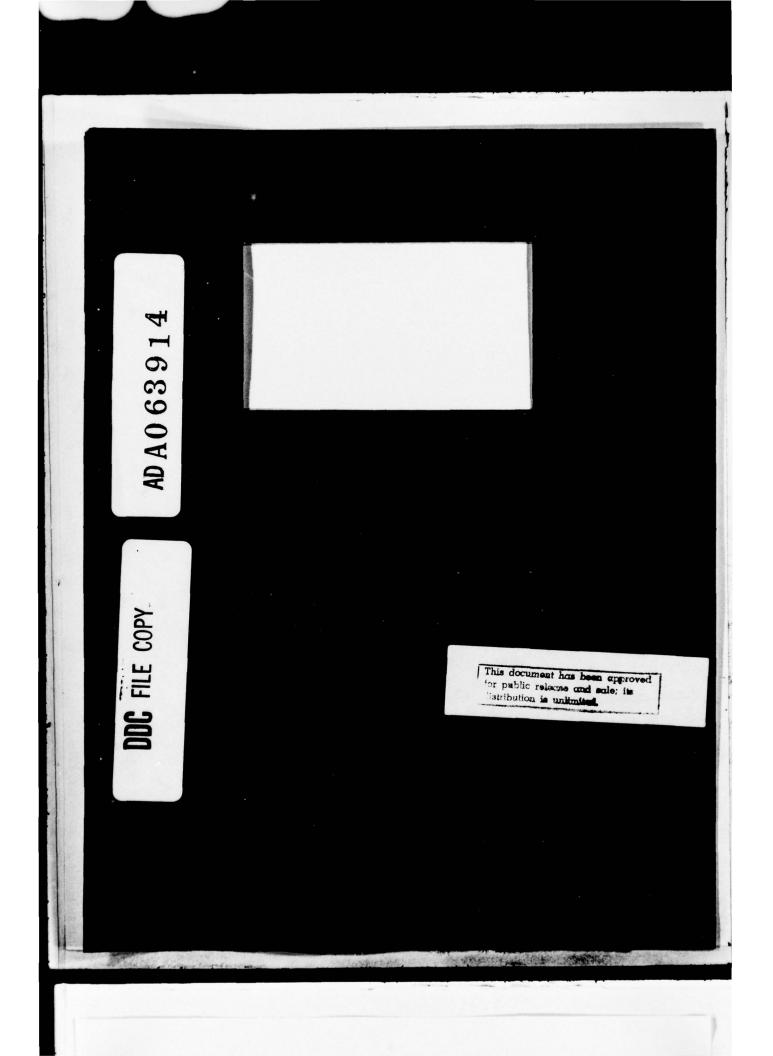
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### FINAL REPORT

"Phytotoxic Hazard of Air Pollution Associated with Munition Production"

C. Ray Thompson - Gerrit Kats

Contract No. DAMD 17-77-C-7015

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND

Technical Monitor Mitchell J. Small



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(Unclassified)

"Phytotoxic Hazard of Air Pollution Associated with Munition Production"

Final Report

C. Ray Thompson - Gerrit Kats

August, 1978

### Supported by

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND Fort Detrick, Frederick, Maryland 21701

> Contract No. DAMD-17-77-C-7015 Statewide Air Pollution Research Center University of California

> > Riverside, California 92521

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Technical Monitor Mitchell J. Small U. S. Army Medical Bioengineering Research and Development Command Fort Detrick, Frederick, MD 21701

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the pollutants, these were: 50 mg/m<sup>3</sup> for NT; 20 mg/m<sup>3</sup> for TNM; 25 mg/m<sup>3</sup> for NM; 20 mg/m<sup>3</sup> for MN, and 50 mg/m<sup>3</sup> for HAC.

Based on low concern concentrations, wheat, alfalfa, tobacco, soybean and corn were injured sufficiently with TNM or HAC to warrant further studies. White oak and scotch pine did not exhibit severe enough injury to warrant further study. Moreover, minimal or no injury was observed on any of the plant species tested with NM, NT, or MN. An index of toxicity, EC50 was devised which represented the dosage of phytotoxicant which caused injury to 50% of all the leaves on an exposed plant population. EC50's of TNM were as follows: wheat 0.68, alfalfa 0.93, tobacco 6.1, soybean 0.69 and corn 2.1 mg/m<sup>3</sup>; SO<sub>2</sub> on wheat 3.35, alfalfa 6.8, tobacco 18.6, soybean 6.8 and corn 21.4 mg/m<sup>3</sup>; HAC on wheat 23.3, alfalfa 7.8, tobacco 41.2, soybean 20.1 and corn 50.1 mg/m<sup>3</sup>. TNM is, in fact, one of the most phytotoxic compounds which has been tested on plants.

The combined effect of  $SO_2$  + TNM and  $SO_2$  + HAc were determined on wheat and alfalfa to find but whether interactions occur. The index of injury used in these tests was the "percent of total leaf area per plant." The results showed that  $SO_2$  + TNM had a small antagonistic interaction with wheat but no interaction with alfalfa.  $SO_2$  + HAc showed no interaction with wheat and a small antagonism with alfalfa.

Due to reproduction limitations, only black and white reprints of photographs of plant injury appear here. Color reprints are available upon request from the Contract Technical Monitor.

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# TABLE OF CONTENTS

Executive Summary	11
Statement of the Problem	1
Background	1
Approach to the Problem	2
Plant Material	4
Greenhouse and Fumigation Facilities	5
Preparation of Plant Material	8
Fumigation Procedure	9
Selection of Concentration of Phytotoxicants	9
Results - Single Compounds	11
Acetic Acid	11
Sulfur Dioxide	12
Tetranitromethane	13
Analytical Evaluation of Single Phytotoxicant Data	13
Results - Combined Compounds	14
Discussion of Results	16
Literature Cited	20
Tables 2 - 9	22 - 29
Figure 1 - Greenhouses	30
Figures 2 - 20 - Data Curves	31 - 49
Figures 21 - 39 - Color Prints	50 - 59
Appendix I - Fumigation Data	60-93

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### Executive Summary

Government owned ammunition plants (AAPs) that produce TNT or RDX emit nitrotoluenes (NT), tetranitromethane (TNM), nitromethane (NM), methyl nitrate (MN), and acetic acid (HAc) from the manufacturing processes, and SO<sub>2</sub> from power generation. These compounds could cause injury to vegetation near the installations. To find out whether these compounds cause vegetation injury and, if so, how much, Contract DAMD-17-77-C-7015 was negotiated with U. C. Riverside.

The procedure was to test the five potential phytotoxicants on seven species of plants. The low concern fumigant levels to be used were: NT 50  $mg/m^3$ , TNM 20  $mg/m^3$ , NM 25  $mg/m^3$ , MN 20  $mg/m^3$ , and HAc 50  $mg/m^3$ . Generally, adverse toxic effects to humans are known to exist at these concentrations. The plant species were wheat, alfalfa, soybean, tobacco, corn, white oak and scotch pine. These species were to be fumigated for 120 min in morning or midday in an "acute" type of exposure after which possible effects would be observed for several hours or days. The intensity of testing would depend upon whether observable effects occurred at low concern fumigant levels. In addition, tests were done with S0<sub>2</sub>, a common background pollutant at AAPs.

The phytotoxicants were bought commercially, except methyl nitrate, which was synthesized in our chemical laboratory. The liquid compounds were injected from Sage syringe pumps into a heated U tube and were evaporated by a stream of warmed air, were further diluted with air from a blower and this atmosphere provided the phytotoxicant mixture for the plant species.

The exposure chambers were translucent plastic covered cylinders 1.83 m diameter X 1.83 m height mounted on a perforated false bottom which contained a layer of activated charcoal. The charcoal adsorbed potentially dangerous compounds such as TNM. The plant species were grown in large pots

in evaporative cooled greenhouses prior to and after fumigation.

The index of injury used to measure plant effects with single phytotoxicants was "percent of number of leaves injured per plant" and the EC50 was that level which produced injury on 50% of the leaves. The data with single fumigants were analyzed by probit analysis.

Visual observations indicated that the five herbaceous species were the only plants which were injured enough for EC50 determinations. The woody perennials were less susceptible at the low concern levels. TNM,  $SO_2$  and acetic acid were the only phytotoxicants that caused injury at or below the specified dosages. TNM was several fold more toxic than  $SO_2$  which was in turn more injurious than HAc. TNM is, in fact, one of the most phytotoxic compound that has been tested on plants. Its toxicity approaches that of the peroxyacyl nitrates that occur in photochemical smog, Table A.

The combined effect of  $SO_2 + TNM$  and  $SO_2 + HAc$  were determined on wheat and alfalfa to find out whether interactions occur. Three concentrations of each phytotoxicant were used;  $SO_2 - zero$ , 5.3 and 10.6 mg/m<sup>3</sup>, TNM zero, 1.25 and 2.50 mg/m<sup>3</sup> and HAc - zero, 8.0 and 16.0 mg/m<sub>3</sub>. The index of plant injury with these combinations was the "percent of total leaf area injured." These experiments were set up in a 3 x 3 incomplete block design and interactions were measured by an analysis of variance.

The results showed that  $SO_2$  + TNM had a small antagonistic interaction with wheat but no interaction with alfalfa.  $SO_2$  + HAc showed no interaction with wheat but a small amount of antagonism with alfalfa.

This study shows that TNM is highly phytotoxic to herbaceous vegetation, some species being more susceptible than others. Woody perennials are less affected.  $SO_2$  and HAc are less toxic in that order. Limited tests with combined phytotoxicants  $SO_2$  + TNM and  $SO_2$  + HAc show no synergistic interaction but either a negative (antagonistic) interaction or no effect.

iii

Table A. Comparative Toxicity of Fumigants to Different Species for 120 Minute Exposure

		HAC			so,			HNT	
SPECIES	Plants	EC50* mg/m <sup>3</sup>	EC50 Range** mg/m <sup>3</sup>	Plants	EC50* mg/m <sup>3</sup>	EC50 Range ** mg/m <sup>3</sup>	Plants	EC50* mg/m <sup>3</sup>	EC50 Range ** mg/m <sup>3</sup>
Wheat	223	23.3	4.7-48.0	187	3.35	0-14.6	326	0.68	0-3.7
Alfalfa	110	7.8	5.8-10.2	228	6.3	3.6-47.6	285	0.93	0-4.77
Tobacco	239	41.2	4.5-79.4	323	13.6	0-132.4	187	6.1	1.14-12.2
Soybean	264	20.1	12.2-28.2	312	6.8	0-14.0	297	0.69	0-4.31
Corn	468	50.1	35.1-65.4	495	21.4	14.3-29.2	403	2.1	0.58-3.61

EC50 - Concentration of phytotoxicant required to cause visible injury in 50% of the leaves of the exposed plant population.

95% Confidence Interval of Concentrations in which true EC50 is expected. Zero values indicate statistical range includes negative values. \*\*

**NOTE:** Conversions to 1 ppm are: HAC, 2.54 mg/m<sup>3</sup>; SO<sub>2</sub>, 2.61 mg/m<sup>3</sup>; TNM, 8.03 mg/m<sup>3</sup>.

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### 1. Statement of the Problem

The U. S. Army needs to determine whether nitrotoluene, tetranitromethane, nitromethane, methyl nitrate and acetic acid pose a hazard to health and plant life as air pollutants. These chemicals may pose a phytotoxic hazard singly, in combination with each other or in combination with a background atmosphere containing  $NO_2$  and  $SO_2$ . Representative plant species that may be affected need to be exposed under known conditions to increasing dosages of each phytotoxicant, singly or in combination, to find out what the effects of these compounds may be on vegetation in the vicinity of Army Ammunition Plants (AAPs). From these determinations, recommendations for ambient air quality standards will be developed.

# 2. Background

The U. S. Army is supplied with explosives from numerous government-owned, contractor-operated ammunition plants. The major high explosives produced are trinitrotoluene (TNT) and cyclotrimethylene trinitramine (RDX). TNT is produced from the nitration of toluene with nitric acid mixed with sulfuric acic or oleum. RDX is produced from the nitrolysis of hexamethylene tetramine by a nitric acid ammonium nitrate mixture in the presence of acetic acid and acetic anhydride. The production of acids for these processes generates considerable amounts of acetic acid, NO2 and SO2 as air pollutants. Additional NO2 and SO2 is produced by the power generating facilities at each AAP. TNT production causes two identified additional air pollutants: nitrotoluene (o-, m- and p-isomers) which is dissolved in spent acids and released to the air during the reprocessing of acids; and tetranitromethane, formed during the destructive oxidation of the intermediate 3,5-dinitrotoluene. Nitromethane and methyl nitrate are volatile by-products formed during cleavage of hexamethylene tetramine in the formation of RDX. The reaction process also causes air emissions of acetic acid.

The following AAPs have the capability to produce the explosives noted:

Holston AAP, Kingsport, TN	RDX
Volunteer AAP, Chattanooga, TN	TNT
Joliet AAP, Joliet, IL	TNT
Radford AAP, Radford, VA	TNT
Newport AAP, Newport, IN	TNT

### 3. Approach to the Problem

The study was intended to screen munitions-generated air pollutants to determine if, when applied singly, or in combination, they are phytotoxic and whether these pollutants enhance the phytotoxic effect of SO<sub>2</sub>. The effects of NO<sub>2</sub> were not considered. For screening purposes, it was specified that a design be devised for a wide range of concentrations to obtain an estimate of the EC50 for each pollutant-plant combination. EC50 was initially defined in terms of permanent foliar lesions that occur on any leaf on 50% of exposed plants. Based on plant responses to each compound, combination test pollutants and concentrations would be selected. Acute tests (one exposure of 120 min applied within a 24-hour period) were intended. Table 1 describes pertinent properties of the pollutants.

Compound*	Mol. Wt.	Wt. Concentratio		Mammalian Toxicity	Stability To Shock	Source - Purity
		mg/m <sup>3</sup>	(PPM)			
HAc	60	50	20	Low	Stable	J. T. Baker Chemicals Glacial, ACS Reag.
MN	77	20	6.4	Low	Explosive	Synthesized in Lab. <sup>†</sup>
NM	61	25	9.8	Low	Stable	Malinkrodt Chem. Works AR
TNM	196	20	2.44	High	Stable	Sigma Chemical Co. Anhydrous
NT	137	50	8.8	Mod.	Mod. Stable	Prescribed mixture of Matheson, Coleman & Bell
so <sub>2</sub>	64			Low	Stable	Matheson Gas Products 99.98% SO <sub>2</sub>

### Table 1. Properties and Sources of Compounds to be Tested

\*HAC = acetic acid, MN = methyl nitrate, NM = nitromethane, TNM = tetranitromethane, NT = nitrotoluene, SO<sub>2</sub> = sulfur dioxide

+Cold absolute MeOH nitrated with conc  $HNO_3 + H_2SO_4$ 

The low-concern concentrations generally represented levels at or above which human toxic effects are known or at which Treshold Limit Values (TLV) have been established<sup>(1)</sup>. An EC50 was to be obtained for all species with each phytotoxicant unless the EC50 proved to be higher than the low concern concentrations cited in Table 1.

