

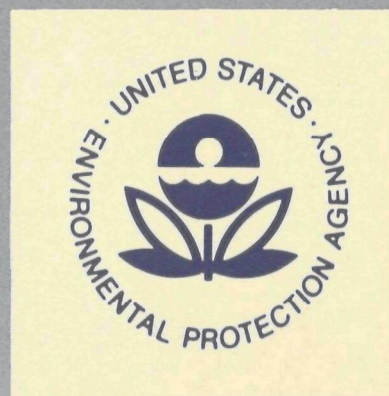
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STAR Series



SCIENTIFIC AND TECHNICAL
ASSESSMENT REPORT
ON PARTICULATE POLYCYCLIC
ORGANIC MATTER (PPOM)



U.S. Environmental Protection Agency
Office of Research and Development
Washington, D.C. 20460

SCIENTIFIC AND TECHNICAL
ASSESSMENT REPORT
ON
PARTICULATE POLYCYCLIC
ORGANIC MATTER (PPOM)

(Program Element 1AA001)

Assembled by

National Environmental Research Center
Research Triangle Park, North Carolina

for

U.S. ENVIRONMENTAL PROTECTION AGENCY
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Washington, D.C. 20460

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PREFACE

Although this report is issued in the Scientific and Technical Assessment Report Series, it differs in several respects from the comprehensive multi-media format that the Series will usually have because it was nearly completed prior to the creation of the STAR series in August 1974.

This document was prepared by a Task Force convened at the direction of Dr. John F. Finklea, Director, U.S. Environmental Protection Agency, National Environmental Research Center (NERC), Research Triangle Park, N. C. Assembly, integration, and production was directed by the Special Studies Staff, NERC-RTP. The objective was to review and evaluate the current knowledge of particulate polycyclic organic matter (PPOM) in the environment, as related to possible deleterious effects upon human health and welfare. Information from the literature and other sources has been considered generally through December 1972.

A report prepared by the National Academy of Sciences, Committee on Biologic Effects of Atmospheric Pollutants, Panel on Particulate Polycyclic Organic Matter served as a primary reference for this report. The National Academy of Sciences' report is based on one prepared under contract to the U. S. Environmental Protection Agency.

The following members served on the NERC Task Force:

James R. Smith, Chairman	Carl G. Hayes
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The substance of the document was reviewed by the National Air Quality Criteria Advisory Committee (NAQCAC) in public sessions on January 18, 1973, March 15, 1973, and May 17, 1973. Members of NAQCAC were:

Mary O. Amdur — Harvard University
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Samuel S. Epstein — Case Western Reserve University
Arie D. Haagen-Smit — California Institute of Technology
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Elmer P. Robinson — Washington State University
Morton Sterling — Wayne County Michigan Health Department
Arthur C. Stern — University of North Carolina
Raymond R. Suskind — University of Cincinnati
Elmer P. Wheeler — Monsanto Company
John T. Wilson — Howard University

NAQCAC members were generally in agreement with the conclusions in this report; however, there were diverse opinions regarding the term carcinogenic as applied to the ambient atmosphere, the concept and application of threshold values, and the adequacy of the Clean Air Act as amended relative to the problem of PPOM in the ambient atmosphere. The differences of opinion centered largely upon a universally acceptable definition of carcinogenic as related to the ambient atmosphere and the term "hazardous air pollutant" as defined in the Clean Air Act. NAQCAC members generally agreed on the need to control the level of PPOM exposure; however, there were diverse opinions concerning control options.

A final formal review of the report was conducted by a Task Force that initially convened on July 16, 1973, under the direction of Dr. Ronald E. Engel of the Office of Research and Development, EPA. Members of the Task Force were:

J. Wesley Clayton, Jr., Chairman	Arnold J. Goldberg
Kenneth L. Bridbord	Robert E. McGaughey
Kenneth Cantor	Robert B. Medz
A. F. Forziati	Jeannie L. Parrish
Thomas L. Gleason	James R. Smith

Review copies of this document also have been provided to other governmental agencies and to industrial and public interest groups.

All comments and criticisms have been reviewed and incorporated in the document where deemed appropriate.

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LIST OF ABBREVIATIONS AND SYMBOLS

A	anthracene	μg	microgram (10^{-6} gram)
Anth	anththrene	μl	microliter (10^{-6} liter)
BaA	benz[a]anthracene	μm	micrometer (10^{-6} meter)
BaP	benzo[a]pyrene	mg	milligram (10^{-3} gram)
BeP	benzo[e]pyrene	min	minute
BghiP	benzo[ghi]perylene	MS	mass spectrometry
BkF	benzo[k]fluoranthene	MT	metric ton
BSO	benzene soluble organics	NAS	National Academy of Sciences
C	Celsius (centigrade)	NASN	National Air Surveillance Networks, EPA
cal	calories	NERC-RTP	National Environmental Research Center, Research Triangle Park, N.C. (EPA)
Ch	chrysene	ng	nanogram (10^{-9} gram)
CHESS	Community Health and Environmental Surveillance System	nm	nanometer (10^{-9} meter)
Cor	Coronene	NO_x	nitrogen oxides
o	degree	P	pyrene
EPA	U.S. Environmental Protection Agency	PAA	polycyclic aza arenes
Fluor	fluoranthene	PAH	polycyclic aromatic hydrocarbons
g	gram	Per	perylene
GC	gas chromatography	pg	picogram (10^{-12} gram)
HPLC	high pressure liquid chromatography	Phen	phenanthrene
hr	hour	POM	polycyclic organic matter
K	Kelvin	PPOM	particulate polycyclic organic matter
kg	kilogram	TLC	thin layer chromatography
km	kilometer	TSP	total suspended particulate
m^3	cubic meter	VPOM	vaporous polycyclic organic matter
Mcal	megacalories (10^6 calories)	yr	year

ABSTRACT

This report is a review and evaluation of the current knowledge of particulate polycyclic organic matter in the environment as related to possible deleterious effects on human health and welfare. Sources, distribution, measurement, and control technology are also considered. Results of an extensive literature search are presented.

Experiments have shown a number of polycyclic organic compounds to be carcinogenic in animals. Although these same compounds have not been proven to be carcinogenic in humans, evidence strongly suggests that they may contribute to the “urban factor”. In American males, the urban lung cancer death rate is about twice the rural rate, even after adjustment for differences in smoking habits. Evidence suggests significant differences between specific urban areas across the United States.

The bulk of the available data is in terms of benzo[a]pyrene; so this compound has been used as an index on particulate polycyclic organic matter. Average seasonal concentrations of BaP in the ambient atmosphere range from less than 1 ng/m³ in nonurban areas to a maximum of 50 ng/m³ in rural areas.

SCIENTIFIC AND TECHNICAL ASSESSMENT REPORT ON PARTICULATE POLYCYCLIC ORGANIC MATTER

1. INTRODUCTION

There is substantial evidence indicating a significant difference between the occurrence of lung cancer in individuals living in urban and nonurban areas even after adjustment for differences in smoking habits. The reasons for this “urban factor” are not known, but there is evidence that high concentrations of some pollutants in urban air might be associated with an increased risk of human cancer. However, the specific causal relationships have not been established. This lack of knowledge constitutes one of the most urgent needs regarding the problem of the health effects of air pollution.

A polluted atmosphere is comprised of a complex mixture of gases and particles originating from both natural and man-made sources. Currently, two classes of polycyclic organic compounds are proven carcinogens in experimental animals, albeit not by the inhalation route. The two—the polycyclic aromatic hydrocarbons and their nitrogen analogs, the aza arenes—are present in the particulate phase in polluted air. Occupational exposure to mixtures containing these compounds has led to well documented cases of lung cancer.

Polycyclic organic matter (POM) is defined as organic matter that contains two or more ring structures which may or may not have substituted groups attached to one or more rings. POM can be separated into two portions:

- Particulate polycyclic organic matter (PPOM) is in solid form at ambient temperatures and is defined as material collected on a glass fiber filter as specified in the *Federal Register* (Vol. 36, No. 84, Part II, pages 8191-8195, April 30, 1971).
- Vaporous polycyclic organic matter (VPOM) is defined as that portion of POM that passes through the filter; it will be covered in a separate document.

The aromatic compounds of POM found in the atmosphere can be subdivided into nine groups:

- *Polycyclic aromatic hydrocarbons.* The polycyclic aromatic hydrocarbons (PAH) usually collected in the particulate form include chrysene, benz[a]anthracene, fluoranthene, the benzpyrenes, the benzo[fluoranthenes], perylene, anthanthrene, dibenzanthracenes, benzfluorenes, the dibenzpyrenes, indeno [1,2,3-cd] pyrene, benzo[ghi] perylene, coronene, and alkyl derivatives of some of these. The latter are usually methyl derivatives. This is of some importance since methylation of a PAH can sometimes increase or confer carcinogenic activity on the molecule.
- *Aza arenes.* Arenes are aromatic hydrocarbons. Aza arenes (arenes containing a ring nitrogen) are usually present in the atmosphere in approximately one order of magnitude lower concentration than the PAH. Those identified in the fraction of airborne particulates extracted by an acidic solvent include acridine, 3-methylacridine, benzquinolines, benzacridines, 11H-indeno [1,2-b] quinoline,

phenanthridine, indeno[1,2,3-ij]-isoquinoline, benzo[Imn]phenanthridine, dibenzacridines, pyridylanthracene, and a large assortment of alkyl derivatives of these compounds. However, the basic fraction of some types of airborne particulates and source samples contains a very large number of unidentified polycyclic compounds.

- *Imino arenes.* Imino arenes contain a ring nitrogen with a hydrogen. Carbazole and some of its methyl derivatives are imino arenes found in urban atmospheres. Both these and the benzocarbazoles are found in air polluted with coal tar pitch. The presence of the carbazoles indicates possible pollution by fumes of coal tar pitch.
- *Carbonyl arenes.* Carbonyl arenes contain one ring carbonyl group. Monocarbonyl compounds found in airborne particulates include 9-acridanone, phenalen-1-one (PO), xanthen-9-one, 7H-benz[de]anthracen-7-one (BO). PO and BO can be readily and quickly separated from particulates and determined.
- *Dicarbonyl arenes.* Dicarbonyl arenes (quinones) isolated from airborne particulate matter include naphthoquinone, anthraquinone, anthanthrone, pyrenequinones, and benzpyrene quinones.
- *Hydroxy carbonyl arenes.* These are ring carbonyl arenes containing hydroxy groups and possibly alkoxy or acyloxy groups. Hydroxy carbonyl compounds found in particulate matter include scopoletin and a variety of flavonols. These are derived from biological material and probably would be found wherever there is natural air pollution.
- *Oxa arenes and thia arenes.* Oxa arenes contain a ring oxygen atom, while thia arenes contain a ring sulfur atom. A large assortment of oxygen-containing heterocyclic hydrocarbons are present in the neutral fraction of airborne particulate matter. Dibenzofuran and dibenzothiophene are examples of oxa and thia arenes, respectively; both are found in airborne particulate matter, although they are more common in the vapor phase.
- *Polychloro compounds.* Among the polychloro compounds found in polluted atmospheres are polychlorobiphenyls, polychloro-p-terphenyls, chlorodibenzofurans, and chlorodibenzo-p-dioxins.
- *Pesticides.* A large variety of pesticides are known. Among the few found in the atmosphere are aldrin, chlordane, and DDT.

POM may be formed in any combustion process involving compounds containing carbon and hydrogen. The amount formed in a given combustion process is dependent upon the "efficiency" of the process—that is, completeness of the oxidation of carbon and hydrogen to carbon dioxide and water, respectively. POM is probably formed in these processes by accretion of carbon-containing free radicals in the reducing atmosphere existing in the center of the flame. Since POM is formed during combustion, it seems clear that most POM in the urban atmospheres originates from man-made sources. There are, however, "natural" sources such as fires set by "natural causes" and possibly decomposition of organic matter.

Much of the POM formed in the course of combustion processes is probably emitted as vapor from the flame. Some vapor remains in the vaporous phase, but some cools and condenses on particles already present in the atmosphere or forms small particles of pure condensate. The primary physical properties that influence the behavior of POM-containing aerosols are particle size, surface area, shape, and density. Current knowledge of each of these factors is limited.

Available data indicate that PPOM is largely associated with particles less than 5 micrometers (μm) in diameter. This range includes the sizes that may affect visibility and cloud and precipitation processes, as well as respiratory intake. One factor that may be important in limiting the size of the smallest particles of PPOM is the Kelvin effect, which says that the equilibrium vapor pressure varies with the radius of curvature of the particles and the surface energy of the volatile material.

