AIR QUALITY CRITERIA FOR HYDROCARBONS

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service

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National Air Pollution Control Administration
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PREFACE

Air quality criteria tell us what science has thus far been able to measure of the obvious as well as the insidious effects of air pollution on man and his environment. Such criteria provide the most realistic basis that we presently have for determining to what point pollution levels must be reduced if we are to protect the public health and welfare.

The criteria we can issue at the present time do not tell us all that we would like to know; but taking all of man's previous experience in evaluating environmental hazards as a guide, we can conclude that improved knowledge will show that there are identifiable health and welfare hazards associated with air pollution levels that were previously thought to be innocuous. As our scientific knowledge grows, air quality criteria will have to be reviewed and, in all probability, revised. The Congress has made it clear, however, that we are expected, without delay, to make the most effective use of the knowledge we now have.

The 1967 amendments to the Clean Air Act require that the Secretary of Health, Education, and Welfare "... from time to time, but as soon as practicable, develop and issue to the States such criteria of air quality as in his judgment may be requisite for the protection of the public health and welfare ... Such criteria shall ... reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on health and welfare which may be expected from the presence of an air pollution agent ..."

Under the Act, the issuance of air quality criteria is a vital step in a program designed to assist the States in taking responsible technological, social, and political action to protect the public from the adverse effects of air pollution.

Briefly, the Act calls for the Secretary of Health, Education, and Welfare to define the broad atmospheric areas of the Nation in which climate, meteorology, and topography, all of which influence the capacity of air to dilute and disperse pollution, are generally homogeneous.

Further, the Act requires the Secretary to define those geographical regions in the country where air pollution is a problem—whether interstate or intrastate. These air quality control regions will be designated on the basis of meteorological, social, and political factors which suggest that a group of communities should be treated as a unit for setting limitations on concentrations of atmospheric pollutants. Concurrently, the Secretary is required to issue air quality criteria for those pollutants he believes may be harmful to health or welfare, and to publish related information on the techniques which can be employed to control the sources of those pollutants.

Once these steps have been taken for any region, and for any pollutant or combination of pollutants, then the State or States responsible for the designated region are on notice to develop ambient air quality standards applicable to the region for the pollutants involved, and to develop plans of action for implementing the standards.

The Department of Health, Education, and Welfare will review, evaluate, and approve these standards and plans and, once they are approved, the States will be expected to take action to control pollution sources in the manner outlined in their plans.

At the direction of the Secretary, the National Air Pollution Control Administration has established appropriate programs to carry out the several Federal responsibilities specified in the legislation. Previously, on February

11, 1969, air quality criteria and control techniques information were published for sulfur oxides and particulate matter.

This publication, *Air Quality Criteria for Hydrocarbons*, is the result of extensive and dedicated effort on the part of many persons—so many that it is not practical to name each of them.

In accordance with the Clean Air Act, a National Air Quality Criteria Advisory Committee was established, having a membership broadly representative of industry, universities, conservation interests, and all levels of government. The committee provided invaluable advice on policies and procedures under which to issue criteria, and provided major assistance in drafting this document.

With the help of the committee, expert consultants were retained to draft portions of this document, while other segments were drafted by staff members of the National Air Pollution Control Administration. After the initial drafting, there followed a sequence of review and revision by the committee, as well as by individual reviewers specially selected for their competence and expertise in the many fields of science and technology related to the problems of atmospheric pollution by hydrocarbons. These efforts, without which this document could not have been completed successfully, are acknowledged individually on the following pages.

As also required by the 1967 amendments to the Clean Air Act, appropriate Federal departments and agencies, also listed on the following pages, were consulted prior to issuing this criteria document. A Federal consultation committee, comprising members designated by the heads of 17 departments and agencies, reviewed the document, and met with staff personnel of the National Air Pollution Control Administration to discuss their comments.

This Administration is pleased to acknowledge the efforts of each of the persons specifically named, as well as the many not named who have contributed to the publication of this volume. In the last analysis, however, the National Air Pollution Control Administration is responsible for its content.

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AIR QUALITY CRITERIA FOR HYDROCARBONS

CHAPTER 1.

INTRODUCTION

Pursuant to authority delegated to the Commissioner of the National Air Pollution Control Administration, *Air Quality Criteria for Hydrocarbons* is issued in accordance with Section 107(b) of the Clear Air Act (42 U.S.C. 1857-18571).

Air quality *criteria* are an expression of the scientific knowledge of the relationship between various concentrations of pollutants in the air and their adverse effects on man and his environment. They are issued to assist the States in developing air quality standards. Air quality criteria are descriptive; that is, they describe the effects that have been observed to occur when the ambient air level of a pollutant has reached or exceeded specific figures for a specific time period. In developing criteria, many factors have to be considered. The chemical and physical characteristics of the pollutants and the techniques available for measuring these characteristics must be considered, along with exposure time and conditions of the environment.

The criteria must consider the contribution of all such variables to the effects of air pollution on human health, agriculture, materials, visibility, and climate. Further, the individual characteristics of the receptor must be taken into account. Table 1-1 is a listing of the major factors that need to be considered in developing criteria.

Air quality *standards* are prescriptive. They prescribe pollutant exposures that a political jurisdiction determines should not be exceeded in a specified geographic area, and are used as one of several factors in designing legally enforceable pollutant emission standards.

This document focuses on gas-phase hydrocarbons and certain of their oxidation products, particularly aldehydes, that are associated with the manifestations of photochemical air pollution. Particulate hydrocarbons, and more specifically polynuclear hydrocarbons, are not treated in this document; these compounds will be considered at a later date in a separate set of air quality criteria. It is important to recognize that the criteria for hydrocarbons rest almost entirely on their role as precursors of other compounds formed in the atmospheric photochemical system and not upon the direct effects of the hydrocarbons themselves. It is for this reason that several of these reaction products are discussed in this document. A companion document, AP-63, *Air Quality Criteria for Photochemical Oxidants,* covers the effects of a class of photochemical reaction products not treated in this document.

This publication reviews the chemical and physical characteristics of hydrocarbons and their degradation products, especially aldehydes, and considers the basic analytical methods used for measuring the atmospheric content of these compounds. A brief review of the sources of hydrocarbons and principles of their control is included. The chemistry of hydrocarbon reactions in the atmosphere is briefly reviewed. The direct effects of hydrocarbons, essentially limited to vegetation damage from ethylene, are discussed. Toxicological data on hydrocarbons and aldehydes are also included.

The National Air Pollution Control Administration is currently advocating the use of the metric system to express atmospheric concentrations of air pollutants, e.g., micrograms per cubic meter ($\mu g/m^3$). In most instances, gaseous pollutants have hitherto been reported on a volume ratio basis, i.e., parts per million

Table 1–1. FACTORS TO BE CONSIDERED IN DEVELOPING AIR QUALITY CRITERIA[a]

- Properties of pollution
  - Concentration
  - Chemical composition
  - Adsorbed gases
  - Coexisting pollutants
  - Physical state of pollutant
    - Solid
    - Liquid
    - Gaseous
  - Kinetics of formation
  - Residence time
- Measurement methods
  - Flame ionization
  - Spectroscopic
  - Gas chromatographic
  - Chemical
  - .
  - .
- Exposure parameters
  - Duration
  - Concomitant conditions, such as
    - Temperature
    - Pressure
    - Humidity
- Characteristics of receptor
  - Physical characteristics
  - Individual susceptibility
  - State of health
  - Rate and site of transfer to receptor
- Responses
  - Effects on health (diagnosable effects, latent effects, and effects predisposing the organism to disease)
    - Human health
    - Animal health
    - Plant health
  - Effects on human comfort
  - Soiling
  - Other objectionable surface deposition
  - Effects on atmospheric properties
  - Effects on radiation and temperature

[a]Adapted from S. Calvert's statement for air quality criteria hearings held by the Subcommittee on Air and Water Pollution of the U.S. Senate Committee on Public Works, July 30, 1968. Published in "Hearings before the Subcommittee on Air and Water Pollution of the Committee on Public Works, United States Senate (Air Pollution 1968, Part 1)."

(ppm). Conversion from volume (ppm) to mass ($\mu g/m^3$) units requires a knowledge of the gas density at the temperature and pressure of measurement, since gas density varies with changes in these two parameters. In this document, 25° C (77° F) has been taken as standard temperature and 760 mm Hg (atmospheric pressure at sea level) as standard pressure. It should be borne in mind that almost all data for the atmospheric hydrocarbons under discussion were originally recorded as ppm.

In general, the terminology employed follows usage recommended in the publication style guide of the American Chemical Society. An appendix to the document includes an explanation of the procedure for converting volume (ppm) to mass ($\mu g/m^3$) units.

The literature has generally been reviewed through October 1969. This document is not intended as a complete literature review and does not cite every published article on the material covered herein. A particular effort was made, however, to relate hydrocarbons to the manifestations of photochemical air pollution. This document summarizes the current scientific knowledge on the role of hydrocarbons with respect to photochemical air pollution and points out the major deficiencies in that knowledge and the need for future research.

The technological and economic aspects of air pollution control are considered in companion volumes to criteria documents. The techniques for control of hydrocarbons, as well as the cost of applying these techniques, are described in two separate documents: AP-66, *Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources,* and AP -68, *Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources.*

CHAPTER 2.

NATURE, SOURCES, AND PRINCIPLES OF CONTROL OF ATMOSPHERIC HYDROCARBONS

A. INTRODUCTION

The class of hydrocarbons covered in this document are those which exist in the atmosphere in the gas phase. Many of these compounds may enter into atmospheric photochemical reaction processes leading to the products and manifestations associated with photochemical air pollution. Excluded are hydrocarbons and other organics associated only with suspended particles in the atmosphere. Even with this restriction, a large number of compounds are involved.

It is significant that most of the principal effects are caused not by hydrocarbons directly, but by compounds derived from the atmospheric reactions of hydrocarbons and their derivatives with other substances.

An appraisal, therefore, of the effects of atmospheric hydrocarbon pollution must be made in relation to the manifestations of photochemical air pollution. Aspects that must be considered include photochemical reactions, the influence of solar irradiation, and meteorological factors relating to the transport and diffusion of air pollutants.

In this chapter, information is presented on hydrocarbon sources and emissions, and on principles of emission control. This information is intended to provide a basic understanding of the nature and importance of sources of hydrocarbons from the standpoint of appraising their contribution to the atmospheric photochemical system. A detailed treatment of technological and economic factors relating to control is not intended; this function is provided by separate documents, AP-66, *Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources,* and AP-68, *Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources.*

B. HYDROCARBON CLASSES

Hydrocarbons are compounds whose molecules consist of atoms of hydrogen and carbon only. All compounds of carbon, except the oxides of carbon, the carbides, and the carbonates, are organic compounds. Hydrocarbons, therefore, are organic compounds, as are many other carbon compounds having additional elements such as oxygen, nitrogen, and chlorine. The hydrocarbons of concern in this document are those gas-phase hydrocarbons which may be encountered in urban atmospheres; of special interest are those hydrocarbons emitted into the atmosphere as contaminants by technological sources.

The volatility of hydrocarbons is approximately determined by their carbon number. Hydrocarbons with a carbon number (that is, number of carbon atoms in each molecule) greater than about 12 are generally not sufficiently abundant to reach troublesome atmospheric concentrations in the gas phase; however, many of these higher hydrocarbons, as particles or in association with particulate matter, are important air contaminants in another context and will be treated in future air quality criteria. Hydrocarbons having a carbon number of 1 to 4 are gaseous at ordinary temperatures, whereas those with a carbon number of 5 or more are liquids or solids in the pure state. (Liquid mixtures of hydrocarbons, such as gasoline, may include some proportion of compounds which, in the pure state, would be either gases or solids.)

Hydrocarbons fall into three classes, which are defined in terms of their general molecular structure: acyclic, alicyclic, and aromatic. Acyclic hydrocarbons are those whose carbon atoms are arranged in chains only, with or without branching chains, but without rings. Aromatic hydrocarbons are all those whose atoms are arranged in benzene rings, that is, six-membered carbon rings with only one additional atom (of hydrogen or carbon) attached to each atom in the ring. Alicyclic hydrocarbons are all those having rings other than benzene rings. A subsidiary classification often used is that of saturated versus unsaturated hydrocarbons. A saturated hydrocarbon is one with each of its carbon atoms boned to four other atoms; an unsaturated hydrocarbon with two or more carbon atoms is bonded to less than four other atoms. Saturated aliphatic hydrocarbons all correspond to the empirical formula C_nH_{2n+2}, where n is the carbon number. Saturated alicyclics with one ring have the formula C_nH_{2n}; those with two rings have the formula C_nH_{2n-2}, and so on.

Detailed discussions of hydrocarbon classes, their properties, and their nomenclature may be found in textbooks on organic chemistry.

C. HYDROCARBON ATMOSPHERIC REACTIONS

1. General Discussion

Reactions of hydrocarbons in the urban atmosphere are important because they give rise to secondary contaminants and reaction intermediates that cause nearly all the detrimental effects of hydrocarbon air pollution. The chemistry of these reactions and their products is not fully known, but existing knowledge is sufficient to explain the most important features of the observed behavior of photochemical air pollution. In a practical sense, adequate prediction of the real effects of controlling hydrocarbon emissions depends on applying both the available knowledge and the relevant scientific principles concerning these reactions.

Hydrocarbons become involved in the photochemical air pollution complex not because of their exposure to sunlight, but because of their reactions with oxygen atoms, excited-oxygen and ozone molecules, and free radicals generated by the action of sunlight on other components in the atmosphere, most particularly nitrogen dioxide. Sunlight alone has no appreciable effect on hydrocarbons in the air; in the absence of such highly reactive matter, hydrocarbons would not be involved in photochemical air pollution.

The speed with which the photochemical air pollution is developed can be related directly to the rates at which the hydrocarbon molecules are attacked by the reactive species and is indicated by the rate of consumption, i.e., the rate of decrease in concentration of hydrocarbons. Thus, in principal, if the rate of consumption of hydrocarbons can be predicted, an expected rate of development of photochemical air pollution can be deduced.

As a consequence of the different reactivities of individual hydrocarbons, it is impossible to predict accurately the rate of consumption of hydrocarbons in photochemical air pollution reactions unless the detailed composition of the hydrocarbon component of the air is known or can be estimated. Knowledge of the total concentration of hydrocarbons is insufficient, since two atmospheres having the same total hydrocarbon measurement may contain individual hydrocarbons of very different reactivity and thus exhibit very different rates of hydrocarbon consumption and photochemical air pollution development.

The total rate of hydrocarbon consumption is the sum of the rates of consumption of all the individual hydrocarbons. Since the individual hydrocarbons have different reactivities, some are consumed much more rapidly than others, and their concentrations change correspondingly faster. Thus the composition of the hydrocarbon component of air after an extended period of exposure to sunlight is quite different from the pre-exposure composition. Stephens and Burleson[1] compared the hydrocarbon composition of an

air sample collected in well-aged photochemical air pollution in Riverside, California, with that of early morning samples in the same vicinity. They found the more reactive components to be reduced by more than 90 percent relative to some of the less reactive compounds,[1] as shown in Table 2-1. Earlier, Neligan analyzed samples of synthetic atmospheres containing diluted automobile exhaust gases before and after simulated sunlight irradiation in the laboratory with similar results,[2] as shown in Table 2-2.

The rate of consumption of each of the individual hydrocarbons in the sum of the rates of the various reactions by which it is consumed. Rates of these reactions depend in principle upon the concentrations of the individual hydrocarbon and the attacking species, and can be estimated (within reasonable limits) by established methods of theoretical chemical kinetics. A detailed treatment of the prediction of gas-phase reaction rates is provided by Benson,[3] who developed methods of estimating rate parameters for many types of reactions involving carbon compounds, including hydrocarbons. These methods have been tested and found surprisingly accurate in a substantial number of reactions for which experimental observations were available. Utilizing these or similar techniques, it should be possible in the near future to develop accurate and scientifically well-based means of accounting for the detailed chemical behavior of hydrocarbon

Table 2–1. HYDROCARBON CONCENTRATIONS IN MORNING AND AFTERNOON AMBIENT AIR SAMPLES, RIVERSIDE, CALIFORNIA, FALL 1968[1]

Hydrocarbon	Concentration, ppm	
	7:30 a.m., PST Sept. 24, 1968	4:10 p.m., PST Oct. 24, 1968
Methane	2.355	2.530
Ethane	0.0636	0.0722
Propane	0.0188	0.0499
Acetylene	0.0770	0.0420
Ethylene	0.0656	0.0179
Propylene	0.0192	0.0013
Methyl acetylene	0.0026	0.0012
1,3-Butadiene	0.0036	0.0003
1-Butene	0.0026	0.0003
Isobutene	0.0052	0.0020
trans-2-Butene	0.0014	<0.0002
cis-2-Butene	0.0014	<0.0002
2-Methyl-1-butene	0.0024	0.0004
Cyclopentene (with 2-Methyl-1, 3-butadiene)	0.0044	0.0008
trans-2-Pentene	0.0024	<0.0002
2-Methyl-2-butene	0.0026	<0.0002
Isobutane	0.0080	0.0197
Butane	0.0276	0.0620
Isopentane	0.0392	0.0412
Pentane (with 3-methyl-1-butene)	0.0224	0.0214
Cyclopentane	0.0032	0.0024
2,2-Dimethyl butane (with 1-pentene)	0.0016	0.0009
2,3-Dimethyl butane	0.0038	0.0019
2-Methyl pentane (with *cis*-2-pentene)	0.0124	0.0096
3-Methyl pentane	0.0084	0.0061
Hexane	0.0090	0.0083

Table 2–2. HYDROCARBON CONCENTRATIONS OF IRRADIATED AND NONIRRADIATED SYNTHETIC ATMOSPHERES CONTAINING DILUTED AUTOMOBILE EXHAUST GASES[2]

	Diluted-nonirradiated				Diluted-irradiated			
Sample No.	1	2	3	4	1A	2A	3A	4A
Fuel, bromine No.	20	30	30	20	20	30	30	20
Exhaust to chamber dilution ratio	1-500	1-500	1-250	1-250	1-500	1-500	1-250	1-250
Components	Concentration, ppm							
Paraffins								
Propane	0.03	0.03	0.02	0.04	0.04	0.02	0.05	0.03
2-Me-Propane	0.02	0.01	0.03	0.02	0.02	0.02	0.02	0.02
n-Butane	0.14	0.13	0.28	0.24	0.15	0.12	0.22	0.19
2-Me-Butane	0.07	0.10	0.19	0.14	0.08	0.08	0.13	0.11
n-Pentane	0.03	0.04	0.07	0.04	0.03	0.03	0.05	0.04
2-Me-Pentane 2,3-Me_2-Butane	0.05	0.05	0.10	0.12	0.06	0.05	0.08	0.09
n-Hexane	0.02	0.02	0.02	0.05	0.02	0.02	0.02	0.02
2,4-Me_2-Pentane	0.01	0.02	0.05	0.02		0.02	0.02	0.02
2-Me-Hexane		0.01	0.03	0.01			0.01	0.01
3-Me_2-Hexane 2,3-Me_2-Pentane		0.01	0.05	0.05		-	0.07	0.03
2,2,4-Me_3-Pentane		0.03	0.03	0.03		0.03	0.05	0.02
Total	0.37	0.45	0.87	0.76	0.40	0.39	0.72	0.58
Olefins								
Propene	0.11	0.13	0.29	0.27	0.04	0.04	0.11	0.11
2-Me-1-Propene 1-Butene	0.04	0.06	0.12	0.09	0.01	0.01	0.03	0.02
trans-2-Butene	0.02	0.01	0.03	0.02	0.005	0.01	0.03	0.02
cis-2-Butene	0.005	0.01	0.01	0.01	0.01	0.005	-	
1-Pentene	0.02	0.005	0.01	0.005	0.005		0.01	-
2-Me-1-Butene	0.01	0.03	0.03	0.02			0.005	0.005
cis-2-Pentene	0.01	0.02	0.02	0.01				
2-Me-2-Butene	0.03	0.06	0.10	0.05	0.01		0.01	
4-Me-1-Pentene		0.005	-				-	
1-Hexene 2-Me-1-Pentene	0.005	0.02	0.02	0.01				
trans-2-Hexene *cis*-3-Hexene	0.005	0.005	0.04	0.01				-
cis-2-Hexene		0.01	0.02	0.005			-	
Cyclopentene		0.01	0.01	0.01				
Total	0.26	0.38	0.70	0.51	0.08	0.07	0.20	0.16
Acetylenes								
Acetylene	0.45	0.62	1.32	0.93	0.43	0.55	1.04	0.79
Me-Acetylene	0.02	0.02	0.04	0.03	0.005	0.01	0.03	0.02
Total	0.47	0.64	1.36	0.96	0.44	0.56	1.07	0.81
Diolefins								
Propadiene		-				-		-
1,3-Butadiene	0.02	0.04	0.06	0.04	0.005		0.01	0.01
Total	0.02	0.04	0.06	0.04	0.01		0.01	0.01

Table 2–2 (Continued). HYDROCARBON CONCENTRATIONS OF IRRADIATED AND NONIRRADIATED SYNTHETIC ATMOSPHERES CONTAINING DILUTED AUTOMOBILE EXHAUST GASES[2]

	Diluted-nonirradiated				Diluted-irradiated			
Sample No.	1	2	3	4	1A	2A	3A	4A
Components	Concentration, ppm							
Aromatics								
Benzene	0.05	0.07	0.18	0.14	0.06	0.08	0.12	0.11
Toluene	0.07	0.14	0.34	0.19	0.09	0.16	0.22	0.19
Total	0.12	0.21	0.52	0.33	0.15	0.24	0.34	0.30
Unresolved compounds								
Ethane[a] Ethylene	0.32	0.33	0.93	0.69	0.34	0.32	0.69	0.58
2,2-Me_2-Butane *trans*-2-Pentene	0.02	0.03	0.03	0.02	0.005	0.005	0.01	0.01
4-Me-2-Pentene 3-Me-Pentane	0.03	0.02	0.04	0.05	0.02	0.02	0.03	0.04
Total	0.37	0.38	1.00	0.76	0.37	0.35	0.73	0.63
Cyclics								
Cyclopentane	0.01	0.01	0.02	0.02	0.01	0.005	0.01	0.01
Me-Cyclopentane	-	0.02	0.04	0.03	-	0.01	0.02	
Cyclohexane	-	0.01		-	-	0.02	0.01	0.01
Total	0.01	0.04	0.06	0.05	0.01	0.04	0.04	0.02
Total hydrocarbons recovered	1.62	2.14	4.57	3.41	1.46	1.65	3.11	2.51

[a]Not detectable, but may be present in small quantities.

gases in urban atmospheres. This will include the prediction of rates of development of secondary contaminants as well as rates of consumption of the various hydrocarbon species in the air. First steps in this direction have already been indicated by Wayne and Ernest[4] with the development of a computer simulation model for the kinetics of photooxidation of propylene.

2. Expected Photooxidation Products

The ultimate products of photooxidation of hydrocarbons in urban air, if a captured parcel of air were to be irradiated by sunlight for a long enough time, would probably be carbon dioxide and water vapor. From the standpoint of ordinary urban atmospheres, these products are of no interest because, aside from their abundance in the natural global atmosphere, no air parcel remains in the urban atmosphere long enough for its hydrocarbons to be fully oxidized. The products of concern in photochemical air pollution are all intermediate products of the complex, i.e., all are capable of further reaction and degradation. They differ in that some react only very slowly and therefore accumulate to appreciable concentrations only if formed at appreciable rates, whereas others react rapidly and are therefore efficiently scavenged, even though their rates of formation may be high. In the following paragraphs, the confirmed and expected (intermediate) products of the photochemical complex are discussed, beginning with those having the longest lives and highest concentrations.

a. Commonly Recognized Products in Photochemical Air Pollution

(1) Ozone.–Best known of the compounds generated in photochemical air pollution is ozone (O_3), a highly reactive and toxic form of oxygen. Because this substance is one of the group of secondary contaminants known

as photochemical oxidants, it is discussed in greater detail in the companion document, AP-63, *Air Quality Criteria for Photochemical Oxidants.* It is important to observe, however, that ozone plays a significant role in the degradation of hydrocarbons, especially the olefinic hydrocarbons. Further, it must be noted that the level and composition of the hydrocarbons in the urban atmosphere, in conjunction with levels of oxides of nitrogen and meteorological factors (including sunshine), determine the concentrations and dosages of ozone that will be reached in photochemical episodes, as they do those of all the secondary contaminants.

(2) Nitrogen Dioxide.—Nitrogen dioxide in photochemical smog is generated primarily by the photooxidation of nitric oxide, which is facilitated by the free radicals generated by photolysis of aldehydes and other secondary contaminants, as well as by the reactions of hydrocarbons with oxygen atoms and other chemical species. This substance will be discussed in a forthcoming air quality criteria document dealing with nitrogen oxides.

(3) Aldehydes.—Aldehydes are major products in the photooxidation of hydrocarbons and in the individual reactions of hydrocarbons with ozone, oxygen atoms, or free radicals. They are dissociated by the ultraviolet fraction of sunlight with the production of alkyl radicals, formyl radicals, and hydrogen atoms. Because the chemical bond between the hydrogen atom and the carbonyl group is weaker than most carbon-hydrogen bonds in hydrocarbon molecules, aldehydes are relatively more susceptible to hydrogen abstraction reactions, which yield acyl radicals or alkyl radicals and carbon monoxide, according to the equations:

$$CH_3CHO + RO \rightarrow CH_3CO + ROH \qquad (2\text{-}1)$$

$$CH_3CO + M \rightarrow CH_3 + CO + M \qquad (2\text{-}2)$$

In urban air, however, the photolysis and all other aldehyde-consuming reactions such as (2-1) are not collectively rapid enough to prevent their accumulation to levels as high as about 0.2 ppm in photochemical air pollution.[5]

Specific aldehydes found in urban air are formaldehyde (HCHO) and acrolein (CH_2CHCHO). Formaldehyde usually accounts for about 50 percent of the estimated total aldehydes in polluted air, and acrolein for perhaps 5 percent.[6,7] The chemical identity of the remaining aldehydes in urban air is unknown, but higher aliphatic aldehydes such as acetaldehyde (CH_3CHO) are probably present.

(4) Peroxyacyl Nitrates.—Peroxyacyl nitrates, $R(CO)OONO_2$, are in the main probably products of the reaction of peroxyacyl radicals with nitrogen dioxide, as in equation (2-3),

$$R(CO)OO + NO_2 = R(CO)OONO_2 \qquad (2\text{-}3)$$

although other reactions, such as acylate radicals with nitrogen trioxide, as in equation (2-4), are not completely excluded.

$$R(CO)O + NO_3 = R(CO)OONO_2 \qquad (2\text{-}4)$$

These compounds are among the products of photochemical air pollution that oxidize certain standard reducing agents and are discussed in AP-63, *Air Quality Criteria for Photochemical Oxidants.* It should be noted that the most abundant member of the class, peroxyacetyl nitrate (frequently abbreviated PAN) is the only one usually detected in atmospheric samples, although smaller amounts of higher homologues are probably present.

PAN may absorb ultraviolet light from the sun, with probable production of free radicals. The specific products of the primary step are not known.

b. *Products of Photooxidation of Hydrocarbons in Experimental Studies*

Laboratory irradiations of synthetic atmospheres provide valuable information in understanding the photochemistry of polluted air because they facilitate the study of rates

and products of reaction of individual hydrocarbons or of mixtures with carefully controlled composition. Further, they can be used to determine quantitatively the relations between reaction rates or product yields and such environmental factors as light intensity, temperature, humidity, and initial reactant concentrations. In many such studies the initial concentrations employed have been larger than those usually found in urban atmospheres, but still small enough to give a reasonably good indication of the relations to be expected under conditions of the ambient atmosphere.

The many studies on irradiated synthetic atmospheres containing hydrocarbons and oxides of nitrogen were thoroughly reviewed by Altshuller and Bufalini in 1965.[8] From that review and reports of subsequent studies,[9,10] it appears that the carbon atoms of photooxidized hydrocarbons can be well accounted for in terms of aldehydes, ketones, carbon monoxide, carbon dioxide, alkyl nitrates, and peroxyacyl nitrates, except that acceptable carbon balances have not been achieved for the photooxidation of aromatic hydrocarbons.

The chemical behavior of irradiated atmospheres containing auto exhaust has been shown to resemble rather closely that of photooxidized mixtures of hydrocarbons and nitric oxide. Ozone and peroxyacyl nitrates are formed, but do not accumulate until nitric oxide is nearly consumed, whereas the aldehydes are produced from the beginning of the irradiation and are always found as major products.

(1) Ozone.—Appreciable ozone concentrations have been observed to result from photooxidation (with nitric oxide or nitrogen dioxide) of many olefins, paraffins (not including methane), and alkylbenzenes. At concentrations of 3 ppm hydrocarbons and 1,230 $\mu g/m^3$ (1 ppm) nitrogen oxide, Schuck and Doyle[11] measured ozone levels between 200 and 1,960 $\mu g/m^3$ (0.1 and 1 ppm) for 25 hydrocarbons, as listed in Table 2-3. At the selected levels of initial concentrations, most of the olefins tested yielded more than 980 $\mu g/m^3$ (0.5 ppm), while most of the paraffins yielded less than that amount. At other levels of initial concentrations, there can be little doubt that different results would be obtained. Altshuller[9] et al. have shown, for example, that in experiments with 3,460 $\mu g/m^3$ (2 ppm) propylene the optimum nitric oxide level for ozone production is about 1,230 $\mu g/m^3$ (1 ppm), which yields 2,160 $\mu g/m^3$ (1.1 ppm) ozone; while, for 6,870 $\mu g/m^3$ (3 ppm) butane, the optimum nitric oxide level is about 125 $\mu g/m^3$ (0.1 ppm), which yields about 1,760 $\mu g/m^3$ (0.9 ppm) ozone.

A simple relation that would permit the prediction of ozone yields, either absolute or relative, from initial concentrations in irradiation experiments has not yet been discovered. There does appear to be a practical limit to the concentration of ozone that can be generated in this way; regardless of what hydrocarbon or mixture of hydrocarbons serves as the substrate for photooxidation and regardless of what initial concentrations or light intensities have been provided, no chamber irradiation has yet produced ozone in excess of 2,940 $\mu g/m^3$ (1.5 ppm), and a few have reached 1,960 $\mu g/m^3$ (1.0 ppm). In urban atmospheres, a level of 1,960 $\mu g/m^3$ (1.0 ppm) has not yet been recorded.

(2) Nitrogen dioxide – All irradiation chamber photooxidations in which nitric oxide is introduced as a reactant show conversion of nitric oxide to nitrogen dioxide at rates dependent on the reactant levels and the hydrocarbon reactivity as well as such experimental variables as light intensity and temperature. Ordinarily the nitrogen dioxide concentration reaches a maximum and then declines somewhat less rapidly than it had previously risen. The time required for nitrogen dioxide concentration to reach this maximum is always less than the time required for ozone to reach a maximum. Some examples are seen in Table 2-3. The degree of conversion (i.e., the ratio of highest observed nitrogen dioxide concentration to the initial

Table 2–3. OZONE LEVELS GENERATED IN PHOTOOXIDATION[a] OF VARIOUS HYDROCARBONS WITH OXIDES OF NITROGEN[11]

Hydrocarbon	Ozone level, ppm	Time, min
Isobutene	1.00	28
2-Methyl-1,3-butadiene	0.80	45
trans-2-Butene	0.73	35
3-Heptene	0.72	60
2-Ethyl-1-butene	0.72	80
1,3-Pentadiene	0.70	45
Propylene	0.68	75
1,3-Butadiene	0.65	45
2,3-Dimethyl-1, 3-butadiene	0.65	45
2,3-Dimethyl-2-butene	0.64	70
1-Pentene	0.62	45
1-Butene	0.58	45
cis-2-Butene	0.55	35
2,4,4-Trimethyl-2-pentene	0.55	50
1,5-Hexadiene	0.52	85
2-Methylpentane	0.50	170
1,5-Cyclooctadiene	0.48	65
Cyclohexene	0.45	35
2-Methylheptane	0.45	180
2-Methyl-2-butene	0.45	38
2,2,4-Trimethylpentane	0.26	80
3-Methylpentane	0.22	100
1,2-Butadiene	0.20	60
Cyclohexane	0.20	80
Pentane	0.18	100
Methane	0.0	

[a]Hydrocarbon concentration (initial) 3 ppm; oxide of nitrogen (NO or NO_2, initial) 1 ppm.

total of both oxides) is often near 100 percent, especially in systems in which the reactions are rapid, as with some of the more reactive olefins and a nitric oxide concentrations near the optimum for ozone production.

(3) Aldehydes and ketones – In all irradiation chamber experiments in which products have been appropriately analyzed, carbonyl compounds have been found among the major products. Table 2-4 shows yields of these compounds for a number of initial hydrocarbons, as tabulated by Altshuller and Bufalini.[8] The yields are shown in relation to initial concentrations in the irradiation chamber; therefore, yields relative to hydrocarbons reacted would be greater than those shown (although perhaps, in some cases, no much greater).

Formaldehyde can be seen (from Table 2-4) to be the most important carbonyl product identified from many of these compounds, forming half or more of the total for each of the 1-alkenes. Acetaldehyde is important as a product from propylene, *cis*- and *trans*-2-butenes, and 2-methyl-2-butene, but not from ethylene, isobutene, or 1,3-pentadiene and 2-methyl-1,3 pentadiene; acetone, from isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. For the olefins cited, the results are consistent with the view that a large fraction of the hydrocarbon molecules that react yield products typical of their reaction with ozone. It appears, however, that some of the formaldehyde ultimately produced may result from the further reactions of other intermediate species in the system, including higher aldehydes.

With alkybenzenes, the yield of carbonyl compounds is smaller,[12] ranging from 0.1 to

Table 2–4. YIELDS OF CARBONYL COMPOUNDS IN EXPERIMENTAL PHOTOOXIDATION OF HYDROCARBONS WITH OXIDES OF NITROGEN[8]

Hydrocarbon	Moles/mole of initial hydrocarbon				Total or other aldehydes
	Formaldehyde	Acetaldehyde	Acrolein	Acetone	
Ethylene	0.35[a], 0-45[b] 0.32[c], 0.45[d]	<0.01[c]			
Propylene	0.40[a], 0.45[e]	0.4[a], 0.15-0.2[e]		0.03-0.05[e]	
1-Butene	0.45[a], 0.4[f]				0.9[a], 0.5[f]
Isobutene	0.7[a], 0.6[b] 0.3-0.45[d], 0.6[e], 0.6[f], 0.5-0.7[g]	0.01[e]		0.6[a], 0.5[d] 0.6[g], 0.25-0.4[e]	
trans-2-butene	0.35[f], 0.35[h]	1.40[a], 1.5[f], 0.9-1.2[h]			
cis-2-butene		0.9[a], 0.8-1.0[d]			1.0[b], 0.9[g]
1,3-Butadiene	0.6[a], 0.6[e], 0.5[f]	~0.01[e]	0.55[a], 0.25[i], 0.2[e]	~0.02[e]	
1-Pentene	0.55[a]				0.4[a]
2-Methyl-2-butene	0.5[a], 0.3[e]	0.75[a], 0.4-0.5[e]		0.45[a], 0.3-0.4[e]	
1,3-Pentadiene	0.65[a]		0.35[a]		1.3[a]
2-Methyl-1,3-Pentadiene	0.55[a]		0.4[a]		0.9[a]
cis-3-hexene					1.0[b], 0.9-1.0[d] 0.9-1.0[g]
2,3-Dimethyl-2-butene	0.25[a]			1.25[a], 0.8-0.9[g], 1.4[j]	
Cyclohexene	0.4[e]				
2,3-Dimethyl-1,3-butadiene	0.65[a]				1.3[a]
3-Heptene	0.8[a]				1.2[a]
Toluene					0.11[k]
p-Xylene	0.15[a]				0.26[b]
o-Xylene					0.22[b]
m-Xylene	0.15[k]				0.25[b], 0.3[k]
1,3,5-Trimethylbenzene	0.15[k]				0.6[b], 0.3[k], 0.4[l]
1,2,4,5-Tetramethylbenzene					0.45[b]

[a]Schuck and Doyle.[11]
[b]Stephens and Scott.[12]
[c]Altshuller and Cohen.[13]
[d]Stephens[14] et al.
[e]Schuck[15] et al.
[f]Sigsby[16] et al.
[g]Stephens.[17]
[h]Tuesday.[18]
[i]Altshuller and Bufalini.[8]
[j]Bufalini and Altshuller.[19]
[k]Leighton.[20]
[l]Vrbaski and Cvetanovic.[21]

0.3 relative to the hydrocarbon reacted. Again, most of the carbonyl product is formaldehyde, with smaller amounts of acetaldehyde reported.

Paraffins also yield carbonyl compounds upon photooxidation. Using 3 ppm of hydrocarbon with 0.6 ppm of nitrogen oxides (nitrogen oxide composition not specified), Altshuller[9] et al. have found formaldehyde, acetaldehyde, propionaldehyde, butanone (methyl ethyl ketone), and a component which may have been acetone; butyraldehyde, or both. Alkanes tested in this study were butane, isopentane, 2-methylpentane, 3-methylhexane, 2,4-dimethylhexane, *n*-nonane, and methylcyclohexane. About 70 percent of isopentane consumed could be accounted for as carbonyl products.

(4) Organic nitrates and nitrites – Of the nitrogen-containing organics produced in irradiation studies, peroxyacetyl nitrate is clearly the most common and most abundant. Table

2-5 shows maximum yields of PAN and alkyl nitrates in irradiation studies with various olefins and alkylbenzenes. Yields of PAN were less than 0.25 mole per mole of initial hydrocarbon, with the exception of *trans*-2-butene and 2,3-dimethyl-2-butene, for which some yields larger than 0.5 were found. Yields of alkylnitrates were uniformly 0.25 or less.

On photooxidation of alkanes (butane, isopentane, 2-methylpentane, 3-methylhexane, 2,4-dimethylhexane, *n*-nonane, and methylcyclohexane), yields of peroxyacetyl nitrate and of alkyl nitrates were about 1 percent or less of the initial hydrocarbon concentration, which was usually 3 ppm in these tests.[9] Individual alkyl nitrates identified were methyl nitrate, ethyl nitrate, propyl nitrate, and isopropyl nitrate. Very small amounts of alkyl nitrites have been reported as products in chamber irradiations,[15] and nitromethane has been found in experiments with reduced oxygen concentrations.[18]

(5) Minor products – Small yields of epoxides, alcohols, esters, and peroxides have been reported.[8] Carbon monoxide is sometimes formed in appreciable yields[11,18] (0.2 to 0.4, relative to initial hydrocarbon), and carbon dioxide has been found in yields up to 0.25, with 2-butene as the substrate.[18] These products probably have been formed in various experiments in which they were not detected, either because the necessary analysis was not done or because the concentrations were below the limits of detection of techniques applied.

D. ESTIMATION OF HYDROCARBON EMISSIONS

1. Emission Levels of Hydrocarbons from Natural Sources

The presence of natural hydrocarbons in the atmosphere, particularly methane, only recently has been established by measurement.[24] Although most of these hydrocarbons arise from biological sources, small and highly localized quantities of methane and a few other lower-molecular-weight hydrocarbons are attributable to geothermal areas, coal fields, and natural gas and petroleum fields, and natural fires.

Table 2–5. YIELDS OF PEROXYACYL NITRATES AND ALKYL NITRATES OBSERVED IN PHOTOOXIDATION OF VARIOUS OLEFINS AND ALKYLBENZENES[8]

Hydrocarbon	Highest yield, relative to initial hydrocarbon	
	PAN	Alkyl nitrate
Ethylene	0	
Propylene	0.25	
1-Butene	0.11	
Isobutene	0.23	0.10
trans-2-Butene	0.51	0.15
cis-2-Butene	0.16	0.12
cis-3-Hexene	0.16	0.12
trans-3-Hexene	0.20	0.14
2,3-Dimethyl-2-butene	0.69	0.25
p-Xylene	0.08	
o-Xylene	0.08	
m-Xylene	0.11	
1,3,5-Trimethylbenzene	0.16	0.15
1,2,4,5-Tetramethylbenzene	0.14	

[a]Stephens and Scott.[12]
[b]Tuesday.[22]
[c]Stephens.[17]
[d]Kopczynski.[23]

Various estimates have been made of the contributions of these natural sources to hydrocarbons in the atmosphere. Koyama has estimated the production rate of methane to be about 3 x 10^8 tons per year.[25] Of this amount, the greatest quantity arises from the decomposition of organic matter at the earth's surface. Ehhalt[26] and Robinson and Robbins,[27] however, conclude that this is a very conservative estimate, since methane generated in swampy and tropical areas was not included.

Volatile terpenes and isoprene constitute a separate class of hydrocarbons for which worldwide natural emission rates have been estimated. Rasmussen and Went[28] have estimated the rate of production of such compounds to be about 4.4 x 10^8 tons per year. Hazes associated with vegetation in many areas of the world, such as the blue haze of the Appalachian Mountain region, have been ascribed to photochemical aerosol formation caused by these substances.

From these estimates, it appears that production of methane from natural sources is roughly equivalent on a weight basis to that of the higher-molecular-weight volatile organics. There is a great difference, however, in their natural background levels, which implies a related difference in the lifetimes of these materials in their global cycles.

There is substantial agreement on the natural background concentration of methane in the atmosphere based upon different methods of measurement and the locations of such measurements. Junge[29] indicates that the worldwide range is 0.8 to 1.1 mg/m^3 (1.2 to 1.5 ppm). This is seen both in optical measurements such as reported by Fink[30] et al. and Goldberg and Muller,[31] and in measurements made by gas chromatography.