The test plant species were to be suitable for growth under controlled conditions and sensitive to air pollutants. Information on the response of these species to SO<sub>2</sub> concentrations should be known. When practicable, indigenous and economically significant plant species in AAP areas were to be included. The species should include at least one representative vegetable crop, grain crop, foliage crop, broad-leaf tree and conifer tree. The final selection was subject to approval by the Government project monitor.

### 4. Plant Material

Seven plant species were selected; white oak, Quercus alba, L, was obtained as one year old, bare root seedlings from Harvest Farms Nursery, Morrison, Tenn.; scotch pine, Pinus sylvestris, L, was obtained as one year old, bare root seedlings from the California Division of Forestry, Placerville, California; alfalfa, Medicago sativa, L, variety Hayden, was obtained from Dr. W. H. Isom, U. S. Department of Agriculture, University of California, Riverside, and the University of Arizona, Phoenix, Ariz. This species had been planted and propagated for 2 years prior to these studies for another purpose. The alfalfa was supplied as 3 mature plants per pot. Corn seed, Zea mays, L variety Early Sunglow, was a medium height sweet corn obtained from W. Atlee Burpee, Riverside, California. Wheat seed, Triticum aestivum, L, variety Inia 66-R was obtained from Dr. W. H. Isom. Soybean seed, Glycine max, Merr, variety Evans, was obtained from Dr. Ben H. Beard, University of California, Davis. Tobacco, Nicotiana tabacum, L, variety Speight G 28, a widely grown commercial variety was obtained from Dr. Howard Heggestad, U. S. Department of Agriculture, Beltsville, MD.

All species names, except <u>Quercus alba</u>, L. were verified by referring to "Recognitition of Air Pollution Injury to Vegetation: A Pictorial Atlas" <sup>(2)</sup>. <u>Quercus alba</u>, L was obtained from "Trees," U. S. Department of Agriculture Yearbook<sup>(3)</sup>.

The oaks and pines were planted individually in pots, 20 x 25 cm, in a 1:1:1 mixture of silt, redwood shavings and peatmoss. They were fertilized by addition of all essential minerals, as salts or solutions, to the pots and were watered with half-strength Hoagland's solution<sup>(4)</sup>. Both species were grown for 12-20 weeks prior to funigation. All plants grew well and showed no injury to the foliage prior to funigation. Three plants per pot of soybeans, wheat, and corn were germinated and grown with the same fertilizer treatment. Tobacco was germinated in vermiculite, transferred to 5 x 5 cm peat pots and when the leaves were 1.5 - 2 cm in length transplanted to 18 x 22 cm pots. A single tobacco plant was used per pot.

The soybeans were grown until they developed 5-7 leaves, 30-40 cm height before fumigation; wheat until 10-15 leaves developed or three tillers per plant, 30-40 cm height; and corn until 5-7 leaves were well formed. Alfalfa, being 2 perennial, was cut, allowed to regrow for about 4 weeks, 35-45 cm height and was fumigated just prior to flowering. Tobacco had 10-15 large, well-developed leaves when fumigated and was 45-55 cm height. These plants were fumigated during a rapidly growing vegetative stage just prior to reproduction.

### 5. Greenhouse and Fumigation Facilities

A large lath house (40' x 80') was covered with clear weatherable polyethylene and provided with activated charcoal filters and blowers. Several thousand seedlings plus the oaks and pines were grown in this greenhouse from small plants until they were ready for fumigation. Other greenhouse space was obtained from existing university facilities in three different buildings. These were also used for germination and propagation of the plants required for fumigation.

Another set of greenhouses was obtained for the actual fumigations. This consisted of two glazed structures shown in Figure 1; greenhouse A with the double doors and B the partly hidden structure to the right. Greenhouse A was used for acclimatizing the plants after moving from the propagation facilities. It was equipped with activated-charcoal filters, evaporative coolers and a mist system to increase humidity. It served as the control chamber. Air was taken from it to supply the fumigation chambers, The fumigation chambers were four cylindrical structures, 1.83 m diameter x 1.83 m height (two chambers are shown in Figure 1) right foreground. They were fabricated from translucent fiberglass with aluminum frames. No interior coating was used. No evidence of reaction of the fiberglass with the phyto-

toxicants was observed. The chambers were mounted with neoprene gasketing on a perforated plywood base. A false bottom tray under the plywood contained a 5 cm layer of activated-charcoal. The charcoal adsorbed fumigants as the air was exhausted, thus preventing escape of potentially toxic compounds. The liquid fumigants (MN, NM, TNM, NT) were used either undiluted or dissolved in suitable non-phytotoxic solvents. They were injected into the evaporation oven (see center foreground Figure 1), with Sage motorized syringe pumps. In the oven the fumigants entered a heated glass U tube filled with glass beads. This spread the fumigant into a thin film from which it was evaporated and diluted by a stream of heated air. The evaporated fumigant was then injected into the vertical duct which carried the incoming air stream to the cylindrical chambers. The air stream was blown in tangentially at the top of the chambers (see black plastic pipe, Figure 1). Baffles were installed inside the chambers to break up the air stream and provide a gentle vortex of air over the plants. The air streams were taken from greenhouse A for all fumigation chambers. Air flows into the fumigation chambers were determined periodically by adding accurately measured volumes of CO or SO2 to the incoming air stream and monitoring the amounts in the chambers. CO was used initially in calibration trials to determine the air flows because of its ease of measurement. Later when SO2 was being used as a fumigant and a Meloy analyzer was available, this gas was used. The four chambers were identical in design and dimensions and all had the same sized ventilation fans. Air flows were 7.4  $m^3/min \pm 2\%$  (1.54 volumes/min) in all chambers.

Safety shielding was installed around the motorized syringes to prevent direct sunlight on the fumigants and protect personnel from explosion hazard. Water was used to dilute acetic acid (HAC) and methanol was used with methyl nitrate and tetranitromethane. Nitromethane and mixed nitrotoluenes were

used undiluted. SO<sub>2</sub> was diluted with dry nitrogen and was injected from low pressure cylinders.

Funigations were conducted during days with either bright or hazy sunshine. Light intensity outside during fumigation was measured periodically with a Yellow Springs Instrument Co. Radiometer Model 65 and averaged about  $1 \times 10^5 \text{ erg/cm}^2$ -sec. In both greenhouse A and the cylindrical fumigation chambers, light levels were about 85% of the intensity outside. Temperatures varied from 18-32°C inside greenhouse A depending upon the particular day. Outside temperatures up to 42°C occurred but evaporative cooling kept the inside to the stated range. Temperatures in the fumigation chambers were essentially the same as in greenhouse A at 18°C but increased to 35° (3° rise) when the greenhouse was 32°.

Relative humidity was kept in the range of 50-90% in the greenhouse and fumigation chambers. During summer this was easily controlled because the plants being conditioned in the receiving greenhouse transpired enough moisture to raise outside humidities of 30-40% to the desired range. However, during fall with dry Santa Ana wind conditions, mist nozzles were activated to raise the moisture in the air to give levels above 50%. The photoperiod was that which prevailed at Riverside, CA from the beginning of single compound fumigations June 23, 1977 until October 18, 1977. The fumigations with the combined phytotoxicants were from November 16, 1977 until February 15, 1978.

Measurement of phytotoxicants in the fumigation chambers was made by three procedures. Acetic acid was trapped in dilute standard alkali in a Greenberg-Smith impinger and the excess was back titrated with standard acid. SO<sub>2</sub> was monitored with a Meloy, Model SA-285, flame emission total sulfur analyzer by sampling directly from the chamber. Methyl nitrate,

nitromethane, tetranitromethane and mixed nitrotoluenes were determined by flame emission with a Hewlett-Packard Gas Chromatograph Model 5710A. Samples were taken from the chamber into 500 ml evacuated glass cylinders. Subsamples were taken for analysis. Sampling was done at randomly selected positions in the chambers both above and below the plant canopy. No differences were measured among the different sampling positions.

Comparisons of projected and measured fumigants in the chambers are shown in Table 2. The variation between the projected and measured concentrations are a few percent which represents a small error compared to the variability of the biological responses being measured.

Acetic acid and mixed nitrotoluenes imparted their respective odors to plants and the fumigation chamber for several hours after fumigation. However, both compounds evaporated and were no longer detected by odor when the equipment was used the following day.

### 6. Preparation of Plant Material

The handling routine of plants prior to fumigation presented some logistical problems. It was necessary to plant the wheat, corn, soybeans and tobacco on a two-week schedule so that plants of a similar age and development were available for successive fumigations. One fifth of the alfalfa plants were cut each week thus providing a mature crop weekly. Oaks and pines were all from the original lots and were used as required. The four annual species were planted in an evaporative cooled propagation greenhouse and were grown until ready for fumigation. They were then hauled in the early morning, by enclosed truck, to greenhouse A, adjacent to the fumigation chambers. Plants were transported only in morning to avoid exposure to photochemical oxidant. In the preconditioning greenhouse A,

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they were exposed to the same control atmosphere as was used during fumigation. The plants remained under these conditions at least for 24 hours after which they were fumigated. Alfalfa was grown in greenhouses with activated charcoal filtered air at a separate location but was conditioned for at least 24 hours in greenhouse A prior to fumigation as were the annuals. The oaks and pines were grown during the entire pre-fumigation period in a plastic covered greenhouse which was covered with shade cloth and supplied with charcoal-filtered air. They were moved and conditioned as were the other species.

### 7. Fumigation Procedure

The plants were moved directly from greenhouse A to the fumigation chambers about 30 minutes prior to beginning the 2-hour fumigation. Ten plants each of tobacco, oak and pine were used. Five pots, each containing 3 plants (15 total), were used with wheat, alfalfa, soybeans and corn. Fumigation schedules were approximately 0900-1100 and 1200-1400. Timing of exposure of 120 min was adhered to in all cases. After treatment in summer, plants were moved to greenhouse B which had charcoal-filtered air to await development of delayed effects. During clear fall weather, when less than 0.03 ppm photochemical oxidant occurred, the plants were allowed to develop symptoms outside in the vicinity of the fumigation chambers.

### 8. Selection of Concentration of Phytotoxicants

Preliminary fumigations with 3 plants of each species were tried with the suggested maximum concentrations of each phytotoxicant to find out whether 0 or 100% injury occurred. If severe (100%) injury was observed a range of concentrations decreasing by a factor of 2 were tried; 1/2, 1/4, 1/8, 1/16 etc., until it appeared that concentrations above and below the EC50 were being used. The plants were evaluated when leaf symptoms were

greatest, usually after 72 hours. The range of concentrations were then narrowed in an attempt to obtain a value at which "50% of the plant population showed at least a single visual lesion on any leaf." This was the initially defined EC50.

Determination of degree of injury with this initial index caused some unexpected problems. The range of concentrations of phytotoxicant which caused observable injury was so narrow that a considerable amount of "all or none" data was obtained. Concurrently we had counted all leaves and recorded the number injured and calculated percent of leaves injured per treatment. At a meeting with the Technical Monitor and consultants in September 1977 it was agreed to adopt the "percent of leaves injured" as the basis for EC50 for single fumigation tests. The percent figures are recorded in the Appendix I, but the actual total number of leaves and those injured on the given treated plant population were used for statistical comparisons of the effect of single fumigants.

Attempts were made to expose the predetermined population of several species to one range of phytotoxicants to avoid multiple fumigations. However, individual sensitivity varied from species to species so much that this was only partially successful. This resulted in many fumigations with a single species.

With the exception of TNM, high levels of toxic fumigants caused immediate leaf color changes when plants were removed from chambers. These became more pronounced and extensive during the subsequent 48-96 hours. The injury was evaluated when leaf symptomatology was greatest, usually about 72 hours after fumigation. No injury symptoms were ever observed on control plants held in greenhouse A.

### 9. Results - Single Compounds

All seven species were fumigated with the six individual fumigants. The low concern concentrations in  $mg/m^3$ : acetic acid (HAc) 50, methyl nitrate (MN) 20, nitromethane (NM) 25, tetranitromethane (TNM) 20, and mixed nitrotoluenes (NT) 50 were used as starting concentrations. Based on existing data, 10.6  $mg/m^3$  (4.0 ppm) SO<sub>2</sub> was used. HAc, SO<sub>2</sub> and TNM caused varying degress of injury at these concentrations but little or no effects were seen with the other fumigants. Nitromethane was tested on two pots each of all species, i.e., two pines, oaks or tobacco plants and 6 each wheat, alfalfa, soybean or corn plants with the following dosages of fumigant; 12.5, 25, 50, 50, 50, and 50 mg/m<sup>3</sup>. Nitrotoluenes were tested with the same numbers of species with the following dosages: 50, 100, 100, 100, and 100 mg/m<sup>3</sup>. Nitromethane and nitrotoluenes had no effect on any species.

Methyl nitrate caused very slight injury at 20  $mg/m^3$  to wheat and more on alfalfa, the most sensitive species, see Figure 39. Twice the low concern level, 40  $mg/m^3$ , caused no injury on soybean, corn, tobacco, oak or pine. Wheat sustained some injury and alfalfa slightly more but both would have EC50's above this dosage, accordingly further trials were dropped. The injury pattern consisted of marginal necrotic spots on alfalfa leaves and distal lesions on wheat. Little intraveinal necrosis was seen.

The injury data observations for all fumigants are presented in Appendix I. 10. <u>Acetic Acid</u>

Beginning trials with HAc at the low concern concentration  $(50 \text{ mg/m}^3)$ showed that alfalfa, soybean and wheat were very sensitive but tobacco and corn were less affected. Continuing experiments showed that this compound caused injury to alfalfa at much lower concentrations, EC50 7.8 mg/m<sup>3</sup>, than to all other species (Table 3). Wheat and soybean were about 3 X as tolerant having EC50s of 23.3 and 20.1 respectively. Tobacco was 4 X as tolerant as alfalfa, and corn was most resistant of the five herbaceous species. Young leaves of the woody species which were not fully expanded or had a full amount of chlorophyll could be injured at about 50  $mg/m^3$  but mature leaves or needles were resistant and the EC50 was above the low concern concentration. The data are shown in Appendix 1.

Injury patterns from HAc fumigation are shown in Figures 21, 22, 23 and 24 on wheat, tobacco, soybean and corn, respectively. Other symptoms are shown in Figure 36 on alfalfa and wheat. The initial symptom present at the end of fumigation was a pronounced water soaked, interveinal wilting. Lesions became grey initially and developed over a period of about 24-72 hours. The affected areas became chlorotic during the subsequent 24-48 hours and eventually assumed the straw color shown in the color plates. If injury was extreme, the entire leaf wilted and became desiccated as is seen on the soybean leaves (Figure 23 upper right). In this case the leaf simply withered without progression to the straw color stage.