PPOM is subject to the same atmospheric processes as other types of airborne particles. It is dispersed in the atmosphere by turbulence and transported by winds. Removal from the atmosphere occurs by sedimentation, deposition by impaction (on rocks, buildings, and vegetation, for example), washout, and rainout. The residence time in dry air varies from 4 to 40 days for particles less than 1 μm in diameter, and 0.4 to 4 days for particles 1 to 10 μm in diameter. The chemical reactivity of PPOM may reduce its half-life to less than 1 day. The primary reactions that shorten the atmospheric life span of PPOM are photooxidation and reactions with oxidants or sulfur dioxide.

Most PPOM measurements are for benzo[a]pyrene (BaP). Concentrations recorded by the National Air Surveillance Networks (NASN) normally are highest during the winter season, apparently because more fuel is burned then. In areas where PPOM concentrations are high, the seasonal variation in concentration is quite pronounced. A wide variation is also observed between different urban areas, suggesting a significant difference in the characteristics of their polluted atmospheres. Early animal experiments carried out with various organic fractions of airborne particles have shown apparent geographic differences in carcinogenic activity, with the highest activity in material from Birmingham and the lowest in material from Los Angeles.

To assess the potential hazards to human health resulting from PPOM in the atmosphere and to make meaningful decisions regarding the necessity and strategies for control, it is necessary to identify the suspect substances and their sources, evaluate the collection and measurement techniques, examine the biological effects, and evaluate the control technology. This report addresses these aspects. A comprehensive review, published by the National Academy of Sciences in 1972 and entitled "Particulate Polycyclic Organic Matter," has provided the basis for much of the material presented here; other information gathered from the literature, however, and results of U. S. Environmental Protection Agency (EPA) research have also been incorporated.

2. SUMMARY AND CONCLUSIONS

2.1 SUMMARY

Evidence is now available confirming that a significant difference exists between urban and nonurban residents in the occurrence of lung cancer and other chronic or latent diseases. The reason for this "urban factor" is not known, but it is probably due to a number of factors. In American males, the urban lung cancer death rate is about twice the rural rate, even after adjustment for differences in smoking habits. A large series of animal experiments carried out with various extracts and fractions of airborne particulates indicate apparent geographic differences in biological activity, with the highest incidence of cancer being associated with material from Birmingham, Alabama, and the lowest with material from Los Angeles, California. This evidence suggests that the pollutant characteristics, and hence the effect upon human health, may be quite different between specific urban atmospheres.

Experiments have shown a number of polycyclic organic compounds to be carcinogenic in animals. Although these same compounds have not been proven to be carcinogenic in humans, evidence strongly suggests that they may contribute to the "urban factor." There are no known data on teratogenicity of PPOM. Work on mutagenicity in higher organisms has been limited, and the results are inconclusive.

Early studies on the biologic effects of environmental POM demonstrated its carcinogenicity and focused subsequent toxicologic laboratory research in that direction. Many screening methods have been devised to evaluate carcinogenicity. These methods have been applied to pure polycyclic compounds representative of those found in the environment, as well as to fractions and mixtures of PPOM collected from urban atmospheres. Inquiries have been made into many of the ramifications of how these compounds reach the cells in which carcinogenesis occurs, what takes place in these cells at the molecular level, and how these sequences may be altered. Little attention has been directed at development of methods to evaluate dose-response relationships which could be applied as criteria for standards.

Polycyclic organic matter (POM) is organic matter that contains two or more ring structures that may or may not have substituted groups attached to one or more rings. POM includes polycyclic aromatic hydrocarbons, polycyclic heterocyclics, and various derivatives. POM can be separated in two portions. Particulate polycyclic organic matter (PPOM) is in solid form at ambient temperatures and is defined as material collected on a glass fiber filter as specified in the *Federal Register* (Vol. 36, No. 84, Part II, page 8191 to 8195, April 30, 1971). Vaporous polycyclic organic matter (VPOM), that portion of POM that passes through the filter, will be covered in a separate document.

PPOM in the atmosphere is produced primarily by incomplete combustion and is thought to be emitted as a vapor from the flame; when cooled, the vapor rapidly condenses on particles already present in the atmosphere or it forms small particles of pure condensate. The bulk of PPOM found in the atmosphere is associated with particles of less than 5 micrometers diameter and hence is respirable. This size range may affect visibility as well as cloud and precipitation processes. Little is known about particle shape, particle density, or number density.

The primary man-made sources of PPOM, measured as benzo[a]pyrene, in the atmosphere over the United States are heat generation—430 metric tons (MT) per year—and open burning of refuse (primarily coal wastes)—500 MT per year. Emissions from coke production may be as high as 150 MT per year, but coke emissions estimates are very uncertain. The highest emission factors are for small and intermediate

hand-stoked coal furnaces. Emissions from mobile sources comprise only a small fraction of the total nationwide emissions.

The mechanisms for removing PPOM from the atmosphere include dry deposition and precipitation. The half-life—that is, the time required for half the material to be removed or destroyed—is estimated at approximately 100 hours under dry conditions, but it may be much shorter. There is evidence that some of the highly reactive compounds are degraded in the atmosphere by reactions with oxidants and by photooxidation.

PPOM is commonly measured in total suspended particulates, benzene-solution organics, and as benzo[a]pyrene (BaP). Ratios of the three vary widely both in urban and nonurban areas. The bulk of the available data is in terms of BaP, so this compound has been used as an index of PPOM pollution. Because it is also known to be extremely carcinogenic to animals, BaP has been used extensively in experimental work. Average seasonal concentrations of BaP in the ambient atmosphere range from less than 1 nanogram per cubic meter (ng/m^3) in nonurban areas to a maximum of $50 \text{ ng}/\text{m}^3$ in urban areas. Local, or short period, concentrations may reach $100 \text{ ng}/\text{m}^3$. Average annual or seasonal concentrations higher than about $2 \text{ ng}/\text{m}^3$ are generally confined to urban areas using coal as the primary fuel. There is large variation among urban areas.

The total suspended particulate (TSP) concentrations in urban atmospheres (measured by High Volume Sampler) range from 100 to 200 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). Benzene-soluble organic particles comprise approximately 8 to 14 percent of the TSP, and BaP approximately 0.01 to 0.2 percent of the benzene solubles.

Although some work has been done on every level of PPOM interaction with biologic materials, much remains to be accomplished. In animal experiments using a number of screening methods, many of the polycyclic aromatic hydrocarbons found in urban atmospheres have been shown to be carcinogenic in varying degrees. Both pure compounds, as well as mixtures of POM with inorganic particulates, have been used. In some cases, the mixtures have been found to be more potent carcinogens than single compounds—for example, BaP and hematite. Little attention has been given to development of methods to evaluate dose-response relationships applicable to ambient air.

POM is a natural component of many plants and plant products and is also produced by many plants and plant products. Evidence indicates that some of the compounds may behave as plant hormones. POM of all types can be metabolized by soil microorganisms and aquatic forms, particularly those associated with polluted water. The incidence of human gastric cancer may correlate with ingestion of plants containing POM.

Since POM is produced primarily by incomplete combustion, control of emissions would logically include improvement in combustion efficiency, removal at the source, and local ordinances. A considerable effort is currently under way to develop control techniques and procedures for the control of particulate matter in the size range less than 2 micrometers. It is expected, although not yet demonstrated, that control of particulates will significantly reduce PPOM emissions if the control device is uniformly effective throughout its collection range.

2.2 CONCLUSIONS

The areas of uncertainty about PPOM are often greater than the areas of knowledge—which attests to the tremendous complexity of the problem. In such an analysis, one quickly becomes keenly aware of the fact that the polluted atmosphere encompasses an aggregate of constituents that individually or in combinations, and in varying degrees, may have a deleterious effect on human health and welfare. When the possible number of combinations is considered, the simple logistics of investigating all individual elements or compounds make the task essentially insurmountable. In a practical sense, one is constrained to use some type of parameter or index to make the problem reasonably tractable; however, such an approach inherently involves a level of risk. In fact, conclusions based upon limited knowledge and data should be

considered tentative. In spite of the uncertainties, a number of specific conclusions related to PPOM in the atmosphere can be drawn with some confidence. These are:

1. There is a significant difference in the occurrence of lung cancer in urban and nonurban residents even after the contribution of smoking has been factored out. The available evidence indicates, although it has not yet been quantified, that PPOM contributes to this increase in cancer among individuals living in urban areas. There also appear to be significant differences between urban areas.
2. Polycyclic aromatic hydrocarbons and heterocyclic compounds constitute a group of known animal carcinogens that are present in the particulate form in the atmosphere.
3. The carcinogenicity of a mixture of compounds may be greater than the sum of that of the individual compounds.
4. Compounds present in the atmosphere may act as tumor-inhibitory or anticarcinogenic agents, although their role is poorly understood at this time.
5. No teratogenic or mutagenic effects have been found in animals, but studies in this area have not been extensive. One might postulate that urban susceptibility to carcinogens may have been induced by mutagenic mechanisms over several generations.
6. The evidence clearly shows that occupational exposure to higher-than-urban concentrations of some polycyclic compounds will increase the incidence of human lung cancer.
7. There is no conclusive evidence that a reduction of benzo[a]pyrene concentration in the ambient atmosphere would necessarily reduce the occurrence of human lung cancer.
8. Dose-response relationships or threshold values have not been established for PPOM in the ambient atmosphere.
9. To date, epidemiologic findings implicate POM in the production of skin and lung cancers. Although most authors cite BaP as the primary human carcinogen, a great deal of work remains in defining the roles of specific polycyclic compounds in producing human disease.
10. Studies to date have suffered from the inability to characterize local air pollution. A sign of this inability has been the tendency to ascribe the total carcinogenic air pollution effect to BaP alone. It is reasonable in many ways to use BaP as an index to air pollution, but PPOM has never been shown to cause human lung cancer and has never even been associated with skin cancers of any kind. For the present, the epidemiologist is not justified in making broad generalizations about local findings.
11. The problem of defining the role of PPOM is complicated by the phenomenon of cocarcinogenesis. It has often been found that even a potent carcinogen is relatively inactive unless coupled with one or more other substances, or cocarcinogens. Furthermore, cocarcinogens can greatly shorten the latent period of carcinogenesis. Known cocarcinogens include ultraviolet radiation, epoxides, lactones, asbestos, and aromatic hydrocarbons. Suspected ones include sulfur dioxide, nitrogen oxides, and ozone. Present data do not warrant intelligent long-range conclusions.
12. There is no documented evidence of deleterious effects of PPOM on materials at ambient levels.
13. The incidence of gastric cancer has been correlated with the ingestion of plant or plant parts containing POM.
14. POM of all types can be metabolized by soil microorganisms and aquatic forms, particularly those associated with polluted water.

15. PPOM is emitted into the atmosphere primarily from incomplete combustion of fuels. The principal sources are heat generation, refuse burning, and uncontrolled coke production. All emission factors are poorly quantified.

16. Few studies have been made on natural emissions of POM. There is some evidence that POM is produced in the decay of organic matter, although the contribution to ambient concentrations is thought to be small.

17. Organic matter in the atmosphere is primarily associated with particulate matter.

18. Rapid and reliable techniques are not available for measurement of PPOM at sources and in the ambient air. Although the use of BaP as an index of PPOM is desirable for some activities, it is not a universally acceptable approach.

19. Adequate PPOM control techniques are not available currently. It is a general consensus of the Task Force Panel that control of particulate emissions from combustion sources will significantly reduce the levels of PPOM in the atmosphere.

3. EMISSIONS

3.1 INTRODUCTION

Discussions of PPOM emissions invariably center on BaP. This compound is singled out for several reasons:

- Considerable emission data are available from a multitude of sources, and emission data for other PPOM compounds are sparse by comparison.
- Since PPOM primarily results from incomplete combustion, a control strategy to improve combustion efficiency will reduce BaP emissions, as well as that of many other PPOM compounds.
- Ambient air data for BaP have been available for several years from NASN.
- Many publications, particularly during the 1960's, describe biological effects of BaP in animals. Concern about the potential carcinogenic effect of BaP has stimulated development of a data bank on the sources of emissions and the ambient air concentrations.

