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PREFACE

Air pollution has received much local attention over the past two years. It is apparent that air pollution is a subject that arouses great emotion and concern for many different reasons, but it is equally apparent that air pollution is a greatly misunderstood phenomenon of modern society.

This symposium was conceived over a year ago when our local Board of Supervisors was in the throes of adopting an air quality maintenance plan. There was great concern then and remains today that Kern County's long time economic leader--Agriculture--did not have adequate input into charting our future.

The purpose of this symposium was to create an awareness that:

- 1. Air pollution does indeed pose an ominous threat to agriculture as we know it today.
- 2. The effects of air pollution on the growing of plants is a subtle thing that has crept upon us and now threatens a large segment of our agricultural economy.
- 3. There are different kinds of air pollution.
- 4. Much remains to be learned about the effects of air pollution on vegetation.
- 5. We all must work together to determine the true extent of this threat through an expanded and enlightened research program.

This symposium was not designed to, nor did we attempt to:

- 1. Identify specific sources of pollution in the Southern San Joaquin Valley.
- 2. Suggest solutions to this growing problem.

It is our hope that when you have studied the contents of this Proceedings you will have a better understanding of air pollution and its effect on agriculture. It is my firm conviction that an informed public and an informed body of decision makers will arrive at enlightened solutions to our mutual concerns.

> J. Hodge Black Farm Advisor County Director

HISTORY OF AIR POLLUTION EFFECTS ON VEGETATION

Dr. O. Clifton Taylor, Associate Director, Statewide Air Pollution Research Center University of California, Riverside

Damage to vegetation is usually one of the earliest indications of an air pollution problem, although the presence of small liquid and solid particles suspended in the atmosphere is often the first tangible evidence one has that man's activities are having a degrading effect on visibility. There is not necessarily a direct relationship between the visible components of pollution and injury to vegetation because for the most part toxic gases are of greatest importance as phytotoxicants. The kind, amount and distribution of air pollution is related directly to population, standard of living, and levels of technology. The problem may be further complicated by meteorological conditions which restrict dispersion and dilution of the emissions. All other factors being equal, air pollution increases as population increases, as the standard of living rises and as the levels of technology increase.

The potential for serious air pollution problems in most of the air basins along our western coast has long been recognized. It is evident that topography and climatic factors which frequently occur in these western basins restrict the dispersion and dilution of toxic gases emitted by industry and transportation units. When this occurs one can expect an air pollutant incident of some magnitude.

Some of the earliest explorers reported observing smoke concentrated in the South Coast Air Basin. The Los Angeles Herald carried an article January 17, 1903, which stated that--"smoke obscured the sun and drove out daylight. It was like meeting a railroad train in a tunnel." Legislation was requested to curtail the amount of smudge from big flues of hotels and bakeries. This emphasizes the fact that without proper ventilation even a few, relatively small sources can be highly objectionable. As population grew, the complaints about poor visibility increased, and in the early 1940's injury to vegetation was observed. During the 1950's, it was clearly established that injury from photochemical oxidants or "smog" was occurring throughout the basin. Surveys in other densely populated valleys along the West Coast revealed that indeed symptoms of oxidant injury on leaves could be found in many areas. Subsequently, similar types of injury were reported near metropolitan centers throughout the country.

Symptoms of "smog" injury to sensitive species of vegetation were identified in and near the cities of Bakersfield, Fresno, Merced and Modesto by Middleton and Paulus (1956). Middleton (1964) reported further that since 1944, when oxidant or smog damage was first seen in the vicinity of Los Angeles, it steadily spread until in 1964 the symptoms could be found in all large cities in the state as well as in all important agricultural regions of California.

The early reports of oxidant or "smog" injury referred to the bronzing, silvering and glazing of the lower leaf surfaces and the diffuse transverse band of collapsed tissue which developed when severe injury occurred. This injury was thought to be produced by some intermediate product when ozone reacted with unsaturated hydrocarbons. Peroxyacetyl nitrate (PAN), the photochemical oxidant responsible for this injury, was not identified until about 1960. It was about the same time that ozone injury was discovered in the field. Some of the injury symptoms produced by ozone were described shortly after the turn of the century, but it was concluded that ozone was so chemically active that it could not possibly exist in the atmosphere in sufficient quantities to injure vegetation. Once ozone injury symptoms were identified in the field and described in the literature, developed countries of the world discovered that similar injury was occurring near their major cities. It is now generally accepted that ozone is responsible for more crop loss in the U.S. than any other air pollutant.

The Cooperative Extension Service and plant pathologists at the University of California, Riverside, worked together from the late 1950's until about 1967 in conducting surveys in the major agricultural regions of California to record incidents of air pollutant injury to vegetation. Many of the Extension personnel in the counties made a special effort to become familiar with the injury symptom syndrome produced by photochemical smog. Reports from the counties were received and collated by an air pollution specialist in the Extension Service. These reports were used in making rough assessments of crop loss. About 1966 an agreement was

reached between the Cooperative Extension Service, the State Department of Food and Agriculture, and the Statewide Air Pollution Research Center of the University of California to transfer the responsibility for assessment of agricultural losses from air pollutants to the Department of Food and Agriculture. Subsequently, training programs were held at Hayward, Davis, Riverside and Parlier to assist the staff of CDFA in developing an expertise in identifying pollutant injury and assessing economic loss. Results of these assessment surveys have been published, Millecan (1971) and (1976). Efforts by the department to assess the impact of pollution on agriculture are continuing.

I need not comment on the urban and industrial growth which has occurred in the San Joaquin Valley in the past 20 years. This is all too familiar to you, and I am sure you are aware of the added pollutants in the atmosphere. It is not surprising that the reports of air pollutant injury are increasing in frequency.

Ozone injury on forest species in Sierra Nevada Mountains was reported by Miller and Millecan (1971) and by Williams, et al. (1977). Williams, et al. (1977) also indicated that elevated ozone levels occurred at three locations in the mountains east of Fresno when monitors were run for five months. The ozone levels in these areas did not, however, exceed the present EPA standard of 0.12 ppm for one hour.

Brewer (1974) reported reduced yield of cotton in field chambers which received ambient air compared with comparable chambers which received air filtered to remove the photochemical oxidants. He concluded that the statistically significant reduction in yield occurred with little or no visible symptoms of foliage injury. This suggests that it would not be possible to assess crop losses, with an acceptable degree of accuracy, based on observations of leaf injury.

Until recently, evaluation of crop loss was directly associated with the amount of foliage injury observed. It is now common knowledge that loss of plant growth and production of marketable product can and does occur with little or no evidence of the characteristic injury symptoms. Consequently, it is difficult to determine if damage is occurring to a particular crop or to evaluate the extent of damage without controlled experiments where results can be compared with plants grown in comparable

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environmental conditions but with the pollutant excluded. Crop loss assessments are further complicated by the wide variation between varieties that frequently occur within a single species. At least now experiments are being designed in many laboratories which should aid in assessing economic losses experienced by farmers operating in polluted areas. Such assessments are critically needed so that control agencies can establish reasonable standards and take steps to provide acceptable controls.

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DOCUMENTED EPISODES OF VEGETATION INJURY IN THE SAN JOAQUIN VALLEY

Dr. Arthur A. Millecan, Jr., Chief, Exclusion and Detection Department, California State Department of Agriculture, Sacramento

It's indeed an honor to be here today to talk about air pollution as it has affected vegetation in the greater San Joaquin Valley. Now, I could very easily say that air pollution is here. We have seen it. We have seen the damage on plants, and that's it, and I could sit down. But I don't think that would be doing justice to you people, especially in view of the fact--as I perceive it--that you're here to find out something about the problems. And so, I hope that I can help accomplish that goal.

First of all, before telling you of what we have seen, I would like to give you some basic background as to our thinking relative to air pollution problems. I think that will help you understand what we're looking for. Dr. Taylor has reviewed very aptly some of the basic principles and some of the phenomena occurring with air pollution, but I would like to restate some of these principles as they affect us. First we look for natural air basins. An air basin is nothing more than a large valley, usually with natural barriers such as mountains.

We look for visual pollution in California. We have been able to see this rather easily. We look for inversions; this is where a warm air mass will move across the cooler air mass and trap the pollutant underneath.

We then look for air movement--how does air move in valleys? And when we consider all of these things together we come up with some kind of understanding of the problem. Theoretically, if we were going to find air pollution damage on plants in the San Joaquin Valley, with what I've said, we would find such in the southeast portion of the valley and on the western slopes of the Sierras.

Now, with these things in mind, we have looked in these areas and there is a very interesting story which goes with that. In about 1969 or 1970, Dr. Paul Miller and I looked for ozone air pollution damage on pines in the southern part of the Sierras, and we found it. It was slight,

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but nonetheless, it was very distinct. Now many people ask me, and I am sure someone here is going to ask me, what in the world are you doing looking at pine trees for air pollution damage when you specialize in agriculture? That's a good question. I want to state that the reason for this is the fact that pines are very sensitive to ozone and are an excellent bio-indicator of the air pollution problem. So, therefore, we look at pines first to see if there are any air pollution problems associated with a particular air mass.

I would emphasize that there are certain things which are basic about pines as bio-indicators. I would mention that some of the varieties of pines are very sensitive, such as the Ponderosa and Monterey pine, and we look for these. By looking at the pines we can tell pretty much what the concentrations of air pollution are. As an example, if you have a very severe concentration of ozone air pollution, the needles on pines will be almost entirely shed. In other words, you may have only a one year retention of needles which gives a foxtail effect to the branch. You can get a two or a three year retention, and with that retention you can see a certain type of marking on the needles which is very indicative of how much pollution is there.

We notice that the symptom from ozone air pollution on pine needles is very specific. After you train your eye for that particular type of symptom, it tells the story. I want to stress that particular aspect because it establishes a basic principle which is used to detect pollution problems in an area. If I suspect that there is pollution within a given area, I look at the pine trees and they give us an indication of how serious the pollution problem might be.

Dr. Miller and I did find damage on pines. It was concentrated at the northern entrance of the Sequoia National Park above Fresno. We watched this particular situation for years and watched that problem expand--it simply became much greater over a much larger area until it was finally quite common. I understand that it has been more difficult to find this year, which is good, but I just relate to you our observation.

If you can go into the mountainous areas and find air pollution damage, then this is a good indication that there could be damage to agricultural crops in the valley, and we put these two things together. We have seen damage in the great central valley. I would report that mostly it has been ozone type damage from air pollution. The symptoms have been very transitory. In other words, we see a problem in one particular area and we might not see it there again for several years. We have seen ozone and PAN air pollution damage in the southeastern edge of the valley where we projected that it would occur. Specifically, we have seen ozone damage on sycamore, on some of the fruitless mulberry; we have seen it on okra--a very sensitive indicator; we have seen it on alfalfa, beans, tomatoes. I reported it once on grapes. We have seen it on cotton. Dr. Brewer will expand upon this latter problem. We can summarize by saying yes, we have seen damage and know the damage has not been consistent on a yearly basis.

Now, we have seen other kinds of damage because there are other kinds of pollutants. We have seen PAN damage on lettuce, especially on Romaine and head lettuce varieties. This has been located primarily south of Bakersfield. The damage on lettuce has been so severe that some fields have been unmarketable from damage by PAN air pollution. I have seen this kind of damage to lettuce at least three times in the last 12 years, and prior to my observations, lettuce damage was reported by Jackson Davidson of the California Cooperative Extension, University of California, Riverside. We have seen other damage from sulphur compounds, especially if you go downwind from some of the fruit drying sheds. On one occasion we have seen mild sulphur dioxide combined with fluoride which damaged crops. This observation was in relation to a large stationary industry in the central valley.

I don't know of any report on air pollution damage in the San Joaquin Valley which has caused more controversy, however, than my particular report on seeing visual damage symptoms on cotton. I have been criticized for that particular report. I have been told that I have a very active imagination and other things, but there were reasons for this particular report. I recognize that the dark stippling or discoloring on the upper surface of the leaves of cotton can be caused by many forms of stress, and yet there was a very typical type of an ozone damage pattern on some of the cotton which we observed. This symptom starts with the basal leaves as a chlorosis and progresses to a very mild stippling, and we took such samples of damage to Riverside to compare. The research people there confirmed it, so I felt pretty good about the statement of cotton damage. I am not going to dwell on this simply because Dr. Brewer today will be discussing his work with cotton, and I would just comment that Dr. Brewer has done a very beautiful piece of work which was and is very much needed.