### 11. Sulfur Dioxide

Sulfur dioxide caused injury to wheat at a low level, EC50 3.35 mg/m<sup>3</sup>. Alfalfa and soybean were equal in sensitivity with EC50's of 6.8 and 6.3 mg/m<sup>3</sup> (Table 3). Tobacco and corn with EC50s of 18.6 and 21.4 mg/m<sup>3</sup> were more than twice as tolerant to SO<sub>2</sub> as the other two species. Young foliage of oak and pine showed some injury at the low concern concentration of 10.6 mg/m<sup>3</sup> but mature leaves and needles were unaffected. EC50's without respect to needle or leaf age would be above the low concern concentration. See Appendix 1.

Injury patterns are shown on alfalfa, tobacco and corn in Figures 25, 26 and 27, respectively. Additional symptoms are shown in Figures 34, 35 and 36 on both wheat and alfalfa.  $SO_2$  caused initial injury which resembled that caused by HAc but the effect was more immediate. After the initial intraveinal water-soaking and wilting occurred, there was more bleaching within the first 24 hours. After 48 hours, injury from  $SO_2$  and HAc looked the same but by 72-96 hours the veins of leaves badly injured by  $SO_2$  were as white as the remaining portion. The age of tissue affected was similar and effects by

both HAc and SO<sub>2</sub> on monocots and dicots looked the same.

### 12. Tetranitromethane

Tetranitromethane was much more phytotoxic than  $SO_2$  to all species, especially to wheat and soybean. They were essentially equal in sensitivity with EC50s of 0.68 and 0.69 mg/m<sup>3</sup>, respectively. Alfalfa was less affected, EC50 of 0.93 mg/m<sup>3</sup>. Corn had an EC50 of 2.1 mg/m<sup>3</sup> or about 3 X as resistant as wheat and soybean, while tobacco was quite resistant with an EC50 of 6.1 mg/m<sup>3</sup>. The injury pattern produced by TNM on all species was very distinctive. No injury symptoms were seen immediately following fumigation. After 24 hours, a greyish stippling occurred, especially on wheat, alfalfa and soybeans. These small lesions either coalesced during the next 48 hours to form larger yellowish spots if injury was severe or remained as a fine stippling with lesser exposure (see Figures 29, 30, 31, 32 and 33).

TNM caused injury to immature pine and oak foliage but didn't injure mature needles or leaves at the low concern concentration. The injury pattern on young oak leaves was similar to that on alfalfa, compare Figures 37 and 29. Young pine needles showed only a non-specific tip burn, Figure 38. EC50's without respect to needle or leaf age would be above the low concern concentration.

# 13. Analytical Evaluation of Single Phytotoxicant Data

The results of the fumigations with single phytotoxicants were analyzed statistically by using raw data numbers of total leaves vs. number injured per treatment. Thus, the total number of leaves on 15 each wheat, alfalfa, soybean and corn plants or 10 each tobacco or oak plants were the basis for the individual data points shown in the printouts of the analyses. The pine represented a special case and only estimates of amount of injury could be made because of the large number of needles.

The results were analyzed by a least sums of squares fit of probit vs. phytotoxicant concentration, see Snedecor and Cochran<sup>(5)</sup>, Sokal and Rohlf<sup>(6)</sup>. The acetic acid data involved are presented on pages 64-71; SO<sub>2</sub> data, pages 74-81; and TNM data, pages 84-91. Fumigations results with leaf percent injuries 5% or below or 95% and above were not included in the fit analysis. There are several problems of statistical rigor with the approach used, such as neglecting dependence of plants within pots and confounding of possible time of year effects. However, given the experimental procedure, the analysis used is considered as valid as any other of higher complexity.

Computer-drawn curves are shown in Figures 6-20 of the fit-lines derived. EC50 results derived from these are summarized in Table 3. The EC50 range presented is the concentration interval in which a true EC50 is expected with 95% confidence. Where data were highly scattered or the slope of the fit line shallow, this interval may be very wide. Thus, several range intervals have a lower bound of 0, since non-positive concentrations have no significance.

### 14. Results - Combined Compounds

The most sensitive species to single fumigants, wheat and alfalfa, were selected for combined fumigations. The plants were grown and fumigated in the same way as were plants tested with single compounds. However, the assessment of injury was different. The <u>percent of total leaf area</u> injured was used. This index allows wider ranges of concentrations of phytotoxicants to be used in which injury is between 5% and 95%.

To demonstrate interaction, the effect of leaf injury by two fumigants applied simultaneously, each at three levels (the first level being zero) was investigated. This is a 3 x 3 factorial design with nine treatments.

The first treatment (zero level of both fumigants) was assumed to be satisfied by conditions in the greenhouse and was omitted, leaving just eight treatments to be performed in the chambers.

Treatment	Fumigant A	Fumigant B
1	0	1
2	0	2
3	1	0
4	second starting	1
5	1	2
6	2	0
7	2	1
8	2	2

However, eight chambers were not available so a balanced incomplete block design, Cochran and  $Cox^{(7)}$  was used with a block size of four chambers.

The plan called for the performance of 14 incomplete blocks so that each fumigation treatment would be replicated 7 times. Ideally, a full replicate in two blocks was scheduled for a day, or when not practical due to weather or logistics, successive working days. In some situations, dosage errors or equipment malfunctions voided the results of a block. Since discovery of a voiding condition could take up to 72 hours, the time interval between two valid blocks in the same replicate was much longer. This is evident in the test result matrix shown in Tables 4 and 5, where the replicate block pairs are identified by the lower-case letters a-g. The balanced incomplete block analysis was carried out on the percent injury with the arcsine transformation to obtain adjusted (for block effects) treatment means and the estimated effective error variances (See Tables 6,7, 8,9). The statistic used was arcsine (percent injury/100)<sup>1/2</sup> expressed in radians. The combinations to be tested were  $SO_2$  + TNM and  $SO_2$  + HAc. The results of treating wheat with  $SO_2$  + TNM (Table 6 and Figure 2) show that only a small degree of antagonism occurred. With alfalfa treated similarly no significant interaction occurred (Table 7 and Figure 3).

The injury symptoms with  $SO_2 + TNM$  on wheat were more typical of  $SO_2$  than TNM. Large areas of straw colored tissue were produced (see Fig. 34) and the veins were also bleached which occurs only with high levels of  $SO_2$ . None of the stippling so characteristic of TNM was seen with the combined phytotoxicants. Treatment of alfalfa with these two phytotoxicants showed similar effects, but some complete killing and bleaching of leaves occurred which wasn't observed with either compound (see Fig. 35).

Treatments combining SO<sub>2</sub> + HAc on wheat had no significant synergistic effect (Table 8 and Figure 4) but with alfalfa a small antagonistic interaction occurred (Table 9 and Figure 5).

Injury symptoms caused by  $HAc + SO_2$  to wheat or alfalfa resembled those of  $SO_2$  more closely than of HAc. Increased bleaching was observed, but the actual pattern was not able to be associated with that of either compound (see Figure 36).

# 15. Discussion of Results

These studies should be recognized as short term, single exposure tests which show what "acute" effects are produced by a single episode. Longer term, lower level fumigations would reveal more nearly what would be expected in the life of a plant near an emission source.

The lack of effect seen with NM and NT at the low concern dosages indicate that these two compounds have a low phytotoxicity. They were readily absorbed during the fumigations, as the strong odor of each compound persisted near the plants for several hours after treatment. However, no wilting or other overt injury symptoms were seen. Haagen-Smit et al.,<sup>(8)</sup> tested NM at 1.0 ppm on several crops including alfalfa and observed no effects. Schott and Worthley<sup>(9)</sup> killed duckweed with 100 ppm o-nitrotoluene in solution of pH 6.3 but not with solution at pH 8.5. One-half this concentration had no effect at either pH.

This lack of toxicity parallels the acute effects on man. Little effects of NM on workers have been observed. The TLV is 100 ppm  $(250 \text{ mg/m}^3)^{(1)}$ . NT is also well tolerated by man but has a much lower TLV, 5 ppm  $(30 \text{ mg/m}^3)^{(1)}$ .

Methyl nitrate was marginally toxic to the most sensitive species, wheat and alfalfa. In solution it is mutagenic to <u>E</u>. <u>coli</u> bacteriophage at 1.33 ppm<sup>(10)</sup> but other published information is unavailable concerning phytotoxicity. If spills of methyl nitrate occurred resulting in air concentration levels about 20 mg/m<sup>3</sup> for several hours, injury to sensitive target species would occur.

Phytotoxicity of HAc has been reported on loblolly pine, <u>Pinus taeda</u><sup>(11)</sup> but dosages are not available. Another study reviewed in  $abstract^{(12)}$  showed reduced shoot growth on red oak, hawthorne, white dogwood and other woody plants at 1.1 mg/m<sup>3</sup>. This latter study must have used much longer exposures than in our work because the levels of HAc caused injury with concentrations about one order of magnitude lower than in this work.

Plants are considerably more sensitive to HAc than man. Whereas our EC50's with different species vary around 10 ppm, Sterner<sup>(13)</sup> concluded that 10 ppm is relatively nonirritating in industrial exposures and the TLV is set at this level<sup>(1)</sup>.

These studies confirm the well documented effects of  $SO_2$ . Thomas<sup>(14)</sup> found alfalfa to be more sensitive than wheat, ratio of 1.0:1.5, but both

species were classified as "sensitive" Differences in susceptibility of different varieties could account for the discrepancy between our results and theirs. Corn, live oak and pine were "resistant." Soybean was injured by fumigating with levels of  $1.3 - 16.0 \text{ mg/m}^3 \text{ SO}_2$  for 30 min<sup>(15)</sup>. The higher level caused acute effects. These results are comparable to our EC50. Tobacco suffered "acute" injury when exposed by Menser and Heggestad in Maryland<sup>(16)</sup> to  $1.3 - 2.6 \text{ mg/m}^3$  of SO<sub>2</sub> for 2 hrs. Leone and Brennan<sup>(17)</sup> fumigated tobacco with 5.4 mg/m<sup>3</sup> SO<sub>2</sub> for 2 hours and observed "moderate" injury. These levels of fumigants are considerably lower than our EC50 of 18.6 mg/m<sup>3</sup>. The greater susceptibility of their plants could be caused by use of different varieties, different stage of growth or higher humidity which occurs regularly in the mid-Atlantic region.

The TNM EC50 of 85 ppb (wheat and soybean) is comparable in toxicity to peroxyacetyl nitrate (PAN). Taylor<sup>(18)</sup> found that one hour fumigation of pinto bean and petunia with 140 ppb PAN cause 55 and 33% injury, respectively, of total leaf area. The time concentration product (140 ppb-hr) is similar to the 170 ppb-hr value corresponding to the above EC50.

The acute mammalian toxicity of TNM vapor has been studied  $^{(19,20)}$ . The studies concluded that TNM is more toxic than NO<sub>2</sub> would be on the basis of equal concentrations of NO<sub>2</sub> (or -NO<sub>2</sub>). A similar situation probably exists with plants. Direct comparisons are not possible but Heck and Tingey as reported by Mudd and Kozlowski<sup>(21)</sup> found that begonia and oats required 8 ppm NO<sub>2</sub> (15 mg/m<sup>3</sup>) for 2 hrs to cause 49 and 40% leaf injury, respectively. Wheat sustained 34% injury after one hour exposure to 13 ppm (25 mg/m<sup>3</sup>). If these data are transposed into the basis that we use for the short time frames, a concentration-time product equivalence is assumed valid. EC50's of 12-15 mg/m<sup>3</sup> are obtained for NO<sub>2</sub>. Thus TNM is perhaps one order of

magnitude more phytotoxic than NO2 to plants.

Emissions of the above studied pollutants have been recorded to a limited extent and levels at the boundary of ammunition plants have been estimated (22). NM at 0.026 mg/m<sup>3\*</sup> is of no consequence. No data are available for mononitrotoluenes but the phytotoxicity is so low that a severe odor problem would occur long before plant injury was observed. MN at 0.42 mg/m<sup>3</sup> is more than one order of magnitude below a possible EC50 and likewise should cause no phytotoxicity. The estimated concentration of HAc at the boundary of Holston AAP was 5.1 mg/m<sup>3</sup>. This is less than the EC50's determined in this study but if 5.1 mg/m<sup>3</sup> HAc in air persisted for several hours or days, phytotoxicity would undoubtedly occur. SO<sub>2</sub> levels of 0.27 ppm are reported at the same site and are below the EC50's which we record but chronic exposures to 0.27 ppm could affect sensitive species. The TNM level of 0.48 mg/m<sup>3</sup> estimated at RAAP could probably cause phytotoxicity to sensitive species if maintained for extended periods such as days or weeks.

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The concentration cited in this paragraph are estimated for a 1-hour average under adverse meteorological conditions for a boundary location most likely to be fumigated. See reference (22) for details.

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Comparison	OI	rrojected	and	measured	rumigants	in	Chambers	

Fumigant	Msmt. Method	Proj. Conc Fumigant	Chambers	Fumigant	Msmt. Method	Proj. Conc. Fumigant	Conc. in Chambers
		mg/m <sup>3</sup>	mg/m <sup>3</sup>	A . 404 mbs		mg/m <sup>3</sup>	mg/m <sup>3</sup>
NM	G.C.	25	26.3	NT	G.C.	50	52.6
		50	47.2			100	89.5
TNM	G.C.	24	25.6	MN	G.C.	20	20.7
		16	16.1, 15.0			40	38.6
		12	11.8, 11.8	HAc	Titr.	80	77.5
			11.8			50	44.2
		8	8.3, 7.5			25	22.4
		6	6.5, 5.8			12	11.3
			5.9, 5.4			10	11.4
		5	4.8, 4.7	so <sub>2</sub>	F.E.	2.67	2.64
		4	4.2, 3.9			1.34	1.31
		3	3.2, 2.7			2.14	2.18
		2	1.9			1.07	1.09

NM	- Nitromethane	MN	- Methylnitrate
TNM	- Tetranitromethane	HAc	- Acetic Acid
NT	- Nitrotoluenes	so2	- Sulfur Dioxide

Table 3. Comparative Toxicity of Fundgants to Different Species for 120 Minute Exposure

		HAC			s02	~		HNL	
SPECIES	Plants	EC50* mg/m <sup>3</sup>	EC50 Range <sup>k‡</sup> ng/u <sup>3</sup>	Plants	EC50t mg/m <sup>3</sup>	EC50 Range** mg/m <sup>3</sup>	Plants	EC50* mg/m <sup>3</sup>	EC50 Range** mg/m <sup>3</sup>
Wheat	223	23.3	4.7-48.0	187	3.35	0-14.6	326	. 0.68	0-3.7
Alfalfa	110	7.8	5.8-10.2	228	6.3	3.6-47.6	285	6.93	0-4.77
Tobacco	239	41.2	4.5-79.4	323	18.6	0-132.4	187	6.1	1.14-12.2
Soybean	264	20.1	12.2-28.2	312	6.8	0-14.0	297	0.69	0-4.31
Corn	468	50.1	35.1-65.4	495	21.4	14.3-29.2	403	2.1	0.58-3.61
				•.					
STATE.									

95% Confidence Interval of Concentrations in which true EC50 is expected. Zero values indicate statistical range includes negative values. \*\*

population.

