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Medical and Biologic Effects of Environmental Pollutants

AP 42  
1.3

# 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

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# 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.<sup>211,373,878,949,1186,1227</sup> 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 estimate<sup>878</sup> 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.<sup>211</sup> 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 |
|---------------|---|------------|-----------------|-----------|
|               | Mobile                                  | Stationary | Natural Sources |           |
| United States | 17.6                                    | 13.9       | 72              | 949       |
|               | 12 <sup>a</sup>                         | 7          | —               | 1186      |
|               | 16.6                                    | 15.4       | —               | 1227      |
|               | 19.8                                    | 17.6       | —               | 211       |
|               | 13.8                                    | —          | —               | 373       |
|               | —                                       | 25.4       | —               | 878       |
|               | World                                   | 34         | 54              | 1026      |

<sup>a</sup>Automobiles 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.<sup>128</sup> Total hydrocarbon emission is expected to continue to decline into the 1980's,<sup>128,373</sup> 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.<sup>373</sup> 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<sup>a</sup>

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

<sup>a</sup>Data from U.S. Environmental Protection Agency,<sup>211</sup> except as noted.<sup>b</sup>Derived from Robinson and Robbins,<sup>102</sup> assuming U.S. methane emission per square mile to be half world rate.<sup>c</sup>Derived from Rasmussen and Went,<sup>100</sup> assuming terpene emission to be uniformly distributed over forested lands of the world.

and 20% from carburetor and fuel tank evaporation.<sup>1186</sup> 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.<sup>1287</sup> A California Motor Vehicle Pollution Control Board (MVPCB) survey of 200 pre-1966 cars showed an average concentration of 828 ppm.<sup>183</sup> A later survey of 583 1966 models with first-generation controls showed an average concentration of 290 ppm.<sup>165</sup> 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.<sup>182</sup> Differences in auto emission have been shown for different altitudes and for cars of different engine size.<sup>730</sup>

The development of gas-chromatographic procedures to measure individual hydrocarbons has greatly increased our understanding of the nature of exhaust gas.<sup>317,541,598,624,825,955</sup> 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 (C<sub>4</sub>) olefins, and sometimes propadiene and

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

| Source           | Estimated Hydrocarbon Emission, million tons/year |             |             |             |            |            |            |
|------------------|---|-------------|-------------|-------------|------------|------------|------------|
|                  | Projected Estimates                               |             |             |             |            |            |            |
|                  | 1955  | 1960        | 1965        | 1970        | 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        |
| <b>TOTAL</b>     | <b>12.1</b>                                       | <b>14.4</b> | <b>15.6</b> | <b>13.8</b> | <b>8.4</b> | <b>4.5</b> | <b>2.9</b> |

<sup>a</sup>Derived from *Environmental Conservation: The Oil and Gas Industries*, Vol. 1. National Petroleum Council, June 1971.<sup>373</sup>

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.<sup>622,874,955</sup> 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. Fleming<sup>412</sup> used blends of isoctane, 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 Biggers<sup>926</sup> used blends of toluene, isoctane, 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.<sup>927</sup> Daniel<sup>282</sup> 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.<sup>321,322,874</sup> 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.*<sup>325</sup> 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.*<sup>1312</sup> concluded that aromatic exhaust emission is linearly related to the aromatic content of the fuel. Similarly, Neligan *et al.*<sup>913</sup> concluded that

TABLE 2-4 Predominant Hydrocarbons in Auto Exhaust

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

<sup>a</sup>Data from Papa.<sup>83</sup><sup>b</sup>Data from Morris and Dishart.<sup>874</sup><sup>c</sup>Data from Jackson.<sup>622</sup><sup>d</sup>Combustion products.<sup>e</sup>Includes 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.<sup>174,195,197,316,318,349,351,841,1084,1164,1165,1178</sup>

Jackson<sup>622</sup> 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<sup>926,927</sup> and Daniel<sup>282</sup> 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.<sup>324,414,447,509,759,951</sup> 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,<sup>759</sup> TEL does not affect the composition of exhaust hydrocarbons.<sup>414</sup>

