AIR POLLUTION ASPECTS

OF

ETHYLENE

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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

- Aeroallergens (pollens)
- Aldehydes (includes acrolein and formaldehyde)
- Ammonia
- Arsenic and Its Compounds
- Asbestos
- Barium and Its Compounds
- Beryllium and Its Compounds
- Biological Aerosols (microorganisms)
- Boron and Its Compounds
- Cadmium and Its Compounds
- Chlorine Gas
- Chromium and Its Compounds (includes chromic acid)
- Ethylene
- Hydrochloric Acid
- Hydrogen Sulfide
- Iron and Its Compounds
- Manganese and Its Compounds
- Mercury and Its Compounds
- Nickel and Its Compounds
- Odorous Compounds
- Organic Carcinogens
- Pesticides
- Phosphorus and Its Compounds
- Radioactive Substances
- Selenium and Its Compounds
- Vanadium and Its Compounds
- Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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ABSTRACT

Ethylene does not appear to present a health hazard to humans or animals. However, ethylene is a phytotoxicant which disrupts the normal function of plant hormones and growth regulators. The effects on plants include growth reduction, epinasty, abscission of flower and leaves, and dry sepal in orchids. Several incidents of plant damage from ethylene air pollution have been reported. Furthermore, ethylene undergoes photooxidation reactions with nitrogen oxides, resulting in the formation of formaldehyde, carbon monoxide, and ozone.

Ethylene air pollution has resulted primarily from automobile exhaust and other combustion sources. However, industrial emissions of ethylene can be a local source. Ethylene is also evolved from plant life.

Ambient air concentration data are limited. Air samples taken recently in California indicate that the average ethylene concentration in large metropolitan areas ranges from 40 to 120 $\mu g/m^3$, with maximums as high as 820 $\mu g/m^3$.

Industrial control methods applicable to other volatile hydrocarbons are suitable for use with ethylene. Ethylene emissions from automobile exhausts present a problem which, although it is under study, has not yet been solved.

Economic losses have been reported among orchid growers

in California and New York, and among cotton growers in Texas.

Methods of analysis for ethylene have been reported in the parts per billion range, using gas chromatographic techniques.

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1. INTRODUCTION

Ethylene (ethene), a colorless hydrocarbon gas of the olefin series, is one of the major growth petrochemicals of the United States and of the world. Ethylene is not toxic to humans or animals, yet despite this fact, it presents a considerable air pollution problem, for two reasons: (1) it is a significant phytotoxicant, and (2) it contributes to photochemically produced air pollution.

Ethylene in the atmosphere has caused substantial damage to several varieties of plants, the most notable of which are commercially grown orchids and other commercial flowers. Documented instances of commercial loss due to ethylene air pollution are known. Although it does not directly attack plant tissues like most other gaseous phytotoxicants, ethylene interferes with the normal function of the plant hormones or growth regulators. This fact is also applied beneficially for the ripening of fruit crops.

Ethylene is the most abundant (based on mole volume) of the photoreactive hydrocarbons in the lower atmosphere. Ethylene undergoes photochemical reactions with nitrogen oxides[6,10,19,47,70,86,95,103] and also reacts with ozone.[18,97] These reactions may contribute to eye irritation in polluted atmospheres. The major products in both reactions are formaldehyde

and carbon monoxide. In addition, the photochemical reaction of ethylene and nitrogen dioxide produces ozone; however, no PAN (peroxyacetyl nitrate) type compound is observed. When the reaction of ethylene-nitrogen dioxide is carried out in the presence of sulfur dioxide, only a small amount of aerosol is found and there is only a slight increase, if any, in the amount of eye irritation.[41,42,47,95] The photooxidation reactivity of ethylene is less than other olefinic hydrocarbons but greater than paraffins, acetylenes, and some aromatic hydrocarbons.[5,106]

The major sources of ethylene production are the chemical industry and the exhaust from automobile engines. As the total production from these two sources is predicted to increase at a steady rate in the foreseeable future, air pollution by ethylene is likely to increase, unless control procedures are implemented.

The physical and chemical properties of ethylene are tabulated in Table 11 in the Appendix.

2. EFFECTS

2.1 Effects on Humans

At concentrations which occur in the ambient atmosphere, ethylene is not toxicologically significant, as it produces no physiological effects on humans or animals. There are no known local or systemic chronic or acute effects. However, ethylene will undergo photooxidation reactions with nitrogen oxides and other substances present in the atmosphere, resulting in products which can have deleterious effects on humans.

At high concentrations, ethylene acts as a simple asphyxiant, and can cause narcosis and unconsciousness. In the presence of sufficient oxygen, ethylene acts as an anesthetic; concentrations of 75 to 90 percent ethylene in oxygen have been used as anesthetics in hospital surgery.[27,72,88]

The only significant hazards in the industrial use of ethylene are its flammability and the possibility of causing asphyxia, due to lack of sufficient oxygen in the work atmosphere.[27,88]

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No information was found in the literature reviewed concerning injury or death of domestic or commercial animals from environmental exposures to ethylene.

2.2.2 Experimental Animals

Luckhardt and Carter[73] exposed several different species of animals--including a mouse, rat, rabbit, guinea pig, and kitten--to concentrations of 75 to 95 percent ethylene in oxygen for periods ranging from 30 to 100 minutes. These doses acted as an anesthetic and produced no notable side effects except nausea, which disappeared after a short time.

Hirschfelder and Ceder[57] studied the effect of ethylene inhalation on the growth rate of rats. The rats were exposed to ethylene at approximately 11,500,000 $\mu g/m^3$ (10,000 ppm)* for 17 days (11 rats, 10 controls); 1,150,000 $\mu g/m^3$ (1,000 ppm) for 63 days (11 rats, 11 controls); and 115,000 $\mu g/m^3$ (100 ppm) for 45 days (5 rats, 5 controls) and 72 days (11 rats, 11 controls). Hirschfelder and Ceder concluded, on the basis of these experiments, that these concentrations of ethylene do not appreciably affect the growth rate of rats. In addition, ethylene added to the drinking water of rats had basically no effect on the rats' growth rate.

