Biologic Effects of Atmospheric Pollutants

PARTICULATE POLYCYCLIC ORGANIC MATTER

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Sources of Polycyclic Organic Matter

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

MECHANISM OF POM FORMATION

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

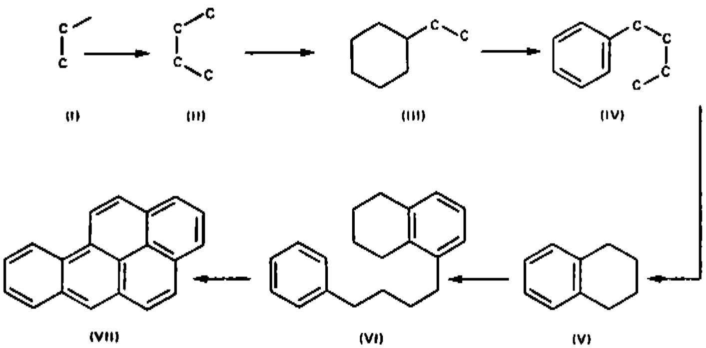

FIGURE 3-1. Mechanism of benzo[a]pyrene formation. (After Badger.[21])

tion of many variables, not the least of which is the presence of a chemically reducing atmosphere, common in the center of flames. In these conditions, radical chain propagation is enhanced, allowing the buildup of a complex POM molecule, such as benzo[a]pyrene. It is important to note that, although methane itself can lead to POM,[102] the formation of these large molecules is favored by the presence of higher-molecular-weight radicals and molecules in the fuel. Obviously, it is unnecessary to break the starting material down completely to a two-carbon radical in order to form benzo[a]pyrene. Any component of the combustion reaction that can contribute intermediate pyrolysis products of the structure required for benzo[a]pyrene synthesis would be expected to lead to increased yields of benzo[a]pyrene. Thus, Badger and Spotswood[22] have shown that in the pyrolysis of alkylbenzenes, including *n*-butylbenzene, enhanced benzo[a]pyrene formation is due primarily to increased concentrations of intermediate structures of types III, IV, and V (Figure 3-1).

Badger also showed conclusively that specific aromatic and diolefinic compounds serve as precursors for other polycyclic organic products. The mechanism in Figure 3-1 is a pathway to benzo[a]pyrene formation, but similar routes could be devised, with somewhat different intermediates, to lead to most of the known POM produced in combustion processes. Badger's work, with its reliance on calculated C—C and C—H bond energies to predict favored pathways and the experimental confirmation of these steps with radioisotopic labeling, provides a clear-cut mechanism for POM formation in the combustion process.

As pointed out by Hoffmann and Wynder,[388] the use of nitrogen atmospheres in Badger's experiments has been criticized for its lack of relevance to the actual combustion of organic molecules. Nonetheless, the conditions are similar to those of the oxygen-deficient environment in flames, and the data are in good qualitative agreement with observed POM combustion products.

NONTECHNOLOGIC SOURCES OF POM

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

TECHNOLOGIC SOURCES OF POM

Large quantities of POM are generated in the vast number of technologic activities that prevail in our society. The contribution of any particular source depends on many factors, including geography, urbanization, and climate; thus, nationwide emission inventories can be misleading. Olsen and Haynes[572] have summarized the available data.

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

Transportation Sources

GASOLINE-POWERED VEHICLES

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

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

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

As will be apparent in the following discussion, most efforts have been directed at estimating the automobile contribution, with less emphasis on trucks and buses. One study[343] is available on benzo[a]-pyrene emission from gasoline-powered trucks; it shows a wide variation in emission factors, from 70 to 1,500 μg/gal.

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

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

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

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

[a] Data from Hangebrauck *et al.*[343]
[b] Data from Begeman and Colucci.[42]

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

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

The effect of oxidizing and reducing atmospheres on incomplete combustion and POM formation is important in estimating vehicular emissions. Recent data[42] indicate that benzo[a]pyrene production at an air : fuel ratio of 10 : 1 is 30 times higher than at a ratio of 14 : 1.

