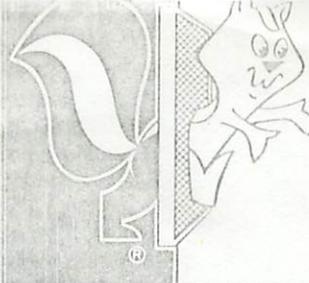


# Purafil®



Ethylene:

## An Urban Air Pollutant

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systems for odor abatement & gaseous filtration

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Ethylene is an unusual air pollutant in that it is a plant hormone. Motor vehicle exhaust is a primary source. In the Washington, D. C., area, ethylene concentrations ranged from 700 ppb in the city center to 39 ppb in areas outside the circumferential beltway. Plants grown in these concentrations of ethylene, using controlled environment chambers, exhibited typical symptoms of ethylene toxicity: reduced growth, premature senescence, and reduced flowering and fruit production. When plants were grown in carbon-filtered ambient air, which was also filtered through  $KMnO_4$  to remove ethylene by oxidation, growth, flowering, and fruit production increased. These observations demonstrate that ethylene air pollution is a continual source of stress for plant growth and development in an urban environment.

The strategy used to demonstrate the existence of a toxic pollutant is straightforward and involves four essential criteria. First, the toxicant must cause damage in terms of growth inhibition, yield reduction, premature senescence, or death. Ethylene, a component of auto exhaust, causes all of these effects according to Abeles.<sup>1</sup>

Second, the gas must be present in the air in sufficient quantity to cause damage. Such presence can be determined by the use of gas chromatography, a technique with sufficient selectivity, precision, and sensitivity to show ethylene levels in air equal to or greater than 10 ppb, a concentration that causes threshold effects on some plants.

Third, it should be possible to reduce the phytotoxic effects of urban air by passage through filters designed to remove ethylene. In this study, filters consisting of  $KMnO_4$  adsorbed on alumina (Purafil\*) were used to oxidize ethylene to ethylene-glycol.

The fourth and most difficult aspect of an air pollution study is to assess the damage to existing urban vegetation. In the case of point sources, such as

industrial ethylene plants,<sup>2</sup> and leaking gas mains,<sup>3</sup> it was relatively simple to prove that ethylene was the phytotoxicant responsible for loss of vegetation. In urban centers, where other pollutants such as ozone and  $SO_2$  exist, identification of the source of damage becomes complex. The problem is compounded further because ozone can increase ethylene production by plants.<sup>4</sup> If drought, insects, or other environmental stresses are superimposed on the air pollution problem, diagnosis of the specific cause of plant injury rapidly becomes impossible. The purpose of this paper is to establish and demonstrate the existence of ethylene air pollution using the criteria of: known dose-response curves, existence of phytotoxic levels, and removal of phytotoxicants by air purification systems. We did not attempt to establish the economic cost of ethylene air pollution. We concur with the idea that resolution of the ethylene air pollution problem ultimately rests on controlling the nature of emissions, especially from urban transportation.

### Materials and Methods

Ethylene was measured with a flame ionization gas chromatograph equipped with 60-cm long  $\times$  0.64-cm diameter copper column filled with alumina. Calibration was accomplished using a reference gas containing 1.3 ppm ethylene in nitrogen supplied by Air Products and Chemicals, Inc. Concentration in a sample was determined

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by comparing peak heights with appropriate dilutions of the reference gas. This instrument can measure as little as 5 ppb ethylene (peak height twice base line noise) in a 2-ml gas sample. Air samples were collected in a 3-ml disposable plastic syringe (JELCO) stoppered with a plastic cap. Ethylene levels inside the sealed syringes remained within 1% of the initial value over a 24-hr storage period.

Plants for the fumigation studies were grown in 0.57 m<sup>3</sup> Teflon plastic-covered chambers. Airflow through the chambers was 0.57 m<sup>3</sup>/min, except for the chamber fitted with the KMnO<sub>4</sub> ethylene filter where the flow rate was 0.28 m<sup>3</sup>/min. A 16-hr photoperiod was supplied by a bank of fluorescent tubes which yielded 12.9 KLx at the floor of the chamber. The temperature and relative humidity of the air with lights on were 24 ± 1°C and 75%; with lights off, they were 20 ± 1°C and 90%.