According to Clayton and Platt,[27] Harvey[54] reported similar results with inhalation experiments using guinea pigs.

The Merck Index[81] gives 950,000 ppm (1,092,500,000 $\mu g/m^3$) ethylene in air as the lethal concentration for mice.

2.3 Effects on Plants

Ethylene ranks as one of the most important phytotoxicants.[32,33,82,83,85] Middleton[82] listed the phytotoxicants in

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*1 ppm ethylene = 1,150 $\mu g/m^3$.

descending order of importance as fluoride, ozone, sulfur dioxide, oxidant, and ethylene. In California, however, ethylene is considered the second[32,64] or third[82] most important phytotoxicant.

2.3.1 Phytotoxicity

The effect of ethylene on plants is unique.[22,27,29,32,56,83] Most gaseous phytotoxicants cause direct, irreversible tissue damage through a caustic action. Ethylene, on the other hand, does not directly attack plant tissue, but rather, interferes with the normal action of the plant hormones and growth regulators. This interference results in morphogenetic and physiological changes in the tissue.

Ethylene produces a wide variety of effects in plants. Some of the important effects of ethylene on plants are: (1) growth retardation; (2) epinasty (downward curvature in the growth of leaves and shoots); (3) the abscission of leaves, buds, and flowers; (4) irregular opening of flowers; (5) senescence of leaves and flowers; (6) inhibition of elongation, and preferential swelling of stems; (7) fading of flowers; (8) blanching of chlorophyll; and (9) hastening of fruit-ripening and coloration. Ethylene can cause plants to lose their ability to orient normally with respect to gravity--the stem assumes a horizontal position (horizontal nutation), as do the secondary roots (plagiogeotropism), and normal growth

movement (circumnutation) ceases. Ethylene may affect the roots by inhibiting growth or may cause formation of lateral roots.

Since orchids are a very sensitive crop, they are readily affected by ethylene, and instances of economic losses from ethylene pollution have often been reported.[25,27,82,83,84] Ethylene generally causes the sepals of orchids to wither and dry without detectable injury to the petals or leaves. The collapse of sepals, which has been termed "dry sepal," is most commonly found with the white-flowered orchids, cattleya, and phalaenopsis. This damage is rarely found with cymbidium, cypripedium, or vanda orchids.

Ethylene also produces beneficial effects which are of commercial importance. Probably the most important of these are the ripening and coloring of fruit.[27,52,115] The fruit is generally exposed to ethylene concentrations of 2,300 to 23,000 $\mu g/m^3$ of air (2 to 20 ppm) with continuous air circulation. Ethylene has also been used in the blanching of celery[55,74] and to accelerate the after-ripening of grain.[11,12]

2.3.2 Sensitivity of Plants

In general, flower crops are more sensitive to ethylene than agricultural crops.[84] The most sensitive is the orchid, particularly the white cattleya, which shows dry sepal injury from as little as 24 hours of exposure to ethylene at 2.3 $\mu g/m^3$

(0.002 ppm).[25,36] Other sensitive plants (showing symptoms of injury at an ethylene concentration of 115 $\mu g/m^3$ or 0.1 ppm) include[25,27,29,69] carnation, African marigold, sunflower, tomato, Chenopodium album, potato, pepper, buckwheat, castor bean, pea, and lemon. Plants that are resistant to ethylene include grasses and lettuce.[104] The phytotoxicity of ethylene may be dependent upon temperature. Thus, roses were found to be sensitive to low concentrations of ethylene only at certain temperatures.[118] At 70°F, petal fall occurs with ethylene concentrations of 11,500 $\mu g/m^3$ (10.0 ppm) after 24 hours; but at 50°F, no abscission occurs with the same concentration and exposure time, nor at 41°F with 46,000 $\mu g/m^3$ (40 ppm) of ethylene after 168 hours.

Some other unsaturated carbon compounds will produce responses similar to those caused by ethylene.[29] Ethylene, however, is a much stronger phytotoxicant than the others, as shown in Table 1.

The reported effects and sensitivities of plants to ethylene have been summarized in Table 12 in the Appendix.

2.3.3 Incidents of Plant Damage

The first recorded case of ethylene plant damage was reported in 1908 by Crocker and Knight.[30] Plants in greenhouses, particularly carnations and tomatoes, were damaged as a result of the ethylene (3 to 4 percent) contained in the illuminating gas used to heat the greenhouses.[29,30] The use of

TABLE 1

COMPARATIVE PHYTOTOXICITY OF UNSATURATED CARBON GASES[29]

Gas	Minimum Concentration of Gas Producing Response (ppm)	
	Sweet Pea[a]	Tomato[b]
Ethylene	0.2	0.1
Acetylene	250	50
Propylene	1,000	50
Carbon monoxide	5,000	500
Butylene		50,000

[a]Effect noted: declination in sweet pea seedlings (3-day exposures).
[b]Effect noted: epinasty in tomato petiole (2-day exposures).

other heating methods eliminated this cause of ethylene plant damage.

In 1957, Hall *et al.*[53] reported damage to cotton and other crops growing near a polyethylene factory in Texas. Air samples taken at this location indicated that the ethylene atmospheric concentration ranged from 560 to 3,450 $\mu g/m^3$ (0.04 to 3 ppm). Symptoms of injury were found on plants as far as 4 miles downwind from the factory, although no ethylene was detected in the atmosphere. On the basis of the plant symptoms, however, it was believed that the concentration of ethylene in the air must have exceeded 3,450 $\mu g/m^3$. The most pronounced damage occurred near the factory and downwind from the factory, the damage decreasing in extent with distance from the source. The symptoms observed included epinasty, growth retardation, early bud development, and abscission of the buds and fruits that resulted in almost total loss in yield in heavily damaged areas.

Ethylene air pollution in the San Francisco and Los Angeles areas has caused much damage to greenhouse plants, particularly orchids, carnations, snapdragons, and roses.[25,27,34,82] The damage usually occurred in winter during periods of stable air conditions and light winds. Similar injury to orchids has been observed in the New York City area and is believed to be at least partly due to ethylene pollution.[36]

Economic losses resulting from these situations are discussed in Section 5.