Some emission controls, however, do affect exhaust hydrocarbon composition. Morris and Dishart<sup>874</sup> 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 C<sub>1</sub> and C<sub>2</sub> hydrocarbons and the near absence of fuel components in the exhaust of the thermal-reactor car. Adams *et al.*<sup>10</sup> 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. Weaver<sup>1293</sup> reported that catalytic reactors selectively oxidize the olefins and aromatics in exhaust, but that the selectivity diminishes with catalyst age. Nebel and Bishop<sup>907</sup> also reported that catalytic reactors may be selective and that methane and ethylene are the most difficult hydrocarbons to oxidize. Jackson<sup>622</sup> found that an engine-modification emission<sup>622</sup> 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<sup>361,364,412</sup> and total aldehyde<sup>364,447,574,741,1164,1293</sup> concentrations in auto exhaust with sensitive chemical tests.<sup>233,685,954,1070</sup> A few investigators have measured benzaldehyde<sup>574,926,927</sup> and phenol,<sup>574</sup> still others have qualitatively identified various aldehydes.<sup>76,365</sup> However, a reasonably complete quantitative analysis of exhaust aldehydes has not been possible until recently, when sophisticated gas-chromatographic techniques were developed.<sup>92,432,934,1255,1342</sup> 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 % |                           |                                       |      | Fracchia <i>et al.</i> <sup>432a</sup> |
|------------------------------|--|---------------------------|---------------------------------------|------|--|
|                              | Wiggs <i>et al.</i> <sup>1312a</sup>       | Oberdorfer <sup>634</sup> | Wodkowsky and Weaver <sup>1342a</sup> |      |  |
| Formaldehyde                 | 66.7                                       | 72.5                      | 59.9                                  | 69.3 | 72.9                                   |
| Acetaldehyde                 | 9.3  | 8.7                       | 14.3                                  | 7.5  | 8.5                                    |
| Propionaldehyde <sup>b</sup> | 15.7                                       | —                         | 0.4                                   | 0.7  | { 6.4                                  |
| Acrolein                     | —  | —                         | 9.8                                   | 2.6  |  |
| Butyraldehydes               | { 3.2                                      | 4.3                       | 0.4                                   | 3.0  | 1.0                                    |
| Crotonaldehyde               | —  | —                         | 0.4                                   | 1.4  | 1.7                                    |
| Valeraldehydes               | —  | —                         | 0.4                                   | —    | 0.4                                    |
| Benzaldehyde                 | 3.2  | 7.0                       | 8.5                                   | 3.3  | —                                      |
| Toluinaldehydes              | 1.9  | 7.2                       | —                                     | 5.9  | 4.3                                    |
| Other                        | —  | 0.3                       | 2.7                                   | 5.2  | —                                      |
| <b>TOTAL</b>                 | 100  | 100                       | 100                                   | 100  | 100                                    |

<sup>a</sup>Exhausts from two different gasolines.<sup>b</sup>Also 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.<sup>1095,1096</sup> 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.*<sup>1090</sup> reported finding mostly propane—plus small amounts of methane, ethane, ethylene, acetylene, and propylene and traces of C<sub>4</sub> hydrocarbons—in the exhaust from automobiles or lift trucks burning LPG. Fleming and Allsup<sup>413</sup> found mostly methane and smaller amounts of other (up to C<sub>4</sub>) 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.<sup>352</sup> The exhaust from Synthane—which was about 10% hydrogen, 88% methane, and less than 0.5% ethane—contained noticeably less C<sub>2</sub> and C<sub>3</sub> 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,<sup>914</sup> 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 C<sub>4</sub> and C<sub>5</sub> 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.<sup>299,348,351,597,623,826,887,1178,1262,1303</sup> Some representative analyses of evaporative emission samples are summarized in Table 2-6. They are not complete analyses, covering only the C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> paraffins, the C<sub>4</sub> and C<sub>5</sub> olefins, and the C<sub>6</sub> and C<sub>7</sub> 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 <sup>1944</sup>                              | Caplan <sup>1944</sup> | Muller<br><i>et al.</i> <sup>1949</sup> | Jackson and<br>Everett <sup>1950</sup> | McEvoy <sup>1950</sup> |
| <b>Paraffins</b>                          |   |                        |   |  |                        |
| <i>n</i> -Butane                          | 11.9  | 9.1                    | 10.5                                    | 23.0                                   | 16.5                   |
| Isobutane                                 | 0.2   | 0.1                    | 0.6                                     | 0.2                                    | 6.5                    |
| <i>n</i> -Pentane                         | 2.0   | 2.0                    | 9.9                                     | 1.5                                    | 7.2                    |
| Isopentane                                | 45.3  | 40.9                   | 17.8                                    | 36.0                                   | 23.2                   |
| <i>n</i> -Hexane                          | 0.2   | 0.3                    | —                                       | 8.7                                    | 0.7                    |
| 2,2-Dimethylbutane                        | 0.1   | 0.0                    | —                                       | —                                      | 0.4                    |
| 2,3-Dimethylbutane                        | 3.0   | 3.2                    | —                                       | 3.7                                    | —                      |
| 2-Methylpentane                           | 2.3   | 2.4                    | —                                       | —                                      | 1.6                    |
| 3-Methylpentane                           | 1.2   | 1.3                    | —                                       | —                                      | 1.6                    |
| <b>Olefins</b>                            |   |                        |   |  |                        |
| 1-Butene                                  | 0.3   | 0.2                    | 0                                       | 4.6                                    | —                      |
| <i>trans</i> -2-Butene                    | 0.5   | 0.5                    | 0.3                                     | 4.8                                    | —                      |
| <i>cis</i> -2-Butene                      | 0.3   | 0.2                    | 0.2                                     | 4.2                                    | 3.2                    |
| <i>cis</i> -, <i>trans</i> -<br>2-Pentene | 1.4   | 1.3                    | 2.7                                     | 1.0                                    | 1.5                    |
| 1-Pentene                                 | 0.3   | 0.3                    | 0.7                                     | —                                      | 5.6                    |
| 2-Methyl-1-butene                         | 0.7   | 0.6                    | 1.7                                     | 0.8                                    | 4.3                    |
| 3-Methyl-1-butene                         | 0.1   | 0.1                    | 0.2                                     | 0.8                                    | —                      |
| 2-Methyl-2-butene                         | 1.6   | 1.6                    | 3.9                                     | 1.2                                    | 7.3                    |
| <b>Aromatics</b>                          |   |                        |   |  |                        |
| Benzene                                   | 0.5   | 0.5                    | 1.8                                     | 0.1                                    | 0.4                    |
| Toluene                                   | 0.5   | 0.8                    | 2.4                                     | —                                      | 0.9                    |
| <b>TOTAL</b>                              | <b>72.4</b>                                       | <b>65.4</b>            | <b>68.2</b>                             | <b>77.1</b>                            | <b>92.7</b>            |
|   |   |                        |   |  | <b>91.3</b>            |
|   |   |                        |   |  | <b>95.1</b>            |