Now, the kind of things which I have been describing are somewhat transitory and leaves the observer open to much criticism. Yet, based upon what we have seen, certain conclusions can be drawn, 1) that pollution is here; 2) that plant effects can be seen; 3) that the trend in pollution is increasing; and 4) that in the future, as Dr. Taylor mentioned, if the population trends increase, pollution levels will also and more plant damage from air pollution will occur.

Because of the opinions being somewhat confusing, transitory and skeptical, we have had to enter into a program of proving scientifically what we have seen. Again, referring to Dr. Brewer's work--I think it is very basic and he will expand upon his work. Dr. Brewer will explain to you how some of the proof comes from the type of approach that he has taken. I would report that the Department of Food and Agriculture also has been faced with this problem. Mr. Ron Oshima has been working with many crops. He works with a particular crop in a chamber in which the air is filtered before it goes into the chamber, so it is clean air. In other chambers he introduces various amounts of pollution for a given period of time during the growth period of that particular plant. Then in other outside areas he places the test plants in maybe 13 or 14 locations which will range in various amounts of pollution, and he records all this information. When through, he comes up with a chart which says in effect, that if you grow a plant in a given amount of pollution during its growing period, the penalties for growing will be so much! He has worked this out on alfalfa, beans and corn; he also has worked with tomatoes and many other crops.

I think the program which you have seen today is excellent. It should evoke some kind of a thought provoking process relative to air pollution and what happens to agriculture. I hope, personally, that air pollution will not increase. I have a personal conviction that it probably will, and I hope I'm wrong. But, I think as a result we are going to see more damage to plants.

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CHEMISTRY OF AIR POLLUTION

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It is now clearly recognized that pollutants in the air have a substantial impact on plant life of all kinds. Some plants show visible symptoms of injury, while others respond principally by losing growth and productivity. In addition to several toxic "primary" pollutants (sulfur dioxide, fluoride ion, ethylene), there are a number of "secondary" toxicants formed by sunlight irradiation of polluted air. Ozone and the peroxyacyl nitrate family (PANs) are the most important of these secondary toxicants.

The reaction which forms ozone and the PANs requires several hours for full development; during this time, contaminated air will drift many miles from an urban source into rural agricultural areas. Damage is then not heaviest near the freeway, but many miles downwind; in California, this usually means inland. These toxicants can only be controlled by reducing the emissions of their precursors, hydrocarbons and nitrogen oxides, which are derived from motor vehicles and other sources. The chemistry of this conversion is complex and shows that control of hydrocarbon is the most effective means to control ozone formation. Paradoxically, the nitric oxide in combustion exhaust gases destroys ozone very rapidly.

Fortunately, hydrocarbon control should also be an effective means of controlling formation of PANs. Unlike ozone, PAN often persists through the night, since it does not react with nitric oxide. This clearly demonstrates carry-over of pollutants from day to day.

Twenty-five years of research have demonstrated that almost all the bad effects of "Los Angeles-type" smog are consequences of a series of chemical reactions which occur in the atmosphere. They are initiated by sunlight and produce quite a different problem than the "coal smoke" problem of eastern cities in earlier years. Unraveling this complex sequence of events has been a fascinating study. We now have a good semi-quantitative understanding of this chemistry, which has implications for control strategy that should not be ignored. This chapter

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will begin with a survey of the "symptoms" of photochemical smog. Then the experimental simulation of smog in the laboratory will be outlined, with emphasis on the development of "symptoms." Then the chemical reactions which account for the observed behavior will be reviewed. It will be shown that these do account for the behavior observed both in the laboratory and in polluted air. Finally, it will be shown how these findings can explain some of the strange aspects of natural smog. Attention will then be drawn to the implications of this complex chemistry for control strategy.

Smog Symptoms

By the term "symptoms," we mean those effects of smog which can be recognized without the use of instruments. They may be listed as follows:

1) Degradation of visibility: Light scattering by tiny droplets of liquid and particles of solids (i.e., aerosol) can reduce the visibility to two miles or less, even when the atmosphere is far too dry for the formation of fog. It is this resemblance to smoke and fog which produced the word "smog."

2) Eye irritation: So long as "smog" was regarded as a combination of the familiar smoke and fog, there was little alarm over possible health implications. Instead, eye irritation, previously a familiar effect of smoke, was a chief complaint. Respiratory irritation is also reported, especially by those exerting themselves.

3) Plant damage: Many varieties of plants (vegetables, trees, grains, ornamentals, etc.) show visible injury symptoms after smog exposure. These symptoms are distinctly different from those of previously recognized pollutants and can be differentiated from damage caused by other stresses (disease, frost, etc.).

4) Odor: Photochemical smog has a distinctive odor which resembles bleach or chlorine.

5) Color: The haze which obscures visibility is usually white, but sometimes--particularly in late winter afternoons--it appears brown or reddish brown.

6) Rubber cracking: Auto tires and other rubber articles crack and deteriorate at points of stress more rapidly in smog areas than

elsewhere. This was one of the first symptoms of photochemical smog recognized, and it provided both a clue to smog chemistry and a procedure for measurement of smog intensity.

Through laboratory study, it has been possible to identify a number of substances in smog which can account for these symptoms. This information is summarized in Table I. In this table, 'M' reveals that the indicated product is a major cause of the proposed symptom; an 'm' indicates that the importance is in doubt. In addition, there may be other contributors to the various symptoms--as yet undiscovered.

TABLE I. Sn	nog Symptoms	and	Products
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				AEROSOL	AEROSOL		
	OZONE	PANs	\underline{NO}_2	<u>(e.g., H₂SO₄)</u>	ALDEHYDE		
Haze	-	-	-	M	-		
Eye irritation	-	M?	-	-	m?		
Respiratory irritation	M?	-	-	m?	_		
Plant damage	М	М	-	-	-		
Odor	М	-	-	-	-		
Color	- '	-	М	m	-		
Rubber cracking	М	-	-	-	· _		
Oxidant	М	m	m	_	-		

"Oxidant" has been added to this table, even though it required chemical equipment for detection, because it has long been used as the distinguishing characteristic and measure of smog intensity. The products as listed at the top of Table I may be briefly described as follows:

1) OZONE is a form of molecular oxygen which contains three atoms of oxygen (0_3) as compared to the two atoms in ordinary oxygen (0_2) as it occurs in air. OZONE is a colorless gas.

2) PANs stands for peroxyacyl <u>n</u>itrates, a family of organic nitrogen compounds with the formula $R'COONO_2$, in which R represents any one of a number of combinations of carbon and hydrogen which are derived from the hydrocarbons. The OO is the "peroxy" part of PANs and is derived from oxygen of the air. The NO_2 is the nitrate part of the molecule and is derived from the nitrogen oxides. In the pure state, PANs are colorless liquids.

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3) NO_2 stands for nitrogen dioxide, a reddish brown gas which is toxic, but not as toxic as ozone.

4) AEROSOL, unlike the other headings, is not a particular chemical substance. Any suspension of liquid droplets or solid particles is an aerosol, regardless of its chemical composition. The only requirement is that the droplets or particles be small enough to remain suspended for an appreciable time. H_2SO_4 is sulfuric acid, which will form an aerosol if it is present as sufficiently small droplets.

5) ALDEHYDE stands for a family of organic compounds with the Q formula RCH, in which R has the same meaning as in the formula for the PANs. Most aldehydes are colorless liquids with fairly strong odors in pure form.

A characteristic feature of smog is that oxidant usually drops to zero at night. Figure 1 shows two oxidant records taken on the carillon tower on the UCR* campus on <u>13</u> September <u>1971</u>. {'Mast'' coulometric analyzers were used to produce these records. In these (and other oxidant analyzers), air is brought into contact with a water solution of potassium

OXIDANT AT UCR CARILLON TOWER





Figure 1. Oxidant maximum at Riverside often occurs long after maximum sunlight.

*UCR - University of California Riverside

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iodide. Any "oxidant" in the air converts some of the iodide ion to iodine. In a "coulometric" analyzer, this iodine is electrically reduced back to iodide ion. The required electric current is then a measure of "oxidant" in the air. More specific measurements (infrared and ultraviolet spectroscopy) have proven that most of this oxidant is ozone (0_3) .

It will be noted in Figure 1 that the two analyzers gave parallel and nearly equal readings and that both recorded zero oxidant at night. Characteristically, maximum oxidant at this inland location (about 60 miles from Los Angeles and a similar distance from the Pacific Coast in Orange County) occurred at about 4:00 p.m. The peak value of 0.55 ppm oxidant, high but not unprecedented, compared with 0.60 ppm recorded by the Riverside County Control District at the same time. The realization that there are no sources of ozone anywhere near large enough to produce concentrations of this magnitude, coupled with the obvious relationship to sunlight, lead to laboratory demonstrations that this and all the other products and symptoms shown in Table 1 could be reproduced by diluting auto exhaust with air and treating the mixture with artificial sunlight.

The Primary Pollutants - Auto Exhaust

Perfect combustion of gasoline with just sufficient air would produce nearly innocuous exhaust gas. The carbon from the fuel would be completely burned to carbon dioxide (CO_2) , and the hydrogen in the fuel would form water (H_20) . No oxygen would be left over, so there would be only nitrogen (and argon) remaining from the air and some sulfur dioxide (SO_2) from the burning of the sulfur compounds which are always in fuel. For a variety of reasons, combustion is not perfect. Exhaust gas contains appreciable hydrocarbon, some of which can be recognized as simply unburned gasoline and some of which is hydrocarbon molecules of smaller size. Even though some fuel is not burned, there is, nevertheless, oxygen also remaining--and some of this, at the high temperatures of combustion, combines with nitrogen to form nitric oxide (NO_x) . A small portion of this combines with additional oxygen to form nitrogen dioxide (NO_2) , either in the exhaust pipe or after dilution with air. Together, these two compounds are referred to as the nitrogen oxides (NO_x) . With hydrocarbon, these oxides are the major primary pollutants which undergo

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reaction in sunlight to form smog. In addition, exhaust contains large amounts of carbon monoxide (CO). This is a health hazard in its own right, but plays little or no role in the production of the symptoms discussed earlier. The sulfur dioxide arising from the fuel plays a role in the atmospheric reactions, particularly in the formation of aerosol haze.

Although automobiles are the major source of these primary pollutants in southern California, other sources contribute substantial amounts of some of them. In particular, power plants and other industries burning high sulfur fuel oil contribute much more sulfur dioxide than automobiles. Nevertheless, auto exhaust can rightly be called "instant smog," because when mixed with air and irradiated with sunlight all the important symptom-causing products are formed. It is this atmospheric reaction which will not be discussed.

Laboratory Irradiation to Form Smog

If one volume of a realistic sample of auto exhaust is diluted with a few thousand volumes of pure air, a mixture will be produced which contains about one ppm of NO; perhaps 0.05 ppm of NO₂; about 2 ppm of hydrocarbon; and perhaps 0.02 ppm of sulfur dioxide. The hydrocarbons will consist of those containing two to ten or twelve carbon atoms. Methane, present in comparatively large amounts even in clean air, plays no part in the subsequent chemistry. This dilute auto exhaust mixture, before irradiation, shows virtually none of the smog symptoms listed in Table I. If allowed to stand in the dark, very little change in the



Figure 2. Ozone accumulates after conversion of NO to NO_2 .

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chemical composition of the mixture is observed. When radiation simulating sunlight is directed into this mixture, the changes shown in Figure 2 are observed. The behavior illustrated in this Figure offers much opportunity for analysis, as well as some implications for control strategy. Points to be noted:

1) Nitric oxide is converted to nitrogen dioxide, even though the former does not absorb sunlight appreciably, while the latter not only absorbs sunlight (ultraviolet) but is photodissociated by it:

$$NO_2 \xrightarrow{UV} NO + O$$
 R1

2) The maximum amount of NO_2 formed in Figure 2 is nearly equal to the sum of the initial NO and NO_2 .

3) As soon as the conversion of NO to NO_2 is complete, the NO_2 begins to disappear. This suggests that formation of other nitrogen-containing products does not occur until NO conversion is nearly complete.

4) Ozone concentrations comparable to those formed in smog can readily be attained, but ozone is not seen until the NO is gone. Depending on the initial mixture, the ozone concentration may still be increasing after six hours of irradiation. This has implications for control strategies. Abatement of sources (by curtailing auto traffic, for example) after the ozone concentration has risen appreciably will have little effect. In Figure 2, there was no addition of reactants after time zero!