2.4 Effects on Materials

Ethylene is not known to corrode or stain material surfaces.

2.5 Environmental Air Standards

According to Patty,[88] "the maximum permissible limit of ethylene in workroom air should not exceed 6,300 mg ethylene/m^3 of air (6,300,000 $\mu g/m^3$) (5,500 ppm), which is 20 percent of the lower flammable limit. The threshold limit for ethylene has been established at 1,150 mg/m^3 (1,150,000 μg) (1,000 ppm)."

The American Industrial Hygiene Association has established ambient air quality standards for ethylene.[45] However, these standards serve only as a guide, since sufficient knowledge is not available at this time to adopt unequivocal standards. The recommended standards are given in Table 2.

The State of California has adopted ambient air quality standards for ethylene of 575 $\mu g/m^3$ (0.5 ppm) for 1 hour or 115 $\mu g/m^3$ (0.1 ppm) for 8 hours.[25,62,106] These are considered "adverse" levels, based on the damage to vegetation. No "serious" or "emergency" levels based on the effects on humans have been set.

Russia has established the ambient air quality standard for ethylene of 3,000 $\mu g/m^3$ (2.3 ppm) for a 24-hour average.[63,106] The permissible standard for a 20-minute average is set at the same value (3,000 $\mu g/m^3$).

TABLE 2

AMERICAN INDUSTRIAL HYGIENE ASSOCIATION RECOMMENDED STANDARDS FOR ETHYLENE[45]

	1-hr Max*		8-hr Max*	
	$\mu g/m^3$	ppm	$\mu g/m^3$	ppm
Rural	287.5	0.25	57.5	0.05
Residential	575	0.50	115	0.10
Commercial	862.5	0.75	172.5	0.15
Industrial	1,150	1.00	230	0.20

*The rural concentrations should not produce adverse effects in the most sensitive plants. The residential concentrations should produce only slight injury to the most sensitive plants.

3. SOURCES

3.1 Natural Occurrence

Ethylene is not normally found in deposits of petroleum or natural gas.

However, ethylene is produced naturally from many, if not all, types of plants. The ethylene can emanate from flowers, fruits, leaves, and stems of a number of plant species.[37,38] Burg[20] recently compiled an extensive list of plants known to produce ethylene; these plants are listed in Table 5 in the Appendix. Biale *et al.*[16] obtained quantitative data on the rates of ethylene production in various fruits (see Table 6 in the Appendix). According to these authors, fruits which did not appear to evolve ethylene have subsequently been shown, by a more sensitive gas chromatography analysis method,[16,21] to produce very small amounts. Akamine[2] found that the vanda orchid produces as much as 3,400 μl/kg-hr of ethylene.

The importance of this biologically derived ethylene in relation to the overall air pollution problem is not known at this time. However, numerous examples are given in the literature in which these emissions caused damage to plants in greenhouses and during storage and shipment.[25,27,29]

3.2 Production Sources

Ethylene is one of the major growth chemicals in the United States and the world.[23] The production in the United States for 1967 was almost 12 billion pounds (see Table 7

in the Appendix). The production has approximately doubled in the last 6 years. This rapid growth rate is expected to continue over the next decade at approximately 10 percent per year.[90] The demand for 1969 and 1971 is projected to be 14.1 and 17.3 billion pounds, respectively.[1,46]

Most of the ethylene produced today is consumed by the producer; only about 25 to 33 percent of the total production is sold to other users.

Presently there are 38 producers of ethylene in the United States (see Table 13 in the Appendix). Over 55 percent of the ethylene production is located in Texas (with 17 plants), while Louisiana is responsible for 28 percent, with eight plants (see Table 14 in the Appendix). The remaining plants are distributed over nine States (including Puerto Rico).

Practically all commercial ethylene is manufactured by the cracking of petroleum fractions or natural gas, usually by means of a pyrolytic process.[23] Small amounts are thus recovered as a by-product of refinery catalytic cracking operations. Some pure ethylene is manufactured from the catalytic dehydrogenation of ethyl alcohol or ethyl ether.

3.2.1 Pyrolytic Processes

Any petroleum fraction, from ethane to heavy gas oil--even to whole crude oil--can be used as the feedstock to produce ethylene. Almost all of the available ethane obtained

from natural gas liquids or from refinery gases is consumed in ethylene production. Other feedstocks commonly used in the United States are liquified petroleum gases (e.g., 95 percent propane and 5 percent butane) and, to a lesser extent, naphtha (crude oil fractions having the boiling range of 90° to 400°F).

The composition of the feedstock and the operating conditions of the pyrolysis reactor determine the amount of ethylene in the final product mixture. Generally, the pyrolysis is conducted at nearly atmospheric pressures and at 1,300 to 1,600°F. Several types of reactor systems are used, including the following:[23] fired tubular heaters, pebble-bed heaters, fluidized-bed cracking regenerative furnaces, the autothermic cracking method, and the catarole catalytic process. The most commonly used method has been the fired tubular heater, which gives ethylene yields of from 24 to 48 percent conversion, depending on the feedstock and conditions. There are many by-products, including hydrogen, paraffins, olefins, diolefins, and aromatic compounds, as well as minor contaminants such as acetylene, propadiene, hydrocarbons, polymers, and acid gases. Thus, recovery, separation, and purification are dependent upon the type and quantity of the different products obtained. Ethylene is recovered by fractional distillation at low temperatures and high pressures, and less commonly, by solvent extraction or absorption.[44,73,92] Sometimes the ethylene is used directly without purification.

3.3 Product Sources

Ethylene is one of the most important petrochemicals in the world.[23] It is used extensively as a raw material in the manufacture of organic chemicals and plastics. One of the most important products is polyethylene, a polymer of ethylene used for packing films as well as for wire insulation, and "squeeze" bottles. Other important chemicals produced from ethylene include ethyl alcohol or ethanol, ethylene oxide, ethylene glycol, ethyl chloride, ethylene dichloride, styrene (via ethylbenzene), and linear alcohols. Table 8 in the Appendix shows the consumption of ethylene in the United States by products. Table 9 in the Appendix shows the major end uses of these chemicals. Plastics have so far been the major product of ethylene, and this use will probably continue to increase in the future.