By adjusting the entrance and exit flow rates, the chambers were held under -2.5-mm water pressure to prevent ethylene in the chambers from escaping into the room—for example, due to a possible small leak around a chamber door. Effluent from the chambers was vented to the outside of the building through an exhaust duct. Ethylene was added to the chambers through high-precision needle valves and flow meters attached to a pressure tank filled with 1% ethylene in nitrogen. The ethylene was diluted to achieve predetermined concentrations. Dilution occurred as the ethylene in the 6.4-mm diameter plastic tubing mixed with air in a 3.7-cm diameter aluminum pipe which supplied the temperature- and humidity-conditioned air to the chambers. Ethylene levels inside the chambers were monitored periodically by a gas chromatograph and were found to be stable within 10% of the desired value.

A KMnO<sub>4</sub> filter was used to remove ethylene from ambient air. The filter consisted of a canister 30-cm high × 30-cm in diameter filled with 3.2-mm diameter Purafil pellets. Purafil is KMnO<sub>4</sub> absorbed on alumina pellets

distributed by H. E. Burroughs and Associates, 3550 Broad Street, Chamblee, Ga. 30341. The Purafil was supported 3 cm from the bottom of the canister by an expanded metal screen covered with 1.6-mm mesh hardware cloth. Entrance and exit ducts of the canister consisted of 3.7-cm diameter pipe. This filter was about 75% efficient, but it reduced the airflow by 50%.

### Results

The results presented here were intended to demonstrate three of the four essential aspects of an air pollution study. We found that ethylene was present over a wide area, that the concentrations of ethylene observed caused plant damage, and that an ethylene filter reduced the damage caused by ambient air.

Figure 1 shows the average daytime concentrations of ethylene in various parts of the Washington, D. C., area during July and August 1972. The ethylene concentrations represent the average of seven or more samples collected between 0900 and 1430 hr. The locations were sampled on different days over a 3-week period from late July to mid-August. Similar results were observed when some of the locations were revisited on different days. No nighttime or weekend samples were collected. At all locations, air samples were taken in open areas as far away as possible from streets or roads.

As expected, the data confirm that ethylene concentrations are highest in areas of heaviest auto traffic. The highest concentrations were observed in downtown Washington. Presumably a survey of other products of auto exhaust, such as nitric oxides and CO, would yield similar results. The ethylene survey indicated in Figure 1 is only an approximation of the ethylene cloud that lies over an urban area. Factors such as meteorological variation and reduced traffic density at night and weekends were not considered and could reduce the values shown.

Figures 2 through 7 depict some effects of ethylene at concentrations that were found in the Washington, D. C., area. In every instance, the

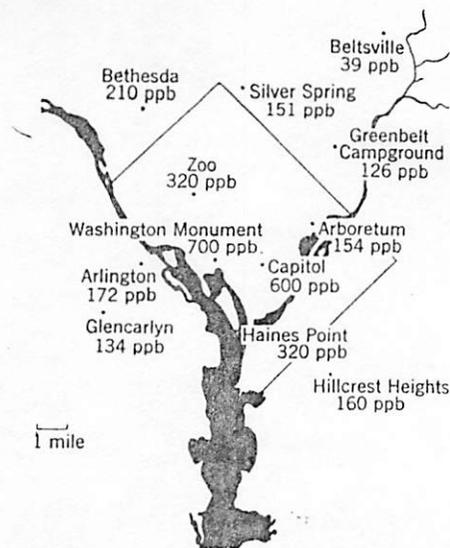


Figure 1. Average daytime concentrations of ethylene during July-August 1972 in Washington, D. C.

