to ozone, the depletion of starch reserves in leaves, to produce antioxidants, activate enzymes, and/or to repair ozone damage to cell membranes, is the physiological response most commonly reported. In studies on tobacco and cotton, plant susceptibility to ozone injury was correlated with foliar carbohydrate level at the time of exposure -- plants sustained greater amounts of ozone-caused leaf injury when carbohydrate levels were lowest. Lee (1965) reported that high levels of sucrose were associated with stomatal closure, which limited ozone uptake and damage expression in tobacco (~5 ppm-hr). In cotton, Ting and Mukerji (1971) suggested that greater amounts of damage resulted from the lack of soluble reserves for repair processes at the time of ozone exposure (~1 ppm-hr). Other crop studies have shown that exposure to ozone reduces both carbohydrate and protein levels relative to levels in plants grown in clean air. In soybean, levels of soluble sugars and starch were reduced by ozone (65 or 95 ppm-hr, Miller et al. 1995), while in cotton and bush bean, ozone-caused reductions in soluble protein were associated with increases in free amino acids (0.5 ppm-hr, Craker and Starbuck 1972, Ting and Mukerji 1971). Exposure to ozone reduced foliar starch and soluble sugar levels in red spruce (~550 ppm-hr, Amundson et al. 1991), starch in primary and secondary needles of loblolly pine (45 ppm-hr, Meier et al. 1990), soluble sugars in white pine and loblolly pine (Wilkinson and Barnes 1973), and total nonstructural carbohydrates and proteins in leaves, stems and roots of *Ulmus americana* (4.5 ppm-hr, Constantinidou and Kozlowski 1979).

8.8.2 Effects of Ozone on Tree Growth

In consideration of the mechanistic relationship between photosynthesis and crop yield (Zelitch 1982), if exposure to ozone causes a decrease in tree photosynthesis (Reich and Amundson 1985), it may also adversely affect on tree growth. Pye (1988) reviewed the responses of 43-tree species to ozone, and postulated that reductions in seedling growth and photosynthesis may be occurring in many parts of the U.S. However, in order to estimate the potential for ozone-caused effects on mature trees and whole-stands from seedling data, several key uncertainties needed to be addressed. For example, seedling growth and physiology is more rapid in seedlings than in mature, and ozone effects tend to be more severe in seedlings due in part to higher rates of ozone uptake. As responses in seedlings are often used to estimate impacts to trees of other age

classes, challenges lie in avoiding major errors in over- or underestimating true impacts on tree growth, wildlife habitat, and forest structure and composition.

In the eastern U.S., studies have focused on the effects of ozone on loblolly pine (e.g., Kelly et al. 1993). Adverse ozone effects in red spruce (400-530 ppm-hr, Amundson et al. 1991; Alscher et al. 1989) and slash pine (~122 ppm-hr, Hogsett et al. 1985) have also been reported, but not in white pine (44 ppm-hr, Reich et al. 1987). For loblolly pine, reductions in aboveground biomass (stem, branches, and leaves) have been found to result from ozone effects on foliage and stem growth. Stem volume reductions of similar magnitude have been reported in two 12-week studies; a 14% reduction was observed after exposure to ~70 ppm-hr (McLaughlin et al. 1994), and a 15% decrease after 45 ppm-hr (Meier et al. 1990). With respect to foliage effects, Adams et al. (1988) found that secondary foliage (new needles) was the most ozone-sensitive biomass component (~190 ppm-hr), which largely accounted for observed reductions in aboveground and whole-plant biomass in five half-sib families. Kress et al. (1992) observed a significant reduction in fascicle retention following exposure to ambient ozone for two-growing seasons (~290 ppm-hr). These workers reported that ambient ozone accelerated the abscission of foliage, such that most foliage abscised before the end of the second growing season. Collectively, the decreases observed on measures of stem and foliage biomass are consistent with the results of Shafer et al. (1987), who found that ambient ozone (~120 ppm-hr) inhibited the growth of three full-sib families by as much as 10% in one growing season. After two growing seasons of exposure to ambient ozone (~240 ppm-hr), seedlings from four full-sib families exhibited about 20% foliar injury and mean growth reductions ranging from 0-19% (Shafer and Heagle 1989). In his review of the loblolly pine growth responses to ozone, Taylor (1994) suggested 12-hr mean threshold concentrations for growth effects on average and sensitive seedlings were in the range of 0.045 and 0.025 ppm, respectively. As such, extant ozone levels in the Southeast are adversely affecting average pines intermittently, and sensitive cohorts frequently. On a regional scale, effects on whole-plant biomass are apparent at exposure levels of ~150 ppm-hr, and a general pattern of biomass suppression with increasing exposure was indicated. Incipient effects were estimated to occur at 97 ppm-hr, and 3% declines in whole-tree biomass were projected for every 100 ppm-hr increase in cumulative exposure.