The importance of combustion efficiency on PPOM emissions is illustrated by plotting BaP emission rates against gross heat input for various coal-fired units (Figure 3-1).¹ Because of the many variables affecting formation of BaP, a wide range of concentrations can be expected from a given size unit. Emissions from units operating with relatively efficient combustion conditions would be expected to fall near the lower boundary of the range, whereas emissions from less efficient combustion processes would fall near the upper boundary. The lower emission rates from the large coal-fired units used by electric power plants can be attributed to the more efficient combustion of fuel obtainable with closely regulated air-fuel ratios and uniformly high combustion-chamber temperatures. The highest emission-rate sources are hand-stoked and underfeed-stoked residential coal-fired heating units.

Comparisons of POM emissions with other products of incomplete combustion indicate that POM emission rates are generally high when carbon monoxide and total gaseous hydrocarbons are high.² The correlations are not consistent enough, however, to warrant their use as a measurement parameter for POM.

In addition to inefficient combustion, another mechanism for the emission of PPOM is vaporization and aeration of substances that contain PPOM. Examples are coal-tar-pitch waterproofing, asphalt hot-road-mix production, and asphalt air-blowing operations. In comparison to incomplete combustion, vaporization and aeration are generally minor sources of PPOM.

3.2 EMISSIONS FROM STATIONARY AND MOBILE SOURCES

Numerous sources were tested for PPOM in the early 1960's as part of a screening program of stationary and mobile sources by the Federal air pollution control program.¹ Ten samples from a variety of source categories thought to emit PPOM were analyzed for: BaP; pyrene (P); benzo[e] pyrene (BeP); perylene (Per); benzo[ghi] perylene (BgHiP); anthanthrene (Anth); coronene (Cor); anthracene (A); phenanthrene (Phen); and fluoranthene (Fluor). Table 3-1 summarizes the sources.

The largest sources of PPOM emissions for heat generation were coal-fired residential furnaces. Table 3-2 shows that low emissions of BaP were associated with low emissions of other PPOM compounds. The lowest

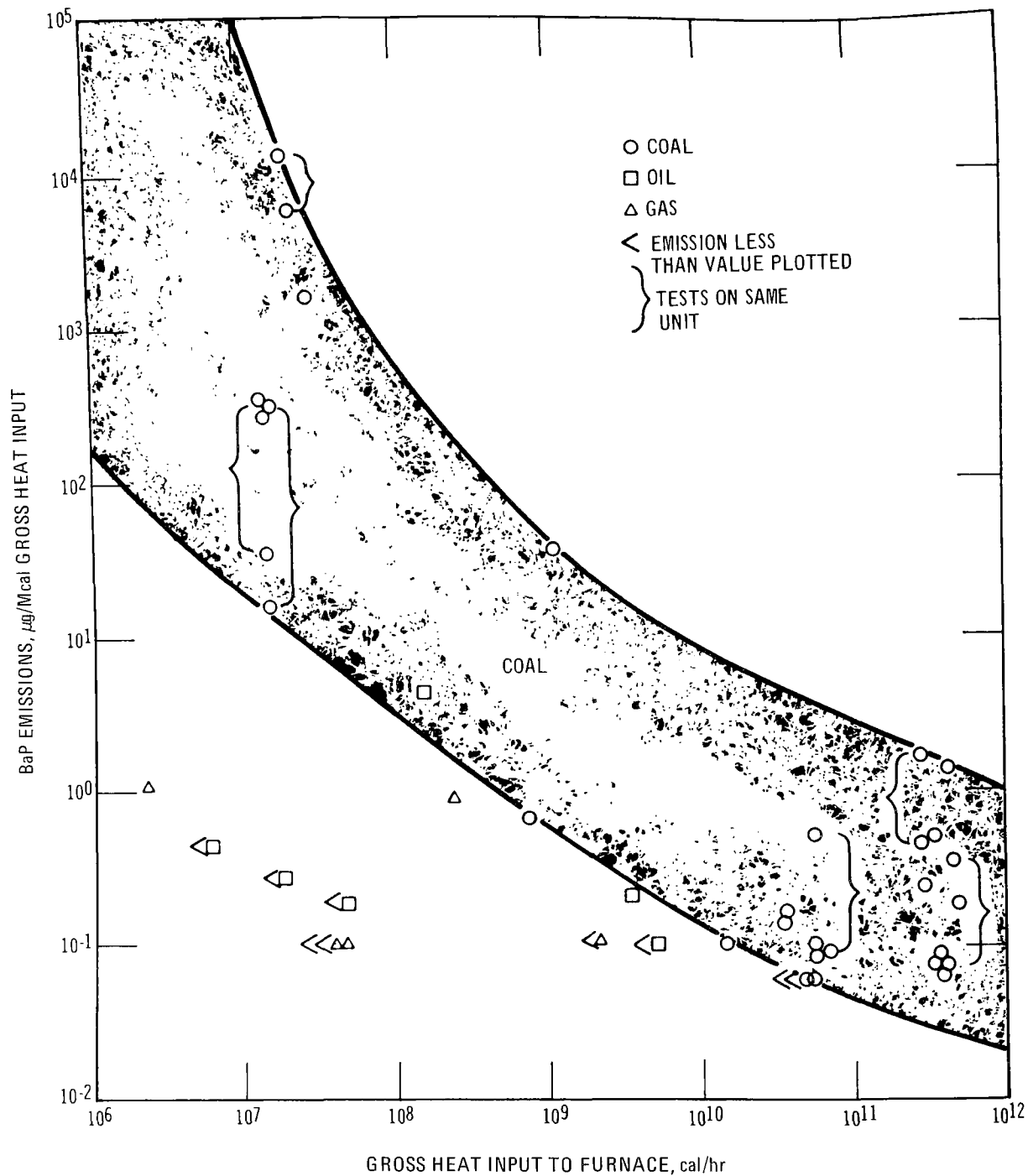


Figure 3-1. Benzo[a] pyrene emissions from coal, oil, and natural gas heat-generation processes.¹

emissions in this category were from coal-fired power plants as shown in Table 3-3. BaP emissions from coal-fired power plants were generally less than 1.6 micrograms per million calories ($\mu\text{g}/\text{Mcal}$) compared to over 1,600 $\mu\text{g}/\text{Mcal}$ for hand-stoked residential furnaces.

Emissions of PPOM from oil- and gas-fired sources were low in comparison to emissions from all coal-fired sources, as shown in Figure 3-1. Detectable concentrations of BaP were found in only two of the six oil-fired units tested. The highest concentration was 3.6 $\mu\text{g}/\text{Mcal}$. Of the five gas-fired sources tested, BaP was detected in two. The highest concentration was 1.1 $\mu\text{g}/\text{Mcal}$. The two gas-fired sources where BaP was detected produced more PPOM than the other three sources, apparently because of improper adjustment of the air-fuel ratio as evidenced by high concentrations of carbon monoxide and total gaseous hydrocarbons.²

PPOM emissions from commercial and municipal incineration and from open-burning of municipal refuse, grass clippings, and automobiles are summarized in Table 3-4. Those from petroleum cracking catalyst regeneration are summarized in Table 3-5. Eight automobiles and four trucks, without emission control devices, representing two popular vehicle makes, were also tested for PPOM. Results are reported in Table 3-6.

Table 3-1. SOURCES SURVEYED FOR PPOM EMISSIONS¹

Source category	Source
Heat generation	Furnaces burning coal, oil, and gas
Refuse burning	Municipal and commercial incinerators Open burning dumps
Miscellaneous industrial processes	
Petroleum catalytic cracking catalyst regeneration	Fluid catalytic crackers Thermofor catalytic crackers Houdrifiow catalytic crackers
Asphalt air-blowing	
Asphalt hot-road-mix manufacture	
Coke manufacture	
Motor vehicle exhaust	Gasoline-burning automobiles and trucks

Table 3-2. PPOM EMISSIONS FROM COAL-FIRED RESIDENTIAL FURNACES¹

Source	Firing method	Fuel rate, kg/hr	Gross heat input, Mcal/hr	Emissions, $\mu\text{g}/\text{Mcal}$ heat input									
				Group 1 ^a							Group 2 ^a		
				BaP	P ^b	BeP	Per	BghiP	Anth	Cor	A ^b	Phen ^b	Fluor ^b
1	Under feed stokers	2.2	25	15	31	21		2		5		115	187
		1.9	25	258	1,190	155	31	242	24	16	278	2,421	1,310
		1.7	25	321	754	234	19	230	12		190	1,389	595
2		2.3	25	266	635	218	22	234	5	13	56	675	1,270
		2.0	25	34	179	31	2	25			5	202	302
3	Hand-stoked	3.6	25	1,587	2,381	397	238	1,190	357	119	2,587	3,968	3,968
4		2.9	25	6,746	10,714	3,452	873	5,556	1,071	194	4,365	9,127	17,063
		2.5	25	13,095	36,111	5,952	1,389	8,730	1,944	385	11,508	29,762	43,651

A blank indicates that the compound was not detected in the sample.

^aAnalytical results are more accurate for Group 1 than Group 2.

^bMinimal values, especially for A and Phen.

Table 3-3. PPOM EMISSIONS FROM COAL-FIRED POWER PLANTS¹

Source	Type of unit	Fuel rate, MT/hr	Gross heat input, Mcal/hr	Emissions, μg/Mcal heat input									
				Group 1 ^a					Group 2 ^a				
				BaP	p ^b	BeP	Per	BghiP	Anth	Cor	A ^b	Phen ^b	Fluor ^b
1	Pulverized coal (vertically fired dry-bottom furnace)	59	388,000	0.12	1.16								1.29
		60	399,000	0.12	0.76								1.19
		43	286,000	0.25	1.04	0.19							1.85
		41	275,000	0.56	0.32	0.34	0.10	0.36					0.37
2	Pulverized coal (front-wall-fired, dry-bottom furnace)	47	331,000	0.09	1.04	0.29		0.07				1.04	0.83
		45	338,000	0.11	0.85								0.07
3	Pulverized coal (tangentially fired, dry-bottom furnace)	57	344,000	0.76	0.76	0.46	0.38	0.81	0.03	0.04		0.19	2.11
4	Pulverized coal (opposed-, downward- inclined burners; wet-bottom furnace)	8	58,000	0.13	0.12	0.38		1.01		0.09			0.19
		10	72,000	0.02	0.06	0.12		0.21		0.02			0.08
		8	60,000	0.02	0.04	0.06		0.14		0.01			0.05
5	Crushed coal (cyclone-fired, wet-bottom furnace)	53	415,000	2.41	10.97	4.44	0.22	2.15		0.01			0.72
		60	469,000	0.56	1.84	0.81		0.27					3.25
6	Spreader stoker (traveling grate)	8	59,000	0.02	0.06	0.06				0.09			0.06
		8	58,000	<0.01	0.03								0.03
		8	58,000	<0.01	0.02								0.01

A blank indicates that the compound was not detected in the sample.

^aAnalytical results are more accurate for Group 1 than Group 2.

^bMinimal values, especially for A and Phen.

Table 3-4. PPOM EMISSIONS FROM INCINERATION AND OPEN BURNING¹

Type of unit	Emissions, $\mu\text{g/kg}$ of refuse charged									
	Group 1 ^a					Group 2 ^a				
	BaP	p ^b	BeP	Per	BghiP	Anth	Cor	A ^b	Phen ^b	Fluor
Municipal incineration 225 MT/day multiple chamber	0.2	17.6	0.8				6.5			21.6
45 MT/day multiple chamber	0.2	4.6	1.3		1.4		1.4			7.3
Commercial incineration 4.8 MT/day single chamber	116.7	704.8	99.1	6.8	198.2	14.5	46.3	103.5	308.4	484.6
2.7 MT/day multiple chamber	572.7	9,251.1	572.7	132.2	1,916.3	174.0	462.6	189.4	130.0	8,590.3
Open burning Municipal refuse	330.4	1,762.1	242.3		154.2					1,607.9
Grass clippings, leaves, branches	352.4	1,762.1	154.2	37.4	160.8	26.4				1,101.3
Automobiles	28,634.4	74,889.9	14,537.4	2,643.2	19,603.5	2,202.6	2,422.9	3,083.7	21,365.6	52,863.4

A blank indicates that the compound was not detected in the sample.

^aAnalytical results are more accurate for Group 1 than Group 2.

^bMinimal values, especially for A and Phen.