addition of as little as 25 ppb of ethylene reduced vegetative growth, and flower and fruit development. Specific effects of ethylene observed at these concentrations include inhibition of stem elongation (Figures 2a, 4), inhibition of leaf expansion (Figure 3), promotion of senescence and abscission (Figures 6, 7), induction of epinasty (Figure 7), and reduction of flowering and fruit set (Figures 2a, 2b, 4, 5; Table I). We also observed a change in sex expression of cucumber flowers from male to female (Table I) and the development of intumescences (hypertrophied lenticels) in ethylene-treated locust. All of the phenomena observed are well-known effects of ethylene. The results confirm our suspicion that continuous exposure to the ethylene concentrations which occur in urban areas will damage, retard, or alter growth and development of plants grown under near optimal laboratory conditions.

The material studied was limited to annual species or tree seedlings because of space limitations inside the growth chambers. However, the material was thought to be fairly representative of

Table I. Effect of ethylene on flower initiation and fruit development.

Concentration	Chris African Violets <sup>a</sup>		A and C Cucumber <sup>b</sup>		Dwarf Bolero <sup>c</sup> Marigold	Cutler Soybean <sup>d</sup>		Red Kidney <sup>e</sup> Bean	
	Initial flrs.	After 10 days	♂ Flrs.	♀ Flrs.	Flrs.	Flrs.	Fruits	Mat. Fruit	Immat. Fruit
Filtered Air	25	31	18	1	5	22	8	8	18
Ambient Air	16	14	14	2	5	16	2	5	5
25 ppb	17	17	3	1	2	2	0	1	4
50 ppb	11	32	3	1	1	0	0	0	0
100 ppb	18	0	0	8	0	0	0	0	0

<sup>a</sup> One plant per treatment.

<sup>b</sup> Average of 2 plants grown as indicated for 46 days.

<sup>c</sup> Average of 2 plants grown as indicated for 70 days.

<sup>d</sup> Average of 4 plants grown as indicated for 50 days.

<sup>e</sup> Average of 4 plants grown as indicated for 44 days.

plants in general. It is possible that mature trees, the dominant form of vegetation in an urban area, would show a higher tolerance for ethylene. It is also possible that damage from ethylene would be less on existing vegetation in an urban setting because of additional stress from edaphic factors, environmental extremes, diseases, and insect damage.

The phytotoxic effects of urban air can be reduced by passage through a filter designed to remove ethylene. Table I summarizes data showing that plants grown in air filtered through about a 75% efficient  $\text{KMnO}_4$  filter formed a greater number of flowers and fruits than those grown in carbon-filtered ambient air in Beltsville, Md. Ethylene levels in Beltsville ranged from 0 to 60 ppb, depending on traffic and meteorological conditions. An average daytime ethylene concentration at the Air Pollution Laboratory was about 39 ppb. Compared to other parts of Washington, air at Beltsville was relatively uncontaminated by ethylene, which accounts for the lack of dramatic improvement in growth after filtering marginally polluted air.

The  $\text{KMnO}_4$  filter is not specific for ethylene; it will also remove nitric oxides,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{O}_3$ . Except for  $\text{O}_3$ , none of the other gases was detected at phytotoxic levels in the vicinity of the Air Pollution Laboratory. To avoid the effect of photochemically generated  $\text{O}_3$ , all air used in the fumigation studies was passed through an activated carbon filter before it entered the growth chambers or ethylene filter.

We can summarize our results by stating that three of the four criteria for demonstrating air pollution damage were met during these experiments. Phytotoxic levels of ethylene occur over a wide area; these levels can cause plant damage; and filtering reduced the phytotoxic effects of urban air. A survey of the existing plant community for air pollution damage remains to be done.