From samples taken in nonurban atmospheres, Stephens and Burleson[32] report methane values averaging 0.93 mg/m^3 (1.39 ppm) over a southern California mountain area during desert winds; they reported similar values for Hawaii. Ethane, ethylene, and acetylene were found at 0.003 ppm or less. Cavanagh[33] et al. found a mean methane concentration of 1.1 mg/m^3 (1.6 ppm) with butane at 0.14 mg/m^3 (0.06 ppm) at Point Barrow, Alaska, whereas Swinnerton[34] et al., during an oceanographic cruise between Washington, D. C., and Puerto Rico, reported a mean methane concentration of 0.83 mg/m^3 (1.25 ppm). Furthermore, these latter authors found that the methane content of ocean water was in equilibrium with that found in the atmosphere.

The lowest hydrocarbon concentrations measured in urban atmospheres are in the same range as the values previously reported for methane in nonurban areas. Data on urban hydrocarbon concentrations were obtained from special gas chromatographic measurements by Altshuller[35, 36] et al., and from total hydrocarbon measurements by flame ionization analyzers from the National Air Surveillance Network, the State of California SCAN network, and the Los Angeles County Air Pollution Control District.

Few measurements of low-molecular-weight hydrocarbons other than methane have been made in nonurban areas, and no accurate statement can be given as to ranges of concentrations for those compounds. Butane concentrations measured at Point Barrow, Alaska, by Cavanaugh[33] et al., and ethane, ethene, and acetylene concentrations measured in southern California mountain areas by Stepehns and Burleson[32] were two to three orders of magnitude lower than concentrations of methane.

Higher-molecular-weight hydrocarbon and other volatile organic compound concentrations have been estimated by Rasmussen and Went[28] on the basis of sensitive gas chromatographic measurements of alpha- and beta-pinene. Pinene content averaged about 0.01 ppm.

Using his own methane production figures and a total instantaneous mass of 4.3 x 10^{15} g in the atmosphere, Koyama[25] calculated an atmospheric average life of 20 years for methane. Ehhalt[26] and Robinson and Robbins[27] consider this an overestimate and suggest that an average life of only a few years is more likely. In contrast with the

estimated life of methane, the lifetime of higher-molecular-weight natural hydrocarbons may be on the order of days to months.

The principal implications of the reported information on abundance of hydrocarbons from natural sources would appear to relate to atmospheric sampling. Since methane is photochemically nonreactive and the other hydrocarbons from natural sources are too low in concentration to be of concern in urban areas, the relatively high concentration of methane as compared to other hydrocarbons of photochemical significance from technological sources makes the use of analytical methods which are specific for methane of critical importance.

In summary, it appears that in nonurban air, background levels of methane are ordinarily in the range of 0.7 to 1.0 mg/m^3 (1.0 to 1.5 ppm), whereas other hydrocarbons, including various terpenes, are each present at levels less than 0.1 ppm.

2. Emission Levels of Hydrocarbons from Technological Sources

a. National Emisison Estimates

Total nationwide emissions of hydrocarbons and related organic compounds to the atmosphere for the year 1968, according to U. S. Public Health Service estimates, amounted to approximately 32 x 10^6 tons.[37] Table 2-6 shows the distribution of this total by major source categories, including percent of relative contribution. Motor vehicles (49 percent), industrial processes (14 percent), and solvent usage (10 percent) constitute by far the most significant sources. According to

Table 2–6. ESTIMATES OF HYDROCARBON EMISSIONS[37] BY SOURCE CATEGORY, 1968[a]

Source	Hydrocarbon emissions, 10^6 tons/yr			Hydrocarbon emissions, Percent of total emissions		
Transportation	16.6			51.9		
Motor vehicles		15.6			48.7	
Gasoline			15.2			47.5
Diesel			0.4			1.2
Aircraft		0.3			1.0	
Railroads		0.3			1.0	
Vessels		0.1			0.2	
Nonhighway use, motor fuels		0.3			1.0	
Fuel combustion-stationary	0.7			2.2		
Coal		0.2			0.7	
Fuel oil		0.1			0.3	
Natural gas		Negligible			Negligible	
Wood		0.4			1.2	
Industrial processes	4.6			14.4		
Solid waste disposal	1.6			5.0		
Miscellaneous	8.5			26.5		
Forest fires		2.2			6.9	
Structural fires		0.1			0.2	
Coal refuse		0.2			0.6	
Organic solvent evaporation		3.1			9.7	
Gasoline marketing		1.2			3.8	
Agricultural burning		1.7			5.3	
Total	32.0			100.0		

[a]These emission estimates are subject to revision as more refined information becomes available.

Mason[38] et al., who reported similar information for the year 1966, approximately 63 percent of the total hydrocarbon emissions arise from urban areas.

b. Regional Emission Estimates

Hydrocarbon emission estimates have been made for 22 major metropolitan areas in the United States.[38] Although information is still quite fragmentary, emissions by area range from 0.05 to 1.3 million tons per year. Table 2-7 shows this information for each of the available areas.

Perhaps of greater significance are the data given in Table 2-8, which provides estimates of the percent of contribution by source catetory to total hydrocarbon emissions in the 22 metropolitan areas included in the study referred to previously. The most significant finding was that while transportation sources accounted for a higher proportion of total hydrocarbon emissions in these metropolitan areas than in the Nation as a whole, the range was extremely wide: 37 to 99 percent.

3. Technological Sources of Hydrocarbons

Hydrocarbon pollutants originate primarily from the inefficient combustion of fuels, particularly the more volatile fuels, such as gasoline, and from the use of hydrocarbons as process raw materials, such as solvents. The sources of hydrocarbons generally are treated in terms of mobile and stationary sources because of the differing control strategies required for each in terms of the engineering, technological, economic, and legal factors that must be taken into account. Mobile sources are chiefly gasoline-powered vehicles, but also include other types of vehicles, including aircraft. Stationary sources primarily

Table 2–7. SUMMARY OF HYDROCARBON EMISSIONS FROM 22 METROPOLITAN AREAS IN THE UNITED STATES, 1967–1968[37]

Location[a]	Population	Area, mi^2	Emissions, 10^3 tons/yr
Los Angeles	7,100,000	41,000	1,270
Philadelphia	5,500,000	4,590	470
San Francisco	4,500,000	7,000	790
Detroit	4,090,000	2,680	480
Washington, D. C.	2,700,000	2,270	310
Boston	2,700,000	1,280	87
Pittsburgh	2,520,000	3,050	95
St. Louis	2,410,000	4,500	330
Hartford	2,290,000	2,650	120
Dallas	2,187,000	8,000	143
Seattle	2,010,000	15,000	170
Houston	2,000,000	7,800	292
Milwaukee	1,730,000	2,630	83
Cincinnati	1,660,000	2,620	55
Buffalo	1,300,000	1,470	130
Kansas City	1,230,000	3,200	230
Providence	1,200,000	1,000	54
Indianapolis	1,050,000	3,080	74
San Antonio	982,000	7,320	71
Dayton	880,000	2,310	64
Louisville	840,000	1,390	46
Birmingham	750,000	1,120	64

[a]Defined on the basis of Standard Metropolitan Statistical Areas; these may include substantial areas which are rural in nature and thus of low population density.

Table 2–8. PERCENT OF TOTAL AREA HYDROCARBON EMISSIONS BY SOURCE CATEGORY, 22 METROPOLITAN AREAS IN UNITED STATES[38]

Source category	Percent of total area hydrocarbon emissions
Transportation	
Average	70.2
Range	37 - 99[a]
Motor vehicles	
Average	66.9
Fuel combustion	
Average	2.8
Range	0 - 18
Power plants	
Average	0.1
Industrial	
Average	2.2
Domestic	
Average	0.5
Process losses	
Average	19.9
Range	1 - 63
Refuse disposal	
Average	7.1
Range	0.4 - 26

[a]More recent estimates indicate that the maximum percent of total area hydrocarbon emissions in the transportation category is somewhat less than 99.

include petroleum and petrochemical operations and solvent usage, with some contribution from waste burning.

a. Carbureted Gasoline Engines

Carbureted gasoline internal combustion engines (i.e., conventional automobile engines) emit air pollutants from four sources: engine exhaust, crankcase blowby, carburetor, and fuel tank. According to a survey conducted on a large number of uncontrolled automobiles, about 60 percent of the unburned hydrocarbons comes from the engine exhaust; another 20 percent of unburned hydrocarbons escapes from crankcase blowby; and an additional 10 percent each results from the evaporation of gasoline from the carburetor and from the fuel tank.[39] Literally hundreds of different hydrocarbons are emitted, primarily in trace quantities.[40] These emissions include organic acids, olefins, and carbonyl compounds.

The quantity and reactivity (or photochemical potential) of the unburned hydrocarbons, as well as the quantity of nitric ocide and carbon monoxide emitted from the automobile exhaust, depend on the engine operation mode[41] (e.g., idle, acceleration, cruising, deceleration), the engine parameters[42] (e.g., compression ratio, spark advance, air-fuel ratio), and the fuel composition.[43]

b. Diesel Engines

The emission from diesel exhaust differs from that of carbureted gasoline engines, mainly because carbureted gasoline engines, in general, operate with a deficiency of combustion air, whereas the diesel engine normally operates with a substantial excess of combustion air and with a substantially higher compression ratio.

The emission of urburned hydrocarbons from diesel exhaust is substantially lower than that from gasoline engines. The higher emission of aldehydes (including formaldehyde),

however, may be partially responsible for the distinctive diesel exhaust odor.[44, 45] Air pollution from crankcase blowby is negligible with diesel engines, since the diesel compresses only air instead of an air and fuel mixture.[41] Practically no air pollution results from evaporation from the fuel system because the volatility of diesel fuel is very low.

c. Gas Turbines and Aircraft Jet Engines

The combustion process in gas turbines and aircraft jet engines differ from that in gasoline and diesel engines mainly in that it occurs at constant pressure (continuous process), low compression ratio, and with a very large excess of combustion air. In general, the exhaust emission is low in unburned hydrocarbons.[46] The main source of pollution from gas turbines and aircraft jet engines is the exhaust. Pollution resulting from evaporation from the fuel tank is minimal because fuels with low volatility are generally used.

d. Stationary Sources

The major stationary sources of hydrocarbons in the United States are the production, processing, storage, and transfer of petroleum products (principally gasoline), and the loss of organic solvents. Relatively smaller quantities arise from the combustion of fuels and refuse.[46]

Potential sources of hydrocarbon emissions in petroleum production and processing include: oil field and refinery leakage, gasoline storage tanks, gasoline loading facilities, air blowing of asphalt, blow-down systems, catalyst regenerators, processing vessels, flares, compressors, pumps, vacuum jets, waste effluent handling equipment, and turnaround operations.

Gasoline distribution and marketing systems emit hydrocarbon vapors from tank truck loading racks, service station tank filling operations, and automobile tank filling operations.

Organic solvents are derived mainly, but not exclusively, from petroleum. They are used in many kinds of operations. Chemical, drug, and pharamceutical manufacturing plants can emit organics from those operations involving the use of organic solvents. Rubber and plastic product manufacturing often involves the use of organic solvent-based adhesives and other solvents that lead to organic emissions. Paints, varnishes, lacquers, undercoatings, etc., are composed of 40 to 80 percent organic solvents that evaporate during or after the application of the coating. Degreasing of manufactured metal items can cause significant organic emissions. Vapor-phase degreasing with trichlorethylene (a hydrocarbon derivative) is the most widely used method, but spray degreasing with other solvents is also used. Drycleaning of clothing utilizes organic solvents and contributes to emissions. The processes by which solvents and solvent-containing materials (e.g., paints and lacquers) are manufactured are also potential sources.

Metallurgical coke plants emit varying amounts of hydrocarbons, depending on the type of furnace, operating methods, maintenance practices used, and other factors. Fuel-burning equipment of all types can emit organics when improperly adjusted, inadequately maintained, or incorrectly operated. Waste disposal by burning can cause hydrocarbon emissions from incomplete combustion. Open burning of refuse is the greatest offender in this category, and inefficient incinerators may also contribute as a source. Miscellaneous sources of organic gases from biological materials include industries employing fermentation, food processing, organic fertilizer processing, wood distillation, and soap manufacturing.

4. Emission Factors

An adequate emission inventory will define the magnitude, frequency, duration, and relative contribution of emissions. For a regional emission inventory, a detailed analysis of all sources of interest would be desirable. It is often necessary, however, to estimate emissions from sources for which detailed data are unavailable. Estimates are arrived at by the use of emission factors, which are based on sampling data, material

balances, and engineering appraisals of sources similar to those in question.

E. PRINCIPLES OF HYDROCARBON EMISSION CONTROL

1. General Principles of Control

The control of hydrocarbon vapors from technological sources rests upon several basic principles. These include: (1) optimization of combustion processes, (2) recovery by mass transfer principles, (3) restriction of evaporative loss, and (4) substitution of process materials and fuels with other having different chemical or physical properties. The application of these principles depends upon whether emissions arise from product storage and transfer, industrial processes, or combustion. Vehicular sources involve a complex mixing of both evaporative and combustion losses.

2. Motor Vehicle Controls

a. Present Controls

(1) Crankcase emission controls–Essentially 100 percent control of crankcase emissions may be achieved by closing off the normal crankcase vents and returning the gases through appropriate piping to the intake manifold. In essence, these gases then dilute the combustion air and are recycled through the combustion process.

(2) Exhaust emission controls – In systems presently in use, the reduction of hydrocarbons in exhaust gases is accomplished by one of two general approaches. The first involves the injection of controlled amounts of additional combustion air at the cylinder exhaust ports in order to oxidize the unburned or partially burned hydrocarbons in the oxygen deficient exhaust gases.

The second and most widely used approach to exhaust gas hydrocarbon control is preventive in nature. It involves a series of integrated engine and engine accessory modifications designed to improve overall combustion efficiency (not to be confused with energy utilization efficiency). The major elements involved in the engine modification approach include: (1) leaner air-to-fuel ratios, (2) improved air-fuel mixing, (3) a more uniform air-fuel mixture distribution, (4) a more precise fuel metering, and (5) improved cylinder combustion conditions.

(3) Evaporative emission controls–Evaporation controls consists of a means for conducting the fuel vapors to either the crankcase or an activated charcoal canister. In the first case, the vapors are merely held in the air space, whereas in the latter, the charcoal actually adsorbs them. The gasoline collected is eventually returned to the induction system for burning in the engine, with the precaution that this be done when it will not interfere with air-fuel mixtures and thus increase exhaust emissions.

b. Proposed Controls

Most restrictive motor vehicle emission controls for hydrocarbons will require the application of control techniques beyond those now in use. First steps might include direct and catalytic exhaust reactors, more drastic engine modification, and fuel alteration.

In the latter approach, volatility would be reduced and less reactive hydrocarbons would be substituted for certain of the components (principally olefins) now commonly present. This type of hydrocarbon control is most effective in reducing evaporative losses and becomes less important where mechanical evaporative controls are used.

In addition to the hydrocarbon control now thought possible with the present four-cycle, spark-ignited, gasoline-fueled, internal combustion engine, other types of motive power have been advanced and publicized. These have sometimes been described as "low emission" systems and include the gas turbine, electric drive, the steam engine, the Stirling engine, and the stratified charge engine. Other suggestions involve the complete substitution of liquefied petroleum gases or, as a special case, liquefied natural gas for gasoline.

Additional proposals for the reduction of hydrocarbon emissions from vehicular sources

include measures other than the use of specific vehicular emission standards. These include: (1) substitution, in part, of public transportation for private motor vehicles; (2) improved road design and traffic control systems, to enable reduction of high-emission stop-and-go driving; and (3) restriction of the use of private vehicles by regulation or by economic incentive.

3. Stationary Source Control

Control principles used for stationary sources of hydrocarbons and related organic substances include: (1) evaporation prevention (including vapor recovery), (2) incineration, (3) adsorption, (4) absorption, (5) condensation, and (6) substitution of less volatile and less photochemically reactive materials in solvents for cleaning and surface coating use. A brief description of the principles involved for each follows.

a. Evaporation Emission Controls

The direct control of hydrocarbon evaporation involves, as a general principle, minimizing liquid-air contact. The major opportunities for this control measure are in the storage and transfer of materials. When such direct control is not possible, vapor recovery systems, which physically move excess vapors to a control unit, may be used. These systems are normally used only with hydrocarbons of rather high vapor pressure.

b. Control by Incineration

The control of hydrocarbon emissions by combustion eliminates product recovery, but by-product heat may sometimes be utilized. It is used only if the products of combustion are innocuous. A successful combustion control process requires adequate heat input, good mixing, and sufficient residence time. Less than optimum conditions may result in only partial combustion.

c. Control by Adsorption

Adsorption is a physical process whereby gas molecules are held on solid surfaces. Certain solids, such as activated alumina, silica gel, and activated carbon, have these properties to the extent that they have practical applications. Adsorbents are for the most part selective in their properties. Polar adsorbents preferentially adsorb water, whereas nonpolar adsorbents are selective for most organic substances. For this reason, activated carbon, a nonpolar adsorbent, is most commonly used to control organic emissions.

d. Control by Absorption

Absorption is the process by which gases or vapors are collected in a relatively nonvolatile liquid absorbent. To be effective, the absorbent should have the capability of holding relatively large quantities of the solute gas at normal temperatures. Because organic absorbents have relatively low capacities, this approach to hydrocarbon control is limited.

e. Control by Condensation

Condensation is the process by which vapors are converted from gases to liquid by cooling. This technique is most suitable for high concentrations of hydrocarbons since substantial quantities of a vapor may coexist with its liquid phase even at the lowest temperature practically obtainable. Condensation for air pollution control is generally used as a pretreatment to reduce the load on a more efficient process such as adsorption or incineration.

f. Control by Substitution of Materials

The substitution of photochemically nonreactive materials as a stationary source control measure has been largely limited to solvents used in degreasing operations, in surface coatings, and in printing inks. In some cases, satisfactory reformulation of products with nonreactive solvents has been difficult, and in other cases the increased costs are greater than those for control equipment.

F. SUMMARY

The hydrocarbons of interest in this document are those that may be encountered in the gas phase in urban atmospheres. In this context, hydrocarbons having a carbon number greater than about 12 are generally not encountered in the atmosphere in sufficiently high gaseous concentrations to be of concern.

Most natural sources of hydrocarbon emissions are biological in nature. A conservative estimate made for the worldwide natural production rate of methane is 3 x 10^8 tons per year. A similar estimate of 4.4 x 10^8 tons per year was made for volatile terpenes and isoprenes. Hydrocarbon background concentration estimates have been made by several authors using a variety of techniques. It appears that nonurban air contains from 0.7 to 1.0 mg/m^3 (1.0 to 1.5 ppm) methane and less than 0.1 ppm each of other hydrocarbons.

Total nationwide technological emissions of hydrocarbons and related organic compounds for the year 1968 were estimated to be 32 x 10^6 tons. Transportation, the largest source category, accounted for 52 percent of this estimate. The miscellaneous source category, principally organic solvent evaporation, was the second largest and represented 27 percent of the total emissions. Industrial processes (14 percent) was third; solid waste disposal (5 percent) was fourth; and fuel combustion in stationary sources (2 percent) was fifth.

Local emissions for 22 metropolitan areas were estimated to range from about 0.05 to 1.3 million tons per year. Transportation sources accounted for 37 to 99 percent of local emissions, and process losses accounted for 1 to 63 percent. Hydrocarbon emissions, therefore, originate primarily from the inefficient combustion of volatile fuels and from their use as process raw materials.

Uncontrolled conventional automobile engines are capable of emitting hydrocarbons by four means: engine exhaust, crankcase blowby, carburetor evaporation, and fuel tank evaporation.

The control of hydrocarbon emissions rests upon the basic principles of: (1) combustion process optimization, (2) recovery by mass transfer, (3) restriction of evaporative loss, and (4) process material and fuel substitution. The first three principles are all applied with varying degrees of success in the control of automobile emissions.

Specific control measures that may be applied to stationary sources include: (1) evaporation prevention, (2) incineration, (3) adsorption, (4) absorption, (5) condensation, and (6) substitution.

G. REFERENCES

1. Stephens, E.R. and F.R. Burleson. Distribution or Light Hydrocarbons in Ambient Air. Presented at the 62nd Annual Meeting of the Air Pollution Control Association. New York. June 22-26, 1969.
2. Neligan, R.E. Hydrocarbons in the Los Angeles Atmosphere. Arch. Environ. Health. *5*:581-591, December 1962.
3. Benson, S.W. Thermochemical Kinetics. New York, John Wiley & Sons, Inc., 1968. 223 p.
4. Wayne, L.G. and T.E. Ernest. Photochemical Smog, Simulated by Computer. Presented at 62nd Annual Meeting of the Air Pollution Control Association. New York. June 22-26, 1969.
5. Scott, W.E. and L.R. Reckner. Atmospheric Reaction Studies in the Los Angeles Basin. Progress Report. November 15, 1968 to January 15, 1969. Scott Research Laboratory. APRAC Project CAPA 7-68. 1969.
6. Altshuller, A.P. and S.P. McPherson. Spectrophotometric Analysis of Aldehydes in the Los Angeles Atmosphere. J. Air Pollution Control Asosc. *13*:109-111, March 1963.
7. Renzetti, N.A. and R.J. Bryan. Atmospheric Sampling for Aldehydes and Eye Irritation in Los Angeles Smog – 1960. J. Air Pollution Control Assoc. *11*:421-424, 427, September 1961.
8. Altshuller, A.P. and J.J. Bufalini. Photochemical Aspects of Air Pollution: A Review. Photochem. Photobiol. *4*(2):97-146, March 1965.
9. Altshuller, A.P. et al. Photochemical Reactivities of N-Butane and Other Paraffinic Hydrocarbons. J. Air Pollution Control Assoc. *19*:787-790, October 1969.
10. Altshuller, A.P. et al. Photochemical Reactivities of Paraffinic Hydrocarbon-Nitrogen Oxide Mixtures Upon Addition of Propylene or Toluene. J. Air Pollution Control Assoc. *19*:791-794, October 1969.
11. Schuck, E.A. and G.J. Doyle. Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide. Air Pollution Foundation. San Marino, Calif. Report Number 29. October 1959. 104 p.
12. Stephens, E.R. and W.E. Scott. Relative Reactivity of Various Hydrocarbons in Polluted Atmospheres. Proc. Amer. Petrol. Inst. *42*:665-670, 1962.

13. Altshuller, A.P. and I.R. Cohen. Presented at the 145th National Meeting of the American Chemical Society. New York. September 1963.
14. Stephens, E.R. et al. Photochemical Reaction Products in Air Pollution. Int. J. Air Water Pollution. *4*(1/2):79-100, June 1961.
15. Schuck, E.A., G.J. Doyle, and J. Endow. Photochemistry of Polluted Atmospheres. Stanford Research Institute. July 1960.
16. Sigsby, J.E. et al. Presented at the 145th National Meeting of the American Chemical Society. New York. September 1963.
17. Stephens, E.R. The Photochemical Olefin – Nitrogen Oxides Reaction. In: Chemical Reactions in the Lower and Upper Atmosphere. New York, Interscience Publishers, 1961, p. 51-69.
18. Tuesday, C.S. The Atmospheric Photooxidation of Trans-Butene-2 and Nitric Oxide. In: Chemical Reactions in the Lower and Upper Atmosphere. New York, Interscience Publishers, 1961, p. 15-49
19. Bufalini, J. J. and A. P. Altshuller. Presented at the 145th National Meeting of the American Chemical Society, Division of Water and Waste Chemistry. New York. September 1963.
20. Leighton, P.A. Photochemistry of Air Pollution. New York, Academic Press, 1961, 300 p.
21. Vrbaski, T. and R.J. Cvetanovic. Relative Rates of Reaction of Ozone with Olefins in the Vapor Phase. Can. J. Chem. *38*:1053-1062, July 1960.
22. Tuesday, C.S. The Atmospheric Photooxidation of Olefins – The Effect of Nitrogen Oxides. Arch. Environ. Health. *7*(2):188-201, August 1963.
23. Kopczynski, S.L. Photooxidation of Alkylbenzene-Nitrogen Dioxide Mixtures in Air. Int. J. Air Water Pollution. *8*:107-120, February 1964.
24. Migeotte, M.V. Spectroscopic Evidence of Methane in the Earth's Atmosphere. Phys. Rev. *73*(5):519-520, March 1, 1948.
25. Koyama, T. Gaseous Metabolism in Lake Sediments and Paddy Soils and Production of Atmospheric Methane and Hydrogen. J. Geophys. Res. *63*(13):3971-3983, July 1, 1963.
26. Ehhalt, D.H. Methane in the Atmosphere. J. Air Pollution Control Assoc. *17*:518-519, August 1967.
27. Robinson, E. and R.C. Robbins. Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants. Stanford Research Institute. February 1968. (Report prepared for American Petroleum Institute, New York, New York).
28. Rasmussen, R.A. and F.W. Went. Volatile Organic Material of Plant Origin in the Atmosphere. Proc. Nat. Acad. Sci. U.S. *53*:215-220, January 1965.
29. Junge, C.E. Air Chemistry and Radioactivity. International Geophysical Series, Van Mieghem, J. (ed.), Vol. 4, New York, Academic Press, 1963. 382 p.
30. Fink, U., D.H. Rank, and T.A. Wiggins. Abundance of Methane in the Earth's Atmosphere. J. Opt. Soc. Amer. *54*:472-474, April 1964.
31. Goldberg, L. and E.A. Muller. The Vertical Distribution of Nitrous Oxide and Methane in the Earth's Atmosphere. J. Opt. Soc. Amer. *43*:1033-1036, November 1953.
32. Stephens, E.R. and F.R. Burleson. Distribution of Light Hydrocarbons in Ambient Air. Presented at the 62nd Annual Meeting of the Air Pollution Control Association. New York. June 22-26, 1969.
33. Cavanagh, L.A., C.F. Schadt, and E. Robinson. Atmospheric Hydrocarbon and Carbon Monoxide Measurements at Point Barrow, Alaska. Environ. Sci. Technol. *3*:251-257, March 1969.
34. Swinnerton, J.W., V. J. Linnenbom, and C.H. Cheek. Distribution of Methane and Carbon Monoxide Between the Atmosphere and Natural Waters. Environ. Sci. Technol. *3*:836-838, September 1969.
35. Altshuller, A.P. and T.A. Bellar. Gas Chromatographic Analysis of Hydrocarbons in the Los Angeles Atmosphere J. Air Pollution Control Assoc. *13*:81-87, February 1963.
36. Altshuller, A.P. et al. Continuous Monitoring of Methane and Other Hydrocarbons in Urban Atmospheres. J. Air Pollution Control Assoc. *16*:87-91, February 1966.
37. National Air Pollution Control Administration, Reference Book of Nationwide Emissions. U.S. DHEW, PHS, CPEHS, NAPCA. Durham, N.C.
38. Mason, D.V. et al. Sources and Air Pollutant Emission Patterns in Major Metropolitan Areas. Presented at the 62nd Annual Meeting of the Air Pollution Control Association. New York. June 22-26, 1969.
39. Data Provided by the National Air Pollution Control Administration, Bureau of Criteria and Standards, NIAPEC, Durham, North Carolina.
40. Grant, E.P. Auto Emissions. Motor Vehicle Pollution Control Board Bulletin. *6*(4):3, 1967.
41. Motor Vehicles, Air Pollution, and Health. A Report of the Surgeon General to the U. S. Congress in Compliance with Public Law 69-498, the Schenck Act. U. S. Dept. of Health, Education, and Welfare, Public Health Service, Division of Air Pollution. Washington, D.C., U.S. Government Printing Office. House Document No. 489, 87th Congress, 2d Session. 1962. 459 p.
42. McReynolds, L.A., H.E. Alquist, and D.B. Wimmer. Hydrocarbon Emissions and Reactivity as Functions of Fuel and Engine Variables (SAE Paper No. 650525). S. A. E. Transactions. *74*:902-911, 1966.

43. Neligan, R.E., P.P. Mader, and L.A. Chambers. Exhaust Composition in Relation to Fuel Composition. J. Air Pollution Control Assoc. *11*:178-186, April 1961.
44. Wetmiller, R.S. and L.E. Endsley, Jr. Effect of Diesel Fuel on Exhaust Smoke and Odor. S. A. E. Transactions. *50*(11):509-520, December 1942.
45. Vogh, J.W. Nature of Odor Components in Diesel Exhaust. J. Air Pollution Control Assoc. *19*(10):773-777, October 1969.
46. Duprey, R.L. Compilation of Air Pollutant Emission Factors. National Center for Air Pollution Control. Durham, N. C. PHS Publication Number 999-AP-42. 1968. 67 p.

CHAPTER 3.

ATMOSPHERIC LEVELS OF HYDROCARBONS AND THEIR RELATED PRODUCTS

A. INTRODUCTION

In the examination of atmospheric hydrocarbon concentrations in relation to photochemical air pollution, several factors must be considered. First, as discussed in Chapter 2, there is an enormous variation in the tendency for different hydrocarbons to enter into the photochemical air pollution reaction sequence. For example, methane is virtuallly inert. Second, the simpler and less laborious atmospheric hydrocarbon detection methods are likely to respond most strongly to methane and other alkanes. Third, methane is often more abundant than all other hydrocarbons combined. There is, in fact, apparently a "geophysical" minimum level of methane, present worldwide, of about 0.7 to 1.0 mg/m^3 (1.0 to 1.5 ppm).[1-3] It is important, then, in assessing photochemical air pollution to be able to discriminate between methane and other more reactive hydrocarbons. Unfortunately, this type of analysis is expensive and time-consuming, so that such data are not abundant. They are available, nevertheless, and in this section such observations are discussed.

B. HYDROCARBONS

Although on occasion all other hydrocarbon concentrations drop to unmeasurably low levels, methane does not. Numerous measurements suggest a worldwide minimum methane concentration of about 0.7 to 1.0 mg/m^3 (1.0 to 1.5 ppm).[3] In inhabited areas, methane levels are often much higher; values of 4 mg/m^3 (6 ppm) or more have been observed.[4]

Yearly averages of monthly maximum 1-hour average total hydrocarbon concentrations recorded at stations that are part of the Continuous Air Monitoring Projects (CAMP) network ranged, for the years 1962 through 1967, from 8 to 17 ppm (as carbon).[5]

Ratios of nonmethane hydrocarbons (as carbon) to methane have been estimated for urban areas, after subtracting 1 ppm from methane values to allow for estimated biogenic background levels.[4] The nonmethane/methane hydrocarbon ratios for several weeks averaged 0.6 in Cincinnati and 1.9 in Los Angeles, although methane values were similar (Figure 3-1). The higher Los Angeles ratios

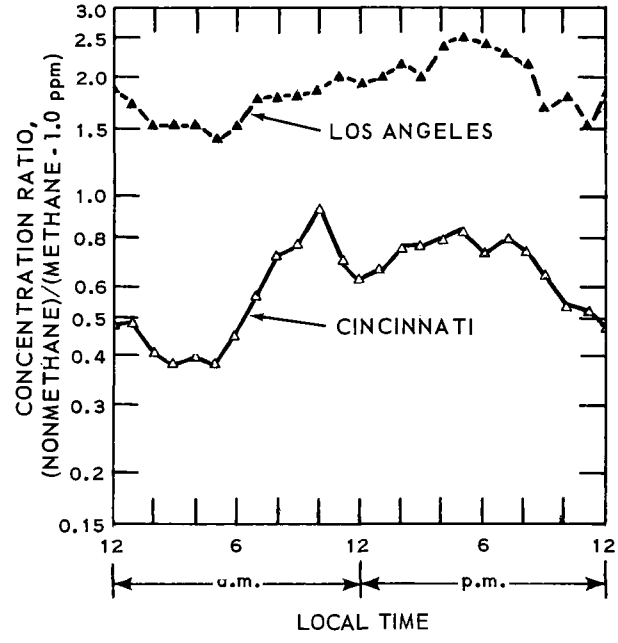

Figure 3-1. Concentration ratios for nonmethane hydrocarbons/methane in Los Angeles (213 hours during October and November, 1964) and Cincinnati (574 hours during September 1964), with 655 μg/m^3 (1 ppm) methane deducted to correct for estimated background biospheric concentration.[4]

may possibly result from local differences in traffic density and solvent losses.

1. Hydrocarbons in Ambient Air

Table 3-1 lists the individual hydrocarbons detected in samples of urban air by gas chromatographic analysis in several investigations.[6-8] Of the 56 compounds detected, 17 were alkanes, 23 alkenes (including two alkadienes), 2 were alkynes, 10 aromatics, 3 cycloalkanes, and 1 was a cycloalkene. The length of this list is limited only by the sensitivity of the analytical methods, and it is certain that many additional hydrocarbon compounds are actually present in urban air. Especially at the higher carbon numbers, the complexity of the chromatographic records becomes so great that the effort to interpret them in terms of individual compounds may be insufficiently rewarding. The listing in Table 3-1 of compounds with carbon numbers of 7 and higher must be considered as only a partial list.

Table 3–1. SOME HYDROCARBONS IDENTIFIED IN AMBIENT AIR

Carbon number	Class	Compound	Reference
1	Alkane	Methane	7
2	Alkane	Ethane	6,7
2	Alkene	Ethylene	6,7
2	Alkyne	Acetylene	6,7
3	Alkane	Propane	6,7
3	Alkene	Propylene	6-8
3	Alkene	Propadiene	7
3	Alkyne	Methylacetylene	7
4	Alkane	Butane	6,7
4	Alkane	Isobutane	6,7
4	Alkene	1-Butene	6,7
4	Alkene	*cis*-2-Butene	6-8
4	Alkene	*trans*-2-Butene	6-8
4	Alkene	Isobutene	6-8
4	Alkene	1,3-Butadiene	6-8
5	Alkane	Pentane	6-8
5	Alkane	Isopentane	6-8
5	Alkene	1-Pentene	6-8
5	Alkene	*cis*-2-Pentene	6-8
5	Alkene	*trans*-2-Pentene	6
5	Alkene	2-Methyl-1-butene	6-8
5	Alkene	2-Methyl-2-butene	6-8
5	Alkene	3-Methyl-1-butene	6
5	Alkene	2-Methyl-1,3-butadiene	6
5	Cycloalkane	Cyclopentane	6,7
5	Cycloalkene	Cyclopentene	6,7
6	Alkane	Hexane	6,7
6	Alkane	2-Methylpentane	6,7
6	Alkane	3-Methylpentane	6,7
6	Alkane	2,2-Dimethylbutane	6,7
6	Alkane	2,3-Dimethylbutane	6,7
6	Alkene	1-Hexene	7
6	Alkene	*cis*-2-Hexene	7
6	Alkene	*trans*-2-Hexene	7
6	Alkene	*cis*-3-Hexene	7
6	Alkene	*trans*-3-Hexene	7
6	Alkene	2-Methyl-1-pentene	7
6	Alkene	4-Methyl-1-pentene	7

Table 3–1 (Continued). SOME HYDROCARBONS IDENTIFIED IN AMBIENT AIR

Carbon number	Class	Compound	Reference
6	Alkene	4-Methyl-2-pentene	7
6	Aromatic	Benzene	7
6	Cycloalkane	Cyclohexane	7
6	Cycloakane	Methylcyclopentane	7
7	Alkane	2-Methylhexane	7
7	Alkane	3-Methylhexane	7
7	Alkane	2,3-Dimethylpentane	7
7	Alkane	2,4-Dimethylpentane	7
7	Aromatic	Toluene	7,8
8	Alkane	2,2,4-Trimethylpentane	7
	Aromatic	*o*-Xylene	8
		m-Xylene	8
		p-Xylene	8
9	Aromatic	*m*-Ethyltoluene	8
		p-Ethyltoluene	8
		1,2,4-Trimethylbenzene	8
		1,3,5-Trimethylbenzene	8
10	Aromatic	*sec*-Butylbenzene	8

All the hydrocarbons above carbon number 4 listed in Table 3-1 are found in gasoline.[9] These and the lower alkenes and acetylenes are also found in automobile exhaust gases. The lower alkanes (methane, ethane, and propane) occur in only trace amounts in auto exhaust gases, but are ordinary constituents of natural gas. Stephens and Burleson have reported that the hydrocarbon composition of their samples resembled that of auto exhaust gases with an addition of natural gas and gasoline vapor.[6] However, samples taken in industrial areas and from near the smoke plume from a brush fire have shown distinctive differences in composition, which should reasonably be attributed to these particular recognized sources. Special studies such as these can be very useful in identifying the importance of various sources as contributors to the pollution of air by hydrocarbons.

2. Diurnal Variation

In Figures 3-2 and 3-3 are shown diurnal patterns for nonmethane hydrocarbons in several cities, averaged over several months.[5,10] In most of these the maximum concentrations at 6:00 to 8:00 a.m. are mainly due to the morning commuter traffic rush. The morning peak is clearest in Denver and Los Angeles, where the automobile is especially important as a means of transportation. Even within a large metropolitan area there may be considerable variation. In Figure 3-3 are shown average diurnal patterns for nonmethane hydrocarbons at three locations in Los Angeles County. There are considerable differences among the three patterns, although the morning maxima are still evident in all. In Table 3-2 the diurnal patterns are given for the C_2 to C_4 hydrocarbons and isopentane, showing the hour-by-hour variations as averaged over some weeks in the Los Angeles smog season. All species listed reach a maximum in the morning, then decline through the midday.[11]

3. Seasonal Variation

Necessary data are not now available for the assessment of seasonal or annual variations in nonmethane hydrocarbon levels. In most instances, total hydrocarbons consist mostly of methane (inert photochemically). Total hydrocarbon concentrations are tabulated for 17 California cities in Table 3-3.[12] It is noteworthy that 14 of these cities show highest hydrocarbon concentrations (averages

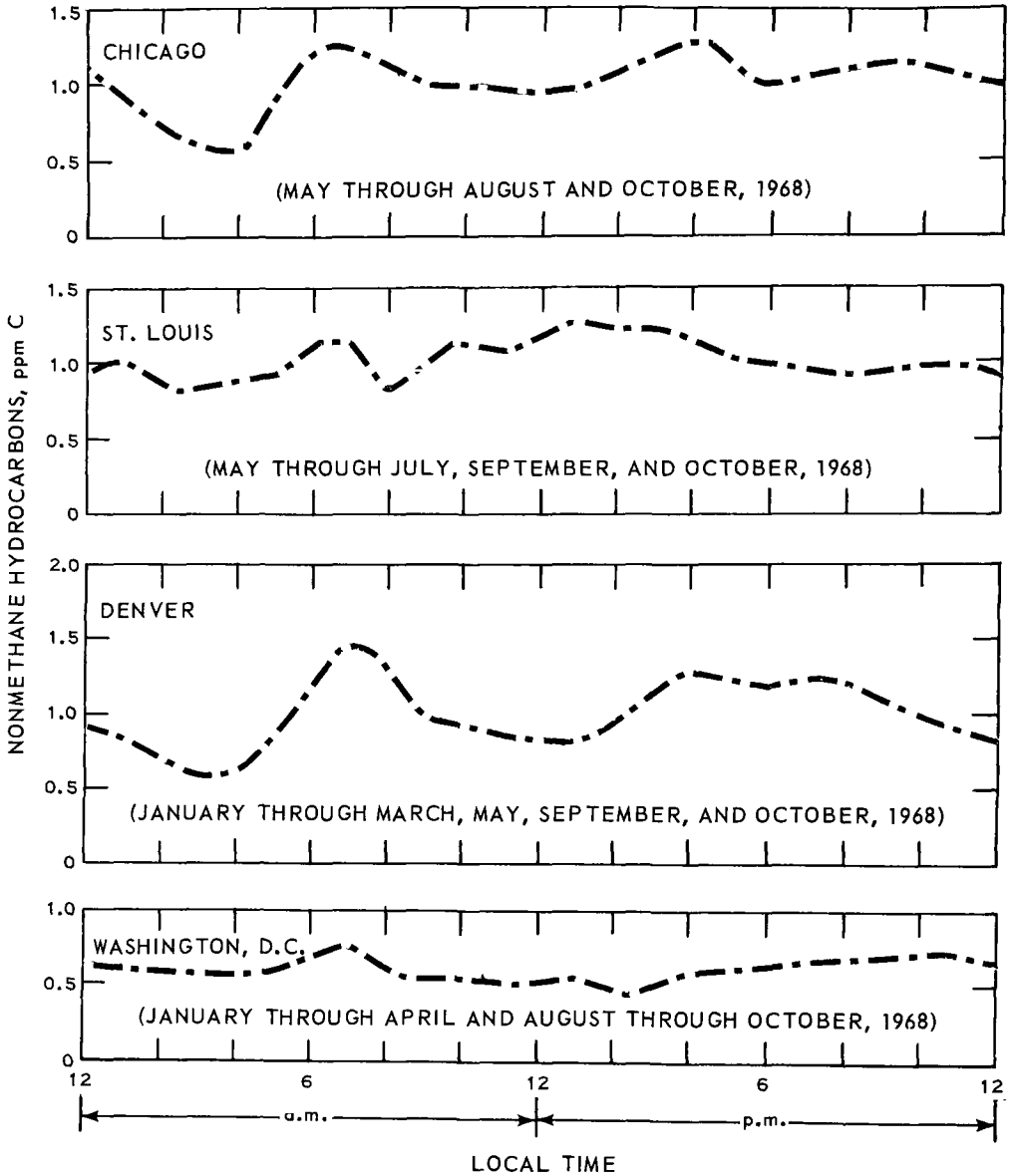

Figure 3-2. Nonmethane hydrocarbons by flame ionization analyzer, averaged by hour of day over several months for various cities.[5]

of maximum hourly averages) in October or November. This is presumably a consequence of the generally similar meteorological conditions along the California Coast. Cities in other parts of the country would be expected to show other patterns, dependent on their particular meteorology.