The proportion of ethylene in the atmosphere which results from these particular sources in not known, except in one isolated case. Hall *et al.*[53] reported damage to cotton from ethylene emissions from a polyethylene plant (see Section 2.3.3).

3.4 Other Sources

Ethylene may form as a by-product from incomplete combustion of hydrocarbons and other organic substances. Thus, ethylene has been found to be one of the components of automobile and diesel combustion emissions (exhaust and blow-by

emissions), incinerator effluents, and agricultural waste combustion gases.

3.4.1 Automobile and Diesel Emissions

Motor vehicle emissions are believed to be the major source of ethylene pollution in California metropolitan areas.[24,25] In Los Angeles, the ethylene emission from automobile exhaust has been estimated at 60 tons per day.

Several studies have been conducted to determine the ethylene concentration in automobile exhaust in relation to the engine operating mode.[28,59,79,110] The data summarized in Table 3 indicate that the ethylene concentration varies considerably with the operating mode--with the deceleration mode producing the most ethylene. In general, automobile exhaust produces approximately 7.8 pounds of ethylene per ton of gasoline consumed.[35]

Hurn *et al.*[59] studied the effect of different fuels on the concentration of ethylene in the automobile exhaust. The composition of the fuel was found to be an important variable in the amount of ethylene produced. The data indicated that the paraffin content--and to a lesser extent, the olefin content--were the main contributors to ethylene formation in the exhaust.

McMichael and Sigsby[80] studied the effect of hot and cold starts in winter and summer using regular and premium fuels. The results indicated that all these variables had only a slight effect on ethylene in the exhaust. The data

TABLE 3

ETHYLENE CONCENTRATION IN AUTOMOBILE EXHAUST

Vehicle	Concentration of Ethylene (ppm)					Reference
	Idle	Acceleration	Cruise	Deceleration	Simulated Traffic Cycle	
1957 Dodge	101	55	230			110
1958 Chevrolet	400	105	190			
1949 Oldsmobile	121	208	310			
1949 Chevrolet	31[a]	166[a]	298[a]	395[a]		
Forklift	66, 80, 194					
Automobile engine	200	270	170	870		28
Automobile engine	188	118 (15-30 mph)	133 (30 mph)	1,030 (50-20 mph)		79
Automobile engine[b]	81	103 (15-30 mph)	93 (30 mph)	39 (50-20 mph)		
1962 V-8	390	168-233 (15-60 mph, 25 sec)	304 (50 mph) 555 (40 mph, 2/3 max torque)	989-2,050 (50-15 mph, 25 sec)	648	59

[a]Total two carbon compounds.

[b]Same engine as above but engine modified by adding air injection, leaner carburetor, and 10° spark retard.

showed that generally ethylene was produced in somewhat greater amounts (a) from cold starts rather than from hot starts, (b) in winter rather than in summer, and (c) from premium fuel rather than from regular fuel.

Although ethylene concentration in the blow-by emissions of automobiles was found to be generally above 155,000 μg/m^3 (100 ppm),[87,100] it was over 310,000 μg/m^3 (200 ppm) in many cases. The concentration of ethylene was less from the blow-by emissions than from the exhaust. Furthermore, the ethylene concentrations varied less with different engine modes in the blow-by emissions than in exhaust analyses.[100]

Two studies reported the concentration of ethylene in diesel exhaust.[71,91] The results (see Table 10 in the Appendix) indicate that the ethylene concentration is usually below 60,000 μg/m^3 (50 ppm) even under heavy loads.

3.4.2 Incinerator Effluents

Effluents of multiple-chamber incinerators usually contain ethylene in concentrations of less than 11,500 μg/m^3 (10 ppm).[49,97,113] When an afterburner is used, the ethylene concentration becomes nearly zero.[49] Single-chamber incinerators were found to have ethylene concentrations of 23,000 to 31,000 μg/m^3.[49] However, inadequately designed incinerators may be a major source of pollution, producing concentrations of ethylene as high as 3,565,000 μg/m^3.[113]

Jerman and Carpenter[61] analyzed gas samples from the

pyrolysis of solid municipal waste. The range of values for the 24 samples was 460,000 to 39,330,000 $\mu g/m^3$ (400 to 34,200 ppm) with an average of 17,855,000 $\mu g/m^3$ (15,700 ppm). Thus, poor or incomplete combustion of solid wastes may be an important source of ethylene pollution.

3.4.3 Burning of Agricultural Wastes

Laboratory studies have been conducted to determine the amount of ethylene emissions produced from burning of agricultural wastes.[17,35] These results are summarized in Table 15 in the Appendix. Field studies confirm that the laboratory data are probably representative of normal field conditions. The results show that moisture content, type of waste, and location, can be variables that determine the amount of ethylene that is produced. For comparison, automobile exhaust produces approximately 7.8 pounds of ethylene per ton of gasoline, or about 2 to 10 times more ethylene per ton than agricultural wastes.[35]

The wastes burned per year in the San Francisco Bay area are as follows: 121,111 tons of fruit prunings, 1,632 tons of barley straw, and 28,140 tons of native brush.[35]

3.5 Environmental Air Concentrations

Only limited data are available on the concentration of ethylene in ambient air.

Several studies have been made in California.[4,27,97]

The data are summarized in Table 4. Scott *et al.*[97] found that the ethylene air concentration in South Pasadena, Calif., appears to correlate with the amount of automobile traffic and with temperature inversions. Altshuller and Bellar[4] collected extensive data on ethylene concentration in Los Angeles for a total of 10 days in September and October 1961. They also noted a peaking in ethylene concentration during the heavy traffic hours, with these high values usually persisting for at least one hour. The maximum for the day generally ranged between 80 and 130 $\mu g/m^3$. It is believed that an unusually high value of 300 $\mu g/m^3$ found late one afternoon was partly due to large forest fires north of Los Angeles. In a 1967 article, Clayton and Platt[27] reported ethylene concentration for three metropolitan areas in California (see Table 4). Although all pertinent information was not given (no data on time, exact location of sampling, or method of analysis), the data indicated a maximum concentration for ethylene of 820 $\mu g/m^3$ in Los Angeles.

