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Section
1.1

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Biologic Effects of Atmospheric Pollutants

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1.1

PARTICULATE POLYCYCLIC ORGANIC MATTER

*Committee on
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Sources of Polycyclic Organic Matter

Polycyclic organic matter (POM) can be formed in any combustion process involving fossil fuels or, more generally, compounds containing carbon and hydrogen. The amount of POM formed will vary widely; efficient, controlled combustion favors very low POM emissions, whereas inefficient burning favors high emissions. This chapter catalogs the more obvious sources of POM emissions to the atmosphere and points out the uncertainties in our information on various source contributions.

MECHANISM OF POM FORMATION

Although the mechanism of POM formation in combustion processes is complex and variable, a relatively clear picture of the overall reaction has emerged, owing primarily to Badger.²¹ Chemical reactions in flames proceed by free-radical paths; in POM formation, a synthetic route is postulated, as shown in Figure 3-1. Radical species containing one, two, or many carbon atoms can combine in rapid fashion at the high temperatures (500-800 C) attained in the flame front. This pyrosynthesis of pyrolysis products is obviously a func-

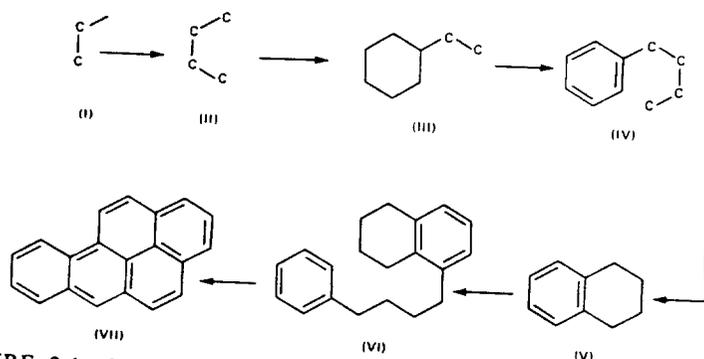


FIGURE 3-1. Mechanism of benzo[a]pyrene formation. (After Badger.²¹)

tion of many variables, not the least of which is the presence of a chemically reducing atmosphere, common in the center of flames. In these conditions, radical chain propagation is enhanced, allowing the buildup of a complex POM molecule, such as benzo[a] pyrene. It is important to note that, although methane itself can lead to POM,¹⁰² the formation of these large molecules is favored by the presence of higher-molecular-weight radicals and molecules in the fuel. Obviously, it is unnecessary to break the starting material down completely to a two-carbon radical in order to form benzo[a] pyrene. Any component of the combustion reaction that can contribute intermediate pyrolysis products of the structure required for benzo[a] pyrene synthesis would be expected to lead to increased yields of benzo[a] pyrene. Thus, Badger and Spotswood²² have shown that in the pyrolysis of alkylbenzenes, including *n*-butylbenzene, enhanced benzo[a] pyrene formation is due primarily to increased concentrations of intermediate structures of types III, IV, and V (Figure 3-1). Badger also showed conclusively that specific aromatic and diolefinic compounds serve as precursors for other polycyclic organic products. The mechanism in Figure 3-1 is a pathway to benzo[a] pyrene formation, but similar routes could be devised, with somewhat different intermediates, to lead to most of the known POM produced in combustion processes. Badger's work, with its reliance on calculated C-C and C-H bond energies to predict favored pathways and the experimental confirmation of these steps with radioisotopic labeling, provides a clear-cut mechanism for POM formation in the combustion process.

As pointed out by Hoffmann and Wynder,³⁸⁸ the use of nitrogen atmospheres in Badger's experiments has been criticized for its lack

of relevance to the actual combustion of organic molecules. Nonetheless, the conditions are similar to those of the oxygen-deficient environment in flames, and the data are in good qualitative agreement with observed POM combustion products.

NONTECHNOLOGIC SOURCES OF POM

Uncontrolled combustion, such as that in forest fires, would be expected to produce POM. Although the requirements for appreciable POM formation can be met in these fires, data on actual emission rates are lacking. The only other nontechnologic source of airborne POM is agricultural burning, but, because it is often planned by man, its contribution is covered below, under "Refuse Burning."

TECHNOLOGIC SOURCES OF POM

Large quantities of POM are generated in the vast number of technologic activities that prevail in our society. The contribution of any particular source depends on many factors, including geography, urbanization, and climate; thus, nationwide emission inventories can be misleading. Olsen and Haynes⁵⁷² have summarized the available data.

Man-made POM emission sources can be broadly separated into transportation or mobile sources and stationary sources. In the transportation category, a major emitter is the conventional gasoline-powered automobile, although all combustion engines contribute to the overall atmospheric POM burden. Because they are ubiquitous and are known to be contributors to POM concentrations in most urban areas, motor vehicles require close scrutiny. The category of stationary sources of POM encompasses a wide variety of processes that can be local contributors to POM concentrations. It has been customary to subdivide this category into heat and power generation, refuse burning, and industrial activities. Indoor POM emissions must also be considered in this assessment.

Transportation Sources

GASOLINE-POWERED VEHICLES

A significant mobile source of atmospheric POM is the conventional automobile, powered by a spark-ignited internal-combustion engine.

The technical literature on vehicular effects is sparse, mainly because of the difficulties associated with the type of experimentation required. In the last few years, results of investigation in this area have been published,⁵²⁸ heightened interest in air pollution has resulted in the initiation of comprehensive programs, which are in various stages of completion. The available published literature and some of the preliminary results from current programs are reflected in this summary. Unpublished or incomplete data are included with the recognition that additional tests may vitiate some of the preliminary judgments.

An assessment of the current vehicular benzo[a] pyrene contribution, compiled from nationwide fuel-consumption data, is summarized in Table 3-1.

As will be apparent in the following discussion, most efforts have been directed at estimating the automobile contribution, with less emphasis on trucks and buses. One study³⁴³ is available on benzo[a]-pyrene emission from gasoline-powered trucks; it shows a wide variation in emission factors, from 70 to 1,500 $\mu\text{g}/\text{gal}$.

The contributions of gasoline-powered vehicles can be separated into vehicular effects and fuel-composition effects. The first category includes the effects of air : fuel ratio or mixture stoichiometry, emission control devices, operating modes, deterioration, and combustion-chamber deposits. The second includes effects of such variables as aromaticity, fuel POM level, additives, and lubricants.

Effects of Vehicular Characteristics Efficient combustion is enhanced by the presence of excess air, i.e., air : fuel ratios greater than stoichiometric. Air : fuel ratios less than stoichiometric lead to

TABLE 3-1 Estimated Benzo[a]pyrene Emission in the United States

Vehicle Type	Fuel Consumed, gal/year	Benzo[a] pyrene Emission Factor, $\mu\text{g}/\text{gal}$	Benzo[a] pyrene Emission, tons/year
Gasoline-powered			
Automobiles	56.4×10^9	170 ^a	10
Trucks	24.2×10^9	$\sim 500^a$	~ 12
Diesel-fuel-powered			
Trucks and buses	5.8×10^9	62 ^b	0.4
Total			~ 22

^a Data from Hangebrauck *et al.*³⁴³

^b Data from Begeman and Colucci.⁴²

the products of incomplete combustion, such as carbon monoxide and unburned and oxygenated hydrocarbons. Before the current concern for reducing vehicular emissions, most vehicles operated with fuel-rich carburetion to promote smooth performance and readily accessible power. Modifications in post-1967 vehicles have resulted in "leaner" fuel-air mixtures and, the data suggest, in significantly lower POM emissions. Table 3-2 shows a compilation of available data; vehicular variables will obviously influence the values shown but should not affect the trends indicated. Automobile exhaust POM is generally referred to in terms of the benzo[a]pyrene emission, primarily because of its cited carcinogenicity and the fact that more data are available on this material than on any other. Data are becoming available on prototype emission control devices, such as thermal reactors and catalytic converters, and a preliminary figure is included for comparison.

It is apparent from these data that the introduction of presently used emission control devices resulted in about an 85% reduction in benzo[a]pyrene emissions from the pre-1965 levels. The data in Table 3-2 have been selected from representative recent research on vehicles operating over cyclic test conditions that approximate driving patterns found in actual customer use. Prototype emission control devices, such as thermal reactors and catalyst systems, result in a continuing downward movement of vehicular POM emissions. Other variables discussed in this section are less important than the vehicle effects.

The effect of oxidizing and reducing atmospheres on incomplete combustion and POM formation is important in estimating vehicular emissions. Recent data⁴² indicate that benzo[a]pyrene production at an air: fuel ratio of 10:1 is 30 times higher than at a ratio of 14:1.

TABLE 3-2 Automotive Benzo[a]pyrene Emission Factors

Source	Benzo[a]pyrene Emission Factors, μg/gal of Fuel Consumed
Uncontrolled car (1956-1964)	170 ^a
1966 Uncontrolled car	45-70 ^b
1968 Emission-controlled vehicle	20-30 ^c
Advanced systems	<10 ^d

^a Data from Hangebrauck *et al.*³⁴³ and Begeman and Colucci.⁴²

^b Data from Gross.³¹⁶

^c Data from Begeman and Colucci⁴² and Gross.³¹⁶

^d Estimated from Hoffman *et al.*³⁸² and Faust and Sterba.³⁶⁴

Hoffman *et al.*³⁸² suggest that benzo[a]pyrene emission is 10 times higher at "rich" carburetion (2.85% CO) than at "lean" carburetion (0.9-1.4% CO). This effect is the central reason for the lower POM emissions from current emission-controlled vehicles. The effect of engine operating temperature is closely related to this aspect; cold engines operate in a "choked" or "rich" condition, indicating that POM emissions would be maximized in cold starts and minimized in hot engine operation.

A clear trend toward higher POM emissions with increasing engine life has been documented by several workers. Hangebrauck *et al.*³⁴³ observed a sharp increase in benzo[a]pyrene emission rates of automobiles as they approached the 50,000-mile age, the rates being about 5 times higher than those of lower-mileage (e.g., 5,000-mile) vehicles. Begeman and Colucci,⁴² who studied oil consumption effects, report a tenfold increase in benzo[a]pyrene emission when oil consumption is increased from 1,600 miles/qt to 200 miles/qt. These workers also found that benzo[a]pyrene from the combustion chamber was preferentially concentrated in the crankcase; eight times more benzo[a]pyrene entered the crankcase than left the exhaust system (at normal oil consumption rates). These data help to explain the higher POM emission rates of older vehicles. As cylinder wear increases, the lubricant concentration in the upper cylinder increases and the heavy lubricant molecules provide convenient intermediates for POM formation.

As vehicles accumulate mileage in normal consumer use, deposits form in the combustion chamber. The nature and composition of these deposits have been shown to influence total hydrocarbon exhaust emissions; as mileage is accumulated, total emissions increase until a stabilized condition is reached at several thousand miles. Gross³¹⁶ has shown that the condition of the deposit exerts a significant effect on POM emission levels; the POM emission levels are about twice as high in a vehicle with stabilized deposits from operation with leaded fuel as in the same vehicle with stabilized deposits from operation with unleaded fuel. Another study³⁸² sees no effect of combustion-chamber deposits on POM emissions.

Effects of Fuel Composition The presence in fuel of precursors of radical intermediates would be expected to facilitate POM formation; i.e., the pyrosynthetic path would be shortened. Conjugated dienes and aromatics in the fuel should provide the maximal enhancement of fuel-related POM formation. The literature does point to fuel

composition as having an important effect, but simple judgments as to the advantages and disadvantages of compositional modifications are confounded by the number of variables in the vehicle-fuel-exhaust-system relation.

Early research on the effects of fuel components on POM emissions pointed clearly to increased aromatic content of fuel as a cause of higher POM exhaust emissions. For example, Boubel and Ripperton⁷⁹ showed that a benzene-fueled engine produced 10–30 times more POM than an engine using *n*-hexane, cyclohexane, or hexene-1. Hoffmann and Wynder³⁹⁰ reported that higher emissions of benzo[a]pyrene and benz[a]anthracene resulted from blends of 50% *o*-xylene and 50% benzene than from gasoline, pure paraffins, and pure olefins. Hoffman *et al.*³⁸² diluted unleaded, high-aromatic gasoline with pure isooctane and achieved dramatic reduction in benzo[a]pyrene emissions. Begeman⁴⁰ reported higher benzo[a]pyrene emissions with test fuels containing high POM and aromatic concentrations than with commercial gasolines. Most of these studies have been carried out with synthetic blends, as opposed to gasolines of conventional compositions. To assess accurately the role of fuel in the question of atmospheric POM, it is imperative to use realistic compositions in consumer driving conditions.

Gross³¹⁶ reports that, when full-boiling-range fuels were used in well-maintained vehicles operated under federal requirements for testing 1968–1971 vehicles, POM emissions increased by 36–74% in an uncontrolled vehicle and 8–34% in an emission-controlled vehicle as fuel aromaticity was increased from 12 to 46%.

A more realistic picture of the effect of gasoline composition can be obtained using Gross's data.³¹⁶ When engine tests using a leaded fuel of low to intermediate aromaticity, with stabilized combustion-chamber deposits, are compared with tests using an unleaded fuel of high aromaticity, also with stabilized deposits, no dramatic effect of fuel aromaticity is apparent. Thus, potential increases in POM emissions due to higher fuel aromaticity are offset by changes in the nature of the combustion-chamber deposits when unleaded fuel is used. These data must be regarded as tentative, because this program is in progress, and other research in progress does not support these conclusions.³⁸² However, the benefits to be gained with future control devices operating on unleaded fuel seem to outweigh greatly the effects of fuel composition, such as aromaticity. Research in this area is aimed at unraveling those effects, which now appear to be more complicated than previously assumed.

The POM content of gasoline has been shown to affect POM emissions from vehicles. Begeman and Colucci⁴¹ estimate that as much as 36% of the benzo[a]pyrene in the exhaust gas can be attributed to the fuel benzo[a]pyrene content; Gross³¹⁶ estimates that 15–30% increases in POM emissions can be obtained when fuel POM is varied between the concentration extremes found in the field. The actual effect was smaller in the controlled vehicle than in the uncontrolled vehicle. These results are consistent with the Badger mechanism outlined previously: High-molecular-weight fuel components and lubricant losses to the combustion chamber will result in higher POM emissions.

DIESEL-FUEL-POWERED VEHICLES

Any critical discussion of the relative contribution of diesel engines to the atmospheric POM concentration must be qualified by the supposition that the vehicle is operated under rated load conditions, i.e., is not overloaded. In normal use, the most objectionable features of diesel operation (soot formation, odor, etc.) are apparent when the engine is overfueled. Begeman and Colucci⁴² have determined that a diesel engine, operated on a bus-driving cycle, emitted 62 μg of benzo[a]pyrene per gallon of fuel. Reckner *et al.*⁶²⁶ showed that POM emissions from a diesel test engine increased with load up to half-load, leveled off, and then dropped sharply at full load. Idle operation resulted in high POM emissions, presumably because of lower combustion-chamber temperatures.

Oil consumption in diesel engines can be somewhat higher than in spark-ignited engines. However, Begeman and Colucci⁴² point out that, because diesel combustion chambers do not operate under vacuum, lubricating oil should not be drawn into the ignition area; thus, POM from this source is probably not significant.

The only published data⁶²⁶ on the effects of fuel characteristics on diesel POM emissions indicate that fuel aromaticity is not related to exhaust POM levels. The test fuels ranged between 5 and 23% aromatic content, with the fuel POM consisting primarily of pyrene, anthracene, and fluoranthene. There was no detectable benzo[a]pyrene.

Although the variables discussed above were evaluated in engine-laboratory conditions, it is apparent that actual on-the-road operation of diesel-powered vehicles can result in higher POM emissions, owing to overloading, poor maintenance, and so on. The objectionable fea-

tures of diesel truck and bus operation, such as smoking and odor, might be associated with higher POM emissions, and additional research in this area should be fruitful.