NOTE: Conversions to 1 ppm are: HAC, 2.54 mg/m<sup>3</sup>; SO<sub>2</sub>, 2.61 mg/m<sup>3</sup>; TNM, 8.03 mg/m<sup>3</sup>.

{

			7 01	X OF TOTAL LEAF AREA INJURED AT INDICATED CONCENTRATIONS of SO <sub>2</sub> and TNM WHEAT	EAF AREA	of SO2 a	AT IND And TNM	ICATED	CONCENT	RATIONS				
NUL - 608	11/16*	11/16* 11/16	11/	11/22	11/23	11/30	12/2	12/2	12/5	12/6	12/7	12/13	12/14	12/16
mg/m3														
0 - 1.25		n		8.1		32		19	13			2.5		20
0 - 2.5	59		•	62	64		45		48		69			53
5.3 - 0	8.1	1.3	7.2	•	20			2.9		2.5				3.9
10.6 - 0			64	and the second		55	86			53	50	88		11
5.3 - 1.25	99		44			11		72	46		73		11	
5.3 - 2.5		51	47		78		69		36			60	48	
10.6 - 1.25				57	83	•		72		84	16	96	16	
10.6 - 2.5	80	92		94		16	96			100			100	
Block	đ	م	υ	υ	p	p	e	a,	f	f	Ą	g	60	60
								÷ •* ,						
Age						ALFALFA	LFA							
HINI - 205	11/16*	11/16	11/21	11/22	11/23	11/30	12/2	12/2	12/5	12/6	12/7	12/13	12/14	12/16
mg/m <sup>3</sup>														
0 - 1.25		1.7		1.1		18		29	11			8.5		12.5
0 - 2.5	88			14	5.8		34		33		37			35
5.3 - 0	•	0.6	5.8		0			22		2.4				8.7
10.6 - 0			36			58	48			58	28	35		50
5.3 - 1.25	56		56			80		50	57		55		49	
5.3 - 2.5		54	69		34		82		70			70	62	
10.6 - 1.25				86	19			86		16	76	95	73	
10.6 - 2.5	ner	86		100		98	16			100			95	
Block * 1977	43	م	U	IJ	P	p	e	a	4	¥	Ą	eg	60	60

Table 4

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# **%** OF TOTAL LEAF AREA INJURED AT INDICATED CONCENTRATIONS of SO<sub>2</sub> and HAC WHEAT

124

					X	WHEAT								
<u>502 - HAC</u>	1/13*	1/13* 1/17 1/18	1/18	1/19	1/23	1/26	1/31	2/1	2/3	2/8	2/10	2/13	2/15	2/1/
mg/m														
0 - 8		1.0	2.2		2.9		1.8		0	1				4.2
0 - 16	24			31	27		16	16	•	37			40	
5.3 - 0		9.9		17	80	0		5.			12			0
10.6 - 0	48		63	2	36	4.2			7.2		75		32	
5.3 - 8	38			42		32.5			42	72		29		45
5.3 - 16		35	88			10.5		21		82		25	87	
10.6 - 8	75		83				16	49			94	67		82
10.6 - 16		74		61			94		06		100	73	95	
Block	đ	đ	م	Ą	v	p	P	e	e	f	f	υ	60	60
			1		AI	ALFALFA								
<u> 502 - HAc</u>	1/13*	1/13* 1/17	1/18	1/19	1/23	1/26	1/31	2/1	2/3	2/8	2/10	2/13	2/15	2/17
_m/8m														
0 - 8		10.5	33.5		8.2		32		2.3	53				41
0 - 16	69			56	74	•	100	41	*	16			89	
5.3 - 0		42		8.2	99	2.2		6.5			30			32
10.6 - 0	32		82		75	13			14		74		99	
5.3 - 8	50			36		53			35	96		87		76
5.3 - 16	0.2	93	06			69		63		100		64.	80	
10.6 - 8	93		96				100	74			86	68		92
10.6 - 16		100		61			100		87		100	100	88	
Block * 1978	•	69	Ą		٩	υ	P	e	U	f	Ŧ	υ	60	60
***														

Sec. 3.

Source	DF	SS	MS	F
so,	(2)	(6.55794776)	3.27897388	160.7***
linear	1	6.3718305	6.3718305	312.2***
quad.	1	.18611726	.18611726	9.123**
TNM	(2)	(4.423120847)	2.211560424	108.4***
linear	1	4.183782972	4.183782972	205.1***
quad.	1	.239337875	.239337875	11.73**
SO <sub>2</sub> + TNM	(4)	(.797331733)	.1993329333	9.771***
S <sub>L</sub> × T <sub>L</sub>	1	.396508	.396508	19.44***
SL x To	1	.0373964	.0373964	1.83 NS
S <sub>0</sub> x T <sub>L</sub>	1	.0030408233	.0030408233	.1491 NS
S <sub>Q</sub> x T <sub>Q</sub>	1	.36038527	.36038527	17.67***
(effective en variance from balanced inco block analysi	n omplete		.02405	

Table 6. Interaction of SO2 and TNM on Wheat, Analysis of Variance

\*\* Stat. sig. at 1% level.
\*\*\*
Stat. sig. at 0.1% level.

			INM		
		0	1.25	2.5	
	0	0	. 3826	.8572	
so2	5.3	.2406	.9259	.8959	adjusted means of data transformed by arcsine
	10.6	.9748	1.246	1.356	√ proportion

			TNM		
		0	1.25	2.5	
	0	0%	13.94%	57.16%	Descendance used from
so2	5.3	5.68%	63.87%	60.96%	Proportions used for Figure 2.
		68.49%	89.82%	95.46%	1

Constant -

Source	DF	SS	MS	F	
so <sub>2</sub>	(2)	(5.455305147)	2.727652574	87.99***	
linear	1	5.454293647	5.454293647	175.9***	
quad.	1	.0010115	.0010115	.03263	NS
TNM	(2)	(5.217389007)	2.608694504	64.15***	
linear	1	5.080036372	5.080036372	163.9***	
quad.	1	.137352635	.137352635	4.43*	
so <sub>2</sub> + TNM	(4)	(.222378986)	.0555947465	1.793	NS
S <sub>L</sub> x T <sub>L</sub>	1	.0000008575	.0000008575	$2.77 \times 10^{-5}$	NS
SL × TO	1	.0324067858	.0324067858	1.045	NS
S <sub>Q</sub> x T <sub>L</sub>	1	.0287749058	.0287749058	.9282	NS
S <sub>Q</sub> × T <sub>Q</sub>	1	.1611964375	.1611964375	5.120*	
(effective er variance from balanced inco			.03100		
block analysi	.s)			and when the	

Table 7. Interaction of SO, and TNM on Alfalfa, Analysis of Variand	Table 7	7.	Interaction	of	SO,	and	TNM	on	Alfalfa,	Analysis	of	Variance
---	---------	----	-------------	----	-----	-----	-----	----	----------	----------	----	----------

\*\* Stat. sig. at 5% level.
\*\*\* Stat. sig. at 0.1% level.

			TNM		
		0	1.25	2.5	
	0	0	.2937	.6589	adducted means of data
so2	5.3	.2010	.8366	.9706	adjusted means of data
	10.6	.6818	1.093	1.340	proportion
		1.45	CEI.	4.569	0.01
		0	1.25	2.5	
	0	0%	8.38%	37.48%	
	5.3	3.99%	55.11%	68.10%	- Proportions used for
	10.6	39.71%	78.86%	94.77%	Figure 3.
			0.000	and the state of	

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Fumigant	DF	SS	MS	F	
so <sub>2</sub>	(2)	(4.87364029)	2.4868201	30.08***	
linear	1	4.86186629	4.86186629	58.81***	
quad.	1	.011774	.011774	.1424	NS
HAc	(2)	(3.35839481)	1.67919741	20.31***	
linear	1	3.11685529	3.11685529	37.70***	
quad.	1	.24153952	.24153952	2.922	NS
SO <sub>2</sub> + HAc	(4)	(.53699007)	.13424752	1.624	NS
SO2, x HACL	1.0000	.05764894	.05764894	.6973	NS
SO2 x HACQ	1	.19079060	.19079060	2.308	NS
SO2 x HACL	1	.28755091	.28755091	3.478	NS
SO <sub>2Q</sub> x HAc <sub>Q</sub>	1 00.000	.00099962	.00099962	.01209	
(effective erro variance from			.08267		
balanced incomp block analysis)					

Table 8. Interaction of SO2 and HAc on Wheat, Analysis of Variance

\*\*\* Stat. sig. at 0.1% level.

			HAc		
		. 0	8	16	
	0	0	.2799	.5711	adjusted means of data
so2	5.3	.4577	.7325	.7685	transformed by arcsine
	10.6	.4944	1.151	1.247	Vproportion
		0	8	16	1.
	0	07	7.63%	29.22%	
	5.3	19.53%	44.72%	48.31%	Proportions used for Figure 4.
	10.6	22.52%	83.39%	89.88%	Figure 4.

Fumigant	DF	SS	MS	F
50,	(2)	(4.70575814)	2.35287907	98.99***
linear	1	4.60480637	4.60480637	193.7***
quad.	1	.10095177	.10095177	4.247*
łAc	(2)	(5.82970642)	2.91485321	122.6***
linear	1	5.79131467	5.79131467	243.6***
quad.	1	.03839175	.03839175	1.615
50 <sub>2</sub> + HAc	(4)	(.92439986)	.231099965	9.722**
SO <sub>2</sub> x HACL	1	.51370767	.51370767	21.61***
SO2 × HACQ	1	.24192933	.24192933	10.18**
SO <sub>2Q</sub> x HAC <sub>L</sub>	1	.11634674	.11634674	4.895*
SO <sub>2Q</sub> x HAc <sub>Q</sub>	1	.05241612	.05241612	2.205
(effective error variance from	35		.02377	
balanced incomple block analysis)	te			

Table 9. Interaction of  $SO_2$  and HAc on Alfalfa, Analysis of Variance

\* Stat. sig. at 5% level. \*\* Stat. sig. at 1% level. \*\*\* Stat. sig. at 0.1% level.

			HAC		
		0	8	16	_
	0	0	.3921	1.088	
so2	5.3	.5662	1.002	1.160	adjusted means of data
	10.6	.8258	1.269	1.372	↓proportion
					-

	0	8	16	
0	0%	14.60%	78.45%	
5.3	28.78%	70.99%	84.05%	- Proportions used for Figure 5.
10.6	54.04%	91.17%	96.10%	rigure 5.

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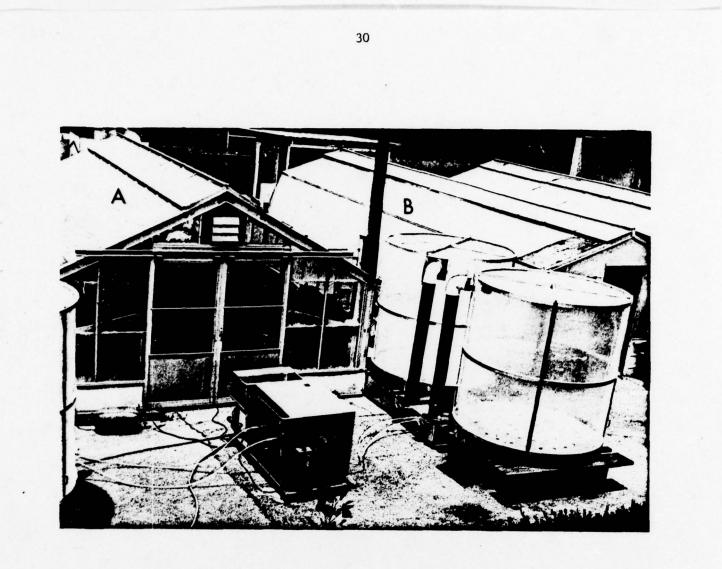
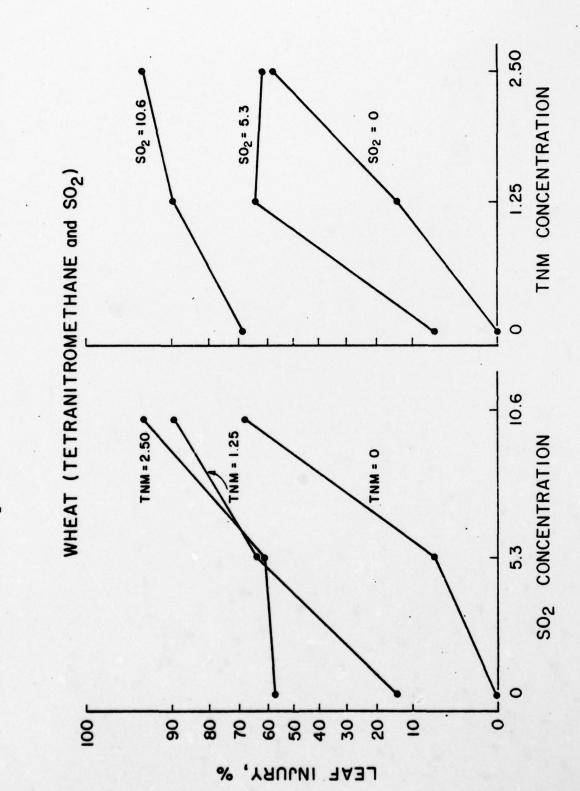


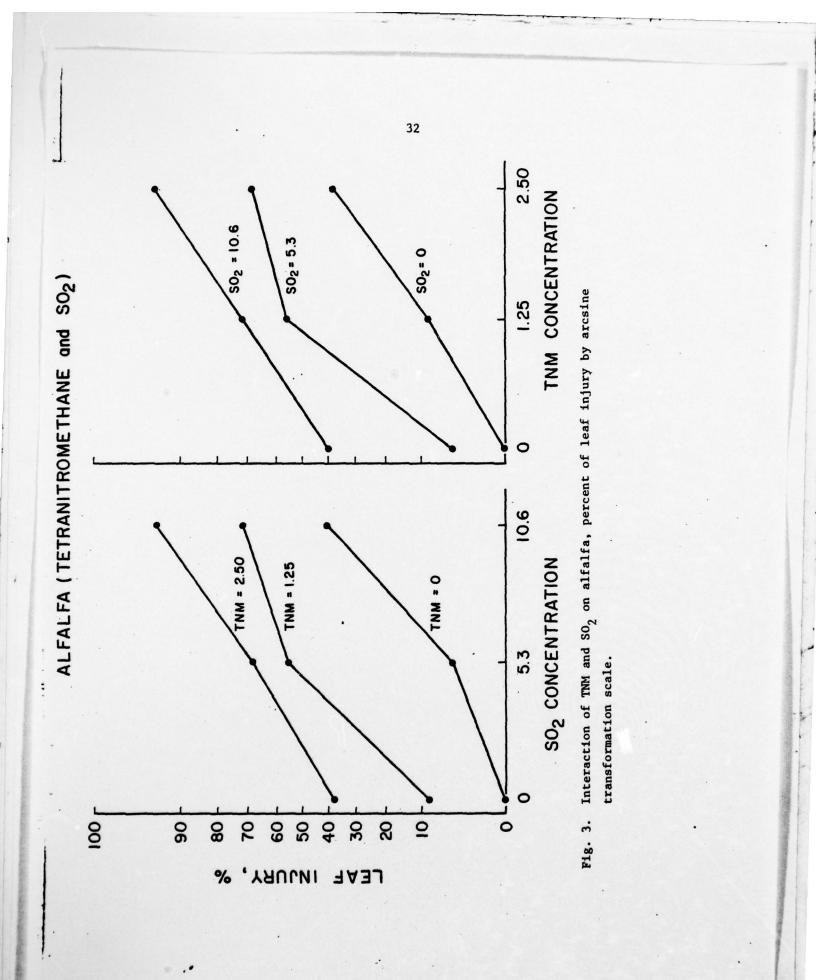
Figure 1 - Greenhouses A and B plus Cylindrical Fumigation Chambers and Volatilizing Oven