TABLE 4

CONCENTRATION OF ETHYLENE IN AMBIENT AIR

Location (California)	No. of Samples	Date	Concentration, $\mu g/m^3$			Reference
			Range	Avg	Max	
South Pasadena	4	12/56	290-580	410	580	97
South Pasadena (at Pasadena Freeway)	1	12/31/56	820			
Los Angeles	125	9/12/61 to 11/14/61	110-150	50	150	4
Los Angeles*	39	(4-month period, 1967?)		120	820	27
Oakland*	73	(10-month period, 1967?)		40		
Ventura*	52	(4-month period, 1967?)		63		

*Data given in ppm and converted to μg by dividing by 2 and multiplying by 1.15.

4. ABATEMENT

Ethylene is one of the many volatile hydrocarbons present in the emissions from combustion engines, petroleum refineries, organic chemical plants, and incinerators. Ethylene poses no peculiar control problem in these emissions and, thus can be controlled by the methods generally used for hydrocarbons. These methods include combustion techniques, adsorption methods, and vapor recovery systems.

Stern[106] discusses the techniques, cost, and efficiency of the control methods for hydrocarbons employed by the petroleum industry. No quantitative data directly pertaining to ethylene emissions from industrial sources were found.

One of the major sources of ethylene air pollution--automobile exhaust--has not yet been effectively controlled. However, programs are in operation for studying the problem of hydrocarbon emissions from automobiles as well as methods for controlling those emissions.

Special control problems may be presented if ethylene evolved from vegetation is an important source--particularly in open fields. Ethylene given off by plant life in confined areas--such as greenhouses, storage areas, and shipping containers--has been controlled by the use of brominated charcoal.[3,50,51]

5. ECONOMICS

No information was found in the literature giving the damage to humans, animals, or materials or the economic losses resulting from ethylene air pollution. However, economic losses due to plant damage from ethylene pollution have been reported. The most significant economic damage is to commercial flower crops, particularly orchids, carnations, roses, and snapdragons.

The flower crop loss from ethylene air pollution in the San Francisco and Los Angeles areas has been reported to run into the hundreds of thousands of dollars annually.[25] In the San Francisco area, the combined loss of three orchid growers amounted to about $70,000 in 1959.[34] In the Los Angeles area, extensive and recurring injury to orchids since the early 1950's has caused orchid production to be moved to the rural areas, away from the ethylene pollution.[82] Heck *et al.*[56] reported extensive damage to a cotton crop near a polyethylene factory in Texas. Cotton downwind and within one mile of the factory was almost totally lost. Ethylene, which appears to be one of the components in New York air pollution, causes damage to orchids in the vicinity of New York.[36]

No information was found on the economic costs of the abatement of ethylene air pollution.

The production and consumption data for ethylene have been discussed in Section 3.

6. METHODS OF ANALYSIS

6.1 Sampling Methods

Ethylene samples can be collected by the grab sampling method, i.e., collection into an evacuated container.[13,35,71,113] Gas chromatography or infrared spectroscopy methods of analysis lend themselves to direct passing of the sample into the instrument without use of collection containers.[4,60,61] Some authors report collecting ethylene in freeze traps,[99] in mercuric solution,[117] and on silica gel.[107]

There are no problems in the collection of ethylene samples other than the normal difficulties in taking and transferring samples. However, in cases in which both ethylene and nitrogen oxides are present in large amounts (e.g., automobile exhaust), a reaction between the two substances may occur in the sampling vessel. This very slow reaction can be reduced to a negligible rate by diluting the sample with dry nitrogen.

6.2 Qualitative and Semi-quantitative Determination Methods

A detector tube method has been described by Kitagawa and Kobayashi[66] which has a sensitivity of about 23,000 $\mu g/m^3$ (20 ppm) with $\pm$ 5 percent error when a 10 cm^3 sample is used. Another adsorbent was reported[68,108] to detect approximately 10 $\mu g/m^3$ (0.01 ppm) ethylene by using a 3,000 cm^3 sample size, which is drawn through the tube at 100 cm^3 per minute.

A portable instrument has been reported to provide a simple and reliable field method for estimating ethylene concentration in the range of 5,700 to 230,000 $\mu g/m^3$ (5 to 200 ppm).[108,109] The air sample is drawn over mercuric oxide at 285°C. The mercury vapor released by the ethylene is passed over a strip of sensitized seleno-cyanate paper at 125°C. The length of the black coloration is used to estimate the amount of ethylene present.

6.3 Quantitative Determination Methods

Gas chromatography methods have found widespread use for determining the presence of ethylene as well as numerous other hydrocarbons.[105] Gas chromatography has gained wide acceptance because it is a simple and rapid technique. With the development of the new packed and open tubular columns, automatic temperature programming, and new types of detectors--particularly the flame ionization detector--one can obtain rapid, efficient separation of many components with a sensitivity in the ppb range and even lower. The commonly used gas chromatographic methods for detecting ethylene employ a silica gel packed column at or near room temperature, with a flame ionization detector.[4,13,14,15,80,110] Other columns that are used include alumina,[35] dimethyl sulfolane,[71] hexadecane,[113] polypak-2,[61] multicolumn techniques,[67,79] and open tubular columns.[60,78] Gas chromatography has been used to determine

ethylene in air samples,[4,15,101] automobile exhaust,[15,60,79,110] blow-by,[100] municipal wastes,[61] agricultural wastes,[35] and incinerator effluents.[113] To increase the sensitivity of this method, some authors also used trapping techniques.[13,43,48,113]

Infrared spectroscopy has been used to determine ethylene in air samples,[97] automobile and diesel exhaust,[71,77,96,102] and incinerators.[116] To obtain a greater sensitivity, very long optical path lengths are needed (e.g., 300 meters),[97] generally making large samples necessary. The absorption peak at 10.5 μ (952cm^{-1}) is normally used, having a sensitivity of greater than 0.1 ppm.