MISCELLANEOUS TRANSPORTATION SOURCES

Quantitative data are generally lacking for diverse mobile sources of POM, such as aircraft engines and various nondiesel two-cycle engines, e.g., lawnmowers, outboard motors, and motorcycles. Aircraft and turbine engine operation has apparently never been surveyed for POM emissions.

A study of POM in the exhaust gas from two-cycle engines has been reported.⁴⁰⁸ Two-cycle engines, which do not have crankcases, operate on a mixture of premixed oil and fuel, the oil being the sole source of lubrication in the system. The data suggest that these engines yield large amounts of benzo[a]pyrene, with an emission factor of 11,000 $\mu\text{g}/\text{gal}$ for an oil : fuel ratio of 1 : 33, and that benzo[a]pyrene yields are a direct function of oil concentration in the fuel. These findings are consistent with the effect of oil consumption on exhaust-gas benzo[a]pyrene found in four-cycle engines.⁴² In the most extreme conditions, the oil : fuel ratio reported by Begeman and Colucci⁴² was 1 : 29. It seems obvious that the presence of higher-molecular-weight components than normally found in the gasoline boiling range has a positive effect on POM formation.

The major noncombustion transportation source of POM is probably the degradation of automobile tires in use. Carbon blacks, used in tire manufacturing, contain POM and other high-molecular-weight organic compounds (S. S. Epstein, personal communication). Marchesani *et al.*⁵¹⁹ estimate that 4.3 tons of rubber particles from tires are emitted per day per million people in the United States. The benzo[a]pyrene contribution from the degradation can be roughly estimated from the analytic data of Falk *et al.*,²⁶⁰ an emission rate of 0.3 lb/day per million people is projected. Although tire degradation does not appear to be a significant source of benzo[a]pyrene, the ultimate burning of used tires and vehicles (which are categorized as refuse burning) may be of far greater importance.

EMISSION CONTROL PROCEDURES

The emission control devices on cars since the 1968 models have reduced benzo[a]pyrene emission factors by about 85%, compared with

uncontrolled vehicles. This reduction is due to the more efficient combustion associated with "leaner" air-fuel mixtures. It is anticipated that these methods will continue in use until the mid-1970's, when more stringent controls on total emissions will be required. At that time, such devices as catalysts or thermal reactors will probably be required, and the mixture stoichiometry will depend on the particular systems chosen. These devices should result in additional reductions in POM emission, as shown in Table 3-2. Reductions in emission of POM to the atmosphere from automobiles can be projected through the 1980-1990 period, as the older cars are removed from service and a greater proportion of vehicles are equipped with advanced emission control systems. Although current work centers on the effects of control devices, operating conditions, and fuel composition, surveillance of vehicles in normal customer usage, including those in poor operating condition, might support the extrapolations made in this section. The emissions from heavier vehicles (such as gasoline- and diesel-powered trucks and buses) seem significant, but little work has been done on defining the emission factors of these vehicles. Knowledge of these factors is clearly needed. There should also be continued efforts to clarify the effects of fuel composition changes, such as trends toward lead removal from gasoline. Although these factors seem to be less important than the vehicle-emission-control system, close scrutiny of them is nonetheless desirable.

Stationary Sources

Polycyclic organic matter is emitted from a vast number of diverse stationary sources. Although the complexity and variety of POM preclude a rigorous assessment of their contribution, it can be seen from compilations of analytic data taken by the U.S. Public Health Service in most of the urban areas of the country that some urban areas close to significant POM sources are subjected to high atmospheric POM concentrations. A recent comprehensive review of POM sources by Hangebrauck *et al.*³⁴³ summarizes the current knowledge of the relative contributions of the various stationary sources. Although emissions from stationary sources consist of a variety of chemical entities, the practice of using benzo[a]pyrene as an indicator of other POM is suggested, owing to the dual factors of the demonstrated carcinogenicity of benzo[a]pyrene and the relatively large amount of published data on it.

HEAT AND POWER GENERATION

Coal, oil, gas, and wood are burned in a variety of installations. Hangebrauck *et al.*³⁴³ concluded that the most important source of benzo[a]pyrene of these four was the inefficient combustion of coal in hand-fired residential furnaces. Data on all four as producers of benzo[a]pyrene are shown in Table 3-3. That efficiency of combustion, and not the fuel used, is the controlling factor is emphasized by the low benzo[a]pyrene emission factor found in power plants burning crushed or pulverized coal. Oil- and gas-burning units used for institutional and home heating, as well as steam for process heating, were also shown to be sources of low POM emission. Although these data are consistent with our knowledge of POM formation processes—i.e., reducing conditions and insufficient oxygen—caution should be used in extrapolating data from some 75 individual sources to the nation as a whole. As will be pointed out, high ambient air

TABLE 3-3 Estimated Benzo[a]pyrene Emission from Heat and Power Generation Sources^a in the United States

Type of Unit	Gross Heat, BTU/hr	Benzo[a]pyrene Emission Factor, $\mu\text{g}/10^6$ BTU	Benzo[a]pyrene Emission, tons/year
Coal			
Hand-stoked residential furnaces	0.1×10^6	1,700,000–3,300,000	420
Intermediate units (chain-grate and spreader stokers)	$60\text{--}250 \times 10^6$	15–40	10
Coal-fired steam power plants	$1,000\text{--}2,000 \times 10^6$	20–400	1
Oil			
Low-pressure air-atomized	0.7×10^6	900	2
Other	$0.02\text{--}21 \times 10^6$	100	
Gas			
Premix burners	$0.01\text{--}9 \times 10^6$	20–200	2
Wood			
		50,000	40

^a Data from Hamburg,³³⁶ Hangebrauck *et al.*,³⁴³ Muhich *et al.*,³⁵⁰ U.S. Department of Agriculture,⁷⁶⁴ U.S. Department of Health, Education, and Welfare,^{767,774} U.S. Department of the Interior,⁷⁷⁷ Wadleigh,⁷⁹⁸ and L. McNab (personal communication).

POM concentrations in a particular region can be associated with local fuel practices. It is apparent that substitution of energy sources that are inherently more efficient than coal combustion in residential units may be a short-term solution in areas of high POM emission.

No firm data are available in the literature on the extent of POM emission from wood-burning combustion units. The growing popularity of home fireplaces, as well as rural heating demands, call for evaluation of this factor. An emission factor of about 50,000 μg of benzo[a]pyrene per million BTU is used to estimate the wood-burning contribution.⁷⁶⁷

The total benzo[a]pyrene emissions from heat and power generation sources shown in Table 3-3 must be regarded as speculative. This applies most directly to the coal- and wood-burning residential usage figures. The possible error in these approximations is such that the contribution of heat and power generation sources to the atmosphere cannot be quantified; an estimate of 500 tons of benzo[a]pyrene emitted per year to the atmosphere appears justified as an upper limit.

REFUSE BURNING

The intentional combustion of solid wastes as a method of disposal, as well as accidental or naturally occurring uncontrollable combustion processes, can contribute significantly to overall POM emissions. Such sources of POM should come under increasing scrutiny in view of the increasing solid-waste disposal problem in the United States today. Unfortunately, the very diversity and nature of these sources has led to great uncertainties as to their actual contributions to atmospheric POM concentrations.

The review by Hangebrauck *et al.*³⁴³ cites benzo[a]pyrene emission factors for municipal and commercial incineration of such wastes as those collected from households, business, and restaurants, as well as for burning of municipal and agricultural refuse and junked automobile parts. Benzo[a]pyrene emissions from these sources vary widely and reflect the importance of efficient combustion in reducing POM emissions. Large (50–250 tons/day) municipal incinerators had benzo[a]pyrene emission factors of 0.1–6 $\mu\text{g}/\text{lb}$ of charged refuse, and commercial (3–5 tons/day) incinerators had factors of 50–260 $\mu\text{g}/\text{lb}$. Data show a benzo[a]pyrene emission factor of about 150 $\mu\text{g}/\text{lb}$ of charged refuse for open burning of municipal wastes, as well as for grass clippings, leaves, etc. Significantly, the destruction of auto

components in test "open-burning" facilities yielded a benzo[a]pyrene emission factor of 1.3×10^4 $\mu\text{g}/\text{lb}$ of refuse.³⁴³

In their summation, Hangebrauck *et al.*³⁴³ conclude that about 20 tons of benzo[a]pyrene are emitted from these sources per year. More recently,^{336,550,764,774,777,798} significantly higher emissions from these sources have been suggested, reflecting higher estimates of total nationwide refuse burning, rather than appreciably different emission factors. These newer data are compiled in Table 3-4. The largest single identified contributor listed is coal refuse bank burning (L. McNab, personal communication), a commonplace occurrence in mining areas. These banks of coal-mining refuse (coal, shale, calcite) can be spontaneously ignited and will burn for long periods in sufficient combustion conditions.

In general, the tonnage figures ascribed to the various refuse burning classifications must be regarded as order-of-magnitude approximations. The highly speculative nature of the emission factors used in the publications cited does not inspire a high level of confidence in the derived estimates. An estimate of 600 tons of benzo[a]pyrene

TABLE 3-4 Estimated Benzo[a]pyrene Emission from Refuse-Burning in the United States

Source of Benzo[a]pyrene	Benzo[a]pyrene Emission, tons/year
Enclosed incineration	
Municipal	<1 ^a
Commercial and industrial	23 ^a
Institutional	2 ^b
Apartment	8 ^a
Open burning	
Municipal	4 ^c
Commercial and industrial	10 ^b
Domestic	10 ^{b,d}
Forest and agricultural	140 ^{d,e}
Vehicle disposal	50 ^f
Coal refuse fires	340 ^g

^a Data from U.S. Department of Health, Education, and Welfare.⁷⁷⁴

^b Data from Muhich *et al.*⁵⁵⁰

^c Data from Olsen and Haynes.⁵⁷²

^d Data from U.S. Department of Health, Education, and Welfare⁷⁷⁴ and Muhich *et al.*⁵⁵⁰

^e Data from U.S. Department of Health, Education, and Welfare,⁷⁷⁴ Wadleigh,⁷⁹⁸ and U.S. Department of Agriculture.⁷⁶⁴

^f Data from U.S. Department of the Interior⁷⁷⁷ and Hamburg.³³⁶

^g Data from L. McNab (personal communication).

emitted per year appears to be the best available value on the basis of current knowledge.

INDUSTRIAL ACTIVITIES

The major direct petroleum-industry source of POM is the catalytic cracking process by which organic molecules in crude oil are broken down into the lighter components used in the manufacture of motor gasoline, heating oil, aviation fuel, etc. The cracking takes place in the presence of a catalyst, which can become deactivated through the deposition of carbon, or coke, on the active sites. It is in the regeneration of the catalyst, through the combustion of the coke on the catalyst surface, that benzo[a]pyrene and other POM are formed. These emissions are finally passed either to the atmosphere or to a carbon monoxide waste-heat boiler. The latter device, originally designed to make use of the waste heat from carbon monoxide gas, functions as a direct-flame afterburner and removes almost all the POM from the effluent being emitted to the atmosphere.

As can be seen from the data in Table 3-5, the contribution of catalytic cracking processes to the atmospheric POM concentrations is a function of the proportion of units equipped with carbon monoxide waste-heat boilers. The various catalytic cracking units listed in the table represent both the moving-bed catalytic systems [Thermoflow (TCC) and Houdriflow (HCC)] and the fluidized-bed system [fluid catalytic cracking (FCC)]. A recent survey⁶²⁷ suggests that a greater proportion of the units are equipped with carbon monoxide boilers than were so equipped in 1967.³⁴³ The results of the later survey show an annual contribution of 6 tons of benzo[a]pyrene from refinery catalytic cracking operations. The total represents a reduction to about one third of previously published estimates.

Another petroleum-industry process of interest is the air-blowing of asphalt. This procedure is designed to yield materials of higher softening point for roofing applications. The effluent from air-blowing may contain many hydrocarbons, including POM. In the one test of an actual process,³⁴³ however, very little benzo[a]pyrene was found in the benzene-soluble fraction of the particulate matter. The total contribution of asphalt air-blowing is estimated at less than 0.01 ton of benzo[a]pyrene per year.

Catalytic cracking of petroleum and air-blowing of asphalt are the most obvious sources of POM emission in the petroleum industry, but there may be miscellaneous other processes that have not been

TABLE 3-5 Estimated Benzo[a]pyrene Emission from Catalytic Cracking Sources^a in the United States

Type of Cracking Unit ^b	Petroleum Consumption, million barrels/year	Benzo[a] pyrene Emission, tons/year
FCC		
no boiler	424	0.08
CO boiler	1,230	0.02
Subtotal	1,654	0.10
HCC		
no boiler	14	3.4
CO boiler	55	0.0
Subtotal	69	3.4
TCC (air-lift)		
no boiler	27	2.4
CO boiler	118	0.0
Subtotal	145	2.4
TCC (bucket-lift)		
no boiler	17	0.0
CO boiler	75	0.0
Subtotal	92	0.0
Total	1,960	5.9

^a Data from Hangebrauck *et al.*³⁴³ and *Oil and Gas Journal*.⁶²⁷

^b FCC, fluid catalytic cracking; HCC, Houdrifiow moving-bed system; TCC, Thermofar moving-bed system.

evaluated. For example, the common refinery practice of flaring waste gas might be a source of POM; modern combustion controls on flares would be expected to remove these sources from consideration.

The industrial emissions cited above were measured directly; that is, the effluent stream itself was analyzed for POM. Many other industrial sources are not amenable to such direct sampling, and indirect means—often imprecise—have been used to estimate their emissions.

Some of the processes considered include coke production in the iron and steel industry; carbon black, coal-tar pitch, and asphalt-hot-road mix processes; and general chemical processes. The analytic procedure used in evaluating all such sources has been to sample the atmosphere in the immediate vicinity of an expected emission source

or complex of sources. This necessarily leads to less accurate estimates than direct sampling. Except for coke production, none of the industrial processes considered above contributes significant amounts of benzo[a]pyrene to the total atmospheric concentration. This conclusion is obscured somewhat by the presence of other local emission sources already discussed, such as residential coal-fired furnaces.

There is evidence⁷¹¹ that high benzo[a]pyrene emissions are associated with the gaseous discharge of coke ovens. In the United States, recent activities of the National Air Sampling Network and the Pennsylvania State Department of Public Health support the belief that iron and steel works do contribute to higher atmospheric benzo[a]pyrene concentrations in the areas surrounding them. Corresponding studies in areas outside the United States^{459,740} lead to similar conclusions. An emission factor, admittedly crude, for benzo[a]pyrene emission from coke effluents has been calculated⁷¹¹ at 1.8 g/ton of coke. Application of this factor to estimated nationwide coke discharges results in a predicted emission of 192 tons/year.

It is obvious that many more industrial processes may contribute to atmospheric benzo[a]pyrene. They will constitute localized sources and can be expected to lead to increased atmospheric concentrations at local sampling sites.

Industrial emission of benzo[a]pyrene is summarized in Table 3-6

INDOOR POM EMISSION

Although the outdoor environment has received a fair amount of study in terms of POM, little is known of the sources and magnitude of the indoor burden. The possible sources in residential structures are improperly vented furnaces and incinerators, tobacco smoke, and leakage from the outdoors. In industrial plants, many of the processes referred to previously can, if not controlled properly, emit POM to the indoor environment.

TABLE 3-6 Summary of Estimated Industrial Benzo[a]pyrene Emission in the United States

Source of Benzo[a]pyrene	Benzo[a]pyrene Emission, tons/year
Petroleum	6
Asphalt air-blowing	<1
Coke production	200

In the only published work, Stocks and co-workers^{726,733} studied polycyclic hydrocarbons and smoke in garages and offices and reported the concentrations of benzo[a]pyrene, benzo[ghi]perylene, pyrene, and fluoranthene. Their data suggest that office sites have 25-70% lower POM concentrations than found in the immediate outdoor environment; the POM concentrations in bus and car garages were at least as high as and usually somewhat higher than those of the ambient air.