<sup>a</sup>Same gasoline at 163 and 177 F.

<sup>b</sup>Calculated values for 140 F.

<sup>c</sup>Different 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's<sup>623</sup> 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.<sup>97</sup> 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.<sup>961,1033,1114</sup>

Possible contamination of blowby from lubricating oil was eliminated in a unique study by Domke, Lindley, and Sechrist.<sup>326</sup> 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 isoctane). They also found oxygenates at about 5 ppm in the blowby, of which only formaldehyde, acetaldehyde, methanol, and ethanol could be identified. Payne and Sigsworth<sup>985</sup> 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 Scanlin<sup>534</sup> 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.*<sup>1254</sup> 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.<sup>251</sup> 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.<sup>770,830</sup>

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  $C_{24}$ .<sup>599,600,769,770,830,848,1009,1263</sup> 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.<sup>769,1009</sup> 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.<sup>599</sup> Linnell and Scott<sup>770</sup> estimated that the light hydrocarbons constitute 10–25% of the total on a molar basis. Hurn and Seizinger<sup>600</sup> reported that the

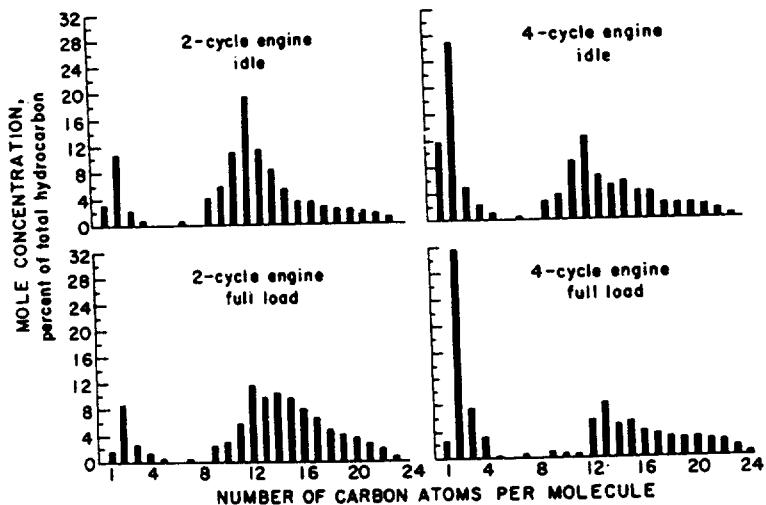


FIGURE 2-1 Distribution of hydrocarbons in diesel exhaust gas. (Reprinted with permission from Hurn and Marshall.<sup>599</sup>)

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.<sup>334,763,1141</sup> Caragay *et al.*<sup>763</sup> reported finding the following hydrocarbon classes in the "oily-kerosene" fraction of diesel-exhaust condensate: indans, tetralins, alkylbenzenes, naphthalenes, indenes, acenaphthenes, and benzothiophenes. Similar types of hydrocarbons were found by Dravnieks *et al.*<sup>334</sup> in a related odor study. Skala *et al.*<sup>1120</sup> 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.<sup>64,360,600,769,770,865,1009,1038,1144</sup> Vogh<sup>1256</sup> 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<sup>360,848,1038</sup> 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.<sup>211</sup> 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