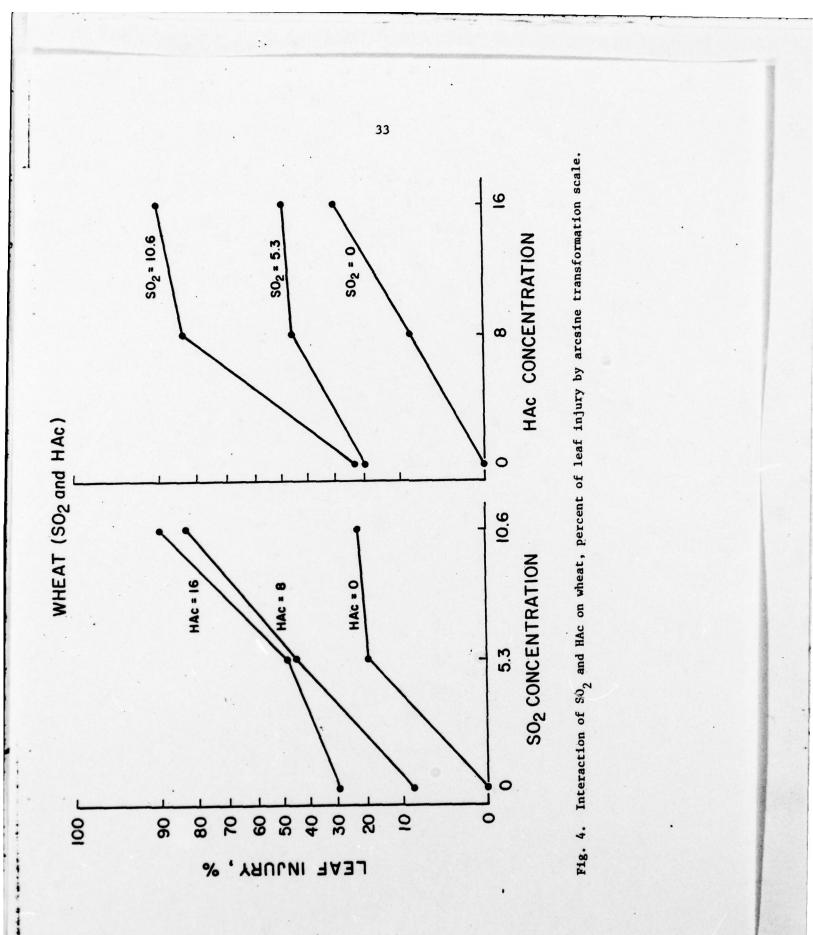
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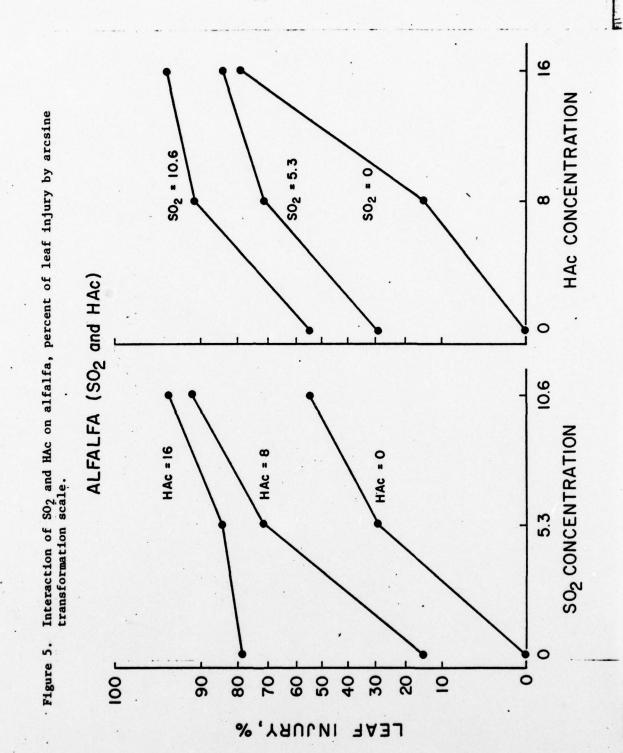


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Fig. 2. Interaction of TNM and SO2 on wheat, percent of leaf injury by arcsine transformation scale.







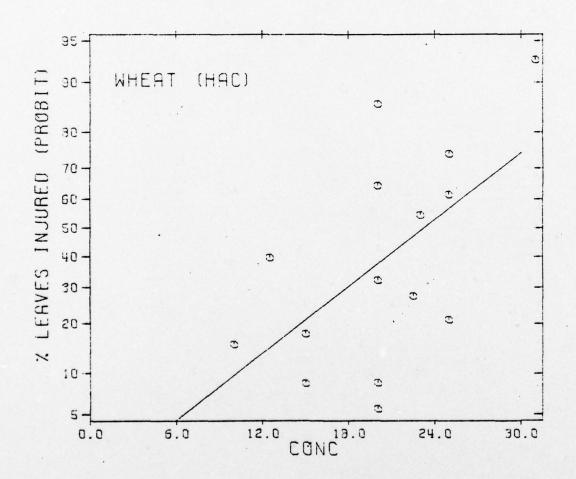


Figure 6. Effect of Acetic Acid on Percent of Leaves Injured With Wheat

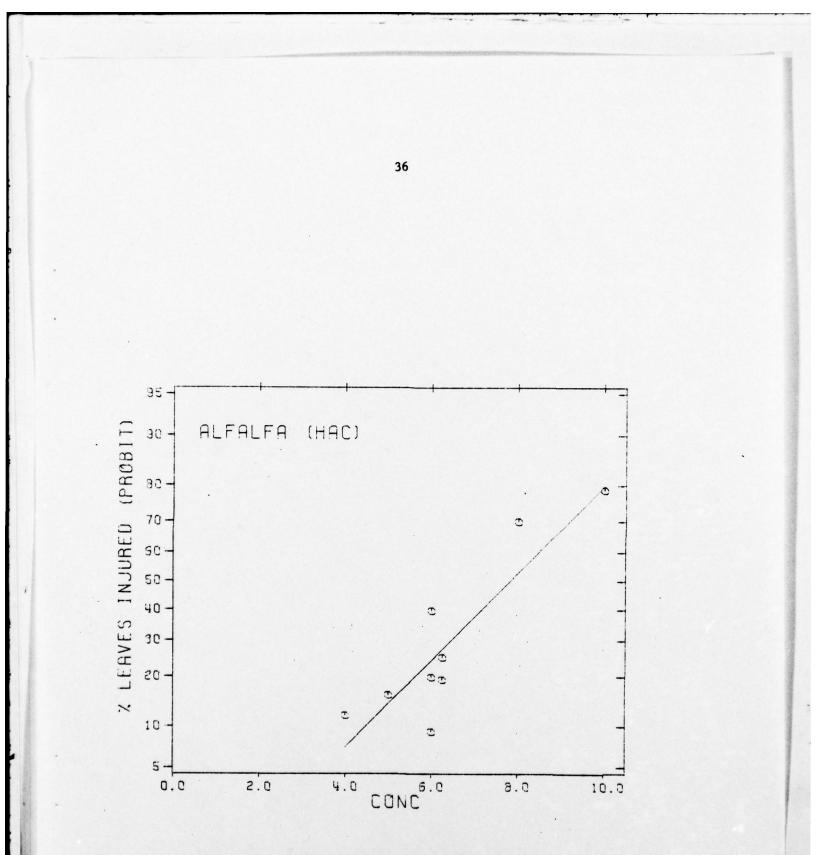


Figure 7. Effect of Acetic Acid on Percent of Leaves Injured With Alfalfa

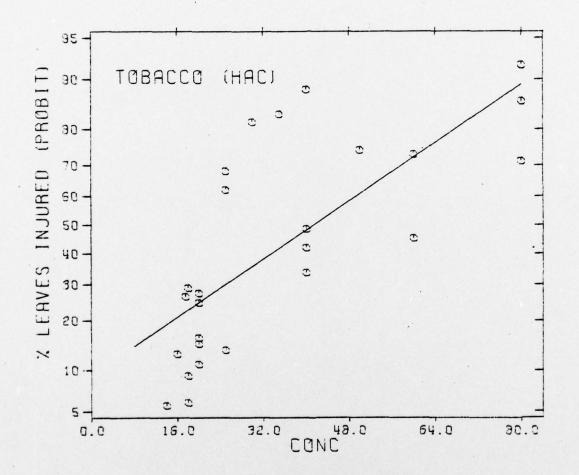


Figure 8. Effect of Acetic Acid on Percent of Leaves Injured With Tobacco

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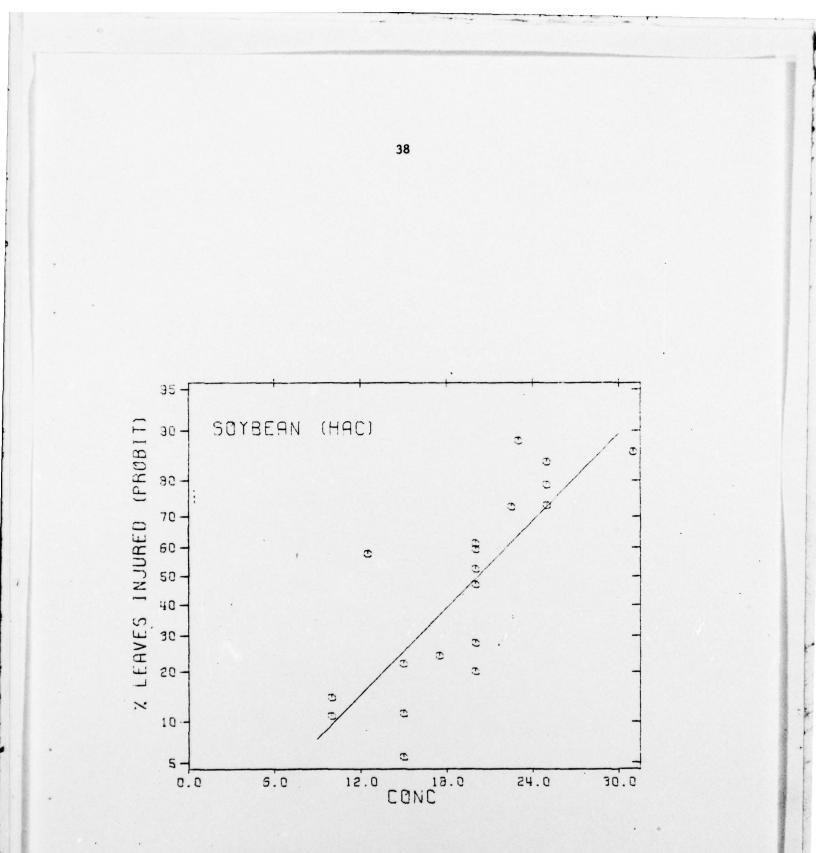


Figure 9. Effect of Acetic Acid on Percent of Leaves Injured With Soybean

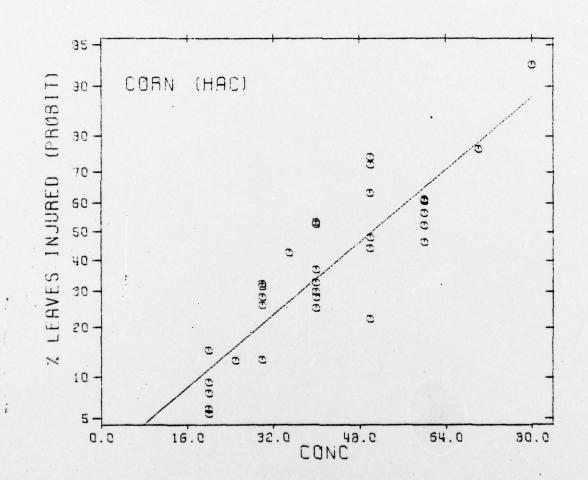


Figure 10. Effect of Acetic Acid on Percent of Leaves Injured With Corn

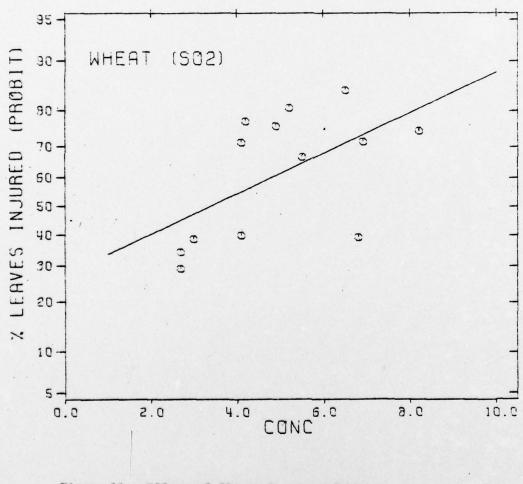


Figure 11. Effect of SO<sub>2</sub> on Percent of Leaves Injured With Wheat

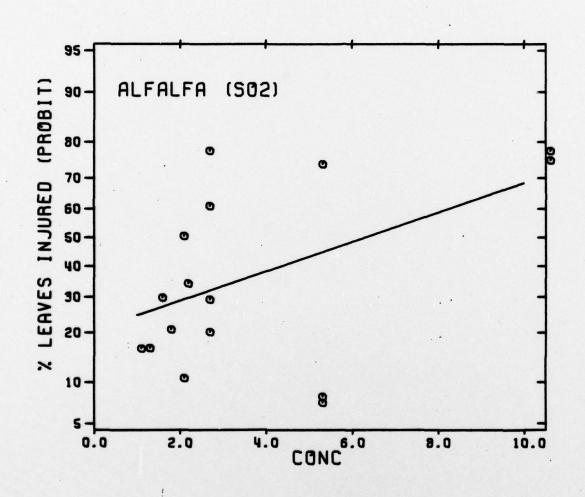


Figure 12. Effect of SO<sub>2</sub> on Percent of Leaves Injured with Alfalfa

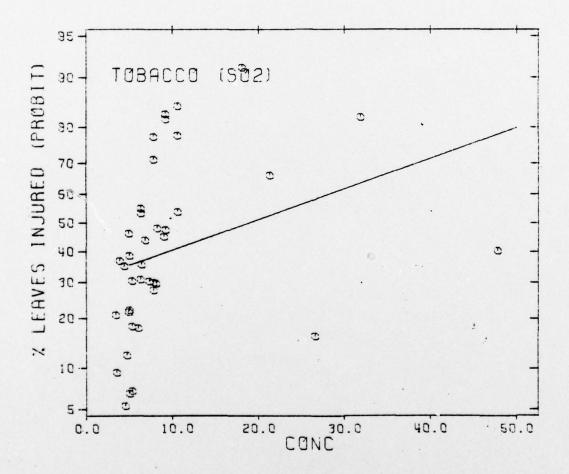
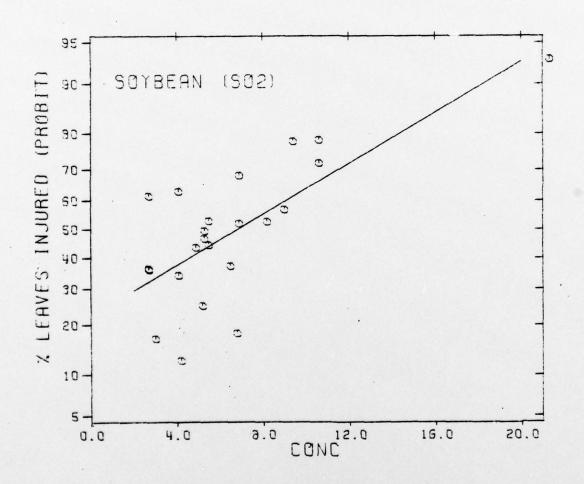
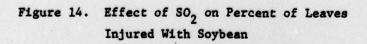