There are further implications of the observations of Figure 2. In the real world, air moves so that this photochemical reaction takes place in a moving air parcel. We can then see why inland areas such as Riverside suffer higher oxidant than source areas such as Los Angeles and Orange County. It simply takes time to develop maximum ozone. The time factor also explains why inland areas such as Riverside experience maximum oxidant long after maximum sunlight intensity (Figure 1).

The San Bernardino mountains, for example, are exposed to high oxidant levels and the pine trees there, 75 miles from Los Angeles, have suffered severe ozone damage. Hemet, Perris, cities in the San Gorgonio pass, and even beyond in Palm Springs, sometimes record oxidant levels as high or higher than Central Los Angeles sometimes after sunset. The reason is that air which reaches these areas has undergone many hours of irradiation. What of the other reaction products? Analysis of the reaction mixture described in Figure 2 shows that PANs and aerosol are also formed predominantly in the second state of the reaction (after the NO_2 maximum). Figure 3 shows this on an expanded concentration scale.



Figure 3. Noxious PAN and visibility-limiting aerosol are formed in the second stage of the reaction.

The same observations we have made regarding ozone apply to these products as well: they can continue to increase long after injection of primary pollutants has stopped. Remote downwind areas suffer more than source areas. Aldehyde is the one product listed in Table I whose formation is not shown in either Figure 1 or 2. It begins to form as soon as the irradiation is started. The five symptom-producing products thus show three different time sequences of formation. Three of the five are formed predominantly in the second stage of the reaction--that is, after the NO₂ maximum. This behavior becomes even more complex when the variations resulting from changes in the initial mixture (relative amounts of NO_x and hydrocarbon, etc.) are considered. But first, the chemical reasons for the behavior shown in Figures 1 and 2 will be explained.

The Photochemistry of Smog

The first law of photochemistry states that only light which is absorbed can cause chemical reaction. To discover the starting point for smog chemistry, those species which absorb sunlight must be ascertained. At low altitudes where most people live, sunlight extends beyond the red end of the visible spectrum (the infrared) and beyond the violet (ultraviolet) down to about 300 nanometers wavelength. With one exception, the substances we have discussed do not absorb visible light (they are not colored), and most of them do not absorb ultraviolet radiation either. Infrared is not sufficiently energetic to break chemical bonds, so only the ultraviolet need be considered. Neither NO nor hydrocarbons absorb ultraviolet within the sunlight range, so we are left with NO₂ as the only strong absorber. Its ultraviolet absorption is merely an extension of the blue absorption, which is responsible for the red color of this gas. This absorption is very strong, and it leads to rupture of the NO₂ molecule already referred to:

$$NO_2 \xrightarrow{UV} NO + O$$
 R1

R2

R3

It has been found that bright sunlight can rupture half of the NO_2 molecules in a sample in about two minutes--a remarkable observation in view of the fact that NO_2 is formed, not destroyed, in real polluted air (Figure 2)! The free atom of oxygen produced by Reaction 1 is far too reactive to simply accumulate in air. It soon finds an oxygen molecule to adhere to and thus form ozone (O_2) :

$$0 + 0_2 + M \longrightarrow 0_2 + M^*$$

{In this equation, M stands for any third molecule (usually nitrogen) which absorbs the energy (as noted by *) of formation of the ozone. Otherwise, the incoming oxygen atom would simply take the place of one of the original atoms of the oxygen molecule.} Measurements show that half the oxygen atoms combine in this way to form ozone in about ten millionths of a second. Thus we have the beginnings of an explanation for the formation of ozone. But now this newly formed ozone molecule soon finds a nitric oxide molecule and returns an atom of oxygen according to Reaction 3:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

This reaction brings us right back to our starting point. Reaction 3 is also very fast and would not allow the accumulation of any significant amount of ozone as long as nitric oxide is present. These three reactions can be expressed as a kind of dynamic equilibrium equation:

$$NO_2 + O_2 \xrightarrow{UV} NO + O_3$$
 R4

The reaction to the right requires ultraviolet radiation, while the back reaction (to the left) proceeds independently of radiation. With

large amounts of NO and only small amounts of NO_2 emitted in combustion gases, the back reaction would predominate and no significant amount of ozone could be formed. Another way to view this dynamic situation is given in Figure 4, wherein each component is represented by a small container:



Figure 4. These three fast reactions form a cycle which is perfectly balanced in the absence of hydrocarbon.

Figure 4 emphasizes the cyclic nature of these fundamental processes. It is simply the transfer of an oxygen atom from NO₂ to an oxygen molecule to form ozone followed by the return of this extra oxygen atom to regenerate the starting materials. Although all three reactions are very rapid, no net change is observed because the cycle is perfectly balanced (in this simple scheme). Reaction 3 produces a change exactly equal but opposite to the change produced by Reaction 1 followed by Reaction 2. It is important to remember that this cycle, which has a turnover time of a few minutes, occurs <u>whenever</u> bright sunlight acts on air containing nitrogen oxides. This is true even if there is little change observed in the concentrations, even in the presence of hydrocarbon and even if no ozone is measureable.

The Role of Hydrocarbon

How then can we account for Figure 2 which shows the conversion of NO to NO_2 followed by the accumulation ozone? The important ingredient

we have omitted is the hydrocarbon, and the behavior of Figure 2 is <u>not</u> observed unless hydrocarbon is present. In its absence only small, slow changes in the initial concentrations of NO and NO₂ are observed, and no appreciable ozone is formed. When hydrocarbons, such as those found in auto exhaust, are present, the conversion of NO to NO₂ as shown in Figure 2 is observed. This occurs in spite of the fact that hydrocarbon does not interact at any significant rate with NO or NO₂ at the low concentrations of dilute auto exhaust. It is clear that somehow hydrocarbons promote the oxidation of NO to NO₂. The term "promote" is used rather than "catalyze" because the hydrocarbon itself is consumed in the process. In fact, those particular hydrocarbons which are consumed most rapidly are just those which are most effective in promoting the conversion of NO to NO₂.

It is evident that something about the <u>process</u> of hydrocarbon oxidation, rather than the simple presence of hydrocarbon, is involved in the conversion of NO to NO_x . The theory of the chemistry of hydrocarbon oxidation is very complex, not fully understood, and cannot be discussed in detail here. A central concept is that of pieces of molecules called "free radicals." These are fragments of molecules which have a free half bond available for reaction. Since this free bond readily combines with others, these free radicals have a very transitory life and are present only in minute concentration. One of the most important free radicals is called peroxyacyl RCOO.

$$RCOO + NO \longrightarrow RCO + NO_2 R5$$

In this formula, R represents a group of carbon and hydrogen atoms derived from a hydrocarbon molecule by removal of one hydrogen atom. This produces an unsatisfied valence (·)('half bond'') which is retained in the peroxyacyl (RCOO·) and in the acyloxy radical (RCO·). At first sight, it might seem that Reaction 5 could have little influence unless it were as fast or faster than the reaction of ozone with NO. But further deliberations show that this is not so, because Reaction 5 converts NO to NO₂ without consuming ozone. It thereby unbalances the neatly balanced cycle shown in Figure 4. This may be described by introducing the dashed line for NO to NO₂ conversion promoted by hydrocarbon (HC) as in Figure 5:



Figure 5. The intermediate formation of peroxy radicals during hydrocarbon oxidation leads to conversion of NO to NO_2 .

Even if this NO oxidation step is 100 or 1000 times slower than the reaction of NO with O_3 , it is important because it removes NO without consuming an equal amount of ozone. This, then, can account for the conversion of NO to NO_2 , which is then followed by the accumulation of ozone. Another way to describe this is to modify equation 4 as follows:

$$NO_2 + O_2 \xrightarrow{UV} NO + O_3 R6$$

HC promoted

Evidence for the presence of the peroxyacyl radical is provided by the formation of PANs according to Reaction 7:

$$CH_3COO + NO_2 \longrightarrow CH_3COONO_2 (PAN) R7$$

This Reaction competes directly with Reaction 5; so long as NO is present in quantity, Reaction 5 takes precedence over Reaction 7. This immediately accounts for two observations previously made:

1) PANs formation is slow in the first stage of the reaction but accelerates as conversion of NO to NO_2 nears completion.

2) The NO_2 disappears rapdily, but only after the peak NO_2 is reached. The effects are both due--at least in part--to the fact that peroxy radicals react preferentially with NO (Reaction 5) rather than NO_2 (Reaction 7) as long as NO is present in larger amounts.

To recapitulate, we have shown how hydrocarbon plays a vital yet indirect role in the formation of ozone and also why the formation of toxic products is largely delayed until the second stage of the reaction. After a brief discussion of aerosol formation, we will return to the effect of changes in amount of hydrocarbon and nitric oxide on symptoms and discuss the implication for control strategy.

Aerosol Formation

Although raw auto exhaust contains some particulate matter (smoke particles), this is not sufficient to degrade visibility significantly when diluted several thousandfold with air. This can be seen in the atmosphere when weather conditions permit the accumulation of unreacted auto exhaust in the early morning hours. For a short time on such mornings before the sun has had time to produce much reaction, analysis shows that high concentrations of auto exhaust are present. In spite of this, the visibility is excellent; if it weren't for instruments showing the presence of hydrocarbon, carbon monoxide, and nitric oxide in concentrations even exceeding those found in smog, the presence of pollution would never be suspected. Mornings like this are rare, since a good purge of the previous day's pollution must be followed by a clear night of low winds to produce a surface inversion to trap the exhaust gases from the morning traffic. This kind of observation clearly shows the crucial role played by photochemistry in developing visibilityreducing aerosols.

In laboratory studies, it has been found that aerosols can be formed by irradiation of dilute auto exhaust or of hydrocarbon/NO₂ mixtures. Aerosol formation is much enhanced by the addition of sulfur dioxide to the mixture. This immediately suggests that sulfuric acid plays a role, since H_2SO_4 is not only very nonvolatile, but it also will absorb water.

$$SO_2 \xrightarrow{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4 \xrightarrow{H_2O} H_2SO_4 \cdot H_2O$$
 (aerosol droplet) R8

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The chemistry of this oxidation is schematic and not fully understood at this time. It is known that the presence of sunlight, hydrocarbons, and nitrogen oxides greatly enhances the oxidation of SO₂.

Calculations show that very small amounts of aerosol (40 micrograms/m³ of aqueous sulfuric acid, equivalent to 0.005 ppm by volume of SO_2) can reduce visibility to two or three miles. It should not be surprising that SO_2 is oxidized in this photochemical reaction; both NO and hydrocarbon are being oxidized. The remarkable observation, as shown in Figure 3, is that this aerosol formation is delayed until the second stage of the photochemical reaction. The first question which might be asked is whether the oxidation of SO_2 is delayed or whether the condensation and growth of sulfuric acid droplets is slowing the process. If NO_2 rather than NO is used as the starting material, there is no delay in aerosol formation--which suggests that the delay is somehow in the chemistry of oxidation of SO_2 to SO_3 and not in droplet formation. Two reactions suggest themselves immediately: oxidation by ozone, or oxidation by PAN.

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Direct experiments show that neither of these is fast enough to be important. Several more complex schemes may be suggested to account for, first of all, the oxidation of SO_2 , and secondly, the delay of this oxidation until the second stage of the photochemical reaction. Since these are quite speculative, they will not be discussed here.

Control Strategies

It is clear that the toxic effects of photochemical smog can only be controlled by reducing the emissions of nitrogen oxides and hydrocarbon. The atmosphere is far too large and far too heavy to consider any scheme for cleaning the air or blowing the dirty air away. But the fact that the toxic effects of smog are photochemically formed and primarily in the second stage of the photochemical reaction has several consequences. The atmospheric reaction contains a remarkable paradox composed of three elements: 1) Ozone and nitric oxide react with each other at a very high rate (Reaction 3). When these two substances are present, each at 0.1 ppm in air, half of each disappears in 18 seconds through Reaction 3 (if not regenerated simultaneously).

2) Nitric oxide is emitted to the atmosphere in large quantities by automobiles and other combustion sources. Combustion gases can contain several thousand ppm of NO.

3) Photochemical smog often contains several tenths ppm of ozone.