### Sources of Atmospheric Hydrocarbon

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.<sup>215</sup> 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

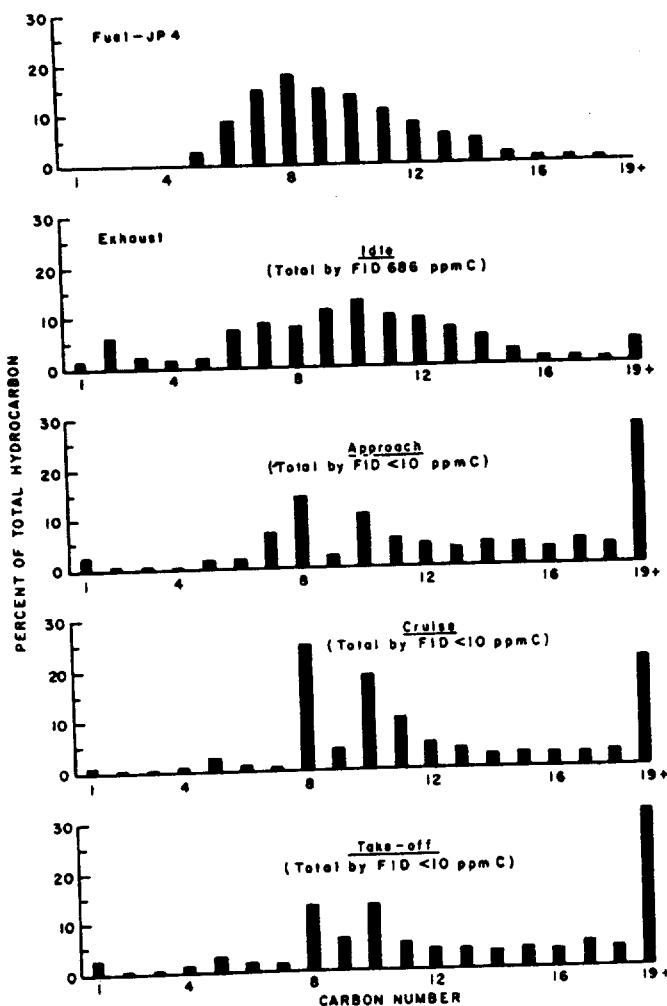


FIGURE 2-2 Distribution of hydrocarbons in jet-aircraft engine exhaust. (Reprinted with permission from Chase and Hurn.<sup>215</sup>)

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.*<sup>250</sup> 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 Rose<sup>714</sup> 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 distribution<sup>215</sup> (Figure 2-2).

Formaldehyde and total aldehyde concentrations in turbine exhaust have been measured,<sup>215,250,714,785</sup> but no detailed aldehyde analyses have been reported. What little information on aldehyde composition is available is conflicting. In one study involving aircraft turbines,<sup>785</sup> 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's<sup>714</sup> 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.<sup>211</sup> 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.<sup>211</sup> 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.<sup>211</sup> 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.*<sup>327</sup> 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 Hurn<sup>350</sup> 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.<sup>350</sup>

#### **STATIONARY MAN-MADE SOURCES OF HYDROCARBON EMISSION**

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

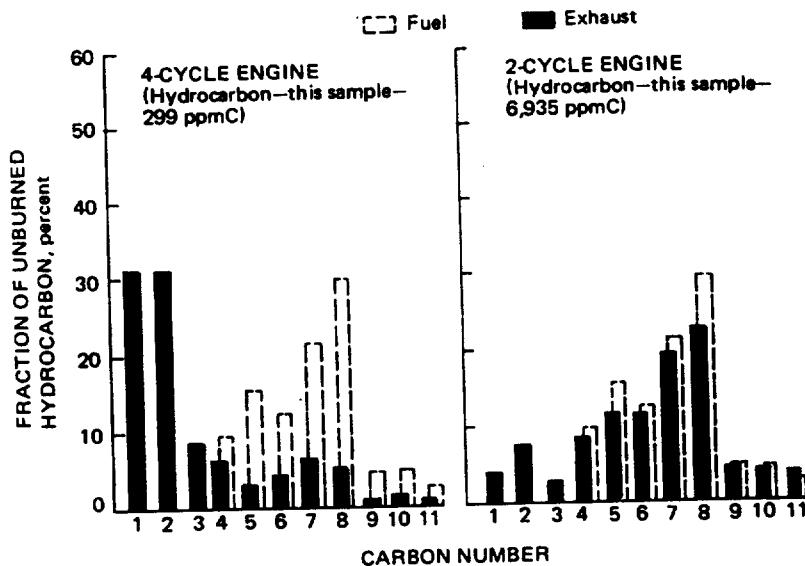


FIGURE 2-3 Distribution of hydrocarbons in exhaust from small utility engines.  
(Reprinted with permission from Eccleston and Hurn.<sup>350</sup>)