#### Discussion

Most contemporary research on plant air pollution has focused on the effects of oxidants,  $\text{SO}_2$ , fluorides, and nitric oxides and has either ignored ethylene or lumped it with a grab bag of gases called hydrocarbons. However, a number of earlier workers were aware of ethylene air pollution, and detailed reviews of Abeles,<sup>1</sup> Clayton and Platt,<sup>5</sup> and Stahl,<sup>6</sup> can be consulted for background data on this problem. Phytotoxic concentrations of ethylene in urban air were described by Scott et al.<sup>7</sup>

Briefly, the history of ethylene air pollution data can be traced to the 1864 report of Girardin<sup>8</sup> who described damage to street trees by illuminating

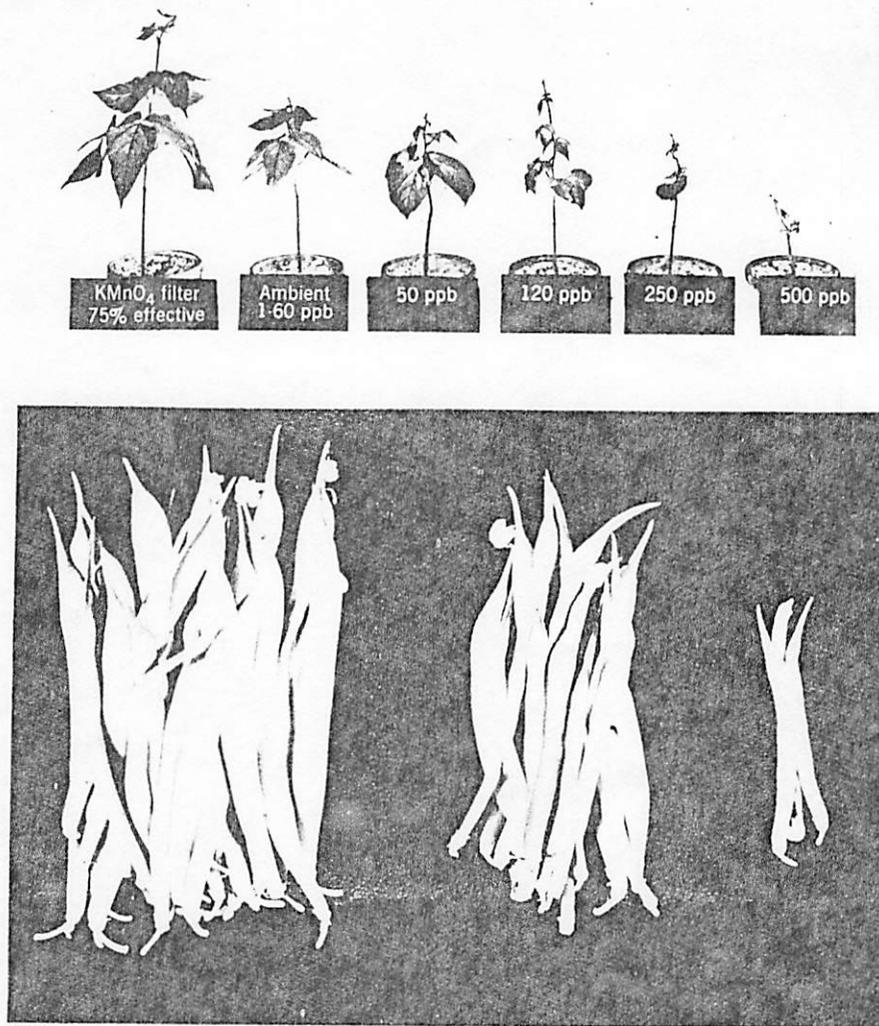


Figure 2. Effect of ethylene on the growth and yield of Red Kidney bean plants. (a) Plants grown for 75 days under the conditions indicated; (b) Yield (left to right) of Red Kidney beans harvested from plants grown in filtered air, ambient air, and air containing 25 ppb ethylene.

gas, containing ethylene, from leaking mains. With increasing use of manufactured gas, the number of reports of shade tree damage increased. Gas from leaking mains in Massachusetts damaged miles of trees in the early 1900's,<sup>9</sup> and it became standard to handle damage claims (\$5-\$150 per tree) out of court. Whole greenhouse crops of roses, carnations, and other flowers have been destroyed by leaking illuminating gas, and settlements of \$90,000 have been reported.<sup>9</sup>

A study of the effects of leaking illuminating gas on plants in 1901 by the Russian plant physiologist, D. N. Neljubov,<sup>10</sup> led to the first report on the physiological effects of ethylene. He demonstrated that this gas was the major cause of the phytotoxic effects of illuminating gas and that threshold effects could be observed at levels as low as 10 ppb. However, the introduction of cheap natural gas, which contains no ethylene, ended these kinds of problems.