The paradox is this: How can this ozone persist in the face of these massive infusions of nitric oxide? As it happened, the answer was understood before the paradox was recognized. It lies in the cyclic nature of the NO_x-O_3 reactions and in the role played by hydrocarbon in converting NO to NO2 as described in the preceding pages. But some further consequences of this scheme should be recognized. When new auto exhaust (or NO from any other source) is added to smog, the ozone content actually goes down--at least temporarily. Observations like this make it doubtful that abatement of sources (such as drastic curtailment of driving) after the ozone concentration has reached substantial levels would actually be beneficial. The air is by then badly contaminated with hydrocarbons and nitrogen oxides, and continued sunlight will continue to produce ozone. In Figures 2 and 3, no additional contaminents were added after the irradiation was started--yet 03, PAN, and aerosol continued to be formed after six hours. Reduction of NO emissions in response to an episode of high oxidant may even lead to increased ozone concentrations as a short-term consequence.

Since both nitrogen oxides and hydrocarbon play roles in the formation of smog, a 3-dimensional or contour diagram is necessary to show the relationship between smog effects (ozone, for example) and initial hydrocarbon and nitrogen oxides concentrations. The simplest such relationship would be <u>if</u> ozone concentrations were proportional to the product of the initial hydrocarbon and nitrogen oxides concentrations. This would be given by a simple equation:

$$(0_3) = k(HC)_0(NO_x)_0$$
E1

In this equation, (0_3) might represent either maximum ozone concentration or ozone dosage during a day's time. The symbols (HC) and

 (NO_x) represent the initial concentrations of hydrocarbon and nitrogen oxides, and k is a proportionality constant. This equation can be plotted to give contours of constant ozone (Figure 6).



Figure 6. <u>Hypothetical</u> relationship between 0_3 and hydrocarbon/NO_x mixture.

If this equation and contour plot were valid, the problem of plotting control strategy would be much simpler. We could say that a twofold reduction in either HC or NO_x would yield a twofold reduction in ozone. <u>Unfortunately, this relationship is not even approximately true</u>. The reasons for its failure are easily found in the chemistry which already has been described. The important points are that hydrocarbon indirectly permits ozone formation by converting nitric oxide to nitrogen dioxide. Most of the bad effects occur after this is complete--that is, in the second stage of the reaction. This being the case, it is not surprising that reduction in either the amount or the reactivity of the hydrocarbon will slow down the NO conversion, prolong the first stage of the reaction and delay the second stage. This is shown by comparison of the upper left and lower left quadrants of Figure 7.

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Figure 7. Hydrocarbon reduction delays ozone formation but prolongs NO_2 exposure. Reduction of NO_x reduces NO_2 but shortens ozone delay.

In contrast, if NO is reduced while hydrocarbon is kept constant, the time necessary to complete the conversion of NO will be reduced, and so ozone will appear <u>sooner</u>. This is shown in the upper right quadrant of Figure 7. The lower right quadrant shows the effect of reducing both NO_x and HC. Time delay to ozone formation is nearly unchanged and so is maximum ozone concentration. This presents us with a dilemma: reduction of hydrocarbon delays ozone formation but enhances total exposure to NO₂ (lower left quadrant). While NO₂ is not as toxic as ozone, it is not harmless; furthermore, in sufficient quantity it will give an objectionable red color to the sky. To abate this hazard, we must reduce NO emissions, but this will shorten the time delay to ozone formation. To sum up: Hydrocarbon control is a good strategy for the control of ozone formation but poor strategy for the control of NO₂ exposure, while NO control is good strategy for the control of NO₂ exposure but poor strategy (perhaps even anti-strategy) for ozone control.

To provide a better guide, several laboratories have irradiated dilute auto exhaust or simulated auto exhaust and followed the formation of ozone. In one such study conducted at the Bureau of Mines in Bartlesville, Oklahoma, total ozone dosage (ppm-min) was measured in six hour irradiation experiments of dilute auto exhaust. The results were shown as a single boundary corresponding to one hour above 0.1 ppm oxidant as shown in Figure 8.





Notice in this diagram that acceptable air quality as judged by ozone dose occupies an area at <u>high</u> NO_x concentrations. This behavior is clearly related to the role of NO in preventing ozone formation. At the lowest hydrocarbon levels, very minute amounts of NO_x suffice to produce ozone over 0.1 ppm.

The boundary between acceptable and unacceptable air quality almost passes through the origin of the plot! In fact, the behavior of the boundary in this crucial area of the diagram (near the origin) is quite difficult to ascertain, since it is necessary to work with extremely tiny amounts of hydrocarbon and nitric oxide. Both the irradiation chamber and the substrate air must be scrupulously clean--otherwise, traces of hydrocarbons and nitrogen oxides from impurities will exceed the amounts added for study. The ability of such small amounts of ingredients to yield appreciable ozone can be understood by remembering that each NO₂ can be photolyzed and regenerated several times, forming ozone on each cycle (Figure 5). Experimentally, it has been found that the ozone concentration after several hours of irradiation may be several times larger than the initial NO concentration. All that is necessary is that sufficient hydrocarbon be oxidized to promote the conversion of NO to NO₂ so that the latter can be rephotolyzed.

Diagrams such as Figure 8 may be used to estimate the reductions needed in emissions to achieve air quality within the air quality standards. In all probability, the amounts of NO_{x} and hydrocarbon emitted in any given area are nearly the same from day to day, and the ratio of the two shows even less variation. Then the atmospheric levels should fall along a narrow band as shown in Figure 8. If these arguments are correct, reductions of both ingredients equally would move the atmospheric levels toward the origin. We are led to the conclusion that extremely low levels of both must be achieved if the oxidant air quality standard is to be achieved. Reduction of emissions by reduction of total vehicle miles (that is, less driving) would reduce HC and NO_x equally toward the origin. Very large reductions would be required to achieve the air quality standard. From Figure 8, it may be concluded that preferential reduction of hydrocarbon would be a far more effective way to attain the air quality standard. It must be remembered that this analysis does not take into account the need to limit NO2 concentrations, since NO_2 is also toxic. The present standard for NO_2 is equivalent to about 0.25 ppm, because medical opinion is that this compound is much Therefore, only modest reductions in NO emissions less toxic than ozone. appear to be required.

Before closing this discussion of atmospheric chemistry and control strategy, some of the uncertainties with regard to Figure 8 should be reviewed:

1) This diagram only expresses one aspect of smog toxicity: ozone dosage. If we considered some other measure of ozone, such as maximum ozone, slightly different conclusions would be reached.

2) Other noxious smog products are not considered. Perhaps we can justify their omission by remembering that many of them (for example, PAN and aerosol) are, like ozone, formed in the second stage of the reaction. They might, therefore, be expected to follow a pattern similar to ozone.

3) How well do these laboratory irradiations imitate the real atmosphere? Figure 8 is based on "batch" experiments in which no additional auto exhaust is added after the experiment is begun. In the real atmosphere, the emission of auto exhaust continues throughout the day. Experimental programs run "dynamically" (with constant addition of auto exhaust) have yielded behavior patterns similar to the batch studies.

4) How significant is the carry-over of pollution from one day to the next? This factor has generally been omitted from laboratory studies, although it is clear that it occurs in the real atmosphere. This "old" smog would have a higher ratio of NO_2 to NO than fresh auto exhaust, and so the first stage of the reaction would be shortened. The extent to which this would modify our conclusions could only be discovered by experiment.

If our knowledge of atmospheric chemistry were purely empirical, so that we had to accept the strange relationships between toxic products and primary pollutants as no more than an experimental observation, it would be very risky to make projections for control strategy in the real atmosphere. But the fact that these observations can be consistently explained in terms of well understood chemical reactions and principals lends much confidence to our application of laboratory findings to the real atmosphere.
METEOROLOGY AND AIR POLLUTION

Thomas R. Crossan, Meteorologist, National Weather Service, Fresno

I know you've been up in the mountains, and alighting from your car you remark, "Isn't the air clean and fresh!" Or, you'we been to the ocean and remark, "Smell the salt in the air." In both cases you were remarking about air pollution. In the first instance the air movement was quite likely still and quiet; in the second, it was moving rapidly onshore. The pine pollen you smelled and enjoyed was added by Mother Nature. So was the salt you noticed in the ocean air. Mother Nature pollutes the air, and she also cleans it! As a generalization, the non-movement of air allows pollutants to collect and movement dissipates them. Meteorology is interested in air movement and, therefore, we in meteorology are into the air pollution problem. As we will shortly see, the weather conditions prevailing in the San Joaquin are conducive to the accumulation of pollutants.

Geography plays a large part in the San Joaquin pollution problem. Virtually all measures of pollution are in volumetric measurements-that is, oxidants in parts per hundred million by volume; carbon monoxide in parts per million by volume. The mountains surrounding the Great Valley of California in effect are restricting the volume of air by walls at least 3,000 feet high and often much higher--they average 12,000 feet high on the east side. As a generalization, the valley is about 400 miles long and 40 miles wide--16,000 square miles for an area. The only outlet from this walled empire at sea level is through the Carquinez Straits toward San Francisco Bay.

So far we have only an area, not a volume. The volume is created when we look at the stability of the air mass contained in the valley, or in the way we look at the inversion. There are two types of inversions that are normal to the San Joaquin Valley--(1) the radiational inversion, and (2) the subsidence inversion. A radiation inversion is caused by the cooling of the air layer near the ground and may extend upward several hundred feet. This is found almost daily the year around during the night and the early morning hours. Little if any vertical mixing takes place within the inversion layer. The inversion is destroyed when the sun's energy warms the lower layers of air and mixing again commences in the vertical.

A subsidence inversion is caused by downward moving air aloft, which is common in the area of high pressure along and off the coast of California land areas. As the air descends, it warms at the rate of 5.5° F per 1,000 feet. It thus arrives at a lower height, warmer than the air surrounding it. This limits vertical mixing of the air, which can take place only when the lower layers are warmer than the layers above.

Let us look quickly at the usual march of temperatures through the day. This will show us the inversion and give us a time frame of reference as well. Beginning the day before the sun rises we know that the lower layers of air near the ground are the coldest with warmer air above. The inversion is near its greatest strength.







Looking at Figure 1, by 9 a.m. the sun has warmed the lower layers of air and we find the base of the inversion off the surface, but there is still an inversion. Even at 11 a.m. a weak inversion usually continues. It isn't until about 1 p.m. that the inversion is gone and the whole mass of air can freely mix. As the sun sets in the afternoon, the reverse is true as the air nearest the ground begins to cool (Figure 2). During the course of the evening the inversion becomes stronger. The top of the inversion then acts like a lid for the free convection of air. It then becomes the third dimension for a volume. I'll generalize at this point and say that for about eight hours a day in the summer (from 11 a.m. say until 7 p.m.) and for about six hours a day in the winter (from 10 a.m. until about 4 p.m.) there is free mixing of the air. The remainder of the time the inversion is present, and pollutants collect below it. The volume is defined, then, for two-thirds to three-fourths of the time as within the mountains and below the inversion.

How do the tops of the inversion change? Mr. Gary C. Franson, the previous air pollution meteorologist at the National Weather Service Office in Fresno, tabulated the airplane flights that have been made over Fresno for the past seven years (July 1, 1972 through May 31, 1979). We have a great wealth of information from his tabulations. Today I'll share with you the figures for the variations of the tops of the inversion and the average mixing heights that were obtained through that period. The mixing height is that height to which mixing was considered possible using the method formulated by George Holzworth. Figure 3 (all future figures will be found at the end of the paper) shows these data. Note that the average top of the inversion doesn't change markedly through the year. It averages a little over 1,700 feet. The mixing height varies much more, rising to the highest point in May at 5,592 feet and the lowest point in December with 1,570 feet. As we generalized above, the area under the bottom curve prevails two-thirds of the time or more, while the upper curve prevails for one-third or less of the time. Our volume is defined, then, at somewhere between 3,000 and 4,500 feet high over the 16,000 square miles--something like 9,600 cubic miles.

When we get down to the basics, the movement of air really is caused by the sun, or, more properly, the energy from the sun and the pressure differences it then creates. The winds in the valley obviously are affected by these pressure differences between the major weather systems on any given occasion. They also are affected by the pressure gradients within the valley, as well as the up and downslope winds into and from the mountains. We all are familiar with the strong winds through the passes from the ocean when the valley is extremely hot. We also are familiar with the strong northerly winds on the west side of the valley when high pressure dominates the Pacific Northwest. These are but a few of the results of pressure gradients on the valley winds.