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  $43.4 \times 10^{15}$  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<sup>a</sup>

| Stationary Source                 | Total Organic Emission,<br>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  |
| <b>TOTAL</b>                      | <b>25.4-26.0</b>                             |

<sup>a</sup>Data from MSA Research Corporation.<sup>478</sup>

wood, LPG, and waste gases.<sup>1229</sup> 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<sup>267,268,458</sup> 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.*<sup>521</sup> 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.*<sup>268</sup> 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 report<sup>1229</sup> 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.*<sup>584</sup> 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.*<sup>217</sup> 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.*<sup>521</sup> 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 George<sup>218</sup> 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.*<sup>1277</sup> 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 survey<sup>1229</sup> estimated the hydrocarbon emission from oil-fired equipment to be about 0.5 lb/ton. Magill and Benolie<sup>1800</sup> 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, but it does produce some organic emission. Chass *et al.*<sup>217</sup> 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.*<sup>217</sup> 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.*<sup>521</sup> 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 George<sup>218</sup> varied from near zero to about 3 lb/ton and averaged 0.5 lb/ton. The consensus values reported by the EPA<sup>1229</sup> 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 Benolie<sup>1800</sup> 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. Hall<sup>510</sup> 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 report<sup>1229</sup> 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.*<sup>441</sup> 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 C<sub>4</sub> and C<sub>5</sub> olefins were also found. Several other investigators have reported a variety of oxygenated organics in wood smoke. Jahnson<sup>629</sup> 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 Sigsby<sup>92</sup> 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 Kap-salopoulou<sup>578</sup> 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 Feldstein<sup>760</sup> 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.<sup>244</sup> The recent development of a continuous coking process may greatly reduce coke-oven emission in the future.<sup>74</sup> The phasing-out of old beehive ovens, from which no attempt is even made to collect the coal tars, will also alleviate the problem.<sup>135</sup>

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.<sup>373</sup> The more volatile C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> 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. Fawcett<sup>391</sup> inventoried the emission from a phthalic anhydride plant and found that it included phthalic anhydride, maleic anhydride, naphthoquinone, benzoic acid, and various aldehydes. Lur'e<sup>792</sup> reported that butadiene, isobutylene, styrene, benzene, and ethyl alcohol vapors are discharged from a synthetic rubber plant. Walter and Amberg<sup>1274</sup> reported that  $\alpha$ -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 Feldstein<sup>761</sup> 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 C<sub>3</sub> and C<sub>4</sub> 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.<sup>1229</sup>

### 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.<sup>1229</sup> 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 Feldstein<sup>1216</sup> 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 C<sub>2</sub>–6 hydrocarbons were found with the less efficient incinerator. Stenburg and co-workers<sup>1150,1151</sup> 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.<sup>1196</sup> Kaiser *et al.*<sup>638</sup> 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.*<sup>1352</sup> 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 Benoliel<sup>1800</sup> 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 Sigsby<sup>92</sup> 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 Kemnitz<sup>459</sup> 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 report<sup>1229</sup> 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. Kreichelt<sup>725</sup> 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.*<sup>441</sup> 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.*<sup>392</sup> for the open burning of land-clearing debris.

Stephens and Burleson<sup>1155</sup> 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.<sup>802</sup> Carbon monoxide and sulfur dioxide are the major gases emitted,<sup>177</sup> 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.<sup>392</sup>

Darley *et al.*<sup>284</sup> 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 C<sub>5</sub>, 1 lb of paraffins below C<sub>6</sub>, and 7 lb of heavier hydrocarbons. Boubel *et al.*<sup>126</sup> reported similar values for the burning of grass and straw in the same apparatus. Gerstle and Kemnitz<sup>459</sup> reported a considerably higher hydrocarbon emission (30 lb/ton) for the open burning of landscape refuse. Feldstein *et al.*<sup>392</sup> 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 C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> 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<sup>a</sup>

| 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                  | <sup>b</sup>                        |
| Chloroethylene          | <sup>b</sup>                        |
| Carbon tetrachloride    | <sup>b</sup>                        |
| Pinene                  | <sup>b</sup>                        |
| Cyclohexyl alcohol      | <sup>b</sup>                        |
| Cyclohexanone           | <sup>b</sup>                        |
| Ethylbenzene            | <sup>b</sup>                        |
| Isobutyl alcohol        | <sup>b</sup>                        |
| Chloromethane           | <sup>b</sup>                        |
| <i>n</i> -Butylacetate  | <sup>b</sup>                        |
| <b>TOTAL</b>            | <b>7,137,500+</b>                   |