4. Community Levels

Since routine air monitoring methods do not yet exist for measuring individual hydrocarbons other than methane, special studies have been required to establish existing levels of individual hydrocarbons. For the most part these studies have involved gas chromatographic analysis of periodic samples, by techniques discussed in Chapter 4.

In Table 3-4 concentrations of many individual hydrocarbons as averaged from more than 200 samples from the Los Angeles atmosphere[10] are tabulated. The great predominance of methane is noteworthy. Even

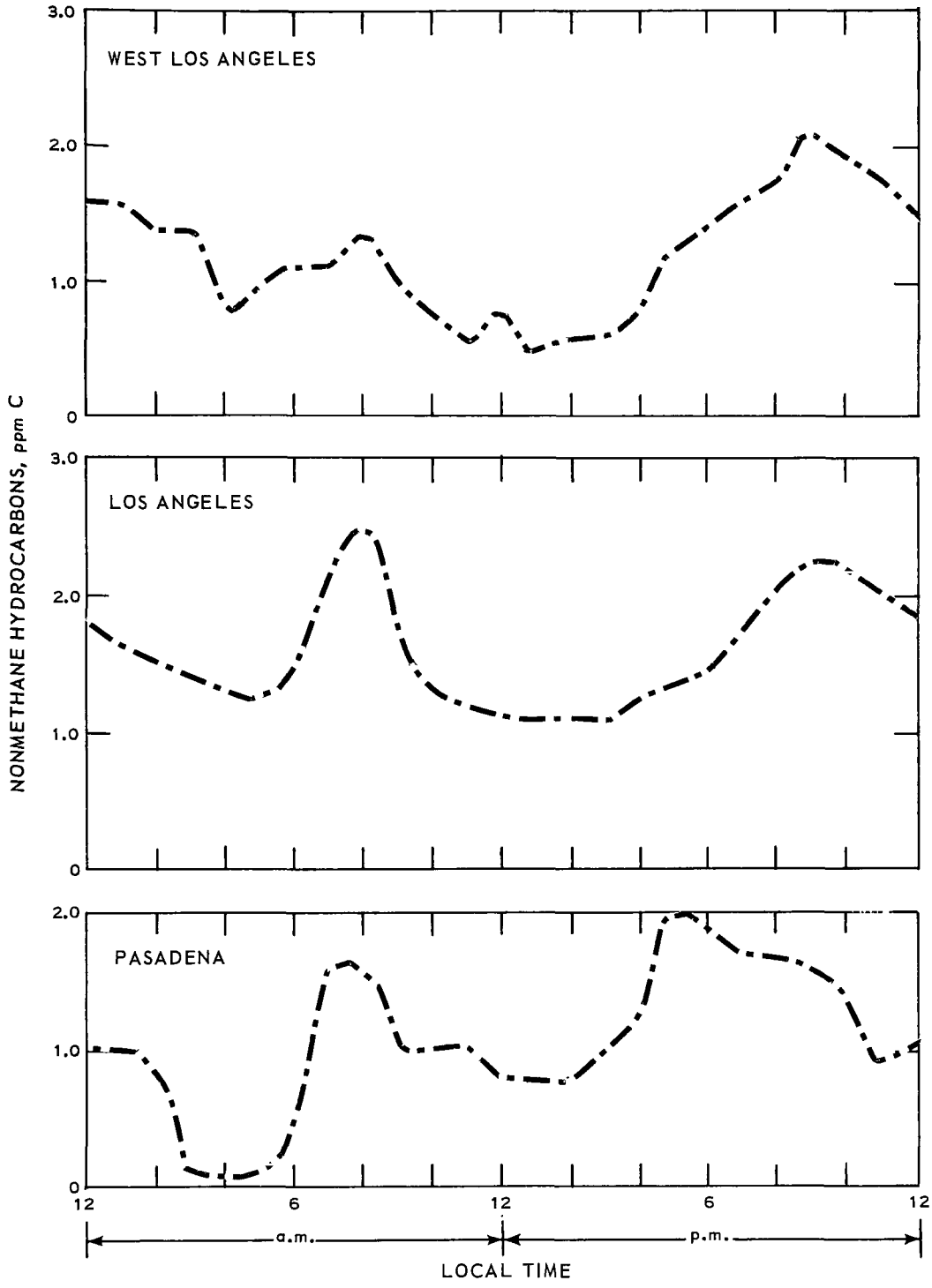

Figure 3-3. Nonmethane hydrocarbons by flame ionization analyzer averaged by hour of day for three Los Angeles county sites, October 1966 through February 1967.[10]

Table 3–2. AVERAGE ATMOSPHERIC LIGHT HYDROCARBON CONCENTRATIONS, BY HOUR, LOS ANGELES, SEPTEMBER THROUGH NOVEMBER, 1967[11]

Local time	No. of days averaged	Hydrocarbon, ppm C								
		Ethane	Ethylene	Acetylene	Propane	Propylene	Isobutane	*n*-Butane	Butylenes	Isopentane
Downtown Los Angeles (DOLA)										
5:00 a.m.	27	0.140	0.031	0.077	0.113	0.025	0.053	0.176	0.032	0.177
6:00 a.m.	28	0.140	0.049	0.112	0.113	0.036	0.061	0.200	0.034	0.224
7:00 a.m.	28	0.151	0.122	0.234	0.125	0.064	0.074	0.300	0.056	0.335
8:00 a.m.	31	0.145	0.102	0.212	0.126	0.054	0.075	0.304	0.049	0.346
9:00 a.m.	15	0.107	0.063	0.141	0.098	0.032	0.063	0.209	0.028	0.249
10:00 a.m.	33	0.126	0.067	0.152	0.118	0.038	0.064	0.260	0.034	0.303
11:00 a.m.	12	0.094	0.039	0.106	0.080	0.025	0.048	0.180	0.021	0.200
Noon	32	0.106	0.039	0.101	0.108	0.020	0.063	0.200	0.015	0.199
1:00 p.m.	16	0.076	0.020	0.068	0.078	0.013	0.044	0.149	0.014	0.162
2:00 p.m.	38	0.094	0.026	0.074	0.097	0.017	0.057	0.156	0.019	0.155
3:00 p.m.	16	0.090	0.026	0.079	0.101	0.016	0.050	0.132	0.020	0.144
4:00 p.m.	34	0.075	0.036	0.095	0.081	0.024	0.046	0.139	0.021	0.141
East San Gabriel Valley (Azusa)										
5:00 a.m.	32	0.143	0.029	0.060	0.087	0.013	0.036	0.101	0.014	0.104
6:00 a.m.	33	0.128	0.017	0.065	0.076	0.015	0.031	0.098	0.012	0.103
7:00 a.m.	30	0.180	0.030	0.103	0.102	0.024	0.041	0.136	0.018	0.144
8:00 a.m.	32	0.118	0.037	0.101	0.084	0.020	0.044	0.149	0.018	0.160
9:00 a.m.	18	0.093	0.031	0.079	0.065	0.015	0.036	0.114	0.015	0.114
10:00 a.m.	32	0.086	0.024	0.069	0.066	0.019	0.040	0.132	0.015	0.136
11:00 a.m.	18	0.090	0.021	0.057	0.062	0.011	0.037	0.107	0.010	0.101
Noon	30	0.089	0.015	0.050	0.058	0.010	0.040	0.098	0.009	0.093
1:00 p.m.	16	0.111	0.016	0.066	0.067	0.018	0.046	0.121	0.017	0.111
2:00 p.m.	42	0.097	0.018	0.064	0.075	0.017	0.050	0.121	0.018	0.117
3:00 p.m.	16	0.092	0.020	0.065	0.075	0.015	0.081	0.175	0.015	0.125
4:00 p.m.	37	0.079	0.021	0.058	0.076	0.014	0.041	0.122	0.014	0.123

on a carbon atom basis, methane constitutes about half the total hydrocarbon. In the remainder, the staturated hydrocarbons (relatively unreactive photochemically) are predominant. These samples were generally taken just before or during the morning traffic rush.

The proportion of aromatic to aliphatic hydrocarbons and some of the proportions among the aromatics have been studied.[13] Table 3-5 shows, again for Los Angeles, averages for concentrations of aromatics observed in the atmosphere over several weeks sampling.

There has been little comparison of hydrocarbon concentrations from various geographical locations. The study of Altshuller[4] et al. compared methane and nonmethane hydrocarbons in Cincinnati and Los Angeles (see Figure 3-1). Stephens and Burleson[6] have determined the hydrocarbon compositions for a number of air samples from widely scattered locations: Hawaii, Denver, New York, and Monterey-Salinas (California), as well as Riverside in Southern California. There are apparently substantial differences in the proportions of individual hydrocarbons present, which may sometimes, but not always, be related to known differences in source contributions and extent of atmospheric reaction.

Laboratory work shows that in the photochemical reaction system the rates of disappearance or reaction of various hydrocarbons differ widely. These differences may be related to some extent to structure: olefins and most aromatics are reactive; higher alkanes are not very reactive; and benzene, acetylene, and lower alkanes are virtually inert.[14] In the atmosphere these differences have been harder to observe. Since the general effects of meteorological dilution and continuing source emission obscure the effects of reaction, Stephens and Burleson[15] studied the changes

Table 3–3. MEAN OF DAILY MAXIMUM HOURLY AVERAGE TOTAL HYDROCARBON CONCENTRATIONS (as ppm methane), 17 CALIFORNIA CITIES, 1968-1969[12]

	1968							1969				
	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
San Francisco Bay Area												
Richmond	5	6	4	6	9[a]	8	9[a]	8	8	7	6	4
San Rafael	4	4	5	6	13[a]	10	9	6	6	8	6	6
San Francisco	5	4	N.A.[b]	5	7[a]	6	6	5	5	5	5	4
Redwood City	N.A.	12	14	16[a]	13	11	9	7	6	7	5	5
San Jose	4	4	4	6	8[a]	8[a]	7	7	5	6	6	5
Central Valley												
Fresno	3	3	3	4	6[a]	5	5	4	4	5	3	3
Bakersfield	7	7	8	10[a]	10[a]	9	10[a]	7	8	7	6	6
Sacramento	4	4	5	5	10[a]	7	7	6	5	7	4	4
Stockton	3	4	4	5	6[a]	4	5	4	3	5	4	4
Central Coast												
Salinas	3	2	3	3	3	4[a]	4[a]	3	3	3	2	N.A.
Monterey	3	2	3	3	4[a]	4[a]	4[a]	4[a]	4[a]	3	3	3
Southern California												
Los Angeles (downtown)	4	5	4	5	6	7[a]	7[a]	6	4	5	4	3
Azusa	4	4	5	5	6[a]	5	5	4	4	5	5	5
Anaheim	4	5	5	6	8	10[a]	10[a]	7	7	7	5	3
Riverside	5	5	7	6	7	7	8	7	9[a]	8	4	4
San Bernardino	4	5	5	6[a]	6[a]	6[a]	6[a]	5	N.A.	6[a]	5	4
San Diego	3	N.A.	4	5	7	7	9[a]	7	6	6	5	3

[a]Highest mean concentration for 12-month period.
[b]N.A. = Not available.

in concentrations in trappped atmospheric samples, artifically irradiated, and found that reactivities were much as expected from laboratory findings. Table 3-6 displays these results.

In another attempt to relate atmospheric hydrocarbon concentrations to other photochemical air pollution effects, Gordon[11] et al. examined the diurnal patterns of several pollutants recorded in the Fall of 1967 at two California sampling sites, downtown Los Angeles and Azusa. The measurements taken were segregated according to the maximum daily oxidant concentration. The high oxidant (HiOx) category included those days on which the maximum oxidant level was above 590 $\mu g/m^3$ (0.30 ppm) at either station. The low oxidant (LoOx) category included those days when neither station reached an oxidant maximum as high as 390 $\mu g/m^3$ (0.20 ppm). Some of the results of this study are shown in Figure 3-4. Acetylene, C_2 to C_4 olefins, and carbon monoxide (curves a, b, and c) all peak at around 8:00 a.m. at both sites on "HiOx" days, and decline rapidly thereafter. Since acetylene and carbon monoxide are known to be very unreactive photochemically, their decrease during the day is attributable to ventilation and a decrease in emissions.

The similar shape for the olefin curve suggests that olefin depletion by reaction is not more important than by other mechanisms. Some of the curves for alkanes (e and f) and oxides of nitrogen (d) peak later and decline much more slowly. This suggests that there is further production of these components from

Table 3–4. AVERAGE HYDROCARBON COMPOSITION, 218 AMBIENT AIR SAMPLES, LOS ANGELES, 1965[10]

Compound	Concentration ppm	Concentration ppm (as carbon)
Methane	**3.22**	**3.22**
Ethane	0.098	0.20
Propane	0.049	0.15
Isobutane	0.013	0.05
n-Butane	0.064	0.26
Isopentane	0.043	0.21
n-Pentane	0.035	0.18
2,2-Dimethylbutane	0.0012	0.01
2-Methylpentane		
2,3-Dimethylbutane	0.014	0.08
Cyclopentane	0.004	0.02
3-Methylpentane	0.008	0.05
n-Hexane	0.012	0.07
Total alkanes (excluding methane)	**0.3412**	**1.28**
Ethylene	0.060	0.12
Propene	0.018	0.05
1-Butane + Isobutylene	0.007	0.03
trans-2–Butene	0.0014	0.01
cis-2–Butene	0.0012	Negligible
1-Pentene	0.002	0.01
2-Methyl-1-Butene	0.002	0.01
trans-2-Pentene	0.003	0.02
cis-2-Pentene	0.0013	0.01
2-Methyl-2-Butene	0.004	0.02
Propadiene	0.0001	Negligible
1,3-Butadiene	0.002	0.01
Total alkenes	**0.1020**	**0.29**
Acetylene	0.039	0.08
Methylacetylene	0.0014	Negligible
Total acetylene	**0.0404**	**0.08**
Benzene	0.032	0.19
Toluene	0.053	0.37
Total aromatics	**0.0850**	**0.56**
Total	**3.7886**	**5.43**

different sources than those emitting acetylene and CO (mainly auto exhausts). Curve g shows oxidation development peaking hours later than other components, as expected for a reaction product. Oxidant levels for Azusa are always equal to or greater than those at downtown Los Angeles, even in morning hours, although primary pollutant levels of hydrocarbons and oxides of nitrogen are higher at downtown Los Angeles until well after noon. This shows the complexity of the reaction system.

These curves also illustrate an apparent anomaly examined by Neligan[7] and by Stephens and Burleson.[6] In qualitative terms auto exhaust, gasoline evaporation, and nat-

Table 3–5. AVERAGE AND HIGHEST CONCENTRATION MEASURED[13] FOR VARIOUS AROMATIC HYDROCARBONS IN LOS ANGELES, 26 DAYS, SEPTEMBER THROUGH NOVEMBER, 1966

Aromatic hydrocarbon	Average concentration, ppm	Highest measured concentration, ppm
Benzene	0.015	0.057
Toluene	0.037	0.129
Ethylbenzene	0.006	0.022
p-Xylene	0.006	0.025
m-Xylene	0.016	0.061
o-Xylene	0.008	0.033
i-Propylbenzene	0.003	0.012
n-Propylbenzene	0.002	0.006
3- and 4-Ethyltoluene	0.008	0.027
1,3,5-Trimethylbenzene	0.003	0.011
1,2,4-Trimethylbenzene, and *i*-Butyl- and *sec*-Butylbenzene	0.009	0.030
tert-Butylbenzene	0.002	0.006
Total aromatics	0.106	0.330

ural gas sources are adequate to explain observed hydrocarbon components. Quantitatively, however, there are more light alkanes present, especially propane, than can be explained by the analysis of samples from these sources. There may be an additional source not yet identified, or the samples used for analysis may not be sufficiently representative.

C. SECONDARY CONTAMINANTS

The photochemical interaction of organic materials in the atmosphere with oxides of nitrogen, leads to numerous products, including oxidants such as ozone, carbonyl compounds, and peroxyacyl nitrates. The oxidants are discussed fully in a separate criteria document, and will therefore only be referred to here as required in the discussion of other aspects of hydrocarbon behavior.

1. Aldehydes

Of all the principal reaction products formed in the atmosphere by photochemical processes, the aldehydes are among the most poorly quantified. By far most of the available data are from Los Angeles, where for the period 1951 through 1957 aldehydes were regularly measured by manual techniques.[16] Total aldehydes was determined by the bisulfite procedure[17] and reported as formaldehyde; formaldehyde was determined by the chromotrophic acid procedure.[18] Table 3-7 shows the range of yearly maximum 1-hour average concentrations obtained over this 7-year period. Typical maximum concentrations were nearer the low end of the range, although insufficient data are available to give a complete characterization.

A study in Los Angeles County during the period July to November of 1960 provided additional data on total aldehydes, formaldehyde, and acrolein.[19] Total aldehydes ranged up to 0.36 ppm for a 10-minute sample, but formaldehyde did not exceed 130 $\mu g/m^3$ (0.10 ppm). Typical aldehyde concentrations were near 0.10 ppm on many days. The maximum acrolein value was 25.2 $\mu g/m^3$ (0.011 ppm), with most values being less than half that amount.

Diurnal variations in aldehydes are apparent for analytical data obtained in Los Angeles from September to November, 1961.[20] These data are shown in Table 3-8. The concentrations show an early rise, a broad plateau or maximum through most of the day, and a decrease in the afternoon. Data

Table 3–6. COMPARISON OF RESULTS FROM ULTRAVIOLET IRRADIATION OF AMBIENT AIR SAMPLES[15]

Compounds	Concentration, ppm					
	12/22/65			3/3/66		
	0 hr	24 hr	% remaining	0 hr	24 hr	% remaining
Ethane	0.0385	0.0384	0.0995	0.0376	0.0352	0.0937
Ethene	0.1342	0.0320	0.0238	0.0512	0.0126	0.0246
Propane	0.0174	0.0152	0.0875	0.0146	0.0114	0.0782
Propene	0.0354	0.0014	0.0040	0.0156	0.0014	0.0090
Propane	0.0216	0.0172	0.0796	0.0130	0.0104	0.0800
Propene	0.0484	0.0020	0.0041	0.0134	0.0006	0.0045
Isobutane	0.0252	0.0172	0.0684	0.0074	0.0048	0.0650
n-butane	0.1190	0.0785	0.0660	0.0448	0.0272	0.0607
Acetylene	0.3105	0.2620	0.0846	0.0696	0.0568	0.0816
1-butene	0.0064	0.0005	0.0078	0.0022	0.0004	0.0181
Isobutene	0.0118	0.0007	0.0059	0.0040	0.0004	0.0100
trans-2-butene	0.0060	0.0	0.0	0.0014	0.0	0.0
Isopentane	0.0936	0.0464	0.0495	0.0276	0.0136	0.0493
cis-2-butene	0.0045	0.0	0.0	0.0010	0.0	0.0
n-pentane[a]	0.0600	0.0300	0.0500	0.0186	0.0058	0.0312
1,3-butadiene	0.0090	0.0	0.0	0.0024	0.0	0.0
Methyl acetylene	0.0095	0.0050	0.0526	0.0020	0.0012	0.0600
2,2-dimethyl butane	0.0023	0.0017	0.0740	0.0006	0.0004	0.0666
1-pentene	0.0050	0.0	0.0	0.0010	0.0	0.0
2-methyl butene-1	0.0089	0.0	0.0	0.0020	0.0	0.0
trans-2-pentene	0.0055	0.0	0.0	0.0016	0.0	0.0
2,3-dimethyl butane	0.0013	0.0010	0.0770	0.0012	0.0010	0.0832
2-methyl pentane[b]	0.0340	0.0140	0.0412	0.0084	0.0036	0.0429
3-methyl pentane[c]	0.0347	0.0088	0.0253	0.0088	0.0022	0.0275
Cyclopentane	0.0060	0.0029	0.0484	0.0014	0.0010	0.0275
n-hexane	0.0250	0.0094	0.0375	0.0072	0.0034	0.0473
Cyclopentene	—	—	—	0.0024	0.0	0.0

[a]Contains 3-methyl butene-1.
[b]Contains *cis*-2-pentene.
[c]Contains 2-methyl butene-2.

from a 1968 study at two sites east of downtown Los Angeles are shown in Figure 3-5 for a single day.[21] In this work it is apparent that formaldehyde contributes the bulk of the aliphatic aldehyde concentration, whereas the acrolein concentration is less than one-tenth that of formaldehyde.

In these few available studies of ambient levels of aldehydes, the ratio of formaldehyde to total aldehydes showed no consistent value, ranging from about 10 percent in one study[19] to 90 percent in another.[21] This inconsistency may be attributable in part to the use of different methods for analyzing aldehydes.

2. Aerosols

Cities in the United State with a population greater than 400,000 have an average atmospheric particulate burden[22] of about 120 $\mu g/m^3$. Characteristics of atmospheric particulates are described in AP-49, *Air Quality Criteria for Particulate Matter.*[22] Some particulate matter is organic and some inorganic. The national average content of suspended particulates from 1960 through 1965 was 6.5 percent benzene-solubles; the total organic content might be several times this, depending on its geographical origin. Some specific comparisons for selected cities are shown in Table 3-9. Total suspended particulates for the cities

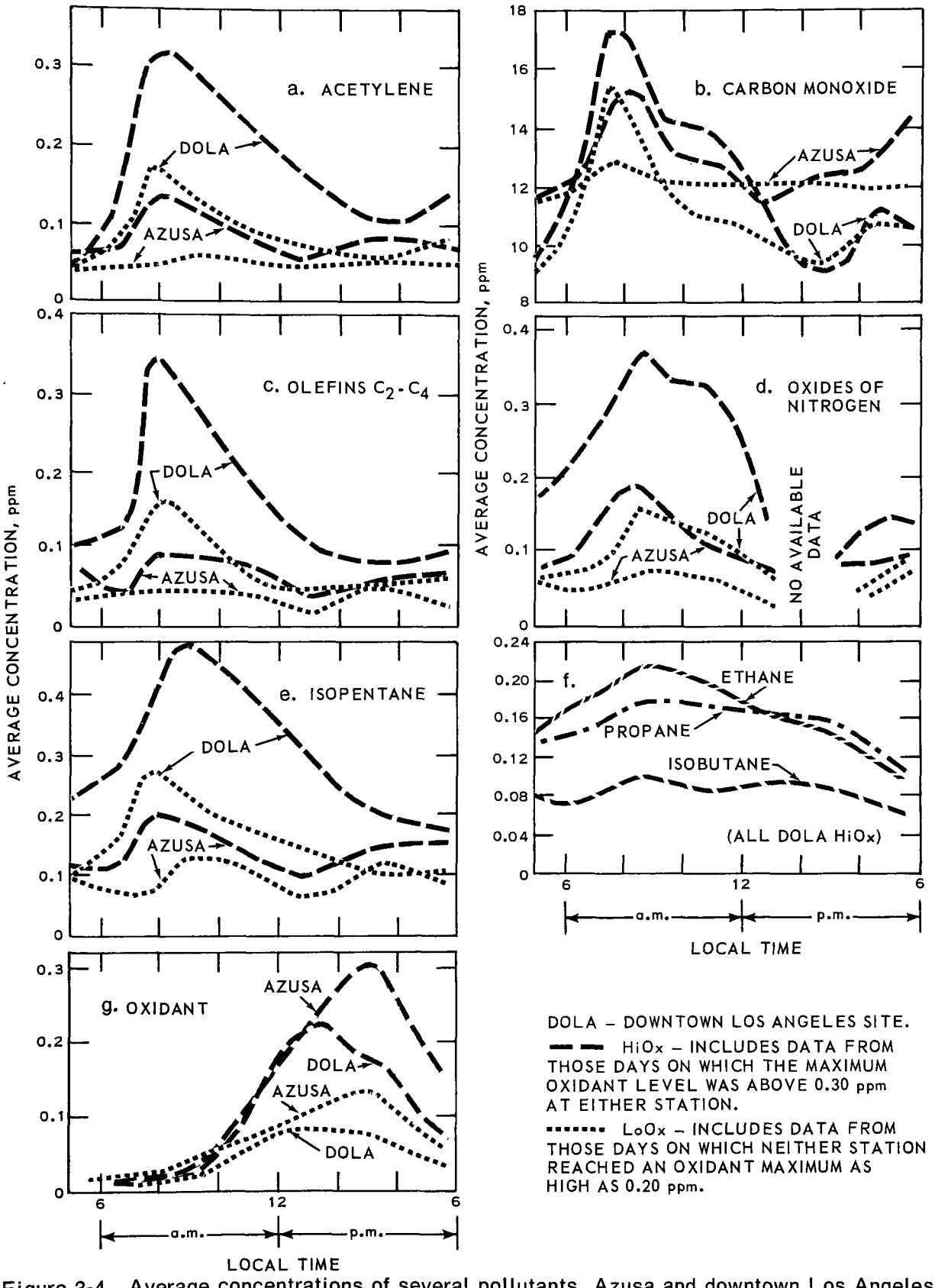

Figure 3-4. Average concentrations of several pollutants, Azusa and downtown Los Angeles, September through November, 1967.[11]

Table 3–7. RANGE OF YEARLY MAXIMUM 1-HOUR AVERAGE CONCENTRATIONS OF ALDEHYDES AND FORMALDEHYDE, LOS ANGELES COUNTY STATIONS, 1951 THROUGH 1957[16]

Year	Concentration range, ppm	
	Formaldehyde	Total aldehydes
1951	0.05 - 0.12	0.26 - 0.67
1952		0.20 - 0.27
1953		0.25 - 1.20
1954		0.39 - 0.80
1955		0.47 - 1.28
1956		0.51 1.30
1957		0.27 - 0.47

shown are comparable, but the amounts of benzene- solubles and of nitrates are highest in Los Angeles, whereas New York has the highest sulfate levels. The Los Angeles loading is produced largely from automobile exhaust with only moderate amounts produced by the consumption of heavy fuel oil (and no coal); in New York much sulfur-containing coal was burned during the period covered.

In Los Angeles, the nitrate content of particulate matter is strikingly higher than in the other cities. There is reason to suspect that this is due to the photooxidation of oxides of nitrogen in the photochemical reaction sequence. The benzene-soluble particulate concentration also is higher in Los Angeles than in any other of 60 standard metropolitan statistical areas of the United States, although Los Angeles ranks only twelfth in total concentrations of particulate matter. This suggests that organic aerosol material, photochemically generated, may be quantitatively significant in the Los Angeles atmosphere.

It has been suggested that sulfur dioxide may be oxidized to sulfates more rapidly in the presence of photochemical oxidants than otherwise. Without further study of emission variables, the available information can yield no evidence on this point.

D. SUMMARY

Air quality within a metropolitan region, on a statistical basis, shows gradients associated with prevailing patterns of wind movement. For primary pollutants, the greatest concentrations are to be found, on the average, in the near vicinity of the most prolific sources of emissions. For the secondary contaminants of the photochemical air pollution complex, the same generalization does not hold. Maximum concentrations of such

Table 3–8. AVERAGE ALDEHYDE CONCENTRATIONS BY HOUR IN LOS ANGELES,[20] SEPTEMBER 25 THROUGH NOVEMBER 15, 1961

Sampling time	Formaldehyde		Acrolein	
	Number of days	Average concentration, ppm	Number of days	Average concentration, ppm
7:00 a.m.	7	0.041	2	0.007
8:00 a.m.	18	0.043	3	0.009
9:00 a.m.	21	0.045	3	0.009
10:00 a.m.	28	0.044	5	0.008
11:00 a.m.	27	0.051	5	0.008
Noon	23	0.044	3	0.005
1:00 p.m.	25	0.041	7	0.008
2:00 p.m.	27	0.034	5	0.007
3:00 p.m.	25	0.026	4	0.004
4:00 p.m.	15	0.019	5	0.004

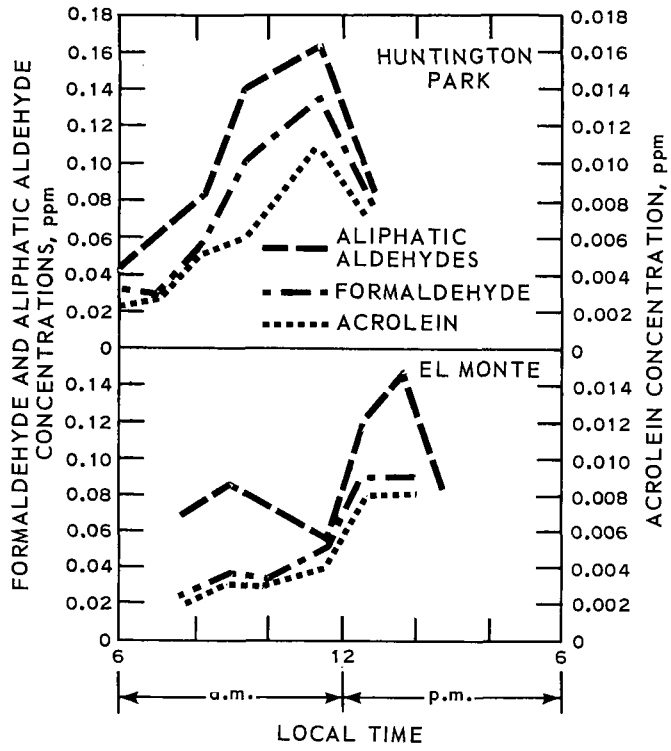

Figure 3-5. Hourly aldehyde concentrations at two Los Angeles sites, October 22, 1968.[21]

Table 3–9. COMPARISON OF COMPOSITION OF SUSPENDED PARTICULATE AIR SAMPLES FROM FIVE UNITED STATES CITIES[22]

Component	Year	Geometric mean concentration, $\mu g/m^3$				
		Los Angeles	Denver	Chicago	New York	Wash.
Total suspended particulates	1961 through 1965	146	147	177	135	104
Benzene-soluble organics, (% of total particulates)	1961 through 1965	15.5 (10.6)	11.7 (8.0)	9.5 (5.4)	10.1 (7.5)	9.4 (9.0)
Nitrates	1962	8.7	1.4	N.A.[a]	N.A.	1.2
	1963	8.3	1.9	1.1	2.3	2.1
	1964	N.A.	2.0	2.0	1.8	1.7
Sulfates	1962	12.9	2.2	N.A.	N.A.	11.0
	1963	6.9	3.6	15.2	25.0	13.1
	1964	N.A.	3.0	16.7	28.7	8.0

[a]N.A. = not available.

photochemical products as aldehydes, nitrogen dioxide, peroxyacyl nitrates, and especially ozone, are very likely to be displaced by 10 or 20 miles from the areas in which the effective primary contaminants were emitted, and residual effects will be observed even farther downwind.

Yearly averages of monthly maximum 1-hour average hydrocarbon concentrations, including methane, recorded continuously in various stations of the CAMP network, have reached 8 to 17 ppm (as carbon), but at least half of this amount is probably the unreactive methane component in all cases. Thus concentrations of 10 ppm (as carbon) or less of nonmethane hydrocarbons can give rise to observed concentrations of secondary photochemical contaminants in urban atmospheres.

In a series of 200 samples taken in one urban location, average concentrations of the most abundant hydrocarbons were as follows (in ppm as carbon): methane, 3.22; toluene, 0.37; *n*-butane, 0.26; *i*-pentane, 0.21; ethane, 0.20; benzene, 0.19; *n*-pentane, 0.18; propane, 0.15; ethylene, 0.12. Among classes of hydrocarbons, the alkanes predominate, even if methane is excluded. They are followed by the aromatics, olefins, acetylene, and alicyclics.

The diurnal variation of hydrocarbon concentrations resembles that of carbon monoxide (at stations in the Los Angeles area) in having a pronounced maximum, which appears usually between 6:00 and 8:00 a.m. PST. It is not, however, parallel to the diurnal variation of secondary contaminants, particularly ozone, which typically show a pronounced maximum in the afternoon. This difference in behavior is characteristic of the photochemical air pollution complex.

Observed concentrations of photochemical oxidants are reviewed in detail in the companion document, AP-63, *Air Quality Criteria for Photochemical Oxidants.* For nonoxidant photochemical secondary contaminants, available information is limited to results of special studies on aldehydes in the Los Angeles area. These show that yearly maximum 1-hour average total aidehyde concentrations range from 0.20 to 1.30 ppm and that the analogous formaldehyde concentrations range from 60 to 150 $\mu g/m^3$ (0.05 to 0.12 ppm). Hourly average acrolein concentrations range from 10 to 270 $\mu g/m^3$ (0.004 to 0.010 ppm) in various other studies. The ratio of formaldehyde to the total aldehyde index has been reported at from about 10 percent to about 90 percent. Much of the variation is undoubtedly caused by the use of different analytical methods in the different investigations.

E. REFERENCES

1. Cavanagh, L. A., C. F. Schadt, and E. Robinson. Atmospheric Hydrocarbon and Carbon Monoxide Measurements at Point Barrow, Alaska. Environ. Sci. Technol. 3:251-257, March 1969.
2. Ehhalt, D. H. Methane in the Atmosphere. J. Air Pollution Control Assoc. *17*: 518-519, August 1967.
3. Swinnerton, J. W., V. J. Linnenbom, and C. H. Cheek. Distribution of Methane and Carbon Monoxide Between the Atmosphere and Natural Waters. Environ. Sci. Technol. *3*:836-838, September 1969.
4. Altshulller, A. P. et al. Continuous Monitoring of Methane and Other Hydrocarbons in Urban Atmospheres. J. Air Pollution Control Assoc. *16*:87-91, February 1966.
5. 1962-1967 Summary of Monthly Means and Maximums of Pollutant Concentrations, Continuous Air Monitoring Projects, National Air Surveillance Networks. U.S.DHEW, PHS, NAPCA. Pub. No. APTD 69-1, April 1969.
6. Stephens, E. R. and F. R. Burleson. Distribution of Light Hydrocarbons in Ambient Air. Presented at 62nd Annual Meeting of the Air Pollution Control Association. New York. June 22-26, 1969.
7. Neligan, R. E. Hydrocarbons in the Los Angeles Atmosphere. Arch. Environ. Health. *5*:581-591, December 1962.
8. Altshuller, A. P. et al. A Technique for Measuring Photochemical Reactions in Atmospheric Samples, Science. (Submitted for publication.)
9. Los Angeles County Air Pollution Control District. A Study of Low Visibilities in the Los Angeles Basin, 1950-1961. Air Quality Report No. 53, 1964.
10. Laboratory Data, 1966-1967. Los Angeles County Air Pollution Control District.
11. Gordon, R. J., M. Mayrsohn, and R. M. Ingels. C_2- C_5 Hydrocarbons in the Los Angeles Atmos-

phere. Environ. Sci. Technol. *2*:1117-1120, December 1968.

12. California Air Quality Data, 1968-1969. California Air Resources Board.

13. Lonneman, W. A., T. A. Bellar and A. P. Altshuller. Aromatic Hydrocarbons in the Atmosphere of the Los Angeles Basin. Environ. Sci. Technol. *2*:1017-1020, November 1968.

14. Altshuller, A. P. and J. J. Bufalini. Photochemical Aspects of Air Pollution: A Review. Photochem. Photobiol. *4*(2):97-146, March 1965.

15. Stephens, E. R. and F. R. Burleson. Analysis of the Atmosphere for Light Hydrocarbons. J. Air Pollution Control Assoc. *17*:147-153, March 1967.

16. Dickinson, J. E. Air Quality of Los Angeles County. Los Angeles County Air Pollution Control District. Los Angeles, Calif. Technical Progress Report, Vol. II. February 1961.

17. Laboratory Methods: Aldehydes. Los Angeles County Air Pollution Control District. California. Method 5-46. 1958.

18. Laboratory Methods: Formaldehyde. Los Angeles County Air Pollution Control District. California. Method 8-53. 1958.

19. Renzetti, N. A. and R. J. Bryan. Atmospheric Sampling for Aldehydes and Eye Irritation in Los Angeles Smog–1960. J. Air Pollution Control Assoc. *11*:421-424. 427, September 1961.

20. Altshuller, A. P. and S. P. McPherson, Spectrophotometric Analysis of Aldehydes in the Los Angeles Atmosphere. JAPCA *13*(3):109-111, 1963.

21. Atmospheric Reaction Studies in the Los Angeles Basin – Vol. I. Scott Research Laboratories, Inc. for Coordinating Research Council, Inc. NAPCA Contract No. CPA 22-69-19. 1969.

22. Air Quality Criteria for Particulate Matter. U.S. DHEW, PHS, EHS, National Air Pollution C ontrol Administration. Washington, D. C. Publication Number AP-49. 1969.

CHAPTER 4.

GENERAL STANDARDIZATION AND ANALYSIS METHODS

A. INTRODUCTION

For most common gaseous air pollutants, the analyst must develop a specific analytical method for one or at most a few related species.[1-3] Thus for many pollutants both simple manual and complex instrumental methods are available. This is not the case with hydrocarbons, for the complexity of the mixture of the compounds that may be present demands more sophisticated instrumentation and techniques for measurement.

One instrumental technique can measure the total hydrocarbon concentration of the atmosphere. The value of the data obtained is severely limited, however, because the high background level of naturally occurring methane obscures the variation in levels of reactive hydrocarbon species, which, because they may participate in photochemical reactions, are usually of principal interest. While simple attempts to eliminate the methane influence have had some success, only specific analysis provides the data needed to delineate properly and fully the nature of atmospheric photochemistry and to evaluate the relative contributions of various sources.[4]

B. CALIBRATION TECHNIQUES

1. Dynamic

Calibration at regular intervals is required for all analytical methods. It may be dynamic or static. Dynamic calibration involves passing known, realistic concentrations of the pollutant in air into the system as if it were an actual sample. This technique may be fairly difficult because of the very low concentrations of some pollutants and the reactivity or condensability of others.

Standard calibration gases in high-pressure steel cylinders are most commonly used to calibrate hydrocarbon analyzers. The gas is diluted in the cylinder to the desired concentration and then fed directly to the analyzer. Common hydrocarbons diluted to atmospheric concentration ranges are available commercially. Commercial mixtures should always be checked against a reference standard; or, if this is not possible, they should at least be checked by an independently calibrated hydrocarbon analyzer.

Various gas dilution systems have been described.[5] A fairly simple method recently developed utilizes permeation tubes;[6] this method is suitable for pollutants that can be condensed at moderate pressures in plastic tubes. The pollutant will effuse through the walls of a tube made of a specific plastic at a rate dependent upon tube surface area and temperature. To generate a known dynamic concentration, air is passed at a known rate over the permeation tube in a thermostated vessel. The tube may be calibrated gravimetrically if it is held at constant temperature, and the permeation rate remains constant as long as the tube contains appreciable liquid.

Another dynamic calibration technique involves the addition of a measured amount of pollutant to a known fixed volume of air in a large vessel. The addition may be made by syringe injection or by crushing a weighed glass ampoule containing the pollutant. If the vessel is rigid, it must be large relative to the amount of sample to be withdrawn. Bags made of plastics, which have the advantage of collapsing as the sample is withdrawn, may also be used. Bags must be made of an inert material to avoid changes in concentration through absorption or reaction with the walls of the bag.

Only dynamic calibration tests the integritiy of intake lines, flow-measuring devices, filters, pumps, and other components of the analyzer that may contaminate or alter the sample before it reaches the sensor.

2. Static

In static calibration, a standard solution of the pollutant, a substance that will generate the pollutant, or the final reaction product may be used. Static calibration is useful for preliminary standardization of a method and for the adjustment of photometric sensors, but the only adequate calibration is by dynamic techniques.

C. METHODS FOR ANALYSIS OF TOTAL HYDROCARBONS

1. Flame Ionization

Originally developed as a detector for gas chromatography, the flame ionization technique (FID) was later adapted for total hydrocarbon analysis.[7] In the technique, a sensitive electrometer detects the increase in ion intensity resulting from the introduction into a hydrogen flame of a sample of air containing any organic compound (e.g., hydrocarbons, aldehydes, alcohols). The response is approximately in proportion to the number of organically bound carbon atoms in the sample. The FID is essentially a carbon atom counter, but its response to carbon atoms in different compounds is nonlinear. As a result, FID data are usually expressed as the calibration gas used: for example, parts per million of carbon as methane. Carbon atoms bound to oxygen, nitrogen, or halogens give reduced or no response. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor; but there is an oxygen effect, which can be minimized by appropriate operating conditions. The instrument also responds to hydrocarbon derivatives approximately according to the proportion of carbon atoms bound to carbon or hydrogen.

The response of the FID is rapid and, with careful calibration, is sensitive to a fraction of a ppm carbon as methane. The variations in response to various hydrocarbons and derivatives must be accounted for in data evaluation.[8] Practically all continuous hydrocarbon analyzers in use today utilize the flame ionization detector as the sensing element. The flame ionization hydrocarbon analyzer is generally accepted by the National Air Pollution Control Administration at the present time as the method of reference for the determination of total hydrocarbons.