In the western U.S., studies have primarily focused on the responses of ponderosa and Jeffrey pine to ozone in the San Bernardino Mountains (Arbaugh et al. 1999) and Sierra Nevada (Peterson et al. 1991). In addition, growth responses in big-cone Douglas fir *(Pseudotsuga macrocarpa)* on the western end of the San Bernardino Mountains (12-hr daytime mean = 0.09 ppm), were also found to be inhibited by ambient ozone (Peterson et al. 1995). In the 1980s, studies conducted in the Sequoia National Forest showed that radial growth in mature ponderosa pine trees, which exhibited ozone injury (symptomatic trees) was 14% lower than in trees without injury (asymptomatic trees) (Williams and Williams 1986). Ozone injury refers to the yellow spotting or “chlorotic mottle” to needles of pine trees exposed to elevated ozone concentrations (Miller and Evans, 1974). In subsequent studies, Peterson and co-workers (1987) in

Sequoia National Park observed a similar level of growth inhibition in symptomatic Jeffrey pine trees (11% lower than asymptomatic trees), which tended to be more pronounced in larger, older trees. However, these workers did not find significant growth reductions in ponderosa pine trees from 1956-1984, which exhibited chlorotic mottle and premature needle senescence (Peterson and Arbaugh 1988, Peterson et al. 1991). The lack of a significant ozone effect may have been due to the presence of ozone-tolerant and -sensitive trees in native forests, and the need to examine a larger number of trees.

At Whitaker's Forest in Kings Canyon National Park, Temple et al. (1993) found that after three-years, well-watered ponderosa pine seedlings exposed to ozone (~900 ppm-hr over three-seasons) exhibited 70% and 48% decreases in two-year-old and one-year-old needle biomass, respectively. While the biomass of current year needles was not reduced, significant decreases were observed in stem diameter (6%) and coarse root dry weight (14%). Total plant dry weight was 14% lower in ozone-exposed plants relative to plants grown in charcoal-filtered air. No significant effects were observed in drought-stressed plants exposed to ozone after three-seasons. This may in part be due to the need to conserve water during periods of drought. Under water-limited conditions, plants may close leaf surface pores that regulate the flow of atmospheric gases into and out of the leaf interior. In doing this, plants balance their need for carbon dioxide for photosynthesis against limiting the amount of cell damage from ozone. Photosynthetic rates in current year needles of well-watered seedlings exposed to 350 ppm-hr ozone in 1990 (the third season) were 40% higher than in plants exposed to charcoal-filtered air. This compensatory response was suggested to result from a higher tissue N level and increased inorganic phosphate cycling as a consequence of the abscission of previous year needles. Temple and Miller (1994) later reported that the reduction in radial growth was correlated with foliar injury in well-watered trees; needles with > 30% injury tended to abscise before the end of the next growing season.