Figure 4 shows the mountains, the cities of the valley and an artist's conception of the prevailing winds. The main reason I show it is to help you identify the coastal passes. Several years ago I analyzed all of the wind data then available in the valley. Figures 5, 6, 7 and 8 show the prevailing winds for October, January, April and July. Let us begin our look in October. We see the prevailing wind from the northwest everywhere except for Visalia. I do not think this is an error. It is showing us that the mountains are beginning to cool now with downslope motion becoming noticeable there already. With the January map we see the down valley wind flow as the prevailing wind--that is to say, many more southwesterly winds. The April map shows a switch to the northwest and with an average of about six m.p.h. The July map shows essentially the same except for an increase in wind speed of some one to two miles an hour. Note that the wind appears to be flowing out faster at Sandberg (along the Ridge Route) than appears possible. It is above the inversion, remember, and in a different drainage, if you will.

Mr. Franson also has drawn some maps that he depicts the normal wind patterns through the course of a day in the warm season (May through October). These Figures 9, 10, 11 and 12 show his ideas. Note two apparent eddies--one around Fresno with a second around Bakersfield-from midnight to 6 a.m. From 6 a.m. to 12 noon the Bakersfield eddy seems decreased in stature, while the Fresno eddy increases somewhat. From noon until 6 p.m. the usual prevailing northwesterly winds take over. It essentially continues through midnight, except note the southeast winds along the Sierra that he had depicted.

We have requested a study of the winds aloft that have been taken simultaneously with the Fresno APOB's. This was done by David Honda in Geography Report Number 114 dated May, 1978. The study was for a period of 17 months where the winter season (from October to March) had two seasons and only one summer season was available. In this study for all of the data available, the maximum wind was above the inversion 58 percent of the time while it was below the inversion only seven percent of the time. Thirty-two percent of the time it was in the region known as the top of the inversion--that is to say, where the temperature was the warmest. This seems to indicate that what is locally known as the low level jet in the San Joaquin Valley is in the main at or above the inversion and not a factor or a part of the valley wind systems.

The San Joaquin Valley can be represented like a jack-in-the-box. The lid is closed a good share of the time. Daily, during the warmer season, and occasionally in the cold seasons, the top opens and some mixing occurs. The majority of the time we valley residents must live in the pollution we create. Mother Nature will not blow it away for us. We must restrict the pollution or adapt ourselves and our crops to it.

Inversion and Mixing Height Data Fresno APOB 7/1/72 - 5/31/79 (Gary C. Franson 6/79)

Mean Mixing Height	1998	3042	4285	5406	5592	5549	4938	4579	4528	3911	2686	1570	1998	4099
Mean Inversion Top	1744	1414	1192	1416	1712	1819	2062	1951	1796	1746	1855	2146	1744	1739







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EFFECTS OF AIR POLLUTION ON MAJOR SAN JOAQUIN VALLEY CROPS: COTTON AND ALFALFA

Dr. Robert F. Brewer, Associate Horticulturist, San Joaquin Valley Agricultural Research & Extension Center, University of California, Parlier

Cotton and alfalfa are two of the most important crops grown in the San Joaquin Valley. Cotton is usually the number one cash crop occupying more than 1.5 million acres and having an average cash value to the growers of approximately \$780 per acre (\$650 for lint and \$130 for seed) for a gross total of 1.17 billion dollars. Picking and processing the cotton adds an additional 7 to 10 percent to its value and creates thousands of jobs. According to the Annual Crop Report for 1978, approximately 70 percent of all the alfalfa hay grown in California is produced between Modesto and the Grapevine. Approximately half a million acres are devoted to this crop in these eight central California counties. With alfalfa averaging approximately seven tons per acre per year from six or seven cuttings, we see a total of approximately 3.5 million tons worth \$315,000,000 based on the current price of \$90 per ton. Money lost is not always proportional to crop lost due to any given cause because many factors, including crop size, determine price; but it is well to remember that one percent of the cotton crop represents almost \$12,000,000--one percent of the alfalfa crop represents \$3,000,000.

Cotton

Small scale exposure chamber experiments in the early 1960's by Taylor and Merserean (1963) established the fact that cotton could be damaged by repeated exposures to ozone, and the symptoms produced were not unlike those observed in the field near Bakersfield, Indio and Phoenix (see Figure 1).

Approximately 10 years later, Brewer and Ferry (1974), placed filtered and non-filtered plastic greenhouse chambers over field cotton at several locations in the San Joaquin Valley and found that the cotton plants in the filtered units always produced more bolls and seed cotton than was produced by comparable plants in the ambient or non-filtered chambers. Differences observed (see Table 1) ranged from five percent in favor of the filtered units at the West Side Field Station near Five



FIGURE 1. OXIDANT INJURY SYMPTOMS ON COTTON LEAVES.

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Location	Year	Variety	Am	oient	Filt	ered	% Dif	ference
			<u>Bolls</u>	Weight	Bolls	Weight	Bolls	Weight
Parlier	1972	SJ-1	7.6	55.3	9.5	68.3	+20.0%	+19.3%
	1973	SJ-1	8.6	55.7	12.4	78.6	+32.2	+29.1
	1974	SJ-4	8.1	49.4	11.9	72.5	+34.4	+31.8
	1974	SJ-4	7.2	68.7	8.9	78.5	+19.1	+12.5
	1976	SJ-2	6.5	40.6	8.7	49.4	+25.3	+17.8
	1976	SJ-4	7.2	39.4	8.7	46.4	+17.2	+15.3
Five Points	1972	SJ-1	11.0	75.3	12.7	82.9	+13.3	+ 9.1
	1973	SJ-1	9.8	63.9	10.9	67.2	+10.1	+ 5.0
	1974	SJ-1	10.0	61.9	11.1	64.5	+ 9.9	+ 4.0
	1974	SJ-2	9.2	53.3	10.6	45.7*	+ 5.6	-16.6
Hanford	1972	SJ-1	14.6	99.0	18.8	124.3	+22.3	+20.3
	1973	SJ-1	7.4	47.6	9.5	58.3	+22.1	+18.3
Strathmore	1973	SJ-1	6.0	30.7	7.5	41.0	+20.0	+25.1
	1975	SJ-2	7.9	45.1	9.1	55.5	+13.2	+18.7
	1976	SJ-4	9.1	48.9	10.8	66.5	+15.7	+26.5
	1976	SJ-5	9.9	59.9	10.9	63.1	+ 9.2	+ 5.1
Arvin	1975 1976	SJ-2 SJ-2**	10.1 10.5	62.5 62.7	$\begin{array}{c} 12.2\\11.6\end{array}$	71.5 66.0	+17.7 + 9.5	+12.6 + 5.0
Mettler	1976	SJ-2	9.0	58.9	10.8	68.9	+16.7	+14.5

Table 1. Effects of Removing Oxidants from Air on Cotton Boll Set at Various Valley Locations

* Severe cabbage looper infestation in filtered unit.

** Very severe verticillium killed plants in early September.

Points to 30 percent more at Kearney Field Station near Reedley. Approximately 20 percent differences were found near Hanford in Kings County, near Strathmore in Tulare County, and near Arvin in Kern County. These early trials used Acala SJ-1. Subsequent experiments from 1974 through 1976 using SJ-2, SJ-3 and SJ-4 indicated increasing smog resistance with each successive release. SJ-2, which still accounts for three-fourths of the valley's cotton acreage, produced 20 percent more cotton in filtered as compared with ambient air at Reedley, and approximately 15 percent more when the pollutants were filtered out near Strathmore and Arvin. When Oshima (1979) and his co-workers at Riverside exposed SJ-2 cotton plants to .025 ppm levels of ozone six hours a day, twice weekly at various stages of growth, they found that both top and root growth were reduced significantly and boll set was depressed 48 percent without any compensatory effect on boll size. Square production was delayed several weeks resulting in similarly delayed boll set. Reductions in net assimilation rates accompanied the exposures to ozone and were deemed responsible for the observed reductions in plant growth.

Results of all greenhouse exposure experiments are clouded by a degree of doubt concerning differences in plant response due to the greenhouse itself. Temperatures, relative humidity and light conditions are usually quite different from those encountered in the field. Comparisons of results obtained with exposures of various species to pollutants in conventional versus open top exposure chambers have indicated that conditions in the former tend to enhance the pollutant effects. For this reason we decided to take a closer look at cotton yield responses using open top growth and exposure chambers. Two varieties of cotton--Acala SJ-2 and SJ-5--were grown at Parlier during the 1978 growing season. Treatments used included 1) filtration of all air entering the chamber, 2) filtration of 1/3 of the air entering the chamber (the remaining 2/3 being ambient air), 3) all ambient or non-filtered air, 4) ambient air to which extra ozone was added to double the ambient ozone level, and 5) outdoor or outside plots to help evaluate the growth chamber effects.

Results of these treatments (see Tables 2, 3 and 4) on Acala SJ-2 indicated a 16 percent beneficial response to filtering out oxidants present in the air at Parlier. When 1/3 of the pollutants were removed yields were increased about seven percent. Doubling the ozone concentration reduced boll set and seed cotton production an additional 25 percent. With Acala SJ-5 there were no significant differences between the ambient and filtered treatments indicating a tolerance to ambient levels of ozone, but when the ambient ozone levels were doubled, boll set was reduced 10 percent and seed cotton nearly 30 percent. In fact, the high ozone treatment had a greater effect on SJ-5 than on SJ-2, indicating that very serious crop reductions should be expected if air quality in the valley deteriorates significantly. Table 2. SJ-2 Boll Counts and Pickings - 1978

Treatment	Boll Count 8/17	9/26	Pickings 10/27	11/27	Season Total	Percent Ambient
Filtered	620	526	319	20	865	113
1/3 Filtered 2/3 Ambient	555	430	367	23	820	107
Ambient	546	475	268	20	763	100
2X Ambient	458	496	188	12	696	91
Outside	437*	84	480	55	619	81

* Plots excessively vegetative due to heavy spring rains.

Table 3. SJ-5 Boll Counts and Pickings - 1978

Treatment	Boll Counts 8/17	9/26	Pickings 10/27	3 11/27	Season Total	Percent Ambient
Filtered	486	399	213	22	634	94
1/3 Filtered 2/3 Ambient	489	379	227	14	620	92
Ambient	482	437	216	21	674	100
2X Ambient	344	382	134	14	530	79
Outside	261*	103	428	62	593	96

* Plot excessively vegetative due to heavy spring rains.

Table 4. Raw Cotton Production - 1978

Treatment	SJ-5	% of Ambient	SJ-2	% of Ambient
Filtered Chamber	2045	94	2873	116
1/3 Filtered 2/3 Ambient Chamber	2026	93	2637	107
Ambient Chamber	2177	100	2471	100
2X Ambient Chamber	1522	70	1901	77
Outside Ambient Chamber	1827*	84	2020	82

* More vegetative than other plots.

Alfalfa

Alfalfa has for many years been considered one of the more sensitive agronomic crops so far as air pollution is concerned. Much of the early work relating SO_2 pollution with crop yields was carried out with alfalfa by Moyer Thomas (1961).

Thompson (1974) and Kats have studied the response of several varieties of alfalfa to air pollution in the Riverside area. Some of their data are summarized in Table 5. Both Hayden, considered sensitive, and Eldorado, considered somewhat tolerant to oxidants, produced significantly less stems with lower leaf to stem ratios and containing less carbohydrates when grown in ambient as compared with filtered air.

Two varieties of alfalfa were planted in the spring of 1979 in the open top growth and exposure chambers at Kearney Field Station previously used for cotton. Treatments included those previously used with cotton plus two others involving the addition of SO_2 gas in subacute concentrations. To date three cuttings have been made on the newly established plots. Results of the second and third cuttings are shown These data indicate that the relatively new variety in Tables 6 and 7. WL-512 is considerably more tolerant to oxidants than the old standby, Moapa. Addition of SO₂ to ambient air was especially limiting on the third cutting of Moapa (24 percent decrease compared with ambient air, 37 percent reduction compared with filtered), but these are preliminary findings on a long term experiment planned for a minimum of three years. If the current trend toward differences ranging from five to 20 percent between filtered and non-filtered treatments persists, we will have a second important crop for which we can predict serious economic damage at current pollution levels in the valley. Cotton, of course, is the other crop for which we now have conclusive data.