Figure 13. Effect of SO<sub>2</sub> on Percent of Leaves Injured With Tobacco





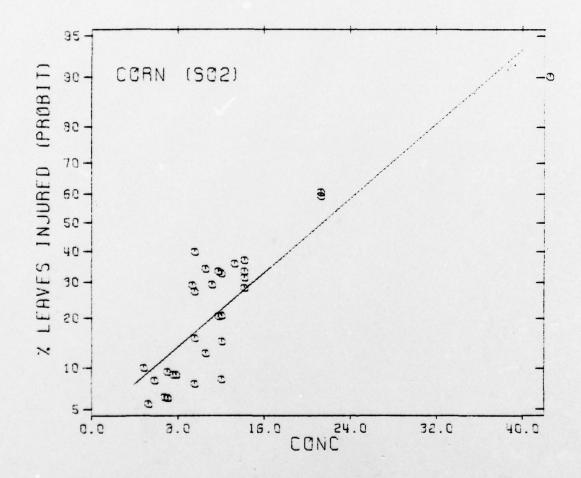
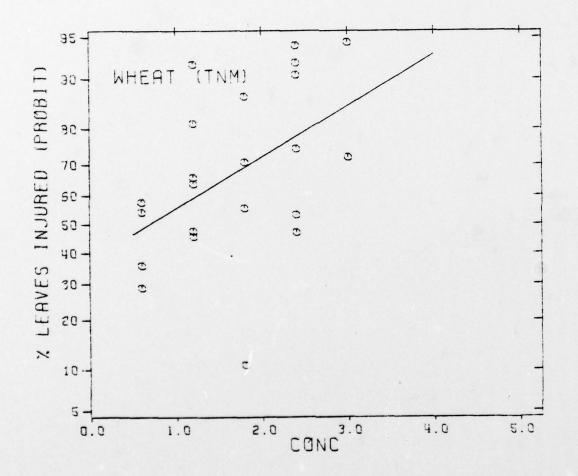
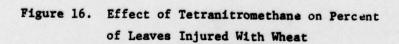
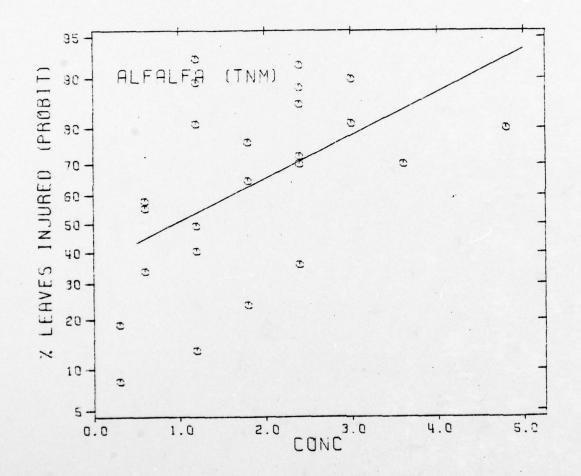
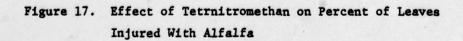


Figure 15. Effect of SO<sub>2</sub> on Percent of Leaves Injured With Corn









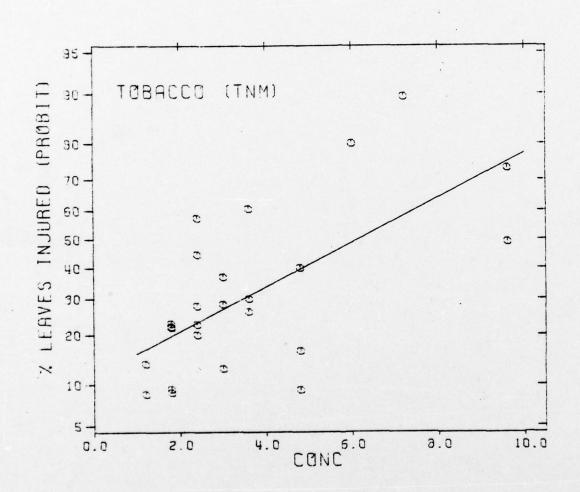


Figure 18. Effect of Tetranitromethane on Percent of Leaves Injured With Tobacco

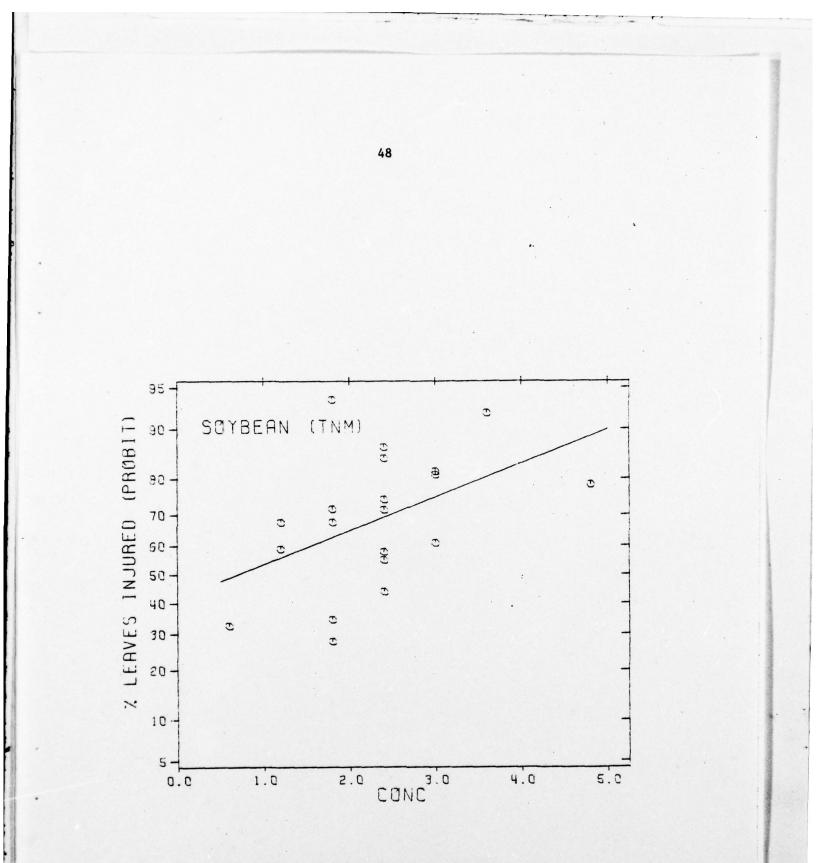
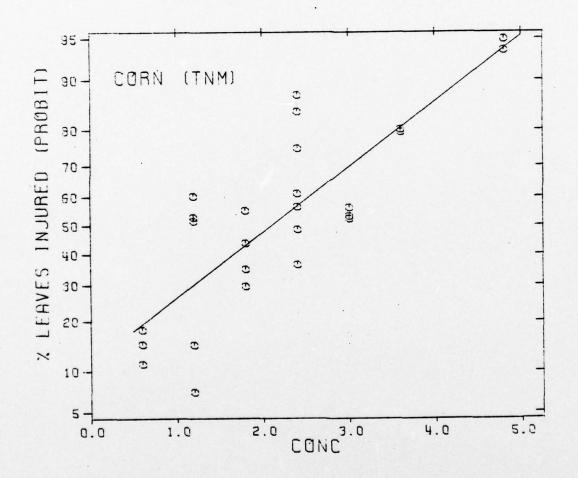


Figure 19. Effect of Tetranitromethan on Percent of Leaves Injured With Soybean



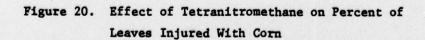




Fig. 21. Extensive acetic acid injury on wheat leaves, 62 mg/m<sup>3</sup> showing straw colored lesions.

Contraction of the

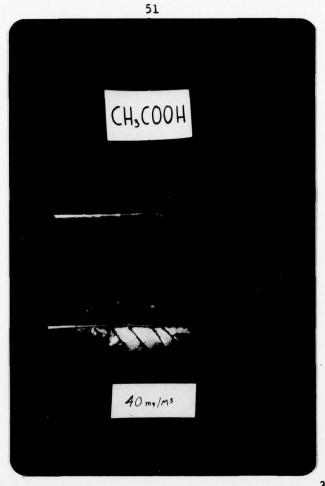


Fig. 22. Severe acetic acid injury on tobacco, 40 mg/m<sup>3</sup>, showing interveinal necrosis.



Fig. 23. Severe acetic acid injury on soybean, 31 mg/m<sup>3</sup>, showing typical interveinal necrosis and complete collapse and desiccation of leaves in upper right.

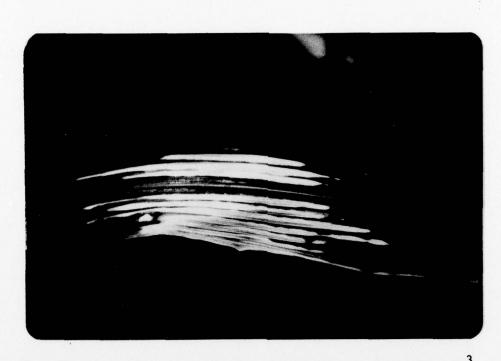


Fig. 24. Typical moderate acetic acid injury on corn,  $50 \text{ mg/m}^3$ .

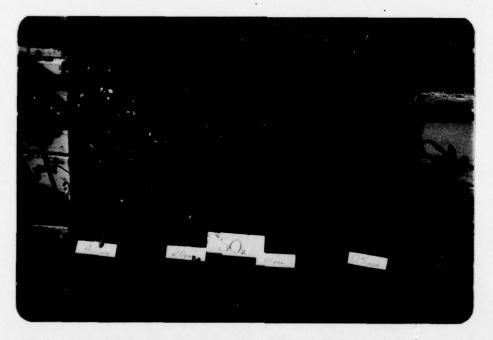


Fig. 25. Effects of four levels of SO<sub>2</sub>, 10.6, 5.3, 2.6 and 1.3 mg/m<sup>3</sup> on alfalfa.



Fig. 26. Effects of four levels of SO<sub>2</sub>, 31.9, 21.3, 10.6 and 5.3 mg/m<sup>3</sup> on tobacco showing extensive bleaching of leaves with highest level.



Fig. 27. Severe SO<sub>2</sub> injury on corn showing extensive bleaching of leaves.



Fig. 28. Moderate injury on alfalfa and wheat with TNM,  $4.0 \text{ mg/m}^3$ .

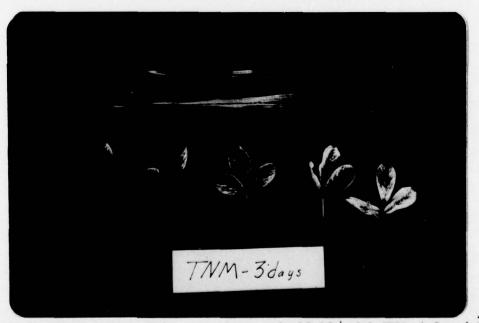


Fig. 29. Moderate to severe injury on wheat and alfalfa with TNM, 4.0 mg/m<sup>3</sup>, showing fine necrotic flecking on wheat and especially alfalfa leaves.

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Fig. 30. Severe injury to soybean, corn, alfalfa, wheat and tobacco with TNM 20 mg/m<sup>3</sup>, showing extensive desiccation of soybean leaves and total bleaching on corn, alfalfa and tobacco leaves

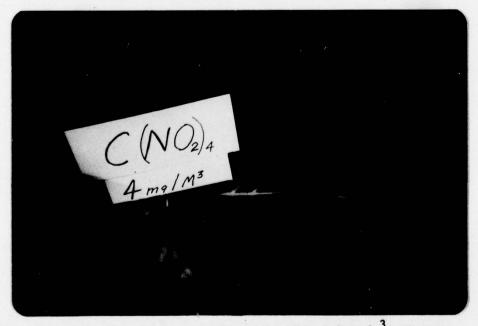


Fig. 31. Moderate injury to tobacco by TNM, 4.0 mg/m<sup>3</sup>, showing fine necrotic flecking.



Fig. 32. Moderate injury to soybean by TNM, 4.0 mg/m<sup>3</sup>, showing fine necrotic flecking on leaves in lower left.



Fig. 33. Moderate injury to corn leaf by TNM, 10  $mg/m^3$ .

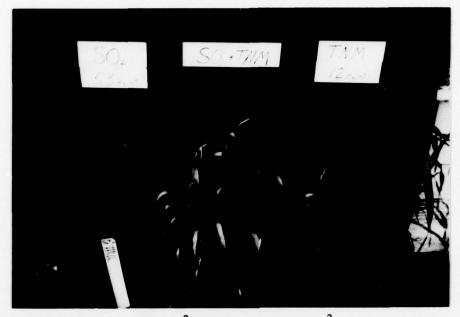


Fig. 34. SO<sub>2</sub>, 5.3 mg/m<sup>3</sup>, and TNM, 1.2 mg/m<sup>3</sup>, singly and combined on wheat.

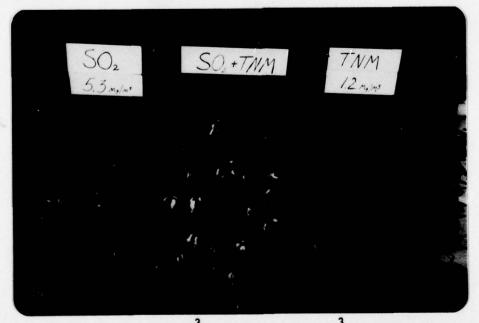


Fig. 35. SO<sub>2</sub>, 5.3 mg/m<sup>3</sup>, and TNM, 1.2 mg/m<sup>3</sup>, singly and combined in alfalfa.