One major source of nonindustrial indoor POM pollution is tobacco-smoking.⁸³¹ During smoking, the mainstream smoke is inhaled and, in the interval between puffs, the sidestream smoke escapes into the environment. The use of one unfiltered cigarette (85 mm) releases 30-50 mg of "tar," which contains 0.10-0.15 μg of benzo[a]pyrene, 0.20-0.30 μg of pyrene, and 0.25 μg of chrysene. In a medium-size room (40 m³), three smokers can pollute the air with 2-4 μg of benzo[a]pyrene, 5-8 μg of pyrene, and 6 μg of chrysene per 1,000 m³ of air. Depending on ventilation and smoking activities, the indoor pollution by cigarette sidestream smoke can be significantly higher; for example, Galůskinová²⁸⁸ reported 28-144 μg of benzo[a]pyrene per 1,000 m³ for a beer hall in Prague.

The most important source of personal air pollution is the mainstream smoke of tobacco products. For example, a smoker of 30 unfiltered cigarettes (popular 85-mm U.S. brand) inhales about 1.0 μg of benzo[a]pyrene daily. Stated differently, 1,000 m³ of cigarette mainstream smoke contain about 100,000 μg of benzo[a]pyrene, compared with 0.01-74 $\mu\text{g}/1,000\text{ m}^3$ found in polluted air. Although the concentration of benzo[a]pyrene in a given volume of air and in the same volume of cigarette smoke are not directly comparable, they do provide some insight into the relative importance of tobacco-smoking in pollution with POM.

EMISSION CONTROL PROCEDURES

Efforts aimed at improving the combustion efficiency of most of the processes covered in this section would be obvious first steps toward control of POM emission. However, the main contributors to the POM emission of heat and power generation are small coal furnaces and wood burning. Neither is economically amenable to better controls, so alternate fuel sources would be the preferred solution.

With regard to refuse burning, more efficient incineration equipment in commercial, industrial, and apartment-building sources would

be appropriate. Their relative contribution diminishes in comparison with open burning, especially coal refuse burning and, to a lesser extent, forest and agricultural burning. Coal refuse burning could simply be eliminated by proper attention to refuse accumulation practices, and intentional forest and agricultural burning could be discontinued.

Polycyclic organic matter emissions from catalytic cracking in the petroleum industry are well on their way to effective control through the increasing use of carbon monoxide waste boilers. The contribution from coking emissions in the iron and steel industry must be more accurately assessed.

The contribution of stationary sources to the total POM emission inventory, although poorly quantified, appears to be large. Latest estimates of gross tonnage are to be viewed as a first approximation and may be valid to within a factor of 10. Even with this qualification, the stationary-source contribution probably accounts for 90% of the total nationwide POM emission. It is important to note that emission by stationary sources is usually highly localized, in contrast with that by mobile sources, and results in high atmospheric POM concentrations in the vicinity of major emitters.

Owing primarily to these localized emissions, comprehensive epidemiologic studies should be initiated in geographic areas that are subject to high atmospheric concentrations of POM. A particularly fruitful study might be done in the Appalachian Mountain-Mississippi River area.

Stationary-source emission factors must be validated and the analysis extended to include as many additional kinds of POM (i.e., other than benzo[a]pyrene) as feasible. In particular, the importance of hand-fired furnaces burning coal or wood must be critically evaluated. Coal refuse burning is in the same category; the large, highly speculative value chosen for this contribution requires verification. Alternate disposal methods for coal refuse should be developed in the interim.

TABLE 3-7 Summary of Benzo[a]pyrene Emission by Stationary Sources in the United States

Source of Benzo[a]pyrene	Benzo[a]pyrene Emission, tons/year
Heat and power generation	~500
Refuse burning	~600
Coke production	200

Emission of POM from coke production also requires scrutiny; alternate manufacturing practices in the iron and steel industry should be developed in case such emission must be controlled.

The best available current data suggest the stationary-source benzo[a]pyrene emission shown in Table 3-7.

GENERAL NATURE OF POM EMISSIONS

Individual POM Emissions

The polycyclic organic molecule mentioned most prominently here has been benzo[a]pyrene. This material has been identified as a prominent constituent of most of the processes discussed and has also been shown to be a potent carcinogen. Although these facts confirm the importance of benzo[a]pyrene, many other materials emitted in the same processes have some carcinogenic activity.

It has been felt that benzo[a]pyrene could be used as an indicator molecule, implying the presence of a number of other components of similar structure. Several workers^{153,667,670,673} have reported numerous types of POM in urban air, including pyrene, anthanthrene, benz[a]anthracene, benzo[fluoranthene], dibenzanthracenes, chrysene, phenylenepyrene, benzoperylene, coronene, fluoranthene, and alkyl derivatives of these compounds, as well as benzopyrenes. (See Table 2-1 for some of these materials and their structures and properties.)

There have been attempts to develop relations between these individual compounds (such as the ratio of benzo[a]pyrene to pyrene and coronene to pyrene) as a function of their source. For example, ratios shown in Table 3-8 have been determined for vehicular emissions, industrial emissions, refuse burning, and heat generation.

It is obvious that these ratios can vary widely as a function of emission source. Before benzo[a]pyrene can be used as an accurate barometer of the entire class of POM, more information on these ratios, as well as on the carcinogenic significance of the other POM molecules, will be required.

Area-Concentration Relations

It is evident that three major stationary sources—coal-fired and wood-fired residential furnaces, coal refuse fires, and coke production—account for more than 90% of the annual nationwide benzo[a]pyrene emission. Of the remaining sources, the transportation contribution

TABLE 3-8 Ratios of Individual POM Molecules by Emission Source

Emission Source	Pyrene: Benzo[a]pyrene	Benzo[ghi]perylene: Benzo[a]pyrene	Benz[a]anthracene: Benzo[a]pyrene
Automobiles ^a	7:1-24:1	2:1-5:1	1:1-2:1
Trucks			
Gasoline-powered ^b	50:1-90:1	—	—
Diesel-fuel-powered ^b	<1:1-50:1	—	—
Catalytic cracking ^c	<1:1-23:1	0.3:1-3:1	—
Incinerators ^c	6:1-16:1	0.2:1-1:1	—
Heat generation ^d	1:1-1,000:1	—	—

^a Data from Gross,³¹⁶ Hangebrauck *et al.*,³⁴³ Hoffman *et al.*,³⁸⁴ Kotin *et al.*,⁴⁵⁵ and Sawicki *et al.*,⁶⁷⁴

^b Data from Hangebrauck *et al.*,³⁴²

^c Data from Hangebrauck *et al.*,³⁴³

^d Data from Falk *et al.*,²⁶⁰

is probably the most significant, in that it pervades all segments of the nation. It is instructive to consider the predominant areas of the country with regard to these stationary sources, as in Table 3-9.

When the areas of major emissions are grouped, it is obvious that POM emissions are very high through the southeastern region along the Appalachian Mountains, as well as in the area to the immediate west as far as the Mississippi River and north to the Great Lakes. Although more quantitative extrapolations are not warranted, we can consider the aerometric data now available through the National Environmental Research Center of the Environmental Protection Agency as indicative of the major urban areas in which POM concentrations may constitute health problems. A survey of the data for the winter of 1969, in which benzo[a]pyrene concentrations are reported,* is enlightening. Of the 40 U.S. cities in which the winter benzo[a]pyrene concentration exceeded $5 \mu\text{g}/1,000 \text{ m}^3$, 34 are in the region just defined, as are 44 of the 53 cities with concentrations in excess of $4 \mu\text{g}/1,000 \text{ m}^3$. The densely populated Northeast and the Far West are conspicuous by their relatively low atmospheric benzo[a]pyrene concentrations; the Los Angeles Basin, with its high vehicle and human population densities, has concentrations of $1.5-3 \mu\text{g}/1,000 \text{ m}^3$.

In the only other set of determinations of relative source contributions to the atmospheric POM burdens, Colucci and Begeman¹⁵³ have calculated that, in Detroit, motor vehicles contribute 5% of the

*Data from National Aerometric Data Bank, P.O. Box 12055, Research Triangle Park, North Carolina 27709.

TABLE 3-9 Contributions to National Totals of Benzo[a] pyrene by Source and State^a

Benzo[a] pyrene Emission Source	State	Fraction of U.S. Total, %	
		State	Group of States
Coal-fired furnaces	Illinois	22	} 58
	Ohio	12	
	Wisconsin	10	
	Michigan	8	
	Indiana	6	
Coal refuse burning	W. Virginia	45	} 90
	Pennsylvania	25	
	Kentucky	} 20	
	Colorado		
	Virginia		
Coke production	Pennsylvania	29	} 79
	Ohio	16	
	Indiana	14	
	Alabama	} 20	
	Maryland		
	W. Virginia		

^a Based on data from Hamburg,³³⁶ L. McNab (personal communication), Muhich *et al.*,⁵⁵⁰ U.S. Department of Agriculture,⁷⁶⁴ U.S. Department of Health, Education, and Welfare,⁷⁶⁷⁻⁷⁷⁴ and U.S. Department of the Interior.⁷⁷⁷

benzo[a] pyrene in the downtown area, 18% of that in the freeway area, and 42% of that in the atmosphere in the suburbs. Similar studies were made in New York City¹⁵¹ and Los Angeles,¹⁵² but the same types of calculations were not possible. In both cases, the data would permit only correlation techniques, which indicate positive statistical relations of benzo[a] pyrene with both automotive and stationary sources.

These data indicate that, in the absence of other major sources, as in some suburban locations, the vehicular contribution may be as high as 50%. Aerometric data indicate that, when this relative vehicular contribution is high, the local atmospheric POM concentrations are low.

The implications of these trends are evident: Epidemiologic data should be obtained in areas of high and low POM concentration to establish the effect of atmospheric contamination by POM. Until such studies are made, the nature and degree of source controls required will be unknown.

SUMMARY AND RECOMMENDATIONS

Polycyclic organic matter can be formed in any combustion process involving hydrocarbons. Naturally occurring POM emission to the atmosphere does not appear to be significant. The major technologic emissions include those from transportation sources and such stationary sources as heat and power generation, refuse burning, and industrial processes.

The internal-combustion engine is a ubiquitous source of POM. Current efforts to reduce total vehicular emissions have reduced POM emissions, and projections of future control levels point toward a continuing and marked decline. However, such projections presuppose properly maintained and operated vehicles; close scrutiny should be directed at the effects of deterioration of automobile emission control devices and the use of diesel-fueled vehicles in overloaded conditions. Research efforts to determine the effects of fuel composition and of advanced emission control devices should be continued. Polycyclic organic matter emissions from aircraft should be assessed, as well as those from local mobile sources, such as two-cycle engines.

POM emissions from major stationary sources are poorly quantified. Available data suggest that coal-fired residential furnaces, coal refuse bank burning, and coke production from the iron and steel industry are responsible for the bulk of the nationwide POM emission. However, serious reservations may be expressed as to the validity and magnitude of these data. It is noted that atmospheric concentrations of POM are high in areas in which the cited sources are concentrated. In addition, effective control procedures for these processes are lacking. Substitution of alternate fuels or more efficient combustion processes and discontinuance of coal refuse storage practices seem to be the only appropriate methods for the restriction of coal-related emission; the emission associated with coke production requires additional research on control procedures and source analysis.

Current data suggest the following relative contributions of major source categories to the total POM emission inventory (expressed in terms of annual estimated benzo[a]pyrene emissions): heat and power generation, 500 tons/year; refuse burning, 600 tons/year; coke production, 200 tons/year; and motor vehicles, 20 tons/year.

These data represent nationwide estimates based on extrapolations from individual source emissions. In specific areas, the relative contribution of any given source may differ significantly from that im-

plied by the nationwide figures. For example, the vehicular source may be the major contributor in suburban areas where other major sources are absent. Epidemiologic studies using source inventory data and ambient atmospheric concentrations are required to assess the importance of control measures in both high and low atmospheric POM areas.

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Medical and Biologic Effects of Environmental Pollutants

AP 42
1.1

VAPOR-PHASE ORGANIC POLLUTANTS

VOLATILE HYDROCARBONS
AND OXIDATION PRODUCTS

*Committee on
Medical and Biologic Effects of
Environmental Pollutants*

DIVISION OF MEDICAL SCIENCES
ASSEMBLY OF LIFE SCIENCES
NATIONAL RESEARCH COUNCIL

NATIONAL ACADEMY
OF SCIENCES

WASHINGTON, D.C. 1976

2

Sources of Atmospheric Hydrocarbon

Total hydrocarbon emission in the United States from mobile (transportation) and stationary man-made source and from natural sources is summarized in Table 2-1.^{211,373,878,949,1186,1227} The differences between estimates are due primarily to differences in underlying assumptions and methods of calculation. Most investigators agree that emission estimates are improving as more is learned about pollution; as a result, the more recent estimates in Table 2-1 are probably the more reliable. In particular, the most recent estimate⁸⁷⁸ of 25.4 million tons/year from stationary man-made sources is significantly higher than all previous estimates because of improved knowledge and the increased number of stationary sources.

One estimate of worldwide hydrocarbon emission is also given in Table 2-1. The U.S. emission is about 40% of the world total for both mobile and stationary man-made sources. Although natural hydrocarbon emission dwarfs man-made emission on a global basis, it generally occurs in relatively unpopulated areas. As a result, tonnage comparisons do not accurately reflect importance.

A detailed hydrocarbon emission inventory for the United States is presented in Table 2-2.²¹¹ This is the latest authoritative inventory that includes both mobile and stationary man-made sources. In discussing the various source categories, the format of Table 2-2 will be followed.

TABLE 2-1 Estimates of Hydrocarbon Emission from Man-Made and Natural Sources

Area	Hydrocarbon Emission, million tons/year			Reference
	Man-Made Sources		Natural Sources	
	Mobile	Stationary		
United States	17.6	13.9	72	949
	12 ^a	7	—	1186
	16.6	15.4	—	1227
	19.8	17.6	—	211
	13.8	—	—	373
World	—	25.4	—	878
	34	54	2,000	1026

^aAutomobiles only.

MOBILE MAN-MADE SOURCES OF HYDROCARBON EMISSION

Motor vehicles are by far the most important mobile man-made source of gaseous hydrocarbons. According to Table 2-2, they account for about 86%, whereas aircraft, railroads, marine vessels, and nonhighway use together account for only 14%. Nationwide total emission from motor vehicles has been decreasing since about 1966, because of the installation on new cars of crankcase control systems in 1963, exhaust control systems in 1968, and evaporative control systems in 1971.¹²⁸ Total hydrocarbon emission is expected to continue to decline into the 1980's,^{128,373} even without additional controls. Some estimates of hydrocarbon emission from automobiles and other mobile sources for the years 1955–1985 are given in Table 2-3.³⁷³ It should be pointed out that these National Petroleum Council estimates are somewhat lower than the Environmental Protection Agency (EPA) estimates in Table 2-2.