<sup>a</sup>Data from MSA Research Corporation.<sup>878</sup><sup>b</sup>Less 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.<sup>858</sup> 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.<sup>176,346</sup> Koyama<sup>722</sup> has estimated the global production of methane as  $2.7 \times 10^{14}$  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's<sup>602</sup> 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. Ehnhalt<sup>355</sup> pointed out that Koyama did not include methane production from swamps, and Robinson and Robbins<sup>1026</sup> 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  $14.5 \times 10^{14}$  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.<sup>18</sup> However, Ehnhalt<sup>355</sup> 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,  $\alpha$ -pinene, and a variety of other terpenes. Ethylene production by plants was noted as early as 1910<sup>254</sup> and rediscovered in 1932.<sup>369</sup> Burg<sup>171</sup> 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.*<sup>110</sup> and in cotton plants by Hall *et al.*<sup>512</sup> 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.<sup>171,172</sup> Ethylene is a plant hormone that is continuously produced in plants and has been linked to fruit ripening.<sup>1,170,265</sup> The ripening of fruits,<sup>110</sup> the fading of flowers,<sup>12</sup> and injury from air pollutants<sup>257</sup> have all been shown to be associated with increased ethylene production. Abeles *et al.*<sup>2</sup> 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 Yakobson<sup>617</sup> 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.

Went<sup>1301</sup> 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, Rasmussen<sup>999</sup> and Rasmussen and Went<sup>1008</sup> reported ambient concentrations of plant volatiles (such as isoprene,  $\alpha$ - and  $\beta$ -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,<sup>1000</sup> it is definite that there are large sources of natural, organic emission in the biosphere. Furthermore, Sanadze and Dolidze<sup>1060</sup> and Rasmussen<sup>996</sup> have identified isoprene as a natural volatile plant product and studied the physiology of isoprene emission.<sup>1007,1059</sup> Table 2-10 lists the various volatile plant products identified by Rasmussen.<sup>999</sup>

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<sup>a</sup>

|                  |                   |
|------------------|-------------------|
| $\alpha$ -Pinene | <i>n</i> -Heptane |
| $\beta$ -Pinene  | Isoprene          |
| Myrcene          | $\alpha$ -Ionone  |
| D-Limonene       | $\beta$ -Ionone   |
| Santene          | $\alpha$ -Irene   |
| Camphene         |                   |

<sup>a</sup>Identified by Rasmussen.<sup>200</sup>

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

Studies of odorous compounds in natural waters<sup>635</sup> 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.<sup>843</sup> Organic nitrogen compounds are also well-known odorous natural products.<sup>173,1153,1176</sup> Wilson *et al.*<sup>1327</sup> 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.*<sup>210</sup> 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;<sup>1314</sup> and methane, ethane, ethylene, propane, propylene, and *n*-butane have been identified as products of the thermal treatment of marine mud slurries.<sup>885</sup>

Man is also a source of volatile organics. Body odors have been studied by the U.S. armed forces.<sup>241,935,1202</sup> 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's<sup>1026</sup> 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's<sup>1008</sup> 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.<sup>2</sup> 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.<sup>1230</sup> 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 1 to 17 ppm. Total hydrocarbons are also routinely measured at over 100 sites in the California air monitoring network.<sup>184</sup> Total hydrocarbon analyses have also been made for shorter periods in specific studies.<sup>32,336,372,1092,1093</sup>

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.<sup>698,948</sup> One method,<sup>948</sup> which discriminates between methane and nonmethane hydrocarbons, has been used<sup>1082,1227</sup> 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 the *Air Quality Criteria for Hydrocarbons*.<sup>1227</sup> 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.<sup>1082</sup>

### Methane

Methane was discovered in the telluric spectrum by Migeotte in 1948.<sup>68</sup> Later spectroscopic measurements established the average methane concentration of the atmosphere to be about 1.5 ppm.<sup>398,475,476</sup> 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.<sup>69,355</sup> Bainbridge and Heidt<sup>69</sup> measured a decrease in the methane concentration at the tropopause, indicating that the stratosphere is a sink for methane. Scholtz *et al.*<sup>1077</sup> 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 Burleson<sup>1155</sup> measured 1.39 ppm in southern California mountain areas during the time hot, dry Santa Ana winds were blowing. Cavanagh *et al.*<sup>210</sup> found an average methane concentration of 1.59 ppm at Point Barrow, Alaska. Swinnerton *et al.*<sup>1180,1181</sup> 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).<sup>68</sup> However, Shearer<sup>1107</sup> has reported measurements at a rural site averaging 0.89 ppm. In inhabited areas, methane concentrations are higher.<sup>32</sup>