Table 3.5. PPOM EMISSIONS FROM PETROLEUM CRACKING CATALYST REGENERATION¹

Source	Type of unit ^b	Sampling point	Process rate, m ³ /stream day	Emissions, µg/m ³ of oil charged ^a									
				Group 1 ^c							Group 2 ^c		
				BaP	p ^d	BeP	Per	BghiP	Anth	Cor	A ^d	Phen ^d	Fluor ^d
1	FCC	Regenerator outlet CO boiler outlet	3,212	277 69	1,069 547	333 132		94					1,006 453
2	FCC	Regenerator outlet CO boiler outlet	7,354	2,893 138	176,101 1,069	22,641 113		2,642 346			13,208	2,515,723	125,786 535
3	HCC	Regenerator outlet CO boiler outlet	5,915	1,289,308 283	823,899 245	1,949,685 610	213,836 30	1,886,792 818	94,340 20	69,182 50	5,786 50	132,075 522	52,201 145
4	TCC (Air lift)	Regenerator outlets	3,116	754,717	817,610	754,717	62,893	452,830	27,673		150,943	490,566	
5	TCC (Air lift)	Regenerator outlets	3,625 3,784	352,201 389,937	1,572,327 1,635,220	352,201 471,698	55,346 34,591	276,730 339,623	8,176 11,321		62,893 69,182	2,213,836 2,075,472	182,390 69,182
6	TCC (Bucket lift)	Regenerator outlets	2,099	195	1,761	516							371

A blank indicates that the compound was not detected in the sample.

^aFresh feed plus recycle.

^bFCC: fluid catalytic crackers; TCC: Thermoform catalytic crackers; HCC: Houdrifiow catalytic crackers.

^cAnalytical results are more accurate for Group 1 than Group 2.

^dMinimal values, especially for A and Phen.

Table 3-6. PPOM EMISSIONS FROM MOTOR VEHICLES¹

Vehicle year	Mileage, km	Emissions, $\mu\text{g}/\text{km}$ traveled									
		Group 1 ^a							Group 2 ^a		
		BaP	p ^b	BeP	Per	BghiP	Anth	Cor	A ^b	Phen ^b	Fluor ^b
Automobiles											
Make A 1962	30,400	3.8	50.1	6.3	<0.3	16.3	1.3	6.3	3.8		24.4
1962	41,600	2.5	43.8	5.0	<0.1	21.9	0.6	6.9	2.5	16.9	24.4
		1.9	8.1	3.1	<0.3	21.3	<0.3	10.6	2.5	28.8	4.4
1959	78,400	2.5	16.9	5.6	<0.6	8.8	<0.3	2.5		2.5	24.4
1956	92,800	13.8	74.4	15.0	<0.6	48.1	1.9	20.0			63.8
4-car average		5.0	41.9	8.1	<0.6	23.8	0.6	9.4	1.3	6.3	31.9
Make B 1964	22,400	2.5	47.5			4.4		4.4	0.6	33.1	26.3
		2.5	41.9	8.8	1.3	5.6	<0.3	5.0	0.6	22.5	20.0
1962	30,400	6.9	88.8	6.3	0.6	40.6	<0.3	12.5	5.0	57.5	41.9
		3.1	78.1	3.8	0.6	30.6		11.9	3.8	20.0	40.6
		2.5	36.3	11.3	1.3	17.5		5.6	2.5	5.6	20.0
1959	84,800	6.9	64.4	20.0	2.5	25.6	0.6	6.9	6.9	30.6	47.5
1957	107,200	21.3	213.1			90.0	3.1	40.0	8.1	46.9	139.4
4-car average		10.0	97.5		1.3	37.5	1.3	16.9	4.4	33.1	61.3
Trucks											
Make A 1963	27,200	>1.6	256.3	>2.5	0.6	58.8		38.1	6.3	162.5	137.5
1956	80,000	81.3	937.5	65.6	12.5	300.0	73.8	150	168.8	643.8	612.5
2-truck average		>41.3	600.0	>33.8	6.3	181.3	36.9	93.8	87.5	406.3	375.0
Make B 1964	9,600	12.0	275.0	24.4	1.9	57.5		23.8	14.4	212.5	193.8
1963	27,200	7.9	400.0	30.0	0.6	95.6		63.8	8.8	181.3	275.0
2-truck average		9.0	331.3	26.3	1.3	67.5		37.5	10.4	200.0	218.8

A blank indicates that the compound was not detected in the sample.

^aAnalytical results are more accurate for Group 1 than Group 2.

^bMinimal values, especially for A and Phen.

PARTICULATE POLYCYCLIC ORGANIC MATTER

The PPOM emissions from an asphalt air-blowing process showed no BaP but did show large concentrations of lower-molecular-weight PPOM, including 3100 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) of pyrene and 220 $\mu\text{g}/\text{m}^3$ of anthracene.³ The source surveyed operated at a rate of 22 metric tons (MT) of asphalt per hour with a stack effluent of 521 cubic meters per minute (m^3/min) at the point of testing.

An asphalt hot-road-mix plant was tested for PPOM. BaP was detected on the inlet of a water spray tower but was not detected on the outlet of this control device. Pyrene, anthracene, and fluoranthene were the only measurable PPOM on the outlet side of the control device. The concentrations were 3, 1.4, and 2.5 $\mu\text{g}/\text{m}^3$ respectively.³ These are minimal concentrations, especially anthracene, since these compounds also are present in the atmosphere as VPOM. The plant was operated at 120 MT/hr of finished mix with a stack effluent of 1158 m^3/min at the point of testing.

Recently, qualitative test results have been reported for the effluent of 20 coke ovens.⁴ Because no source test data were available in the publication, emission rates cannot be determined. The following compounds were found: fluoranthene, pyrene, benz[a] anthracene, chrysene, benzanthrone, BaP, and benzo[e] pyrene. Two investigators have measured BaP at various positions in coke oven operations.^{5,6} These studies were not designed specifically to determine emission factors for coke ovens, but the values obtained were used to estimate emissions from coke ovens. The estimates ranged from 0.05 to 153 MT of BaP per year. No reliable emissions estimates can be derived from these data.

3.3 STATIONARY AND MOBILE SOURCE EMISSION DATA LIMITATIONS

Table 3-7 reports a BaP emission inventory made by the National Academy of Sciences (NAS). (A more up-to-date inventory became available as this document went to press. It is presented in the Appendix.) NAS estimated that 90 percent of the annual nationwide BaP emissions came from three stationary combustion sources—coal-fired and wood-fired residential furnaces, coal refuse burning, and coke production.

Residential coal furnaces were the major source of BaP emitting 380 MT/yr. However, the emission factors used by NAS were based on studies which tested only two hand-stoked and two underfeed-stoked residential furnaces.¹

Coal-fired steam power plants were estimated to emit only 1 MT per year of BaP. All tests, however, were conducted on conventional type boilers (30 to 40 percent excess combustion air) available during the early 1960's.^{1,8} To meet EPA's nitrogen oxides standard for new fossil-fuel-fired steam generation plants, two-stage combustion boilers are viewed as a most promising replacement to conventional type boilers. In two-stage combustion, the first stage operates below the stoichiometric air requirements for complete combustion of the fuel. This condition, incomplete combustion, favors formation of POM. In addition, overall excess combustion air is normally around 10 percent for two-stage combustion of coal. This lower excess combustion air may result in reduced oxidation of POM in the second stage if this material is formed in the first stage. No test results are reported in the literature for BaP or other POM from two-stage combustion.

Wood-burning home fireplaces were estimated by NAS to contribute 36 MT/yr of BaP. This estimate, however, is speculative, since no firm data were available in the literature.

Enclosed incineration contributes 31 MT/yr and open burning of domestic and municipal wastes 22 MT/yr. Extensive testing has been conducted on these source types.

NAS listed coal refuse fires at 308 MT/yr. The information was from personal communication, however, with no reference to published data.⁷

Table 3-7. ESTIMATED BENZO[a] PYRENE EMISSIONS IN UNITED STATES, 1968^{7,a}

Source type	Emissions, MT/yr
Stationary sources	
Coal, hand-stoked and underfeed-stoked residential furnaces	380
Coal, intermediate-size furnaces	9
Coal, steam power plants	1
Oil, residential through steam power type	2
Gas, residential through steam power type	2
Wood, home fireplaces	36
Enclosed incineration, apartment through municipal type	31
Open burning, domestic and municipal waste	22
Open burning, coal refuse	308
Open burning, vehicle disposal	45
Open burning, forest and agriculture	127
Petroleum catalytic cracking	5
Coke production	0.05 to 153 ^b
Asphalt air-blowing	<1
Asphalt hot-road-mix plant	<1
Mobile sources	
Gasoline-powered, automobiles and trucks	20
Diesel-powered, trucks and buses	<1
Rubber tire degradation	9
Aircraft	No estimate
Lawn mowers and motorcycles	No estimate

^aEstimated BaP emissions for 1972 are given in the Appendix at the end of the document.

^bRange of values based upon figures obtained from three separate studies not designed specifically to determine emission factors from coke ovens.^{5,6} Original value reported in Reference 7 was 180 MT.

NAS suggested that open burning of vehicles emitted 45 MT/yr of BaP. This level appears high in view of the fact that States now ban open burning. Furthermore, use of enclosed auto incineration and auto crushers for preparation and disposal of vehicles should result in lower BaP emissions than suggested by NAS.

Forest fires and agricultural burning were estimated by NAS to emit 127 MT/yr.⁷ Using new data from the U.S. Forest Service on the extent of forest and agricultural burning, EPA calculated that 9.5 MT per year of BaP are emitted from these sources.

PPOM emissions from fast service restaurants specializing in charcoal broiling have not been evaluated but may be significant because broiling results in incomplete combustion (as is apparent from the dense smoke emissions), the transport distance between the source and receptor is minimal, and a rapid growth has occurred in the fast-service restaurant business.

Gasoline-powered automobiles and trucks were reported by NAS to emit an estimated 20 MT/yr. This estimate is based on studies for uncontrolled motor vehicles surveyed before 1964.^{1,9} NAS indicated emission control devices on automobiles since 1968 models have reduced BaP emissions by 85 percent, compared with uncontrolled vehicles surveyed before 1964. Furthermore, large reductions in BaP emissions should result from control measures instituted to meet hydrocarbon and carbon monoxide standards scheduled for mid-1970's. Emissions from uncontrolled automobiles (prior to 1964) were 45 μg per liter of fuel, versus 5 to 8 for 1968 emission-controlled cars and less than 3 for the advanced systems of the mid-1970's.

NAS reported no BaP emission data for aircraft. Recent Russian studies on a modern aircraft engine showed releases into the atmosphere of from 2,000 to 10,000 μg of BaP per minute.¹⁰

NAS did not estimate emissions from lawn mowers and motorcycles. NAS data for a two-cycle engine, however, suggest large BaP emissions—2900 μg per liter of fuel. This source should not be ignored since the transport distance between source and receptor is short and the emission rate is potentially high.

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4. MEASUREMENT TECHNIQUES

4.1 INTRODUCTION

This chapter is concerned primarily with measurement of aromatic hydrocarbons (arenes) and their heterocyclic analogues containing 2 or more rings. Some discussion of polycyclic aza arenes (PAA) as well as a few other types of PPOM and VPOM is included. This chapter reviews and comments on methods from the viewpoint of an EPA scientist experienced in the field. More detailed information is provided by the National Academy of Sciences¹ review and a selected list of references.²⁻⁶

4.2 PROPERTIES AFFECTING THE MEASUREMENT OF POM

4.2.1 Boiling Point

The organic material in the atmosphere can be subdivided into gases, vapors, and particles mainly on the basis of volatility. Thus, material that is a liquid or solid on the laboratory shelf at room temperature and pressure but a gas in the atmosphere is classified as a vapor. PPOM is collected on filters, while VPOM is collected by methods more suitable for lower boiling materials. On this basis, some material is part vapor and part particulate; the equilibrium is affected by temperature and the collection media. Airborne particulate matter is by definition the material collected on standard glass fiber filters with a standard High Volume sampler as specified in the *Federal Register* (Vol. 36, No. 84, Part II, pages 8191-8195, April 30, 1971).

Separation is another factor affected by the volatility of POM. In gas chromatography, for example, separation of compounds of similar polarity is based mainly on differences in their volatility. Consequently, compounds that have similar boiling or sublimation points are hard to separate—for example, chrysene from benz[a]anthracene and benzo[a]pyrene from benzo[e]pyrene. In addition, some spots on thin layer chromatography chromatograms can volatilize if left too long—pyrene, for example.

4.2.2 Solubility

Differences in solubility of the POM family from other types of compounds in various solvents can be used to concentrate the POM. This property is also used in selectively extracting POM from particulates.