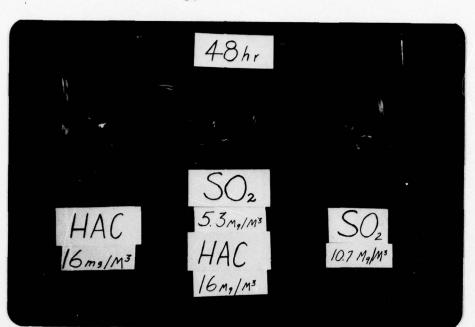


Fig. 36. Effects of HAc, 16.0 mg/m<sup>3</sup> and SO<sub>2</sub> 10.6 mg/m<sup>3</sup> singly and in combination on wheat and alfalfa leaves.

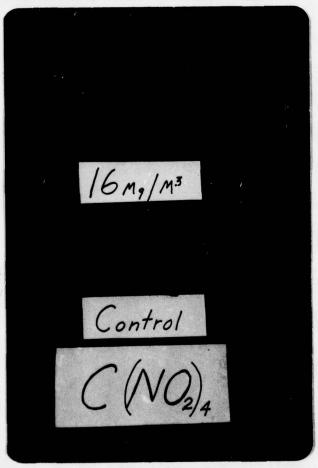


Fig. 37. Effect of TNM, 16.0 mg/m<sup>3</sup>, on young oak leaf showing stipple and interveinal necrosis.

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 $C(NO_2)_4$  $20_{mg}/M^2$ 

Fig. 38. Effect of TNM on young scotch pine needles showing necrosis of tip.

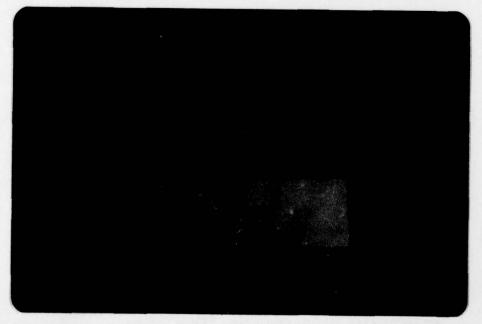


Fig. 39. Effect of MN on alfalfa and wheat leaves showing distal and marginal injury on wheat and marginal injury on alfalfa.

## APPENDIX I

Data showing fumigation dates, concentrations, number of plants injured and percent leaves injured for six phytotoxicants and seven plant species.

WEATER AND ADDRESS STREET, CO.

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Date	Conc mg/m <sup>3</sup>	# Plants	# Injured	% Leaves Injured	
7/18/77	50	2 pots each	0	0	
7/18/77	25	"	0	0	
7/18/77	12.5	"	0	0	
7/20/77	50	"	0	0	
8/31/77	50	"	0	0	
8/31/77	50	"	0	0	

Effects of Fumigating Plants with Nitromethane

\*

Effects of Fumigating Plants with Mixed Nitrotoluenes

All Species\*

Date	Conc mg/m <sup>3</sup>	# Plants	# Injured	. * .	% Leaves Injured
7/21/77	50	2 pots each	0		0
7/21/77	100	"	0		0
7/22/77	100	"	0		0
9/1/77	100	"	0		0
9/1/77	100		0		0

\* 2 each oak, pine, tobacco; 6 each wheat, alfalfa, soybean and corn.

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Effects of Fumigating Plants With Methyl Nitrate

		WILLAL		
Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>	20114	19	
9/2/77	40.0	6	6	11.
"	40.0	6	6	23
	40.0	6	6	35
"	40.0	6	0	0
9/8/77	20.0	15	1	1
"	20.0	15	6	7
	20.0	15	5	5
10/11/77	40.0	10	0	0
	20.0	10	0	0
	10.0	10	0	0
	5.0	10	0	0
10/12/77	40.0	10	0	. 0
	20.0	10	0	0
	10.0	10	0	0
	5.0	10	0	0

WHEAT

\* 8/31/77 - All species - 2 plants each - no injury 9/2/77 - Corn, soybean, oak, pine, tobacco - fumigated with 40 mg/m<sup>3</sup> - no injury Effects of Fumigating Plants With Methyl Nitrate

				109102	
Date	Conc.	# Plants	# Injured	% Leaves Injured	
Date	mg/m <sup>3</sup>				
9/2/77	40.0	6	6	23	
	40.0	6	6	30	
"	40.0	6	6	47	
	40.0	5	5	46	
9/8/77	20.0	15	13	33	
	20.0	13	12	38	
	20.0	13	13	48	
10/11/77	40.0	10	0.	0	
"	20.0	10	. 0	0	
"	10.0	10	0	0	
	5.0	10	0	. 0	
10/12/77	40.0	10	0	0	
	20.0	10	0	0	
	10.0	10	0	0	
н .	5.0	10	. 0	0	

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Date	Conc.	# Plants	# Tedured	% Leaves Injured
Date	mg/m <sup>3</sup>	r Idits	Injured	Injured
6/21/77	50.0	15	15	100
"	31.0	15	15	93
"	23.0	15	15	54
6/24/77	25.0	15	12	74
"	12.5	15	10	40
"	6.3	15 /	0	0
"	3.1	15	0	0
7/1/77	20.0	15	15	65
"	15.0	15	13	18
	10.0	15	0	0
"	5.0	15	0	. 0
7/5/77	25.0	15	12	21
"	20.0	14	4	9
"	15.0	15	0	0,
"	10.0	15	0	0
7/8/77	25.0	15 '	15	61
"	20.0	15	15	32
"	15.0	14	9	8
"	10.0	15	0	0
7/12/77	25.0	15	15	100
"	20.0	<b>15</b>	15	86
"	15.0	15 🌍	*	*
"	10.0	15	11	15
7/13/77	22.5	15	13	27
	20.0	15	6	6
	17.5	15	7	5
	10.0	15	3	2

Effects of Fumigating Plants With Acetic Acid

WHEAT

\* Rejected - improper fumigation

Effects of Fumigating Plants With Acetic Acid

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
6/22/77	50.0	10	10	100
	25.0	10	10	100
"	12.5	10	10	100
	6.3	10	10	25
6/23/77	25.0	10	10	100
"	12.5	10	10	100
	6.3	10	5	19
"	3.1	10	2	3
7/7/77	10.0	15	15	79
	8.0	15	15	70
"	6.0	15	12	39
"	4.0	15	8	12
7/13/77	6.00	15	7	9
"	5.0	15	0	0
"	4.0	15	0	0
"	3.0	15	0	0
7/14/77	6.0	15	8	20
"	5.0	15	11	16
<b>N11</b>	4.0	15	0	0
	3.0	15	0	0
			0.81	

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besit of	the state	#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>°</sup>			
6/22/77	50.0	10	10	74
"	25.0	10	5	13
н	12.5	10	0	0
7/6/77	40.0	10	10	88
н.	35.0	10	9	84
"	30.0	10	10	82
"	25.0	10	10 ·	62
7/12/77	25.0	10	10	68
"	20.0	10	10	25
n	15.0	10	6	6
"	10.0	10	0	0
7/13/77	20.0	6	6	27
	17.5	6	5	26
"	15.0	6	3	4
7/21/77	18.0	10	10	29
	16.0	10	5	5
"	14.0	10	4	5
"	12.0	10	0	0
7/22/77	20.0	9	7	16
11	18.0	9	5	9
"	16.0	9	4	13
	14.0	9	2	5
7/26/77	18.0	10	6	6
"	16.0	10	5	4
	14.0	10	2	2
	12.0	10	0	0
10/12/77	80.0	10	10	92
u	40.0	10	10	42
	20.0	10	8	15
	10.0	10	0	0

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TOBACCO

Effects	ot	Fumigating	Plants	With	Acetic	Acid	
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Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
11/1/77	80.0	10	10	86
u	60.0	10	10	73
"	40.0	10	10	48
	20.0	10	7	11
11/2/77	80.0	10	10	71
."	60.0	10	10	45
"	40.0	10	10	34
"	20.0	10	0	0

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1/3/77 vi

77/2/77

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
6/21/77	50.0	15	15	. 99
	31.0	14	14	86
	23.0	14	14	88
6/24/77	25.0	14	14	73
	12.5	14	14	58
	6.3	15	0	0
	3.1	15	0	0
7/1/77	\$20.0	15	8	28
"	15.0	14	2	5
	10.0	15	0	0
	5.0	15	0	0
7/5/77	25.0	14	*	*
	20.0	15	5	20
	15.0	15	0	0
	10.0	15	0	0
7/8/77	25.0	15	15	79
	20.0	15	15	54
	15.0	15	11	22
	10.0	15	2	2
7/12/77	25.0	15	15	84
	20.0	18	16	59
	15.0	15	*	*
	10.0	15	9	14
7/13/77	22.5	14	14	73
	20.0	15	13	47
"	17.5	15	9	24
	15.0	15	4	11

Effects of Fumigating Plants With Acetic Acid

\* Rejected - improper fumigation

SOYBEANS

		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
10/12/77	80.0	15	15	100
"	40.0	15	15	100
	20.0	15	15	61
	10.0	15	8	11

SOYBEANS

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Effects of Fumigating Plants With Acetic Acid CORN

		#	#	% Leaves
Date	Conc. mg/m <sup>3</sup>	Plants	Injured	Injured
6/22/77	50.0	15	14	63
"	25.0	15	0	0
"	12.5	15	0	. 0
6/23/77	25.0	15	1	2
"	12.5	15	0	0
"	6.3	15	0	0
	3.1	15	0	0
6/30/77	60.0	15	15	56
"	50.0	15	15	44
"	40.0	15	13	30
	30.0	14	7	13
7/1/77	60.0	15	15	46
H	50.0	15	10	22
	40.0	15	14	25
"	30.0	15	14	28
7/5/77	70.0	15	15	77
"	60.0	15	14	52
	50.0	15	15	72
н .	40.0	15	15	53
7/8/77	50.0	15	15	48
"	40.0	15	12	- 28
	30.0	15	13	26
	20.0	14	4	15
7/12/77	50.0	15	15	74
	40.0	15	15	53
	30.0	15	12	32
	20.0	15	5	5
7/14/77	35.0	15	15	43
"	30.0	15	12	31
	25.0	15	8	13
	20.0		3	

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Effects of Fumigating Plants With Acetic Acid

			#	#	% Leaves
	Date	Conc.	Plants	Injured	Injured
		mg/m <sup>3</sup>			
1 -	10/13/77	80.0	14	14	100
		60.0	15	15 .	61
	"	40.0	15	13	33
	"	20.0	15	6	8
2 -	10/13/77	80.0	12	12	93
	"	60.0	12	12	61
	"	40.0	14	13	37
	n	20.0	13	6	9

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Effects o	f Fum	igating	Plants	With	Acetic	Acid	
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		#	#	% Leaves*
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
6/24/77	25.0	2	0	0
	12.5	2	0	0
7/11/77	50.0	4	3	14
7/27/77	50.0	9	6	39
	45.0	10	10	54
	40.0	10	10	51
	35.0	10	10	59
10/13/77	80.0	5	4	6
	60.0	5	0	0
	40.0	6	0	0
	20.0	5	0	0
10/14/77	80.0	5	4	23
	60.0	5	0	0
	40.0	4	0	0
"	20.0	5	1	15
11/2/77	80.0	5	0	0
"	60.0	5	0	0
	40.0	5	0	0
"	20.0	5	0	0
11/7/77	80.0	5	0	0
	60.0	5	0	0
"	40.0	5	0	0
	20.0	5	0	0
11/9/77	80.0	5	4	18
	60.0	5	0	0
<b>"</b> "	40.0	5	• • •	0
"	20.0	5	0	0

WHITE OAK

\* % young leaves injured

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ANY WARDERSON MEN STREET

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
6/24/77	25.0	2	0	0
	12.5	2	0	0
7/11/77	50.0	6	6	83
7/14/77	35.0	4	4	95
7/26/77	30.0	. 5	0	• 0
	28.0	5	0	0
"	26.0	5	0	0
"	24.0	5	0	0
LO/13/77	80.0	5	5	86
	60.0	5	5	30
"	40.0	4	3	20
"	20.0	5	0	0
10/14/77	80.0	5	5	78
"	60.0	5	4	34
"	40.0	6	0	0
	20.0	5	0	0
11/2/77	80.0	5	5	12
"	60.0	5	0	0
n	40.0	5	0	0
"	20.0	5	0	0
11/7/77	80.0	5	3	7
	60.0	5	0	0
	40.0	5	0	0
	20.0	. 5	0	0
11/9/77	80.0	5	4	21
	60.0	5	1	2
	40.0	5	0	0
	20.0	5	0	0

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Effects of Fumigating Plants With Acetic Acid SCOTCH PINE

\* % young needles injured

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Effects of Fumigating Plants With SO2

	Lo rel rel	#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
7/27/77*	10.6	6	6	100
	5.3	6	6	22 ·
"	2.7	6	0	0
"	1.3	6	0	0
7/28/77*	18.1	6	6	100
"	9.0	6	6	54
	4.5	6	3	5
	2.1	6	0	0
7/29/77	9.4	15	15	100
"	8.2	15	15	75
n	6.8	15	15	39
	4.9	15	15	76
8/2/77	6.5	14	14	85
H	5.2	14	14	- 81
H	4.2	15	15	77
u	3.0	13	13	39
8/18/77	6.9	15	15	71
H	5.5	12	12	67
"	4.1	14	14	40
"	2.7	13	13	34
8/19/77	6.9	15	15	100
	5.5	15	15	100
	4.1	15	15	71
	2.7	14	14	29
8/24/77	2.7	15	0	0
	2.1	15	0	0
	1.5	15	0	0
	0.9	15	0	0

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WILL	1.1	L 1	

\* Omitted from probit analyses, preliminary fumigations.