2. Spectrophotometric Methods

Spectrophotometric methods are usually applied to samples concentrated by freeze-out or other techniques. The principal problem encountered with their use is one of calibration. In many cases hexane is chosen as a calibration compound to represent the whole hydrocarbon class. In infrared spectrophotometric methods, the reading is made at about 3.4 minus, which is the carbon-hydrogen bond stretch wavelength. At this wavelength, more weight is given to saturated hydrocarbons, which are rich in carbon-hydrogen bonds, than to unsaturates. The absorbance at other infrared wavelengths can be read and correction made for certain principal components, such as methane, acetylene, and ethylene.[1-3]

Nondispersive infrared spectrophotometric instruments have similar limitations. Because instrument sensitivity is low, atmospheric analysis without freeze-out requires very long cell path lengths.[1-3]

D. METHODS FOR ANALYSIS OF SPECIFIC HYDROCARBONS

1. Subtractive Columns

a. Nonmethane Hydrocarbons

In typical polluted air samples the principal hydrocarbon component, methane, is usually more abundant than all other hydrocarbons combined. Methane, however, is inert in photochemical reactions. It is therefore desirable to measure methane separately to permit an estimation by difference of the nonmethane hydrocarbons.[9] In one technique, a carbon column is treated with methane until it "breaks through," that is, until no more

methane is absorbed, although other hydrocarbons are still retained.[10] This column becomes a "methane only" analyzer when it is used to absorb nonmethane hydrocarbons before analysis of the sample by a flame ionization analyzer. If the methane analyzer is run in parallel or in alternation with a conventional total hydrocarbon analyzer, methane and total hydrocarbons are measured and, by difference, the nonmethane hydrocarbon concentration may be calculated. Thus a somewhat better approximation of the reactive fraction is provided.[11,12]

b. Reactive Hydrocarbons

Fractionation of organic compound contaminants can be useful when it results in separate determinations of classes of compounds having significantly different reactivities in the photochemical air pollution complex. Such a system, described by Klosterman and Sigsby,[13] permits separate determination of three groups: (1) olefins and acetylenes, both aliphatic and alicyclic as well as, presumably, aromatic; (2) aromatics excluding benzene; and (3) other hydrocarbons, including benzene. The members of the first group are scrubbed from a sample stream by a column containing firebrick supporting mercuric sulfate; those of the second group are removed by palladium sulfate. The first column also removes alcohols, ketones, and organic acids; the second is effective in scrubbing aldehydes, ethers, and esters. Though at present it is only used in the analysis of automobile exhausts, the system shows promise for use in conjunction with other hydrocarbon analyzers, including flame ionization and gas chromatographic units, in giving a complete definition of the nature of hydrocarbon pollution.

2. Gas Chromatography

Gas chromatography (GC) is the only available method for specific atmospheric hydrocarbon analysis.[12,14] With flame ionization detection, it is sensitive in the ppb range. Through the judicious choice of columns and temperatures, almost any desired separation of components can be effected.

Very little data except those from California are available on ambient levels of individual hydrocarbons, and none are available on a tinuous basis. Two factors tended to produce this situation: GC data are in a form most tedious to reduce to meaningful information; and, until recently, automation of data reduction was not possible and the manpower needed to process the volume of raw data manually was not available.

Qualitative identification of the many overlapping peaks is difficult. An unknown can be identified, however, by comparing the chromatogram with that of reference compounds run under the same operating conditions, or by attaching a qualitative detector such as an infrared or mass spectrometer to the GC output. Both approaches require highly trained personnel.

For type separations using GC, subtractive columns may be used before or after the unit. Examples are mercuric perchlorate and silver sulfate – sulfuric acid columns, which are used to remove unsaturates and pass paraffins.[12] The use of subtractive columns simplifies an analysis in which individual components of different hydrocarbon types overlap or interface in the chromatogram.

3. Spectrometric Methods

Both infrared and mass spectrometric methods are capable of considerable discrimination among hydrocarbons, but the low sensitivity required for ambient air monitoring often necessitates a freeze-out or concentration step. The operation and maintenance of either instrument is demanding and expensive, and data reduction is complicated. Infrared spectra may be used to determine the proportions of various olefin types, various aliphatic carbon-hydrogen types (primary, secondary or tertiary), and some aromatic types.[15] The mass spectrometer can differentiate paraffin, olefin plus naphthene, and aromatic groups; in restricted narrow fractions it may permit analysis for individual components.[16,17]

4. Methods for Olefins

A number of methods for olefin determination by colorimetric or coulometric techniques are available. The colorimetric reagents include phosphomolybdate[18] p-dimethylaminobenzaldehyde in sulfuric acid.[19] A coulometric analyzer based on the reaction of olefins with bromine was used successfully in several studies.[20]

E. METHODS FOR ANALYSIS OF GASEOUS ALDEHYDES AND KETONES

1. General

Limitations of methodology allow measurement of only a few specific oxygenated organics. Except for one formaldehyde procedure,[21] there are no automated measurement methods for these contaminants. Only manual colorimetric procedures employing bubblers for sampling are available. The methods used for measurement of carbonyls (aldehydes and ketones) are mostly based on condensation reactions.[22] There is no single method that reliably measures total carbonyls or aldehydes. Sampling of oxygenates is difficult because of their water solubility and their ready condensation or adsorption in the system.

2. Bisulfite Method

The bisulfite aqueous reagent[23] forms moderately stable complexes with lower-molecular-weight aldehydes and methyl ketones.[24] Heavier aldehydes are too insoluble for complex formation, and most ketones form unstable complexes. After complex formation, the excess reagent is destroyed and the complex is broken up. The released bisulfite is analyzed by iodimetry. This method is only moderately sensitive. Bisulfite reagent is also used as a collection absorber for other methods because the carbonyls are readily liberated by acidification of the complex.

3. Other Condensation Reagents

Among the condensation reagents that will react with carbonyl compounds[1-3] are: cyanide, hydroxylamine, phenylhydrazine, 2,4-dinitrophenylhydrazine, Schiff's reagent,[21] 2-hydrazinobenzothiazole, 3-methyl-2-benzothiazole hydrazone (MBTH), and chromotropic acid.[25] The Schiff's reagent and chromotropic acid methods can result in good precision and sensitivity for formaldehyde measurement when used with current analytical procedures. The MBTH method is good for aliphatic aldehydes (including formaldehydes), but purity of the MBTH is a constant problem. Since it reacts with both aldehydes and ketones,[26-28] 2,4-dinitrophenylhydrazine is one of the more general carbonyl reagents used.[29] Colorimetric determinations with 2,4-dinitrophenlhydrazine are complicated by shifts in wavelength with type of carbonyl compound; gravimetric analyses with 2,4-dinitrophenylhydrazine are lengthy and too insensitive for atmospheric work.

Formaldehyde, generally found to be the predominant carbonyl compound in the atmosphere, is very water soluble and in most derivatives is not typical of aldehydes as a class. For this reason it is often desirable to use a procedure specific for formaldehyde (such as the chromotropic acid method),[25,30] and then determine total aldehydes or carbonyls by another method, attempting to allow for the amount of formaldehydes found independently.

The unsaturated aldehyde, acrolein, has also received special attention because, like formaldehyde, it is a known lacrimator found in measurable concentration in photochemically polluted air. The method used most commonly is colorimetric and employs a 4-hexylresorcinol reagent, which is specific and sensitive.[31]

The chromotropic acid method for aldehydes and the MBTH method for total aldehydes and ketones are the most widely used methods and are recommended by the National Air Pollution Control Administration as the reference methods for analysis of these compounds.

F. SAMPLE COLLECTION AND HANDLING

Samples for hydrocarbon measurement must occasionally be collected in the field and

returned to a central laboratory for analysis. The manner in which they are transported must be chosen so as to prevent deterioration in storage and transit. Evacuated glass vessels or inert plastic bags are sometimes used for the collection of grab samples.[32]

For condensable pollutants, a freeze-out technique may be used. The air is passed through a trap immersed in a cold bath (ice or liquid air) suitable for condensing the materials of interest. Sometimes the trap is packed with an inert solid absorbent. Later the trap is connected to the detector and warmed up to volatilize the sample. In this method, the normally large quantities of water vapor in air also condense. The water can cometimes be removed by a drying agent if the pollutant of interest is not also affected as a result. In most instances, these grab samples can be analyzed by the techniques described above.

G. AEROSOL MEASUREMENTS

The particulate material observed in photochemical air pollution (in addition to that portion of solid particulates found even in the absence of a photochemical reaction system) is partially liquid in character. In a sample the moisture and other evaporable liquid generally present make weight and volume estimates difficult and dependent on the recent sample history. Prolonged passage of sample air over the aerosol may evaporate part of the colllected material. The weight of a collected photochemical aerosol also depends on the relative humidity to which it has been exposed between time of collection and weighing.[33] The extent to which gaseous photochemical reaction products condense to liquid and perhaps solid materials, or condense onto solid particulate material, is very uncertain.

Thus aerosol collection, separation by particle size, and characterization are difficult. Most of the conventional collection methods are suitable for solid particulates, but have very uncertain effects on liquid aerosols. Methods based on light scattering do not affect the particles appreciably, but are hard to relate to known particulate sizes and densities. The reader is referred to AP-49, *Air Quality Criteria for Particulate Matter*[34] for a detailed discussion of aerosol sampling and analysis techniques.

H. SUMMARY

With a few exceptions, atmospheric hydrocarbon measurements are made with continuous, relatively complex instruments. Increasing demands for detailed data on specific compounds will reinforce this trend.

Continuous analysis instrumentation demands dynamic calibration techniques. Standard gases for this purpose are commercially available, may be generaged by permeation tubes or dilution systems, or may be prepared in large containers.

Flame ionization analyzers are sensitive, reliable, and suitable for the continuous measurement of total hydrocarbons. They are generally accepted as the method of choice by the National Air Pollution Control Administration. They fail, however, to give the specific detailed information required for a thorough understanding of the atmospheric photochemical problem. Attempts to further define the hydrocarbon mixture by using pretreatment columns to measure only methane or various reactive classes have met with some success in limited application.

Spectrometric techniques both for total and specific analyses are complex and generally insensitive; they require sample concentration steps or long path lengths.

Gas chromatrographic analysis provides the requisite sensitivity and specificity for the quantitation of individual hydrocarbons. Difficulties in qualitative analysis and data handling have limited the application of GC to short-term studies for the most part, and no continuous data are available.

Carbonyl compounds, specifically aldehydes and ketones, can be measured by several manual colorimetric techniques, but few actual data are available.

I. REFERENCES

1. Hendrickson, E. R. Air Sampling and Quantity Measurements. In: Air Pollution, Stern, A. C.

(ed.), Vol. II, 2d ed. New York, Academic Press, 1968. p. 3-52.
2. Katz, M. Analysis of Inorganic Gaseous Pollutants. In: Air Pollution, Stern, A. C. (ed.), Vol. II, 2d ed. New York, Academic Press, 1968. p. 53-114.
3. Lodge, J. P. Production of Controlled Test Atmospheres. In: Air Pollution, Stern, A. C. (ed.), Vol. II, 2d ed. New York, Academic Press, 1968, p. 465-483.
4. Lodge, J. P., Jr. et al. The Use of Hypodermic Needles as Critical Orifices in Sampling. J. Air Pollution Control Assoc. *16*:197-200, April 1966.
5. Thomas, M. D. and R. E. Amtower. Gas Dilution Apparatus for Preparing Reproducible Dynamic Gas Mixtures in Any Desired Concentration and Complexity. J. Air Pollution Control Assoc. *16*:618-623, November 1966.
6. O'Keefe, A. E. and G. C. Ortman. Primary Standards for Trace Gas Analysis. Anal. Chem. *38*:760-763, May 1966.
7. Andreatch, A. J. and R. Feinland. Continuous Trace Hydrocarbon Analysis by Flame Ionization. Anal. Chem. *32*:1021-1024, July 1960.
8. Bruderreck, H., W. Schneider, and I. Halasz. Quantitative Gas Chromatographic Analysis of Hydrocarbons with Capillary Columns and Flame Ionization Detector. Anal. Chem. *36*:461-473, March 1964.
9. Altshuller, A. P. An Evaluation of Techniques for the Determination of the Photochemical Reactivity of Organic Emissions. J. Air Pollution Control Assoc. *16*: 257-260, May 1966.
10. Ortman, G. C. Monitoring Methane in Atmosphere with a Flame Ionization Detector. Anal. Chem. *38*:644-646, April 1966.
11. Altshuller, A. P. et al. Continuous Monitoring of Methane and Other Hydrocarbons in Urban Atmospheres. J. Air Pollution Control Assoc. *16*:87-91, February 1966.
12. Altshuller, A. P. Atmospheric Analysis by Gas Chromatography. In: Advances in Chromatography, Giddings, J. C. and R. A. Keller (eds.), Vol. 5. New York, Marcel Dekker, Inc., 1968. p. 229-262.
13. Klosterman, D. L. and J. E. Sigsby, Jr. Application of Subtractive Techniques to the Analysis of Automotive Exhaust. Environ. Sci. Technol. 1:309-314, April 1967.
14. Pierce, L. B. and P. K. Mueller. Analysis of Atmospheric Hydrocarbons by Gas Chromatography. Presented at the 10th Conference on Methods in Air Pollution and Industrial Hygiene Studies. San Francisco. February 19-21, 1969.
15. Mader, P. P. et al. Determination of Small Amounts of Hydrocarbons in the Atmosphere. Anal. Chem *24*:1899-1902, December 1952.
16. Shepard, M. et al. Isolation, Identification and Estimation of Gaseous Pollutants in Air. Anal. Chem. *23*:1431-1440, October 1951.
17. Weaver, E. R. et al. Interpretation of Mass Spectra of Condensates from Urban Atmospheres. J. Res. Nat. Bur. Stand. *59*(6):383-404, December 1957.
18. MacPhee, R. D. Use of Molybdates for Estimating Amounts of Olefinic-Type Hydrocarbons in the Air. Anal. Chem. *26*:221-225, January 1954.
19. Altshuller, A. P. and S. F. Sleva. Spectrophotometric Determination of Olefins. Anal. Chem. *33*:1413-1420, September 1961.
20. Nicksie, S. W. and R. E. Rostenbach. Instrumentation for Olefin Analysis at Ambient Concentrations. J. Air Pollution Control Assoc. *11*:417-420, September 1961.
21. Lyles, G. R., F. B. Dowling, and V. J. Blachard. Quantitative Determination of Formaldehyde in the Parts per Hundred Million Concentration Level. J. Air Pollution Control Assoc. *15*:106-108, March 1965.
22. Altshuller, A. P. et al. Analysis of Aliphatic Aldehydes in Source Effluents and in the Atmosphere. Anal. Chim. Acta. *25*(2):101-117, August 1961.
23. Laboratory Methods: Aldehydes. Los Angeles County Air Pollution Control District. California. Method 5-46. 1958.
24. Wilson, K. W. Fixation of Atmospheric Carbonyl Compounds by Sodium Bisulfite. Anal. Chem. *30*:1127-1129, June 1958.
25. Altshuller, A. P., D. L. Miller, and S. F. Sleva. Determination of Formaldehyde in Gas Mixtures by the Chromotropic Acid Method. Anal. Chem. *33*:621-625, April 1961.
26. Sawicki, W. et al. The 3-Methyl-2-Benzothiazolone Hydrazone Test. Sensitive New Methods for the Detection, Rapid Estimation, and Determination of Aliphatic Aldehydes. Anal. Chem. *33*:93-96, June 1961.
27. Altshuller, A. P. and L. J. Leng. Application of the 3-Methyl-2-Benzothiazolone Hydrazone Method for Atmospheric Analysis of Aliphatic Aldehydes. Anal. Chem. *35*:1541-1542, September 1963.
28. Hauser, T. R. and R. L. Cummins. Increasing Sensitivity of 3-Methyl-2- Benzothiazolone Hydrazone Test for Analysis of Aliphatic Aldehydes in Air. Anal. Chem. *36*:679-681, March 1964.
29. Jones, L. A., J. C. Holmes, and R. B. Seligman. Spectrophotometric studies of Some 2,4-Dinitrophenylhydrazones. Anal. Chem. *28*:191-198, February 1956.
30. Laboratory Methods: Formaladehyde. Los Angeles County Air Pollution Control District. California. Method 8-53. 1958.

31. Cohen, I. R. and A. P. Altshuller. A New Spectrophotometric Method for the Determination of Acrolein in Combustion Gases and in the Atmosphere. Anal. Chem. *33*:726-733, May 1961.
32. Schuette, F. Plastic Bags for Collection of Gas Samples. Atmos. Environ. *1*: 515-519, July 1967.
33. Lundgren, D. A. and D. W. Cooper. Effect of Humidity on Light-Scattering Methods of Measuring Particle Concentration. J. Air Pollution Control Assoc. *19*: 243-247, April 1969.
34. Air Quality Criteria for Particulate Matter. National Air Pollution Control Administration. Washington, D.C. Publication Number AP-49. 1969.

CHAPTER 5.

RELATIONSHIP OF ATMOSPHERIC HYDROCARBONS TO PHOTOCHEMICAL AIR POLLUTION LEVELS

A. INTRODUCTION AND GENERAL DISCUSSION

As discussed in detail in the companion document, AP-63, *Air Quality Criteria for Photochemical Oxidants,* health effects (including eye irritation), vegetation damage, material damage, and visibility reduction have all been associated with the products that result from the interaction of hydrocarbons within the nitrogen dioxide atmospheric photolytic cycle. The major objective of this chapter is to delineate the quantitative relationships existing between hydrocarbon concentrations and their photooxidation products, and thus to relate hydrocarbon concentrations to the effects of photochemical air pollution. In one sense this objective has been accomplished in considerable detail in the laboratory, as is described in AP-63. Yet for a variety of reasons, these laboratory results cannot be quantitatively extrapolated to ambient atmospheres. Because of experimental limitations, most laboratory results relate to hydrocarbon and nitrogen oxide concentrations that are somewhat higher than those observed in ambient atmospheres. An additional factor of importance is that detailed analytical procedures used in laboratory experimentation have not been readily available for routine air monitoring. Thus, until recently, most air monitoring systems have had to rely on a total hydrocarbon measurement that contained a sizeable fraction of photochemically nonreactive compounds. Without additional information as to the composition of this total hydrocarbon mixture or, more important, its compositional variability in the atmosphere, it is difficult to appraise the significance of any apparent relationship in the atmosphere between total hydrocarbon concentrations and photochemical effects. Since 1966, however, several of the CAMP stations have been routinely measuring methane as well as total hydrocarbons. This is a relatively important advance since methane, a photochemically inactive hydrocarbon, is known to comprise 50 percent or more of the total hydrocarbon measurement.

Wherever possible in this chapter, an attempt has been made to correlate photochemical products with the nonmethane hydrocarbon concentrations. In lieu of such nonmethane data, as is the case in the Los Angeles area, an approximate correction for methane was used based on the determined ratio of total hydrocarbon to methane. It must be kept in mind that even the measurement of nonmethane hydrocarbons is not as specific as the photochemistry demands. Thus the proportion of photochemically active hydrocarbons in this nonmethane hydrocarbon total is subject to change on a long-term basis, because the methods of hydrocarbon control have differing efficiencies for individual hydrocarbons. Such effects will eventually, over a period of years, change the relative composition of the ambient hydrocarbon mixture. It is possible, for example, to use control methods that are more efficient for nonreactive hydrocarbons. Thus, the amount of reduction in the photochemically reactive fraction will be less than that indicated by the nonmethane hydrocarbon measurement. The opposite effect is also possible, since a control method may be chosen that is more efficient for the photochemically reactive hydrocarbons. In this discussion, the relationship that is developed between nonmethane hydrocarbons and

oxidant levels must be recognized as subject to change due to changes in the relative proportions of photochemically reactive hydrocarbons in ambient air. On the other hand, such a change in the composition of the ambient hydrocarbons will necessarily be slow; several years may pass before these variations can be demonstrated. More specific methods for measuring the photochemically reactive fraction of atmospheric hydrocarbons are under development and may soon be available for monitoring purposes.

Most of the available information concerning the photochemical system has been discovered by laboratory investigation of simulated atmospheres. As previously discussed in AP-63, *Air Quality Criteria for Photochemical Oxidants*, it has not been apparent how such results are to be extrapolated to ambient atmospheres. Recent improvements in techniques, however, are permitting experimental simulation of hydrocarbon - oxides of nitrogen mixtures that are characteristic of the concentrations found in ambient atmospheres; therefore, less extrapolation is being required. Thus, the findings of a study conducted by the Bureau of Mines for the National Air Pollution Control Administration will soon be published and will present the results of simulated-atmosphere studies using diluted automobile exhaust in which the total hydrocarbon concentration varied from 0.1 to 5 ppm C. The oxides of nitrogen concentration in these studies varied from 0.08 to 0.27 ppm. Simulated-sunlight irradiation of these mixtures under static conditions indicates that an hourly average concentration of 0.1 ppm oxidant can be achieved when the total hydrocarbon value is in the range of 0.1 to 0.4 ppm C. These results represent the closest simulation of ambient atmospheres to date. While certain unknowns still exist relative to extrapolation of such laboratory data, it is of interest to note the similarity of these results with those subsequently shown to be associated with ambient atmospheres at certain CAMP stations.

There are several principles based on laboratory experimentation that are applicable to the analysis of ambient air data. Although the reactions are complex and incompletely understood, the products of photochemical reactions and their effects are relatively well delineated. Each hydrocarbon capable of interacting within the NO_2 photolytic cycle leads to predictable and invariable products. The most common hydrocarbon products of photochemical reactions are aldehydes and ketones. Among the minor products, the most important in terms of effects are the peroxyacyl nitrates and the peroxybenzoyl nitrates. Certain of these products are known to contribute to specific effects associated with photochemical air pollution. Aldehydes, notably formaldehyde and acrolein, and the peroxynitrates are associated with eye irritation. Similarly, ozone and the peroxynitrates may be associated with health effects, vegetation damage, or damage to materials.

Perhaps the least understood effect is that of visibility reduction resulting from the presence of photochemically formed atmospheric aerosols. It is known, however, that certain aromatic hydrocarbons interacting within the NO_2 photolytic cycle lead to the formation of such aerosols. Furthermore, and perhaps of more importance, it is known that some aspect of the photochemical complex leads to the rapid oxidation of sulfur dioxide to form sulfuric acid aerosols.

B. ANALYSIS OF AEROMETRIC DATA

Prior studies of air monitoring data have largely been limited to the application of correlation analyses and to the attempted use of empirical relationships. Good correlation has been demonstrated between oxidant concentrations and reported eye irritation[1] and measured visiblity reduction.[2] These results are surprising in a sense, since on a day-to-day basis, the correlations are rather poor. The observed relationships do illustrate certain characteristics of air monitoring data that are of prime importance and utility in studying atmospheric data. Perhaps the most important characteristic is that the observed correlations

are largely a function of the dominating influence of meteorological variables relating to dispersion and dilution. A second important characteristic is that the correlation between oxidant concentrations and additional manifestations of photochemical smog is generally good because the oxidants, the eye irritants, and the visibility-reducing aerosols are all products of, and thus dependent variables in, one set of photochemical reactions. The third characteristic is the additional dominating influence of the macro-meteorological factors on the concentrations of both precursors and products. As yet there is no model with which the relationship among emissions, their ambient air concentrations, and their photochemical products can be delineated.

In the absence of such a model, rather limited attempts have been made to establish empirical relationships. From the practical viewpoint of control, an empirical relationship that delineates the relationship between ambient hydrocarbon levels and subsequent oxidant levels would be quite adequate, since the established correlation between oxidant concentrations and both eye irritation and visibility reduction means that a clear definition of the hydrocarbon-oxidant relationship also establishes a relationship between hydrocarbons and eye irritation and hydrocarbons and visibility reduction.

The closest approach, albeit undefinitive, to establishing the required relationship has been achieved by directly comparing the relationship between early morning total hydrocarbon concentrations with the subsequent maximum daily oxidant concentration. There are three problems associated with this approach. The first problem is that until recently insufficient evidence was available to show that measurements of total hydrocarbons and the photochemically reactive hydrocarbon fraction could be related. As previously indicated, this problem has been partially solved by measuring both total hydrocarbons and methane at certain of the CAMP stations.

Evaluating data from only the 6:00 to 9:00 a.m. period reveals several relationships. In Philadelphia, for example, the ratio of nonmethane hydrocarbons to total hydrocarbons on the 71 days investigated in the 1966 to 1968 period was 0.3 ± 0.1. In Washington, D.C., for 78 days during the same time period. this ratio was 0.2 ± 0.1. In Denver, a study of 32 days during the 1967 and 1968 period yielded a ratio of 0.4 ± 0.1. During a portion of 1968, NAPCA measured nonmethane and total hydrocarbons in downtown Los Angeles. In this study during the 6:00 to 9:00 a.m. period for 38 days, the hourly values were determined. The average ratio of nonmethane to total hydrocarbon was 0.50, with a range of 0.43 to 0.54. These Los Angeles ratios are partially a function of time of the day and day of the week. A review of these findings indicates that it is possible in certain cases to use these ratios to approximate the nonmethane hydrocarbon concentration. Nevertheless, a direct measurement is less subject to error. Wherever possible in this discussion, directly measured nonmethane hydrocarbon values have been used. In the initial development of the relationship between hydrocarbon and oxidant concentrations, however, it has been necessary to use the uncorrected total hydrocarbon values, since such measurements comprise the bulk of available data. For the Los Angeles station, no nonmethane data are available. Thus, where data from this station are used on a nonmethane basis, they have been corrected by use of the independently determined ratio. In any event, the Los Angeles data do not affect the direct determination of the association between hydrocarbon and oxidant levels discussed later in this chapter. The Los Angeles data are useful primarily because they demonstrate locational independence of the hydrocarbon-oxidant relationship, they illustrate the predominance of macro-meteorological variables, they delineate the limit of oxidant concentrations resulting from certain hydrocarbon concentrations, and they show the air quality relationship that exists between widely separated stations within a given metropolitan area.

A second problem is the implied assumption inherent in comparing early morning

hydrocarbon levels with the maximum oxidant concentrations occurring several hours later. The implication is that the measurement of air quality at a specific point is a good quantification of the air quality of the air mass covering large segments of the metropolitan area. The results of correlation analyses and the dominance of macro-meteorological factors would tend to support such an implication. Yet, fortunately, one need not rely on such supposition, since this question is directly amenable to investigation. A study of data from several stations within a given area is necessary, and such data for the Los Angeles area have been examined. Examination of data from June 1962 to June 1963 shows that there generally exists a very close and definable relationship between oxidant values measured at various points over a 600-square-mile area.[3] The correlation between air quality measurements at various stations within this area exhibited a standard deviation of less than 10 percent.

Again it seems quite clear that the macrometeorological variables are dominant influences on the ambient air quality and, therefore, account for the close correlation between ambient concentrations at widely separated points within a metropolitan area. Further examination of these Los Angeles data indicates that changes in human activities could account for as much as 20 percent of the variation in hydrocarbon levels and resultant oxidant levels on a day-to-day basis. The total range in hydrocarbon and oxidant concentrations, however, varies up to 200 percent, again illustrating the importance of meteorological variables on hydrocarbon and oxidant levels. This direct examination of the air quality of a metropolitan air mass supports the concept that early morning hydrocarbon levels measured at a single point are proportional to the hydrocarbon levels responsible for oxidant concentrations observed at the same single point later in the day.

A third problem relates to the choice of early morning hydrocarbon concentrations in preference to, for example, the concentration found at the time of peak oxidant levels. Reflection shows that examination of the 6:00 to 9:00 a.m. time period constitutes the most conservative approach; and, in addition, it is most consistent with current knowledge of the reactions involved. It is considered conservative, since this time period usually corresponds to the peak hydrocarbon concentrations (see Chapter 3, Figures 3-2 and 3-3) prior to the development of the peak oxidant level. Thus, adoption of any other hydrocarbon concentration would lead to an association of even lower hydrocarbon values with the peak oxidant level than those herein demonstrated. This 6:00 to 9:00 a.m. technique is consistent with knowledge of the facts, i.e., that the measured hydrocarbon during this period must contain that fraction of photochemically reactive compounds that contribute most to the oxidant peak. Comparison of peak oxidant concentrations with the hydrocarbon levels at the time of this oxidant peak is of dubious value, since it is known from atmospheric analysis that most of the photochemically reactive hydrocarbons have disappeared from the mixture by this time. Variations in the chosen time period have also been taken into consideration.

Changes in human activities on weekends frequently shift the time of peak hydrocarbon concentration by an hour or more; but if the measurements were extended to cover the 6:00 to 10:00 a.m. period for the entire week, the overall result would be an association of slightly lower hydrocarbon values with a given oxidant concentration. Alternately, only that hour when the peak hydrocarbon concentration occurs might be chosen. This, however, has additional problems that are less consistent with facts. Such a choice ignores the fact that it is not a single hour's emissions that contribute the photochemically reactive compounds. It, likewise, ignores the fact that a peak in the 6:00 to 7:00 a.m. period will contribute much less to the subsequent maximum oxidant concentration than an 8:00 to 9:00 a.m. peak. It has also been considered that the 3-hour period chosen should be shifted, wherever applicable on weekends, to conform to the hydrocarbon peak. Such a system

has associated problems, however, since any time beyond 9:00 a.m. is definitely entering the period in which the photochemically reactive hydrocarbons are disappearing. Additionally, and more important, is the fact that even when such a system is adopted, it does not yield significantly different results over those obtained by using only the 6:00 to 9:00 a.m. period. It is obvious that because of the dominance of the meteorological factors, a relationship between hydrocarbon and oxidant values will be obtained almost regardless of what hydrocarbon values are chosen. Yet, the known facts must not be ignored, and on this basis, the 6:00 to 9:00 a.m. average hydrocarbon concentration appears most realistic and practical for the purpose of establishing a relationship between ambient hydrocarbon and oxidant concentrations.

Demonstrating that a relationship between early morning hydrocarbons and maximum daily oxidant can be expected still leaves that relationship to be defined. There is more interest in the limits of such a relationship than in mean values. Specificially, it is desirable to know the maximum oxidant concentration that can be associated in ambient atmospheres with a given hydrocarbon concentration. Delineation of this upper limit can be approached in several ways, but the simplest way, without making additional assumptions, is to examine all available individual days.[4] In such an examination, the only restriction that must be observed is that the data for each day be examined for validity and that the limitations of measurement techniques be taken into account. This latter item applies mainly to the oxidant measurement. The instruments in common use were designed to measure oxidant in the 0 to 1,960 $\mu g/m^3$ (0-1 ppm) concentration range. Therefore, the meaning of oxidant values below approximately 135 $\mu g/m^3$ (0.07 ppm) becomes questionable. In this treatment of data, the examination has been restricted to oxidant values greater than 135 $\mu g/m^3$ (0.07ppm). Reflection shows that this restriction will have no effect on the results, since maximum rather than minimum effects are being sought. It is apparent that the lower limit in all cases will be near zero, since the data include days of no sunshine.

In order to make use of the largest possible number of days, the first examination is based on total hydrocarbon values (Figure 5-1). A total of 326 applicable days was available during the 1966 through 1968 time period in Denver, Cincinnati, Philadelphia, and Washington, and during the May through October 1967 period at the downtown Los Angeles station. The downtown Los Angeles data were used here, since the location of the station more nearly corresponds to that of the CAMP stations, i.e., it is centrally located in a metropolitan area. When these maximum daily oxidant values are plotted as a function of early morning hydrocarbon concentration, the result is as shown in Figure 5-1. The most striking feature of this relationship is that, apparently, an upper limit exists of the maximum daily oxidant concentration as a function of hydrocarbon concentration. Furthermore, the data in Figure 5-1 suggest that the oxidant-hydrocarbon relationship is largely independent of metropolitan area. Several points relative to the results illustrated in Figure 5-1 require discussion. For example, it becomes obvious why a large number of days must be considered. With only a small number of data points available, a scatter diagram with no clear indication of the upper limit line would be obtained. Even with 326 days of available data, it can be noted that delineation of the upper limit above 3 ppm hydrocarbon becomes difficult. A second point to be considered is the suggested independence of this upper limit of metropolitan geographic area. Considering that meteorological factors are dominating the relationship and that the magnitude of meteorological factors affecting dispersion and dilution varies widely between metropolitan areas, one would not expect such an independence. A closer examination of Figure 5-1 yields additional detail regarding this subject. For example, it will be noted that above a hydrocarbon level of 3 ppm C, the Los Angeles data, and to a lesser extent the Denver data, dominate the relationship. Extending this observation, it is noted that

the Los Angeles data contribute very few points below 3 ppm C hydrocarbon. This is to be expected, since the meteorological factors restricting dilution and dispersion are more intense in the Los Angeles region. Thus, although imprecisely defined in Figure 5-1, there must exist an ordering of metropolitan areas in terms of maximum possible oxidant values that is essentially dictated by the mixing and dispersion factors. This ordering of areas can, of course, be affected by hydrocarbon emission rates on a unit-area basis. Differences in such rates in the central portions of large metropolitan areas, however, are not likely to be great. A check on such emission rates yields a value of approximately 3 tons per square mile per day for both Washington, D.C., and Los Angeles.

The single major feature not yet discussed in relation to Figure 5-1 is the influence of sunlight intensity. Examination of the data points in the vicinity of the upper limit line shows such data to be almost exclusively confined to the June through August period when sunlight intensities in the United States are at their highest and are essentially independent of latitude. While latitude during these months has little contribution, altitude does. Thus at Denver, which is at 5,000 feet elevation, one might expect a 10 to 15 percent increase in sunlight intensity over that observed at sea level.[5] On the other hand, laboratory experimentation indicates that intensity changes of this magnitude have more of an effect on rates of reactions than on ultimate concentrations of products. In reality, the changes in ground level incident sunlight intensity caused by the polluted atmosphere itself can be much greater than the 10 to 15 percent change produced by a change in altitude. Studies conducted in the Los Angeles area during October 1965 indicate a 50 percent drop in incident solar radiation at ground level over that observed at a 5,000-foot elevation.[6] If only 15 percent of this change is attributed to altitude, then 35 percent must be attributed to absorption within the polluted air mass. In any event, the data in Figure 5-1 do not indicate any unusual characteristic of the Denver data.

In examining Figure 5-1, it is difficult to see the relationship for a single station. A search of the available data indicates the Denver station has the most applicable points. These data for 126 days are shown in Figure 5-2. The only point to note in relation to these data is the already predicted tendency for the plot to deteriorate into a scatter diagram with indefinite delineation of the upper limit on oxidant as the number of data points is decreased.

As indicated previously, it is possible to apply, in an approximate manner, the determined ratio of nonmethane hydrocarbon to total hydrocarbons to the data in Figures 5-1 and 5-2. Because these ratios are variable, however, it is better to use the nonmethane values whenever possible. These nonmethane values are obtained by subtracting the methane concentration from the total hydrocarbon concentration. Since both measured concentrations have a precision of ± 0.1 ppm C, their difference, i.e., nonmethane hydrocarbons, has doubtful significance when it is less than 0.3 ppm C. In the 1966 to 1968 period, there were 125 days of valid data at Washington, Philadelphia, and Denver when the oxidant concentration was greater than 135 $\mu g/m^3$ (0.07 ppm) and the nonmethane hydrocarbon concentration was greater than or equal to 200 $\mu g/m^3$ (0.3 ppm C).

These points are shown in Figure 5-3. Also plotted are the upper limit data points from Los Angeles data that have been corrected, since no directly determined nonmethane values were available, by use of the previously determined ratio. Little can be said concerning the relative ranking of cities, since only 18 days were available from Denver as compared to 56 from Philadelphia and 51 from Washington.

The data of most interest in Figure 5-3 are those in the vicinity of 200 $\mu g/m^3$ (0.1 ppm) maximum hourly oxidant concentration. It is quite apparent that the 6:00 to 9:00 a.m. early morning nonmethane hydrocarbon value

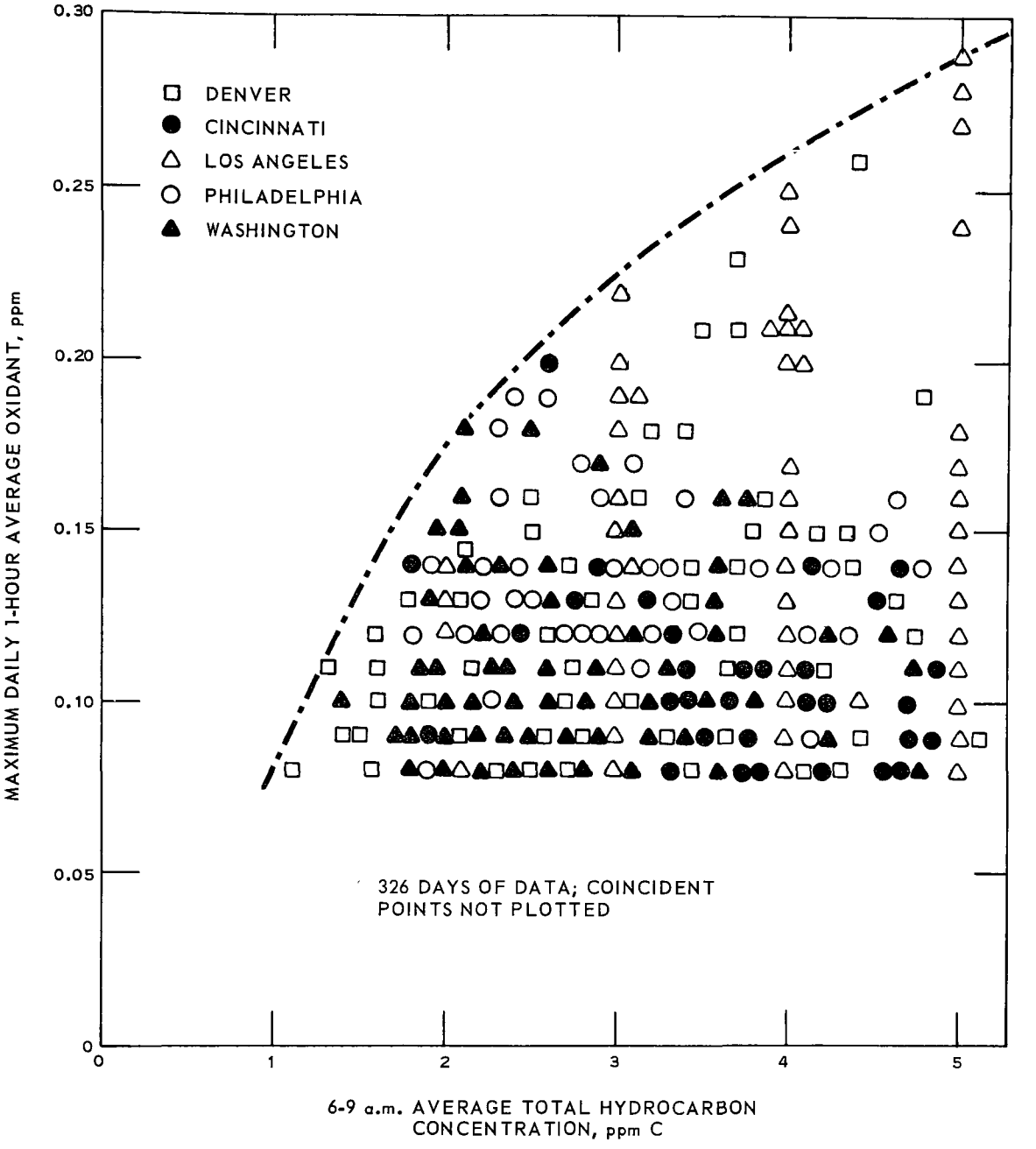

Figure 5-1. Maximum daily oxidant as a function of early morning total hydrocarbons, 1966-1968 for CAMP stations; May through October 1967 for Los Angeles.

must be below 200 $\mu g/m^3$ (0.3 ppm C) if the maximum 1-hour average oxidant concentration is to be kept below 200 $\mu g/m^3$ (0.1 ppm.). It will be noted that this is a conservative approach that depends on direct examination of the data rather than extrapolation. Obviously extrapolation would yield a lower hydrocarbon value, but such extrapolation cannot be justified.