4.2.3 Reactivity to Oxidants in the Presence of Light

Polycyclic aromatic hydrocarbon (PAH) compounds containing a linear structure are more readily oxidized than those without such a structure. Therefore, hydrocarbons such as tetracene and pentacene are usually not found in the atmosphere, although angular compounds such as benz[a]anthracene and chrysene are.

The stability of PAH suspended in the atmosphere depends on molecular structure, the amount of available light, and the presence of oxidizing pollutants. For example, half-lives of less than a day to several days have been given for BaP on soot in sunlight. However, BaP within the soot particle would probably have a much longer half-life. The smaller PAH would disappear from soot in sunlight at a more rapid rate than the larger ones. Summer temperatures would accelerate this loss.

4.2.4 Stability

The stability of PAH collected on a glass fiber filter has been studied. No tetracyclic and larger PAH were lost with 2 hours of collection at 1.2 cubic meters per minute (m^3/min) followed by 2 hours of filtered air at 1.2 m^3/min drawn through the sample. Some tetracyclic PAH, but no larger PAH, were lost with 24 hours of collection followed by 24 hours of treatment with filtered air. Even when air was pulled through the filter for 3 weeks, the pentacyclic and larger PAH showed little, if any, loss.

PAH collected on glass fiber filter paper are stable for at least 3 weeks if they are pentacyclic or larger. The concentrations of tricyclic and tetracyclic PAH decrease under these conditions. Periods of filter storage longer than 3 weeks are not advisable.

The residue obtained from extraction of the filter and careful evaporation to dryness is stable for at least 6 years if kept at 5°C and in the dark.

The stability of PAH on an adsorbent is strongly affected by the type of adsorbent and by the length of exposure to light. Ultraviolet light can accelerate the decomposition. On some adsorbents, some PAH can decompose within a few minutes under ultraviolet light; with other adsorbents much longer exposure is necessary. For this reason, yellow plastic sheeting, which filters out light less than 400 nanometers in wavelength, is used over any source of light during thin layer chromatographic analysis of PAH.

4.3 COLLECTION

High-volume filtration samplers are used routinely to collect atmospheric particulate matter on fiber glass filters for periods of 24 hours or more. This type of sampling is adequate for determining the concentration of PPOM and of individual polycyclic compounds. The collection and retention of some compounds of POM in this manner will be affected by temperature, air flow rate, and particulate composition.

4.4 INTERFACIAL TECHNIQUES

4.4.1 Extraction

Extraction of the PAH from particulates is usually accomplished by a 5- to 8-hour Soxhlet extraction with benzene or cyclohexane at the boiling point. A more efficient and simpler procedure is to extract the filter ultrasonically at room temperature for about 15 minutes; in this procedure, polycyclic aromatic compounds can decompose. If care is not used in the evaporation of the solvent, extensive decomposition can occur.

4.4.2 Sublimation

PAH can be sublimed off the filters, collected, and analyzed; or it can be sublimed into a gas chromatograph, separated, and analyzed. A piece of the filter can be used or it can be shredded into fine particles ultrasonically or with a Wiley mill.

4.4.3 Direct Assay

An effluent in the vapor form can be separated on a gas chromatograph (without a collection step) and assayed in the gas phase using a fluorescence detector and/or a mass spectrometer-computer system. Fluorescence detectors are available for gas phase and liquid phase, but the interfacing needs to be developed and improved. Another problem to be resolved is the incomplete separation of some of the PAH.

4.5 SEPARATION

Because of the large quantity of POM compounds present in urban airborne particles, separation methods are necessary. In the evolution of methods, the survival of any separation technique is dependent on ease of handling, separation time, improved recovery, and reliability of the procedure. Cost factors require the investigation of inexpensive separation methodology.

4.5.1 Liquid-Liquid Extraction

4.5.1.1 PAH—Liquid-liquid extraction has been used to concentrate the PAH and separate them from interfering groups. Pure solvents and hydrocarbon standards must be used. The PAH can be separated from the aliphatic hydrocarbons by distribution of the organic particulates between cyclohexane and nitromethane (or dimethylsulfoxide or dimethylformamide), hexane and dimethylformamide (or dimethylsulfoxide), acetonitrile and hexane, or nitromethane and carbon disulfide. PAH can be separated from aliphatic hydrocarbons and the polar molecules by distribution of the organic extract between cyclohexane and dimethylformamide (or dimethylsulfoxide) and back-extraction from the latter layer with cyclohexane after addition of water.

4.5.1.2 Aza Arenes—The basic fraction containing a number of aza arenes is obtained by extracting an ether solution of the organic particulates with 20 percent aqueous sulfuric acid, neutralizing this latter solution with solid sodium carbonate, and extracting this mixture with chloroform.

4.5.2 Column Chromatography

4.5.2.1 PAH—Column chromatography is probably the best preliminary method for separating an unknown mixture so as to ascertain its composition in terms of PAH. The method has been in use for the past 20 years. Unfortunately, 12 to 24 hours are necessary for a separation. With the help of thin layer chromatography, absorption spectrophotometry, and spectrophotofluorimetry, a large number of arenes can be characterized. The weaknesses lie in the extended period of time necessary for such an investigation and the difficulty of identifying the alkyl derivatives.

4.5.2.2 Aza Arenes—Molecular characteristics of aza arenes useful in their separation are: (1) the size, shape, and steric property of the molecule, and (2) the polar effect of the structure on the capability of the ring nitrogen to bind to the adsorbent and to the eluting solvents. Thus, isomers such as the benzoquinolines, the benzacridines, and the dibenzacridines are readily separated from each other.

4.5.3 Paper Chromatography

Paper chromatography has been used in the past, but because it takes many hours for a separation, it is rarely used in routine assay of POM.

4.5.4 Instant Thin Layer Chromatography

Instant thin layer chromatography, a form of paper chromatography that permits fast separations, is primarily used in the analysis of benzanthrone and phenalenone. In 18 minutes, these compounds are readily separated from the many thousands of pollutants in organic particulates on glass fiber paper impregnated with silica gel. If necessary, a crude estimation of these compounds can be accomplished by visual comparison with standards. Otherwise, assay involves elution and fluorimetric estimation.

4.5.5 Thin Layer Chromatography

A large number of separations of POM are possible with thin layer chromatography (TLC).⁷ With the help of spectrophotometric and fluorometric techniques, a large variety of POM assays are available. With two different types of adsorbents on a plate, two widely differing types of separation are possible. Thus, it is

possible with such a plate to separate BaP and other penta- and hexa-cyclic arenes from each other. As yet gas chromatography cannot do this. The problem is that good technique is necessary, and routine assays of a large number of samples for PAH would be difficult. Direct examination of the spots with fluorescence scanners might solve the problem, however.

4.5.6 High Pressure Liquid Chromatography

Much better separation of pentacyclic and large PAH is obtained with the high pressure liquid chromatography than with gas chromatography. Separation can be completed in 15 to 30 minutes. Although standard PAH have been separated, the technique has not yet been applied successfully to ambient air particulates. This type of separation should be possible for the proper cleanup of the sample. The method has also been used successfully to separate standard mixtures of aza arenes.

4.5.7 Gas Chromatography

4.5.7.1 PAH—The gas chromatography (GC) system is superior for separating VPOM and, when allied with ultraviolet absorption spectrophotometry or some form of mass spectrometry, could evolve into one of the better state-of-the-art separation methods for the PPOM. Although some fine GC separations have been reported, difficulties have arisen in attempting to use these procedures routinely. Thus far, no satisfactorily proven method is available to separate benzo[a]pyrene from benzo[e]pyrene and chrysene from benz[a]anthracene.

For the near future, the best system for routine separation consists of column chromatographic cleanup of the organic particulates and then GC followed by ultraviolet spectrophotometric assay.

4.5.7.2 Aza Arenes—A few methods are available for the separation of standard aza arenes. Some work has been done with programmed temperature and coated high resolution glass capillary columns. About a dozen aza arenes were identified in ambient air particles by this technique.

4.5.8 Temperature Programming

Using a gas chromatograph with temperature programming from 20 to 400°C and a high resolution mass spectrometer interfaced with a digital computer, qualitative and quantitative results (in $\mu\text{g}/\text{m}^3$) can be obtained for a large number of pollutants in a short period of time. The VPOM and PPOM identified by this method in atmospheric aerosols are listed in Table 4-1. Although this is a good beginning, no data are available on the reliability of the identification and quantitative results.

Table 4-1. POM IDENTIFIED IN COLLECTED POLLUTANTS BY MEANS OF TEMPERATURE PROGRAMMING AND MASS SPECTROMETRY

Naphthalene	Benzo[a] pyrene
Methyl naphthalene	Perylene
2,3-Dimethylnaphthalene	Benzo[ghi] perylene
Trimethylnaphthalene	Dibenz[a,h] anthracene
Acenaphthene	Coronene
Anthracene	Acridine
Phenanthrene	Benzo[f] quinoline
Fluoranthene	Carbazole
Pyrene	2,6-Naphthoquinone
Benzo[c] phenanthrene	9,10-Anthraquinone
Benzo[a] anthracene	9-Xanthenone
Chrysene	

4.6 ANALYSIS

A decrease in the total analysis time and an improvement in sensitivity and accuracy have been the criteria in the evolution of the methodology and instrumentation for the determination of POM. Cost also plays an important role, however. The objective has been to develop simple, inexpensive methods of estimation as well as sophisticated, more accurate methods. The various types of separation methods described previously have been used by themselves or in combinations and with individual measuring methods described in this section. Many of the methods discussed below are reviewed in a paper by Sawicki.⁸

Pure standards of POM are needed for all analytical methods. For calibration, it is necessary to run recovery experiments and/or use an internal standard. In recovery experiments, the pure standard compound is added to the mixture as close to the first stage as possible. Internal standard compounds that do not interfere in the analysis are added to the mixture and assayed with the POM. For PAH analysis, s-triphenyl benzene or a PAH containing carbon-14 can be used as an internal standard, especially in gas chromatography.

4.6.1 Polynuclear Aromatic Hydrocarbons

4.6.1.1 Ultraviolet Spectrophotometry—The method that has been used most frequently in the routine analysis for PAH consists of column chromatography followed by ultraviolet-visible absorption spectroscopic scanning of the fractions to permit characterization and assay. This procedure, accompanied by thin layer chromatography and spectrophotofluorimetry, is probably the best way to initiate a study of unknown mixtures for PAH. Although this method takes too much time for routine analysis, it can be used following GC separation to analyze the GC fractions for the individual PAH. The best separations can probably be achieved by column chromatography with long columns; however, the time of separation is increased.

4.6.1.2 Spectrophotofluorimetry—This method can be used after column chromatographic, gas chromatographic, and two-dimensional thin layer chromatographic separations.⁹ Care must be exercised to minimize quenching phenomena, intensity enhancement, and excimer formation—especially on dry chromatograms.

The Shopl'skii procedure, which has been used extensively in the USSR, consists of column chromatography followed by fluorescence analysis at low temperatures. Internal reference standards are used for the determination of individual PAH's. The present method is long and tedious and could be improved.

Another method that has been used consists of two-dimensional TLC followed by direct fluorimetric scanning. This procedure can be automated.

4.6.1.3 Direct Fluorimetry—This procedure involves drawing the air samples through a liquid bubbler followed by fluorescence assay of the liquid in terms of anthracene. The main problem in using this crude method is the effect of the various components of the mixture on the intensity and wavelength positions of the characteristic emission bands. A fluorescence detector can be used in the gas or liquid phase to obtain total PAH values. A wide range of sensitivities for different PAH is also available. Such a detector has been used in the direct gas phase analysis of automotive exhaust for total PAH.

4.6.1.4 High Pressure Liquid Chromatography—High pressure liquid chromatography (HPLC) has high potential, especially with cleanup of the sample followed by HPLC using an ultraviolet or fluorescence detector. With automated procedures for spectral scanning and assay of the fractions, HPLC could be developed into a fast routine method.

4.6.1.5 Gas Chromatography—Probably the best state-of-the-art routine technique, which could be developed within 6 months, would involve sample cleanup, followed by GC and ultraviolet spectral assay of

the GC fractions. The simplest method would be temperature programming, or controlled sublimation of the particulate fraction into a gas chromatograph for direct assay.

Several available methods employ procedures for extracting the organic material from the particles followed by a preliminary cleanup of this material and GC analysis. Because of the conflicting claims made by various investigators, these methods need to be evaluated impartially before they are adopted as routine techniques.