### Other Individual Hydrocarbons

#### REMOTE LOCATIONS

There have been few measurements of individual hydrocarbons in remote locations. Cavanagh *et al.*<sup>210</sup> 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'Angio<sup>1215</sup> showed that there is a complex mixture of organic vapors in remote locations. Rasmussen and Went<sup>1008</sup> have identified isoprene,  $\alpha$ -pinene,  $\beta$ -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. Rasmussen<sup>906</sup> and Rasmussen and Hutton<sup>1004</sup> have also analyzed volatile organics in the ambient air in the humid tropics. Stephens and Burleson<sup>1155</sup> 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. Neligan<sup>911</sup> analyzed 16 early-morning samples collected in central Los Angeles for C<sub>2-4</sub> 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 Bellar<sup>19</sup> measured methane, C<sub>2-5</sub> hydrocarbons, and C<sub>6-8</sub> 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 Leonard<sup>912</sup> reported the concentrations of a dozen C<sub>6-10</sub> 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<sub>1-7</sub> hydrocarbons in Los Angeles are summarized in *Air Quality Criteria for Hydrocarbons*.<sup>1227</sup> Stephens and Burleson<sup>1154</sup> analyzed the atmosphere in Riverside, California, for C<sub>1-6</sub> 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.*<sup>1156</sup> presented results of C<sub>1-7</sub> 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.*<sup>779</sup> measured methane, total hydrocarbons, and individual C<sub>6-10</sub> 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.*<sup>483</sup> followed the diurnal patterns of individual C<sub>2-5</sub> hydrocarbons in downtown Los Angeles and Azusa in the fall of 1967. Altshuller *et al.*<sup>31</sup> measured the full range of individual C<sub>1-10</sub> 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. Williams<sup>1316</sup> has identified over 30 hydrocarbons on the University of British Columbia campus, and some measurements from Japan are available.<sup>941</sup> Grob and Grob<sup>497</sup> have qualitatively identified 108 C<sub>6-20</sub> organics in the air of Zurich, Switzerland. Scott

TABLE 2-11 Average and Highest Concentrations of Various Aromatic Hydrocarbons in Los Angeles<sup>a</sup>

| 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,<br>isobutylbenzene, and <i>sec</i> -<br>butylbenzene | 9                              | 30         |
| <i>tert</i> -Butylbenzene  | 2                              | 6          |
| <b>TOTAL</b>   | <b>106</b>                     | <b>330</b> |

<sup>a</sup>Data from Lonneman *et al.*<sup>779</sup>

TABLE 2-12 Aliphatic Hydrocarbon and Alkylbenzene Concentrations in  
Downtown Los Angeles (DLA) and Azusa<sup>a</sup>

| Hydrocarbon   | Concentration, ppb (by volume)                |       |                 |       |   |       |
|---|---|-------|-----------------|-------|---|-------|
|   | Concentration below Which 10% of Values Occur |       | Overall Average |       | Concentration Exceeded by 10% of Values |       |
|   | DLA   | Azusa | DLA             | Azusa | DLA                                     | Azusa |
| <b>Aliphatic hydrocarbons</b>                         |   |       |                 |       |   |       |
| 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     |
| <b>Alkylbenzenes</b>                                  |   |       |                 |       |   |       |
| 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 <sub>6</sub> and C <sub>7</sub> alkylbenzenes | 3   | 1     | 12              | 6     | 23                                      | 13    |

<sup>a</sup>Data from Shiebler et al.

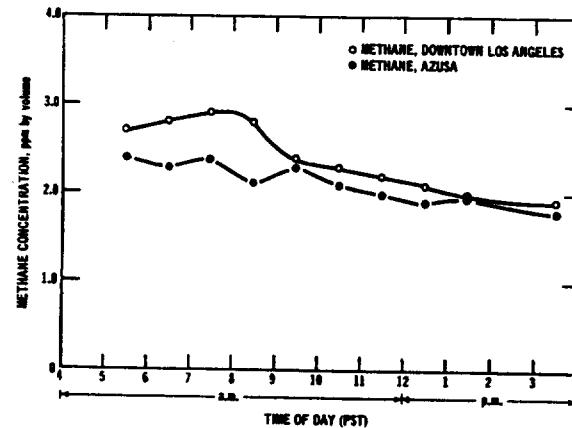


FIGURE 2-4 Diurnal variations in average hourly methane concentrations in downtown Los Angeles and Azusa. (Figures 2-4 through 2-7 reprinted with permission from Altshuller *et al.*<sup>31</sup>)