In the San Bernardino Mountains, radial growth responses in ponderosa pine have varied over the period from 1925-1991 (Arbaugh et al. 1999). From 1925-1949, radial increment growth rates exhibited an increasing trend, reaching a maximum in about 1945. A decreasing trend was observed from 1950-1974, due in part to the combined effects of drought and high ambient ozone. Impacts were most severe in trees > 100-years old. From 1975-1991, radial growth responses appear to have recovered to levels similar to those in the 1930s, which coincides with an increase in precipitation amount, but only slight declines in ambient ozone.

8.8.3 Effects of Ozone on Winter Hardiness

Over centuries, extremes in regional climate have largely defined the conditions that forest trees must adapt to, in order to thrive in a particular location. In California, ponderosa pine trees, which retain their foliage year-round, have developed strategies to minimize the potentially growth-limiting impacts of low-soil moisture in the summer and cold air temperature in the winter. A key factor in a tree's ability to limit the impacts of freezing temperatures in winter is the

accumulation of carbohydrates that minimize cell damage due to ice formation (e.g., Alscher et al. 1989). In the presence of ozone, negative impacts on photosynthesis and carbon allocation could hinder efforts to produce and store the carbohydrates involved with avoiding injury from exposure to cold temperatures.

As tree species that retain their foliage year-round, conifers undergo a suite of morphological and physiological activities to increase frost hardiness each autumn. These activities include decreasing rates of photosynthesis, accumulating polyunsaturated fatty acids (e.g., 18:4 fatty acids, Wolfenden and Wellburn 1991), increasing levels of antioxidants (e.g., glutathione (GSH), Hausladen et al. 1990) and soluble sugars (e.g., raffinose and sucrose, Alscher et al. 1989, Amundson et al. 1991, Barnes et al. 1990). At the physiological level, it has been suggested that the effects of cold temperature are comparable to the impacts of ozone, since both cause increases in reactive oxygen species. The increase in reactive oxygen species caused by cold temperatures occurs as a result of the freezing of extracellular water during the first autumn frosts. In periods of prolonged chilling, the temperature of extracellular water continues to decrease, with a concomitant increase in oxygen solubility. Ultimately, oxygen concentrations equilibrate across plant cell membranes, and at higher oxygen tensions, the rate of intracellular superoxide formation may be enhanced. For ozone, reactive oxygen species are formed upon dissolution to the substomatal cavity (Skärby et al. 1998).

Ozone-caused decreases in frost hardiness have been suggested to result from cell membrane damage during the growing season in high-elevation Norway spruce forests in Europe (Barnes and Davison 1988). Trees, which were damaged by ozone in summer, may be predisposed to greater amounts of freezing injury and winter desiccation than trees that were not affected by ozone. Additionally, ozone may also increase susceptibility to winter chilling by increasing rates of dark respiration, leading to decreased levels of ethanol-soluble sugars (e.g., raffinose, Barnes et al. 1990). With respect to lipids, Wolfenden and Wellburn (1991) reported that ozone may interfere with the biosynthesis of 18:4 fatty acids during frost hardening by inhibiting the Δ^5 desaturation of oleate. In cold temperatures, a high proportion of polyunsaturated fatty acids allows membranes to maintain fluidity and to remain semi-permeable. Thus, if trees are unable to achieve a prescribed level of lipid unsaturation in autumn, membrane dysfunctions may occur in subsequent winter months, leading to more extensive damage to cell membranes and loss of cell integrity.

8.8.4 Overview of Potential Ozone Effects on Western Pines in California

8.8.4.1 Ozone's Role in Forest Health/Productivity

Reports of oxidant-caused injury to pines in California forests date back to the 1950s in southern California (Richards et al. 1968), and the 1970s in the Sierra Nevada (Miller and Millecan 1971). At the cell/tissue level, the development of chlorotic mottle and/or necrotic flecks constitutes a loss of photosynthetically active leaf area, and in some cases, a net decrease in whole-plant carbon