4.6.1.6 Mass Spectrometry—Many variations of mass spectrometry (MS) are used in the analysis of PAH. A large amount of data can be obtained.¹⁰ The GC-MS method has been used in the analysis of VPOM and PPOM in cigarette smoke and in airborne particles. Many POM compounds have been characterized in the fractions from the column chromatographic analysis of extracts of organic particulates with the help of high resolution mass spectrometry.

One procedure involves TLC followed by MS. Using internal standards and an integrated ion current technique, the detection limit was reported to be 0.05 picogram (pg) of BaP, 0.01 pg of benzo[ghi]perylene, and 0.01 pg of coronene.

With the help of internal standards and a controlled evaporation rate, an organic particulate fraction can be analyzed directly for the PAH content. With this procedure, the PAH in a sample can be determined within 10 minutes with sensitivity as low as 0.5 ng.

The various types of mass spectrometric techniques should be evaluated in the analysis of VPOM and PPOM — for example, chemical ionization MS, field ionization MS, and field desorption MS.

4.6.1.7 Flame Ionization Detector—When properly used, the flame ionization technique should produce accurate total PAH values; however, the sensitivity may vary for different compounds.

4.6.1.8 Discussion—Liquid chromatography, gas chromatography, and mass spectrometry are evolving rapidly. They are the hope of the future in terms of sophisticated automated measurements. It is possible that with mass spectrometry, in particular, a large amount of data can be made available. EPA has access to mass spectral signatures of about 15,000 organic compounds, several of which are in the PPOM group.

4.6.2 Benzo[a]pyrene

Some form of separation is necessary before BaP can be determined. Some of the measuring techniques are discussed here.

4.6.2.1 Ultraviolet Spectrophotometry—Probably the best characterization method for BaP consists of alumina column chromatographic separation of the pentane-ether extracts followed by an absorption spectral scan of its ultraviolet spectrum in pentane. In this solvent, BaP shows a highly distinctive triplet at 377, 379, and 382 nm. No other hydrocarbon gives this triplet in pentane.

Separation by sublimation, column chromatography, thin layer chromatography, or gas chromatography can be used preliminary to analysis. With proper cleanup, a high pressure liquid chromatographic procedure for BaP could be developed.

4.6.2.2 Room Temperature Fluorimetry—This method of analysis is approximately 100 to 1000 times more sensitive than the ultraviolet spectral method and provides a high order of selectivity for BaP. One disadvantage is that invalid results from unrecognized quenching effects could be obtained. This could affect the position and intensity of fluorescence emission bands used in characterization and assay.

Separation procedures used preliminary to analysis include liquid-liquid extraction, column chromatography, TLC sublimation, and GC. One of the most sensitive methods consists of TLC followed by

elution and fluorimetric analysis of a sulfuric acid solution of the benzpyrene fraction. Probably the best separation method for BaP consists of two-dimensional TLC on alumina-cellulose acetate. BaP is separated from all other hydrocarbons and can be eluted and analyzed fluorimetrically as the neutral compound or as the cationic salt. At least 20 μg of a benzene-soluble fraction would be necessary; the lower limit of detection would be about 10 ng of BaP.

4.6.2.3 Low Temperature Fluorimetry—Following any of the separation methods described previously, BaP could be analyzed by low temperature fluorimetry. Since the bands would be much more intense and much narrower, the analysis would be much more sensitive and highly selective. A disadvantage is that the liquid nitrogen is required.

4.6.2.4 Shopl'skii Effects—In Shopl'skii procedure, quasilinear spectra are obtained from frozen crystalline solutions wherein the dimension of the solute molecule is approximately equal to that of the solvent molecule. BaP with a molecular length of 1.0 nm gives its sharpest spectrum in n-heptane (1.0 nm). For example, pyrene in methylcyclopentane has several bands at room temperature — 70 lines at 88° and 120 lines at 9°K. An internal standard must be used in the method, and only the best separation techniques should be used. Increased sensitivity and selectivity are obtained with the method, but very low temperatures are required.

4.6.2.5 Direct Spectrophotofluorimetry—After one- or two-dimensional TLC, BaP can be assayed directly on the plate by direct spectrophotofluorimetry. This is a convenient method of characterization and assay.

4.6.2.6 High Pressure Liquid Chromatography—This method could be used as a fast survey method for BaP after proper cleanup.

4.6.2.7 Gas Chromatography—A method of assay involving either sublimation or ultrasonic extraction followed by gas chromatography should be developed.

4.6.2.8 Mass Spectrometry—This method of assay could be used following any of the methods of separation previously described, but it would be too expensive to be used for the analysis of BaP.

4.6.2.9 Colorimetry—The method employs a piperonal test on the nonpolar organic fraction of airborne particles. A fairly good correlation has been obtained between the piperonal value and the BaP concentration in a large number of samples. The main disadvantage of the method is the use of highly corrosive trifluoroacetic acid.

4.6.3 Polycyclic Aza Arenes

Probably the best way to examine an unknown mixture for polycyclic aza arenes (PAA) is to isolate the basic fraction, chromatograph it through an alumina column, scan each fraction spectrally from 200 to 500 nm, quantitate by the base-line method, separate each fraction by TLC, and scan each spot fluorimetrically before and after elution and before and after addition of acid.

Estimation of PAA is by alumina column chromatography UV-visible absorption spectrophotometry, or by gas chromatography. Pure standards have to be used throughout these procedures. When standards are not available, analysis is impossible.

Some of the individual PAA are readily assayed by TLC-fluorimetry using fluorescence-quenching methods to eliminate the fluorescence of interferences.

4.6.4 Monocarbonyl Arenes

Both TLC and instant TLC methods have been used to analyze monocarbonyl arenes fluorimetrically. At least 15 μg of the organic particulate fraction is necessary for the analysis of phenalenone and benzanthrone; the detection limit is about 20 ng phenalenone and 10 ng benzanthrone.

4.6.5 Residue Analysis

In all analytical methods, blanks should be run routinely. Benzene should be reagent grade and redistilled. PAH is not normally found in the routinely purified solvents, however, in fluorescence methods of analysis, impurities will affect results. Therefore, glass distilled solvents must be used in this type of analysis.

4.6.6 Precision and Accuracy

No universally acceptable quantitative values are available for the precision and accuracy of measurement techniques for POM. A limited discussion of the precision and accuracy of some of the methods treated here is given in the Intersociety Committee Manual.¹¹ For example, based upon 11 determinations using 560 µg BaP/g extract, the relative standard deviation was calculated to be ± 7 percent. The elution of pure BaP from activated alumina was 95 percent (± 5 percent) efficient based upon more than 20 determinations. Unfortunately these limited data do not provide a realistic basis for conclusions regarding the accuracy of ambient atmospheric measurements. Accuracy data reported in the literature are usually based upon the recovery of added material or the recovery of an added radioactive standard. However, this is no guarantee that what is found in the test mixture is representative of what was in the ambient atmosphere. The accuracy of ambient air measurements is highly dependent upon collection techniques and instrument efficiency as well as analytical methodology. Accuracy of measurement also may vary with different POM compounds. Consequently, it is not necessarily meaningful to talk about the accuracy of ambient air data. It is perhaps more meaningful to view the program in terms of relative precision and sensitivity, although this also has not been well established. It seems to be a rather general consensus among those actively engaged in ambient measurements that a sensitivity of ± 0.1 ng/m³ and a relative precision within ± 25 percent are reasonable values for concentrations well within the range of detectability. One may be reasonably confident in using published ambient air data on POM in categorizing the concentration values as high, medium, or low. In a practical sense, this is the way the data are used. It is questionable, however, whether one would be justified in using the data to evaluate second order terms in sophisticated mathematical models involving kinetics or atmospheric transport.

4.7 REFERENCES

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5. CONCENTRATIONS IN AMBIENT AIR

5.1 INTRODUCTION

In 1961 Sawicki and co-workers compiled a list of some 60 polycyclic organic compounds identified as either being present in the air or as emitted to the air from a few familiar sources. This list, partially updated during preparation of this document by the addition of several aza heterocyclics and other compounds, is presented in Table 5-1. The potential carcinogenicity of a compound is indicated if so reported in the Public Health Service survey of organic compounds for carcinogenicity.² A thorough search of recent literature would probably provide sufficient newly identified compounds to double the length of the list. As presented, this list of almost 100 compounds is adequate to illustrate the complexity of PPOM and define the enormous effort required to bring order out of the existing state of chaos. The problems of accuracy in measurement as discussed in section 4.6.6 are a further complication that must be considered.

5.2 EARLY MEASUREMENTS OF AMBIENT PARTICULATE POLYCYCLIC AROMATIC HYDROCARBONS

The first large-scale attempt to measure ambient air concentrations of PAH was made by Sawicki and co-workers³ who conducted two studies of BaP content. One involved the analysis of samples collected from January through March 1959 at 94 urban and 28 nonurban NASN sampling stations. None of its results is presented here because of its preliminary nature and short period covered.

Table 5-1. POLYCYCLIC COMPOUNDS FOUND IN AIR, CIGARETTE SMOKE, AND EXHAUST GASES^{1,2}

Compound	Occurrence ^a
Naphthalene	A T
2-Methylnaphthalene	A T
Alkyl naphthalenes	A
Azulene	A T
Acenaphthene	A T
Acenaphthylene	A T
Dibenzofuran	A
Carbazole	A
Dibenzothiophene	A
Fluorene	A T
Anthracene (A) ^b	A T
Phenanthrene	A T
2-Methylanthracene	T
11H-Benzo[b] fluorene	A
11H-Benzo[a] fluorene	A T
7H-Benzo[c] fluorene	A
Fluoranthene (Fluor) ^b	A T
8-Methylfluoranthene	T
Alkyl fluoranthene	T

Table 5-1. (continued). POLYCYCLIC COMPOUNDS FOUND IN AIR, CIGARETTE SMOKE, AND EXHAUST GASES^{1,2}

Compound	Occurrence ^a
Naphthacene	G
Benz[a]anthracene (BaA) ^{b,c}	A T
Chrysene (Ch) ^{b,c}	A T
Alkyl chrysene	T
Benzo[c]phenanthrene ^c	T
Pyrene (P) ^b	A T G D
1-Methylpyrene	A T
4-Methylpyrene	T
2,7-Dimethylpyrene	A
Naphtho[2,1,8,7-klmn]xanthene	T
10,11-Dihydro-9H-benzo[a]cyclopent[i]anthracene	T
2,3-Dihydro-1H-benzo[a]cyclopent[h]anthracene	T
7H-Dibenzo[c,g]carbazole ^c	T
Benzo[b]fluoranthene ^c	A T G D
Benzo[ghi]fluoranthene	A T
Benzo[j]fluoranthene ^c	A T
Benzo[k]fluoranthene (BkF) ^b	A T G D
2-Methylfluoranthene ^c	T
Methylfluoranthene	T
Benzo[a]naphthacene	T
Dibenzo[b,h]phenanthrene	T G D
Dibenz[a,h]anthracene ^c	T
Benzo[a]pyrene (BaP) ^{b,c}	A T G D
Methylbenzo[a]pyrene	T
Hydroxybenzo[a]pyrene	T
Benzo[a]pyrenequinone	A
Benzo[e]pyrene (BeP) ^{b,c}	A T
Perylene (Per)	A T
Dibenzo[a,1]naphthacene	A G D
Dibenzo[a,j]naphthacene	T
Naphtho[2,1,8-qr]naphthacene (Naphtho[2,3-a]pyrene) ^b	T
Phenalen-1-one	A
Dibenzo[a,i]pyrene ^c	A T
Dibenzo[a,e]pyrene	T G D
Dibenzo[cd,jk]pyrene (anthanthrene) ^b	A T G D
Dibenzo[cd,jk]pyrene-6,12-dione (anthanthrone) ^b	A
Benzo[ghi]perylene (BghiP) ^b	A T G D
Dibenzo[b,pqr]perylene	G
Coronene (Cor) ^b	A T
Dibenzo[a,h]pyrene ^c	A T
Tribenzo[a,i]fluorene	T
13H-Dibenzo[a,i]fluorene	T
Dibenzo[a,c]naphthacene	T
Benzo[h]quinoline	A
Ra-Benzo[h]quinoline ^d	A
Rb-Benzo[h]quinoline ^d	A
Benz[c]acridine	A G
Ra-Benz[c]acridine ^d	A
Rb-Benz[c]acridine ^d	A
Dibenz[a,h]acridine ^c	A T

Table 5-1. (continued). POLYCYCLIC COMPOUNDS FOUND IN AIR, CIGARETTE SMOKE, AND EXHAUST GASES^{1,2}

Compound	Occurrence ^a
Ideno[1,2,3-ij] isoquinoline	A G
Phenanthridine	A
11H-Indeno[1,2-b] quinoline	A
Acridine	A
Benzo[f] quinoline	A
Ra-Benzo[f] quinoline ^d	A
Rb-Benzo[f] quinoline ^d	A
Benz[a] acridine ^d	A
Rb-Benz[a] acridine ^d	A
Dibenz[a,j] acridine ^c	A T
Rb-Dibenz[a,j] acridine	A
7H-Benz[de] anthracen-7-one	A
Indeno[1,2,3-cd] pyrene ^c	A
Dibenz[e,1] pyrene ^c	A
Xanthene-9-one	A
Dibenz[a,i] acridine	A

^aA: air; T: tobacco smoke; G: gasoline exhaust; D: diesel exhaust.