It will be recalled that data from the Los Angeles downtown station were used because the location more nearly corresponded to the location of the CAMP sites. Previous investigations, however, have clearly demonstrated

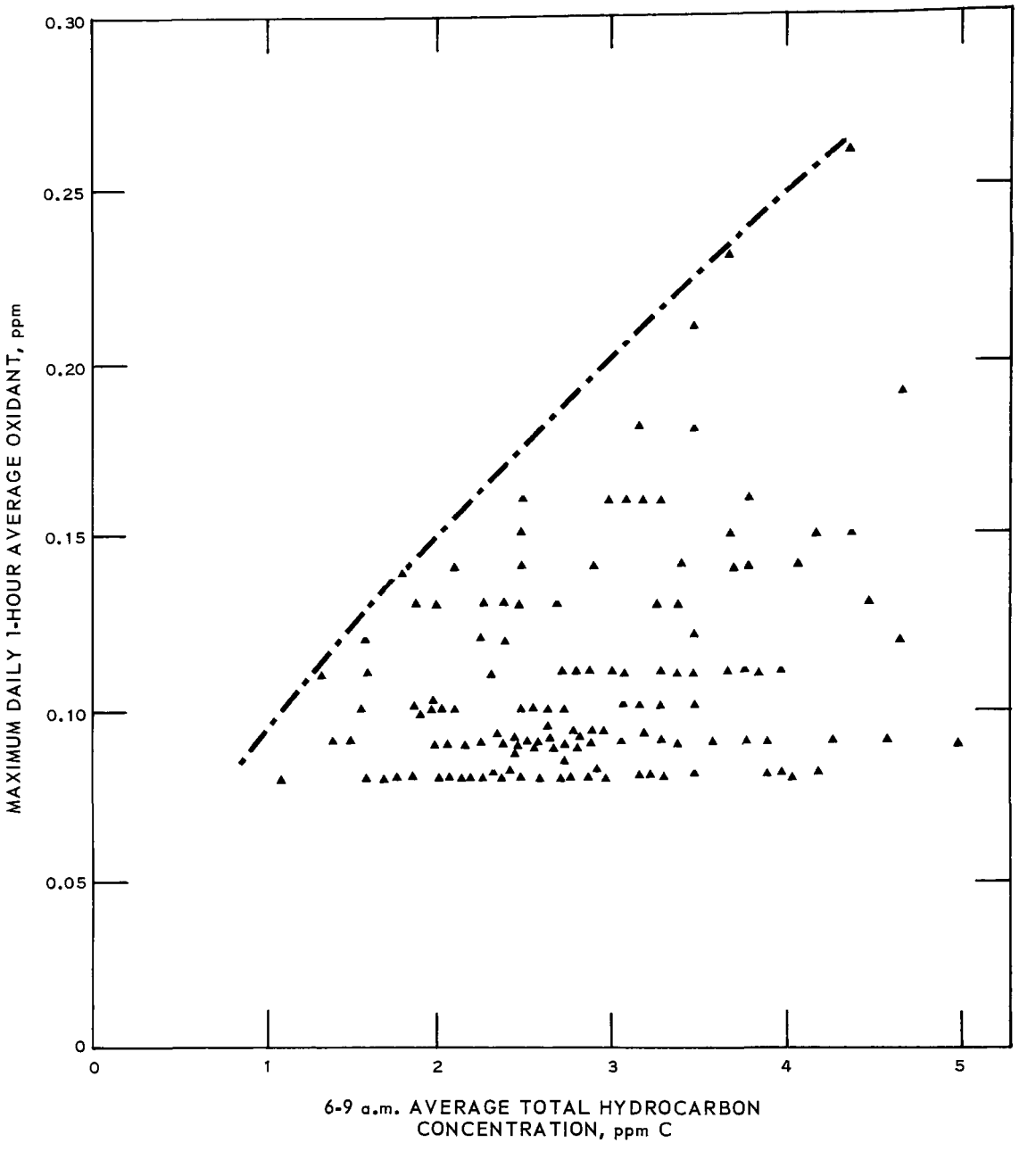

Figure 5-2. Maximum daily oxidant as a function of early morning total hydrocarbons, Denver, 1966-1968.

that this particular Los Angeles site does not, on the average, experience the highest oxidant values in this metropolitan area.[3] It is appropriate at this point to further explore this Los Angeles phenomenon, since the same facts probably apply to the CAMP sites and thus have implication for the value of nonmethane hydrocarbon that can be associated with 200 $\mu g/m^3$ (0.1 ppm) maximum 1-hour average oxidant concentration. The relative location of selected Los Angeles air monitoring stations is shown in Figure 5-4. The average wind direction is northeasterly, which is fortunate because data from three stations in line with this wind direction are available. These stations, as shown in Figure 5-4, are

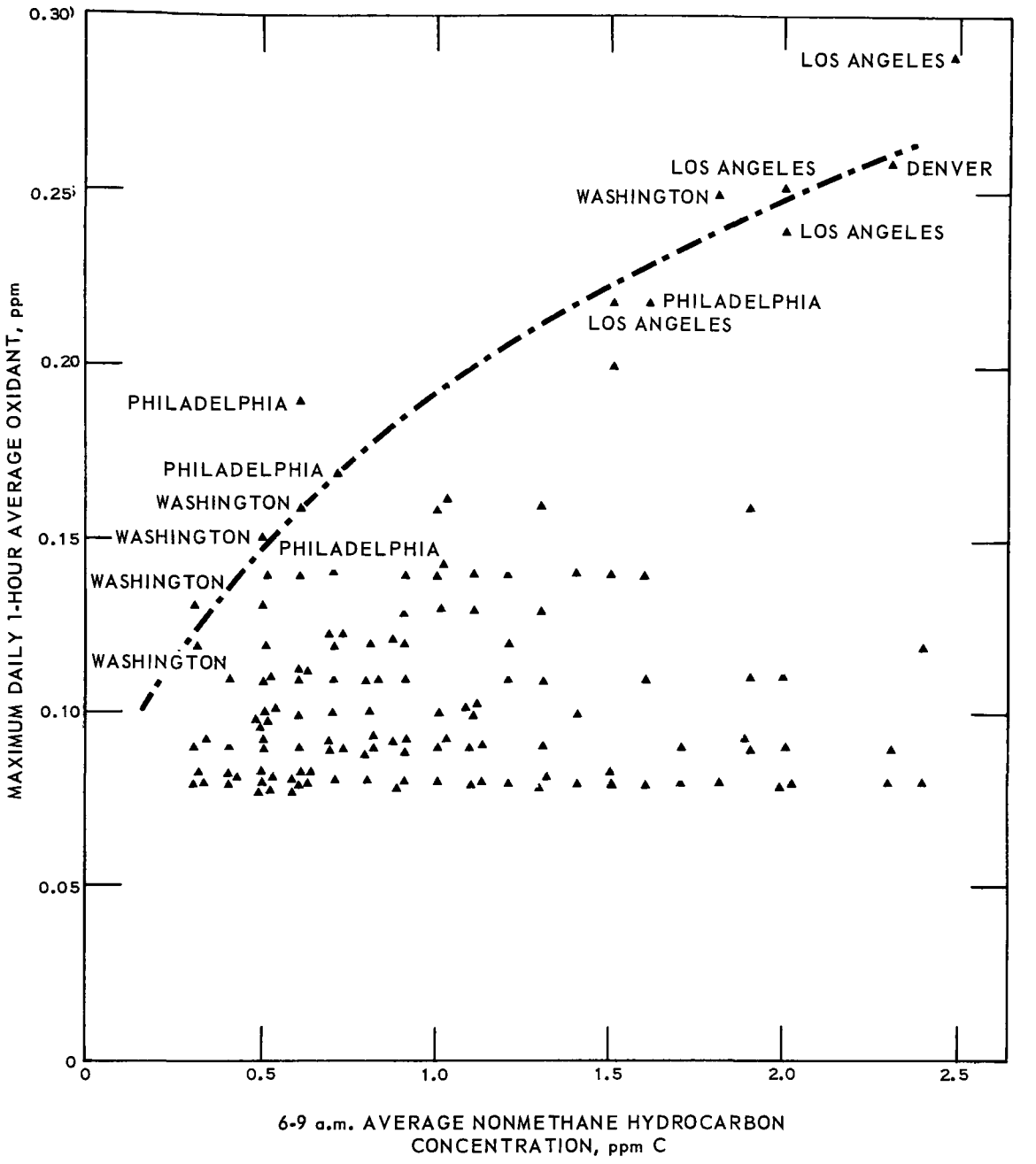

Figure 5-3. Maximum daily oxidant as a function of early morning nonmethane hydrocarbons, 1966-1968 for CAMP Stations; May through October 1967 for Los Angeles.

located in downtown Los Angeles, at the University of Southern California (USC) Medical School, and at Pasadena. This arrangement of stations thus permits examination of the contribution to oxidant values from upwind sources. Using the May through October data for 1967, the upper limit line of oxidant concentration for these three stations was determined. When these data are plotted on one graph, the result is as shown in Figure 5-5. The results demonstrate that the more restrictive the vertical dispersion factors, as evidenced by higher hydrocarbons and maximum oxidants, the greater the contribution to oxidant levels from upwind sources. The greatest pollutant transfer is, as expected,

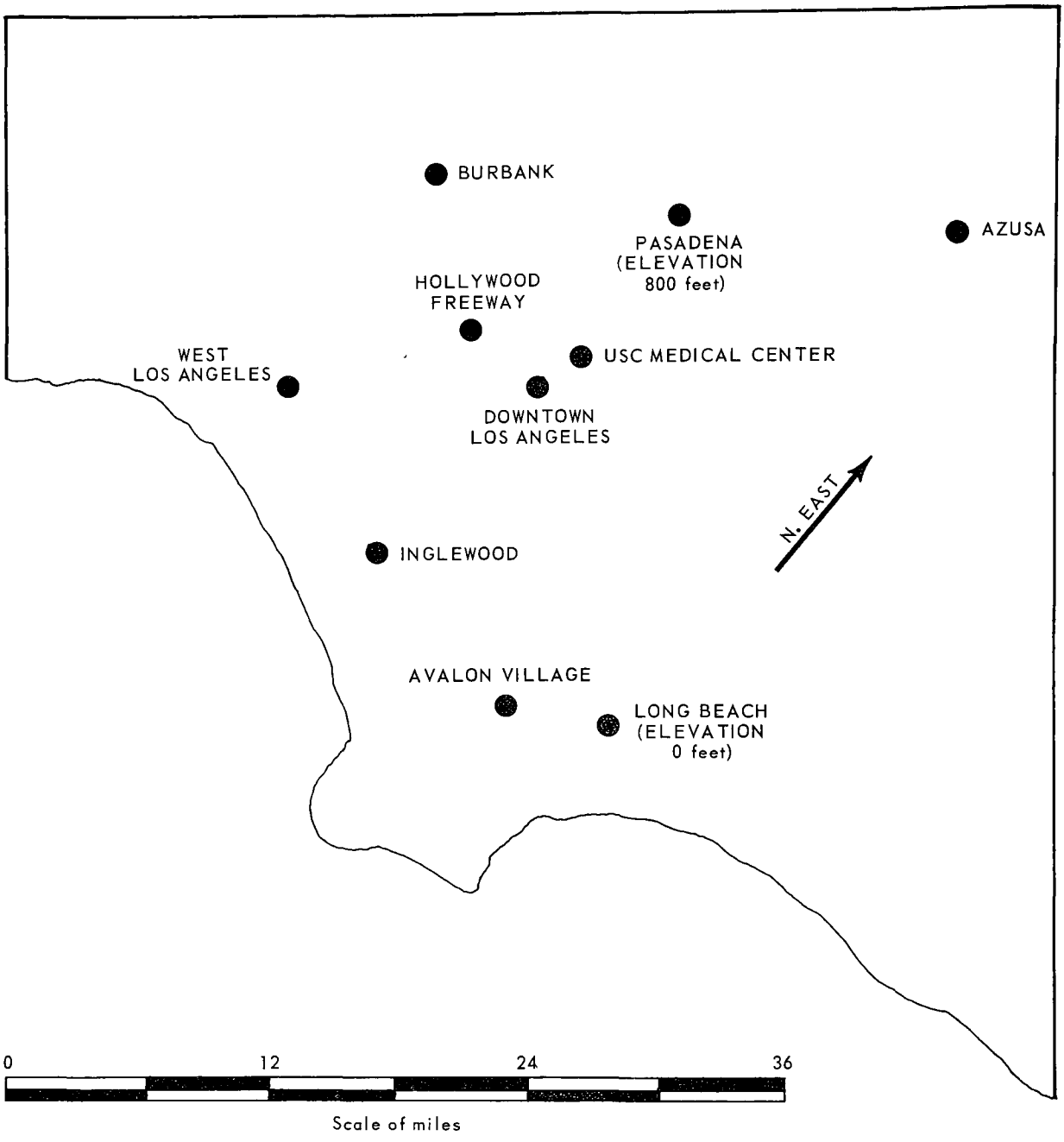

Figure 5-4. Location of selected Los Angeles County air monitoring stations.

from downtown Los Angeles to the USC Medical Center, a distance of only 3 miles. In contrast, much less transfer occurs between the USC Medical Center and the Pasadena station, a distance of 10 miles. It is noted that as the curves in Figure 5-5 are extrapolated to 200 $\mu g/m^3$ (0.1 ppm) oxidant, the contribution of upwind sources tends toward a minimum. Since most of the relationships in Figures 5-3 and 5-5 are a function of meteorological variables, it appears that dispersion rates become greater at the lower hydrocarbon values. Thus, at oxidant concentrations of 200 $\mu g/m^3$ (0.1 ppm), the

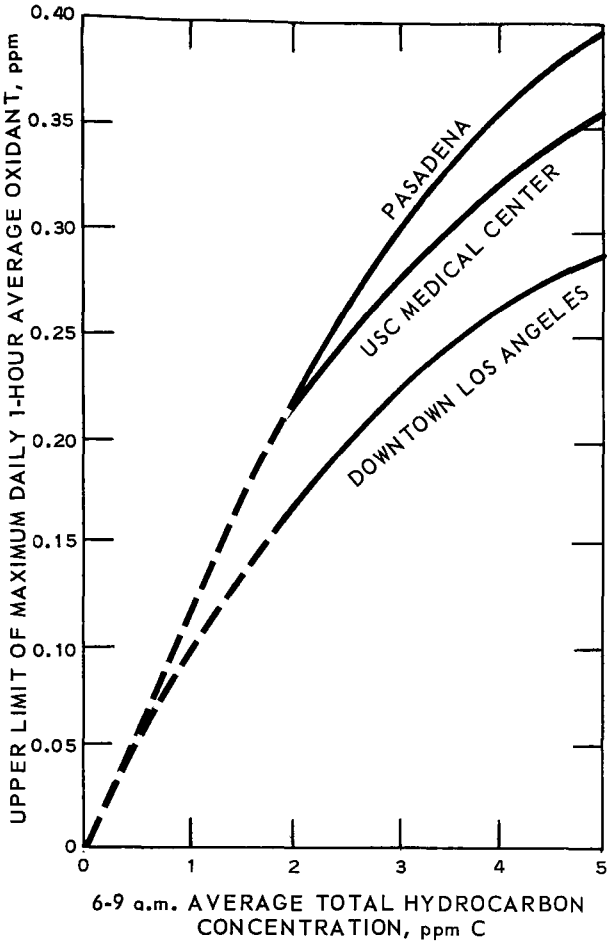

Figure 5-5. Upper limit of maximum daily oxidant at three Los Angeles County stations, May through October 1967.

contributions from sources more than 3 miles distant appear to be counterbalanced by high dispersion rates. The air mass at the CAMP sites studied would appear to have much higher dispersion rates than the Los Angeles atmosphere. Therefore, upwind oxidant contributions may also be minimal at these sites. This latter concept is based on analogy, however, and not on known facts. A more definitive evaluation of this phenomenon in the CAMP cities must await evaluation of the results from multi-station sites in those cities.

Based on the observed association, it should be possible to estimate by city the percent of the time the maximum oxidant potential is attained. Again, however, the available data severely limit such estimations. Combined data for Washington, Denver, and Philadelphia for the 125 days shown in Figure 5-3 indicate that when the oxidant concentration was equal to or greater than 135 $\mu g/m^3$ (0.07 ppm) and the nonmethane hydrocarbon concentration was equal to or greater than 0.3 ppm, the maximum oxidant potential was achieved about 8 percent of the time. Since Figure 5-3 contains only about 11 percent of all days for these cities for a 3-year period, it follows that for all days in the 3-year period the maximum oxidant potential was achieved on less than 1 percent of the days.

C. SUMMARY

The development of a model to relate emission rates of hydrocarbons to ambient air quality and then to the secondary products of photochemical reactions has proved to be an elusive problem. Because of this lack of an appropriate model, the relationship between hydrocarbon emissions and subsequent maximum daily oxidant levels must be approached empirically. The empirical approach adopted is a comparison of 6:00 to 9:00 a.m. average hydrocarbon values with hourly maximum oxidant values attained later in the day. This approach has validity only because of the dominating influence of the macro-meteorological variables on both the concentrations of precursors and photochemical products. Furthermore, this approach can yield useful information only when a large number of days are considered; this guarantees the inclusion of all possible combinations of emission rates, meteorological dilution and dispersion variables, sunlight intensity, and ratios of precursor emissions. When maximum daily oxidant values from such an unrestricted data base are plotted as a function of the early morning hydrocarbons, a complete range of oxidant values—starting near zero and ranging up to finite and limiting values—is observed. Given data for a sufficient number of days, it becomes apparent that the maximum values of attainable oxidant are a direct function of the early morning hydrocarbon concentration. This upper limit of the maximum daily oxidant concentration is depen-

dent on the metropolitan geographical area only to the extent that differences in meteorological variables exist between these areas. Thus, the data from all cities can be plotted on one graph when defining the oxidant upper limit as a function of early morning hydrocarbon.

In defining this oxidant upper limit, all available data relating directly measured nonmethane hydrocarbon values to maximum daily oxidant concentrations have been used. Direct observation of this limit in the vicinity of 200 $\mu g/m^3$ (0.1 ppm) daily maximum 1-hour average oxidant concentrations shows that in order to keep the oxidant below this value, the 6:00 to 9:00 a.m. average nonmethane hydrocarbon concentration must be less than 200 $\mu g/m^3$ (0.3 ppm C). This maximum oxidant concentration potential may be expected to occur on about 1 percent of the days.

D. REFERENCES

1. U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration. Air Quality Criteria for Photochemical Oxidants. Publication No. AP-63. Raleigh, North Carolina, 1970.

2. Renzetti, N.A. and V. Gobran. Studies of Eye Irritation Due to Los Angeles Smog 1954-1956. Air Pollution Foundation Report No. 29. San Marino, California. July 1957.

3. Schuck, E.A., J.N. Pitts, and J.K.S. Wan. Relationships Between Certain Meteorological Factors and Photochemical Smog. Air and Water Pollut. Int. J., 10:689-711, 1966.

4. Schuck, E.A. et al. Relationship of Hydrocarbons to Oxidants in Ambient Atmospheres. Accepted for publication in J. Air Pollution Control Assoc. *20*(5), May 1970.

5. U.S. Department of Commerce, Environmental Science Services Administration. Climatological Data. Volume 18, No. 7. Asheville, North Carolina. July 1967.

6. U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration. Pilot Study of Ultraviolet Radiation in Los Angeles, October 1965. Publication No. 999-AP-38. Cincinnati, Ohio. 1967.

CHAPTER 6.

EFFECTS OF HYDROCARBONS AND CERTAIN ALDEHYDES ON VEGETATION

A. INTRODUCTION

Ethylene is one of the major petrochemicals in the United States as well as a major product of auto exhaust; and it appears to be the gaseous hydrocarbon presenting the greatest hazard to vegetation. Ethylene is a significant phytotoxicant, and it contributes to the formation of photochemical air pollution.

Around the turn of the century, plant physiologists and commercial greenhouse operators noted that illuminating gas escaping in greenhouses caused malformations of certain plants and injuries to flowers.[1-3] Of the hydrocarbons tested, only ethylene produced injury at the relatively low concentrations associated with such leaks. Later, ethylene attributed to illuminating gas leaks was found to injure orchid blossoms.[4]

Ethylene from various sources has been reported to be responsible for considerable losses of flowers in California[5] and of cotton in Texas.[6] Research has demonstrated that ethylene is produced naturally within tissues of plants and serves as a hormone in regulating growth, development, and the other processes such as the ripening of fruit. Considerable investigation has been done in this area, and the subject has recently been reviewed.[7-9] Thus, ethylene is unique in being both an endogenous plant-growth regulator and a serious phytotoxic air pollutant. As indicated by Crocker,[1] ethylene has long been recognized as a growth modifier rather than a highly lethal gas that can readily kill tissue. As early as 1913, Knight and Crocker[10] suggested that ethylene, and perhaps other carbon-containing gases, be considered phytotoxic.

Photochemical reactions with certain olefins in the atmosphere are known to produce phytotoxic secondary products, but there is no evidence that the olefins *per se* cause an added or reduced response of plants to these secondary reaction products.[11]

Although ethylene has the unique role of both an endogenous plant hormone as well as an exogenous phytotoxicant, the principal concern here is with the latter function. The extensive literature on the former role is covered in detail by Burg,[7] Hansen,[8] and Pratt and Goeschl.[9]

B. RELATIVE IMPORTANCE OF HYDROCARBON GASES IN CAUSING INJURY TO VEGETATION

Because ethylene is both a phytotoxic atmospheric pollutant and a growth regulator, the comparative activity of other hydrocarbons in each of these areas is of interest. Crocker[12,13] et al. found that exposure to 115 $\mu g/m^3$ (0.1 ppm) ethylene for a given time produced epinasty in sensitive plants. The relative concentrations of acetylene, propylene, and 1-butene that produce the same degree of response as ethylene are given in Table 6-1. In this table, the activity of ethylene is defined as 1 with respect to the other hydrocarbons tested. Methane, ethane, propane, butane, 1,3-butadiene, and benzene ring compounds had no effect.

Zimmerman[14] studied growth inhibition of tobacco by ethylene, propylene, acetylene, and l-butene and found no effects from 1-butene at the highest level used. Burg and Burg[15] found that concentrations of 115 $\mu g/m^3$ (0.1 ppm) ethylene inhibited elongation in peas. They compared the relative effectiveness of propylene, acetylene, 1-butene,

Table 6–1. RELATIVE CONCENTRATIONS OF SEVERAL UNSATURATED HYDROCARBONS THAT PRODUCE BIOLOGICAL RESPONSE SIMILAR TO THAT PRODUCED BY ETHYLENE[16]

Compound	Abscission	Inhibition of growth		
		Pea stem[a]	Tobacco[b]	Epinasty[c]
Ethylene	1	1	1	1
Propylene	60	100	100	500
Acetylene	1,250	2,800	100	500
1-Butene	100,000+	270,000	2,000	500,000
1,3-Butadiene	100,000+	5,000,000	--	--

[a]Reference 15.
[b]Reference 14.
[c]Reference 12.

and 1,3-butadiene on the same response. Methane, *cis*-2-butene, *trans*-2-butene, and isobutene were inactive.

Abeles and Gahagan[16] found that 115 $\mu g/m^3$ (0.1 ppm) ethylene produced about one-half maximum abscission. This response was then studied using propylene, acetylene, 1-butene, and 1,3-butadiene. As shown in Table 6-1, these authors tabulated their results along with others[12,14,15] to show the relative concentrations of five hydrocarbons that would produce similar activity.

Heck and Pires[17] fumigated a number of plants with 10, 100, and 1,000 ppm of 11 hydrocarbons for periods of from 1 to 3 weeks and noted various responses of the test plants. Only ethylene, acetylene, and propylene had adverse effects. The activity of the three gases has been rated[16] in the order noted in Table 6-1. Acetylene and propylene were considerably less effective than ethylene. Methane, ethane, propane, butane, 1-butene, 1, 3-butadiene, isobutane, and isobutene were inactive.

From the reports cited, ethylene is the only hydrocarbon that should have adverse effects on vegetation at ambient concentrations of 1 ppm or less. The hydrocarbon gases most nearly approaching the activity of ethylene are acetylene and propylene, but concentrations of at least 60 to 500 times that of ethylene are required to produce adverse effects. Stephens and Burleson[18] and Stephens[19] et al. have reported that ambient concentrations of ethylene in congested urban areas were 25 to 150 $\mu g/m^3$ (0.02 to 0.13 ppm), and propylene concentrations were considerably lower, 5 to 50 $\mu g/m^3$ (0.003 to 0.03 ppm). Ethylene concentrations are, therefore, within the range that will produce harmful effects on vegetation.

C. EFFECTS OF ATMOSPHERIC ALDEHYDES ON VEGETATION

Aldehydes are a major reactant product of the photochemical complex and, as such, have been of some interest to investigators studying the effects of air pollutants on vegetation. Haagen-Smit[20] et al. reported abnormal injury to several sensitive plant species after exposure to fairly high concentrations of several aldehydes, but concluded that injury seen on natural vegetation was not caused by aldehydes. Stephens[21] et al. reported injury to plants from irradiated propionaldehyde but no injury from irradiated *cis*-2-butene plus ozone where acetaldehyde was a major product. Hindawi and Altshuller[22] and Altshuller[11] et al. reported injury to sensitive plants after exposure to irradiated propionalaldehyde with and without added nitrogen dioxide, although traces of nitrogen dioxide were present even when not added. They reported no injury after similar exposures to formaldehyde, even though oxidant levels with both aldehydes were sufficiently high to produce plant injury.

Brennan[23] et al. reported injury to

petunias that correlated well with total atmospheric aldehyde levels (including ketones), even when oxidant levels were low. This work has been criticized because of the analytical procedure used and laboratory reports on irradiated formaldehyde-nitrogen dioxide mixtures.[22]

Results to date suggest that atmospheric aldehydes *per se* are not important phytotoxicants, but that products from the irradiation of propionalaldehyde and higher-molecular-weight saturated aldehydes in the presence of nitrogen oxides may cause injury to plants.

D. SYMPTOMS OF EFFECTS OF ETHYLENE ON VEGETATION

Ethylene enters plant leaves during the course of the normal gas exchange required for growth. For this reason, the site of the primary response is in the leaves. In some cases, petals and sepals of flowers may be affected, but these are actually modified leaves. Responses may range from the death of plant parts to very subtle changes within the leaf cells that can be detected only by complex biochemical and histological methods.

Effects may be described in three broad categories: (1) *acute,* identified by tissue collapse and death (necrosis) of leaf parts and usually accompanied by rapid change in leaf color; (2) *chronic,* identified by the slow development of mild or severe symptoms over a long period, such as chlorosis without death of cells; and (3) *growth suppression and/or alternation,* identified by a change in the normal growth pattern of the plant, without obvious symptoms on the leaves.[24,25] Premature leaf fall (abscission) may occur following chronic injury or may be found with no noticeable leaf injury.

The drying of the orchid sepals is the only acute symptom associated with exposure of plants to ethylene.

Chronic injury is often nondescript and usuallly appears as an early senescence of sensitive tissue. It cannot be used to distinguish the effects of ethylene from other pollutants or from injury caused by other factors such as disease, insects, nutritional disorders, or climatic conditions.

A variety of growth abnormalities have been associated with the exposure of plants to ethylene. In 1901, Neljubow notes, illuminating gas containing about 1,145 $\mu g/m^3$ (1 ppm) ethylene caused retarded elongation, an oblique growth toward the horizontal, and a radial swelling or thickening of the stem in seedling plants.[1,9,13] These three responses were later termed the "triple response" by Knight and Crocker.[26] They suggested that these responses be used to detect the presence of ethylene.

Harvey[3] noted that illuminating gas caused leaves of castor bean to grow in a downward direction and suggested that this epinastic response could also be used to detect ethylene because the plant responded to as little as 115 $\mu g/m^3$ (0.1 ppm). Doubt[2] also reported epinastic growth, as well as leaf abscission, in a variety of plants. Subsequently, the effects of illuminating gas on a variety of plants were studied, and the responses were consistently associated with ethylene.[27-30]

Abscission and loss of apical dominance, which results in a spreading vine-like growth instead of an upright plant, have been reported.[1,24] Since complaints of epinasty by commercial growers are uncommon, there is no evidence that epinasty *per se* seriously affects the health of plants.

Ethylene causes color changes in leaves and flowers and death of flower parts. These responses are in contrast to the effects of other phytotoxic pollutants that normally cause rather characteristic markings on affected plant leaves. Most of the reports of adverse effects from ethylene involve flower crops grown in greenhouses.[1,31] The first extensive injury to a field-grown crop was a 1957 report on cotton by Hall[6] et al.

Growth suppression may occur when plants are exposed to dosages of ethylene less than those that cause chronic injury or growth abnormalities. Experiments using carefully controlled air are required to demonstrate this effect, since it is virtually impossible to detect under field conditions. In most cases., growth suppression can be explained on the basis of

the effect of the pollutants on biochemical and physiological systems of the plant.[32-34]

Perhaps the most characteristic symptoms of ethylene injury are the drying of orchid sepals, the closing of carnation flowers (sleepiness), and the shattering of snapdragon petals. Thus, acute symptons caused by other pollutants can not be confused with symptoms caused by ethylene. Chronic symptoms characteristic of natural senescence, however, may be confused with ethylene injury and with certain chronic symptoms associated with sulfur dioxide, ozone, PAN, and several other common pollutants. Accordingly, these effects could not be related to a specific pollutant.

As noted by Brandt and Heck,[24] other factors may produce effects that could be confused with ethylene. Wilting of leaves due to water stress, bacterial wilts, or root rots resembles epinasty. These factors, as well as nutritional imbalance and early senescence, cause leaf chlorosis. The latter factors could cause premature abscission of leaves and flowers.

E. ESTIMATES OF ECONOMIC LOSS (DAMAGE) ASSOCIATED WITH ETHYLENE INJURY TO VEGETATION

The scattered information that exists on economic losses due to ethylene relates mostly to flower crops. Hall[6] et al. reported that the yield of cotton was meager within 1 mile of an industrial source, but the decline in monetary value of the crop was not assessed. Darley[4] et al. reported that during 1959 the combined damages incurred by three orchid growers in Northern California amounted to $70,000. James[35,36] surveyed losses in the San Francisco Bay area. Data supplied up to 1964 by several cooperating orchid growers indicated an annual loss ranging from $60,000 to $100,000. Reduction in profit suffered by carnation growers in 1963 was estimated at $700,000. A value for snapdragon losses was not given, but they were quite severe. Although information is not available for other parts of the country, it can be assumed that comparable losses with respect to flower crops could occur in those urban areas where elevated levels of ethylene occur.

For purposes of using plants to assess losses from ethylene pollution, the best indicators at present are orchids and possibly carnations and snapdragons. Brandt and Heck[24] have suggested the additional use of cowpea and cotton because of their relatively high sensitivity.

F. DOSE-INJURY RELATIONSHIPS FOR VARIOUS PLANTS EXPOSED TO ETHYLENE

In early investigations, dose-injury relationships for vegetation were studied with illuminating gas and/or ethylene. When comparative tests were made, the concentration of ethylene in the illuminating gas was approximated for parallel experiments with ethylene alone. These experiments were conducted in chambers without air exchange, and concentrations in many experiments ranged from over 1,145 mg/m^3 (1,000 ppm) to less than 1,145 μg/m^3 (1 ppm). Modern analytical techniques were not available, but many early investigators produced valid results and, as noted by Abeles and Gahagan,[16] some of these results compare favorably with later work. More recent studies on ethylene have been performed in chambers with dynamic airflow systems and better analytical methods. Concentrations approaching 1,145 mg/m^3 (1,000 ppm) have been used, but most experiments have utilized lower levels. In general, only the lowest concentrations of the exposure range are considered in discussing the experimental results in this section.

Because a carnation grower complained that the flowers in his greenhouse did not open normally, or once open would close again, Crocker and Knight[27] investigated this phenomenon and found that ethylene in illuminating gas was responsible. A 3-day exposure to 115 μg/m^3 (0.1 ppm) ethylene prevented the flowers from opening, and a 12-hour exposure to 575 μg/m^3 (0.5 ppm) caused flowers to close. Darley[4] et al. reported that the minimum exposure required

to close the flowers was 115 $\mu g/m^3$ (0.1 ppm) for 6 hours.

Zimmerman[29,30] et al. and Crocker[12,13] et al. have exposed a number of plants for various periods of time. Epinasty occurred on the sensitive plants after a 3-hour exposure to 3,435 $\mu g/m^3$ (3 ppm) and after a 24-hour exposure to about 345 $\mu g/m^3$ (0.3 ppm). Exposure to as little as 1.15 $\mu g/m^3$ (0.001 ppm) for 20 hours caused epinasty on African marigold, the most sensitive species studied. A 5-day exposure to 1,145 $\mu g/m^3$ (1 ppm) produced yellowing along the veins of rose leaves. Of some 202 species tested, 44 percent reacted adversely to ethylene. Long exposure periods were required for abscission of plant parts. Rose leaf abscission began after exposure to 350 $\mu g/m^3$ (0.3 ppm) for 120 hours, while 11,450 $\mu g/m^3$ (10 ppm) induced the same response in 24 hours.

Darley[4] et al. found that 115 $\mu g/m^3$ (0.1 ppm) for several hours induced dropping of the flower buds on tomato and pepper plants.

Hitchcock[28] et al. reported that all varieties of several species in the lily family were retarded in growth when exposed for 7 days to about 855 $\mu g/m^3$ (0.75 ppm) ethylene contained in illuminating gas. Crocker[1] later reported 25 to 50 percent growth inhibition of four species exposed to 115 $\mu g/m^3$ (0.1 ppm) ethylene for 4 weeks.

Davidson[5] found that when a concentration of 115 $\mu g/m^3$ (0.1 ppm) ethylene was exceeded for 8 hours, injury to Cattleya orchids (dry sepal) was usually more severe than that normally occurring in greenhouses. At 575 to 1,145 $\mu g/m^3$ (0.5 to 1 ppm) for 20 hours, buds remained closed and the tissues collapsed within 2 to 4 days. Dry sepal injury occurred at a concentration of 45 $\mu g/m^3$ (0.04 ppm) for 8 hours and 25 $\mu g/m^3$ (0.02 ppm) for 24 hours. The lowest exposure at which injury occurred was 6 $\mu g/m^3$ (0.005 ppm) for 24 hours.

Darley[4] et al. found that the minimum ethylene concentrations for injury to orchids at 1-, 6-, and 24-hour exposures to be 345, 57.5, and 11.5 $\mu g/m^3$ (0.3, 0.05, and 0.01 ppm), respectively. They also fumigated snapdragons and found that exposure to 575 $\mu g/m^3$ (0.5 ppm) for 1 hour caused the petals to fall from the flowers.

Heck and Pires[37] exposed 89 species of horticultural and agronomic crops to the relatively high concentrations of 2,290, 5,750, and 11,450 $\mu g/m^3$ (2, 5, and 10 ppm) ethylene for 10 days. Based on the severity of a variety of symptons, they categorized the plants according to six broad groups. Plants typical of the six groups, from the most sensitive to the least sensitive, were cowpea, cotton, squash, soybean, radish, and grasses, respectively. The most marked responses exhibited by cowpea were epinasty, chlorosis, and death of the older leaves. These symptoms later extended to the younger leaves, and death of plants was common. Squash leaves were chlorotic and necrotic, with evidence of growth inhibition, but the plants were not killed. There was no injury to soybean, but growth was retarded. Grasses were not injured and the principal effect observed was the reduction of leaf elongation. Twenty-two of the species flowered during the exposure; floral injury developed on all of them and was quite severe on 18.

The only occurrence of ethylene injury to field grown crops was reported by Hall[6] et al. on cotton in Texas in 1957. Fields of cotton in the vicinity of a polyethylene manufacturing plant were severely affected, those within 1 mile giving negligible yield due to abscission of the fiber-bearing squares. Lateral buds were stimulated, which resulted in a prostrate, vine-like growth rather than a normal, upright plant. Concentrations of ethylene about the source ranged from 45 to 3,435 $\mu g/m^3$ (0.04 to 3 ppm). Injury occurred in the areas with the higher concentrations. In controlled experiments under static conditions, defoliation occurred in 48 to 72 hours with 11,450 to 114,500 $\mu g/m^3$ (10 to 100 ppm).

Heck[38] et al. conducted detailed fumigation experiments on cotton, wherein plants were exposed to 690 $\mu g/m^3$ (0.6 ppm) for various periods up to 3 months. Though the

plants were seriously affected, the field symptoms noted in the previously reported study were not duplicated, especially the prostrate growth habit. Among the more significant responses after 1 month were an approximate 50 percent reduction in plant height and leaf size, an increase in leaf abscission, an increase in the number of nodes, and an abscission of squares. Leaf chlorosis was not pronounced, but leaves were badly curled and developed a granular texture on their surfaces.

A summarization of the dose-response data is given in Table 6-2. Listings of plants

Table 6–2. DOSAGE-RESPONSE RELATIONSHIPS OF VARIOUS PLANTS TO ETHYLENE

Response	Dosage: Concentration, $\mu g/m^3$	Dosage: Concentration, ppm	Dosage: Time	Reference
Abscission				
Cotton leaves, square	46-3,435	0.04-3.0	Not stated	Hall[6] et al.
Cotton leaves	685	0.6	1 month	Heck[38] et al.
Pepper and tomato flower buds	115	0.1	Less than 8 hr	Darley[4] et al.
Rose leaves	345	0.3	120 hr	Zimmerman[30] et al.
	11,450	10.0	24 hr	
Snapdragon petals	575	0.5	1 hr	Darley[4] et al.
Chlorosis on leaves				
Cotton (slight)	685	0.6	1 month	Heck[38] et al.
Cowpea	2,290	2.0	1 day	Heck and Pires[37]
Rose	1,145	1.0	5 days	Zimmerman[30] et al.
Death of plant				
Cowpea	2,290	2.0	10 days	Heck and Pires[37]
Dry sepal injury				
Orchids (severe)	115	0.1	8 hr	Davidson[5]
Orchids (typical)	46	0.04	8 hr	
	23	0.02	24 hr	
Orchids (slight)	5.75	0.005	24 hr	
	345	0.3	1 hr	Darley[4] et al.
	57.5	0.05	6 hr	
	11.5	0.01	24 hr	
Epinasty				
African marigold	1.15	0.001	20 hr	Crocker[12] et al.
Various plants	345	0.3	24 hr	Zimmerman[29] et al.
	3,435	3.0	3 hr	
	2,290	2.0	10 days	Heck and Pires[37]
Flowers do not open				
Carnation	115	0.1	3 days	Crocker and Knight[27]
Orchid	575-1,145	0.5-1.0	20 hr	Davidson[5]
Flowers close				
Carnation	115	0.1	6 hr	Darley[4] et al.
	575	0.5	12 hr	Crocker and Knight[27]
Growth inhibition				
Cotton	685	0.6	1 mo	Heck[38] et al.
	46-3,435	0.4-3.0	Not stated	Hall[6] et al.
Lily family	860	0.75	7 days	Hitchcock[28] et al.
Various plants	2,390	2.0	10 days	Heck and Pires[37]
Loss of apical dominance				
Cotton	46-3,435	0.04-3.0	Not stated	Hall[6] et al.

according to sensitivity can be found in several references.[12,13,24,29,30,37]

G. NEED FOR FURTHER RESEARCH

There appears to be sufficient evidence available to confirm the belief that ethylene is the only hydrocarbon that affects vegetation at known ambient concentrations. To produce comparable effects, the concentrations required of the other active gases, acetylene and propylene, are at least 100 times that of ethylene.

The range of plant responses induced by ethylene is known and has been confirmed by many investigators. Since the principal effect at reported ambient concentrations is on plant growth, more information is needed concerning the long-term economic effects of concentrations less than 345 $\mu g/m^3$ (0.3 ppm) on a wide variety of greenhouse and field crops. Heck and Pires[37] have examined a large number of crops exposed to ethylene, but the concentrations were relatively high and the exposure to ethylene was for only 10 days. Heck[38] et al. observed a significant reduction in the growth of cotton at 690 $\mu g/m^3$ (0.6 ppm) over a period of 1 to 3 months, but were able to examine only the one species. These results indicate the direction that continued research should take.

The possible synergistic action of ethylene in combination with other pollutants, particularly those occurring in the photochemical complex, should be investigated. Heck[39] observed no synergistic effect on several species; however, Menser and Heggestad[40] reported that a mixture of ozone and sulfur dioxide caused injury to tobacco when the same concentrations acting alone had no effect. Consequently, research in this area is also needed.

H. SUMMARY

Hydrocarbons were first recognized as phytotoxic air pollutants about the turn of the century as a result of complaints of injury to greenhouse plants from illuminating gas. Ethylene was shown to be the injurious component. Renewed interest in hydrocarbons, and ethylene in particular, occurred in the mid-1950's when ethylene was found to be one of the primary pollutants in the photochemical reaction complex. Research on several unsaturated and saturated hydrocarbons proved that only ethylene had adverse effects at known ambient concentrations. It is noteworthy that the activity of acetylene and propylene resemble more closely that of ethylene than do other similar gases, but 60 to 500 times the concentration is needed for comparable effects.

In the absence of any other symptom, the principal effect of ethylene is to inhibit growth of plants. Unfortunately, this effect does not characterize ethylene because other pollutants at sublethal dosages, as well as some diseases and environmental factors, may also inhibit growth.

Epinasty of leaves and abscission of leaves, flower buds, and flowers are somewhat more typical of the effects of ethylene, but the same effects may be associated with nutritional imbalance, disease, or early senescence. Perhaps the most characteristic effects are the dry sepal wilt of orchids and the closing of carnation flowers. Injury to sensitive plants has been reported after exposure to ethylene concentrations of 1.15 to 575 $\mu g/m^3$ (0.001 to 0.5 ppm) for an 8- to 24-hour time period.

Economic loss has not been widely documented except among flower growers in California, where damage to orchids and carnations has been assessed at about $800,000 annually. More research needs to be done on economic losses sustained in field and greenhouse crops from long exposures to very low concentrations of ethylene.

I. REFERENCES

1. Crocker, W. Growth of Plants. New York, Reinhold Publishing Corp., 1948. 459 p.
2. Doubt, S. L. The Response of Plants to Illuminating Gas. Botan. Gaz. *63*(3) 209-224, March 1917.
3. Harvey, E. M. The Castor Bean Plant and Laboratory Air. Botan. Gaz. *56*(5): 439-442, November 1913.
4. Darley, E. F. et al. Plant Damage by Pollution Derived from Automobiles. Arch. Environ. Health, *6*:761-770, March 1963.