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

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

[a] Data from Hangebrauck *et al.*[343] and Begeman and Colucci.[42]
[b] Data from Gross.[316]
[c] Data from Begeman and Colucci[42] and Gross.[316]
[d] Estimated from Hoffman *et al.*[382] and Faust and Sterba.[264]

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

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

As vehicles accumulate mileage in normal consumer use, deposits form in the combustion chamber. The nature and composition of these deposits have been shown to influence total hydrocarbon exhaust emissions; as mileage is accumulated, total emissions increase until a stabilized condition is reached at several thousand miles. Gross[316] has shown that the condition of the deposit exerts a significant effect on POM emission levels; the POM emission levels are about twice as high in a vehicle with stabilized deposits from operation with leaded fuel as in the same vehicle with stabilized deposits from operation with unleaded fuel. Another study[382] sees no effect of combustion-chamber deposits on POM emissions.

Effects of Fuel Composition The presence in fuel of precursors of radical intermediates would be expected to facilitate POM formation; i.e., the pyrosynthetic path would be shortened. Conjugated dienes and aromatics in the fuel should provide the maximal enhancement of fuel-related POM formation. The literature does point to fuel composition as having an important effect, but simple judgments as to the advantages and disadvantages of compositional modifications are confounded by the number of variables in the vehicle-fuel-exhaust-system relation.

Early research on the effects of fuel components on POM emissions pointed clearly to increased aromatic content of fuel as a cause of higher POM exhaust emissions. For example, Boubel and Ripperton[79] showed that a benzene-fueled engine produced 10–30 times more POM than an engine using *n*-hexane, cyclohexane, or hexene-1. Hoffmann and Wynder[390] reported that higher emissions of benzo[a]-pyrene and benz[a]anthracene resulted from blends of 50% *o*-xylene and 50% benzene than from gasoline, pure paraffins, and pure olefins. Hoffman *et al.*[382] diluted unleaded, high-aromatic gasoline with pure isooctane and achieved dramatic reduction in benzo[a]pyrene emissions. Begeman[40] reported higher benzo[a]pyrene emissions with test fuels containing high POM and aromatic concentrations than with commercial gasolines. Most of these studies have been carried out with synthetic blends, as opposed to gasolines of conventional compositions. To assess accurately the role of fuel in the question of atmospheric POM, it is imperative to use realistic compositions in consumer driving conditions.

Gross[316] reports that, when full-boiling-range fuels were used in well-maintained vehicles operated under federal requirements for testing 1968–1971 vehicles, POM emissions increased by 36–74% in an uncontrolled vehicle and 8–34% in an emission-controlled vehicle as fuel aromaticity was increased from 12 to 46%.

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

The POM content of gasoline has been shown to affect POM emissions from vehicles. Begeman and Colucci[41] estimate that as much as 36% of the benzo[a]pyrene in the exhaust gas can be attributed to the fuel benzo[a]pyrene content; Gross[316] estimates that 15–30% increases in POM emissions can be obtained when fuel POM is varied between the concentration extremes found in the field. The actual effect was smaller in the controlled vehicle than in the uncontrolled vehicle. These results are consistent with the Badger mechanism outlined previously: High-molecular-weight fuel components and lubricant losses to the combustion chamber will result in higher POM emissions.

DIESEL-FUEL-POWERED VEHICLES

Any critical discussion of the relative contribution of diesel engines to the atmospheric POM concentration must be qualified by the supposition that the vehicle is operated under rated load conditions, i.e., is not overloaded. In normal use, the most objectionable features of diesel operation (soot formation, odor, etc.) are apparent when the engine is overfueled. Begeman and Colucci[42] have determined that a diesel engine, operated on a bus-driving cycle, emitted 62 μg of benzo[a]pyrene per gallon of fuel. Reckner *et al.*[626] showed that POM emissions from a diesel test engine increased with load up to half-load, leveled off, and then dropped sharply at full load. Idle operation resulted in high POM emissions, presumably because of lower combustion-chamber temperatures.

Oil consumption in diesel engines can be somewhat higher than in spark-ignited engines. However, Begeman and Colucci[42] point out that, because diesel combustion chambers do not operate under vacuum, lubricating oil should not be drawn into the ignition area; thus, POM from this source is probably not significant.

The only published data[626] on the effects of fuel characteristics on diesel POM emissions indicate that fuel aromaticity is not related to exhaust POM levels. The test fuels ranged between 5 and 23% aromatic content, with the fuel POM consisting primarily of pyrene, anthracene, and fluoranthene. There was no detectable benzo[a]-pyrene.