^bAbbreviations used for most common compounds in ().

^cReported by PHS to have carcinogenic activity.

^dR-alkyl groups: substituted alkyl groups; Ra and Rb: various substitutes.

The other study was more intensive; monthly composite samples from several different sites in nine cities collected from July 1958 through June 1959 were analyzed in detail.

The monthly average BaP concentration for each city for the 12-month period is shown in Table 5-2. Except for New Orleans, the highest concentrations of BaP were found during the colder months. The greatest ranges in concentrations from winter to summer occurred in the coal-burning or heavily industrialized cities of Birmingham and Nashville.

Data for ambient concentrations of eight different PAH compounds for the winter (January and February) and summer (July) for seven of the nine cities are given in Table 5-3. There was a distinct contrast between winter and summer concentrations, with summer concentrations generally considerably lower. The New Orleans data appeared anomalous for some of the compounds, although at best only rough comparisons can be made on the basis of a single month's data for each season.

5.3 ROUTINE MEASUREMENTS OF BaP ON SUSPENDED PARTICULATE MATTER COLLECTED BY NASN

For several years, the benzene-soluble organics (BSO) of quarterly composite samples of suspended particulate matter collected by the approximately 250 NASN stations have been analyzed for BaP. Data for urban stations are listed in Table 5-4 and for nonurban stations in Table 5-5.^{4,5} The data, in the form of annual arithmetic averages, are listed only for years with four quarters of valid data. Thus the values are as representative as possible of the entire year.

Table 5-2. BENZO [a] PYRENE CONTENT OF THE AIR OF SELECTED CITIES³
(ng/m³)

City	1958						1959					
	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June
Atlanta	1.6	4.0	4.0	-	15	12	9.9	7.4	2.1	2.1	-	3.6
Birmingham	6.4	6.1	10	20	34	74	34	25	23	18	5.9	6.3
Cincinnati	3.9	1.3	2.5	15	14	18	18	18	26	-	2.0	2.1
Detroit	6.0	4.1	-	18	19	20	28	31	16	12	7.4	3.4
Los Angeles	0.5	0.4	1.2	1.2	4.1	13	6.6	5.3	1.1	0.5	0.8	0.8
Nashville	1.4	-	6.6	30	55	40	25	-	-	9.0	3.4	2.1
New Orleans	2.0	4.1	4.1	3.9	3.6	3.9	6.0	4.1	2.6	3.3	5.6	2.6
Philadelphia	3.5	1.9 ^a	3.6	7.1	12	12	8.8	6.4	6.4	-	3.4	2.5
San Francisco	0.25	0.38	1.1	-	3.0	7.5	2.3	2.4	1.3	0.8	0.8	0.9

^aCorrected value based on Figure 3 of reference 3 and comments by the senior author of reference 3.

Table 5-3. POLYCYCLIC AROMATIC COMPOUNDS IN THE AIR OF SELECTED CITIES¹
(ng/m³)

City	BghiP	BaP	BeP	BkF	P	Cor	Per	A	Total
Winter 1959									
Atlanta	8.9	7.4	4.7	6.0	6.0	4.3	1.1	0.5	38.9
Birmingham	18	25	10	13	17	3.5	5.5	2.2	94.2
Detroit	33	31	23	20	36	6.4	6.0	2.0	146.4
Los Angeles	18	5.3	8.1	5.7	6.0	12	1.6	0.2	56.9
Nashville	17	25	14	15	30	4.6	4.4	1.8	111.8
New Orleans	7.3	4.1	6.4	3.9	2.3	27	0.8	0.1	27.6
San Francisco	7.5	2.3	2.9	1.7	1.9	4.9	0.3	0.1	21.6
Summer 1958									
Atlanta	5.1	1.6	1.5	1.3	0.7	2.5	0.4	0.2	13.3
Birmingham	8.3	6.4	5.9	4.6	2.1	2.4	2.1	0.3	32.1
Detroit	9.5	6.0	5.3	4.9	2.8	1.8	1.7	0.4	32.4
Los Angeles	2.3	0.5	0.6	0.5	0.3	2.2	0.03	0.0	6.4
Nashville	3.4	1.4	1.2	1.0	0.6	1.3	0.2	0.1	9.2
New Orleans	4.6	2.0	3.1	1.8	0.3	2.5	0.4	0.1	14.8
San Francisco	2.6	0.3	0.5	0.2	0.1	1.6	<0.1	0.02	5.4

Table 5-4. ANNUAL AVERAGE AMBIENT BENZO [a] PYRENE CONCENTRATIONS
AT NASN URBAN STATIONS^{4,5}
(ng/m³)

Station	1966	1967	1968	1969	1970
Alabama					
Birmingham	18.5				
Gadsden	3.5		2.4	1.8	2.5
Huntsville		3.1	2.7	1.8	1.6
Mobile	6.5		4.2	2.6	
Montgomery		2.3	2.9	2.0	1.3
Alaska					
Anchorage	2.3	1.9	1.7	1.3	0.8
Arizona					
Phoenix	1.7	2.5	2.1	2.2	
Tucson	0.6	0.7	0.7	0.5	0.4
Arkansas					
Little Rock	1.2	0.9	0.9	1.1	0.7
West Memphis	1.1	2.2	2.2	2.4	0.6
California					
Burbank	2.5			2.9	1.9
Glendale		1.0	1.6	1.6	1.0
Long Beach		2.1	2.1	2.3	1.0
Los Angeles	2.1	1.3	1.8	1.9	1.2
Oakland	2.7	1.7	1.6	1.6	1.0
Ontario			0.9	0.6	0.6
Pasadena	1.8		2.3		0.7
Riverside			1.3	0.8	0.7
Sacramento			1.4	1.8	0.7
San Bernardino			1.0	0.9	0.8
San Diego	1.7	1.6	1.2	1.4	0.7
San Francisco	1.1	1.5	1.8	1.2	0.6
Colorado					
Denver	2.3	2.4	2.3	2.5	2.2
Connecticut					
Hartford	2.3	2.1	1.4	2.0	1.4
New Haven	3.5	1.9	1.4	2.1	1.2
Delaware					
Newark	1.0	1.4	0.9		0.4
Wilmington	2.2	2.7	1.9	1.7	1.1
District of Columbia					
Columbia	2.4	1.9	1.9	4.3	
Florida					
Jacksonville			2.9	2.3	1.4
Tampa			1.5	1.0	0.5

**Table 5-4 (continued). ANNUAL AVERAGE AMBIENT BENZO [a] PYRENE
CONCENTRATIONS AT NASN URBAN STATIONS^{4, 5}
(ng/m³)**

Station	1966	1967	1968	1969	1970
Georgia Atlanta	1.4	3.0	1.8	1.9	0.9
Hawaii Honolulu	0.2	0.5	0.6	0.6	0.2
Idaho Boise City	3.5	2.4	2.0	6.0	1.1
Illinois Chicago Springfield	3.3	3.0	3.1 1.1	3.9 1.3	2.0 0.9
Indiana East Chicago Hammond Indianapolis Muncie New Albany South Bend Terre Haute	6.8 3.9 10.4 2.4 5.4 2.2	5.7 2.5 5.7 1.6 2.6 3.7	1.9 2.1 4.1 3.7	6.8 3.3 5.2 4.3 3.7 4.0	5.3 1.7 2.3 3.7 2.4 2.8
Iowa Davenport Des Moines Cedar Rapids	3.2 2.5	2.7 0.8	1.1 0.7	1.7 0.9	0.9 0.7 0.3
Kansas Kansas City Topeka Wichita	1.2 0.8	0.5 0.5	1.2 0.7 1.0	1.1 0.4 0.7	2.4 0.3 0.5
Kentucky Ashland Covington Lexington Louisville	10.5 3.1 2.5	1.9 1.8 2.1	9.3 3.6 3.0 2.7	10.9 4.1 1.9	6.7 4.4 1.6
Louisiana New Orleans	2.3	1.8	1.6	1.5	1.1
Maine Portland			2.3		1.1
Maryland Baltimore	2.8	3.8	2.3	2.8	2.1

Concentrations in Ambient Air

Table 5-4 (continued). ANNUAL AVERAGE AMBIENT BENZO [a] PYRENE
CONCENTRATIONS AT NASN URBAN STATIONS^{4,5}
(ng/m³)

Station	1966	1967	1968	1969	1970
Massachusetts Worcester			1.7	1.5	1.6
Michigan Detroit	4.7	5.4	5.1	3.9	2.6
Flint		1.4	0.8	1.7	1.5
Grand Rapids		2.8	3.4	1.7	0.9
Trenton			1.4	1.6	0.8
Minnesota Duluth	2.2		2.7	2.1	1.1
Minneapolis	1.6	1.3	1.1	1.4	0.6
Moorhead	0.7		0.9	1.0	1.6
St. Paul	1.8	2.3	1.8	1.8	1.0
Missouri Kansas City			1.8	1.6	1.1
St. Louis		2.3		3.3	
Montana Helena		0.8	0.9	0.5	
Nebraska Omaha	2.7	1.3	1.9	1.6	1.0
Nevada Las Vegas	1.3	1.1	1.4		
Reno		4.6	3.1		
New Hampshire Concord	0.6	1.5	1.0	0.7	0.6
New Jersey Camden	3.0		1.6	2.4	1.9
Glassboro	0.7	0.8	1.2	1.1	1.2
Jersey City	4.2	3.5	2.3	2.7	4.7
Marlton	1.2	1.6	1.3		1.4
Newark	2.1	3.3	2.1	1.8	1.5
Patterson		1.9	2.0	1.2	1.2
Perth Amboy	2.1	2.1	1.2	1.2	1.0
Trenton	2.2		1.0	1.5	1.1
New Mexico Albuquerque	2.0	1.9	1.8	1.1	1.1
New York New York City	4.1	3.9		3.6	3.0

**Table 5-4 (continued). ANNUAL AVERAGE AMBIENT BENZO[a] PYRENE
CONCENTRATIONS AT NASN URBAN STATIONS^{4,5}**
(ng/m³)

Station	1966	1967	1968	1969	1970
North Carolina					
Charlotte	5.7	6.3	5.6	4.9	1.9
Durham			8.0	3.4	3.9
North Dakota					
Bismarck			0.9	1.0	0.4
Ohio					
Akron	4.1	3.7	3.0		
Cincinnati	3.6	1.9	1.8	2.9	2.6
Cleveland	3.1	2.9	3.0	3.8	2.8
Columbus	2.9	1.7	2.2	2.7	1.6
Dayton	2.7	3.7	2.4	1.9	1.5
Toledo	1.8	1.9	1.8	1.5	1.4
Youngstown	7.3	8.2	5.6	9.9	7.1
Oklahoma					
Oklahoma City	1.5	0.7	0.7	0.7	0.9
Tulsa	0.7	0.6	0.8	0.5	0.8
Oregon					
Eugene		2.4			
Medford		4.8	8.2	4.1	
Portland	3.3	3.5	4.1	2.6	2.3
Pennsylvania					
Allentown		1.8	1.2	1.9	2.4
Altoona		29.5	18.0	22.3	19.3
Bethlehem		2.9	2.1	2.0	2.7
Harrisburg			1.3	1.5	1.5
Lancaster	2.3				
Philadelphia	3.8	5.9	2.9	4.0	2.4
Pittsburgh	4.9	7.0	6.3	13.8	5.9
Reading	2.3	2.9	2.4	1.8	1.6
Scranton		5.2	6.1	7.7	2.9
Warminster	0.9	2.2	0.9	1.0	
West Chester		1.1	1.0	1.3	
Wilkes Barre			1.6	1.5	1.3
York		1.8	1.9	2.0	1.2
Rhode Island					
East Providence		1.6	1.2	1.2	1.2
Providence	3.6	2.8	2.0	2.2	2.1
South Carolina					
Columbia		4.2	6.2	1.3	
Greenville	5.0		18.6	7.0	3.4