Gasoline-Powered Motor Vehicles

Gasoline-powered vehicles account for about 99% of all vehicular hydrocarbon emission; diesels account for the remainder. Of the emission from gasoline-powered vehicles (automobiles) in 1967, an estimated 55% came from exhaust, 25% from the crankcase (blowby),

TABLE 2-2 Hydrocarbon Emission by Source Category, United States, 1969^a

Source	Hydrocarbon Emission, million tons/year	
Mobile (transportation)		
Motor vehicles, gasoline	16.9	
Motor vehicles, diesel	0.2	
Aircraft	0.4	
Railroads	0.1	
Vessels	0.3	
Nonhighway use	<u>1.9</u>	19.8
Fuel combustion—stationary		
Coal	0.1	
Fuel oil	0.1	
Natural gas	0.3	
Wood	<u>0.4</u>	0.9
Industrial processes		
Primary metals	0.3	
Petroleum refining	2.3	
Chemical processing	0.8	
Other	<u>2.1</u>	5.5
Solid-waste disposal		
On-site incineration	0.5	
Open dumps, burned	1.2	
Teepee burners	<u>0.3</u>	2.0
Miscellaneous		
Forest fires	2.9	
Structural fires	0.1	
Coal-refuse banks	0.1	
Agricultural burning	1.7	
Solvent evaporation	3.1	
Gasoline marketing	<u>1.3</u>	<u>9.2</u>
TOTAL POLLUTION		37.4
Natural		
Methane	50 ^b	
Terpenes	22 ^c	
Ethylene	0.04	
TOTAL POLLUTION		<u>72.0</u>
PLUS NATURAL		109.4

^aData from U.S. Environmental Protection Agency,²¹¹ except as noted.

^bDerived from Robinson and Robbins,^{102b} assuming U.S. methane emission per square mile to be half world rate.

^cDerived from Rasmussen and Went,^{100b} assuming terpene emission to be uniformly distributed over forested lands of the world.

and 20% from carburetor and fuel tank evaporation.¹¹⁸⁶ Presumably, this breakdown was for cars without any emission controls. Today, with emission controls on many cars, the proportions are different.

EXHAUST EMISSION

Several investigators have measured exhaust emission from car fleets. One of the earliest studies was a Coordinating Research Council (CRC) field survey in which the average exhaust hydrocarbon concentration (hexane equivalent) of 160 pre-1956 model cars from the Los Angeles area was reported to be 1,375 ppm.¹²⁸⁷ A California Motor Vehicle Pollution Control Board (MVPCB) survey of 200 pre-1966 cars showed an average concentration of 828 ppm.¹⁸³ A later survey of 583 1966 models with first-generation controls showed an average concentration of 290 ppm.¹⁶⁵ On the basis of its own two surveys and other data, the California MVPCB estimated the average hydrocarbon emission from automobiles to be 11.0 g/mile before controls and 3.4 g/mile for 1966 models with first-generation controls.¹⁸² Differences in auto emission have been shown for different altitudes and for cars of different engine size.⁷³⁰

The development of gas-chromatographic procedures to measure individual hydrocarbons has greatly increased our understanding of the nature of exhaust gas.^{317,541,598,624,825,955} We now know that exhaust gas contains low-molecular-weight hydrocarbons that are not present in the fuel, as well as fuel components. The low-molecular-weight hydrocarbons include methane, ethane, ethylene, acetylene, propylene, the four-carbon (C₄) olefins, and sometimes propadiene and

TABLE 2-3 Estimated Hydrocarbon Emission from Automobiles and Other Mobile Pollution Sources, United States, 1955-1985^a

Source	Estimated Hydrocarbon Emission, million tons/year						
	1955	1960	1965	1970	Projected Estimates		
					1975	1980	1985
Automobiles	9.9	12.0	13.0	11.0	5.9	2.4	0.9
Trucks and buses	1.2	1.4	1.7	1.9	1.7	1.4	1.4
Aircraft	0.3	0.3	0.2	0.3	0.2	0.1	0.1
Off-highway	0.7	0.7	0.7	0.6	0.6	0.6	0.5
TOTAL	12.1	14.4	15.6	13.8	8.4	4.5	2.9

^aDerived from *Environmental Conservation: The Oil and Gas Industries*, Vol. 1. National Petroleum Council, June 1971.³⁷³

methylacetylene. The fuel components include hydrocarbons heavier than butane and may number over 100. Typically, the low-molecular-weight hydrocarbons constitute 40–60% of the total (by volume), although the exact proportions depend on many engine-fuel variables.

The predominant hydrocarbons in gasoline exhaust have been reported in three studies, each of which covered a wide range of conditions and included many analyses.^{622,874,955} The three agree remarkably well (Table 2-4), considering the diversity of the investigations. The low-molecular-weight hydrocarbons—methane, ethylene, acetylene, and propylene—are high on each list. Toluene and isopentane seem to be the major fuel components.

Fuel composition obviously will affect exhaust composition, but the fuel components in exhaust do not exactly match the original fuel. Some fuel hydrocarbons are preferentially burned, and some others are formed in the engine. To avoid undue complexity, some investigators have used simple hydrocarbon fuels to study the relations between fuel composition and exhaust composition. Fleming⁴¹² used blends of isooctane, isooctene, and *m*-xylene and found that the exhaust may contain (aromatic) hydrocarbons heavier than those in the original fuel and that fuel paraffins produce more exhaust olefins than do fuel olefins. Ninomiya and Biggers⁹²⁶ used blends of toluene, isooctane, and *n*-heptane and showed that the air:fuel ratio greatly affects the yields of aromatic products (ethylbenzene, styrene, benzene, benzaldehyde, and toluene) formed from these blends. The effects on other exhaust hydrocarbons (low-molecular-weight products and some heavier olefins) were reported in an earlier study.⁹²⁷ Daniel²⁸² found methane, ethylene, ethane, acetylene, propylene, and propane in the exhaust from a single-cylinder engine burning pure propane. The concentrations depended greatly on the air:fuel ratio, spark timing, volumetric efficiency, and compression ratio.

The effect of gasoline composition on exhaust composition has been studied extensively by Dishart and his co-workers.^{321,322,874} They concluded that ethylene is formed from saturates and olefins—propylene and butene primarily from saturates, and diolefins primarily from olefins—and that additional amounts of toluene, benzene, and xylenes are formed from higher aromatics and additional 2-methyl-2-butene from higher saturates. Doelling *et al.*³²⁵ concluded that gasoline composition had no effect on the total hydrocarbon concentration in exhaust, but that the percentages of aromatics, olefins, and paraffins in exhaust were correlated with fuel composition. Wigg *et al.*¹³¹² concluded that aromatic exhaust emission is linearly related to the aromatic content of the fuel. Similarly, Neligan *et al.*⁹¹³ concluded that

TABLE 2-4 Predominant Hydrocarbons in Auto Exhaust

Hydrocarbon	Fraction of Total Exhaust Hydrocarbons, vol %		
	62-Car Survey ^a	15-Fuel Study ^b	Engine-Variable Study ^c
Methane ^d	16.7	18	13.8
Ethylene ^d	14.5	17	19.0
Acetylene ^d	14.1	12	7.8
Propylene ^d	6.3	7	9.1
<i>n</i> -Butane	5.3	4	2.3
Isopentane	3.7	4	2.4
Toluene	3.1	5	7.9
Benzene ^d	2.4	—	—
<i>n</i> -Pentane	2.5	—	—
<i>m</i> - and <i>p</i> -Xylene	1.9	—	2.5
1-Butene ^d	1.8	3 ^e	6.0 ^e
Ethane ^d	1.8	—	2.3
2-Methylpentane	1.5	—	—
<i>n</i> -Hexane	1.2	—	—
Isooctane	1.0	—	—
All others	22.2	30	26.9

^aData from Papa.⁸⁶⁵^bData from Morris and Dishart.⁸⁷⁴^cData from Jackson.⁸²²^dCombustion products.^eIncludes isobutylene.

fuel olefinic exhaust emission is proportional to the olefin content of the fuel, but that the nature and concentration of the light, cracked products are independent of the olefin content of the fuel. Many others have investigated fuel composition effects, frequently expressing their results in terms of photochemical reactivity.^{174,195,197,316,318,349,351,841,1084,1164,1165,1178}

Jackson⁸²² has reported the effects of the air:fuel ratio and spark timing on the concentrations of about 10 exhaust hydrocarbons. This is the only comprehensive engine-variable study using gasoline as fuel, although Ninomiya and co-workers^{926,927} and Daniel²⁸² investigated engine variables with pure hydrocarbon fuels. In each of these three studies, the effect of engine variables was different for different hydrocarbons.

The use of tetraethyl lead (TEL) as a gasoline antiknock agent tends to increase exhaust hydrocarbon emission, both directly and indirectly, by promoting the buildup of engine deposits.^{324,414,447,509,759,951} The direct lead effect increases hydrocarbon emission by about 5%; the indirect (deposit) effect, by an additional 7%, according to the sum-

mary study of Leikkanen and Beckman,⁷⁵⁹ TEL does not affect the composition of exhaust hydrocarbons.⁴¹⁴

Some emission controls, however, do affect exhaust hydrocarbon composition. Morris and Dishart⁸⁷⁴ compared an uncontrolled car, a modified-combustion car, an air-injection car, and an advanced thermal-reactor car. The greatest differences they found were the high percentage (87%) of C₁ and C₂ hydrocarbons and the near absence of fuel components in the exhaust of the thermal-reactor car. Adams *et al.*¹⁰ also found significantly higher percentages of methane and ethylene and lower percentages of aromatics in the exhaust of a lean-reactor car, compared with that of an unmodified car of the same model. Weaver¹²⁹³ reported that catalytic reactors selectively oxidize the olefins and aromatics in exhaust, but that the selectivity diminishes with catalyst age. Nebel and Bishop⁹⁰⁷ also reported that catalytic reactors may be selective and that methane and ethylene are the most difficult hydrocarbons to oxidize. Jackson⁸²² found that an engine-modification emission⁸²² control system increased the photochemical reactivity of exhaust, but that an air-injection system had no effect.

Exhaust gases contain organic compounds besides hydrocarbons, such as aldehydes, ketones, alcohols, ethers, esters, acids, and phenols. These partial-oxidation products are called oxygenates. The total oxygenate concentration is about one-tenth the total hydrocarbon concentration. Aldehydes are generally believed to be the most important class of oxygenates.

Many investigators have measured formaldehyde^{361,364,412} and total aldehyde^{364,447,574,741,1164,1293} concentrations in auto exhaust with sensitive chemical tests.^{233,685,954,1070} A few investigators have measured benzaldehyde^{574,926,927} and phenol;⁵⁷⁴ still others have qualitatively identified various aldehydes.^{76,365} However, a reasonably complete quantitative analysis of exhaust aldehydes has not been possible until recently, when sophisticated gas-chromatographic techniques were developed.^{92,432,934,1255,1342} The results of several of these detailed analyses are summarized in Table 2-5. They agree very well, considering that different engines, gasolines, and, to some extent, analytic techniques were used. Formaldehyde is by far the predominant aldehyde, constituting about 60–70% of the total (on a volume basis); acetaldehyde is next, at about 10%; and propionaldehyde, acrolein, benzaldehyde, and the tolualdehydes are all found in appreciable amounts. As might be expected, the nature of the gasoline burned influences the aldehydes formed.

There is almost no published information on noncarbonyl oxygenates, such as ethers, alcohols, epoxides, and peroxides. Seizinger and

TABLE 2-5 Exhaust Aldehyde Analyses

Aldehyde	Fraction of Total Exhaust Aldehydes, vol %					
	Wiggs <i>et al.</i> ^{1312a}	Obertorffe ¹³¹⁴	Wodkowski and Weaver ^{1342a}	Fracchio <i>et al.</i> ⁴³²		
Formaldehyde	66.7	72.5	70.2	59.9	69.3	72.9
Acetaldehyde	9.3	8.7	7.2	14.3	7.5	8.5
Propionaldehyde ^b	15.7	—	0.4	{ 7.0	0.7	{ 6.4
Acrolein	{ 3.2	—	9.8	—	2.6	—
Butyraldehydes	—	4.3	0.4	3.0	1.0	1.7
Crotonaldehyde	—	—	0.4	1.4	0.4	0.4
Valeraldehydes	—	—	0.4	—	—	—
Benzaldehyde	3.2	7.0	8.5	3.3	5.4	4.3
Tolualdehydes	1.9	7.2	—	5.9	3.1	—
Other	—	0.3	2.7	5.2	10.0	5.8
TOTAL	100	100	100	100	100	100

^aExhausts from two different gasolines.

^bAlso includes acetone of unknown proportion.

Dimitriades measured 10 aldehydes, six ketones, and 16 noncarbonyl oxygenates in exhaust from 22 different simple fuels, each containing one, two, or three hydrocarbons.^{1095,1096} They developed computational formulas from their data that can be used to estimate the oxygenate concentrations in gasoline exhaust.

The use of liquefied petroleum gas (LPG) or natural gas as a motor fuel does not in itself eliminate or even reduce exhaust hydrocarbon emission. These fuels, however, produce less complex exhaust than gasoline. Schwartz *et al.*¹⁰⁹⁰ reported finding mostly propane—plus small amounts of methane, ethane, ethylene, acetylene, and propylene and traces of C₄ hydrocarbons—in the exhaust from automobiles or lift trucks burning LPG. Fleming and Allsup⁴¹³ found mostly methane and smaller amounts of other (up to C₄) hydrocarbons in the exhaust from an automobile burning natural gas. They attributed the nonmethane hydrocarbons primarily to the ethane in natural gas. This was confirmed by Eccleston and Fleming's study in which natural gas and a synthetic pipeline gas derived from coal (Synthane) were compared as motor fuels.³⁵² The exhaust from Synthane—which was about 10% hydrogen, 88% methane, and less than 0.5% ethane—contained noticeably less C₂ and C₃ hydrocarbons than the exhaust from natural gas, whose composition was 89% methane, 9% ethane, and 2% propane and butane. The photochemical reactivity of the Synthane exhaust was also significantly lower. The exhausts from both the natural gas and Synthane contained small amounts of an unidentified aldehyde (or aldehydes).

EVAPORATION LOSSES

The evaporation of gasoline from carburetors and fuel tanks has been greatly reduced for 1971 and later automobiles, compared with older models, by 88% according to one estimate,⁹¹⁴ owing to the installation of evaporation control systems. Evaporative emission is still significant, however, because many older cars are in use.

Evaporative emission consists of the lighter components of gasoline, primarily C₄ and C₅ hydrocarbons. As many investigators have pointed out, the exact composition depends on the gasoline used, the temperature it attains, and the degree of "weathering" or prior evaporation.^{299,348,351,597,623,826,887,1178,1262,1303} Some representative analyses of evaporative emission samples are summarized in Table 2-6. They are not complete analyses, covering only the C₄, C₅, and C₆ paraffins, the C₄ and C₅ olefins, and the C₆ and C₇ aromatics. The light paraffins and light olefins constituted about 70% of the carburetor emission and about 90% of the fuel-tank emission in these samples. Isopentane and *n*-

TABLE 2-6 Partial Analysis of Carburetor and Fuel-Tank Evaporation Losses

Hydrocarbon	Fraction of Total Evaporated Hydrocarbons, vol. %									
	Carburetor					Fuel Tank				
	Wade ^{1,2,3}	Caplan ^{1,2}	Müller <i>et al.</i> ^{1,2,3}	Jackson and Everett ^{1,2,3}	McEwen ^{1,2,3}	Wade ^{1,2,3}	Caplan ^{1,2}	Müller <i>et al.</i> ^{1,2,3}	Jackson and Everett ^{1,2,3}	McEwen ^{1,2,3}
Paraffins	11.9	9.1	23.0	16.5	30.5	48.5				
<i>n</i> -Butane	0.2	0.1	0.2	6.5	2.7	3.6				
Isobutane	2.0	2.0	1.5	7.2	8.6	6.9				
<i>n</i> -Pentane	45.3	40.9	36.0	23.2	26.4	20.3				
Isopentane	0.2	0.3	8.7	0.7	1.8	1.5				
<i>n</i> -Hexane	0.1	0.0		0.1						
2,2-Dimethylbutane	3.0	3.2	3.7	1.6	2.6	1.6				
2,3-Dimethylbutane	2.3	2.4		1.9	3.4	2.4				
2-Methylpentane	1.2	1.3		1.1						
3-Methylpentane										
Olefins	0.3	0.2		4.6						
1-Butene	0.5	0.5	0.9	4.8	3.2	2.2				
<i>trans</i> -2-Butene	0.3	0.2		4.2						
<i>cis</i> -2-Butene										
2-Pentene	1.4	1.3	1.0	1.5	2.9	2.0				
1-Pentene	0.3	0.3		5.6						
2-Methyl-1-butene	0.7	0.6	0.8	4.3	4.5	2.8				
3-Methyl-1-butene	0.1	0.1		0.8						
2-Methyl-2-butene	1.6	1.6	1.2	7.3	3.4	2.7				
Aromatics										
Benzene	0.5	0.5	0.1	0.4	0.4	0.3				
Toluene	0.5	0.8		0.4	0.9	0.3				
TOTAL	72.4	65.4	77.1	92.7	91.3	95.1				

¹Same gasoline at 163 and 177 F.