Table 5. Alfalfa Response to Smog -	Riverside	
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Treatment	Variety	Thompson Leaf/Stem Ratio	& Kats, Er Stem/Pot 8/5	nv. Sci. & Tech Yield % of Ambient	h. 10;1237. 1976 Carbohydrate G/100G
Filtered	Hayden	48.3	113	173	43.6
Ambient	Hayden	40.8	82	100	37.3
Filtered	Eldorado	48.0	116	150	45.8
Ambient	Eldorado	42.1	88	100	44.1

Table 6. Alfalfa Yields - Moapa - 1979

Treatment	Weight 2nd Cutting	Percent of Ambient	Weight 3rd Cutting	Percent of Ambient
Filtered	4507g	109	3913g	122
Ambient	4150	100	3211	100
Ambient + SO ₂	4126	99	2455	76
1.5 X AO3	3617	87	2981	93
Outside	3809	92	3443	107

Table 7. Alfalfa Yields - WL-512 - 1979

Treatment	Weight 2nd Cutting	Percent of Ambient	Weight 3rd Cutting	Percent of Ambient
Filtered	4589g	104	4751g	105
Ambient	4434	100	4524	100
Ambient + SO ₂	4264	96	4120	91
1.5 X AO ₃	4096	92	4174	92
Outside	4006	90	4356	96

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EFFECTS OF AIR POLLUTION ON POTATOES GROWN IN CALIFORNIA

Dr. Ken W. Foster, Geneticist, University of California, Riverside

"Speckle-leaf" of potato, a disease best characterized by glazed spots on leaf lower surfaces, has been in the San Joaquin Valley for several years. The affliction is probably gradually increasing in severity, with air pollution the main causal factor. Potato fields in Kern County, especially if late planted and/or in the Arvin-Edison district, usually are affected to the greatest degree. Distinct varietal differences in susceptibility to speckle-leaf have consistently been noted. White Rose, Norgold Russet, Russet Burbank, and Kennebec usually show few symptoms. The varieties Centennial Russet and Red La Soda are frequently moderately to severely affected. In addition to the named varieties, numerous advanced selections in the industry-supported Variety Development Program also have shown speckle-leaf. Therefore, the problem will likely continue.

The observed varietal differences are consistent with our results and with research conducted in other U. S. potato production areas, i.e., ozone appears to be responsible for a majority of the problem in California while sulfur dioxide, although less damaging than ozone, may be significant. Neither PAN nor sulfur dioxide appear to be related directly to speckle-leaf.

Controlled environment exclusion studies were carried out in Riverside in 1978 on the speckle-leaf sensitive cultivar 'Centennial', a russet-skinned type of considerable importance to Kern County. Activated carbon was used to filter various proportions of ozone from ambient Riverside air. Plants grown in plastic chambers were exposed to the various levels of ozone. Sulfur dioxide was also injected into half of the chambers at each ozone dose. Plants growing in completely filtered air developed no speckle-leaf symptoms, remaining green and vigorous throughout the 120 day experiment. Plants grown in unfiltered air developed symptoms early in growth, and the severity of damage increased until premature plant death occurred. The differences in foliar symptoms were reflected in large effects on tuber yield. Plants growing in completely filtered air developed no speckle-leaf symptoms, remaining green and vigorous throughout the 120 day experiment. Plants grown in unfiltered air developed symptoms early in growth, and the severity of damage increased until premature plant death occurred. The differences in foliar symptoms were reflected in large effects on tuber yield. Plants growing in filtered air yielded approximately twice as much as those receiving the maximum ambient treatment (Figure 1). Sulfur dioxide may have contributed additional damage, but the ozone response was dominant. The quality components, dry matter percentage and sugar concentrations, were not significantly affected. Tuber protein percentage in the heavily damaged plants was increased, but not sufficiently to offset reduced yield. Thus, total protein yield also was decreased.



Figure 1. Effects of carbon filtration on tuber yield of Centennial Russet plants grown at UCR.

A second approach to analyzing yield losses attributable to oxidant air pollutants, e.g., ozone, is through the use of antioxidant compounds. These are chemicals which, through poorly understood mechanisms, reduce injury to treated plants exposed to oxidant pollutants. We have utilized an antioxidant designated "EDU" or "DPX-4891*" to obtain yield loss estimates in moderately sized field plots. The material was applied as a preplant soil treatment and as a foliar spray. Experiments with EDU have been conducted at UCR in 1978 and 1979, and at four Kern County locations in 1979. The Riverside experiments were grown at much higher ozone levels than the Kern County ones, but ozone levels at the latter sites are similar to those in other U. S. potato production areas plagued by pollution damage. Riverside thus provides an excellent site for testing both the efficacy of EDU and varietal differences in susceptibility.

The EDU tests each featured Centennial (susceptible) and White Rose (resistant) cultivars. EDU was very effective in reducing foliar injury to Riverside-grown Centennial plants (Figure 2), but no effects were observed on White Rose. Tuber yields showed similar trends, with large effects being observed on Centennial, but essentially none on White Rose (Table 1). An increased number of tubers, especially marketable tubers, accounted for much of the higher yields of treated Centennial plants (Table 2).

The Kern County experiments in which EDU was tested in 1979 were conducted in growers' fields in the following four areas: 1) Off Kimberlina Road near wasco; 2) On Seventh Standard Road, 3 miles west of California Highway 99; 3) On Rancho Road south of Arvin; and 4) On Weedpatch Highway just south of Weedpatch. The results were less dramatic than, but consistent with, those at Riverside. Marketable tuber yield of Centennial was increased an average of 18 percent, while White Rose was not affected by EDU treatment (Table 3). A somewhat unexpected result was the apparent consistency over locations. From previous ozone data, we predicted that the more southern sites (site numbers 3 and 4), which were also planted later, would show greater treatment effects. The prediction was not realized, but actual ozone levels (not monitored in 1979) may not have varied as expected. None of the sites developed what would be considered a severe case of speckle-leaf, but treatment induced differences in severity were observed. However, the two later

* E. I. Du Pont de Nemours and Company

tests were rather low yielding and factors other than ozone may have been limiting.

Figure 2. Effects of EDU on visual ozone damage to Centennial Russet plants grown at UCR.





		Tuber yield, cwt/acre						
Cultivar	Treatment	>12 oz.	4-12 oz.	<4 oz.	culls	Total marketable	Total	Specific gravity
Centennial	T0 T1 T2	0 15 17	60 180 230	96 83 80	2 4 4	60 200 240	160 290 330	1.062 1.073 1.075
White Rose	${}^{T}_{T_{1}}$	34 42 51	260 240 240	70 74 57	91 109 103	290 285 290	460 470 450	1.072 1.073 1.074
	$S_{\overline{x}}$	7	10	9	7	10	10	0.001
(T): (C): T x	reatments ultivars C	NS ** NS	** ** *	NS * NS	NS ** NS	** ** **	* ** **	** **

Table 1. Effects of antioxidant treatment on performance of Centennial and White Rose grown at Riverside in 1979

*, ** Significant at 5 and 1% levels, respectively.

 T_0, T_1, T_2 are untreated, recommended rate, and twice recommended rate, respectively.

	, ,	Tuber no./	olot
Cultivar	Treatment [†]	Marketable	Total
Centennial	${}^{\mathrm{T}}_{{}^{\mathrm{T}}_{2}}^{\mathrm{T}}$	13 54 60	89 121 126
White Rose	${}^{\mathrm{T}}_{{}^{\mathrm{T}}_{1}}_{{}^{\mathrm{T}}_{2}}$	54 55 63	146 164 134
S	Γ	5	5
(T)reatments (C)ultivars T x C		** ** **	** ** **

Table 2. Effects of antioxidant treatments on tuber number of Centennialand White Rose grown at Riverside in 1979.

** Significant at 1% level.

⁺ T₀, T₁, T₂ are untreated, recommended rate, and twice recommended rate, respectively.

Table 3. Effects of antioxidant treatment on performance of Centennial and White Rose averaged over four Kern County locations in 1979.

Cultivar	Treatment	Total yield, cwt/acre	Percent marketable	Specific gravity
Centennial	Check	240	78.7	1.083
	Treated	280	79.5	1.084
White Rose	Check	445	78.7	1.080
	Treated	440	80.8	1.081
Centennial		**	NS	NS
White Rose		NS	NS	NS

** Significant at 1% level.

In summary, ozone can significantly reduce yields of sensitive potato cultivars in important potato producing areas of California. In certain areas, sulfur dioxide may cause additional yield losses. Speckle-leaf damage may be reduced by planting resistant cultivars (for market classes in which they are available) and by early planting if susceptible cultivars are grown. Mean daily and mean daily maximum ozone concentrations increase markedly during spring months, peaking between June 1 and August 1 in the Arvin area (Figure 3 shows 1976-77 values; ARB data). Early planting thus decreases crop exposure to ozone.



Figure 3. Seasonal trends of daily mean and daily maximum ozone concentrations at Arvin in 1976 and

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EFFECTS OF AIR POLLUTANTS ON VEGETABLE CROPS GROWN IN THE SAN JOAQUIN VALLEY

Dr. James P. Bennett, Assistant Professor, Department of Vegetable Crops, University of California, Davis

How sensitive are vegetable crops to air pollutants? How likely is it that damage is occurring in the San Joaquin Valley? Is anything known about how the pollutants in the valley affect plant growth and yield? These are some of the questions I would like to try to answer very briefly with specific references to vegetable crops grown in this area.

Table 1 lists the million dollar vegetable crops grown in 1978 in Kern County (Department of Agriculture, Kern County).

Table 1:	KERN COUNTY MILLION	DOLLAR VEGETABLE	<u>CROPS</u> , <u>1978</u>
	(\$ million)		(\$ million)
Potatoes	48.4	Cantaloup	5.5
Carrots	25.9	Watermelon	3.2
Lettuce	18.1	Other melons	3.0
Onions	15.0	Dry Beans	2.8
Tomatoes	8.3	Garlic	2.3

I will discuss how ozone (O_3) affects most of these except potatoes (see paper by Ken Foster) because a great deal of research has been done with this pollutant. Very little is known about the effects of sulfur dioxide (SO_2) on these crops because the research has not yet been done. Some field crops, e.g. alfalfa and soybean, are known to be sensitive to SO_2 and in potato it is known that tubers from SO_2 polluted areas do not grow as well as tubers from non-polluted areas, indicating there is a carry-over effect on subsequent years' yields. I will confine the rest of my comments to the effects of O_3 .

Sensitivity can be studied by subjecting as many varieties of a crop as possible to a single high concentration dose of a pollutant and then ranking the responses of the test plants. Table 2 gives two such rankings for lettuce and snap beans, the former based on the response of 36 plants of each variety being exposed to .70 ppm 0_3 for 1-1/2 hours (Reinert <u>et al</u>. 1972) while the latter were based on visible injury scores produced by exposure to ambient air pollution in New Jersey (Brennan and Rhodes, 1976).

Table 2: VARIETAL RANKINGS FOR SENSITIVITY TO OZONE

LETTUCE		SNAP BEAN
Dark green Boston	High	Tempo
Grand Rapids		White half runner
Imperial 456		Tenderwhite
Butter crunch		Bush blue lake
Big Boston		Honey gold
Romaine		Rich green
Black seeded Simpson		Provider
Great Lakes		Greensleeves
(Based on 36 plants exposed		Contender
to .70 ppm for 1.5 hours)		Green Isle
		Greenway
		Slenderwhite
		Mohawk

Long Tendergreen

Gold crop

Low

(Based on vis. injury from ambient New Jersey air)

Neither study included the opposite companion study to determine if the rankings were consistent. That is, the lettuce study did not include plantings in the field to be exposed to ambient air and the snap bean study did not include plants exposed to controlled fumigations of a single pollutant.

It is also known that the difference in response between the most sensitive and the most tolerant varieties is not the same for each crop. Table 3 shows that this difference can range from 18 percent for radish to 63 percent for tomato (Reinert <u>et al.</u>, 1972). This means that you cannot compare rankings between species, and that the most sensitive variety of one species will not show the same response as the most sensitive variety of another species after exposure to the same concentration of pollutant.

A study on tomato sensitivity in southern California found that foliar injury rankings did not correlate at all with yield reduction rankings (Oshima <u>et al.</u>, 1977a, b). Plants of four varieties were grown in the field along a pollution gradient and ranked for both visible injury

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Table 3: <u>PERCENT</u> <u>DIFFERENCE</u> <u>IN</u> <u>INJURY</u> <u>BETWEEN</u> <u>MOST</u> <u>SENSITIVE</u>

AND TOLERANT VARIETIES

Crop	% Difference after exposure to .70 ppm 0 ₃ for 1.5 hours
Tomato	63
Soybean	42
Lettuce	36
Radish	18

and final yield. It was also found that the yield rankings in the polluted and non-polluted areas were not correlated. For example, Earlypak was found to be resistant to visible injury development but it yielded poorly at the polluted site compared to the other varieties which showed damage. Thus one cannot extrapolate from foliar injury screening studies to yield responses in the field.