5. Davidson, O. W. Effects of Ethylene on Orchid Flowers. Proc. Amer. Soc. Hort. Sci. *53*:440-446, May 1949.
6. Hall, W. C. et al. Ethylene Production by the Cotton Plant and Its Effects Under Experimental and Field Conditions. Physiol. Plant. (Copenhagen). *10*(2):306-317, 1957.
7. Burg, S. P. The Physiology of Ethylene Formation, In: Ann Rev. Plant Physiol., Machlis, L. (ed.), Vol. 13. Palo Alto, Calif., Annual Reviews, Inc., 1962. p. 265-302.
8. Hansen, E. Postharvest Physiology of Fruits. In: Ann Rev. Plant Physiol., Machlis, L. (ed.), Vol. 17. Palo Alto, Calif., Annual Reviews, Inc., 1966. p. 459-480.
9. Pratt, H. K. and J. D. Goeschl. Physiological Roles of Ethylene in Plants. In: Ann. Rev. Plant Physiol., Machlis, L. (ed.), Vol. 20. Palo Alto, Calif., Annual Reviews, Inc., 1969. p. 541-584.
10. Knight, L. I. and W. Crocker. Toxicity of Smoke. Botan. Gaz. *55*: 337-371, May 1913.
11. Altshuller, A. P. et al. Products and Biological Effects from Irradiation of Nitrogen Oxides with Hydrocarbons or Aldehydes under Dynamic Conditions. Int. Jour. Air Wat. Poll. *10*:81-98, 1966.
12. Crocker, W., A. E. Hitchcock, and P. W. Zimmerman. Similarities in the Effects of Ethylene and the Plant Auxins. Contributions from Boyce Thompson Institute. *7*(3):231-248, July-September 1935.
13. Crocker, W., P. W. Zimmerman, and A. E. Hitchcock. Ethylene-Induced Epinasty of Leaves and the Relation of Gravity to It. Contributions from Boyce Thompson Institute. *4*(2):177-218, June 1932.
14. Zimmerman, P. W. Anaesthetic Properties of Carbon Monoxide and Other Gases in Relation to Plants, Insects, and Centipedes. Contributions from Boyce Thompson Institute. *7*(2):147-155, April-June 1935.
15. Burg, S. P. and E. A. Burg. Molecular Requirements for the Biological Activity of Ethylene. Plant Physiol. *42*:144-152, January 1967.
16. Abeles, F. B. and H. E. Gahagan, III. Abscission: The Role of Ethylene, Ethylene Analogues, Carbon Dioxide, and Oxygen. Plant Physiol. *43*:1255-1258, August 1968.
17. Heck, W. W. and E. G. Pires. Growth of Plants Fumigated with Saturated and Unsaturated Hydrocarbon Gases and Their Derivatives. Texas Agri. Exp. Sta. Misc. Publ. No. 603. 1962. 12 pp.
18. Stephens, E. R. and F. R. Burleson. Analysis of the Atmosphere for Light Hydrocarbons. J. Air Pollution Control Assoc. *17*:147-153, March 1967.
19. Stephens, E. R., E. F. Darley, and F. R. Burleson. Sources and Reactivity of Light Hydrocarbons in Ambient Air. Proc. Div. Refining, Amer. Petrol. Inst. *47*: 466-483, 1967.
20. Haagen-Smit, A. J. et al. Investigation on Injury to Plants from Air Pollution in the Los Angeles Area. Plant Physiol. *27*:18-34, 1952.
21. Stephens, E. R. et al. Photochemical Reaction Products in Air Pollution. Int. Jour. Air Wat. Poll. *4*: 79-100, 1961.
22. Hindawi, I. J., and A. P. Altshuller. Plant Damage Caused by Irradiation of Aldehydes. Science. *146*:540-542, 1964.
23. Brennan, E. G., I. A. Leone, and R. H. Daines. Atmospheric Aldehydes Related to Petunia Leaf Damage. Science. *143*:818-819, 1964.
24. Brandt, C. S. and W. W. Heck. Effects of Air Pollutants on Vegetation. In: Air Pollution, Stern, A. C. (ed.), Vol. I, 2d ed. New York, Academic Press, 1968. p. 401-443.
25. Thomas, M. D. Gas Damage to Plants. Ann. Rev. Plant Physiol. *2*:293-322, 1951.
26. Knight, L. I. and W. Crocker., Toxicity of Smoke. Bot. Gaz. *55*:337-371, 1913.
27. Crocker, W. and L. I. Knight. Effect of Illuminating Gas and Ethylene Upon Flowering Carnations. Botan. Gaz. *46*(4):259-276, October 1908.
28. Hitchcock, A. E., W. Crocker, and P. W. Zimmerman. Effect of Illuminating Gas on the Lily, Narcissus, Tulip, and Hyacinth. Contributions from Boyce Thompson Institute. *4*(2):155-176, June 1932.
29. Zimmerman, P. W., A. E. Hitchcock, and W. Crocker. The Response of Plants to Illuminating Gas. Proc. Amer. Soc. Hort. Sci. 27:53-56, December 1930.
30. Zimmerman, P. W., A. E. Hitchcock, and W. Crocker. The Effect of Ethylene and Illuminating Gas on Roses. Contributions from Boyce Thompson Institute. *3*(3): 459-481, September 1931.
31. Hasek, R. F., H. A. James, and R. H. Sciaroni. Ethylene—Its Effects on Flower Crops. Florists' Rev. *144*(3721):21, 65-68, 79-82, March 27, 1969; *144* (3722):16-17, 53-56, April 3, 1969.
32. Darley, E. F. and J. T. Middleton. Problems of Air Pollution in Plant Pathology. Ann. Rev. Phytopathology. *4*: 103-118, 1966.
33. McCune, D. C. et al. Concept of Hidden Injury in Plants. In: Agriculture and the Quality of Our Environment, Brady, N.C., (ed.), 33-44. Amer. Assoc. Adv. Sci., 1967.
34. Taylor, O. C. and F. M. Eaton. Suppression of Plant Growth by Nitrogen Dioxide. Plant Physiol. *41*:132-135, 1966.
35. James, H. A. Flower Damage—A Case Study. San Francisco Bay Area Air Pollution Control District. California Information Bulletin Number 8-63. 1963.

36. James, H. A. Commercial Crop Losses in the Bay Area Attributed to Air Pollution. San Francisco Bay Area Air Pollution Control District. California. 1964.
37. Heck, W. W. and E. G. Pires. Effect of Ethylene on Horticultural and Agronomic Crops. Texas Agri. Exp. Sta. Misc. Publ. Number MP-613. 1962. p. 3-12.
38. Heck, W. W., E. G. Pires, and W. C. Hall. The Effects of a Low Ethylene Concentration on the Growth of Cotton, J. Air Pollution Control Assoc. *11*:549-556, December 1961.
39. Heck, W. W. Plant Injury Induced by Photochemical Reaction Products of Propylene-Nitrogen Dioxide Mixtures. Jour. Air Poll. Control. Assoc. *14*:255-261, 1964.
40. Menser, H. A. and H. E. Heggestad. Ozone and Sulfur Dioxide Synergism: Injury to Tobacco Plants. Science. *153*(3734):424-425, July 22, 1966.

CHAPTER 7.

TOXICOLOGICAL APPRAISAL OF HYDROCARBONS AND ALDEHYDES

A. INTRODUCTION

Studies of atmospheric chemistry have shown that hydrocarbons enter into and promote the formation of photochemical air pollution, and thus contribute to the development of eye irritation and other associated manifestations. In the description of the effects of these atmospheric hydrocarbons, it is insufficient to regard the reported effects of each hydrocarbon compound alone; the discussion must include due consideration of the potential of these compounds under certain atmospheric conditions to form more hazardous derivatives.

Many gaseous hydrocarbons in the atmosphere are intimately involved in the formation of formaldehyde and other aldehydes, ketones, peroxyacetyl nitrate (PAN), and other oxidants, primarily through atmospheric photochemical reactions. Because the formation of aldehydes in photochemical air pollution is so closely related to the presence of hydrocarbons, a review of the toxicological effects attributed to aldehydes is included here.

Although concentrations of aldehydes – especially formaldehyde and acrolein – and PAN encountered in ambient air are not likely to produce severe health effects, they undoubtedly contribute to the eye irritation experienced in photochemical air pollution.[1,2] Because the presence of gaseous hydrocarbons in ambient air can lead to the formation of the eye irritants as a result of photochemical reactions, a discussion of the relevant toxicological studies of eye irritation is also included in this chapter.

The present state of knowledge does not demonstrate any direct effects of the gaseous hydrocarbons in the ambient air on populations, although many of the effects attributed to photochemical oxidants are indirectly related to ambient levels of these hydrocarbons. Thus the effects of hydrocarbons in the ambient air on groups of people living or working in a community or area cannot be directly assessed in epidemiological studies.

B. TOXICOLOGY OF HYDROCARBON COMPOUNDS

1. General Discussion

Experimental hydrocarbon toxicology is fraught with difficulties not found in the study of the toxicology of other groups of compounds. Hydrocarbons in the presence of nitric oxide (or nitrogen dioxide) and ultraviolet irradiation (sunlight) react to form various toxic compounds. The toxicity of hydrocarbons may be of lesser importance than the toxicity of their reaction products.

Hydrocarbons, at concentrations found in ambient air, have rarely been observed to have direct physiological effects on humans or animals, although effects have been noted at higher levels. Concentrations well above those in the atmosphere have been used in most of the studies discussed below. The results are included here only as a guide to orient the reader in developing a perspective on the photochemical air pollution complex.

2. Aliphatic Hydrocarbonss

In general, members of the aliphatic hydrocarbon series are biologically and biochemically inert, i.e., they produce no detectable functional or subclinical alterations.[3] The lower members, with the exception of methane and ethane, are gases that tend to

have anesthetic properties; this is particularly true of the unsaturated (olefin) compounds. Ethylene, propylene, and acetylene have all been used as anesthetics, and available evidence indicates that these gases are rapidly eliminated from the lungs in the unchanged state. These hydrocarbons must usually be present in relatively high concentrations before noticeable effects are produced, as is illustrated in Tables 7-1 and 7-2.

3. Alicyclic Hydrocarbons

Toxicologically, the alicyclic hydrocarbons resemble their open-chain relatives, the aliphatic hydrocarbons. In general, they are anesthetics and central nervous system depressants with a relatively low order of toxicity. They do not tend to accumulate in body tissues; thus cumulative toxicity from repeated exposure to low atmospheric concentrations is improbable. An overwhelming acute exposure resulting in prolonged unconsciousness, anoxia, and convulsions may result in central nervous system sequelae and has been described only following exposure to volatile aliphatic hydrocarbons.[5]

Laboratory experiments[5] concerning the toxicity of cyclohexane and methylcyclohexane are summarized in Tables 7-3, 7-4, and 7-5.

4. Aromatic Hydrocarbons

Members of the class of aromatic hydrocarbons are biochemically active. The vapors are much more irritating to the mucous membranes than equivalent concentrations of the aliphatic or alicyclic hydrocarbons, and systemic injury can result from their inhalation. Table 7-6 summarizes the effects of acute and chronic exposure to the aromatic hydrocarbons on the laboratory animal and man. Hematological abnormalities have also been associated with the aromatic hydrocarbons.[6] The chronic effects of inhaling benzene over a prolonged period of time may be important in the industrial use of this chemical, and anemia and leukopenia are often associated with chronic benzene poisoning. Greenburg[7] did complete blood studies on 102 workmen exposed to benzene in the rotogravure industry. A positive diagnosis of chronic benzene poisoning, varying in severity, was made in 74 men. In this group were men with clinical benzene poisoning whose blood studies were normal, and also men with serious blood abnormalities in the complete absence of signs or symptoms of benzene poisoning. Signs and symptoms may include headache, dizziness, fatigue, loss of appetite, irritability, nervousness, and nosebleed or other hemorrhagic manifestations.

Toluene, on the other hand, is a more powerful narcotic and is more acutely toxic than benzene, although it does not have the hematological effects attributed to benzene.[8] It appears that the acute toxicity of the xylenes is even greater than that of benzene or toluene.[6]

5. Summary

Experimental data obtained from animal and human research indicate that:

1. The aliphatic and alicyclic hydrocarbons are generally biochemically inert, though not biologically inert. These compounds are only somewhat reactive at concentrations hundreds to thousands of times above those levels found in the atmosphere. No effects have been reported at levels below 500 ppm.

2. The aromatic hydrocarbons are biochemically and biologically active. The vapors are much more irritating to the mucous membranes than equivalent concentrations of the aliphatic or alicyclic groups. Systemic injury can result from the inhalation of vapors of the aromatic compounds, and hematological abnormalities are especially associated with chronic benzene inhalation. No effects, however, have been reported at levels below 25 ppm.

C. TOXICOLOGY OF ALDEHYDES

1. General Discussion

Although aldehydes are widely used in industrial situations, and despite the potential of aldehydes as air pollutants, comprehensive studies of the toxicological effects on human and animals exposed to these compounds are lacking. There have been almost no long-term

Table 7–1. TOXICITY OF SATURATED ALIPHATIC HYDROCARBONS (THROUGH OCTANE)[4]

Hydrocarbon	Concentration, ppm											
	100,000	50,000	40,000	30,000	20,000	15,000	10,000	5,000	2,000	1,000	500	0
Methane Ch_4	No effect											
Ethane C_2H_6		No effect										
Propane C_3H_8	No irritation noticed Dizziness in a few min.				Odor not detected		No symptoms after brief exposure					
Butane C_4H_{10}							Drowsiness in 10 min	Odor not detectable				
Pentane C_5H_{12}	Narcosis in 5-60 minutes							Odor readily detectable; No irritation or symptoms in 10 min		TLV[a]		
Hexane C_6H_{14}			Convulsions and death	Narcosis				Dizziness, giddiness, in 10 min	No symptoms in 10 min		TLV[a]	
Heptane C_7H_{16}					Convulsions, death in 30-60 min	Narcosis in 30-60 min		In 4 min: marked vertigo, hilarity, incoordination	Slight vertigo in 4 min		TLV[a]	
Octane C_8H_{18}							Narcosis in 30-90 min	In 15 min: uncontrolled hilarity or stupor			TLV[a]	

[a]TLV – threshold limit value.

Table 7-2. TOXICITY OF UNSATURATED ALIPHATIC HYDROCARBONS[4]

Hydrocarbon	Concentration, ppm											
	350,000	300,000	200,000	100,000	50,000	40,000	20,000	8,000	5,500	5,000	4,000	1,000
Ethylene									MPL[a]			
Propylene											MPL[a]	TLV[b]
1-Butene											MPL[a]	
1,3-Butadiene											MPL[a]	
2-Methyl-1,3-butadiene								Irritation of eye and upper respiratory tract in man				
Acetylene	Unconsciousness in in 5 min.	Incoordination	Marked intoxication	Slight intoxicating effect on man						MPL[a]		

[a]MPL - maximum permissible limit in workroom air.

[b]TLV - threshold limit value.

Table 7-3. COMPARATIVE EFFECTS OF SINGLE EXPOSURE TO 61.8 mg/m^3 (18,000 ppm) CYCLOHEXANE VAPOR IN AIR[5]

Animal	Time to produce effect, min		
	Trembling	Disturbed equilibrium	Complete recumbency
Mouse	5	15	25
Guinea pig	Slight	—	—
Rabbit	6	15	30
Cat	—	11	18-25

Table 7-4. COMPARATIVE EFFECTS OF CHRONIC EXPOSURE TO CYCLOHEXANE VAPOR IN AIR[5]

Animal	Concentration		Daily exposure, hr	Exposure, days	Effects
	ppm	mg/m^3			
Rabbit	434	1,491	8	130	No effect
Rabbit	786	2,710	6	50	Minor microscopic changes in kidneys and liver
Monkey	1,243	4,270	6	50	No effect
Rabbit	3,330	11,439	6	50	No fatalities or signs of injury
Rabbit	7,400-18,500	25,419-63,548	6	10	Some fatalities

Table 7-5. COMPARATIVE EFFECTS OF CHRONIC EXPOSURE TO METHYLCYCLOHEXANE VAPOR IN AIR[5]

Animal	Concentration,		Daily exposure, hr	Exposure, days	Effects
	ppm	mg/m^3			
Rabbit	241	996	24	70	No effect
Rabbit	1,162	4,659	24	70	No effect
Rabbit	2,800	11,228	24	70	No effect
Rabbit	3,300	13,233	5	70	Minor evidence of kidney and liver injury
Rabbit	5,600	22,456	6	28	No fatalities; lethargy in 50%
Rabbit	7,300	29,273	6	14	25% fatalities
Rabbit	10,000	40,100	6	14	100% fatalities

Table 7-6. COMPARATIVE EFFECTS OF ACUTE AND CHRONIC EXPOSURE TO AROMATIC HYDROCARBON VAPORS IN AIR[6]

Compound	Subject	Concentration, ppm	Concentration, mg/m^3	Daily exposure, hr	Exposure, days	Effect
Benzene	Man	25	80	Acute	-----	Threshold limit value (TLV)
	Man	100	319	Acute	-----	Mucous membrane irritation
	Mice	370	1,180	Acute	-----	Threshold for affecting the central nervous system
	Man	3,000	9,570	Acute	-----	Endurable for 1/2 - 1 hour
	Mice	4,700	14,993	Acute	-----	Prostration
	Mice	7,400	23,606	Acute	-----	LC_{50}
	Man	7,500	23,925	Acute	-----	Dangerous after 1/2 - 1 hour
	Mice	14,100	44,979	Acute	-----	LC_{100}
	Rats	17,800	56,782	Acute	-----	LC_{100}
	Man	20,000	63,800	Acute	-----	Fatal after 5-10 minutes
	Man	50-100	188-377	Acute	-----	No effect
Toluene	Man	200	753	8	1	Mild fatigue, weakness, confusion, skin parethesias
	Man	300	1,130	8	1	Symptoms more pronounced
	Man	400	1,506	8	1	Also: mental confusion
	Man	600	2,259	3	1	Also: nausea, headache, dizziness
	Man	600	2,259	8	1	Also: loss of coordination, staggering gait, pupils dilated
	Mice	2,700	10,166	Acute	-----	Prostration
	Mice	6,700	25,226	Acute	-----	LC_{50}
	Mice	9,500	35,768	Acute	-----	LC_{100}
	Rat	13,500	50,828	Acute	-----	LC_{100}
Styrene	Man	100	418	Acute	-----	Threshold limit value (TLV)
	Guinea pig	650	2,714	8	180	No effect
	Rat	1,300	5,428	8	180	Eye & nasal irritation only
	Rabbit	1,300	5,428	8	180	Eye & nasal irritation only
	Guinea pig	1,300	5,428	8	180	10% deaths
	Guinea pig & rat	2,500	10,438	8	1	Some fatalities; varying degree of weakness, stupor, incoordination, tremor, unconsciousness (in 10 hrs.)
	Guinea pig & rat	5,000	20,875	1	1	Unconsciousness in 1 hour
	Guinea pig & rat	10,000	41,750	1/2 - 1	1	Unconsciousness in 10 minutes; deaths in 30-60 minutes
Xylene	Mice	174	755	Acute	-----	Threshold for affecting central nervous system
	Man	200	868	Acute		Threshold limit value (TLV)
	Rat & rabbit	690	2,995	8	130	No hematological effects

Table 7-6 (continued). COMPARATIVE EFFECTS OF ACUTE AND CHRONIC EXPOSURE TO AROMATIC HYDROCARBON VAPORS IN AIR[6]

Compound	Subject	Concentration, ppm	Concentration, mg/m^3	Daily exposure, hr	Exposure, days	Effect
	Rabbit	1,150	4,991	8	55	Decreased leukocytes & red blood cells; increased platelets
	Mice	4,699	20,394	Acute	------	Prostration
	Mice	9,200	39,928	Acute	------	LC_{50}
	Mice	12,650	54,901	Acute	------	LC_{100}
	Rat	17,250	74,865	Acute	------	LC_{100}

studies in experimental animals, and much of the available information on the toxicity of aldehydes pertains either to the effects from single, acute exposures of animals, or to industrial exposures to high concentrations rather than to levels of aldehydes as they occur in the ambient air. Aldehydes, however, are among the contributors to the eye irritation observed during photochemical smog.

2. Mechanisms of Toxicity

The general and parenteral toxicities of the aldehydes appear to be related primarily to their irritant properties. Reports from occupational exposures have failed to indicate the presence of serious cumulative effects, although primary irritant reactions and contact dermatitis are occasionally seen. Four basic types of effects of aldehydes are reported: primary irritation, sensitization, anethesia, and pathological effects.

a. Primary Irritation of the Skin, Eyes, and Respiratory Mucosa

The principal effect of low concentrations of aldehydes on humans and animals is primary irritation of the mucous membranes of the eyes and the upper respiratory tract, particularly the nose and throat, as well as irritation of the skin. Animal studies indicate that high concentrations can also injure the lungs and other organs of the body. The irritant properties are well documented, being possessed in varying degrees by nearly all of the aldehydes, although the unsaturated (olefinic) and the halogenated aldehydes generally cause more noticeable irritation than saturated aldehydes, while aromatic and heterocyclic aldehydes generally cause less irritation than saturated aldehydes.[9,10] The irritant effect decreases with increasing molecular weight (within a given aldehyde series), and thus decreases with increasing chain length.[10,11] The lower aldehydes act chiefly on the eyes and upper respiratory tract, while the higher, less soluble aldehydes, tend to penetrate more deeply into the respiratory tract and may affect the lungs.[12]

b. Sensitization

Certain aldehydes have been reported to cause allergic reaction. Animals or humans who respond either to concentrations of aldehydes lower than established thresholds or to concentrations that ordinarily do not affect others are said to be sensitized. Direct sensitization of the skin or respiratory tract to aldehyde vapors is uncommon, and asthmatic-like symptoms are very rarely caused by inhalation of aldehydes.[10]

c. Anethesia

Most aldehydes posses anesthetic properties,[10,12,13] the degree of activity decreasing with increasing molecular weight in each aldehyde group. The quantities of aldehydes that can be tolerated by inhalation, however, are so rapidly metabolized that no anesthetic symptoms occur.

d. Pathological Effects

The principal pathological changes found in animals exposed to high concentrations of aldehyde vapors are those of damage to the respiratory tract and pulmonary edema.

Multiple hemorrhages and alveolar exudates may occur, although these effects are ordinarily not observed during experimental aldehyde intoxication. High dosages of compounds such as formal and furfural have been reported to cause various changes in the liver, kidneys, and central nervous system, but there has been no confirmation of this type of action in human industrial exposures. In fact, the aldehydes as a group invoke only a weak response in the experimental animal or in man. Alveolar thickening, minor areas of pulmonary consolidation, minimal parenchymal lung damage, and only rare evidence of residual damage have been reported following aldehyde inhalation, although a decrease in the muco-ciliary activity of the tracheobronchial tree is noted at low concentrations. Acute pathological changes or definitive cumulative organic damage to tissues other than those that may be associated with primary irritation or sensitization are only rarely noted.[10] The fact that aldehdyes are readily metabolized in the body[14] probably accounts for this lack of cumulative damage.

3. Formaldehyde and Acrolein

a. General Discussion

In the field of air pollution, major interest centers on two specific aldehydes, formaldehyde and acrolein. Their effects on humans are known, and their concentrations are generally higher than those of other aldehydes present in the atmosphere. In addition, some reports suggest that they contribute to the odor[15-19] as well as the eye irritation commonly experienced in photochemical air pollution. The concentrations of these two compounds have been shown to correlate with the intensity of odor of diesel exhaust and the intensity of eye irritation during natural and chemically produced air pollution.[15,17,19] The eye irritation potential of aldehydes is further discussed in Section D.3 of this chapter.

b. Formaldehyde

(1) Human studies – The principal effect of formaldehyde vapor on humans appears to be irritation of the mucous membranes of the eyes, nose, and other portions of the upper respiratory tract,[10,12,20-23] although skin irritation can also occur. Repeated exposures may result in chronic irritation of these organs[12,20] as well as inflammation of the eyelids.[20] Symptoms that have been observed from nonfatal exposures to formaldehyde include lacrimation, sneezing, coughing, dyspnea, a feeling of suffocation, rapid pulse, headache, weakness, and fluctuations in body temperature. Reported responses of man to formaldehyde are summarized in Table 7-7. Several reports indicate that irritation of the eyes and upper respiratory tract can first be detected at formaldehyde levels of 12 to 1,230 $\mu g/m^3$ (0.01 to 1.0 ppm).[1,10,24,26-28] Although there are variances as to the exact irritant and odor thresholds, it should be noted that researchers tend to be in agreement that these values may be well below 1,230 $\mu g/m^3$ (1 ppm) of formaldehyde vapor. Variables involved in the experiments, which include the measurement of a subjective response, individual differences in sensitivity, previous exposures, the nature of the synthetic atmospheres, and the apparatus utilized, can easily result in multiple values for the same measurement. Fortunately, there has been an attempt to minimize the number of variables in an effort to consistently replicate experimental results as demonstrated in the reports of experimental exposures to formaldehyde or acrolein.

On the other hand, according to Fassett,[10] no discomfort is noted until concentrations of 2,460 to 3,690 $\mu g/m^3$ (2 to 3 ppm) are reached, at which time a very mild tingling sensation may be detected in the eyes, nose, and posterior pharynx. Since some tolerance occurs, repeated 8-hour exposures to 2,460 to 3,690 $\mu g/m^3$ are possible. At 4,920 to 6,150 $\mu g/m^3$ (4 to 5 ppm), the discomfort increases rapidly, with mild lacrimation occurring in most people.[10] This level may be tolerated fairly well for periods of 10 to 30 minutes by some, but not all people; longer exposures to this level are unpleasant. Elkins[32] reported complaints of eye irritation from acclimatized

Table 7-7. REPORTED SENSORY RESPONSES OF MAN TO FORMALDEHYDE VAPORS

Concentration, μg/m³	Concentration, ppm	Exposure time	Response	Reference
70	0.060	---	Odor threshold (Russian literature)	Melekhina[24, 25]
80	0.065	---	Chronaximetric response threshold	Melekhina[24, 25]
98	0.08	---	Cortical reflex threshold	Melekhina[24, 25]
410-1,110	0.33 - 0.9	---	Irritant threshold	Bourne[26] Roth[27] Morrill[28]
615 1,230	0.5 - 1.0	---	Odor threshold	Stern[29] Fassett[10]
2,460 - 3,690	2.0 - 3.0	8 hr	Tolerable; mild irritation of eyes, nose, and posterior pharynx	Fassett[10]
4,920 - 6,150	4.0 - 5.0	10-30 min	Intolerable to most people; mild lacrimation; very unpleasant	Fassett[10]
6,150	5.0		Severe irritation to throat	Walker[20, 30]
12,300	10.0	Few min	Profuse lacrimation	Fassett[10]
24,600	20.0	15-30 sec	Lacrimation	Barnes[31]
24,600	20.0	30 sec	Irritation of nose and throat	Barnes[31]
24,600	20.0	1-2 min	Sneezing	Barnes[31]

[a]This table excludes several studies of eye irritation, which are discussed in Section D.3 of this chapter.

persons when the maximal concentration was from 6,150 to 7,380 μg/m³ (5 to 6 ppm), although eye irritation was noted in unacclimatized persons upon exposure to much lower levels. At a concentration of 12,300 to 24,600 μg/m³ (10 to 20 ppm), breathing becomes difficult, coughing occurs, and burning of the nose and throat becomes more severe, and extensive irritation of the trachea is evident.[10] On exposure to clean air, lacrimation subsides promptly, but nasal and respiratory irritation may persist for an hour or more. The concentration at which serious inflammation of the bronchi and upper respiratory tract would occur is not known, but inhalation of high concentrations has caused laryngitis, bronchitis, and bronchopneumonia.[20] Based on the above findings, it has been estimated that exposure to 61,500 to 123,000 μg/m³ (50 to 100 ppm) for 5 to 10 minutes might be expected to cause serious injury.[10]

(2) Industrial exposures – Some additional observations on formaldehyde toxicology have been gathered from occupational exposures. Harris[33] studied 25 men engaged in the manufacture of urea-formaldehdye and phenolformaldehyde resins. Exposures varied from 5 to 18 years, and, as a general rule, the concentrations were well below 12,300 μg/m³ (10 ppm). Dermatitis was found in only four of the men. In another group of about 150 to 200 men engaged in the manufacture of urea-formaldehyde resins, glues, molding powders,

etc., Harris[33] was able to uncover three distinct lesions. Some workers developed a sudden eczematious reaction of the face, neck, scrotum, flexor surfaces of the arms, and eyelids, which in some instances appeared only a few days after commencing work. Another eczematous type of reaction that only appeared after years of exposure started in the digital areas of the back of the hands, wrists, forearms, and parts of the body exposed to friction from clothing. A third type of reaction included a combination of the first two types. Many other descriptions of formaldehyde dermatitis have appeared in the literature, but these have generally been related to situations wherein there was direct contact with either liquid solutions, solid materials, or resins containing free formaldehyde; hence these exposures are not analagous to air pollution situations.

According to Fassett,[10] skin sensitization from exposures to formaldehyde vapors is very rare; furthermore, no cases of authentic pulmonary sensitization have occurred. Individuals who have already developed an eczematous skin sensitization, however, may subsequently have a skin reaction upon exposure to formaldehyde vapors. All fatal poisonings attributed to formaldehyde have resulted from ingestion.[21]

In 1969, the American Conference of Government Industrial Hygienists set the 8-hour threshold limit value (TLV) at 6,150 $\mu g/m^3$ (5 ppm) and the American Industrial Hygiene Association recommended that ambinet levels of formaldehyde should not exceed 125 $\mu g/m^3$ (0.1 ppm).[34,36]

(3) Animal studies – Irritation of the eyes, respiratory tract, and skin also occurred during animal experimentation. Higher concentrations, long exposure periods, and postmortem examinations, however, have resulted in information that would have been unavailable if studies had been limited to human volunteers.

Murphy[37] found that rat-liver alkaline phosphatase activity was increased after an 18-hour exposure to 4,300 $\mu g/m^3$ (3.5 ppm) formaldehyde vapor. At higher concentrations, injury to the lungs and other organs may occur in addition to causing prompt and severe irritation of the eyes and respiratory tract. Salem and Collumbine[38] exposed groups of 50 mice, 20 guinea pigs, and 5 rabbits simultaneously to 23,400 $\mu g/m^3$ (19 ppm) formaldehyde vapor and other aldehydes for periods of up to 10 hours. Upon sacrificing the animals at the end of this time, hemorrhages and edema were found in the lungs, and evidence of hyperemia and perivascular edema was noted in the liver. Skog[39] exposed rats to 98,400 $\mu g/m^3$ (80 ppm) formaldehyde for up to 31 minutes. In nonlethal exposures, most rats appeared to recover fully within 2 or 3 days. Postmortem examination of those animals killed by the vapors showed expanded edematous and hemorrhagic lungs, fluid in the pleural and peritoneal cavities, pneumonic consolidation, distended alveoli, and ruptured alveolar septa.

The response of pulmonary function upon exposure to formaldehyde has been studied with normal and tracheotomized animals.[40-43] Formaldehyde inhalation has resulted in an increased flow resistance and tidal volume, with a decrease in the respiratory rate. Amdur[40] noted that the results in tracheotomized animals were similar to, but of a greater magnitude than, those observed with normal animals. This was attributed to the tracheal cannula, which prevents removal of formaldehyde by the nasal and upper airway routes. Davis[42] noted, however, that tracheotomized animals had elevated respiratory rates accompanied by decreased tidal volumes. These findings were ascribed to the fact that the receptors for those responses observed in the normal animals are in the upper airway (i.e., larynx and above), while these same receptors are not exposed to the irritant when the tracheal cannula is in place.

Low levels of formaldehyde can cause cessation of ciliary activity.[44-46] In one study, exposure to 3,690 $\mu g/m^3$ (3 ppm) for 50 seconds or 615 $\mu g/m^3$ (0.5 ppm) for 150 seconds caused cessation of the ciliary beat in the anesthetized respiratory tract of tracheotomized rats.[45]

Gofmekler[47] continuously exposed pregnant rats to 1,125 $\mu g/m^3$ (0.1 ppm) or 1,020 $\mu g/m^3$ (0.83 ppm) formaldehyde vapor. The mean duration of pregnancy was prolonged by 14 to 15 percent as compared to pregnant control rats, while a decrease in the number of fetuses per female was found with the higher concentration. Furthermore, the exposure to formaldehyde appeared to cause an increase in the weight of the thymus, heart, kidneys, and adrenals in the offspring. The author concluded that this effect was apparently a compensatory reaction to unfavorable environmental conditions. On the other hand, the hepatic and pulmonary systems (organs directly affected upon inhalation of formaldehyde) weighed less than those of control animals.

Effects caused by the inhalation of formaldehyde may be modified if an aerosol is also present. La Belle[48] exposed mice to a formaldehyde level of 15,375 $\mu g/m^3$ (12.5 ppm) in the presence of nine different aerosols, including solids and liquids. The time for 50 percent survival of the mice (ST_{50}) was measured, and the results are shown in Table 7-8. Significant increases in the death rate and in the severity of pulmonary edema were found with some of the aerosols. The authors suggest that the active aerosols exerted a synergistic effect when combined with the formaldehyde vapor.

Amdur[41,49] also investigated the response to inhalation of formaldehyde in the presence and absence of sodium chlorid aerosols (appproximately 0.04 micron in diameter). Guinea pigs were exposed to formaldehyde concentrations varying from approximately 86 to 57,800 $\mu g/m^3$ (0.07 to 47 ppm) with and without the presence of 10,000 $\mu g/m^3$ of sodium chloride aerosol. Statistically significant increases in "respiratory work" as a result of the exposure to aerosol were found only when the formaldehyde concentration was greater than 370 $\mu g/m^3$ (0.3 ppm). Moreover, when compared with the pure vapor, the formaldehyde-aerosol mixture significantly prolonged the period necessary for recovery after

Table 7-8. SURVIVAL TIME OF MICE EXPOSED TO 15,375 $\mu g/m^3$ (12.5 ppm) FORMALDEHYDE[a] IN PRESENCE OF AEROSOLS[48]

Aerosol	Aerosol size, microns	Aerosol concentration, μg/liter	ST_{50},[b] min	Significance[c]
Triethylene glycol	1.8	2210	71	++
Ethylene glycol	2.0	2920	168	0
Mineral oil	2.1	1420	72	++
Glycerin	2.0	1280	114	++
Sodium chloride	2.6	2320	114	+
Dicalite	3.3	420	118	+
Celite[d]	2.9	360	102	++
Attapulgus clay[e]	3.3	960	157	0
Santocel CF[f]	2.7	310	145	0

[a] ST_{50} was 147 minutes for mice exposed to this concentration of formaldehyde without aerosols.

[b] Time for 50 percent survival of mice.

[c] 0 = no significance, + = significant, ++ = highly significant.

[d] Diatomaceous earth.

[e] Highly absorptive clay.

[f] Commercial silica gel.

discontinuation of the exposure. Further experiments indicated that flow resistance rapidly increased as the aerosol concentration was raised from 0 to 30,0000 $\mu g/m^3$. The author concluded that sodium chloride aerosol, which is itself inert, can potentiate the response to formaldehyde and prolong its effect as compared with the response to the pure vapor. This may be due to the concentrating effect of sodium chloride on formaldehyde, which results in very high aldehyde concentrations surrounding the small sodium chloride aerosol.

c. Acrolein

(1) Human studies – Acrolein, like most other unsaturated aldehydes, is much more irritating and toxic than the saturated aliphatic aldehydes.[10] Its vapors are highly toxic to humans and extremely irritating to the eyes and respiratory tract.[10,12,50-52] No cases of chronic toxicity are known,[10,52,53] although repeated contact with the skin may produce chronic irritation and dermatitis. Symptoms reported from inhalation of acrolein include lacrimation, swelling of the eyelids, shortness of breath, pharyngitis, laryngitis, bronchitis, oppression in the chest, somnolence, and asthma.[10,23,51,53] The reported responses of man to acrolein vapors are summarized in Table 7-9.

Concentrations of acrolein as low as 675 $\mu g/m^3$ (0.25 ppm) can cause moderate irritation of the eyes and nose in 5 minutes.[52,53,57] Sim,[11] Cook,[58] Henderson,[59] and Hines[57] have reported that lacrimation occurred within 20 seconds after exposure to 1,880 $\mu g/m3$ (0.67 ppm), and began within 5 seconds after exposure to 2,800 $\mu g/m^3$ (1.04 ppm). After 2 to 3 minutes at the latter concentration, eye irritation is quite noticeable, becoming almost intolerable after 4 to 5 minutes. Smith[52] and Henderson[59] reported that moderate eye and nasal irritation is produced from a 5-second exposure to 14,795 $\mu g/m^3$ (5.5 ppm), and that a 20-second exposure is quite painful. Exposure to 58,640 $\mu g/m^3$ (21.8 ppm) is immediately intolerable to humans.[52,59] Pulmonary edema has been reported at this level,[53] and a fatality related to inhalation of 403,500 $\mu g/m^3$ (150 ppm) acrolein vapor for 10 minutes was noted by Prentiss.[51]

The American Conference of Governmental Industrial Hygienists and the AIHA recommended that ambient levels of acrolein vapor should not exceed 27 $\mu g/m^3$ (0.01 ppm) in order to prevent sensory irritation.[34,35]

(2) Animal studies – Smaller concentrations of acrolein are needed to produce similar effects when compared to saturated aldehydes. The acrolein exposure time of mice for 50 percent survival (ST_{50}) is 87 minutes, approximately one-half that for formaldehyde (147 minutes), and approximately 0.005 that for propionaldehyde, while the one-half hour lethal concentration for 50 percent of rats exposed to acrolein (LC_{50}) is 130 $\mu g/m^3$ (0.05 ppm) and approximately one-sixth of that for formaldehyde (815 $\mu g/m^3$ or 0.67 ppm).[10] Mice and rats are found to react to acrolein even at very low levels.[48] Gusev[60] exposed groups of rats to 150 $\mu g/m^3$ (0.06 ppm), 510 $\mu g/m^3$ (0.19 ppm), and 1,520 $\mu g/m^3$ (0.57 ppm) acrolein in air over a period of several weeks. The rats exposed to 1,520 $\mu g/m^3$ for 24 days showed a loss of weight, changes in conditioned reflex activity, a decrease in cholinesterase activity of whole blood, a fall of coproporphyrin excretion in the urine, and an increase in the number of luminescent leukocytes in the blood. When rabbits were exposed to 1,520 $\mu g/m^3$ continually for 30 days, there was no apparent effect, though increasing the level to 5,110 to 6,995 $\mu g/m^3$ (1.9 to 2.6 ppm) for 4 hours resulted in enzyme alterations in eye tissue.[61,62] Murphy[37] also reported an increase in alkaline phosphatase activity in the liver of rats exposed to similar levels.

The damage to the lungs and other organs attributed to formaldehyde in the previous section may also be induced by acrolein.[38,39] Skog[39] described immediate onset of severe respiratory difficulty with evidence of primary irritation of the eyes and upper respiratory tract in various animals following the inhalation of acrolein. Pulmonary edema and

Table 7-9. REPORTED SENSORY RESPONSES OF MAN TO ACROLEIN VAPORS

Concentration, μg/m³	Concentration, ppm	Exposure time	Response	Reference
525-800	0.20-0.30	—	Odor threshold	Leonardos[54]
600	0.22	—	Dark adaptation response threshold	Plotnikova[55]
1,500	0.56	—	Respiratory rhythm and wave amplitude response threshold	Plotnikova[55]
1,750	0.61	—	Chronaximetric response threshold	Plotnikova[55]
1,880	0.67	20 sec	Lacrimation	Sim[11]
2,690	1.0	1 min	Slight nasal irritation	Smith[52]
2,690	1.0	2 to 3 min	Slight nasal irritation and moderate eye irritation	Smith[52]
2,690	1.0	2 to 3 min	Eye and nose irritation	Guest[50]
2,690	1.0	4 to 5 min	Moderate nasal irritation; practically intolerable eye irritation	Smith[52]
2,800	1.04	5 sec	Lacrimation	Sim[11]
4,500	1.7	3 to 4 min	Profuse lacrimation (practically intolerable)	Smith[52]
14,795	5.5	5 sec	Slight odor; moderate eye and nasal irritation	Smith[52]
14,795	5.5	20 sec	Painful eye and nasal irritation	Smith[52]
14,795	5.5	60 sec	Marked lacrimation; vapor practically intolerable	Smith[52]
58,640	21.8	Immediately	Intolerable eye and nasal irritation	Smith[52]
403,500	150	10 min	Lethal	Prentiss[51]

marked damage to bronchial epithelium were the principal pathological lesions. Smythe[63] found that a 4-hour inhalation of 21,520 μg/m³ (8 ppm) acrolein killed one of six rats, while Pattle[64] found that 50 percent of mice and guinea pigs had died after exposure to 28,245 μg/m³ (10.5 ppm) for 6 hours. At this concentration, exposure of cats for 3-1/2 hours caused respiratory irritation, salivation, lacrimation, and mild narcosis, although the animals returned to normal within 2 to 3 hours after the exposure.[65] Lung damage, however, was still observed in rats 6 months after exposure to 538,000 μg/m³ (200 ppm) acrolein for 10 minutes each week for 10 weeks.[66]

Murphy[67] used levels more nearly equivalent to industrial exposures in order to determine effects on respiratory function in guinea pigs. The animals were exposed to 1,615 μg/m³ (0.6 ppm), and the results indicated that acrolein vapors increased the pulmonary flow resistance and tidal volume while decreasing the respiratory rate. The magnitude of these effects increased as the acrolein concentration was raised; and the effects were reversible upon return to clean air. The increased flow resistance was felt to be due to bronchoconstriction mediated through reflex cholinergic stimulation.

La Belle[48] exposed mice to 16,140 μg/m³ (6 ppm) acrolein in the presence and absence

Table 7-10. SURVIVAL TIME OF MICE EXPOSED TO 16,150 $\mu g/m^3$ (6 ppm) ACROLEIN[a] IN PRESENCE OF AEROSOLS[48]

Aerosol	Aerosol size, microns,	Aerosol concentration, μg/liter	ST_{50},[b] min	Significance[c]
Triethylene glycol	1.8	380	73	0
Ethylene glycol	2.0	500	106	0
Mineral oil	2.1	240	69	+
Glycerin	2.0	220	94	0
Sodium chloride	2.6	390	71	+
Dicalite	3.3	70	91	0
Celite[d]	2.9	60	99	0
Attapulgus clay[e]	3.3	160	78	0
Santocel CF[f]	2.7	50	65	+

[a]ST_{50} was 87 minutes for mice exposed to this concentration of acrolein without aerosols.
[b]Time for 50 percent survival of mice.
[c]0 = no significance, + = significant.
[d]Diatomaceous earth.
[e]Highly absorptive clay.
[f]Commercial silica gel.