With the increasing scarcity of natural gas and the reintroduction of manufactured gas, these problems will eventually recur. Gas leakage from distribution systems has been estimated to be about 10%.<sup>11</sup>

The major source of ethylene in the air is automobile exhaust, which consists of about 1000-500 ppm ethylene. In the U. S. in 1966, auto exhaust produced 12 million metric tons of ethylene.<sup>12</sup> Manufacturing, fires, and other sources contributed an additional 4 million tons. Plants also produce ethylene, but they were estimated to produce only 20,000 metric tons a year.

Most ethylene is released in urban areas and rates of production for Detroit, Washington, and San Francisco have been estimated at 32, 24, and 20 metric ton/mi<sup>2</sup>/yr, respectively.<sup>13</sup> Reports of crop damage from urban ethylene production are associated primarily with greenhouse operation.

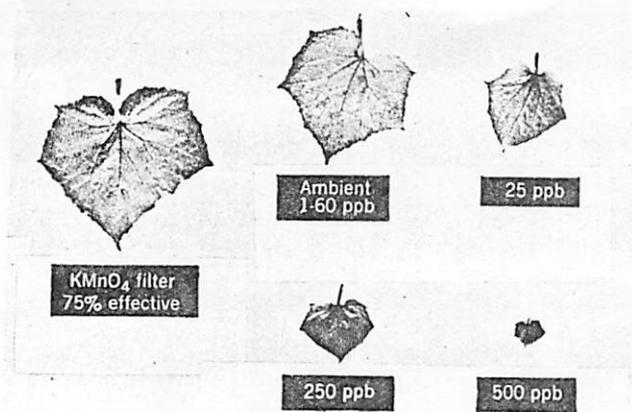


Figure 3. Effect of ethylene on the growth of A and C cucumber. Appearance of leaves from the 3rd node of 21-day-old plants.



Figure 4. Effect of ethylene on the growth of Nainari 60 spring wheat. Plants were grown for 90 days in the ethylene concentration indicated.

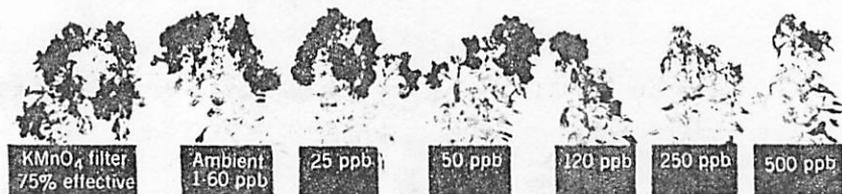


Figure 5. Effect of ethylene on flowering of Pink Cascade petunias. Plants were initially grown in ambient air for 60 days before exposure to ethylene concentrations indicated for an additional 6 days.

California orchid growers reported increasing losses of flowers from 1952 to 1962,<sup>14</sup> and a number of growers have ceased commercial production of blooms. Losses amounting to hundred of thousands of dollars have been reported in a number of cases: Clayton and Platt<sup>5</sup>; Barth<sup>13</sup>; Cottrell<sup>15</sup>; James<sup>14</sup>; Weidensaul and LaCasse.<sup>16</sup>

Ethylene is normally absent or present in only small amounts (<5 ppb) in rural air. In cities, maximum concentrations of 100 ppb or more have been reported frequently, Altshuller and Bellar<sup>17</sup>; Barth<sup>13</sup>; Clayton and Platt<sup>5</sup>; Gordon et al.<sup>18</sup>; Scott et al.<sup>7</sup> A number of investigators have observed high levels of ethylene (4 ppm) in the air downwind from forest and brush fires.<sup>19</sup> Darley et al.<sup>20</sup> estimated that burning of agricultural wastes in California gave rise to 136 metric tons of ethylene in 1966. Ethylene from such fires probably does not cause widespread damage, though plants in the immediate vicinity of the smoke can respond to the gas. Before the introduction of naphthalene-acetic acid, pineapple growers set fire to brush alongside pineapple fields to produce ethylene to accelerate floral initiation.<sup>21</sup>