²Calculated values for 140 F.

³Different gasolines.

butane were by far the predominant hydrocarbons, together accounting for an average of about 50% of the total. It seems safe to generalize that isopentane and *n*-butane account for the major portion of all gasoline evaporation losses. The amounts of other paraffins and olefins varied from sample to sample, largely because of differences in gasoline composition.

The analyses in Table 2-6 confirm Jackson and Everett's⁹²³ conclusion that fuel-tank emission is richer in the lighter components than carburetor emission. Presumably, this is because the gasoline in the carburetor is "distilled" at a higher temperature.

BLOWBY

Blowby or crankcase emission has been practically eliminated; all 1963 and later model cars have been equipped with positive crankcase ventilation (PCV). The PCV cure for this problem and the importance of blowby hydrocarbon emission were first recognized by Bennett and his co-workers.⁹⁷ They measured hydrocarbon concentrations of around 10,000 ppm and flow rates of a few cubic feet per minute for blowby and concluded that blowby accounted for about 40% of the total hydrocarbon emission from automobiles. They also found that blowby is predominantly carbureted mixture (85%) plus some combustion gases (15%) and that fuel composition determines which hydrocarbons are emitted from the crankcase. Later studies by other investigators essentially confirmed their findings on blowby composition.^{961,1033,1114}

Possible contamination of blowby from lubricating oil was eliminated in a unique study by Domke, Lindley, and Sechrist.³²⁶ Using an oilless engine with Teflon parts, they found that blowby hydrocarbon composition was roughly 50% aromatics, 35% saturates, and 15% olefins, regardless of the air:fuel ratio or the fuel used (gasoline or isooctane). They also found oxygenates at about 5 ppm in the blowby, of which only formaldehyde, acetaldehyde, methanol, and ethanol could be identified. Payne and Sigsworth⁹⁶⁵ also detected oxygenates, as well as hydrocarbons, in blowby gases, although they did not recognize the importance of blowby as an emission source of their early (1952) study.

Hass and Scanlin⁵³⁴ measured the blowby rates of 500 cars of various makes and ages and determined the flow-rate percentiles for various engine sizes. This basic information has been useful to designers of PCV systems. Voelz *et al.*¹²⁵⁴ tested over 75,000 vehicles in 15 metropolitan areas and found that 17% of the PCV systems needed maintenance and that 3.6% of the cars were discharging some crankcase fumes to the atmosphere. In a smaller survey of 483 cars in Cincinnati, Ohio, 29%

needed PCV maintenance and 5% were discharging some crankcase fumes.²⁵¹ The detailed data from these surveys suggest that the PCV systems in actual use are about 98% effective.

Diesel-Powered Motor Vehicles

As indicated in Table 2-2, diesel-powered motor vehicles account for about 1% of the hydrocarbon emission from all motor vehicles and about 1% from all mobile sources. Diesel emission originates exclusively from the exhaust; blowby and evaporative emission is practically nil.^{770,830}

The gaseous hydrocarbon fraction of diesel exhaust is extremely complicated. Many investigators have shown that it consists of light, cracked hydrocarbons and heavy fuel-like components up to about C_{24} .^{599,600,769,770,830,848,1009,1263} Except for methane, the light, cracked hydrocarbons are almost all olefins. Ethylene, acetylene, and propylene are the predominant light hydrocarbons, with smaller amounts of C_4 olefins and even smaller amounts of C_5 and C_6 olefins.^{769,1009} Figure 2-1 shows the bimodal carbon-number distribution of diesel-exhaust hydrocarbons; interestingly, the proportions of light hydrocarbons are greater for the four-cycle engine than for the two-cycle engine.⁵⁹⁹ Linnell and Scott⁷⁷⁰ estimated that the light hydrocarbons constitute 10–25% of the total on a molar basis. Hurn and Seizinger⁶⁰⁰ reported that the

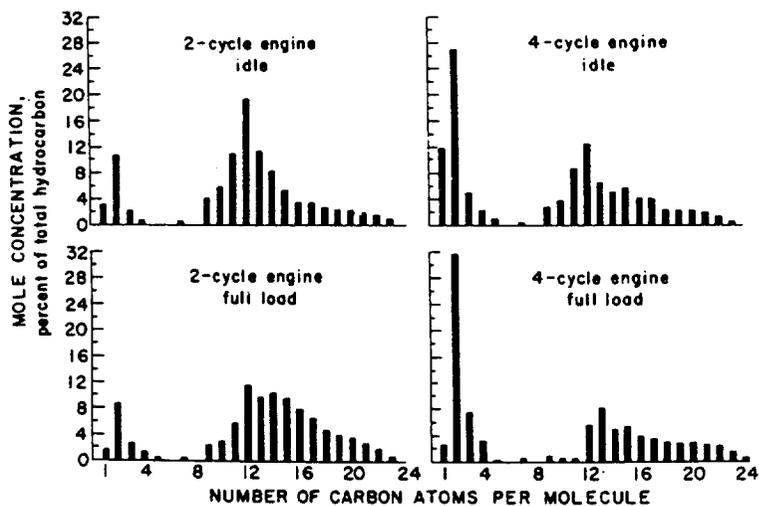


FIGURE 2-1 Distribution of hydrocarbons in diesel exhaust gas. (Reprinted with permission from Hurn and Marshall.⁵⁹⁹)

proportions of light hydrocarbons are highest when the total hydrocarbon concentration is lowest.

Most of the analytic work on heavy hydrocarbons (C_{10-24}) has been directed toward identifying the odorous components.^{334,763,1141} Caragay *et al.*⁷⁶³ reported finding the following hydrocarbon classes in the "oily-kerosene" fraction of diesel-exhaust condensate: indans, tetralins, alkylbenzenes, naphthalenes, indenenes, acenaphthenes, and benzothiophenes. Similar types of hydrocarbons were found by Dravnieks *et al.*³³⁴ in a related odor study. Skala *et al.*¹¹²⁰ identified several high-molecular-weight aromatic carbonyl compounds in diesel exhaust that they believe are important odorants. At present, we can say only that the fuel-like fraction of diesel exhaust consists of at least several hundred compounds; most of them are found in the fuel, but some—important to the odor problem—are formed during combustion.

Low-molecular-weight aldehydes have also been found in diesel exhaust. Formaldehyde and to a lesser extent acrolein have been reported most often.^{64,360,600,769,770,865,1009,1038,1144} Vogh¹²⁵⁶ measured the following aldehydes in one diesel-exhaust sample: formaldehyde (18.3 ppm); acetaldehyde (3.2 ppm); acrolein, acetone, propionaldehyde, and isobutyraldehyde (2.9 ppm); *n*-butyraldehyde (0.3 ppm); crotonaldehyde and valeraldehyde (0.4 ppm); hexaldehyde (0.2 ppm); and benzaldehyde (0.2 ppm). The proportions were not greatly different from those shown in Table 2-5 for diesel auto exhaust.

Several investigators^{360,848,1038} have attempted to correlate total aldehyde or formaldehyde concentration with diesel-exhaust odor, with limited success.

Other Mobile Sources

AIRCRAFT

Hydrocarbon emission from aircraft is estimated to be 400,000 tons/year, or about 2% of the emission from all mobile sources.²¹¹ This estimate includes only gaseous hydrocarbons, not smoke or soot, although smoke is considered to be the major air pollution problem for aircraft.

Jet aircraft are by far the most important type from a fuel-consumption standpoint. In general, hydrocarbon emission from turbine engines is considerably lower than from comparable-sized reciprocating engines, and the concentrations are very much lower, owing to the large air consumption of turbine engines. Like those from reciprocating engines, the hydrocarbons in turbine-engine exhaust consist of light, cracked

products plus fuel-like components. Figure 2-2 shows the carbon-number distribution of the hydrocarbons in the exhaust from an aircraft turbine and in the fuel (JP-4) burned to produce the exhaust.²¹⁵ The proportions of light hydrocarbons are much lower than for reciprocating engines powered by either gasoline or diesel fuel. Turbine-engine exhaust is unusual in another way, as shown in Figure 2-2: the

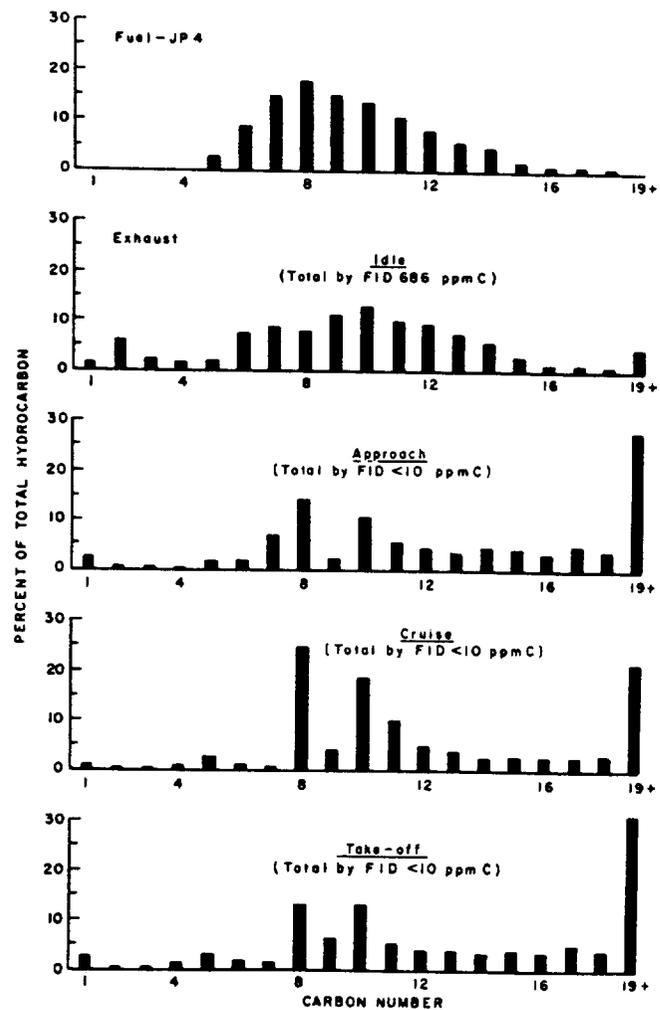


FIGURE 2-2 Distribution of hydrocarbons in jet-aircraft engine exhaust. (Reprinted with permission from Chase and Hurn.²¹⁵)

polymerization of the fuel components to form heavy hydrocarbons (C_{19} and heavier). Fuel polymerization does not occur in gasoline or diesel engines to nearly so great an extent, if it occurs at all. The C_{19} and heavier hydrocarbons in turbine exhaust are probably particulate, rather than gaseous.

Cornelius *et al.*²⁵⁰ measured the concentrations of individual hydrocarbons in the exhaust from an automotive turbine engine, but reported only that their average photochemical reactivity "compared favorably" with that of gasoline-engine exhaust hydrocarbons. Korth and Rose⁷¹⁴ measured individual hydrocarbons in the exhaust from a turbine-powered automobile operated on unleaded gasoline. Compared with those from a conventional automobile (and adjusted for differences in air consumption), the turbine exhaust concentrations were very much lower for C_{1-5} olefins and C_{1-5} paraffins, slightly lower for C_{6-8} paraffins, and slightly higher for benzene. Moreover, the exhaust from the turbine car did not contain any aromatics above C_8 , whereas the exhaust from the conventional car, operated on the same gasoline, did contain higher aromatics. The proportion of light olefins in the turbine exhaust was much less than that in the conventional exhaust. This agrees with Chase and Hurn's carbon-number distribution²¹⁵ (Figure 2-2).

Formaldehyde and total aldehyde concentrations in turbine exhaust have been measured,^{215,250,714,785} but no detailed aldehyde analyses have been reported. What little information on aldehyde composition is available is conflicting. In one study involving aircraft turbines,⁷⁸⁵ formaldehyde constituted about 70% of the total aldehyde, about the same proportion as in gasoline- or diesel-powered engine exhaust. However, in Korth and Rose's⁷¹⁴ study of the turbine-powered automobile, formaldehyde constituted only 10% of the total aldehyde.

RAILROADS

Hydrocarbon emission from railway locomotives is only about 100,000 tons/year.²¹¹ Because locomotives are almost all diesel-powered, the character of their emission is essentially the same as that of diesel-powered vehicles, previously discussed.

MARINE VESSELS

Hydrocarbon emission from ships, barges, and other vessels is estimated at about 300,000 tons/year.²¹¹ Larger vessels are powered by oil-fired and to a lesser extent coal-fired steam engines. Because no

information is available about the gaseous emission from such vessels (although smoke is a problem on the Great Lakes), they cannot be discussed further here. Smaller vessels are usually diesel-powered. The character of their emission is essentially the same as that of diesel-powered vehicles. The special case of outboard motors is discussed in the following section, because they are similar in design to internal-combustion engines in some off-highway uses.

OFF-HIGHWAY USE

This category includes large construction equipment, farm tractors, snowmobiles, trail bikes, outboard motors, electric generators, garden tractors, power lawn mowers, and chain saws. Hydrocarbon emission from these sources is about 1.9 million tons/year, or about 10% of all mobile-source emission.²¹¹ Off-highway emission appears to be increasing.

Many large off-highway vehicles and machines, such as heavy construction equipment and farm tractors, use gasoline or diesel engines that are very similar to those in motor vehicles. Their emission is probably also similar, so they will not be discussed further. However, many small off-highway vehicles and machines use small gasoline engines, which in general are less efficient and emit larger quantities of hydrocarbons than larger engines. Donohue *et al.*³²⁷ estimated the hydrocarbon emission from these small engines at 169,000 tons/year for the United States. This is about 9% of the emission from all off-highway sources and less than 1% of the emission from all mobile sources. Eccleston and Hurn³⁵⁰ tested 36 small utility engines and found the average hydrocarbon emission to be 8 g/hp-hr for four-cycle engines and 140 g/hp-hr for two-cycle engines. This large difference was attributed partly to the lower average size of the two-cycle engines, but mostly to the fact that two-cycle engines are scavenged by unburned fuel-air mixture. This scavenging action not only increases the total hydrocarbon concentration in the exhaust, but alters the composition. As shown in Figure 2-3, two-cycle engine exhaust contains a much higher proportion of fuel components.³⁵⁰

STATIONARY MAN-MADE SOURCES OF HYDROCARBON EMISSION

Many industrial, commercial, and domestic activities emit gaseous hydrocarbons and other organic compounds to the atmosphere. These

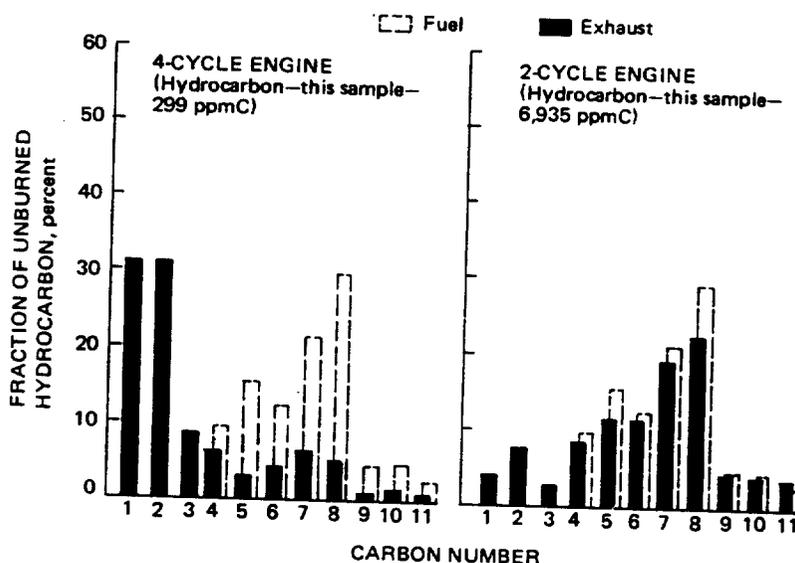


FIGURE 2-3 Distribution of hydrocarbons in exhaust from small utility engines. (Reprinted with permission from Eccleston and Hurn.³⁵⁰)

sources, both numerous and widespread, include all kinds of fuel burning, solvent usage, and waste-disposal operations, as well as the more obvious chemical processing and petroleum refining and marketing. The total hydrocarbon emission from these sources is shown in Table 2-2. According to this 1969 estimate, stationary sources in the United States discharge 17.6 million tons of hydrocarbon per year, compared with 19.8 million tons from mobile sources. A more recent (1971) survey estimates stationary-source emission at slightly more than 25 million tons/year; it is summarized in Table 2-7 and is considerably different from the 1969 survey and presumably more accurate.