The study also investigated the causes of the yield reductions. In general, a decrease in fruit size occurred as pollution increased. The most marketable fruit were produced during the period of lowest production and the greatest production occurred late in the season during the time of lower marketability (fresh market tomatoes). Thus air pollution cannot only lower biological yield, it also can cause a depressed seasonal harvest for the grower and lead to a loss of early market advantage.

Turning to snap beans, a study of cultivar sensitivities to 0_3 both in the field and the greenhouse did show a consistent ranking between the two (Brennan and Rhodes, 1976). It was found that damage usually occurred following exposure to .04 ppm for only six or seven hours. This is a very low level which probably is found in the Central Valley today. Injury was noted to increase on older leaves throughout the growing season. This means that the crop may be more sensitive when it's older and larger yield losses could occur if more oxidant events occur during that time. Damage was consistently observed in the field when the 0_3 concentration exceeded .03 ppm only 6-22 percent of the time and when the peak hourly concentrations ranged from .045-.098 ppm. Damage also was correlated with high 0_3 peaks that occur one or two days previously and these peak concentrations were observed to increase with time. Finally, it was observed that the cultivars most sensitive to 0_3 were also most resistant to rust. The authors cautioned that the two were not causally related and exceptions to the rule occurred.

The sensitivity of onions to 0_3 is not clearly understood. In Ontario, flecking occurs on the leaves in the field following exposure to .15 ppm for only four hours (Wukasch and Hofstra, 1977). This is not an uncommon dose for California. However, in a study in a greenhouse with two-week-old plants, no visible injury developed even after exposure to .20 ppm up to 24 hours daily for four weeks (Ormrod <u>et al.</u>, 1971)! This dramatically emphasizes the difficulty we have in trying to extrapolate from greenhouse studies to the field. It is often thought that greenhouse conditions would predispose plants to greater injury, yet this evidence suggests the opposite. The best explanation for this problem is that the extremely low wind speeds in greenhouses and growth chambers does not break the boundary layer around leaves preventing pollutant uptake, thus causing the plants to be exposed to less pollutant than they would get outdoors where wind speeds are higher.

Ozone (pphm-hr)	Top dry weight (g)	Necrotic leaf dry weight (g)	Necrotic leaf percent	
		ONION		
0	.84	.06	7.0	
100-1	.79	.06	7.3	
100-4	.62	.06	9.5	
		CUCUMBER		
0	3.95	.21	5.5	
100-1	3.78	.25	6.5	
100-4	2.80	.58	20.8	

Table 4: EFFECTS OF OZONE ON ONION AND CUCUMBER

Based on two-week-old plants, greenhouse grown. Onions showed no visible injury after four weeks of exposure to .20 ppm O_3 up to 24 hours daily.

NOTE: In Ontario, flecking occurs on onions in the field after exposure to .15 pp. 0_3 for four hours.

The effects of 0_3 on onions and cucumbers grown and fumigated simultaneously are shown in Table 4 (Ormrod <u>et al.</u>, 1971). It is clear that following the exposure to a very high concentration of 0_3 (1 ppm) cucumbers are more sensitive than onions. The latter showed a 26 percent yield loss with only 9.5 percent necrosis while the former had a 29 percent yield loss with almost 21 percent necrosis at the highest 0_3 dose. It also is evident that the dry weight loss is not correlated with the amount of necrosis, a fact that also has been observed in lettuce and spinach. When the same onion variety was grown in the field, the 0_3 stress increased infection of the leaves by botrytis. The application of an anti-oxidant and a fungicide provided better control than either one alone. One can conclude from this that 0_3 -stressed plants are more susceptible to disease.

Table 5 shows the results of a study where both spinach and lettuce were grown simultaneously in controlled environment chambers and fumigated six hours daily with 0, .08 and .18 ppm 03 at 50 and 80 percent relative humidity for 32-35 days (Bennett, 1979). In lettuce, there was no effect of 0_3 on senescent leaves or visible injury, yet yield losses ranged from 25-43 percent, depending on humidity. In spinach, percent senescent leaves increased 3.6 to 47 times due to 0_3 yet yield losses ranged from 16 to 54 percent. It does not seem reasonable to assume that if no visible injury occurs on a plant there will be no effect on yield. Yield losses can occur with or without any visible injury symptoms. The lettuce plants were also significantly smaller and more tender, rendering them unmarketable, regardless of a weight loss and without visible injury. This occurred even at an average one-hour 03 concentration that is below the California one-hour standard and inside a growth chamber, where they are presumably less susceptible as we have learned earlier. It is clear that the standard does not protect this crop from significant yield losses if the same 03 concentrations and humidity conditions were to occur in the field. Furthermore, under conditions that were favorable for lettuce, the spinach grew poorly and showed a greater 03 response. One could conclude from this that unfavorable growth conditions make plants more susceptible to 0_3 . The results also show that spinach yield losses due to 0_3 were greater at 50 percent humidity than

		SPINACH	[
Humidity	O	FW	LA	#LVS	%DL
50	໐ັ	57	. 70	59	.2
	.08	39	.53	35	3.4
	. 18	26	.40	30	9.4
80	0	24	.32	42	5.5
	.08	20	. 30	39	9.6
	.18	18	.21	31	20.0
		LETTUCE	<u>_</u>		
50	0	170	3.66	55	11.0
	.08	188	5.04	69	9.0
	.18	127	3.54	52	11.0
80	0	174	3.95	77	10.0
	.08	122	2.88	60	10.0
	.18	99	2.57	60	10.0

Table 5. EFFECTS OF OZONE AND RELATIVE HUMIDITY ON SPINACH AND LETTUCE

at 80 percent while lettuce yield losses followed the opposite pattern. Thus it may be that generalizations about losses in more humid versus dry environments are not possible because responses are crop specific.

Carrots also are quite sensitive to 0_3 . We exposed containergrown carrot plants intermittently to .19 and .25 ppm 0_3 throughout their growth period of 108 days and found the results shown in Table 6 (Bennett and Oshima, 1976). Total biomass decreased 30 percent in the high 0_3 treatment but root weight decreased 46 percent while leaf weight was unchanged. On a percentage basis roots accounted for over 56 percent of the total dry weight in the unfumigated control treatment but only about 40 percent in the high 0_3 treatment. The decrease in root weight was found to be directly proportional to the increase in chlorosis in the leaves and a model relating the two predicted that 1.5 g of root tissue is lost for every gram of chlorotic leaf dry weight caused by 0_3 injury. One can conclude that root crops may be more seriously affected by oxidants than leafy vegetable crops.

Ozone (ppm)	Leaf length (cm)	Root length (cm)	Total No. leaves	% chlorotic leaves	Total fresh wt. (g)	Total dry wt. (g)	Root dry wt. (g)	Leaf dry wt. (g)	% dry wt.	Root wt. Ratio	Root shoot ratio
Control	45.7a ^z	21.9a	34.la	2a	351a	44.5a	24.9a	19.6a	13a	.56a	1.23a
0.19	50.2ab	19.9a	39.2a	14b	272Ъ	39.la	16.9b	22.2a	14a	.43b	.73Ъ
0.25	52.4b	20.1a	39.8a	28c	244b	32.6b	13.4b	20.0a	13a	.41c	.60b

Table 6. EFFECTS OF OZONE FUMICATION ON CARROT PLANTS

^z Mean separation in columns by Duncan's multiple range test, 5% level.

What can 0_3 do to the quality of vegetable crops? One study of the effects of 0_3 on cabbage, carrots, corn, lettuce, strawberries and tomatoes found that solids were decreased in carrots, corn, tomatoes and increased in cabbage (Pippen <u>et al.</u>, 1975). Fiber and ash content increased in cabbage, but decreased in tomato. No consistent pattern emerged for carbohydrate or protein (nitrogen) contents in response to 0_3 . Some vitamins were affected, most notably vitamin C, thiamine and niacin, which actually increased in some of the vegetables. Although the survey indicated that 0_3 did not have a major or generally deleterious impact on crop quality, it did indicate some areas where 0_3 influenced some components. Obviously a lot more work is needed in this area.

I hope it is clear by now that the vegetable crops in the San Joaquin Valley are sensitive to the pollutants that are found there. I believe we can say with 100 percent certainty that air pollution is damaging agriculture in the Central Valley, but we cannot say how much, when and where it is occurring. Estimates of damage vary widely in the millions of dollars because there are many ways of calculating the losses. Experts disagree on many things in this field and I would like to list eight of them for you in the hopes that by bringing them out in the open we can focus more attention on them.

Experts disagree on the significance of long-term, low level doses versus short, high concentration doses in affecting final yield. While there is general agreement that there are thresholds for visible injury development, the existence of a threshold for yield losses is quite controversial. The adequacy of generalized dose-response curves in predicting the response to a particular concentration and exposure duration and time also is questionable. What is needed are families of curves for selected air pollutant concentrations, but this takes a great deal of time and money to produce.

The acceptability of greenhouse and chamber fumigation studies is still being debated. Do such studies over- or under-estimate the impact of pollutants in the field? A great deal more research is needed in this area. We disagree on the adequacy of pollution trade-offs for mitigation of impact. If the trade-off ratio is not substantially larger than one it will not lead to a net air quality benefit and damage to agriculture will continue unabated. This is also important because many investigators are not yet convinced of the significance of long-distance transport of pollutants. Several studies have not documented the existence of increased rather than decreased amounts of oxidants downwind of power plant plumes and urban areas. This means that areas far removed from sources of pollution actually may experience higher pollution doses than those in proximity to the sources.

Our air pollution standards were set for single gas effects, but many studies now have come out showing that mixtures of pollutants can cause more damage than either pollutant alone. The problem facing air quality experts is how to set a combined gas standard for protecting vegetation.

Agricultural burning is becoming a significant pollution source in this state and controversy exists over what to do about it. Agricultural burning can release ethylene, dust, and hydrocarbons which can generate smog. If burning is to continue, how do we separate the smog due to burning from the smog from other sources? In evaluating impact we would like to be able to attribute the impact to its various sources.

What do plants do after they've experienced an episode of high air pollutants? Do they recover? There is now some evidence that some crops can recover from an acute episode depending on the stage of development that the crop was in. Obviously this can lead to overestimates of air pollution impact.

Finally, does a "fertilizer" effect indeed occur, and if so, how widespread is it? Is NO_2 as important as SO_2 in fertilizing soils? What determines whether these compounds are metabolized as nutrients or whether they alter the acidity of the soil? This is an area of research where most of the questions are unanswered and a great deal of work is needed.

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EFFECTS OF AIR POLLUTANTS ON TREE AND VINE CROPS IN CALIFORNIA

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During the 1940's and '50's citrus growers observed progressively declining yields in southern California, and because Kaiser Steel at Fontana was known to emit fluoride, the company was suspected of causing extensive crop injury. However, automobile population had increased rapidly and the company blamed automobile smog.

An elaborate field study was done in which commercially producing lemon and navel orange trees were tested to determine the effects of ambient air pollutants on water use (transpiration) and apparent photosynthesis. The entire trees were enclosed in plastic covered greenhouses and were supplied various fractions of the atmosphere to find out whether ozone, peroxyacyl nitrates, or fluorides were causing deleterious effects. The results showed that the total photochemical smog complex reduced the rate of water use by lemon trees and also reduced the rate of apparent photosynthesis. Fluoride levels occurring in the atmosphere caused no detectable effects. In addition, the same studies measured the following responses: growth; weight of prunings; leaf drop; fruit drop; and yield of mature fruit. The results showed that overall growth was not affected significantly. Leaf drop was significantly less in lemons where carbon filtered air was supplied to the trees. A similar trend was present in oranges, but was not significant statistically. Fruit drop in navel oranges was significantly less in carbon filtered air than in ambient. Yield of fruit is also reduced significantly by photochemical oxidants, sometimes by as much as 50 percent.

The continuous exposure of navel orange trees to 0.5 and 1.0 ppm of nitrogen dioxide for 35 days caused severe defoliation and leaf chlorosis. Exposure of the trees to 0.25 ppm and lower levels caused increased leaf drop and reduced fruit yield.