Table 7-11. AIR QUALITY STANDARDS FOR FORMALDEHYDE[36]

Country	Basic standard			Permissible levels (<4 hr)		
	Concentration,		Time period, hr	Concentration,		Time period, min
	$\mu g/m^3$	ppm		$\mu g/m^3$	ppm	
West Germany	36	0.03	0.5	84	0.07	30
Russia	14.4	0.01	24	42	0.03	20
Czechoslovakia	18	0.01	24	60	0.04	30

Table 7-12. AIR QUALITY STANDARDS FOR ACROLEIN[35]

Country	Basic standard			Permissable levels (< 4 hr)		
	Concentration,		Time period, hr	Concentration,		Time period, min
	$\mu g/m^3$	ppm		$\mu g/m^3$	ppm	
West Germany	10	0.003	0.5	25	0.009	30
Russia	100	0.03	24	300	0.11	20

of various aerosols (see discussion in Section C.3.b). The results are shown in Table 7-10. where it can be seen that significant increases in the death rate were observed in some cases.

d. Sensory Physiology and Central Nervous System Responses

In the U.S.S.R., maximum air pollution levels have been rigidly set according to the principle ". . . . . that the ambient air should not contain odors to be imposed on the population against its wishes. . . ."[68] Russian studies to develop acceptable levels of formaldehyde and acrolein in the air were conducted in the mid-1950's with this principle as a guideline. Limits were based on the subjective reactions of human volunteers. The threshold* for odor perception and mucosal irritation in these subjects was found to be about 800 $\mu g/m^3$ (0.30 ppm) for acrolein and about 70 $\mu g/m^3$ (0.06 ppm) for formaldehyde. The allowable concentrations of acrolein and formaldehyde as adopted by the Russian government in 1957 were established as 300 $\mu g/m^3$ (0.11 ppm) and 42 $\mu g/m^3$ (0.03 ppm), respectively (Tables 7-11 and 7-12), levels about one-half the respective threshold values.[39,68]

Between 1956 and 1962, Russian scientists attempted to define the level of formaldehyde or acrolein that could trigger specific receptors of the respiratory system (including the nose). The striking sensitivity of the respiratory receptors, particularly those concerned with olfaction, to the action of minimal concentrations of chemical substances has long been known. This sensitivity is partially explained by the fact that the olfactory receptors of the upper respiratory tract are located at the point where outside air is first exposed to the internal organism, thus exerting a sentinel action in this area.[68]

The varied responses to the aldehydes discussed in this section, although not strictly within the realm of classical toxicology, are included because the data closely relate to the biological considerations of this review. The practical ramifications and toxic implications of neurophysiological responses, however, have not been adequately explored. One must exercise caution in the interpretation of such data, since there have been no replicative studies to confirm the reported neurophysiological responses, and information concerning experimental conditions has certainly been less than adequate.[69]

Alterations in optical chronaxy+ resulting from stimulation of the receptors in the respiratory system have been used extensively in Russia to examine the allowable limits of atmospheric pollutants.[24,25,55,70] No change in optical chronaxy has been noted when either of the aldehydes was administered to volunteers in concentrations equal either to their allowable limits or their threshold levels. Levels of formaldehyde exceeding threshold values (i.e., concentrations greater than 70 $\mu g/m^3$ or 0.06 ppm) have consistently elicited changes in the optical chronaxy, while acrolein concentrations twice the threshold level (i.e., 1750 $\mu g/m^3$ or 0.61 ppm) have been necessary to initiate chronaxy changes.

Information on optical chronaxy has been substantiated by studies based on the adaptation of the eye to darkness.[24,25,55,70] The Hagel adaptometer, an instrument that measures increasing light sensitivity of the visual organ while the subject is in darkness, was used. Test subjects were exposed to various concentrations of the aldehyde vapors; and the average sensitivity to light was computed

*The term threshold concentration applies to that vapor level just perceptible by either odor or irritation. Subthreshold implies that the level of exposure of the particular aldehyde cannot be detected by subjective evidence of either odor or irritation.

+Weak electrical current applied to the eyeball gives rise to the sensation of a flash of light. For each subject there is a maximum intensity of stimulation below which the sensation of light is not perceived. The intensity threshold, expressed in units of electrical potential (i.e., volts), is called the rheobase. For chronaxy determination, electrical current twice the intensity of the rheobase is used. A stimulating current of two rheobases causes light sensation only when it is sufficiently prolonged. This value, which is the time threshold necessary for the appearance of light sensation, is called optical chronaxy.

utilizing a curve illustrating the change of dark adaptation with time. It was shown that following the inhalation of air containing 600 to 650 $\mu g/m^3$ (0.22 to 0.24 ppm) acrolein, a fall in the curve of eye sensitivity to light was noted. Thus, acrolein concentrations not perceivable by odor had an effect on the central nervous system by eliciting reflex changes in the functional state of the brain cortex. Changes in eye sensitivity to light, therefore, appear to be a more sensitive measurement of the effect of acrolein than does odor perception or optical chronaxy. Remarkable as it may seem, the complex nerological processes that cause cortical stimulation are initiated under the influence of a subjectively nonperceivable odor. On the other hand, subthreshold and threshold levels of formaldehyde have consistently failed to produce changes in dark adaptation, and it is only when the formaldehyde level has reached 98 $\mu g/m^3$ (0.08 ppm) that changes in dark adaptation consistently occur. Thus, both odor perception and optical chronaxy have proved to be more sensitive indexes of the effect of formaldehyde than has dark adaptation.

The Russian data are concerned wholly with the effect of the aldehydes upon the interrelationship of sensory modalities and cerebral cortical function. The Russians have found that odor perception is not the most sensitive index of acrolein concentrations, as acrolein is detected by dark adaptation at levels consistently below that perceived by odor. It has taken twice the threshold concentration of acrolein, however, to elicit a positive response using the optical chronaxy method. On the other hand, odor perception, dark adaptation, and optical chronaxy have all been equally sensitive in determining perceptible levels of formaldehdye.

The Russian results, however, do not confirm ose noted by American researchers. Ameri- ı reports have also demonstrated that acro- is more active and requires smaller concentrations to achieve the similar effects of formaldehyde, and this remains unaccountable at the present time.

4. Acetaldehyde and Other Aldehydes

Acetaldehyde is almost nonirritant to man at levels less than 90 mg/m^3 (50 ppm). The LC_{50} for rats appears to be about 36,000 mg/m^3 (20,000 ppm) for 30-minute exposures.[39] At this level, the animals rapidly became excitable, but after about 15 minutes were in a pseudoanesthetic state; survivors usually recovered rapidly. The principal finding at autopsy has been pulmonary edema. Smythe[63] found that rats survived 4 hours after inhalation of 14,400 mg/m^3 (8,000 ppm) but died from 28,800 mg/m^3 (16,000 ppm); and Iwanoff[65] observed that cats inhaling 505 mg/m^3 (280 ppm) showed no noticeable effects even after 7 hours, though temporary irritation of the air passages was observed at 1,980 mg/m^3 (1,100 ppm).

Human studies have shown that acetaldehyde can be readily detected at concentrations well below 90 mg/m^3 (50 ppm), while some individuals can perceive it at about 45 mg/m^3 (25 ppm), Silverman,[71] Sim,[11] and Pattle[64] have found that the majority of volunteers exposed for 15 minutes to 90 mg/m^3 (50 ppm) showed some signs of eye irritation, while all subjects had red eyes and transient conjunctivitis upon inhalation of 360 mg/m^3 (200 ppm) acetaldehyde. Eye irritation and, to a lesser extent, nose and throat irritation appear to be the only signs reported during industrial exposures. The American Conference of Governmental Industrial Hygienists set the 8-hour TLV for acetaldehyde at 360 mg/m^3 (200 ppm),[35] although no ambient levels were recommended.

There has been little research concerning the toxicology of the remaining aldehyde compounds. Fasset[10] has summarized the reported toxicity data on exposures of animals to aldehyde (Table 7-13). It should again be pointed out that the aldehyde concentrations used in these experiments were far above those encountered in ambient air.

As is the case with animal studies, very little has been published concerning the toxicological effects of aldehydes on man. Table 7-14 summarizes the data available.

Table 7-13. TOXICITY OF INHALED ALDEHYDES TO RATS[10]

Compound	Concentration, mg/m^3	Concentration, ppm	Time, hr	Mortality
Saturated aliphatic aldehydes				
Propionaldehyde	19,000	8,000	4	5/6
	142,500	60,000	0.3	3/3
	61,750	26,000	0.5	LC_{50}
n-Butyraldehyde	22,280	8,000	4	1/6
	167,100	60,000	0.5	LC_{50}
Isobutyraldehyde	22,280	8,000	4	1/6
n-Valeraldehyde	168,960	48,000	1.2	3/3
	4,930	1,400	6	0/3
2-Methylbutyraldehyde	224,785	67,000	0.3	3/3
	12,750	3,800	6.0	0/3
	3,500	1,043	6.0	0/3
Unsaturated aliphatic aldehydes				
Methacrylaldehyde (Methacrolein)	725	250	4	5/6
Crotonaldehyde	----	a	(1 min)	0/6
(β-Methyl acrolein)	4,010	1,400	0.5	LC_{50}

[a]Concentrated vapor.

Table 7-14. TOXICITY OF ALDEHYDES TO HUMANS

Compound	Concentration, mg/m^3	Concentration, ppm	Time, min	Comments	Reference
Crotonaldehyde	11.7	4.1	10	Lacrimation after 30 seconds; no increase during 10 min.	Sim[11]
Crotonaldehyde	11.5	4.0	a	Highly irritant; causes lacrimation	Pattle[64]
Propionaldehyde	475.0	200.0	a	Almost nonirritating	Pattle[64]
Propionaldehyde	317.3	134.0	30	Mildly irritating to mucosal surface; occasional comment of odor present.	Sim[11]
Butyraldehyde	640.5	230.0	30	No irritation noticed	Sim[11]
Butyraldehyde	557.0	200.0	a	Almost nonirritating	Pattle[64]
Isobutyraldehyde	576.5	207.0	30	No irritation; some nausea	Sim[15]

[a]Not given.

5. Summary

The most characteristic and important effect of aldehydes, particularly of low-molecular-weight aldehydes in both humans and animals is the primary irritation of the eyes, upper respiratory tract, and skin. Aldehyde concentrations have been shown to correlate with the intensity of odor of diesel exhaust and to some extent with the intensity of eye irritation during natural and chemically produced smogs. The effects attributable to aldehyde inhalation, however, have been produced only by concentrations far above the levels found in ambient air. In fact, aldehyde levels referred to as "low" in toxicological reports are usually much greater than concentrations routinely found in ambient air.

The observed symptoms in humans resulting from inhalation of "low" concentrations of aldehydes include lacrimation, coughing, sneezing, headache, weakness, dyspnea, laryngitis, pharyngitis, bronchitis, and dermatitis. In most cases, the general and parenteral toxicities of these aldehydes appear to be related mainly to these irritant effects. The unsaturated aldehydes are several times more toxic than the corresponding aliphatic aldehydes, and toxicity generally decreases with increasing molecular weight within the unsaturated and aliphatic aldehyde series. Sensitization has occurred from contact with formaldehyde solutions and other aldehydes, although sensitization of the respiratory tract is produced rarely, if at all, by inhalation of aldehydes. The anesthetic properties of aldehydes are generally overshadowed by their stronger irritant effects. Furthermore, concentrations that can be tolerated via inhalation can usually be metabolized so rapidly that systemic symptoms do not occur.

Animal experiments have shown that aldehydes can affect respiratory functions, causing such effects as an increase in flow resistance and tidal volume and a decrease in the respiratory rate. Exposure of animals to high concentrations of aldehydes (20 to 80 ppm, depending on the compared inhaled) has been shown to produce edema and hemorrhage in the lungs and fluid in the pleural and peritoneal cavities.

Animal experiments have also indicated the existence of possible synergistic effects between aldehydes and aerosols. Thus, acrolein and formaldehyde in the presence of certain inert aerosols appeared to be more toxic to mice than the pure compounds themselves.

Formaldehyde appears to be detectable by odor or physiological response (optical chronaxy) at concentrations of the order of 70 to 80 $\mu g/m^3$ (0.06 to 0.065 ppm). Estimates of the threshold for irritation vary over a wide range, with values between about 12 and 1,130 $\mu g/m^3$ (0.01 to 0.9 ppm). Concentrations between 2,460 and 3,690 $\mu g/m^3$ (2 to 3 ppm) are unpleasant, while concentrations around 5,000 $\mu g/m^3$ (4 ppm), and the threshold for optical chronaxy (4 ppm) are intolerable to most people after a few minutes.

Acrolein seems more irritating than formaldehyde, although published reports are at variance on this point. The odor is detectable at concentrations as low as 525 $\mu g/m^3$ (0.20 ppm), and the threshold for optical chronaxy is reported at 1,750 $\mu g/m^3$ (0.61 ppm), much higher than that of formaldehyde. Concentrations of 2,690 $\mu g/m^3$ (1 ppm) are definitely irritating, and acrolein at a concentration of 4,580 $\mu g/m^3$ (1.7 ppm) is practically intolerable.

Acetaldehyde is much less irritating than formaldehyde; its irritant threshold appears to be near 10,000 $\mu g/m^3$ (50 ppm). No physiological effects are known at levels that may be anticipated in the atmosphere. There is little information available on the toxicity of other aldehyde compounds.

Additional information on the eye-irritant potential of aldehydes, notably formaldehyde and acrolein, is included in Section D.3 of this chapter.

D. HYDROCARBON-MIXED ATMOSPHERE EXPERIMENTATION

1. Introductory Discussion

It has already been noted that the hydrocarbons found in the atmosphere are degraded

to other atmospheric compounds during ultraviolet irradiation. To assess the toxicological effects of mixtures generated by this process, researchers have exposed experimental animals to either irradiated auto exhaust, polluted air, or various synthetic atmospheres, all of which provide the milieu necessary for hydrocarbon reactivity. It must be emphasized, however, that there is not always a well-defined hydrocarbon-oxidant interrelationship during these mixed atmosphere experiments. Often, the primary effect is directly related to the oxidant level, although the hydrocarbon concentration in the synthetic atmosphere may be directly responsible for the oxidant concentration upon irradiation. Thus, it is often quite difficult to define the relative importance of either of these groups of pollutants.

The results of several experiments relating such mixed atmospheres to pulmonary function and to eye irritation are reviewed in this section. Additional studies on the effects of photochemical oxidants on pulmonary function are included in the companion document, AP-63, *Air Quality Criteria for Photochemical Oxidants.*

2. Changes in Pulmonary Function

Studies have been carried out to show the effect of both ambient air and diluted auto exhaust on pulmonary function in laboratory animals. Murphy[72] exposed guinea pigs to irradiated and nonirradiated auto exhaust for periods of 4 hours. Tidal volume, respiratory rate, and flow resistance were measured before, during, and after exposure. Comparison of concentrations in irradiated and nonirradiated atmospheres of approximately equal dilution ratios showed the photochemical formation of aldehydes, nitrogen dioxide, and total oxidant at the expense of nitric oxide and olefins. Flow resistance and tidal volume increased while the respiratory rate decreased during exposure to irradiated exhaust; the response to nonirradiated exhaust was relatively small. These functions rapidly returned to baseline levels following exposure. The data suggest that components of the exhaust other than photochemical reaction products play a role in the functional changes observed. The largest response was observed in an atmosphere containing 2,950 $\mu g/m^3$ (2.4 ppm) formaldehyde, 540 $\mu g/m^3$ (0.2 ppm) acrolein, 160 $\mu g/m^3$ (0.8 ppm) ozone, and 5,075 $\mu g/m^3$ (2.7 ppm) nitrogen dioxide. Special fumigation studies[72] revealed that the effects produced could be nearly quantitatively simulated by exposing animals to 1,615 $\mu g/m^3$ (0.6 ppm) acrolein, while ozone alone at 1,370 $\mu g/m^3$ (0.7 ppm) produced a negligible effect on one parameter (flow resistance), and on the other two (respiratory frequency and tidal volume) it caused responses in the opposite direction from those observed in the irradiated exhaust exposure.

In these experiments, the authors noted that changes in pulmonary function were best correlated with the aldehyde content of the exhaust when compared with other routinely measured agents. Even at an exhaust dilution of 1,000:1, with hydrocarbon concentrations well within the range reported for community pollution levels, the same effects were detectable. In tests at this lower concentration, the total oxidant level was about 785 $\mu g/m^3$ (0.4 ppm), formaldehyde was nearly 615 $\mu g/m^3$ (0.5 ppm), and the olefin content was estimated to be about 900 $\mu g/m^3$.

The likelihood that oxidants were not responsible for these effects was increased to near certainty by a comparison of the effects of irradiated exhaust at a dilution of 1,140:1 with those of nonirradiated exhaust at a dilution ratio of 150:1. Although no oxidant was present in the latter case, the effects of the two conditions on the respiratory function parameters were virtually identical, as shown in Table 7-15. These results indicate that the effective agents are present in raw exhaust gases and are multiplied in quantity by the photochemical effects of irradiation. Since qualitatively identical pulmonary effects are produced by acrolein and similar effects by formaldehyde, the hypothesis that the effects are caused by aldehydes may be entertained.

Table 7-15. COMPARISON OF THE EFFECTS OF IRRADIATED EXHAUST WITH THOSE OF NONIRRADIATED EXHAUST ON PULMONARY FUNCTION PARAMETERS[72]

	Nonirradiated	Irradiated		
Air: Exhaust ratio	150:1	1,140:1	360:1	150:1
Effect on:				
Flow resistance	+30%	+26%	+29%	+113%
Respiratory frequency	-17%	-17%	-20%	33%
Tidal volume	+ 6%	+ 4%	+12%	+ 25%

Swann[73,74] also measured the flow resistance in guinea pigs. The animals were located at three stations within the los Angeles area; at each station one group was exposed to filtered air while the second was exposed to ambient air. Flow resistance was consistently elevated in the group exposed to ambient air when oxidant levels were sufficiently elevated in the atmosphere. Such pollutants as nitric oxide, carbon monoxide, and low-molecular-weight hydrocarbons were presumably unaffected by the charcoal filters, but oxidants and some aldehydes were probably removed. It is, therefore, impossible to decide which components of the smoggy atmosphere were specifically responsible for the effects observed.

3. Eye Irritation

Of the compounds thus far identified in ambient air, only formaldehyde, acrolein, and peroxyacyl nitrates have been shown to be eye irritants. In laboratory experiments on the photooxidation of alkylbenzenes, peroxybenzoyl nitrate is formed. This substance has been shown to be an especially potent eye irritant[75] and may, therefore, be one of the species contributing to this manifestation in the ambient atmosphere.

Renzetti and Bryan[76] determined concentrations of formaldehyde, acrolein, and PAN in photochemical smog in conjunction with eye irritation determinations made by a quantal response technique. Figure 7-1 shows the regression line relating reported eye irritation to total aldehyde concentrations in these air samples, indicating a remarkably good log plot for aldehyde concentrations between 0.035 and 0.35 ppm. Figure 7-2 shows similar information for formaldehyde; the course of the best-fit line is somewhat less clear than for total aldehydes (Figure 7-1). For acrolein, the apparent relationship was nonlinear; samples with acrolein concentrations of more than 40 $\mu g/m^3$ (0.015 ppm) corresponded to less irritating atmospheres, on the average, than those with acrolein in the range from 8 to 40 $\mu g/m^3$ (0.003 to 0.015 ppm).

Measuring eye irritation by a threshold response method in chamber studies with irradiated auto exhaust, Buchberg[77] found a strong correlation with formaldehyde concentration. In a special comparison using one subject, however, the formaldehyde threshold was found to be 13,530 $\mu g/m^3$ (11 ppm), while the formaldehyde measured in the irradiated synthetic atmosphere at the threshold was only 1,230 $\mu g/m^3$ (1 ppm). The best sets of variables for multiple correlation were those which included either formaldehyde concentrations or hydrocarbon consumption. In these tests, initial concentrations of hydrocarbons ranged from 3.5 to 35 mg/m^3 (1 to 10 ppm as hexane, by nondispersive infrared detector), while the decrease due to reaction was from 0.42 to 11 mg/m^3 (0.12 to 2.9 ppm). Associated initial oxides of nitrogen ranged from 0.4 to 6 ppm, and formaldehyde generated was never more than 3,075 $\mu g/m^3$ (2.5 ppm).

Studies with irradiated synthetic atmospheres containing auto exhaust gases were also reported by Tuesday[78] et al. Using a severity scale for the measurement of eye irritation, they found high correlation (r = 0.80) with formaldehyde and noted a linear relation

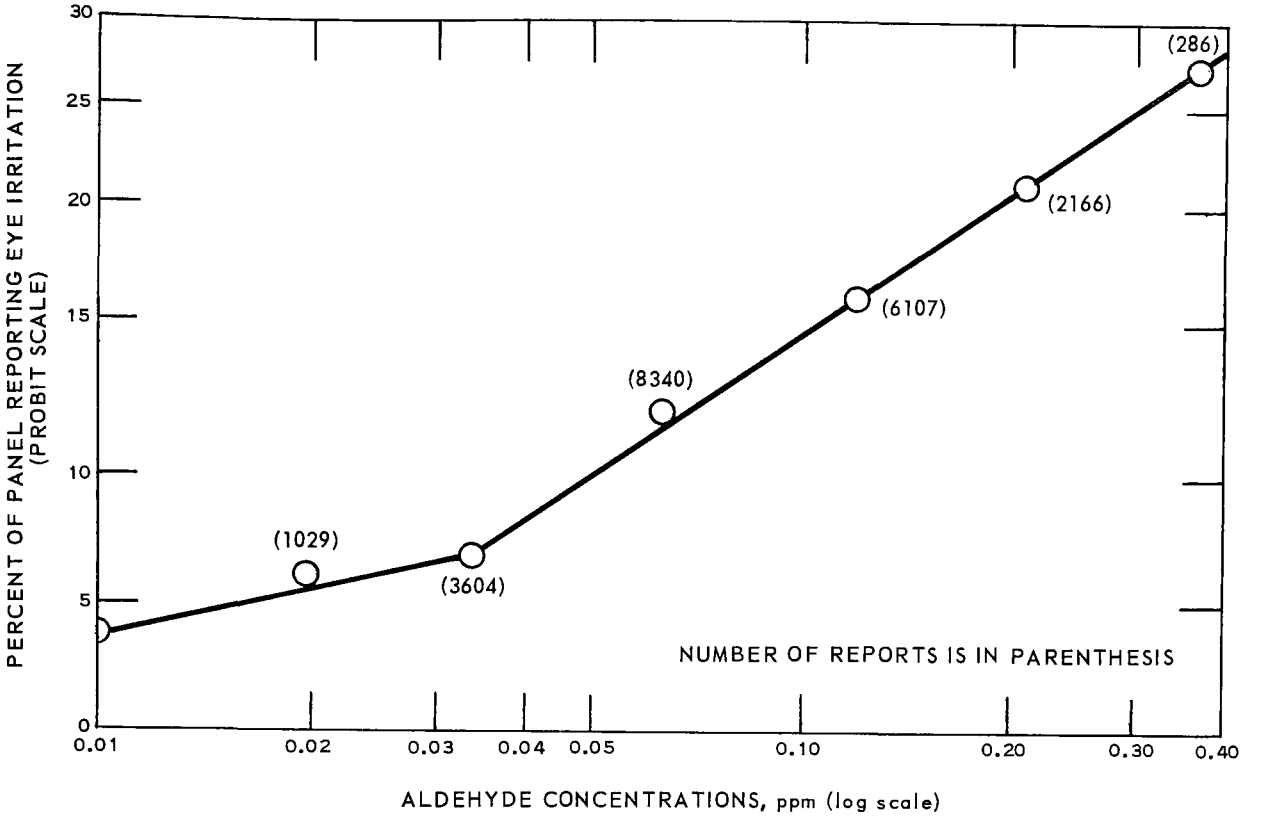

Figure 7-1. Regression curve of the effect of atmospheric concentrations of total aldehyde on panel eye irritation.[76]

between formaldehyde accumulation and initial hydrocarbon concentration. They concluded that formaldehyde concentration might serve as a useful index of eye irritation, even though formaldehyde was probably not the sole agent in these atmospheres.

In these experiments, very little eye irritation was experienced. the highest average panel rating being 0.6 on a scale in which 1 represented "light" eye irritation. Initial hydrocarbon concentrations ranged from 1.1 to 9.2 mg/m^3 (0.3 to 2.6 ppm as hexane, by nondispersive infrared detector), and oxides of nitrogen from 0.1 to 1.1 ppm. Formaldehyde concentrations were obtained up to 370 μg/m^3 (0.3 ppm), and reports of eye irritation occurred with formaldehyde as low as 185 μg/m^3 (0.15 ppm).

An extensive series of irradiations of synthetic atmospheres containing auto exhausts was performed by Hamming[79] et al., using exhaust gases generated by six fuels of carefully defined composition. The study confirmed that changes in the composition of gasoline are reflected in changes in the composition of exhaust gases produced and in changes in the level of eye irritation developed on irradiation. It was concluded that the potential of exhaust gases for eye irritation might be raised or lowered, but could not be eliminated by controlling the composition of gasoline. More specifically, there was a definite tendency for eye irritation to increase with increasing fuel olefin content for fuels of equal aromatic content and to increase with increasing aromatic content for fuels of equal olefin content. With fuels of equal aromatic content, increasing fuel olefins resulted in increased pentenes and higher olefins in the exhaust, but had little effect on ethylene, propylene, and butenes. Some of the observed increases in eye irritation, therefore, must be attributed to products of reaction of these higher olefins in the atmosphere.

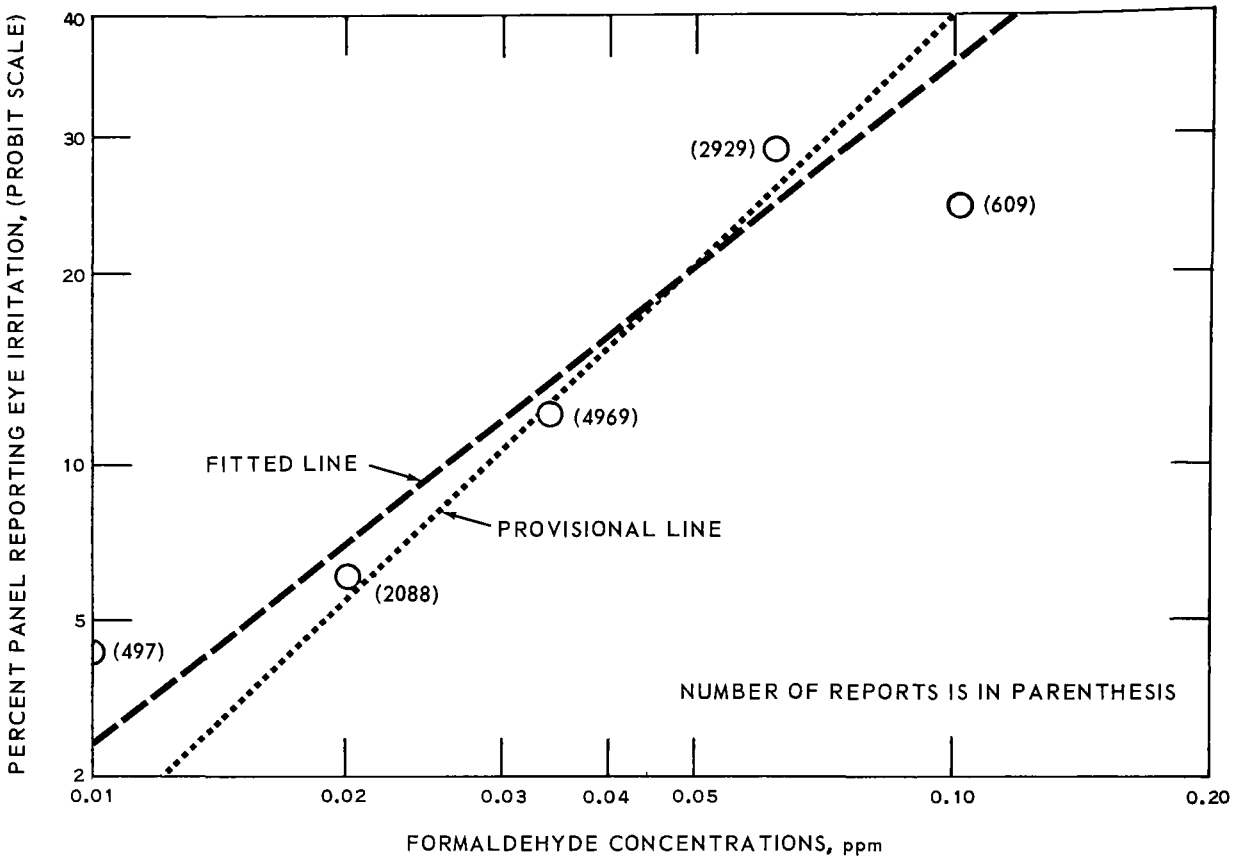

Figure 7-2. Regression curve of the effect of atmospheric concentrations of formaldehyde on panel eye irritation.[76]

With fuels of equal olefin content, increasing aromatic content decreased the production of ethylene, propylene, butenes, and higher olefins in automobile exhaust, but strongly increased the production of nitric oxide. Aromatic components in the exhaust were not measured, but were presumably higher with the more aromatic fuels. Although complicated by the effect of changing nitric oxide content, this suggests that aromatic hydrocarbons in the exhaust are also effective precursors for the generation of eye irritants. Although the relation of eye irritation to formaldehyde produced in this study was not specifically examined, a table of peak values of formaldehyde concentration shows that exhaust from the high-aromatic fuel, which had a high eye irritation potential, nevertheless produced much less formaldehyde when irradiated than did exhaust from the high-alkylate fuel, which had a low eye irritation potential. From this it is clear that formaldehyde concentration is not the only determinant of eye irritation in these synthetic atmospheres. Peroxybenzoyl nitrate is a probable further contributor, especially in the tests discussed here.

Another extensive series of irradiations of synthetic atmospheres was performed by Romanovsky[80] et al. In one series of tests, the hydrocarbon utilized was propylene; in another, a mixture of ethylene, propylene, isobutene, and gasoline was used; in a third, auto exhaust was used. The response-delay method was used to measure eye irritation. Utilizing all tests regardless of the initial hydrocarbon composition, the correlation coefficient for log of response time with log of formaldehyde concentration was -0.82, indicating that formaldehyde may have accounted

for a large portion of the variance in eye-irritation results. Formaldehyde levels found in the irridated atmospheres ranged from about 125 to 4,920 $\mu g/m^3$ (0.1 to 4 ppm). Since in these tests nitric oxide was treated as a major independent factor, it was important to evaluate the effects of initial hydrocarbons and nitric oxide separately, if possible. For this purpose, the data were fitted by curvilinear second- and third-degree equations with interaction terms, by a least-squares method, with the results shown in Figure 7-3. In this diagram, the dashed lines enclose the points representing initial concentrations for all the experiments with propylene as the photo-oxidation substrate (66 tests in all), and the contours represent constant levels of a derived index of eye irritation as computed from the equation of best fit to the data.

The form of the curves in Figure 7-3 indicates that for any given propylene level, maximum eye irritation should be obtained for nitric oxide initial concentrations of 2,460 to 3,690 $\mu g/m^3$ (2 to 3 ppm), but that the degree of eye irritation encountered ought to be determined primarily by the propylene level. The fact that propylene is sufficiently reactive to be largely consumed in these irradiations suggests that eye irritation is cuased by formaldehyde or some other product showing parallel behavior—that is, a product whose formation is approximately proportional to the consumption of propylene.

Multiple correlation coefficients with eye irritation as the independent variable were 0.85 for the tests with propylene and 0.54 for those with the olefin-gasoline mixture. Thus the initial levels of contaminants allowed a much better prediction of eye irritation results for the propylene system, accounting for two-thirds of the experimental variance as compared with only one-third for the mixed-hydrocarbon system. At the same time, formaldehyde peaks could be predicted very well (multiple correlation coefficient = 0.97) and equally well for each system. It therefore appears that eye irritation in the mixed-hydrocarbon system was significantly affected by some factor not paralleling the formaldehyde concentration. Such a factor might possibly be peroxyacyl nitrates, which begin to accu-

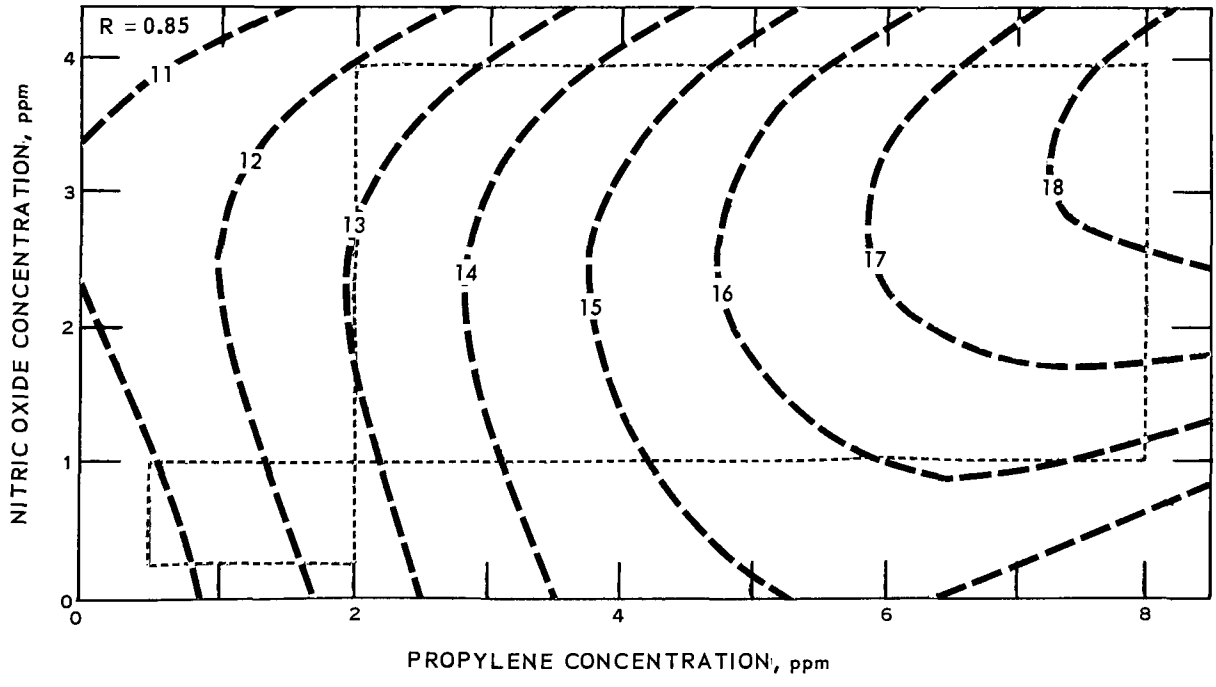

Figure 7-3. Effects of varying concentrations of propylene and nitric oxide on eye irritation.[80]

mulate in photooxidation systems only after the nitric oxide has been consumed; or it might be some irritant not yet recoginzed.

Schuck and Doyle[81] contended that eye irritation observed in their irradiated synthetic atmospheres could be accounted for by formaldehyde and acrolein. They compared observed values for 24 different hydrocarbons, with calculated values based on assigned contributions for unit concentrations of the two aldehydes, with resonable agreement resulting. The contributions were calculated on the basis of tests with the individual aldehydes. In the evaluation tests, 3,435 $\mu g/m^3$ (1.5 ppm) acrolein gave an eye irritation severity of 15 (maximum possible 24), and 4,920 $\mu g/m^3$ (4 ppm) formaldehyde gave a severity of 16. The compounds were therefore assigned values of 10 and 4 (severity units per ppm), respectively.

If these factors are applied to the aldehyde concentrations measured in the atmosphere by Renzetti[76] (discussed above), predicted values of the severity index are of the order of magnitude of 0.3 for days when 50 percent of the panelists reported eye irritation. If 50 percent of the members of the panel employed by Schuck[81] reported eye irritation in a given test, the severity index for that test would be at least 4. Thus there appears to remain a discrepancy amounting to a factor of at least 10 between the observed concentrations of formaldehyde and acrolein in the atmosphere and those that would be needed, using this formulation, to account for the observed effects.

In an attempt to explain this discrepancy, Schuck[1] et al. conducted irradiations of synthetic atmospheres containing nitrogen dioxide and ethylene or propylene, in conjunction with determination of eye irritation potential both by severity index and by response time, as well as observations on the blink rate of subjects exposing their eyes. When propylene was used, the regression of severity index against formaldehyde concentration was linear, with an intercept of 3 for zero formaldehyde. When ethylene was the hydrocarbon, however, the relation appeared significantly nonlinear, with values for formaldehydes less than 370 $\mu g/m^3$ (0.3 ppm) approaching the "pure air" average severity of about 5 (See Figure 7-4). The investigators interpreted these results as indicating that formaldehyde concentrations as low as 12 $\mu g/m^3$ (0.01 ppm) could cause eye irritation.

A possibility which has been suggested to account for the discrepancy between observed irritation and observed concentrations of irritants is a synergistic effect of aerosols on gasoues eye irritants. To test this hypothesis, Doyle[82,83] measured the eye irritation effects of six olefin nitrogen oxide mixtures irradiated with and without added sulfur dioxide. These experiments indicated that the aerosols formed did not increase, but on the average decreased, the eye irritation effects developed by the irradiation.

A series of 29 hydrocarbons, including 12 aromatic hydrocarbons, was studied in irradiations of synthetic atmospheres by Heuss.[75] It was found that, under the conditions chosen, the aromatic hydrocarbons produced more eye irritation than most nonaromatic compounds; in particular, styrene and β-methylstyrene were more potent that any other hydrocarbons in the list, as shown in Table 7-16. In this series, eye irritation showed no correlation with formaldehyde. The eye irritation potency utilized by these authors is based on a linear transformation of average panel response time.

Further investigation revealed the presence, in some of the systems containing aromatic compounds, of peroxybenzoyl nitrate.[75] This compound was found to be a lacrimator almost 200 times as potent as formaldehyde; in photooxidation of styrene, it accumulated to a concentration of 0.4 ppm. It is, therefore, probable that this substance caused most of the eye irritation in some or all of these irradiations of aromatic hydrocarbons. It is also probable that the same substance is formed in urban atmospheres and is responsible for some of the eye irritation observed in photochemical smog.

Altshuller,[84] studying irradiated synthetic atmospheres containing alkylbenzenes, found

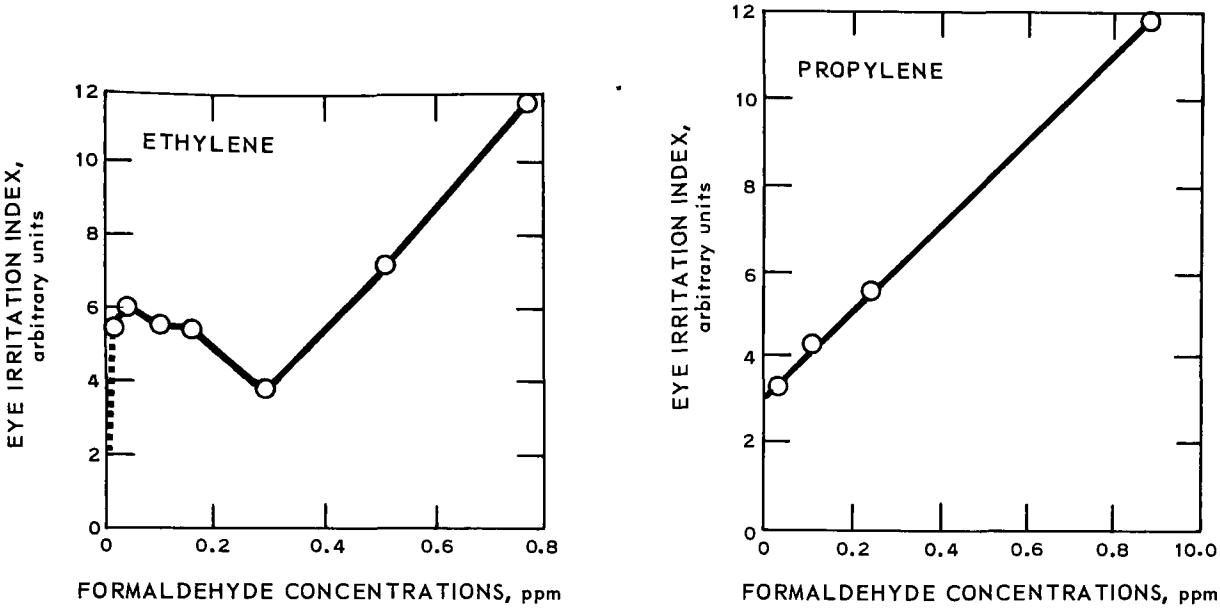

Figure 7-4. Average reported eye irritation intensities of 12 subjects during photooxidations with ethylene and propylene, related to observed formaldehyde concentrations.[1]

Table 7-16. EYE IRRITATION POTENCY OF VARIOUS HYDROCARBONS IN IRRADIATED SYNTHETIC ATMOSPHERES[75]

Hydrocarbon	Potency[a]	Hydrocarbon	Potency
n-Butane	0	*m*-Xylene	2.9
n-Hexane	0	1,3,5-Trimethylbenzene	3.1
Isooctane	0.9		
tert-Butylbenzene	0.9	1-Hexene	3.5
Benzene	1.0	Propylene	3.9
Ethylene	1.0	Ethylbenzene	4.3
1-Butene	1.3	Toluene	5.3
Tetramethylethylene	1.4	*n*-Propylbenzene	5.4
cis-2-Butene	1.6	Isobutylbenzene	5.7
Isopropylbenzene	1.6	*n*-Butylbenzene	6.4
sec-Butylbenzene	1.8	1,3-Butadiene	6.9
2-Methyl-2-butene	1.9	α-Methylstyrene	7.4
trans-2-Butene	2.3	Allylbenzene	8.4
o-Xylene	2.3	β-Methylstyrene	8.9
p-Xylene	2.5	Styrene	8.9

[a]Conditions: Hydrocarbon 2 ppm, nitric oxide 1 ppm for all except styrene, α-methylstyrene, β-methylstyrene, and allylbenzene (for those, hydrocarbon was 1 ppm, nitric oxide 0.5 ppm).

eye irritation panel responses of the same magnitude as those in propylene photooxidation, but mainly somewhat smaller. Toulene, *m*-xylene, and 1,3,5-trimethylbenzene showed eye irritation response greater than ethylene, while *o*-xylene gave less. The same workers[85] reported that eye irritation could also be produced by irradiating synthetic atmospheres containing 615 $\mu g/m^3$ (0.5 ppm) nitric oxide and 14.3 mg/m^3 (6 ppm) butane or 13.9 mg/m^3 (3 ppm) 2,4-dimethylhexane. In similar systems, 3 ppm of butane (7.1 mg/m^3), isopentane (8.9 mg/m^3), 2-methylpentane (10.3 mg/m^3), 3-methylhexane (12 mg/m^3), methylcyclohexane (12 mg/m^3), or *n*-nonane (15.6 mg/m^3) did not yield irritation significantly above that obtained with background air. In the system with 14.3 mg/m^3 (6 ppm) butane, it was noted that eye irritation was produced even with nitric oxide levels that were high enough to inhibit appreciable accumulation of oxidants, presumably including peroxyacyl nitrates. The authors concluded that paraffinic hydrocarbons, acetylene, and benzene do not contribute appreciably to eye irritation in photochemical air pollution.