Ethylene concentration has been determined by mass spectrometry in air samples[99] and automobile exhaust.[28,93,114]

A manometric technique has been used for determining small amounts of ethylene.[117] A mercuric perchlorate solution containing the collected ethylene is acidified in a closed system, and the released ethylene is determined by the change in pressure. The sensitivity is approximately 0.2 ml of ethylene per 2 ml of solution.

The chemical methods developed for quantitative determination of olefins[7,8,9,76,85] are not generally applicable to ethylene because of the lack of reactivity of the ethylene and the low sensitivity of the product formed with ethylene.

7. SUMMARY AND CONCLUSIONS

Ethylene does not appear to be toxic to humans or animals or cause damage to materials in the concentrations that have been found in air. In fact, 75 to 90 percent ethylene in oxygen has been used as an anesthetic in hospital surgery with no adverse side effects.

However, low concentrations of ethylene do have a pronounced effect on plant life. Unlike most gaseous phytotoxicants, which attack the plant tissue, ethylene disrupts the normal processes of the plant hormones or growth regulators. This disruption results in morphogenetic and physiological changes in the plant. The response to ethylene varies widely with different species of plants. Some of the commonly observed effects are growth reduction; epinasty; abscission of flowers, buds, and leaves; discoloration; and abnormal growth patterns.

Another important aspect of ethylene air pollution is the photooxidation products created by reaction of ethylene with nitrogen oxides in the atmosphere. Although ethylene is not as reactive as many other hydrocarbons, it is the most abundant (on a mole basis) of the "reactive" hydrocarbons present in the atmosphere. The major products formed from the photooxidation of ethylene are formaldehyde and carbon monoxide.

The major source of ethylene air pollution in large metropolitan areas appears to be emissions from combustion,

particularly automobile exhaust. It has been estimated that in Los Angeles, ethylene emissions from automobile exhaust amount to 60 tons per day. No information was found on the contribution of industrial sources to ethylene pollution. Approximately 55 percent of the commercial ethylene is produced in Texas. Moreover, in one case, a polyethylene factory was shown to be a local source of ethylene pollution.

Ethylene is also produced by plant life. The importance of this source is not known in the case of open fields, but in confined areas such as greenhouses or plant storage containers, damage has been reported to certain species of plants, particularly orchids.

Only limited information is available concerning the amount of ethylene in the atmosphere. Air samples recently taken in California indicate that the average ethylene concentration for metropolitan areas ranges from 40 to 120 $\mu g/m^3$ (0.04 to 0.1 ppm). The maximum value observed has been as high as 800 $\mu g/m^3$ (0.7 ppm).

The methods used for control of volatile hydrocarbons are applicable to ethylene. These include combustion, adsorption, and vapor recovery systems. No information was found on the cost of abatement.

Economic losses from plant damage due to ethylene have been reported in the literature. Greenhouse plants, particularly orchids, appear to be most affected.

Ethylene can be determined in the ppb range by the available gas chromatographic techniques.

Based on the material presented in this report, further studies in the following areas are suggested:

(1) Determination of the concentration of ethylene in the ambient air of more cities than have been studied so far, particularly in areas of high population density.

(2) Evaluation of the importance of commercial sources, combustion sources (e.g.,automobiles, incinerators), and biological sources to ethylene air pollution.

(3) Determination of the effects of ethylene on different plant species under closely simulated ethylene atmospheric conditions (i.e., dynamic conditions, concentrations of ethylene varying with time, presence of other atmospheric contaminants).

(4) Determination of the importance of photooxidation reactions of ethylene in air pollution.

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APPENDIX

APPENDIX

TABLE 5

MAJOR ORGANS OF VARIOUS PLANT SPECIES PRODUCING ETHYLENE[20]

I. Flowers		
broccoli	gardenia	orchid
calceolaria	gladiolus	pelargonium
carnation	hollyhock	petunia
chrysanthemum	iris	rose
cotton	larkspur	snapdragon
dahlia	lilac	tulip
dandelion	lily	verbena
diplotaxis	lily of the valley	violet
	marigold	

II. Fruits		
apple	hawthorn	pear
avocado	lemon	pecan
banana	lime	persimmon
cantaloupe	loquat	pineapple
cherimoya	mango	plum
cotton	nectarine	sapodilla
eggplant	orange	squash
feijoa	passion fruit	tangerine
grapefruit	pea	tomato
green pepper	peach	

III. Leaves and Leafy Stems		
asparagus	milk thistle	rose
celery	onion	spinach
dandelion	peony	tomato
hollyhock	potato	virginia creeper
lettuce	rhubarb	yellow calla

IV. Seeds	
lima bean	pea

TABLE 5

MAJOR ORGANS OF VARIOUS PLANT SPECIES PRODUCING ETHYLENE
(Continued)

V. Roots and Tubers		
beet	potato	rutabaga
kohlrabi	radish	turnip
VI. Fungi		
Blastomyces dermatididis	*Penicillium digitatum*	*Saccharomyces cerevisiae*
Fulsarium osysporum f. lycopersicum		

TABLE 6

MAXIMUM RATES OF ETHYLENE PRODUCTION BY VARIOUS FRUITS[16]

Fruit	Variety	Temp (°C)	C_2H_4 µl/Kg hr
Tropical			
Banana	Gros Michel	20	4
Mango	Haden	20	Trace*
Papaya		25	37
Pineapple		25	Trace*
Subtropical			
Avocado	Fuerte	20	88
Cherimoya	Booth	20	186
Feijoa	Coolidge	20	50
Lemon	Eureka	25	Trace*
Orange	Valencia	25	Trace*
Orange	W. Navel	20	Trace*
Persimmon	Hachiya	20	2
Sapote	Pike	20	129
Temperate			
Apple	McIntosh	20	112
Pear	Bartlett	20	122
Pear	Bosc	20	29
Peach	Hale	20	36

*Determined by more recent techniques.