Although the variables discussed above were evaluated in engine-laboratory conditions, it is apparent that actual on-the-road operation of diesel-powered vehicles can result in higher POM emissions, owing to overloading, poor maintenance, and so on. The objectionable features of diesel truck and bus operation, such as smoking and odor, might be associated with higher POM emissions, and additional research in this area should be fruitful.

MISCELLANEOUS TRANSPORTATION SOURCES

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

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

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

EMISSION CONTROL PROCEDURES

The emission control devices on cars since the 1968 models have reduced benzo[a]pyrene emission factors by about 85%, compared with uncontrolled vehicles. This reduction is due to the more efficient combustion associated with "leaner" air–fuel mixtures. It is anticipated that these methods will continue in use until the mid-1970's, when more stringent controls on total emissions will be required. At that time, such devices as catalysts or thermal reactors will probably be required, and the mixture stoichiometry will depend on the particular systems chosen. These devices should result in additional reductions in POM emission, as shown in Table 3-2. Reductions in emission of POM to the atmosphere from automobiles can be projected through the 1980–1990 period, as the older cars are removed from service and a greater proportion of vehicles are equipped with advanced emission control systems. Although current work centers on the effects of control devices, operating conditions, and fuel composition, surveillance of vehicles in normal customer usage, including those in poor operating condition, might support the extrapolations made in this section. The emissions from heavier vehicles (such as gasoline- and diesel-powered trucks and buses) seem significant, but little work has been done on defining the emission factors of these vehicles. Knowledge of these factors is clearly needed. There should also be continued efforts to clarify the effects of fuel composition changes, such as trends toward lead removal from gasoline. Although these factors seem to be less important than the vehicle-emission-control system, close scrutiny of them is nonetheless desirable.

Stationary Sources

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

HEAT AND POWER GENERATION

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

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

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

[a] Data from Hamburg,[336] Hangebrauck *et al.*,[343] Muhich *et al.*,[550] U.S. Department of Agriculture,[764] U.S. Department of Health, Education, and Welfare,[767,774] U.S. Department of the Interior,[777] Wadleigh,[798] and L. McNab (personal communication).

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

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

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

REFUSE BURNING

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

The review by Hangebrauck *et al.*[343] cites benzo[a]pyrene emission factors for municipal and commercial incineration of such wastes as those collected from households, business, and restaurants, as well as for burning of municipal and agricultural refuse and junked automobile parts. Benzo[a]pyrene emissions from these sources vary widely and reflect the importance of efficient combustion in reducing POM emissions. Large (50–250 tons/day) municipal incinerators had benzo[a]pyrene emission factors of 0.1–6 μg/lb of charged refuse, and commercial (3–5 tons/day) incinerators had factors of 50–260 μg/lb. Data show a benzo[a]pyrene emission factor of about 150 μg/lb of charged refuse for open burning of municipal wastes, as well as for grass clippings, leaves, etc. Significantly, the destruction of auto components in test "open-burning" facilities yielded a benzo[a]pyrene emission factor of 1.3×10^4 µg/lb of refuse.[343]

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

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

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

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

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

[b] Data from Muhich *et al.*[550]

[c] Data from Olsen and Haynes.[572]

[d] Data from U.S. Department of Health, Education, and Welfare[774] and Muhich *et al.*[550]

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

[f] Data from U.S. Department of the Interior[777] and Hamburg.[336]

[g] Data from L. McNab (personal communication).

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

INDUSTRIAL ACTIVITIES

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

As can be seen from the data in Table 3-5, the contribution of catalytic cracking processes to the atmospheric POM concentrations is a function of the proportion of units equipped with carbon monoxide waste-heat boilers. The various catalytic cracking units listed in the table represent both the moving-bed catalytic systems [Thermofor (TCC) and Houdriflow (HCC)] and the fluidized-bed system [fluid catalytic cracking (FCC)]. A recent survey[627] suggests that a greater proportion of the units are equipped with carbon monoxide boilers than were so equipped in 1967.[343] The results of the later survey show an annual contribution of 6 tons of benzo[a]pyrene from refinery catalytic cracking operations. The total represents a reduction to about one third of previously published estimates.