assimilation during the growing season. Depending on the extent of needle injury, energy and carbohydrate allocations to maintenance respiration during winter could be considerable if injured needles are retained by the plant as sources for initiating new needle growth in the spring. Since ozone is known to accelerate leaf senescence, it may also be a factor that influences the number of needle whorls retained by a tree after several successive years of exposure. At the tissue/organ level, the stress imposed by ozone on the plant shoot requires greater resource allocations to defense, repair, and homeostasis during the growing season to sustain plant productivity (Grulke 1999, McLaughlin and Shriner 1980). Greater energy and carbohydrate allocations to the shoot for detoxification and repair are balanced against reduced allocations to root growth, starch storage, winter hardiness, and pest tolerance. On an annual-basis, the net effect of these compensatory reductions in C-allocation on tree health are expected to be minor, but if they occur over 5-10 consecutive years, the potential for severe, growth-limiting tree damage could be high. Adverse impacts are expected to be greater for western pines, as opposed to cedar and fir species, which may emerge as the dominant species in mixed conifer forests over the next century (Peterson et al. 1991).

Rosenbaum et al. (1994) examined the extent to which critical levels for ozone, nitrogen dioxide and sulfur dioxide, developed by the United Nations-Economic Commission for Europe (UN-ECE), were exceeded in the U.S. Average ozone concentrations at 99% of monitored sites exceeded the 7-hr (0.025 ppm) and 8-hr (0.03 ppm) critical levels, and the 1-hr level (0.075 ppm) was exceeded at 50% of sites. As noted above, forest lands in California are among the sites exceeding the UN-ECE critical levels for ozone, and these results are consistent with the findings of Olson et al. (1992), who concluded that ozone is the primary pollutant of concern in western U.S. forests. Over the next 50-years, forest exposures to ozone and atmospheric N in California may continue to occur at levels that can cause adverse plant and soil responses, based on current knowledge. Although the results from tree surveys suggest that exposure to ozone is a contributing factor to reduced pine growth in mixed conifer forests across the state, the interactive effect of other possible contributing factors (e.g., rising rates of atmospheric N deposition and increasing levels of carbon dioxide) are not known.

8.8.4.2 Conclusions

Throughout California, ambient ozone levels are expected to decrease through 2010 as a result of proposed hydrocarbon and NO_X control measures in the California State Implementation Plan. In consideration of Beyers et al. (1992) and Bytnerowicz et al. (1989a), mixed conifer forests in the Sierra Nevada and SoCAB are exposed to ~250 or ~350 ppm-hr ozone, respectively, during the growing season. In postulating a worse case scenario, sustained annual exposures to ozone in the range of 250-350 ppm-hr would accelerate leaf senescence, and symptomatic trees may only retain 2-3 whorls of needles. While tree health would be impacted to a significant extent, the effects may not be as great as those projected for loblolly pine in the Southeast (Taylor 1994). A key uncertainty is the co-deposition of atmospheric N-containing compounds, which

may exacerbate the deterioration of forest health at ozone-affected sites if soil N-saturation occurs within the next 50-100 years (Takemoto et al. 2001).

Table 8-14 Ambient Ozone Concentrations at Background and Rural U.S. Forest Sites

Concentration (ppm)	Site Location	Type of Value	Reference
~0.015	American Samoa	Annual average	Lefohn et al., 1990
~0.04	Apache National Forest, AZ	Annual average	Lefohn et al., 1990
0.03-to-0.045	"Rural U.S. forests"	Growing season, 12-hr mean	Lefohn et al., 1990; Taylor and Hanson, 1992
0.05-to-0.07	Mixed conifer forests, western Sierra Nevada	May-to-October, 12-hr mean (1991-1994)	Carroll, 1991; 1992; Carroll and Dixon, 1993; 1995
0.05-to-0.06	Whitaker's Forest, Sierra Nevada	Growing season, 12-hr mean	Temple et al., 1992
~0.06	Shirley Meadow, Sierra Nevada	Growing season, 12-hr mean (1989-1990)	Takemoto et al., 1997
~0.06	Barton Flats, San Bernardino Mountains	May-to-October, 12-hr mean (1991-1994)	Miller et al., 1996a
~0.09	Camp Paivika, San Bernardino Mountains	May-to-October, 12-hr mean (early 1980s)	Miller et al., 1986