Ethylene levels in air are controlled by the rate of production, dilution, and removal by sinks in the air and soil. Ethylene is removed from the air by a number of mechanisms, including reaction with ozone and photolysis with nitric oxides. In the latter case, ethylene, unlike other hydrocarbons, does not give rise to the production of peroxyacetyl nitrate, a secondary air pollutant. Ethylene, along with other hydrocarbons, can also be removed from the air by microbial decomposition in the soil.<sup>12</sup> Plants do not consume ethylene and do not contribute to air purification of this gas.

The relative efficiency of these sinks and their ultimate capacity for air purification are now known. However, their capacity obviously is not exceeded by present rates of production, because ethylene levels in rural air are still low.

Ethylene has no effect on humans or other animals until levels of 80% or more are present. These concentrations will induce sleep and, in fact, ethylene was used as an anaesthetic before less explosive anaesthetic gases were developed.

The data presented here confirm the observations of other workers as to the dose-response curve for ethylene. In general, threshold effects for ethylene on plants start at 10 ppb, half maximal effects occur at 100-500 ppb, and saturation occurs at 1000-10,000 ppb. These facts must be kept in mind when air quality standards are prepared. According to standards of the California State Board of Health, maximum levels of ethylene are 500 ppb for 1 hr

and 100 ppb for 8 hr.<sup>22</sup> Air quality standards proposed by the American Industrial Hygiene Association<sup>23</sup> are similar for residential areas and are lower by one-half for rural areas. If damage to vegetation is to be avoided, these standards should be decreased by a factor of 10. The available data have shown a significant amount of damage to plants exposed to 25 ppb ethylene and higher. Ethylene is only one part of the urban air mix, and, under conditions capable of generating 500 ppb ethylene, other aspects of air quality have also degraded to the point where ethylene values represent only a part of the total problem.

#### Acknowledgments

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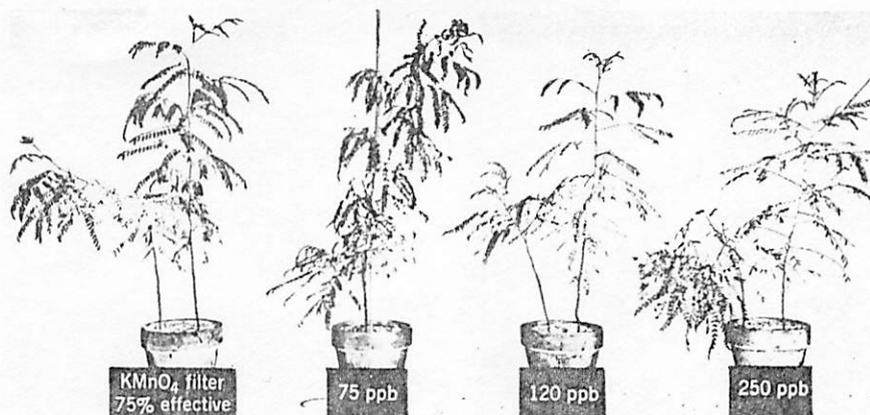


Figure 6. Effect of ethylene on honey locust seedlings. One-year-old seedlings were grown in ambient air for 30 days and then transferred to concentrations of ethylene shown for 30 days. Ethylene-treated plants show characteristic yellowing and abscission of leaflets.



Figure 7. Senescence and epinasty of ethylene-treated Bonny Best tomatoes. Plants were grown in ambient air for 30 days before a 7-day fumigation at ethylene levels indicated. The concentrations of ethylene used were (left to right): filtered air, ambient air, 50 ppb, 100 ppb, 200 ppb, and 450 ppb.

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