Another petroleum-industry process of interest is the air-blowing of asphalt. This procedure is designed to yield materials of higher softening point for roofing applications. The effluent from air-blowing may contain many hydrocarbons, including POM. In the one test of an actual process,[343] however, very little benzo[a]pyrene was found in the benzene-soluble fraction of the particulate matter. The total contribution of asphalt air-blowing is estimated at less than 0.03 ton of benzo[a]pyrene per year.

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

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

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

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

[b] FCC, fluid catalytic cracking; HCC, Houdriflow moving-bed system; TCC, Thermofar moving-bed system.

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

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

Some of the processes considered include coke production in the iron and steel industry; carbon black, coal-tar pitch, and asphalt-hot-road mix processes; and general chemical processes. The analytic procedure used in evaluating all such sources has been to sample the atmosphere in the immediate vicinity of an expected emission source or complex of sources. This necessarily leads to less accurate estimates than direct sampling. Except for coke production, none of the industrial processes considered above contributes significant amounts of benzo[a]pyrene to the total atmospheric concentration. This conclusion is obscured somewhat by the presence of other local emission sources already discussed, such as residential coal-fired furnaces.

There is evidence[711] that high benzo[a]pyrene emissions are associated with the gaseous discharge of coke ovens. In the United States, recent activities of the National Air Sampling Network and the Pennsylvania State Department of Public Health support the belief that iron and steel works do contribute to higher atmospheric benzo[a]-pyrene concentrations in the areas surrounding them. Corresponding studies in areas outside the United States[459,740] lead to similar conclusions. An emission factor, admittedly crude, for benzo[a]pyrene emission from coke effluents has been calculated[711] at 1.8 g/ton of coke. Application of this factor to estimated nationwide coke discharges results in a predicted emission of 192 tons/year.

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

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

INDOOR POM EMISSION

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

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

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

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

One major source of nonindustrial indoor POM pollution is tobacco-smoking.[831] During smoking, the mainstream smoke is inhaled and, in the interval between puffs, the sidestream smoke escapes into the environment. The use of one unfiltered cigarette (85 mm) releases 30–50 mg of "tar," which contains 0.10–0.15 μg of benzo[a]pyrene, 0.20–0.30 μg of pyrene, and 0.25 μg of chrysene. In a medium-size room (40 m^3), three smokers can pollute the air with 2–4 μg of benzo[a]pyrene, 5–8 μg of pyrene, and 6 μg of chrysene per 1,000 m^3 of air. Depending on ventilation and smoking activities, the indoor pollution by cigarette sidestream smoke can be significantly higher; for example, Galůskinová[288] reported 28–144 μg of benzo[a]pyrene per 1,000 m^3 for a beer hall in Prague.

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

EMISSION CONTROL PROCEDURES

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

With regard to refuse burning, more efficient incineration equipment in commercial, industrial, and apartment-building sources would be appropriate. Their relative contribution diminishes in comparison with open burning, especially coal refuse burning and, to a lesser extent, forest and agricultural burning. Coal refuse burning could simply be eliminated by proper attention to refuse accumulation practices, and intentional forest and agricultural burning could be discontinued.

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

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

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

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

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

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

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

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

GENERAL NATURE OF POM EMISSIONS

Individual POM Emissions

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

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

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

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

Area-Concentration Relations

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

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

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

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

[b] Data from Hangebrauck *et al.*[342]

[c] Data from Hangebrauck *et al.*[343]

[d] Data from Falk *et al.*[260]

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

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

In the only other set of determinations of relative source contributions to the atmospheric POM burdens, Colucci and Begeman[153] have calculated that, in Detroit, motor vehicles contribute 5% of the

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

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

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

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

benzo[a]pyrene in the downtown area, 18% of that in the freeway area, and 42% of that in the atmosphere in the suburbs. Similar studies were made in New York City[151] and Los Angeles,[152] but the same types of calculations were not possible. In both cases, the data would permit only correlation techniques, which indicate positive statistical relations of benzo[a]pyrene with both automotive and stationary sources.

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

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

SUMMARY AND RECOMMENDATIONS

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

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

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

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

These data represent nationwide estimates based on extrapolations from individual source emissions. In specific areas, the relative contribution of any given source may differ significantly from that implied by the nationwide figures. For example, the vehicular source may be the major contributor in suburban areas where other major sources are absent. Epidemiologic studies using source inventory data and ambient atmospheric concentrations are required to assess the importance of control measures in both high and low atmospheric POM areas.