Table 8-15 Comparison of Ozone Exposures (ppm-hr) Used in Plant Effect Studies

Tree Species	Selected Response(s)	Ozone Exposure	Reference
Loblolly pine	Reductions in foliar starch and stem volume	45 ppm-hr; 0.15 ppm, 5-hr/day, 5-day/wk, 12-wks	Meier et al., 1990
Loblolly pine	Greater C-retention in the shoot	50 ppm-hr; 0.12 ppm, 7-hr/day, 5-day/wk, 12-wks	Spence et al., 1990
Loblolly pine	Reduction in stem volume	~70 ppm-hr; 0.04 ppm (24-hr mean), 90 days	McLaughlin et al., 1994
Loblolly pine	Decrease in photosynthesis	100-150 ppm-hr; 0.034 ppm (24-hr mean), 37 wks	Richardson et al., 1992
Loblolly pine	Reduction in growth	~120 ppm-hr; 0.05 ppm, 12-hr/day, 150-days	Shafer et al., 1987
Loblolly pine	Decrease in secondary foliage mass	~190 ppm-hr; 0.08 ppm (24-hr mean), 14 wks	Adams et al., 1988
Loblolly pine	Reduced fascicle retention	~290 ppm-hr; 0.03 ppm (24-hr mean), 6-mo, 2-seasons	Kress et al., 1992
Loblolly pine	Greater C-retention in shoot	~800 ppm-hr; 0.06 ppm (24-hr mean), 3-seasons	Kelly et al., 1993

Ponderosa pine	Decrease in photosynthesis	81 ppm-hr; 0.15 ppm , 9-hr/day, 60-days	Miller et al., 1969
Ponderosa pine	Decrease in photosynthesis	81 ppm-hr; 0.30 ppm, 9-hr/day, 30-days	Miller et al., 1969
Ponderosa pine	No significant effect on photosynthesis	140-340 ppm-hr; 0.06 ppm (24-hr mean), 6-7 months	Bytnerowicz and Takemoto, 1989
Ponderosa pine	Intermittent de-creases in photo-synthesis in 2nd growing season	~500 ppm-hr; 0.06 ppm (24-hr mean), 2-seasons	Takemoto et al., 1997
Ponderosa pine	No significant effect on photosynthesis	~600 ppm-hr; 0.06 ppm (24-hr mean), 3-seasons	Beyers et al., 1992
Red spruce	Reductions in foliar carbohydrates	~400-530 ppm-hr; 0.06 ppm (24-hr mean), 2-seasons	Amundson et al., 1991
Slash pine	Decrease in stem growth	~122 ppm-hr; 0.08 ppm (7-hr mean), 111-days	Hogsett et al., 1985
White pine	No significant growth effect	44 ppm-hr; 0.14 ppm, 7-hr/day, 3-day/wk, 15 wks	Reich et al., 1987

Figure 8-1 Location of forest/ozone research sites in California.

8.9 Effects on Materials

The very great chemical reactivity of ozone results in significant damage to a wide range of materials, including rubber, plastics, paint, and metals. In areas experiencing high ambient concentrations, ozone can shorten material lifespans, increase maintenance costs, and progressively damage functional or cosmetic aspects of materials. Based on results from chamber and field studies, such damage includes increased rates of loss of physical integrity of rubber and other elastomers, corrosion of metals and electrical components, erosion and discoloration of paint, fading and reduction of tensile strength of fabrics, and soiling and spalling of nonmetallic building materials. Ozone damage to these materials leads to costs for producers and consumers in two general classes:

1) accelerated replacement and repair costs, as when the service life of a material is impaired of appearance is degraded; and

2) increased avoidance costs, as when industries (e.g., tires, plastics, dyes) substitute processes and materials, or use additives and reformulation, in order to avoid or minimize losses.