The composition of organic emission from various stationary sources is discussed in the following sections.

Fuel Combustion

The fuel burned by all stationary combustion sources in the United States during 1968 was the equivalent of 43.4×10^{15} Btu, of which 30% was provided by coal, 17% by distillate and residual fuel oil, 48% by natural gas, and 5% by miscellaneous fuels, such as coke, lignite,

TABLE 2-7 Most Recent (1971) Estimates of Organic Emission from Stationary Sources in the United States^a

Stationary Source	Total Organic Emission, million tons/year
Solvent evaporation	7.1
Solid-waste combustion	4.5
Agricultural burning	4.2
Forest fires	2.4-3.0
Petroleum storage and marketing	2.2
Petroleum production and refining	2.0
Chemical processing	1.4
Other industrial processing	~1
Fuel combustion	0.4
Coal-refuse burning	0.2
TOTAL	25.4-26.0

^aData from MSA Research Corporation.²⁷⁸

wood, LPG, and waste gases.¹²²⁹ The major uses of fuel are in electric power plants, industrial processing, and space heating. In general, the gaseous hydrocarbon and other organic emission from specific stationary combustion sources is lower than and very different from those of specific automotive sources.

COAL

Electric power plants account for most of the coal burned in the United States. Cuffe, Gerstle, and their co-workers^{267,268,458} reported hydrocarbon emission from several large coal-fired power plants to be between 0.1 and 0.2 lb/ton of fuel burned. Hangebrauck *et al.*⁵²¹ reported similar values for large power plants and considerably higher values (1-3 lb/ton) for coal-fired industrial boilers. Formaldehyde emission from the same units ranged from about 0.001 to 0.006 lb/ton of fuel, or about 1-2% of the hydrocarbon emission, and so appears to be unimportant. However, organic acids are important and actually exceed hydrocarbon emission in this type of equipment. Cuffe *et al.*²⁶⁸ reported an average value of 12.4 lb of organic acid (as acetic) per ton of fuel burned for one large coal-fired plant. This was almost 70 times the hydrocarbon emission from the same plant. An EPA report¹²²⁹ stated that hydrocarbon emission from coal-fired equipment ranges from 0.3 lb/ton for large utility boilers to 3 lb/ton for commercial and domestic

furnaces. Hovey *et al.*⁵⁸⁴ reported that organic emission from the combustion of hard coal was only one-eighth that from soft coal.

No information is available on the composition of the hydrocarbons or organic acids that are discharged from coal-burning equipment.

FUEL OIL

Electric power plants, oil refineries, industrial plants, and space heating account for most of the fuel oil burned in the United States. Like that from coal-burning equipment, gaseous hydrocarbon and other organic emission from oil burners is very low. Chass *et al.*²¹⁷ reported hydrocarbon emission from oil-burning power plants, industrial boilers, and domestic and commercial furnaces to be about 0.2 lb/ton; aldehyde and ketone emission, about 0.15 lb/ton; and other organic emission (presumably organic acids), 0.4–0.8 lb/ton. The hydrocarbon and other organic emission from oil-fired equipment in petroleum refineries was about 1 and 3 lb/ton, considerably greater than from the other sources. Hangebrauck *et al.*⁵²¹ reported hydrocarbon emission of about 0.3 lb/ton and formaldehyde emission of about 0.006 lb/ton for large oil-fired equipment; emission from smaller equipment was somewhat higher—about 1.0 and 0.03 lb/ton, respectively. Chass and George²¹⁶ measured aldehyde emission from about 30 small industrial burners operated on oil, gas, or both. The oil-fired burners discharged 0.1–6.7 lb of aldehydes per ton of fuel burned and averaged 1.0 lb/ton. Wasser *et al.*¹²⁷⁷ studied the effect of excess air on the emission from a small domestic oil burner. The hydrocarbon emission was very low under optimal conditions—about 0.06 lb/ton—but increased to over 30 lb/ton when the air was reduced to stoichiometric proportions. An EPA literature survey¹²²⁹ estimated the hydrocarbon emission from oil-fired equipment to be about 0.5 lb/ton. Magill and Benoliel⁸⁰⁰ reported somewhat higher emission for large oil-fired units than those quoted above in their early (1952) study.

NATURAL GAS

Space heating accounts for most of the natural gas consumed in the United States, although power plants and industrial processes are important users. Natural gas is considered to be clean-burning fuel, and it does produce some organic emission. Chass *et al.*²¹⁷ reported negligible hydrocarbon emission from gas-fired power plants, industrial boilers, and commercial and domestic heaters. Aldehyde emission from the same sources was less than 0.1 lb/ton, and other organic

emission (presumably organic acids) was between 0.1 and 0.2 lb/ton. Chass *et al.*²¹⁷ reported appreciably higher emission for gas-fired units in petroleum refineries than for other gas-fired units, as they did for oil-fired equipment. Hydrocarbon emission reported by Hangebrauck *et al.*⁵²¹ for gas-fired equipment varied from 0.14 to 3.8 lb/ton; formaldehyde emission, from 0.005 to 0.12 lb/ton. Aldehyde emission from the small gas-fired burners tested by Chass and George²¹⁶ varied from near zero to about 3 lb/ton and averaged 0.5 lb/ton. The consensus values reported by the EPA¹²²⁹ were about 2.0 lb/ton for hydrocarbons, 0.15 lb/ton for aldehydes, and 0.2 lb/ton for other organics for gas-fired power plants and industrial boilers; emission was somewhat lower for domestic and commercial heating units. Magill and Benolie⁸⁰⁰ reported that the emission of all three organic classes was between 2 and 3 lb/ton for gas-fired equipment; no difference was noted between large and small units.

Methane is presumably the predominant hydrocarbon in the effluent from gas-fired equipment, but there are no published data to confirm this. Hall⁵¹⁰ reported that formaldehyde, acetaldehyde, and formic acid are produced when natural gas is burned in appliances with a deficiency of air.

WOOD

Wood is used as an industrial fuel only where it is a readily available by-product. Hydrocarbon emission from burning it depends on the proportions of wood and bark, the moisture content, and how well the furnace is designed and maintained. An EPA report¹²²⁹ gave typical emission from the combustion of wood in industrial boilers as 2 lb of hydrocarbon per ton and 0.5 lb of carbonyl per ton; these values are comparable with those reported for the combustion of other fuels.

Fritschen *et al.*⁴⁴¹ measured total hydrocarbon emission of 2–4 lb/ton from the burning of pine slash samples in laboratory apparatus. Methane was the predominant hydrocarbon, but smaller amounts of ethylene, ethane, acetylene, and propylene and traces of C₄ and C₃ olefins were also found. Several other investigators have reported a variety of oxygenated organics in wood smoke. Jahnsen⁶²⁹ found 29 different organics in the effluent from hickory sawdust that was burned in Pyrex apparatus. Acetic acid was the principal organic acid; methyl alcohol, the principal alcohol; diacetyl, the principal carbonyl; and guaiacol and 2, 6-methoxypyrogallol, the principal phenols. Bellar and Sigsby⁹² identified methyl alcohol, ethyl alcohol, acetone, acetaldehyde, acrolein, propyl alcohol, 2-methylpropyl alcohol, and butyl alcohol in the

effluent from a trench incinerator burning wood. Hoff and Kapsalopoulou⁵⁷⁸ reported finding 18 different alcohols, aldehydes, ketones, and ethers and benzene and toluene in the low-boiling fraction of smoke from a hickory fire used to smoke meats. Levaggi and Feldstein⁷⁶⁰ measured amounts of formaldehyde, acetaldehyde, and acetone in parts per million and smaller amounts of propyl alcohol and methylethylketone in the effluent from a wood-burning fireplace.

SUMMARY

Some typical fuel combustion emission values are shown in Table 2-8. The purpose is to show the composition of the gaseous organic emission from different combustion sources, not to compare different fuels. Organic acids are the major constituent, followed by hydrocarbons and aldehydes. This is an entirely different order from auto exhaust, in which hydrocarbons are predominant, aldehydes secondary, and organic acids negligible.

It should be pointed out that the nationwide hydrocarbon emission summarized in Table 2-2 does not include organic acids, at least for the fuel combustion sources. On the basis of 1968 U.S. consumption of the three fuels and the emission values in Table 2-8, an additional 4.5 million tons of organic acids are emitted, of which 3.5 million tons are from coal, 0.5 million tons from oil, and 0.5 million tons from gas. These must be considered only rough estimates, but they do indicate that fuel combustion is a more important source of organic emission than implied in Table 2-2 or Table 2-7.

Industrial Processes

A wide variety of organic pollutants are emitted by industrial processes. Some of the more important are discussed below.

PRIMARY METALS

The production of coke is the main source of gaseous hydrocarbon emission associated with the primary metals industry. Coke-oven gases contain aromatic hydrocarbons and phenols, as well as inorganic pollutants. The emission occurs principally when coal is charged to the oven and when the coke is quenched and removed.²⁴⁴ The recent development of a continuous coking process may greatly reduce coke-oven emission in the future.⁷⁴ The phasing-out of old beehive ovens, from which no attempt is even made to collect the coal tars, will also alleviate the problem.¹³⁵

TABLE 2-8 Typical Emission of Several Classes of Compounds from Stationary Combustion Sources

Compounds	Emission, lb/ton of fuel		
	Coal	Oil	Gas
Hydrocarbons	0.3	1.0	1.0
Aldehydes	unknown	0.5	0.5
Formaldehyde	0.003	0.006	0.008
Organic acids	10	~5	2

PETROLEUM REFINING

Various refinery processing and storage operations discharge hydrocarbons to the atmosphere. Good design and housekeeping minimize this emission, however.³⁷³ The more volatile C₄, C₅, and C₆ hydrocarbons probably account for most of the refinery emission. Petroleum refineries also discharge small amounts of organic sulfur compounds.

CHEMICAL PROCESSING

Many chemical processing plants discharge a variety of organic compounds to the atmosphere, depending on their operations. Fawcett³⁹¹ inventoried the emission from a phthalic anhydride plant and found that it included phthalic anhydride, maleic anhydride, naphthoquinone, benzoic acid, and various aldehydes. Lur'e⁷⁹² reported that butadiene, isobutylene, styrene, benzene, and ethyl alcohol vapors are discharged from a synthetic rubber plant. Walter and Amberg¹²⁷⁴ reported that α -pinene, methyl alcohol, and, to a lesser extent, acetone are the major organic compounds emitted from kraft paper mills (sulfur compounds excluded). No organic compound or group of compounds predominates in chemical plant emission.

OTHER INDUSTRIAL SOURCES

Levaggi and Feldstein⁷⁶¹ measured aldehyde emission from a variety of small industrial operations, such as coffee roasting, printing, paint spraying, and foundry-core preparation, many of which involved ovens and after burners. They found amounts of formaldehyde, acetaldehyde, and acetone in parts per million and smaller amounts of acrolein and other C₃ and C₄ aldehydes. The emission from many of these and from other small industrial operations arises from the use of chemical

solvents. The EPA has compiled air pollutant emission rates for a variety of industrial processes.¹²²⁹

Solid-Waste Disposal

The per capita solid-waste load in the United States is about 10 lb/day, about half of which is disposed of by incineration.¹²²⁹ This incineration produces a wide variety of organic air pollutants, whose amount and composition depend greatly on the nature of the wastes and how they are burned.

DOMESTIC, MUNICIPAL, AND INDUSTRIAL INCINERATORS

These incinerators vary widely in size, design, and effectiveness. In general, large, fully engineered units, many of which have stack controls, discharge smaller amounts of pollutants than small, domestic units. Tuttle and Feldstein¹²¹⁶ reported much lower hydrocarbon emission from an adequately designed multichamber incinerator than from an inadequately designed incinerator; methane and ethylene were the predominant hydrocarbons from both units, but many other C₂₋₆ hydrocarbons were found with the less efficient incinerator. Stenburg and co-workers^{1150,1151} reported hydrocarbon emission of 1–2 lb/ton of refuse burned and formaldehyde emission of 0.01–0.02 lb/ton for a medium-sized multichamber incinerator. Carotti and Kaiser's data for a large municipal incinerator indicate hydrocarbon emission of about 0.2 lb/ton, aldehyde emission of about 0.1 lb/ton, and organic acid emission of about 3 lb/ton; most of the hydrocarbon was methane and ethylene.¹⁹⁹ Kaiser *et al.*⁶⁵⁹ reported somewhat higher values for an apartment-house incinerator: organic acids, 18 lb/ton; esters, 10 lb/ton; aldehydes, 4 lb/ton; and benzene and phenol, about 0.1 lb/ton each. In addition, Kaiser *et al.* detected smaller amounts of methane, ethylene, propylene, acetaldehyde, methyl alcohol, ethyl alcohol, acetone, and unidentified higher-molecular-weight products totaling about 0.6 lb/ton. Still higher emission was reported by Yocum *et al.*¹³⁵² for a backyard incinerator burning a high proportion of garden clippings: methyl alcohol, 9–23 lb/ton; ethylene, 8–61 lb/ton; acetone, > 8 lb/ton; methane, 23–150 lb/ton; acetylene, 4–73 lb/ton; olefins, > 6 lb/ton; carbon disulfide, > 3 lb/ton; benzene, > 3 lb/ton; organic acids, > 4 lb/ton; phenols, > 8 lb/ton; and aldehydes, 5–64 lb/ton. Magill and Benoliel⁸⁰⁰ reported organic emission of several hundred pounds per ton for domestic incinerators burning paper or grass clippings, compared with only 1–2 lb/ton for municipal incinerators.

Bellar and Sigsby⁹² measured individual oxygenates in the effluent from a trench incinerator burning wood. They found a much wider range of products when no forced air was added. With forced air, methyl and ethyl alcohol predominated. Bellar and Sigsby noted that the ratio of alcohols to aldehydes was considerably greater in the incinerator effluent than in auto exhaust.

OPEN BURNING

Gerstle and Kemnitz⁴⁵⁹ reported the following emission values from the open burning of municipal refuse, landscape refuse, and automobile components: hydrocarbons, 30 lb/ton; organic acids, 15 lb/ton; and formaldehyde, 0.01–0.10 lb/ton. An EPA report¹²²⁹ showed that organic emission from open burning is generally higher than that from incineration.

TEEPEE BURNERS

Teepee (or wigwam) burners are large conical structures in which industrial and municipal wastes are burned. They are used only when more efficient (and costly) incinerators are not available. Kreichelt⁷²⁵ reported that many teepee burners do not receive enough air for good combustion, because of poor maintenance or inadequate blowers. The organic emission from teepee burners depends on the waste material burned and is generally greater than that from incinerators, but less than that from open burning.