Later, mature navel orange trees were exposed to ambient and two times ambient air levels of NO_2 for eight months from blooming to picking time to find out whether this pollutant is causing injury to citrus.

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There was no visible evidence of injury. Leaf drop was greater and yield of fruit was less in ambient air containing photochemical smog than in trees which received carbon-filtered air or carbon-filtered air to which ambient or two times ambient levels of NO_2 were added. The addition of either of the two levels of NO_2 had no statistical effect on leaf drop or yield. Ambient levels of NO_2 which occur in the Los Angeles Basin probably are without effect on citrus.

Young navel orange trees and branches of a mature tree were enclosed and exposed for two years at Riverside, California, to activated carbonfiltered air, carbon-filtered air plus ambient levels of peroxyacetyl nitrate (PAN), or ambient air. The growth of the young trees was reduced by the addition of synthetic PAN at levels in ambient air. Leaf drop increased. With enclosed branches, significantly less growth occurred with PAN. Trends toward reduced yield of mature fruit were seen. Shortterm apparent photosynthesis was not affected by fumigating a young tree with 20-80 ppb of PAN.

Zinfandel grapes were exposed to ambient (smoggy) air and carbonfiltered air near Cucamonga, California, for two seasons. During the first year the chlorophyll content of leaves, individual berry weight, sugar content of grape juice, and growth where higher in carbon-filtered air. Yield of grapes was marginally affected. But during the second year, the above responses occurred and yield increased from 3.1 kg in ambient air to 8.1 kg in carbon-filtered air. The flower buds had been damaged by oxidant on all vines prior to the first year's trials, thus obviating differences during the first year.

Continuous fumigation of alfalfa (Medicago sativa L), Thompson Seedless grapes (Vitis vinifera), lettuce (Lactuca sativa), sugar beets (Beta vulgaris), California buckeye (Aesculus californica), Ponderosa pine (Pinus ponderosa), and Douglas fir (Pseudotsuga menziesii) with 3000 parts per billion (ppb) H_2S in greenhouses caused leaf lesions, defoliation, reduced growth, and death of sensitive species. Three hundred ppb caused lesser but similar effects. Sulfur accumulated in leaves depending upon dosage. Faster growing plants accumulated sulfur more rapidly. Lower levels of H_2S , 30 ppb and sometimes 100 ppb, caused significant stimulation in growth of lettuce, sugar beets, and alfalfa. The

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stimulation occurred at certain times of year and may be influenced by temperature and/or humidity.

CARB'S ROLE IN CALIFORNIA'S AIR QUALITY DILEMMAS

Dr. Marjorie Evans, Member, California Air Resources Board, Sacramento

I want to talk to you today about the air quality control regulator's job--how it seems to me.

What do we do as members of the Air Resources Board? We sort through facts, testimony, and situations to make decisions on the effects of pollutants on people's health and on vegetation. Those decisions are called standards. We also consider and sometimes decide on appropriate pollution controls: what are appropriate technological controls; where they are most appropriate; when they should be required; and who should require them. The basic responsibility for that is in the district, right here. Sometimes when we see--for whatever the reason may be-that a district is slow, we use our statutory authority to direct that action be taken.

Our biggest task is dealing with conflicting interests in a reasonable way. That, in the end, is what being a good regulator is all about--taking a tough situation and making it the best possible for everybody. There nearly always are conflicting interests. Some people have to meet pollution controls, and that hurts. It costs money, it takes time, it's just a general hassle. Other people are directly hurt by the pollution. Their health is hurt, their crops are hurt. Interestingly enough, farmers are in both positions. Their crops are hurt, so they would like the air pollution to be controlled. On the other hand, they contribute substantially to it when they are burning field trash; they would prefer not to be controlled, and the city people are the hurt ones.

The ideal, of course, is no pollution. What is actually happening here in the San Joaquin Valley--as elsewhere in the state--is that population is increasing and each person generates pollution. Moreover, there is an added effect--the amount of pollution generated per person is increasing. Why? We each drive our cars more than we did 10 or 20 years ago. The general level of material welfare is higher. That is to say, we have more things in our houses--more washing machines, more TV sets, and more clothes--and just the manufacture and use of those things creates more pollution.

And we still have incomplete control methods. For many sources we work for 90-95 percent control. Nevertheless, given the large and growing population of the state and the Valley and the large amount of industrial and economic activity, our level of control isn't enough.

We are not about, or not able, to control population, for at this stage of the state's history, population size control presents an immense political and sociological problem. Most people are not motivated to control the amount of pollution per person, even though this could be done without a decrease of the standard of living. So, given the difficulty of controlling either population or per capita pollution, the burden of control falls on business and industry. That means control on utilities, people who paint or drill oil wells, filling stations, dry cleaners, refiners, automobiles, and agricultural burning.

Let me repeat. As long as we can't control the population size, and as long as we can't control or reduce the amount of pollution per person by lowering material consumption, we are going to have source control. If the population keeps increasing and the per capita pollution keeps increasing, the amount of pollution control is going to in-This is too bad, because business and industry cry for certainty. crease. They complain, 'You put this control on us five years ago and now here you are with some new thing." And the new thing that has been thought of is there because it controls to a greater degree. I don't know how to handle this dilemma in a uniformly satisfactory way. I hope that we are about to move into a time where our controls are as tight as we are ever going to have to ask them to be. But, I can tell you one thing--there are a lot of chemical engineers in this country who are going to make a very good living devising good ways of avoiding the production of pollution in the first place, and removing what is produced in the second place.

Here is my approach as these matters come before the Board. There are four things which are important and for which I am alert during hearings.

First is health. Second is long term economic soundness, i.e., over a 10, 20, or 100 year period. Third is short term economic soundness--what happens this year and next year. And fourth is an aspect more difficult to define in a few words. It is the quality of the earth, on the assumption that it is immoral, if you will, to damage the earth beyond repair.

I view the retention of agriculture as being part of this fourth aspect. It is conceivable to me as a chemist that we could make all of our food out of Kern County oil. There really isn't anything to stand in the way of that from a chemist's point of view. But I find that offensive because I think agriculture, the growing of things, is good in itself.

Now let us call to mind some examples of conflicts among these four things I have mentioned. History gives us some. Centuries ago there were goats pasturing in the boot of Italy and parts of Greece. They were needed for the economic short run life quality of a given family, so it was good for the short run from an economic point of view. The long term economic effect was bad. Those of you who have been there know how bare the slopes are, and the reason is that the short term economic well-being of the family led to a long term devastation of the land by the grazing goat. A similar thing, involving humans rather than animals, took place in Great Britain, parts of Greece and Scotland where oak forests were cut down to build ships. Now, instead of forests and rangeland, one finds plains and mountains without trees.

An example closer to home in terms of time and geography is the acid rain which is experienced in Europe and Canada and the United States. In the short term it is to industry's economic disadvantage to control sulphur dioxide and nitrogen oxides. In the long term, those products, when they get into the air and are converted to acidic substances, have decimated--in some places have wiped out--fish in the lakes in Sweden and in the Eastern United States. Grasses, too, show susceptibility to damage. This has escalated to a political issue between Canada and the United States, because each produces that kind of pollutant and it slips across to the other country. It is clearly in the long term not economically sound. When I sit in a hearing I try to assemble data on these four points and balance them in a reasonable and helpful way. What helps me most of all is to hear precise and sound information on the effect of pollution on health, vegetation and economics, and on the availability of controls. What you've heard this morning is an excellent example of the kind of information which we need if we are to make judgments on more than a hunch of what's right for the world.

We surely are learning more every day about the effects of pollutants on health and vegetation. This is partly because scientific people have gotten smarter about choosing the goals of their research. It is partly because of the wide availability of very exact instruments and methodologies which now make possible excellent scientific research in the very difficult areas of the effects of air contaminants on people and plants. It is also a fact that emission controls are improving both as to the extent of pollutant prevention and cleanup, and as to cost.

As far as the agricultural effects of air pollution, we know how important it is to California. I would like to emphasize some things I have heard in the presentations this morning so that you see what seems important.

The most drastic adverse effect of pollutants on a plant is its death. This is something we may never observe--you, as farmers, or I in my vegetable garden. The next most severe effect is leaf damage or loss, a kind of visible damage that has been used as an indicator for 50 years. Recently other parameters have been shown to be relevant to crop marketability; for example, fruit weight, protein content and sugar content. Researchers are now developing even more sensitive indicators of damage by monitoring plants at different stages of growth. A delay in crop maturation can mean that you lose your contract price, or are in disadvantageous competition with sales from other regions. And let us not forget the evidence suggesting that a gradual elimination of native grasses, native vegetation or trees, very difficult for us to spot from day to day, is going on. This poses enormously serious long-term problems like the goat problem in Italy and Greece. It seems clear that low concentrations of certain pollutants will initiate plant population shifts. That can convert valuable forest or pasture land into land of lower quality and productive capacity. You probably are familiar with the idea of choosing resistant crops to reduce disease. As you have heard today, it is also becoming rather common to select stocks or seeds resistant to certain air pollutants. However, such selection—while it provides protection for the problem at hand—may have unexpected drawbacks in terms of crop quality or susceptibility to unexpected disease problems. We might be buying a short term economic benefit for a long term economic loss.

Now by way of illustration of how the Air Resources Board goes about its job, I want to talk a bit about the setting of a combined sulphur dioxide-ozone standard.

In 1977 the Board held hearings on the setting of sulphur dioxide standards. We heard evidence on the effects on both health and vegetation. We eventually set a standard for sulphur dioxide (in combination with ozone or particulates) as related to health. We did not set a standard for SO_2 for vegetation, and I want to tell you why we did not and where I think we are now.

There was clear evidence as to the bad effects on vegetation of sulphur dioxide and sulphur dioxide in combination with oxidants and also, perhaps, with particulates. My uncertainty was as to the concentration level at which harmful effects occurred. It seemed to me that the evidence was not clear enough at that time to set a quantitative standard, and also it seemed to me that in view of the importance to those who would be controlled as well as to the agricultural industry, we could wait to let more research be done. For one thing, we did not have extensive testimony from agricultural spokesmen that you were being harmed. There was time, it appeared, to do necessary research.

Here were some of the points at issue. There was testimony to the effect that SO₂ and oxidant in combination were harmful to certain plants. There was other testimony to the effect that the evidence was faulty. These latter people argued that laboratory studies do not accurately reflect field conditions. They also occasionally argued that field studies carried out in a certain way did not accurately reflect field results. It seemed clear to me that the scientists needed to get back into their laboratories and think through the best ways to do the research so that their experimental conditions accurately reflected the plants' experience. You heard this morning some of the results.

Another point of argument was related to plant variety. Those opposing a standard argued that experiments showing harmful effects were all on overly sensitive plants. They suggested that farmers not grow overly sensitive plants in the valley. Another argument was over how to define damage. An old measure was crop weight reduction. It has become clear that there is more to it than that. Failure to thrive, sugar content and effects at different stages during a plant's life also are important. At the time of the hearing the criteria were not well developed. Today you heard--for the first time I think--results of research directly aimed at trying to be clear about criteria of damage.

Yet another argument revolved around acid rain. The first subargument was about whether it can occur in California. There were people who said it could and did; others said it could not and did not; and some said even if it does, it does no harm either because of the soil content or because the plants aren't affected. I felt we need more precise information on all scores.

And another argument was over whether it is legitimate to apply research and field results from elsewhere in the world to California. The argument was made that California is a special place and the fact that eastern plants are hurt by sulphur dioxide and oxidants doesn't mean that western plants will be. Thus it was claimed that research has to be done in California on crops that grow in California.

Finally, there was evidence presented that SO_2 was good for crops, not bad.

Well, I have been interested and very pleased with what I have heard this morning. The research seems appropriately designed, and is yielding the data we need to decide what sort of standards, if any, need to be enacted to protect agricultural and forest land. It is my intention, because agriculture should be nurtured and preserved in California, that we take action soon to reconsider the problems posed to agriculture by air pollution, and to set out protective standards.

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In closing, I suggest you keep your eyes open for damage, and if you think you have something significant to report, let the Farm Bureau, the agricultural commissioner, the air pollution control officer, and the Air Resources Board hear about it. We need to know about it and we need to know what your views are. Thank you very much. It is a real pleasure to be here in Bakersfield. It is a good meeting and has been a pleasure to meet all of you.