TABLE 7

PRODUCTION OF ETHYLENE IN UNITED STATES, 1958-1967[111]

Year	Production (1,000 lbs)	Amount Sold (1,000 lb)
1958	4,149,233	737,346
1959	5,099,056	2,941,228
1960	5,448,094	3,251,813
1961	5,655,785	3,360,619
1962	6,282,908	3,978,634
1963	7,517,552	2,208,259
1964	8,641,202	2,377,368
1965	9,569,885	2,714,873
1966	11,241,085	3,276,767
1967	11,854,515	3,353,371

TABLE 8

ETHYLENE CONSUMPTION IN UNITED STATES, 1950, 1960, 1970[23]

Derivative	Percent of Ethylene Consumption		
	1950	1960	1970*
Ethanol, synthetic	34	19	11
Ethyl chloride and Ethylene dichloride	15	13	8
Ethylene oxide and Glycol	30	27	22
Polyethylene	5	29	43
Styrene	12	10	9
Others	4	2	7
Total	100	100	100

*Projected.

TABLE 9

TRENDS IN ETHYLENE CONSUMPTION BY END USE IN UNITED STATES[23]

End Use	Percent of Total Ethylene Growth 1950-1960	1960-1970*
Plastics and resins (e.g., polyethylene and polyester)	43.2	63.4
Detergents (straight chain alcohols)	4.8	4.2
Antifreeze (ethylene glycol)	13.8	2.9
Elastomers (ethylene-propylene rubber, styrene-butadiene rubber)	2.7	5.8
Solvents (chlorinated ethylene)	8.8	6.9
Additives (tetraethyl lead, ethylene dibromide)	3.5	0
Synthetic fibers (polyesters)	1.2	1.5
Miscellaneous	22.0	15.3
	100	100

*Projected.

TABLE 10

ETHYLENE IN DIESEL EXHAUST[71,91]

RPM	Load	Ethylene (ppm, dry basis) 4-cycle engine[a]	2-cycle engine[b]
500	0		15
600	0		6.85, 10.1
740	0	16	
800	[c]	12.2, 14.2	
1,000	1/4		4.20, 7.2
	Full	40	
1,050		8.93, 9.52	
1,200	0	14	
	1/4	10	10
	1/2	11	10.7, 21.0
	3/4	14	
	Full	30	
1,300	[c]	13.7, 19.4	
1,500	0	12	
	1/4	8	
	1/2	13	
	3/4	13	
	Full	38	
1,520	[c]	18.5, 14.2	
1,600	3/4		23.9, 31.9
	Full		56
1,780	[c]	27.3, 29.6	
1,800	0	13	
	1/4	12	
	1/2	12	
	3/4	21	
	Full	44	
2,200	Full		30.2, 35.1
600 to 2,200	0		82.8

[a]6-cylinder, 300 Hp turbocharged.
[b]6-cylinder, 220 Hp.
[c]Load provided by a club propeller; load a function of rpm.

APPENDIX

TABLE 11

GENERAL INFORMATION AND PROPERTIES OF ETHYLENE[81]

Synonyms	Ethene, elayl, olefiant gas, etherin
Molecular formula	C_2H_4, CH_2CH_2, $H_2C{=}CH_2$
Molecular weight	28.05 (85.63% carbon, 14.37% hydrogen)
Normal state, color odor	Colorless gas with sweet odor
Boiling point (760 mm)	-103.9° C
Melting point	-169.4°C (solidifies at -181°C)
Specific gravity (liquid, 0°C)	0.610
Vapor density (air = 1)	0.98
Water solubility	0.25 v/v* H_2O (0°C) 0.11 v/v* H_2O (25°C)
Flammability	Burns with a luminous flame
Autoignition temperature	543°C
Explosive limits	Lower: 3% by vol in air Upper: 34% by vol in air

*v/v = volume per volume.

TABLE 12

SUMMARY OF REPORTED EFFECTS OF ETHYLENE ON PLANTS

Species	Concentration (ppm)	Exposure Time (hr)	Effects or Comments	Reference
Vanda orchids	1	24	Fading of flowers	3
Antirrhinum majus	0.5	1	Abscission of flowers	25
Cattleya sp. orchids, buds	0.01	24	Sepal tissue collapse	
	0.05	6		
	0.3	1		
Cattleya orchids	0.002	24	Sepal tissue collapse	36
	0.1	8		
Chenopodium album	0.05		Epinasty	31
Dianthus caryophyllus	0.10	6	Inhibited flower opening	25
Fagopyrum sagittatum (*F. esculentum*)	0.05		Epinasty	31
Gossypium hirsutum	0.6	720	Reduction in growth and yield	56
Itelianthus annuus	0.05		Epinasty	31
Lathyrus odoratus	0.2	72	Epinasty	
Lilium regale	4.0		Growth retardation and epinasty	58

TABLE 12

SUMMARY OF REPORTED EFFECTS OF ETHYLENE ON PLANTS (Continued)

Species	Concentration (ppm)	Exposure Time (hr)	Effects or Comments	Reference
Lycopersicon esculentum	0.1	48	Growth retardation	31
Narcissus sp.	2.0	72	Growth retardation	58
	4.0	72	Growth retardation and leaf curl	
Rosa sp.	0.33	120	Epinasty and leaf abscission at room temperature	118
	10.0	24	Petal fall at 70°F, none at 32°, 40°, and 50°	
	40.0	24	Epinasty at 70°F	
	40.0	48	Epinasty and leaf abscission at 70°F	
	40.0	168	No abscission at 41°F	
Solamon tuberosum	0.05	16	Epinasty	38
Tagetes patula	0.05		Epinasty	31
Tulipa gesneriana	4.0		Leaf roll	58
Tomato	0.1	48	Leaf epinasty	29
	0.04	3 to 4	Leaf epinasty of mature leaves	
African marigold	0.001		Leaf epinasty	
Lemons	0.025-0.05		Epinasty	89

(continued)

TABLE 12

SUMMARY OF REPORTED EFFECTS OF ETHYLENE ON PLANTS (Continued)

Species	Concentration (ppm)	Exposure Time (hr)	Effects or Comments	Reference
Datura stramonium	0.1		Close to limit for response	40
Lycopersicum esculentum	0.2		Epinasty of leaves	
Begonia luminosa	8		Slight epinasty	
Sweet peas	0.1		Inhibited elongation of the epicotyl	30
	0.4		Production of triple response; horizontal nutation and swelling	