Miscellaneous Stationary Sources

The following sources account for over half the total gaseous organic emission from all stationary sources. Solvent evaporation is the largest single stationary source, 7.1 million tons/year according to the most recent EPA estimates (Table 2-7). Solid-waste combustion and agricultural burning are the next most important stationary sources.

FOREST FIRES

It is nearly impossible to measure emission from a forest fire, but at least one study has been made under field conditions closely simulating forest fires. Fritschen *et al.*⁴⁴¹ measured the gaseous organic emission from the burning of several acres of mature Douglas fir trees. They identified 25 different organics, ranging in molecular weight from that of ethylene to

that of xylene; the most significant were ethylene, ethane, propylene, propane, methyl alcohol, and ethyl alcohol. Acetone, benzene, and toluene were also found in most of the samples. They estimated the total hydrocarbon emission from forest fires at 2–4 lb/ton burned, on the basis of these and other laboratory tests. This is considerably lower than the 166-lb/ton estimate of Feldstein *et al.*³⁹² for the open burning of land-clearing debris.

Stephens and Burleson¹⁵⁵ reported an excess (compared with normal air) of olefins over paraffins in the air near a brush fire in Riverside, California; this finding is consistent with the results of laboratory studies on the combustion of agricultural wastes.

STRUCTURAL FIRES

The gaseous organic emission from structural fires, like that from forest fires, can be only roughly estimated. It is probably similar in composition to the emission from wood combustion and municipal-waste incineration and includes both hydrocarbons and oxygenated compounds.

COAL-REFUSE BANKS

Smoldering coal-refuse banks are a conspicuous source of air pollution in mining areas.⁸⁰² Carbon monoxide and sulfur dioxide are the major gases emitted,¹⁷⁷ but some organics are also produced. The composition of the gaseous organics is not known.

AGRICULTURAL BURNING

Agricultural wastes—such as cut grass and weeds, straw, felled trees, and other debris—are often disposed of by open burning. The relatively low temperatures associated with open burning tend to increase the emission of gaseous organics, compared with incineration.³⁹²

Darley *et al.*²⁸⁴ measured the hydrocarbon produced by burning fruit prunings, barley straw, and native bush in a special tower that simulated field conditions. The average hydrocarbon emission from these agricultural wastes was about 13 lb/ton, of which 2 lb consisted of ethylene, 3 lb of other olefins below C₅, 1 lb of paraffins below C₆, and 7 lb of heavier hydrocarbons. Boubel *et al.*¹²⁶ reported similar values for the burning of grass and straw in the same apparatus. Gerstle and Kemnitz⁴⁵⁹ reported a considerably higher hydrocarbon emission (30 lb/ton) for the open burning of landscape refuse. Feldstein *et al.*³⁹² reported still higher values for the open burning of land-clearing debris. They estimated

(from other incinerator tests) total gaseous organic emission at 166 lb/ton, of which 30 lb would consist of ethylene, 30 lb of other olefins, 36 lb of saturated hydrocarbons, 11 lb of aromatic hydrocarbons, and 59 lb of oxygenated organics. Many of the low-molecular-weight alcohols and aldehydes in wood smoke are probably produced by the open burning of agricultural wastes.

SOLVENT EVAPORATION

Some of the more important uses of solvents include dry cleaning, surface coatings, metal degreasing, and chemical processing. Most solvents evaporate eventually, either inadvertently or by plan, and end up in the atmosphere. Therefore, the overall composition of solvent emission can be deduced accurately from usage data.

The usage or consumption of different solvents in the United States for 1968 is shown in Table 2-9. Petroleum naphtha, a generic name for hydrocarbon mixtures of varied composition and volatility, is by far the most important solvent from a tonnage standpoint, accounting for about 60% of the total usage. No other solvent accounts for more than 4%. In all, hydrocarbon-based solvents account for 70% of the total usage; ketones and other oxygenated hydrocarbons, 14%; and chlorinated hydrocarbons, 16%. It should be pointed out that the data in Table 2-9 indicate only the quantities of various chemicals consumed as solvents, rather than total amounts produced or consumed in all uses.

GASOLINE MARKETING

Vapor breathing losses from storage tanks at refineries and bulk plants and vapor displacement during filling of tank trucks, service station tanks, and automobile tanks account for almost all the emission associated with gasoline marketing. The vapor lost from breathing and filling consists primarily of the more volatile C₄, C₅, and C₆ hydrocarbons. The analyses of automobile evaporation losses shown in Table 2-6 are probably typical of gasoline marketing emission. Various control devices and practices minimize vapor losses at most storage facilities, but there are no vapor loss controls at retail service stations.

NATURAL SOURCES OF ATMOSPHERIC HYDROCARBONS

Many natural processes emit hydrocarbons to the atmosphere. The major natural sources that have been identified and for which quantita-

TABLE 2-9 Estimated Solvent Usage in the United States, 1968^a

Solvent	Quantity Used As Solvent, tons/year
Petroleum naphtha	4,325,000
Perchloroethylene	285,000
Ethyl alcohol	265,000
Trichloroethylene	245,000
Toluene	240,000
Acetone	205,000
Xylenes	180,000
Fluorocarbons	175,000
Methylethylketone	160,000
1,1,1-Trichloroethane	140,000
Methylene chloride	140,000
Methyl alcohol	135,000
Ethylene dichloride	120,000
Ethylacetate	85,000
Cyclohexane	80,000
Methylisobutylketone	75,000
Hexanes	65,000
Benzene	50,000
<i>n</i> -Butyl alcohol	45,000
Nitrobenzene	25,000
Turpentine	20,000
Isopropylacetate	20,000
Ethyl ether	20,000
Monochlorobenzene	15,000
Isopropyl alcohol	10,000
Diethylene glycol	5,000
Methylacetate	5,000
Cresols	2,500
Phenol	^b
Chloroethylene	^b
Carbon tetrachloride	^b
Pinene	^b
Cyclohexyl alcohol	^b
Cyclohexanone	^b
Ethylbenzene	^b
Isobutyl alcohol	^b
Chloromethane	^b
<i>n</i> -Butylacetate	^b
TOTAL	7,137,500+

^aData from MSA Research Corporation.⁵⁷⁸^bLess than 2,500.

tive estimates are available are biologic decomposition of organic matter, seepage from natural gas and oil fields, and volatile emission from plants. However, information in the literature indicates that there are many other natural sources of hydrocarbons and oxygenates that have not been considered heretofore. Techniques sensitive enough to measure the minute concentrations of hydrocarbons and oxygenates present in remote areas have only recently become available. For example, methane, the predominant hydrocarbon in the atmosphere, was first identified as a trace constituent of the atmosphere as late as 1948.⁸⁵⁸ As more-sensitive analytic techniques become available and more effort is channeled into attempts to understand the characteristics and role of natural emission, one would expect more and more minor sources (particularly in the biosphere) to be identified. This section discusses the major natural sources for which quantitative estimates are available and indicates some of the minor sources that have been identified.

Methane is produced in the anaerobic bacterial decomposition of organic matter in swamps, lakes, marshes, paddy fields, etc.^{176,346} Koyama⁷²² has estimated the global production of methane as 2.7×10^{14} g/year (300 million tons/year), on the basis of his measurements of methane fermentation in various soils and lake sediments under controlled experimental conditions. Koyama estimated that paddy fields contribute two-thirds of the methane production and used Hutchinson's⁶⁰² estimate of enteric fermentation in animals to account for one-sixth. The other one-sixth of the methane in Koyama's estimate came from coalfields and soils in grassland and forest areas. Ehhalt³⁵⁵ pointed out that Koyama did not include methane production from swamps, and Robinson and Robbins¹⁰²⁶ pointed out that methane production in humid, tropical areas should also be considered. Robinson and Robbins have estimated the production from swamps and humid tropical areas and added it to Koyama's figure to derive an estimate of methane production of 14.5×10^{14} g/year (1.6 billion tons/year).

Methane is the predominant hydrocarbon in natural gas; seepage from gas, oil, and coal fields constitutes another source.¹⁸ However, Ehhalt³⁵⁵ considered measurements of the carbon-14 content of atmospheric methane and concluded that up to 25% of the atmospheric methane is from "dead" carbon and could have come from oil-field seepage or the combustion of fossil fuels; 75% is of recent biogenic origin.

Our understanding of the natural sources of methane is still highly limited; as a result, current estimates of global production remain speculative.

Plants release a variety of volatile organic substances, including ethylene, isoprene, α -pinene, and a variety of other terpenes. Ethylene production by plants was noted as early as 1910²⁵⁴ and rediscovered in 1932.³⁶⁹ Burg¹⁷¹ has compiled an extensive list of plants that have been shown to produce ethylene. Rates of production of ethylene in various fruits have been measured by Biale *et al.*¹¹⁰ and in cotton plants by Hall *et al.*⁵¹² Although some of the fruits were thought to produce no ethylene, later measurements by a more sensitive gas-chromatographic method have shown that very small amounts are produced.^{171,172} Ethylene is a plant hormone that is continuously produced in plants and has been linked to fruit ripening.^{1,170,265} The ripening of fruits,¹¹⁰ the fading of flowers,¹² and injury from air pollutants²⁵⁷ have all been shown to be associated with increased ethylene production. Abeles *et al.*² have estimated the natural production of ethylene from plants in the United States at 20,000 tons/year.

Other organic plant volatiles have not been studied as extensively. Ivanov and Yakobson⁶¹⁷ have reviewed the Russian literature and reported that a considerable number of plant species release low-molecular-weight hydrocarbons, aldehydes, and a wide variety of essential oil components.

Went¹³⁰¹ hypothesized that the decomposition of carotenoids (lipochromes) and phytol results in emission of volatile organics to the atmosphere and that the fate of terpenes synthesized in plants is volatilization into the air. Went estimated that a total of 175 million tons of volatile organic material was emitted to the atmosphere of the whole world each year. Later, Rasmussen⁹⁹⁹ and Rasmussen and Went¹⁰⁰⁸ reported ambient concentrations of plant volatiles (such as isoprene, α - and β -pinene, limonene, and myrcene) in air at remote sites. From the average concentration they measured (10 ppb), Rasmussen and Went estimated the global production of plant volatiles at 438 million tons/year. Although the estimates of worldwide terpene emission need considerable refinement,¹⁰⁰⁰ it is definite that there are large sources of natural, organic emission in the biosphere. Furthermore, Sanadze and Dolidze¹⁰⁶⁰ and Rasmussen⁹⁹⁶ have identified isoprene as a natural volatile plant product and studied the physiology of isoprene emission.^{1007,1059} Table 2-10 lists the various volatile plant products identified by Rasmussen.⁹⁹⁹

From the available estimates of methane and terpene emission, it is clear that worldwide natural hydrocarbon emission is about 2 billion tons/year. However, there is evidence that many other organic volatiles are naturally emitted to the atmosphere. These may be only trace amounts emitted on a local scale, but the total worldwide production can be very large.

TABLE 2-10 Volatile Plant Products^a

α -Pinene	<i>n</i> -Heptane
β -Pinene	Isoprene
Myrcene	α -Ionone
D-Limonene	β -Ionone
Santene	α -Irene
Camphene	

^aIdentified by Rasmussen.⁹⁹⁹

Although natural gas consists predominantly of methane, it also contains varying amounts of ethane, propane, and butane and traces of heavier hydrocarbons.¹⁸ It has been reported that trace quantities of ethane, acetylene, ethylene, propane, and propylene are present as products of methane fermentation.¹⁷⁵

Studies of odorous compounds in natural waters⁶³⁵ have shown that organic sulfur compounds—such as methylmercaptan, dimethylsulfide, isobutylmercaptan, and *n*-butylmercaptan—are produced. In addition, geosmin has been identified as a natural product.⁸⁴³ Organic nitrogen compounds are also well-known odorous natural products.^{173,1153,1176} Wilson *et al.*¹³²⁷ have found that ethylene and propylene are produced in illuminated cell-free distilled water or natural seawater systems to which dissolved organic matter produced by phytoplankton has been added. Furthermore, Cavanagh *et al.*²¹⁰ consider the small quantities of *n*-butyl alcohol, acetone, and ethyl alcohol in Point Barrow, Alaska, as products of a fermentation process in the tundra cover. Aldehydes have been identified as products of an illuminated mixture of plant extracts, oxygen, and water;¹³¹⁴ and methane, ethane, ethylene, propane, propylene, and *n*-butane have been identified as products of the thermal treatment of marine mud slurries.⁸⁸⁵

Man is also a source of volatile organics. Body odors have been studied by the U.S. armed forces.^{241,935,1202} Some atmospheric contaminants identified during a 30-day manned experiment are low-molecular-weight aliphatic acids and aldehydes, in addition to hydrocarbons and other compounds.

The annual hydrocarbon emission from natural sources in the United States can be estimated from the preceding information. If natural methane emission is uniform in all land areas, Robinson and Robbins's¹⁰²⁶ estimate of worldwide methane emission (1.6 billion tons/year) can be used to calculate a U.S. emission of 100 million tons/year. The assumption that natural methane is emitted uniformly from all land areas is probably in error, in that emission rates are higher in tropical

than in nontropical areas. More realistically, assuming that the U.S. methane emission rate is half the world average, the U.S. natural methane emission would be 50 million tons/year. Similarly, if Rasmussen and Went's¹⁰⁰⁸ estimate of worldwide terpene emission (438 million tons/year) is based on uniform distribution over the forested areas of the world, the U.S. emission would be 22 million tons/year. Emission of ethylene from plants in the United States has been estimated at 20,000 tons/year.² Combining these estimates indicates a natural hydrocarbon emission in the United States of about 72 million tons/year.

ATMOSPHERIC CONCENTRATIONS OF GASEOUS HYDROCARBONS AND OXYGENATES

Many hydrocarbons are present in the atmosphere, and the exact composition varies enormously from place to place, but methane is the predominant hydrocarbon found in all locations. In remote areas, it is predominant by far. In populated areas, other hydrocarbons are present, but methane has the highest concentration.

Total Hydrocarbon Concentrations

The flame ionization detector, which measures total organically bound carbon, has been used to measure total hydrocarbon concentrations in various cities. It has been used in the Continuous Air Monitoring Program (CAMP) network since 1962.¹²³⁰ Yearly average carbon concentration ranges from 1.43 ppm in Washington, D.C., in 1962 to 3.3 ppm in Chicago in 1962, and yearly maximal 1-hr averages range from 8 to 17 ppm. Total hydrocarbons are also routinely measured at over 30 sites in the California air monitoring network.¹⁸⁴ Total hydrocarbon analyses have also been made for shorter periods in specific studies.^{32,336,372,1092,1093}

Because the total hydrocarbon measurement does not discriminate between photochemically active hydrocarbons and methane, which is relatively inert, various techniques to separate the hydrocarbon mixture into classes have been developed.^{698,948} One method,⁹⁴⁸ which discriminates between methane and nonmethane hydrocarbons, has been used^{1082,1227} to relate nonmethane hydrocarbons to oxidants formed in urban atmospheres. Diurnal patterns of nonmethane hydrocarbons at some CAMP and Los Angeles County sites are presented in *Air Quality Criteria for Hydrocarbons*.¹²²⁷ Ratios of nonmethane hydrocarbons to total hydrocarbons are reported to vary from 0.2:1 in Washington, D.C., to 0.5:1 in Los Angeles.¹⁰⁸²

Methane

Methane was discovered in the telluric spectrum by Migeotte in 1948.⁶⁵⁸ Later spectroscopic measurements established the average methane concentration of the atmosphere to be about 1.5 ppm.^{398,475,476}

From these spectroscopic measurements, which average over the entire air column, it was tentatively concluded that methane is uniformly distributed throughout the atmosphere, except for local variations near the surface. However, vertical profiles have shown that the methane concentration is somewhat variable in time and space.^{69,355}

Bainbridge and Heidt⁶⁹ measured a decrease in the methane concentration at the tropopause, indicating that the stratosphere is a sink for methane. Scholtz *et al.*¹⁰⁷⁷ have shown that the methane concentration near the stratopause is, indeed, less than 0.05 ppm (by volume).