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Effects of Fumigating Plants With SO2

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
- 10- 1				
7/27/77	10.6	2	0	0
	5.3	3	0	. 0
"	2.7	3	0	0
"	1.3	3	0	0
7/28/77	18.1	4	4	100
"	9.0	4	4	100
"	4.5	4	0	0
	2.1	4	0	0
8/23/77	6.9	15	15	100
	5.5	15	15	100
n	4.1	15	15	100
	2.7	15	15	100
8/24/77	2.7	15	15	78
"	2.1	12	8	11
	1.5	15	5	5
	0.9	5	0	0
8/25/77	2.7	21	11	29
	2.2	19	7	34
н	1.8	20	11	21
"	1.3	17	10	16
9/1/77	2.7	15	15	61
"	2.1	15	15	50
	1.6	12	12	30
"	1.1	15	14	16
9/2/77	3.2		8	
9/2///	2.9	8 7	8	100
				100
	2.5	8	8	100
	2.1	8	8	100

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Effect of Fumigating Plants With SO2

		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
•	mg/m <sup>3</sup>			
10/5/77	10.6	15	15	75
	5.3	15	3	7
"	2.7	15	0	0
	1.3	15	0	0
10/6/77	10.6	15	15	78
n	5.3	15	7	8
<b>n</b> ·	2.7	15	· 1	1
n	1.3	15	0	0
10/10/77	10.6	15	15	100
	5.3	15	15	74
	2.7	15	10	20
	1.3	15	0	0

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Effect of Fumigating Plants With SO2

TOBACCO

		#	#	% Leaves
Date	Conc. mg/m <sup>3</sup>	Plants	Injured	Injured
7/27/77	10.6	5	- 5	78
"	5.3	5	3	7
	2.7	5	0	0
	1.3	5	0	0
7/28/77	18.1	5	5	91
"	9.0	5	5	45
	4.5	5	1	5
	2.1	. 5	0	0
7/29/77	9.2	10	10	82
"	8.2	10	10	48
	6.8	10	6	44
	4.9	10	8	22
8/2/77	7.3	10	9	30
"	6.0	10	7	18
	4.7	10	6	12
	3.3	10	2	3
8/5/77	8.1	10	10	30
	7.8	10	9	28
	6.4	10	10	. 36
	5.0	10	3	5
8/15/77	9.2	10	10	48
	7.8	10	10	30
	6.3	10	10	31
	5.0	10	4	7
8/19/77	9.2	8	8	83
	7.8	8	8	78
"	6.3	7	7	55
	5.0	7	5	22
8/22/77	7.8	9	9	71
"	6.3	9	9	53
"	5.0	9	9	39
"	3.5	9	6	9
9/1/77	4.9	7	7	46
"	4.4	7	7.	35
	3.9	7	7	37
"	3.4	. 7	7	21

-VAL TROOM - CONTRACTOR

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
9/27/77	47.8	9	8	40
	37.2	10	2	4
	26.6	10	5	16
H	20.0	10	2	3
9/30/77	31.9	10	10	98
	21.3	9	9	100
u	10.6	10	10	85
u	5.3	10	6	30
11/17/77	31.9	10	10	82
	21.3	10	10	66
н	10.6	10	10	54
	5.3	10	8	19

Effect of Fumigating Plants With SO2

TOBACCO

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Effects of Fumigating Plants With SO2

Date	Conc.	# Plants	# Injured	% Leaves Injured
·	mg/m <sup>3</sup>		a sa	
7/27/77	10.6	4	4	78
	5.3	6	6	47
	2.7	6	0	0
0.0	1.3	6	0	0
7/28/77	18.1	6	6	100
9 m	9.0	6	6	57
6 H	4.5	6	0	0
	2.1	6	0	Q
7/29/77	9.4	14	14	78
	8.2	15	15	53
	6.8	14	9	18
	4.9	15	14	44
8/2/77	6.5	15	13	37
	5.2	15	11	25
	4.2	14	5	12
	3.0 .	14	8	17
8/18/77	6.9	15	15	68
	5.5	15	15	53
	4.1	15	15	63
	2.7	15	15	61
8/19/77	6.9	15	15	52
	5.5	15	15	44
	4.1	15	15	34
	2.7	15	15	36
9/30/77	21.3	15	15	93
"	10.6	15	15	72
	5.3	15	14	49
	2.7	15	14	36

SOYBEANS

		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
7/29/77	9.4	14	9	29
"	8.2	14	3	4
"	6.8	14	4	6
u	4.9	15	7	10
8/8/77	11.8	15	12	20
"	7.9	15	7	9
u	5.9	15	6	8
	4.8	15	2	2
8/9/77	13.3	16	15	36
"	11.8	15	14	33
"	11.2	15	12	29
"	7.6	17	7	9
8/10/77	14.2	16	15	31
	12.1	18	6	8
"	9.6	18	10	15
	7.1	17	0.05	6
8/23/77	14.2	15	12	33
	12.1	16	6	15
"	9.6	15	5	8
	7.1	15	0	0
8/24/77	14.2	15	12	37
"	12.1	15	12	33
"	9.6	14	13	40
	7.1	15	7	9
8/25/77	14.2	13	12	28
	12.1	17	10	21
	9.6	18	15	27
"	7.1	14	4	6

Effects of Fumigating Plants With  $SO_2$ 

80

	Date	Conc.	# Plants	# Injured	% Leaves Injured
	Date	mg/m <sup>3</sup>	TIGACO	Injulu	Injuice
1 -	9/29/77	42.6	18	18	90
	"	21.3	15	15	59
	"	10.6	15	12	34
	"	5.3	15	6	5
2 -	9/29/77	31.9	14	14	95
	"	21.3	15	15	61
	"	10.6	15	8	12

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Effects of Fumigating Plants With SO2

CORN

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>			
7/27/77	10.6	2	0	0
	5.3	2	0	0
	2.7	2	0	0
	1.3	2	0	0
7/28/77	18.1	2	2	68
	9.0	2	1	28
"	4.5	2	0	0
	2.1	2	0	0
8/23/77	14.1	2	0	0
8/24/77	14.1	2	1	6
9/29/77	31.9	5	4	17
"	21.3	5	2	10
"	10.6	5	0	0
	5.3	5	0 .	0

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Effects of Fumigating Plants With SO2

### WHITE OAK

10/10/77

10/11/77

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# \* % young leaves injured

10.6

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10.6

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# Effects of Fumigating Plants with $SO_2$

		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
7/27/77	10.6	2	0	0
ii	5.3	2	0	0
	2.7	2	0	0
	1.3	2	0	0
7/28/77	18.1	2	1	7
	9.0	2	1	48
н	4.5	2	0	0
"	2.1	2	0	0
3/23/77	14.2	2	2	100
3/24/77	12.1	3	2	<7
	9.6	3	2	20
"	7.1	3	2	<7
9/30/77	21.3	5	4	43
	10.6	5	0	0
"	5.3	5	0	0
	2.7	5	0	0
0/10/77	10.6	5	0	0
"	5.3	5	0	0
0/11/77	10.6	5	0	0
"	5.3	5	0	0

+ Casted

公共由

SCOTCH PINE

\* % young needles injured

		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
9/8/77	12.0	6	6	100
9/13/77	2.4	15	15	47
	1.8	14	6	11
"	1.2	15	0	0
"	0.6	15	0	. 0
9/15/77	3.6	15	15	96
"	3.0	15	15	95
"	2.4	15	15	91
"	1.8	15	15	71
9/21/77	3::0	15	15	98
	2.4	15	15	96
	1.8	15	15	87
"	1.2	15	15	46
9/21/77	3.0	15	15	72
"	2.4	15	15	. 53
	1.8	15	15	55
"	1.2	15	15	48
10/4/77	4.8	15	15	92
"	2.4	15	15	. 75
"	1.2	15	15	64
"	0.6	14	14	54
10/7/77	4.8	15	15	100
"	2.4	15	15	97
	1.2	15	15	92

#

Effects of Fumigating Plants With Tetra Nitro Methane

WHEAT

VERSELE LED

		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>		170	
- 10/14/77	2.4	15	15	94
	1.2	14	14	66
"	0.6	14	14	29
"	0.3	15	9	5
- 10/14/77	2.4	15	15	96
"	1.2	15	15	81
"	0.6	15	15	36
"	0.3	15	1	1

WHEAT

		#	#	% Leaves
Date	Conc.	Plant	Injured	Injured
	mg/m <sup>3</sup>			
9/8/77	12.0	6	6	100
9/9/77	6.0	6	6	100
"	4.8	6	6	80
"	3.6	6	6	70
"	2.4	6	6	70
9/13/77	2.4	15	15	36
	1.8	15	14	24
"	1.2	15	14	13
"	0.6	15	3	2
9/21/77	3.0	14	14	90
"	2.4	5	5	85
"	1.8	15	12	. 65
"	1.2	14	13	40

"	1.8	15	12	
"	1.2	14	13	
#2 - 9/21/77	3.0	9	9	
"	2.4	8	8	
"	1.8	8	8	
"	1.2	9	9	
10/4/77	5.0	15	15	
"	2.4	15	15	
"	1.2	15	15	
"	0.6	15	14	
#1 - 10/14/77	2.4	15	15	
"	1.2	15	15	
"	0.6	15	15	
"	0.3	15	6	
#2 - 10/14/77	2.4	15	15	

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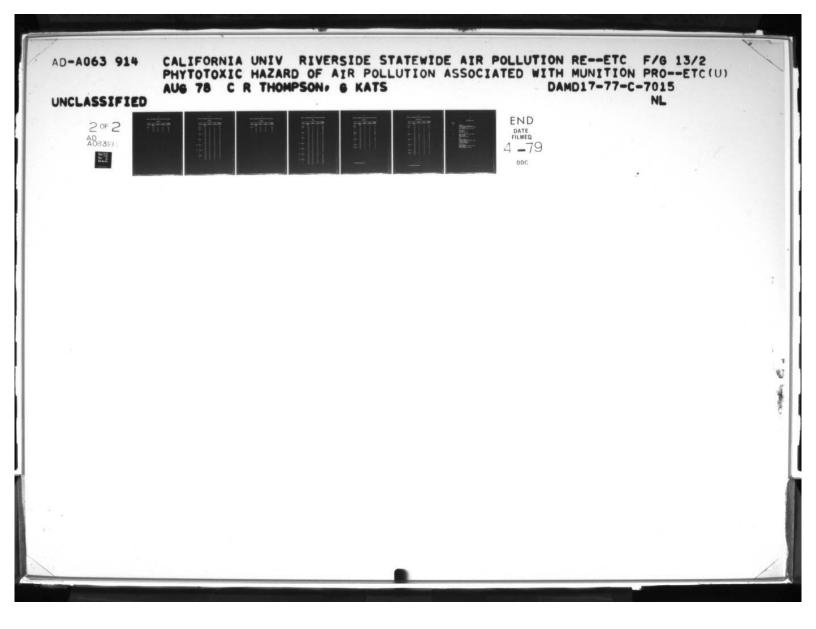
		#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
9/8/77	12.0	2	2	100
9/9/77	6.0	3	3	80*
u	4.8	3	3	40*
"	3.6	3	3	30
"	2.4	3	3	20
9/12/77	2.4	10	. 10	45
"	1.8	10	. 9	23
"	1.2	10	6	14
**	0.6	10	0	0
9/14/77	3.6	10	10	61
"	3.0	9	9	37
"	2.4	. 9	9	57
"	1.8	9	9	22
9/20/77	3.0	5	4	28
"	2.4	5	4	23
"	1.8	5	3	9
	1.2	5	2	9
9/20/77	3.0	7	6	13
"	2.4	7	5	28
"	1.8	7	3	9
	1.2	7	1	1
10/5/77	9.6	10	10	49
	4.8	10	5	9
"	2.4	10	2	4
	1.2	10	0	0
10/6/77	9.6	10	10	73
	4.8	10	5	16
"	2.4	10	0	0
	1.2	10	0	0

TOBACCO

\* % leaf injury - old leaves

and the second second

87



Lange and	na manford	#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
10/7/77	14.4	10	10	100
	7.2	10	10	90
	3.6	10	9	26
"	1.8	10	8	22
				10/0/07
			1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	
			a start and	
		60,000 \$ 1		

TOBACCO

		SOYBEAN		
Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>		han a state of the second	
9/8/77	12.0	6	6	100
9/12/77	2.4	15	14	58
	1.8	15	12	34
'n	1.2	15	0	0
"	0.6	15	0	0
9/14/77	3.6	14	14	97
"	3.0	15	15	82
	2.4	15	15	71
	1.8	15	15	68
9/15/77	3.6	15	15	92
"	3.0	15	15	98
"	2.4	15	15	. 87
"	1,8	15	15	94
- 9/21/77	3.0	15	15	81
"	2.4	15	12	44
	1.8	14	11	28
"	1.2	15	1	2
- 9/21/77	3.0	15	15	61
"	2.4	15	15	73
"	1.8	15	15	72
"	1.2	14	14	59
10/4/77	4.8	15	14	78
	2.4	15	15	55
	1.2	15	0	0
	0.6	15	0	0

COUDEAN

89

· · · · · ·	Sugar Star	#	#	% Leaves
Date	Conc.	Plants	Injured	Injured
	mg/m <sup>3</sup>			
10/7/77	4.8	15	15	100
"	2.4	15	15	85
".	1.2	15	15	68
n	0.6	15	15	32
				st.
	25			
		4		
		1		

Date	Conc.	# Plants	# Injured	% Leaves Injured
	mg/m <sup>3</sup>		The loss	
9/8/77	12.0	6	6	100
9/9/77	6.0	6	6	100
	4.8	6	6	100
	3.6	6	6	80
	2.4	6	6	75
9/13/77	2.4	15	15	84
"	1.8	15	12	55
"	1.2	14	13	53
о <b>н</b>	0.6	15	11	15
9/14/77	3.6	14	14	79
n	3.0	15	15	53
	2.4	15	14	61
0.0	1.8	15	12	44
9/20/77	3.0	15	14	52
	2.4	14	11	36
	1.8	14	12	29
	1.2	14	7	15
9/20/77	3.0	14	14	56
	2.4	15	15	56
	1.8	14	11	35
"	1.2	14	5	7
10/4/77	4.8	15	15	94
	2.4	15	15	49
	1.2	15	15	52
	0.6	15	7	11
10/4/77	4.8	14	14	95
"	2.4	15	15	88
"	1.2	14	13	60
	0.6	12	11 1 1 7 1 2 W	18

CORN

Effects of	Fumigating	Plants	With	Tetra	Nitro	Methane	

Date	Conc.	# Plants	# Injured	% Leaves Injured
Date	mg/m <sup>3</sup>	Flants	Injured	Injured
9/8/77	12.0	2	0	0
9/977	6.0	2	0	0
	4.8	2	0	0
	3.6	2	0	0
	2.4	2	0	0
9/22/77	7.2	3	3	100
10/17/77	9.6	5	3	39*
	4.8	5	0	0
	2.4	5	0	0
u	1.2	5	0	0
10/18/77	9.6	5	5	32*
	4.8	5	0	0
	2.4	5	0	0
	1.2	5	0	0
10/21/77	19.2	5	0	0
	9.6	5	0	0
10/24/77	19.2	5	0	0
	9.6	5	0	0

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WHITE OAK

## \* % young leaves injured

.

Date	Come	#	#	% Leaves
Date	Conc. mg/m <sup>3</sup>	Plants	Injured	Injured
9/8/77	12.0	2	2	45
9/9/77	6.0	2	2	40
"	4.8	2	0	0
	3.6	2	0	0
"	2.4	2	0	0
9/22/77	7.2	10	6	52
	6.0	10	4	24
	4.8	10	3	6
"	3,6	10	5	20
10/17/77	9.6	5	0	0
".	4.8	5	0	0
	2.4	5	0	0
	1.2	5	0	• 0
10/18/77	9.6	5	0	0
	4.8	5	0	0
"	2.4	5	0	0
	1.2	5	0	0
10/21/77	19.2	5	0	0
"	9.6	5	0	0
10/24/77	19.2	5	0	0
"	9.6	5	0	0

\* % young needles injured

93

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