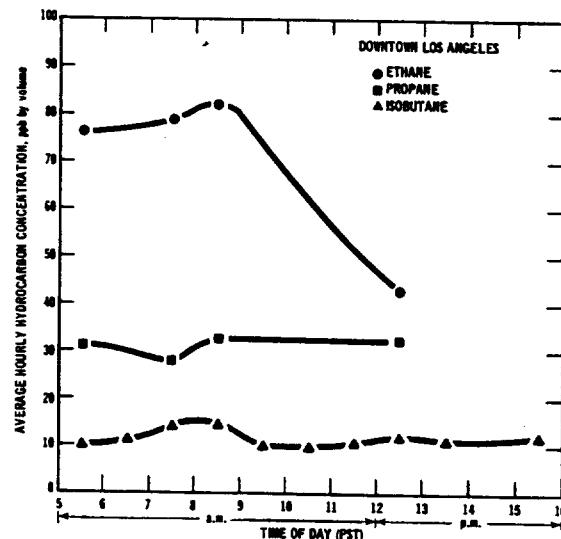


FIGURE 2-5 Diurnal variations in average hourly concentrations of ethane, propane, and isobutane in downtown Los Angeles.

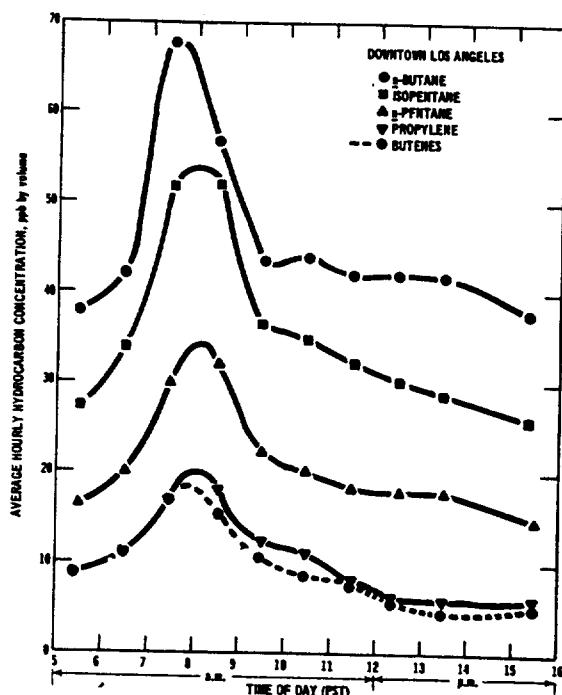


FIGURE 2-6 Diurnal variations in average hourly concentrations of *n*-butane, isopentane, *n*-pentane, propylene, and butenes in downtown Los Angeles.

Research Laboratories<sup>1092,1093</sup> has measured individual C<sub>1-10</sub> hydrocarbons at various sites in New York, as well as Los Angeles, but has not analyzed the results in detail. Lonneman and Kopczynski<sup>780</sup> have determined atmospheric hydrocarbon compositions in Los Angeles, Denver, and New York. Stephens and Burleson<sup>1155</sup> 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<sub>3-5</sub> paraffins that resemble gasoline vapor. Samples taken in industrial areas and near brush fire showed distinct differences in composition.

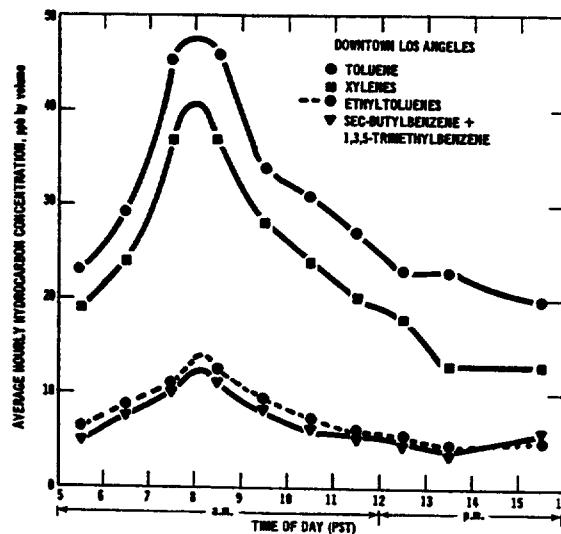


FIGURE 2-7 Diurnal variations in average hourly concentrations of toluene, xylene, ethyltoluene, *sec*-butylbenzene, and 1,3,5-trimethylbenzene in downtown Los Angeles.

### 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.<sup>18,191,765,821,1299</sup> Levy<sup>765</sup> 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 Pate<sup>775</sup> and Fischer *et al.*<sup>402</sup> 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.<sup>11</sup> Stahl<sup>11,43</sup> 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.<sup>1014,1092,1093</sup> 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.<sup>1349</sup>

There are few atmospheric measurements of oxygenates other than aldehydes, primarily because suitable analytic methods are lacking. However, Bellar and Sigsby<sup>92</sup> have qualitatively identified methyl alcohol, acetaldehyde, and acetone in ambient air near motor-vehicle traffic.