TABLE 13

UNITED STATES PRODUCERS OF ETHYLENE[90]

Company	Location	Estimated Annual Capacity, 1968 (Million Pounds)	Onstream in 1969 and Considering for Early 1970's[a] (Million Pounds)
Allied Chem. Corp. and Wyandotte Chems. Corp.	Geismar, La.	600	
Amoco Oil Co.	Alvin, Tex.		750
Atlantic Richfield Co.	Wilmington, Calif.	100	
Celanese	Bayport, Tex.		(500)
Chemplex Co.	Clinton, La.	500	
Cities Service Co. and Columbian Carbon Co.	Lake Charles, La.	420	
Commonwealth Oil Refining Co., and PPG Industries, Inc.	Penuelas, P.R.		1,000
Continental Oil Co. Petrochemical Dept.	Lake Charles, La.	500	
Dow Chem. Co.	Bay City, Mich.	170	
	Freeport, Tex.	1,400	
	Plaquemine, La.	610	300
E.I. duPont de Nemours & Co., Plastics Dept.	Orange, Tex.	750	
Eastman Kodak Co. Texas Eastman Co., Div.	Longview, Tex.	450	
El Paso Natural Gas Co. and Rexall Drug & Chem. Co.	Odessa, Tex.	400	
Enjay Chem. Co.	Baton Rouge, La.	1,000	
	Baytown, Tex.	90	
	Bayway (Linden), N.J.	175	25
B. F. Goodrich Chem. Co.	Calvert City, Ky.	250	
Gulf Oil Corp.	Cedar Bayou, Tex.	400	
	Port Arthur, Tex.	425[b]	900
Jefferson Chem. Co.	Port Neches, Tex.	470	

(continued)

TABLE 13

UNITED STATES PRODUCERS OF ETHYLENE (Continued)

Company	Location	Estimated Annual Capacity, 1968 (Million Pounds)	Onstream in 1969 and Considering for Early 1970's[a] (Million Pounds)
Mobil Oil Corp. Petrochemicals Div.	Beaumont, Tex.	485	500
Monsanto Co., Hydrocarbons & Polymers Div.	Alvin, Tex.	600	
	Texas City, Tex.	100	
National Distillers and Chem. Corp., U.S. Industrial Chems. Co.	Tuscola, Ill.	350	
Northern Natural Gas	Joliet, Ill.		(500)
Olin Mathieson Chem. Corp. Chems. Div.	Brandenburg, Ky.	90	
Phillips Petroleum Co.	Sweeny, Tex.	600	
Phillips Petroleum Co. and Houston Natural Gas Products Co.	Sweeny, Tex.	500	
Shell Oil Co.	Deer Park, Tex.	275[b]	
	Norco, La.	500	
	Torrance, Calif.	75	1,000
Sinclair-Koppers Co.	Houston, Tex.	500	
Sun Oil Co.	Marcus Hook, Pa.		(500)
SunOlin Chem. Co.	Claymont, Del.	225	(50)
Union Carbide Corp. Chems. and Plastics Operations Div.	Institute, W. Va.	350	
	Ponce, P.R.	200[b]	1,200
	Seadrift, Tex.	900	
	South Charleston, W. Va.	400	

(continued)

TABLE 13

UNITED STATES PRODUCERS OF ETHYLENE (Continued)

Company	Location	Estimated Annual Capacity, 1968 (Million Pounds)	Onstream in 1969 and Considering for Early 1970's[a] (Million Pounds)
Union Carbide Corp. Chems. and Plastics Operations Div.	Taft, La.	500	
	Texas City, Tex.	750[b]	1,200
	Torrance, Calif.	150	
	Whiting, Ind.	275	

[a]Quantities in parenthesis are under consideration for early 1970's.
[b]May be shut down when new plant comes onstream.

TABLE 14

ETHYLENE CAPACITY BY STATES[90]

State	Capacity (Million Pounds)	Percent	Number of Plants
Texas	9,095	55	17
Louisiana	4,630	28	8
West Virginia	750	4.5	2
Illinois	350	2.1	1
Kentucky	340	2.1	2
California	325	2.0	3
Indiana	275	1.7	1
Delaware	225	1.4	1
Puerto Rico	200	1.2	1
New Jersey	175	1.0	1
Michigan	170	1.0	1
Total	16,535	100.0	38

TABLE 15

ETHYLENE EMISSIONS FROM BURNING OF AGRICULTURAL WASTES

Material	Ethylene (lb/ton of material)	Collection Location	Comments	Reference
Blue grass	2.4	Willamette Valley, Oregon	5% moisture, dry	17
Perennial Rye grass	1.4	" "	6% moisture, dry	
Bent grass	0.9	" "	2% moisture, dry	
Annual Rye grass	0.6	" "	9% moisture, dry	
Fescue grass	1.2	" "	9% moisture, dry	
Orchard grass	0.7	" "	15% moisture, dry	
Blue grass	1.2	" "	23% moisture, dry-green	
Perennial Rye grass	3.4	" "	71% moisture, dry-green	
Bent grass	3.1	" "	60% moisture, dry-green	
Annual Rye grass	0.6 1.8	" " " "	20% moisture, dry-green 55% moisture, dry-green	
Fescue grass	1.8	" "	66% moisture, dry-green	
Orchard grass	2.1 2.3	" " " "	66% moisture, dry-green 47% moisture, dry-green	

TABLE 15

ETHYLENE EMISSIONS FROM BURNING OF AGRICULTURAL WASTES (Continued)

Material	Ethylene (lb/ton of material)	Collection Location	Comments	Reference
Rice straw	1.7	San Joaquin Valley California		35
Barley straw	2.2	" "		
Native brush	0.7 3.5 5.5	" " " " " "	Dry Dry-green Green	
Cotton	0.3	" "		
Fruit prunings	0.8	San Francisco Bay Area, California (1965)		
Native brush	1.2	" "		
Fir chips	0.2	" "		
Redwood chips	0.2	" "		
Fruit prunings	2.7	San Francisco Bay Area, California (1966)		
Native brush	0.9	" "		