4. Summary

a. Pulmonary Function

Pulmonary function tests are found to be altered following the exposure of experimental animals to either smog or irradiated auto exhaust. Caution must be taken, however, on drawing conclusions from these studies, since hydrocarbons are but one of several type pollutants inhaled by the animals. The following results have been previously discussed:

1. Exposure to ambient air in Los Angeles during episodes of photochemical smog produces a temporary increase in pulmonary airflow resistance in guinea pigs.

2. During short-term exposure to irradiated auto exhaust, the following changes in pulmonary function may be observed in guinea pigs: increased tidal volume, increased minute volume, and increased flow resistance,* with a decrease in the respiratory rate. The parameters return to normal immediately following exposure.

b. Eye Irritation

Consideration of the facts and findings cited in the section on eye irritation may justify some conclusions as to the relation of eye irritation to contaminant levels in photochemical smog:

1. The effective eye irritants are products of the photochemical reactions. These include, as identified eye irritants, formaldehyde, acrolein, peroxyacyl nitrates, and peroxybenzoyl nitrate.

2. The precursors of the eye irritants are hydrocarbons (as well as other organic compounds) in combination with oxides of nitrogen. Alkylbenzenes and olefins are more effective precursors than paraffins, benzene, and acetylenes.

3. The secondary contaminants causing eye irritation in the atmosphere are not known with certainty. Although it is possible that the compounds named above are the only irritants of importance in the atmosphere, this has not been demonstrated.

4. Concentrations of formaldehyde in irradiated synthetic atmospheres or in ambient atmospheres tend to be well correlated with observations of eye irritation. This is especially true for series of observations in which there is little change in the composition of the hydrocarbon substrate. But where relative proportions of paraffins, olefins, and aromatics are changed, the correlation is impaired.

5. Eye irritation severity developing as a result of irradiating atmospheres contaminated with hydrocarbons and oxides of nitrogen tends to reflect the concentration of hydrocarbon prescursors more directly than that of the oxides of nitrogen.

---

*When the irradiated exhaust contains 9,000 to 13,000 $\mu g/m^3$ of olefinic hydrocarbons, about 2,460 $\mu g/m^3$ (2 ppm) formaldehyde, and 540 $\mu g/m^3$ (0.2 ppm) acrolein, total expiratory flow resistance may be doubled.

6. The development of eye irritation in irradiated atmospheres is not strictly parallel to the accumulation of oxidants or ozone. Eye irritation can be appreciable while concentrations of oxidants are still negligible.

E. SUMMARY

Hydrocarbon air pollutants enter into and promote the formation of photochemical smog, and thus contribute to the development of eye irritation and other manifestations. They are intimately involved in the formation of formaldehyde and other aldehydes and ketones, and of various oxidants, including peroxyacetyl nitrate. In developing air quality criteria, the potential of the hydrocarbons under certain atmospheric conditions to form more hazardous derivatives must be discussed also.

Experimental data resulting from the exposure of animals and humans to various hydrocarbon compounds indicate that:

1. The aliphatic and alicyclic hydrocarbons are generally biochemically inert, though not biologically inert, and are only reactive at concentrations of 10^2 to 10^3 higher than those levels found in the ambient atmosphere. No effects have been reported at levels below 500 ppm.

2. The aromatic hydrocarbons are biochemically and biologically active. The vapors are more irritating to the mucous membranes than equivalent concentrations of the aliphatic or alicyclic groups.Systemic injury can result from the inhalation of vapors of the aromatic compounds; no effects, however, have been reported at levels below 25 ppm.

Aldehydes are one of the primary contributors to the eye irritation noted during photochemical smog; and, because there is a direct relationship between aldehydes and hydrocarbons as determined through various atmospheric reactions, a review of aldehyde toxicology was included in this chapter. Experimental data indicate:

1. Aldehyde concentrations have been correlated with the intensity of eye irritation during natural and laboratory-produced photochemical smogs. Formaldehyde appears to be detectable by odor or physiological response (optical chronaxy) at concentrations in the order of 70 $\mu g/m^3$ (0.06 ppm). The threshold for eye irritation by formaldehyde has been estimated by various investigators to be between 12 and 1,230 $\mu g/m^3$ (0.01 to 1.0 ppm). Acrolein can be detected by odor and eye irritation at concentrations as low as 600 $\mu g/m^3$ (0.25 ppm), but the threshold for optical chronaxy is reported as 1,750 $\mu g/m^3$ (0.75 ppm).

2. Formaldehyde at a concentration of 2,460 $\mu g/m^3$ (2 ppm) has been associated with a doubling of the total expiratory resistance of guinea pigs exposed to irradiated atmospheres of automobile exhaust gases.

3. Acetaldehyde is much less irritating than formaldehyde; its irritant threshold appears at concentrations of about 10,000 $\mu g/m^3$ (50 ppm). No physiological effects are known at levels that may be anticipated to occur in the ambient atmosphere.

In general, the most characteristic and important effect of aldehydes for both humans and animals is primary irritation of the eyes, upper respiratory tract, and skin. The unsaturated aldehydes are several times more toxic than the corresponding aliphatic aldehydes; toxicity generally decreases with increasing molecular weight within the unsaturated and aliphatic aldehyde series. Animal experiments have shown that aldehydes can affect respiratory functions, causing such effects as an increase in flow resistance and tidal volume and a decrease in the respiratory rate. Animal experiments have also indicated that acrolein and formaldehyde, in the presence of certain inert aerosols, appeared to be more toxic to mice than the pure compounds themselves.

Pulmonary function and eye irritation have also been evaluated by the exposure of experimental animals and humans to various mixed atmospheres that had the characteristic of providing the milieu necessary for hydrocarbon reactivity. Experimental data indicate:

1. Exposure of guinea pigs to ambient Los Angeles air may produce a temporary increase in pulmonary airflow resistance. Exposure of guinea pigs to laboratory-irradated auto exhaust causes as increased tidal volume, minute

volume, and flow resistance, with a decrease in the respiratory rate. These parameters return to normal immediately following exposure.

2. The precursors of the eye irritants are hydrocarbons (as well as other organic compounds) in combination with oxides of nitrogen; the alkylbenzenes and olefins are more effective precursors than paraffins, benzene, and acetylenes. The products of photochemical reactions that have been identified as effective eye irritants are formaldehyde, acrolein, peroxyacyl nitrates, and peroxybenzoyl nitrate.

F. REFERENCES

1. Schuck, E.A., E.R. Stephens, and J.T. Middleton. Eye Irritation Response at Low Concentrations of Irritants. Arch. Environ. Health. *13*(5):570-575, November 1966.
2. Renzetti, N.A. and E.A. Schuck. Preliminary Observations on the Relationship Between Eye Irritation in Synthetic Systems and in the Atmosphere. J. Air Pollution Control Assoc. *11*:121-124, March 1961.
3. Dickens, F. Biological Aromatization of Hydro-Aromatic Compounds. In: Biochemical Society Symposia No. 5, Williams, R.T. (Ed.). London, Cambridge University Press, 1950. p. 66-84.
4. Gerarde, H. Aliphatic Hydrocarbons. In: Industrial Hygiene and Toxicology, Patty, F.A. (ed.). Vol II. New York, Interscience Publishers, Inc., 1963.
5. Gerarde, H. Alicyclic Hydrocarbons. In: Industrial Hygiene and Toxicology, Patty, F.A. (ed.), Vol. II. New York, Interscience Publishers, Inc., 1963.
6. Gerarde, H. Aromatic Hydrocarbons. In: Industrial Hygiene and Toxicology, Patty, F.A. (ed.), Vol. II. New York, Interscience Publishers, Inc., 1963.
7. Greenburg, L. et al. Benzene (Benzol) Poisoning in the Rotogravure Printing Industry in New York City. J. Ind. Hyg. Toxicol. *21*(8):395-420, October 1939.
8. Greenburg, L. et al. The Effects of Exposure to Toulene in Industry. J. Amer. Med. Assoc. 118*(8):573-578,* February 21, 1942.
9. Community Air Quality Guides. Aldehydes. Amer. Ind. Hyg. Assoc. J. *29*(5):505-512, September-October 1968.
10. Fasset, D.W. Aldehydes and Acetals. In: Industrial Hygiene and Toxicology, Patty, F.A. (ed.), Vol. II. New York, Interscience Publishers, Inc. 1963.
11. Sim, V. M. and R. E. Pattle. Effect of Possible Smog Irritants on Human Subjects. J. Amer. Med. Assoc. *165*(15):1908-1913, December 14, 1957.
12. Sax, N. I. Dangerous Properties of Industrial Materials. New York, Reinhold Publishing Corp., 1968.
13. Skog, E. Anaesthetic and Haemolytic Action of Lower Aliphatic Aldehydes and Their Effect on Respiration and Blood Pressure. Acta Pharmacol. Toxicol. (Copenhagen). *8*(3):275-289, 1952.
14. Williams, R. T. Detoxification Mechanisms, 2d ed. New York, John Wiley & Sons, Inc., 1959. 796 p.
15. Elliott, M. A. and R. F. Davis. Composition of Diesel Exhaust Gas. S.A.E. Quart. Transactions. *4*(3):330-346, July 1950.
16. Rounds, F. G. and H. W. Pearsall. Diesel Exhaust Odor–Its Evaluation and Relation to Exhaust Gas Composition (SAE Paper No. 863). In: Vehicle Emissions, Vol. 6. New York, Society of Automotive Engineers, Inc., 1964. p. 45-69.
17. Wetmiller, R. S. and L. E. Endsley, Jr. Effect of Diesel Fuel on Exhaust Smoke and Odor. S.A.E. Transactions. *50*(11):509-520, December 1942.
18. Fracchia, M. F., F. J. Schuette, and P. K. Mueller. A Method for Sampling and Determination of Organic Carbonyl Compounds in Automobile Exhaust. Environ. Sci. Technol. *1*:915-922, November 1967.
19. Renzetti, N. A. and R. J. Bryan. Atmospheric Sampling for Aldehydes and Eye Irritation in Los Angeles Smog–1960. J. Air Pollution Control Assoc. *11*:421-424, 427, September 1961.
20, Properties and Essential Information for Safe Handling and Use of Formaldehyde. Chemical Safety Data Sheet SD-1. Manufacturing Chemists Assoc., Washington, D.C. April 1960.
21. Formaldehyde: Its Toxicity and Potential Dangers. Public Health Rept. Suppl. *18*: 1945.
22. Haggard, H. W. Action of Irritant Gases Upon the Respiratory Tract. J. Ind. Hyg. *5*(10):390-398, February 1924.
23. Motor Vehicles, Air Pollution, and Health. A Report of the Surgeon General to the U. S. Congress in Compliance with Public Law 89-493, The Schenck Act. U. S. Dept. of Health, Education, and Welfare, Public Health Service, Division of Air Pollution. Washington, D. C. U. S. Government Printing Office. House Document No. 489, 87th Congress, 2d Session. 1962. 459 p.
24. Melekhina, V. P. Maximum Permissible Concentrations of Formaldehyde in Atmospheric Air. In: USSR Literature on Air Pollution and Related Occupational Diseases, Levine, B. S., Vol. 3. Washington, D. C., Dept. of Commerce, 1960. p. 135.

25. Melekhina, V. P. Hygienic Evaluation of Formaldehyde as an Atmospheric Air Pollutant. In: USSR Literature on Air Pollution and Related Occupational Diseases. Levin, B.S., Vol. 9. Washington, D. C., Dept. of Commerce, 1962. p. 9.
26. Bourne, H. G., Jr. and S. Seferian. Formaldehyde in Wrinkle-proof Apparel Produces Tears for Milady, Ind. Med. Surg. *28*:232-233, May 1959.
27. Roth, H. P. and E. A. Swenson. Physiological Studies of Irritant Aspects of Atmospheric Pollution. Los Angeles County Air Pollution Control District. California. 1957.
28. Morrill, E. E., Jr. Formaldehyde Exposure from Paper Process Solved by Air Sampling and Current Studies. Air Conditioning, Heating, Vent. *58*:94-95, July 1961.
29. Air Pollution, Stern, A. C. (ed.), Vol. I, 2d ed. New York, Academic Press, 1968. 694 p.
30. Walker, J. F. Formaldehyde, 3d ed. New York, Reinhold Publishing Corp., 1964. 701 p.
31. Barnes, E. C. and H. W. Speicher. The Determination of Formaldehyde in Air. J. Ind. Hyg. Toxicol. *24*(1):10-17, January 1942.
32. Elkins, H. B. Maximum Acceptable Concentrations. A Comparison in Russia and the United States. Arch. Environ. Health. *2*:45-49, January 1961.
33. Harris, D. K. Health Problems in the Manufacture and Use of Plastics. Brit. J. Ind. Med. *10*(4):255-268, October 1953.
34. Hygienic Guide Series. Dichlorodifluoromethane. Amer. Ind. Hyg. Assoc. J. *29*(5):513-516, September-October 1968.
35. Threshold Limit Values for 1967. Adopted at the 29th Annual Meeting of the American Conference of Governmental Industrial Hygienists. Chicago. May 1-2, 1967.
36. Air Pollution, Stern, A. C. (ed.), Vol. III, 2d ed. New York, Academic Press, 1968, 866 p.
37. Murphy, S. D., H. V. Davis, and V. L. Zaratzian. Biochemical Effects in Rats from Irritating Air Contaminants. Toxicol. Appl. Pharmacol. *6*(5):520-528, September 1964.
38. Salem, H. and H. Cullumbine. Inhalation Toxicities of Some Aldehydes. Toxicol. Appl. Pharmacol. *2*(2):183-187, March 1960.
39. Skog, E. A Toxicological Investigation of Lower Aliphatic Aldehydes. I. Toxicity of Formaldehyde, Acetaldehyde, Propionaldehyde, and Butyraldehyde; as well as of Acrolein and Crontonaldehyde. Acta Pharmacol. Toxicol. (Copenhagen). *6*(4): 299-318, 1950.
40. Amdur, M. O. The Physiological Response of Guinea Pigs to Atmospheric Pollutants. Int. J. Air Water Pollution. *1*(3):170-183, January 1959.
41. Amdur, M. O. The Effect of Aerosols on the Response to Irritant Gases, Inhaled Particles and Vapours. In: Proc. Int. Symp., Oxford, Eng. 1960. p. 281-292.
42. Davis, T. R. A., S. P. Battista, and C. J. Kensler. Mechanism of Respiratory Effects During Exposure to Guinea Pigs to Irritants. Arch. Environ. Health. *15*:412-419, October 1967.
43. Murphy, S. D. and C. E. Ulrich. Multi-Animal Test System for Measuring Effects of Irritant Gases and Vapors on Respiratory Function of Guinea Pigs. Amer. Ind. Hyg. Assoc. J. *25*(1):25-28, January-February 1964.
44. Cralley, L. V. The Effect of Irritant Gases Upon the Rate of Ciliary Activity. J. Ind. Hyg. Toxicol. *24*(7):193-198, September 1942.
45. Dalhamn, T. Mucous Flow and Ciliary Activity in Trachea of HealthyRats and Rats Exposed to Respiratory Irritant Gases (SO_2, H_3N, HCHO). Acta Physiol. Scand. (Stockholm). Suppl. 123. *36*:1-161, 1956.
46. Kensler, C. J. and S. P. Battista. Chemical and Physcial Factors Affecting Mammalian Ciliary Activity. Amer. Rev. Resp. Dis. *93*:93-102, March 1966.
47. Gofmekler, V. A. Effect of Embryonic Development of Benzene and Formaldehyde in Inhalation Experiments [Embriotropnoe deistvie benzola i formal'degiela pri ingalyatsionnom puti vozdeistviya v eksperimente]. Hyg. Sanit. *33*:327-332, January-March 1968.
48. La Belle, C.W., J.E. Long, and E. E. Christofano. Synergistic Effects of Aerosols. Arch. Ind. Health. *11*:297-304, April 1955.
49. Amdur, M. O. The Physiological Response of Guinea Pigs to Atmospheric Pollutants. Int. J. Air Water Pollution. *1*(3):170-183, January 1959.
50. Guest, H. R., B. W. Kiff, and H. A. Stansbury, Jr. Acreolein and Derivatives. In: Kirk-Othmer Encyclopedia of Chemical Technology Standen, A. (ed.), Vol. 1, 2d ed. New York, Interscience Publishers, 1963. P. 255-274.
51. Prentiss, A. M. Chemicals in War. New York, McGraw-Hill Book Co., Inc., 1937. 739 p.
52. Acrolein. Smith, C. W. (ed.). New York, John Wiley & Sons, Inc., 1962. 273 p.
53. Properties and Essential Information for Safe Handling and Use of Acrolein. Chemical Safety Data Sheel SD-85. Manufacturing Chemists Assoc., Washington, D. C. 1961.
54. Leonardos, G., D. A. Kendall, and N. J. Bernard. Odor Threshold Determinations of 53 Odorant Chemicals. J. Air Pollution Control Assoc. *19*:91-95, February 1969.
55. Plotnikova, M. M. Acrolein as an Atmospheric Air Pollutant. In: USSR Literature on Air Pollution and Related Occupational Diseases, Levine,

B. S., Vol. 3. Washington, D. C., Dept. of Commerce, 1960. p. 188.
56. Yant, W. P. et al. Acrolein as a Warning Agent for Detecting Leakage of Methyl Chloride from Refrigerators. Bureau of Mines. Washington, D. C. Report of Investigation Number 3027. July 1930, 11 p.
57. Hine, C. H. et al. In: Proceedings of the Air Pollution Medical Research Conference, Los Angeles, December 4, 1961.
58. Cook, W. A. Maximum Allowable Concentrations of Industrial Atmospheric Contaminants. Ind. Med. *14*:936-946, November 1945.
59. Henderson, Y. and H. W. Haggard. Noxious Gases and the Principles of Respiration Influencing Their Actions, 2d ed. New York Reinhold Publishing Corp., 1943. 294 p.
60. Gusev, M. I. et al. Determination of the Daily Average Maximum Permissible Concentration of Acrolein in the Atmosphere [K obosnovaniyu srednesutochnoi predel'no dopustimoi konstentratsii akroleina v atmosfernom bozdukhe]. Hyg. Sanit. *31*:8-13, January-March 1966.
61. Mettier, S. R. et al. A Study of the Effect of Air Pollutants on the Eye. Arch. Ind. Health. *21*:1-6, January 1960.
62. Hine, C. H. et al. Eye Irritation for Air Pollution. J. Air Pollution Control Assoc. *10*(1):17-20, February 1960.
63. Smyth, H. F., Jr. Hygienic Standards for Daily Inhalation. Amer. Ind. Hyg. Assoc. Quart. *17* (2):129-185, June 1956.
64. Pattle, R. E. and H. Cullumbine. Toxicity of Some Atmospheric Pollutants. Brit. Med. J. *2*(4998):913-916, October 20, 1956.
65. Iwanoff, N. Experimentelle Studien Uber den Einfluss Technisch und Hygienisch Wichtiger Gase und Dampfe auf den Organismus. Arch. Hyg. Bakteriol. (Munich). *73*:338, 1911.
66. Catilina, P., L. Thieblot, and J. Champeix. Experimental Lesions of the Respiratory System in Rats from the Inhalation of Acrolein [Lesions Respiratoires Experimentales par Inhalation d'Acroleine Chez le Rat]. Arch. Mal. Prof. (Paris). *27*:857-867. December 1966.
67. Murphy, S. D., D. A. Klingshirn, and C. E. Ulrich. Respiratory Response of Guinea Pigs During Acrolein Inhalation and Its Modification by Drugs. J. Pharmacol. Exp. Therap. *141*(1):79-83, July 1963.
68. Ryazanov, V. A. Sensory Physiology as Basis for Air Quality Standards. The Approach Used in the Soviet Union. Arch. Environ. Health *5*(5):480-494, November 1962.
69. Amdur, M. O. The Influence of Aerosols Upon the Respiratory Response of Guinea Pigs to Sulfur Dioxide. Amer. Ind. Hyg. Assoc. Quart. *18*(2):149-155, June 1957.
70. Plotnikova, M. Basic Investigations for the Determination of the Limit of Allowable Acrolein Concentration in Atmospheric Air. In: Limits of Allowable Concentrations of Atmospheric Pollutants, Book 4, Ryazanov, V. A. (ed.). Office of Technical Services, Washington, D. C. 1960.
71. Silverman, L., H. F. Schulte, and M. W. First. Further Studies on Sensory Response to Certain Industrial Solvent Vapors. J. Ind. Hyg. Toxicol. *28*(6):262-266, November 1946.
72. Murphy, S. D. et al. Effects on Animals of Exposure to Auto Exhaust. Arch. Environ. Health. *7*(1):60-70, July 1963.
73. Swann, H. E. et al. Biological Effects of Urban Air Pollution: II. Chronic Exposure of Guinea Pigs. Arch. Environ. Health. *11*(6): 765-769, December 1965.
74. Swann, H. E. and O. J. Balchum. Biological Effects of Urban Air Pollution: IV. Effects of Acute Smog Episodes on Respiration of Guinea Pigs. Arch. Environ. Health. *12*:698-704, June 1966.
75. Heuss, J. M., and W. A. Glasson. Hydrocarbon Reactivity and Eye Irritation. Environ. Sci. Technol. *2*:1109-1116, December 1968.
76. Renzetti, N. A. and R. J. Bryan. Atmospheric Sampling for Aldehydes and Eye Irritation in Los Angeles Smog–1960. J. Air Pollution Control Assoc. *11*:421-424, 427, September 1961.
77. Buchberg, H. et al. Studies of Interacting Atmospheric Variables and Eye Irritation Thresholds. Int. J. Air Water Pollution. *7*(4/5): 257-280, June 1963.
78. Tuesday, C. S. et al. Paper No. 65-19. Presented at the Annual Meeting of the Air Pollution Control Association. Toronto. June 1965.
79. Hamming, O. J. et al. Gasoline Composition and the Control of Smog. Joint Study by Western Oil and Gas Association and Los Angeles County Air Pollution District. Los Angeles Country Air Pollution Control District. Los Angeles, Calif. 1961.
80. Romanovsky, J. C., R. M. Ingels, and R. J. Gordon. Estimation of Smog Effects in the Hydrocarbon-Nitric Oxide System. J. Air Pollution Control Assoc. *17*:454-459, July 1967.
81. Schuck, E. A. and G. J. Doyle. Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide. Air Pollution Foundation. San Marino, Calif. Report Number 29. October 1959. 104 p.
82. Doyle, G. J., N. Endow, and J. L. Jones. Sulfur Dioxide Role in Eye Irritation. Arch. Environ. Health. *3*(6):657-667, December 1961.
83. Doyle, G. J. and J. L. Jones. Automobile Exhaust–Gas Aerosols: A Review of Studies Conducted at Stanford Research Institute. J. Air Pollution Control Assoc. *13*: 365-367, August 1963.

84. Altshuller, A. P. et al. Chemical Aspects of the Photooxidation of the Propylene - Nitrogen Oxide System. Environ. Sci. Technol. *1*:899-922, November 1967.

85. Altshuller, A. P. et al. Photochemical Reactivities of N-Butane and Other Paraffinic Hydrocarbons. J. Air Pollution Control Assoc. *19*:787-790, October 1969.

CHAPTER 8.

SUMMARY AND CONCLUSIONS

A. INTRODUCTION

This document focuses on gas-phase hydrocarbons and certain of their oxidation products, particularly aldehydes, that are associated with the manifestations of photochemical air pollution. Particulate hydrocarbons, and more specifically polynuclear hydrocarbons, are not treated in this document. It is important to recognize that the criteria for hydrocarbons rest almost entirely on their role as precursors of other compounds formed in the atmospheric photochemical system and not upon direct effects of the hydrocarbons themselves. A companion document, AP-63, *Air Quality Criteria for Photochemical Oxidants,* covers the effects of a class of photochemical reaction products not treated in this document.

B. SOURCES, NATURE, AND PRINCIPLES OF CONTROL OF ATMOSPHERIC HYDROCARBONS

Most natural sources of hydrocarbon emissions are biological in nature. A conservative estimate made for the worldwide natural production rate of methane is 3×10^8 tons per year. A similar estimate of 4.4×10^8 tons per year has been made for volatile terpenes and isoprenes. It appears that nonurban air contains from 0.7 to 1.0 mg/m^3 (1.0 to 1.5 ppm) methane and less than 0.1 ppm each of other hydrocarbons.

Total nationwide technological emissions of hydrocarbons and related organic compounds for the year 1968 were estimated to be 32×10^6 tons. Transportation represented the largest source category and accounted for 52 percent of this estimate. The miscellaneous source category—principally organic solvent evaporation—was the second largest and represented 27 percent of the total emissions. Industrial processes (14 percent) was third; solid waste disposal (5 percent) was fourth; and fuel combustion in stationary sources (2 percent) was fifth.

Local emission estimates for 22 metropolitan areas ranged from about 0.05 to 1.3 million tons per year. Transportation sources accounted for from 37 to 99 percent of local emissions, and process losses accounted for from 1 to 63 percent. Hydrocarbon emissions, therefore, originate primarily from the inefficient combustion of volatile fuels and from their use as process raw materials.

The control of hydrocarbon emissions rests upon the basic principles of: (1) combustion process optimization, (2) recovery by mass transfer principles, (3) restriction of evaporative loss, and (4) process material and fuel substitution. The first three principles are all applied with varying degrees of success in the control of automobile emissions.

C. ATMOSPHERIC LEVELS OF HYDROCARBONS AND THEIR RELATED PRODUCTS

Yearly averages of monthly maximum 1-hour average hydrocarbon concentrations including methane, recorded continuously in various stations of the Continuous Air Monitoring Projects, have reached maximum hourly values of 8 to 17 ppm (as carbon), but at least half of this amount is probably the photochemically unreactive methane component in all cases.

In a series of 200 samples taken in one urban location, average concentrations of the most abundant hydrocarbons were as follows

(in ppm as carbon): methane, 3.22; toluene, 0.37; *n*-butane, 0.26; *i*-pentane, 0.21; ethane, 0.20; benzene, 0.19; *n*-pentane, 0.18; propane, 0.15; and ethylene, 0.12. Among classes of hydrocarbons, the alkanes predominate, even if methane is excluded. They are followed by the aromatics, olefins, acetylenes, and alicyclics.

The diurnal variation of hydrocarbon concentrations resembles that of carbon monoxide (at stations in the Los Angeles area) in having a pronounced maximum appearing usually between 6:00 and 8:00 a.m.

For nonoxidant photochemical secondary contaminants, available information is limited to results of special studies on aldehydes in the Los Angeles area. These show that yearly maximum 1-hour average total aldehyde concentrations range from 0.20 to 1.30 ppm and that the analogous formaldehyde concentrations range from 60 to 150 $\mu g/m^3$ (0.05 to 0.12 ppm). Hourly average acrolein concentrations range from 10 to 270 $\mu g/m^3$ (0.004 to 0.010 ppm) in various studies. The ratio of formaldehyde to the "total" aldehyde index has been reported at from about 10 to 90 percent; it is likely that an appreciable part of the variation is caused by the use of different analytical methods or procedures in the different investigations.

D. SAMPLING AND STANDARDIZATION METHODS FOR MEASUREMENT OF HYDROCARBONS

With few exceptions, atmospheric hydrocarbon measurements are made with relatively complex instruments that operate continuously. Continuous instrumentation demands dynamic calibration techniques. Standard gases for this purpose are available or may be generated by permeation tubes or dilution systems, or prepared in large containers.

Flame ionization analyzers are sensitive and reliable and are suitable for the continuous measurement of total hydrocarbons. They are generally accepted as the method of choice by NAPCA. They cannot, however, give the specific detailed information required for a thorough understanding of the atmospheric photochemical problem. Attempts to further define the hydrocarbon mixture by using pretreatment columns to measure only methane or various reactive classes have met with some success but limited application.

Spectrometric techniques both for total and specific analysis are complex and generally insensitive.

Gas chromatographic analysis provides the requisite sensitivity and specificity for the quantitation of individual hydrocarbons. Difficulties in qualitative analysis and data handling have limited the application of GC to short-term studies for the most part, and no continuous data are available.

Carbonyl compounds, specifically aldehydes and ketones, can be measured by several manual colorimetric techniques, but very little actual data are available.

E. RELATIONSHIP OF ATMOSPHERIC HYDROCARBONS TO PHOTOCHEMICAL AIR POLLUTION LEVELS

The development of a model to relate emission rates of hydrocarbons to ambient air quality and thence to the secondary products of photochemical reactions has proved to be an elusive problem. Because of this lack of an appropriate model, the relationship between hydrocarbon emissions and subsequent maximum daily oxidant levels has been approached empirically by a comparison of 6:00 to 9:00 a.m. average hydrocarbon values with hourly maximum oxidant values attained later in the day. This approach has validity only because of the dominating influence of the macro-meteorological variables on both the concentrations of precursors and photochemical products. Furthermore, this approach can only yield useful information when a large number of days are considered, thus guaranteeing the inclusion of all possible combinations of emission rates, meteorological dilution and dispersion variables, sunlight intensity, and ratios of precursor emissions. When maximum daily oxidant values from such an unrestricted data base are plotted as a function of the early morning

hydrocarbons, a complete range of oxidant values starting near zero and ranging up to a finite and limiting value is observed. Given data for a sufficient number of days, it becomes apparent that the maximum values of attainable oxidant are a direct function of the early morning hydrocarbon concentration. This upper limit of the maximum daily oxidant concentration is dependent on the metropolitan geographical area only to the extent that differences in meteorological variables exist between these areas. Thus the data from all cities can be plotted on one graph when defining the oxidant upper limit as a function of early morning hydrocarbon concentrations.

In defining this oxidant upper limit all available data relating directly measured nonmethane hydrocarbon concentrations to maximum daily oxidant concentrations have been used. Direct observation of this limit in the vicinity of 200 $\mu g/m^3$ (0.1 ppm) daily maximum 1-hour average oxidant concentration shows that in order to keep the oxidant below this value, the 6:00 to 9:00 a.m. average nonmethane hydrocarbon concentration must be less than 200 $\mu g/m^3$ (0.3 ppm C). This maximum oxidant concentration potential may be expected to occur on about 1 percent of the days.

F. EFFECTS OF HYDROCARBONS AND CERTAIN ALDEHYDES ON VEGETATION

Hydrocarbons were first recognized as phytotoxic air pollutants about the turn of the century as a result of complaints of injury to greenhouse plants from illuminating gas. Ethylene was shown to be the injurious component. Renewed interest in hydrocarbons, and ethylene in particular, occurred in the mid-1950's when ethylene was found to be one of the primary pollutants in the photochemical smog complex. Research on several unsaturated and saturated hydrocarbons proved that only ethylene had adverse effects at known ambient concentrations. Acetylene and propylene more nearly approach the activity of ethylene than do other similar gases, but 60 to 500 times the concentration is needed for comparable effects.

In the absence of any other symptom, the principal effect of ethylene is to inhibit growth of plants, Unfortunately, this effect does not characterize ethylene because other pollutants at sublethal dosages, as well as some disease and environmental factors, will also inhibit growth.

Epinasty of leaves and abscission of leaves, flower buds, and flowers are somewhat more typical of the effects of ethylene, but the same effects may be associated with nutritional imbalance, disease, or early senescence. Perhaps the most characteristic ethylene effects are the dry sepal wilt of orchids and the closing of carnation flowers. Injury to sensitive plants has been reported at ethylene concentrations of 1.15 to 575 $\mu g/m^3$ (0.001 to 0.5 ppm) during time periods of 8 to 24 hours.

G. TOXICOLOGICAL APPRAISAL OF HYDROCARBONS AND ALDEHYDES

Hydrocarbon air pollutants enter into and promote the formation of photochemical smog and thus contribute to the development of eye irritation and other manifestations. They are intimately involved in the formation of formaldehyde and other aldehydes and ketones, and of various oxidants, including peroxyacetyl nitrate. In developing air quality criteria, there must be due consideration of the potential of the hydrocarbons under certain atmospheric conditions to form more hazardous derivatives.

Experimental data resulting from the exposure of animals and humans to various hydrocarbons compounds indicate that:

1. The aliphatic and alicyclic hydrocarbons are generally biochemically inert, though not biologically inert, and are only reactive at concentrations of 10^2 to 10^3 higher than those levels found in the ambient atmosphere. No effects have been reported at levels below 500 ppm.

2. The aromatic hydrocarbons are biochemically and biologically active. The vapors are more irritating to the mucous membranes than equivalent concentrations of the aliphatic or alicyclic groups. Systemic injury can result from the inhalation of vapors of the aromatic compounds; no effects, however, have been reported at levels below 25 ppm.

Pulmonary function and eye irritation have been evaluated by the exposure of experimental animals and humans to various mixed atmospheres that had the characteristic of providing the milieu necessary for hydrocarbon reactivity. Experimental data indicate:

1. Exposure of guinea pigs to ambient Los Angeles photochemical smog produces a temporary increase in pulmonary airflow resistance. Exposure of guinea pigs to laboratory-irradiated auto exhaust causes an increased tidal volume, minute volume, and flow resistance, with a decrease in the respiratory rate. These parameters return to normal immediately following exposure.

2. The precursors of the eye irritants are hydrocarbons (as well as other organic compounds) in combination with oxides of nitrogen; the alkylbenzenes and olefins are more effective precursors than paraffins, benzene, and acetylenes. The products of photochemical reactions that have been identified as effective eye irritants are formaldehyde, acrolein, peroxyacyl nitrates, and peroxybenzoyl nitrate. In general, the most characteristic and important effect of aldehydes for both humans and animals is primary irritation of the eyes, upper respiratory tract, and skin. The unsaturated aldehydes are several times more toxic than the corresponding aliphatic aldehydes, and toxicity generally decreases with increasing molecular weight within the unsaturated and aliphatic aldehyde series. Animal experiments have shown that aldehydes can affect respiratory functions, causing such effects as an increase in flow resistance and tidal volume and a decrease in the respiratory rate. Animal populations, although many of the effects attributed to photochemical smog are indirectly related to ambient levels of these hydrocarbons.

Experimental data on specific aldehydes have indicated:

1. Aldehyde concentrations have been correlated with the intensity of eye irritation during natural and laboratory-produced photochemical smog. Formaldehyde appears to be detectable by odor or physiological response (optical chronaxy) at concentrations in the order of 70 $\mu g/m^3$ (0.06 ppm). The threshold for eye irritation by formaldehyde has been estimated by various investigators to be between 12 and 1,230 $\mu g/m^3$ (0.0 1 to 1.0 ppm). Acrolein can be detected by both odor and eye irritation at concentrations as low as 600 $\mu g/m^3$ (0.25 ppm), but the threshold for optical chronaxy is reported as 1,750 $\mu g/m^3$ (0.75 ppm).

2. Formaldehyde at a concentration of 2,460 $\mu g/m^3$ (2 ppm) has been associated with a doubling of the total expiratory resistance of guinea pigs exposed to irradiated atmospheres of automobile exhaust gases.

3. Acetaldehyde is much less irritating than formaldehyde; its irritant threshold appears at concentrations of about 10,000 $\mu g/m^3$ (50 ppm). No physiological effects are known at levels that may be anticipated to occur in the ambient atmosphere.

H. CONCLUSIONS

The conclusions that follow are derived from a careful evaluation of the studies cited in this document, representing the National Air Pollution Control Administration's best judgment of the effects that may occur when various levels of hydrocarbons are reached in the ambient air. Additional information from which the conclusions were derived, and qualifications that may enter into consideration of these data, can be found in the appropriate chapters of this document.

1. Our present state of knowledge does not demonstrate any direct health effects of the

gaseous hydrocarbons in the ambient air on populations, although many of the effects attributed to photochemical smog are indirectly related to ambient levels of these hydrocarbons.

2. Injury to sensitive plants has been reported in association with ethylene concentrations of from 1.15 to 575 $\mu g/m^3$ (0.001 to 0.5 ppm) over a time period of 8 to 24 hours (Chapter 6).

3. Examination of air quality data indicates that an early morning (6:00 to 9:00 a.m.) concentration of 200 $\mu g/m^3$ (0.3 ppm C) nonmethane hydrocarbon can be expected to produce a maximum hourly average oxidant concentration of up to 200 $\mu g/m^3$ (0.1 ppm) (Chapter 5).

I. RESUME

Studies conducted thus far of the effects of ambient air concentrations of gaseous hydrocarbons have not demonstrated direct adverse effects from this class of pollution on human health. However, it has been demonstrated that ambient levels of photochemical oxidant, which do have adverse effects on health, are a direct function of gaseous hydrocarbon concentrations; and when promulgating air quality standards for hydrocarbons, their contribution to the formation of oxidant should be taken into account.

An analysis of 3 years of data collected in three American cities shows that on those several days a year when meteorological conditions were most conducive to the formation of photochemical oxidant, nonmethane hydrocarbon concentrations of 200 $\mu g/m^3$ (0.3 ppm C) for the 3-hour period from 6:00 to 9:00 a.m. might produce an average 1-hour photochemical oxidant concentration of up to 200 $\mu g/m^3$ (0.10 ppm) 2 to 4 hours later. The hydrocarbon measurements were confined to 200 $\mu g/m^3$ (0.3 ppm C), or above, because of instrumentation limitations. However, if the functional relationship between the hydrocarbon and photochemical oxidant measurements were extended to include the lowest levels at which photochemical oxidant has been observed to adversely affect human health, the corresponding hydrocarbon concentration would be approximately 100 $\mu g/m^3$ (0.15 ppm C).

APPENDIX.

CONVERSION BETWEEN VOLUME AND MASS UNITS OF CONCENTRATION

The physical state of gaseous air pollutants at atmospheric concentrations generally may be described by the ideal gas law:

$$pv = nRT \qquad (1)$$

where:

- p = absolute pressure of gas
- v = volume of gas
- n = number of moles of gas
- T = absolute temperature
- R = universal gas constant

The number of moles (n) may be calculated from the weight of pollutant (w) and its molecular weight (m) by:

$$n = \frac{w}{m} \qquad (2)$$

Substituting equation (2) into equation (1) and rearranging yields:

$$v = \frac{wRT}{pm} \qquad (3)$$

Parts per million refers to the volume of pollutant (v) per million volumes of air (V).

$$ppm = \frac{v}{10^6 V} \qquad (4)$$

Substituting equation (3) into equation (4) yields:

$$ppm = \frac{w}{V} \quad \frac{RT}{pm10^6} \qquad (5)$$

Using the appropriate values for variables in equation (5), a conversion from volume to mass units of concentration for methane may be derived as shown below.

T = 298°K (25°C)
p = 1 atm
m = 16 g/mole
R = 8.21×10^{-2} ℓ-atm/mole° K

$$ppm = \frac{w(g) \times 10^6 \ (\mu/g)}{V(\ell) \times 10^{-3} \ (m^3/\ell)}$$

$$\frac{8.21 \times 10^{-2} \ (\ell\text{-atm/mole}^\circ K) \times 298(^\circ K)}{1(atm) \times 16 \ (g/mole) \times 10^6}$$

$$1 \ \mu g/m^3 = 1.53 \times 10^{-3} \ ppm$$

$$1 \ ppm = 655 \ \mu g/m^3$$

In the text reference is made both to ppm as carbon (ppm C) and to ppm as methane. On a ppm-by-volume basis these two terms are equivalent, since methane has only a single carbon atom. In converting such measurements from volume to mass units, therefore, the molecular weight of methane is used.

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