Materials that can be adversely affected by ozone include elastomers, paints, fabrics, dyes, artists' pigments, and various types of plastics such as polyethylene. The discussion that follows briefly describes ozone damage for each of these types of materials.

8.9.1 Elastomers

A number of commercially important rubber-based products are fabricated from unsaturated elastomers with well-known sensitivities to ozone damage. These materials include tires, rubber seals, pharmaceutical goods, and many others. Of the materials listed, vehicle tires have been identified as the single major user of elastomers with associated significant economic costs resulting from effects of ozone.

Oxidation affects tires most significantly by causing cracks to develop in the tire sidewalls. Some types of flexible unsaturated rubber are placed over the strength-bearing cords in a tire's sidewall. However, such unsaturated rubber can be susceptible to ozone damage. In order to minimize such damage, tire manufacturers add anti-oxidant materials to such rubber formulations. Benefits from reduced concentrations of ozone can be expected both by tire manufacturers and by tire retreading firms. The manufacturers would benefit by decreasing the quantity of anti-oxidant required to protect vehicle tires through predicted use lifetimes, and tire retreaders would benefit through increased numbers of usable tire carcasses (Rowe, et al., 1986).

8.9.2 Paints

Past studies have shown that of various paints only vinyl and acrylic coil coatings are affected (Haynie, et al., 1976), and that this impact has a negligible effect on the useful life of the material coated. Another more recent study has found that the costs associated with premature replacement of acrylic and vinyl coil coatings were minimal and could not be attributed to pollutants alone (McCarthy, et al., 1981). The results of an EPA study indicated that the possible effect of ozone on latex paint was masked by the effects of other pollutants and environmental factors (Haynie and Spence, 1984).

8.9.3 Fabrics

Ozone has an adverse effect on cotton, nylon, and acrylic fibers and reduces breaking strength of these fibers. The degree of reduction in strength depends upon the moisture present. The effect of ozone on the economic life of fabric material is extremely uncertain. However, it is believed to be quite small (Rowe, et al., 1986).

8.9.4 Dye Fading

Oxidants cause certain sensitive dyes to fade. Research suggests that the magnitude of oxidant-caused dye fabric fading varies significantly with temperature, relative humidity, location of exposure, type and area of exposure, and variation in seasons. A nationwide field exposure study of dye fabric samples showed that one of the highest rates of fabric fading occurred in Los Angeles (Ajax, et al., 1967). Another nationwide field study conducted at the same sites indicated that two-thirds of exposed fabrics showed evidence of dye fading (Beloin. 1972, 1973).

8.9.5 Artists' Pigments

Pigments in artists' paints have been tested under controlled conditions. A recent laboratory study exposed seventeen pigment samples and two Japanese woodblock prints to 0.40 ppm of ozone in a controlled test chamber for three months. The study concluded that several artists' pigments when applied on paper will fade if exposed to an atmosphere containing ozone at the concentrations found in photochemical smog (Shaver, et al., 1983). Indoor-outdoor ozone monitoring in a Pasadena art gallery confirmed that ozone concentrations half as high as those outdoors can be found in art galleries that lack a chemically protected air conditioning system. Under those conditions, it would take roughly six years to accumulate an ozone exposure equivalent to the study's chamber experiment. A more recent study was conducted to further assess the risk of color fading hazard for works of art. Twenty-seven artists' pigments were exposed to ozone for three months. This study found that many types of pigments were susceptible to fading when exposed to ozone. Several ozone-resistant pigments were also identified in the study (Drisko, et al., 1984). Because art work often requires protection for hundreds of years, ozone concentrations in unprotected buildings may pose a significant risk of damage to many art collections.

8.10 Conclusions

Elevated concentrations of ozone can cause adverse effects on agricultural crops, forest trees and materials at current ambient levels. The proposed health-based ozone standards will also provide protection to crops, forests and materials.

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