A number of ground-level measurements of natural background methane concentrations in remote areas have been reported. Stephens and Burleson¹¹⁵⁵ measured 1.39 ppm in southern California mountain areas during the time hot, dry Santa Ana winds were blowing. Cavanagh *et al.*²¹⁰ found an average methane concentration of 1.59 ppm at Point Barrow, Alaska. Swinnerton *et al.*^{1180,1181} measured a mean concentration of 1.25 ppm during an oceanographic cruise between Washington, D.C., and Puerto Rico and concentrations between 1.25 and 1.50 ppm over the Pacific Ocean and on the island of Hawaii. All these measurements agree with Junge's estimate of the worldwide range (1.2–1.5 ppm).⁶⁵⁶ However, Shearer¹¹⁰⁷ has reported measurements at a rural site averaging 0.89 ppm. In inhabited areas, methane concentrations are higher.³²

Other Individual Hydrocarbons

REMOTE LOCATIONS

There have been few measurements of individual hydrocarbons in remote locations. Cavanagh *et al.*²¹⁰ found fractional parts-per-billion concentrations of benzene, pentane, butane, ethane, ethylene, acetaldehyde, and acetone at Point Barrow, Alaska. They also found *n*-butyl alcohol at about 100 ppb, which they attributed to biologic sources. Turk and D'Angio¹²¹⁵ showed that there is a complex mixture of organic vapors in remote locations. Rasmussen and Went¹⁰⁰⁸ have identified isoprene, α -pinene, β -pinene, limonene, and myrcene in the ambient air in remote locations in North Carolina, Virginia, Missouri, and Colorado. They measured terpene concentrations from 2 to 50 ppb and found that ambient concentrations increased with temperature and light intensity.

Particularly high concentrations were found when conditions associated with the death of cells were present, such as the dying of leaves in autumn and the mowing of meadows. Rasmussen⁹⁹⁶ and Rasmussen and Hutton¹⁰⁰⁴ have also analyzed volatile organics in the ambient air in the humid tropics. Stephens and Burleson¹¹⁵⁵ measured parts-per-billion concentrations of ethane, ethylene, and acetylene in the mountains of southern California during Santa Ana winds.

POPULATED LOCATIONS

Although the hydrocarbon composition of the ambient air in populated areas has been studied by a number of investigators, only the Los Angeles basin has been studied extensively. Neligan⁹¹¹ analyzed 16 early-morning samples collected in central Los Angeles for C_{2-4} hydrocarbons. He compared his results with the composition of auto exhaust and showed that they were similar. However, he did find a relative excess of light paraffins in the atmosphere, compared with the composition of auto exhaust. He attributed these to natural gas leakage. Altshuller and Bellar¹⁹ measured methane, C_{2-5} hydrocarbons, and C_{6-8} aromatics on separate days in downtown Los Angeles in the fall of 1961. They followed changes in concentrations during the day and showed that methane concentrations between 2 and 3 ppm were common, confirmed Neligan's finding that light paraffins are more abundant in the Los Angeles atmosphere than in auto exhaust, and showed that aromatic hydrocarbons contribute appreciably to the total hydrocarbon concentration.

Neligan and Leonard⁹¹² reported the concentrations of a dozen C_{6-10} aromatics at five sites in Los Angeles and concluded that aromatics contribute significantly to the total hydrocarbon loading of urban atmospheres. The average results from over 200 early-morning analyses of C_{1-7} hydrocarbons in Los Angeles are summarized in *Air Quality Criteria for Hydrocarbons*.¹²²⁷ Stephens and Burleson¹¹⁵⁴ analyzed the atmosphere in Riverside, California, for C_{1-6} hydrocarbons. Here, too, an abundance of light paraffins was found in the atmosphere, compared with auto exhaust. Because this phenomenon appeared to be more pronounced in the afternoon, Stephens and Burleson suggested that natural gas losses, gasoline evaporative losses, and possibly seepage from oil fields could contribute to the effect. In a later paper, Stephens *et al.*¹¹⁵⁶ presented results of C_{1-7} analyses from various locations in Riverside, the San Francisco Bay area, and southern California oil fields. They concluded that gasoline evaporation alone could not account for the excess paraffins, but that natural gas leakage, seepage from oil fields, and gasoline evaporation all contribute.

Lonneman *et al.*⁷⁷⁹ measured methane, total hydrocarbons, and individual C₆₋₁₀ aromatics in 136 samples from Los Angeles during the fall of 1966. The average and maximal concentrations are shown in Table 2-11. Toluene was the most abundant aromatic, followed by *m*-xylene and benzene. Gordon *et al.*⁴⁸³ followed the diurnal patterns of individual C₂₋₅ hydrocarbons in downtown Los Angeles and Azusa in the fall of 1967. Altshuller *et al.*³¹ measured the full range of individual C₁₋₁₀ hydrocarbons in downtown Los Angeles and Azusa in the fall of 1967. The average concentrations of a number of individual hydrocarbons are shown in Table 2-12. Diurnal patterns for various individual hydrocarbons are shown in Figures 2-4 through 2-7. Although many hydrocarbons are present in urban atmospheres, Altshuller *et al.* found that methane and 10 other hydrocarbons (ethane, ethylene, acetylene, *n*-butane, isopentane, propane, toluene, *n*-pentane, *m*-xylene, and isobutane) account for about 90% of the total hydrocarbon loading.

The hydrocarbon composition of urban areas other than Los Angeles is not so well known. Williams¹³¹⁶ has identified over 30 hydrocarbons on the University of British Columbia campus, and some measurements from Japan are available.⁹⁴¹ Grob and Grob⁴⁹⁷ have qualitatively identified 108 C₆₋₂₀ organics in the air of Zurich, Switzerland. Scott

TABLE 2-11 Average and Highest Concentrations of Various Aromatic Hydrocarbons in Los Angeles^a

Aromatic Hydrocarbon	Concentration, ppb (by volume)	
	Average	Highest
Benzene	15	57
Toluene	37	129
Ethylbenzene	6	22
<i>p</i> -Xylene	6	25
<i>m</i> -Xylene	16	61
<i>o</i> -Xylene	8	33
Isopropylbenzene	3	12
<i>n</i> -Propylbenzene	2	6
3- and 4-Ethyltoluene	8	27
1,3,5-Trimethylbenzene	3	11
1,2,4-Trimethylbenzene, isobutylbenzene, and <i>sec</i> - butylbenzene	9	30
<i>tert</i> -Butylbenzene	2	6
TOTAL	106	330

^aData from Lonneman *et al.*⁷⁷⁹

TABLE 2-12 Aliphatic Hydrocarbon and Alkylbenzene Concentrations in Downtown Los Angeles (DLA) and Azusa^a

Hydrocarbon	Concentration, ppb (by volume)					
	Concentration below Which 10% of Values Occur			Concentration Exceeded by 10% of Values		
	DLA	Azusa	Overall Average	DLA	Azusa	DLA
Aliphatic hydrocarbons						
Methane	1,700	1,500	2,100	2,200	3,500	3,000
Ethane + ethylene	40	34	102	65	180	100
Acetylene + propane	30	18	76	43	120	65
Propylene	3	1	10.5	4	21	8
<i>n</i> -Butane	20	9	46	21	80	35
Isobutane	5	3	12	7	20	12
1-Butene + isobutene	2	1	5.5	3.5	10	5
2-Butene	1	1	2	1	5	2
1,3-Butadiene	1	1	2	1	5	2
<i>n</i> -Pentane	8	4	21	10	35	16
Isopentane	12	7	35	16	56	26
1-Pentane + 2-methyl-1-butene	—	—	3	—	—	—
Nonane + decane	2	1	5	3	8	6
Alkylbenzenes						
Toluene	10	6	30	14	50	23
Ethylbenzene	1	1	5	2.5	9	4
<i>p</i> -Xylene	2	1	5	2	10	4
<i>o</i> -Xylene	2	1	6.5	3	11	6
<i>m</i> -Xylene	4	2	12	5.5	21	10
Propylbenzenes	2	1	4.5	3	8	6
Ethyltoluenes	3	1	7.5	3	15	7
Other C ₈ and C ₁₀ alkylbenzenes	3	1	12	6	23	13

^aData from Altshuler et al.²¹

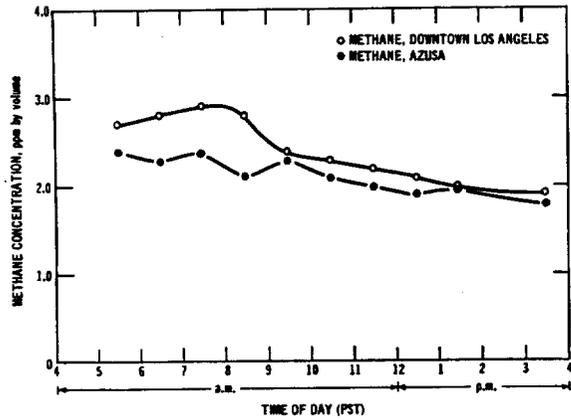


FIGURE 2-4 Diurnal variations in average hourly methane concentrations in downtown Los Angeles and Azusa. (Figures 2-4 through 2-7 reprinted with permission from Altshuller *et al.*³¹)

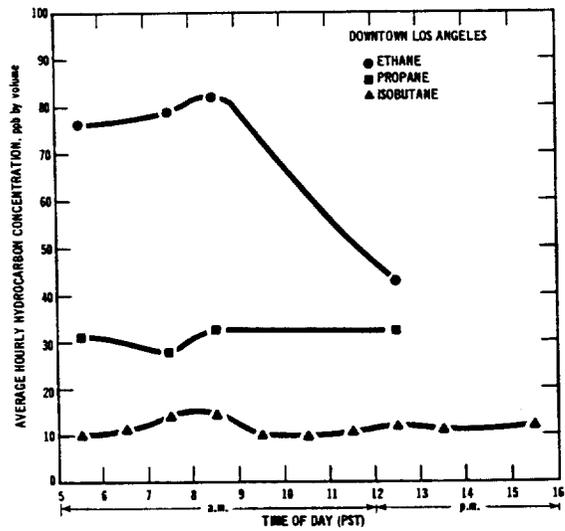


FIGURE 2-5 Diurnal variations in average hourly concentrations of ethane, propane, and isobutane in downtown Los Angeles.

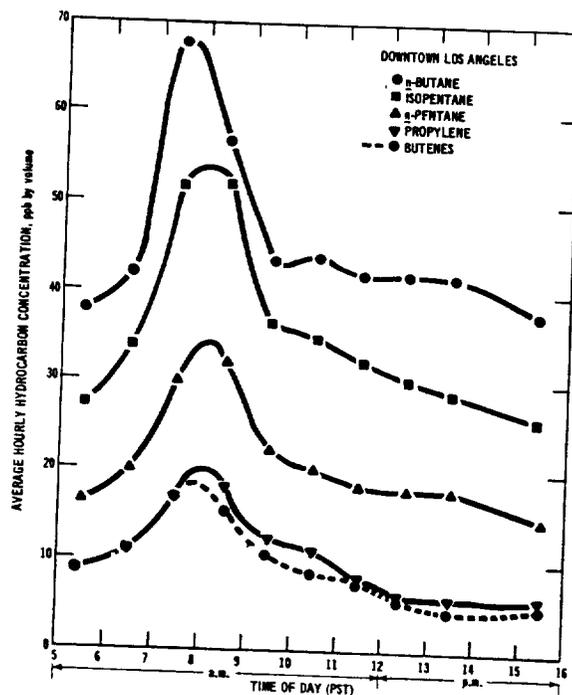


FIGURE 2-6 Diurnal variations in average hourly concentrations of *n*-butane, isopentane, *n*-pentane, propylene, and butane in downtown Los Angeles.

Research Laboratories^{1092,1093} has measured individual C_{1-10} hydrocarbons at various sites in New York, as well as Los Angeles, but has not analyzed the results in detail. Lonneman and Kopczynski⁷⁸⁰ have determined atmospheric hydrocarbon compositions in Los Angeles, Denver, and New York. Stephens and Burleson¹¹⁵⁵ have measured the composition of light hydrocarbons in samples from Hawaii, Denver, New York, and Riverside and the Salinas Valley, California. They concluded that, as long as samples are not deliberately taken near sources of hydrocarbon pollution, the composition resembles that of auto exhaust, with the addition of natural gas and of C_{3-5} paraffins that resemble gasoline vapor. Samples taken in industrial areas and near a brush fire showed distinct differences in composition.

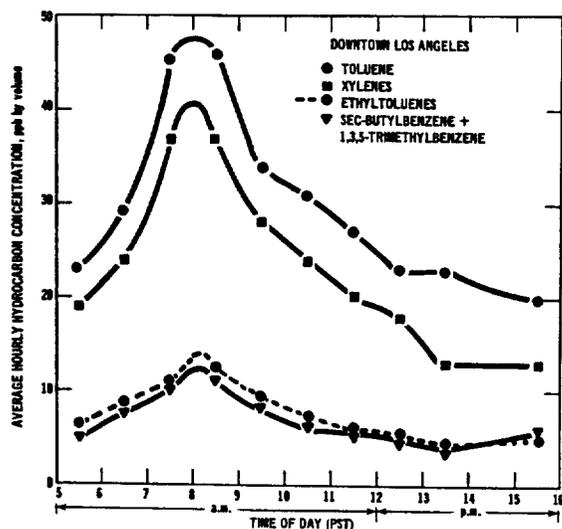


FIGURE 2-7 Diurnal variations in average hourly concentrations of toluene, xylene, ethyltoluene, *sec*-butylbenzene, and 1,3,5-trimethylbenzene in downtown Los Angeles.

Aldehydes and Other Oxygenates

A number of investigators have predicted that formaldehyde should be naturally present in the atmosphere as an intermediate in the oxidation of methane.^{18,191,765,821,1299} Levy⁷⁶⁵ calculated a steady-state daytime concentration of 2 ppb. These predictions are generally confirmed by the few aldehyde measurements that have been made in remote areas. Lodge and Pate⁷⁷⁵ and Fischer *et al.*⁴⁰² measured aldehyde concentrations between 1 and 10 ppb in the jungles of Panama and in Antarctica. Although their method measured total aldehydes, it seems reasonable to assume that formaldehyde was the major, if not the only, aldehyde present. Thus, there is some evidence that formaldehyde is a natural constituent of the atmosphere at a few parts per billion.

The source of aldehyde data for populated areas is the U.S. National Air Surveillance Networks (NASN), which measured total aldehydes on an experimental basis in 1967. Insufficient data were obtained from this pilot study, however, to permit the computation of annual averages. The study was discontinued after 1967. The average estimated concentra-

tions at 30 urban sites ranged from less than 0.01 to 0.06 ppm; the average daily maximal concentrations ranged from 0.01 to 0.13 ppm.¹²² Stahl¹¹⁴³ has compiled atmospheric aldehyde data for the years before 1967. Some indication of the composition of atmospheric aldehydes can be obtained from total aldehyde, formaldehyde, and acrolein measurements made in the Los Angeles area.^{1014,1092,1093} Formaldehyde was the predominant aldehyde, accounting for over 50% of the total, whereas acrolein accounted for only about 5%. Formaldehyde has also been measured in the air of Tokyo, Japan.¹³⁴⁹

There are few atmospheric measurements of oxygenates other than aldehydes, primarily because suitable analytic methods are lacking. However, Bellar and Sigsby⁹² have qualitatively identified methyl alcohol, acetaldehyde, and acetone in ambient air near motor-vehicle traffic.