Concentrations in Ambient Air

**Table 5-4 (continued). ANNUAL AVERAGE AMBIENT BENZO [a] PYRENE
CONCENTRATIONS AT NASN URBAN STATIONS^{4,5}
(ng/m³)**

Station	1966	1967	1968	1969	1970
Tennessee					
Chattanooga	8.4	22.9	7.4	4.2	5.5
Knoxville		7.0	9.8	4.7	
Memphis	1.7	1.6	1.3	0.7	1.4
Nashville	5.5	7.0	6.0	2.8	3.6
Texas					
Dallas	1.4			2.0	1.9
Houston	0.9				1.2
San Antonio	0.6	1.4	0.9	0.6	1.0
Utah					
Ogden	0.5		0.8	0.7	2.5
Salt Lake City	1.2	0.7	1.0	0.7	1.4
Vermont					
Burlington	0.8		0.7	0.5	0.7
Virginia					
Danville	3.2		2.5	1.8	2.7
Hampton		2.2	1.5	0.9	1.1
Lynchburg		9.2	8.7	6.3	4.5
Norfolk	2.8	3.5	4.9	3.9	1.8
Portsmouth		7.7	10.2	3.4	4.9
Richmond		5.2		2.2	2.1
Roanoke		7.5	7.7	5.3	6.2
Washington					
Seattle	2.7	1.8	2.0	1.6	1.5
West Virginia					
Charleston	3.4		4.6	2.6	2.1
Wisconsin					
Kenosha			1.4	1.7	1.3
Madison			1.3		1.1
Milwaukee	4.1		4.7	4.0	2.5
Superior			3.3	1.6	1.5
Wyoming					
Casper			0.9	0.6	0.4
Cheyenne	0.5		0.6	0.5	0.4

**Table 5-5. ANNUAL AVERAGE AMBIENT BENZO [a] PYRENE
CONCENTRATIONS AT NASN NONURBAN STATIONS^{4,5}
(ng/m³)**

Station	1966	1967	1968	1969	1970
Arizona					
Grand Canyon	0.3	0.2	0.2	0.2	0.1
Maricopa County		0.2	0.5	0.3	0.3
Arkansas					
Montgomery County	0.3	0.1	0.2	0.2	0.1
California					
Humboldt County	0.4	0.4	0.3	0.5	0.1
Idaho					
Butte County			0.2	0.1	0.1
Indiana					
Monroe County	0.5		0.5	0.3	0.2
Parke County	0.9		0.4	0.3	0.4
Maine					
Acadia Natl Park	0.2		0.3	0.1	0.2
Missouri					
Shannon County		0.2	0.2	0.2	0.2
Montana					
Glacier Natl Park		0.3	0.4	0.4	
Nebraska					
Thomas County	0.2		0.2	0.1	0.1
Nevada					
White Pine County	0.1		0.1	0.1	0.1
New Hampshire					
Coos County	0.2	0.2	0.2	0.1	0.1
New York					
Jefferson County	0.2		0.2	0.3	0.2
North Carolina					
Cape Hatteras	0.2		0.2	0.1	0.2
Oklahoma					
Cherokee County	0.2	0.2	0.2	0.2	0.2
Oregon					
Curry County	0.1	1.1	0.1	0.1	0.1
Pennsylvania					
Clarion County	1.5	2.1	1.0	1.2	1.2

Concentrations in Ambient Air

**Table 5-5 (continued). ANNUAL AVERAGE AMBIENT BENZO [a] PYRENE
CONCENTRATIONS AT NASN NONURBAN STATIONS^{4,5}
(ng/m³)**

Station	1966	1967	1968	1969	1970
Texas Matagorda County	0.3	0.1	0.2	0.1	0.3
Vermont Orange County	0.9		0.3	0.3	0.2
Virginia Shenandoah Natl Park	0.9	0.3	0.3	0.3	0.2

With only an occasional exception, the annual averages for the urban sites were remarkably consistent from year to year for the period covered. Study of the data uncovers a number of facts: ambient levels are not necessarily related to city size; cities like Los Angeles with high BSO levels generally attributed to auto exhaust emissions and subsequent photochemical reactions do not necessarily have high ambient concentrations of BaP; high concentrations are usually associated with heavily industrialized coal-burning cities (Birmingham, Ashland, Pittsburgh); highest concentrations are exhibited in Altoona, which relies on coal for heating purposes, and because of meteorological and geographical factors, is subject to frequent fumigations from this source during the winter months. Many urban areas enjoy low ambient levels because of the lack of contributing sources.

Concentrations at the nonurban stations were quite low, with the more remote stations (Idaho, Nevada, Oregon) approaching minimum detectable levels. The higher levels occurring at the Clarion County, Pennsylvania, station were no doubt due partly to its location downwind from the Pittsburgh-Youngstown-Akron-Cleveland industrial complex. Domestic heating systems in the area may also contribute, although these sources were probably minor as this station exhibits no pronounced seasonal pattern, as Figure 5-1 shows.

Seasonal variations at three urban and two nonurban NASN sites over a 2-year period are graphically shown in Figure 5-1. The graph not only shows the difference between sites but dramatically demonstrates the influence of community parameters on the seasonal pattern as well.

The ratios of BaP concentrations to total suspended particulate (TSP) and BSO concentrations have been computed for each of 3 years for approximately 100 urban and 19 nonurban NASN stations. These ratios are shown in Table 5-6 and 5-7. To provide whole numbers for easier comparisons, the BaP/TSP ratio has been multiplied by 100,000 and the BaP/BSO ratio by 10,000. Although many differences can be detected by comparison of Tables 5-4 and 5-5 to 5-6 and 5-7, there are certain similarities. For Altoona and Ashland, which have high BaP concentrations, both ratios for each city were high also. Pittsburgh and Youngstown, with fairly high BaP levels, showed high BaP/BSO ratios, indicating the high BaP content of the BSO fraction. Tucson, with low BaP levels, showed low ratios. Los Angeles had unusually low BaP/BSO ratios because of the low levels of BaP and the high concentrations of BSO characteristic of that city. Most of the nonurban stations appeared to follow the same general pattern, with Clarion County, Pennsylvania, again having unusually high ratios in both cases.

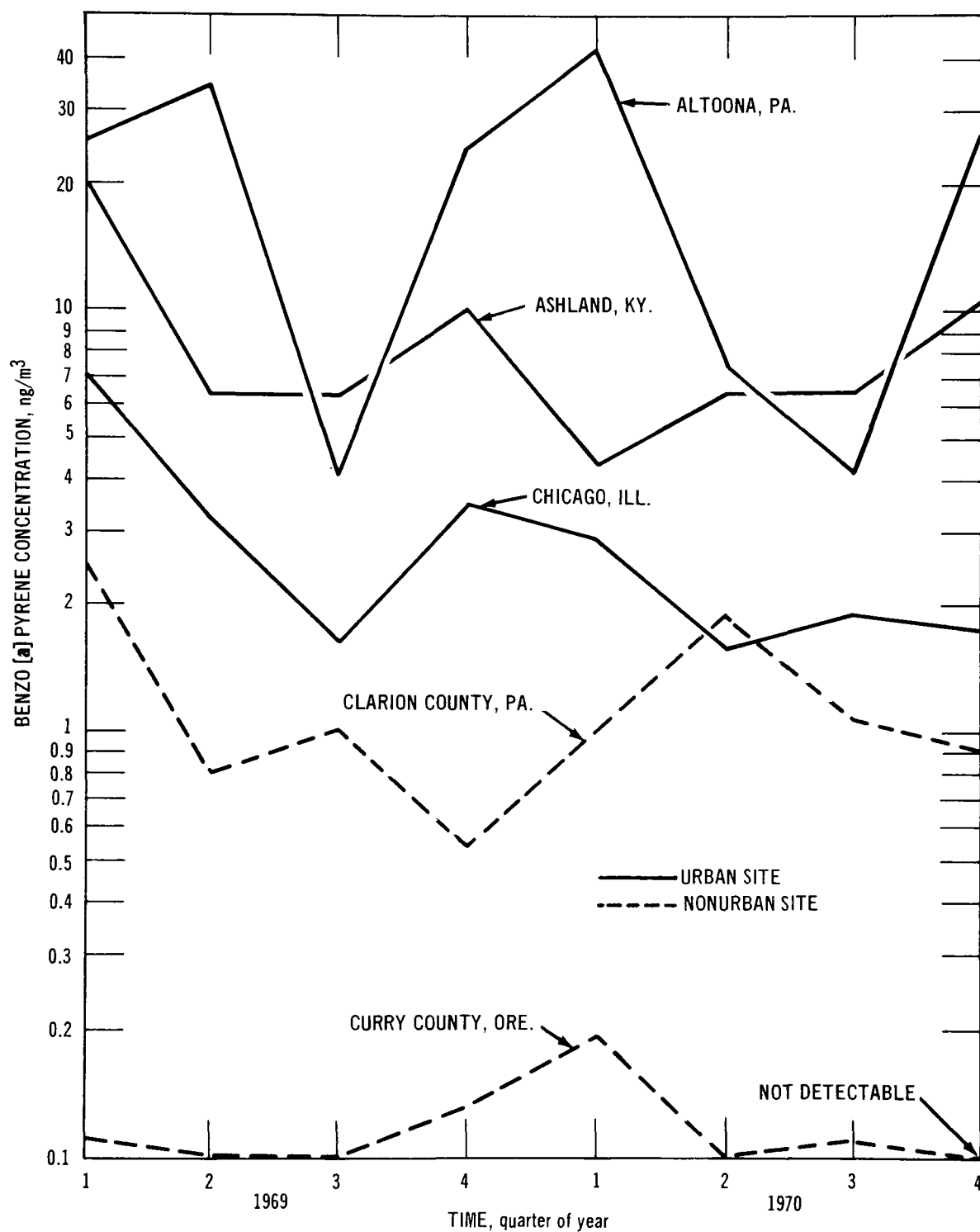


Figure 5-1. Seasonal variations of benzo[a] pyrene at selected NASN stations.

5.4 BIRMINGHAM, ALABAMA, STUDY

During 1964 and 1965, Hauser and coworkers⁶ carried out a detailed study of POM from samples collected at 10 different sites in Birmingham and suburbs. Seasonal composites comprised of 30 to 50 individual samples were obtained for each of the 10 sites, extracted with benzene, and the benzene soluble fraction was analyzed for 10 different PAH compounds. Annual average concentrations for each compound for each site are shown in Table 5-8; the seasonal average of each hydrocarbon for the Greater Birmingham area is given in Table 5-9; and interrelationships between the different polycyclics, the particulate sample, and the benzene soluble fraction are shown in Table 5-10. Table 5-10 suggests that, in situations comparable to those existing in Birmingham, measurement of any one of the polycyclic hydrocarbons would provide a data base for use in computing concentrations of any of the others with some degree of accuracy. It must be recognized, however, that extrapolation from one urban atmosphere to another is not possible because of the variations in the emissions from different sources.

Table 5-6. RATIOS OF BENZO [a] PYRENE TO TOTAL SUSPENDED PARTICULATES AND TO BENZENE-SOLUBLE ORGANICS AT NASN URBAN STATIONS^{4,5}

Station	BaP/TSP ^a			BaP/BSO ^a		
	1968	1969	1970	1968	1969	1970
Alabama						
Gadsden	2.6	2.8	3.1	2.9	4.6	6.4
Huntsville	4.3	2.8	2.4	4.7	4.2	4.0
Montgomery	3.6	2.4	1.4	2.8	2.6	2.1
Alaska						
Anchorage	2.2	1.2	0.9	3.1	2.3	1.8
Arizona						
Tucson	0.9	0.6	0.4	1.9	1.7	1.2
Arkansas						
Little Rock	1.2	1.3	0.9	1.6	1.8	1.7
West Memphis	2.5	3.0	0.7	3.7	4.6	1.7
California						
Glendale	1.6	2.1	1.1	1.3	1.9	1.4
Long Beach	1.6	2.0	1.0	1.6	2.8	1.9
Los Angeles	1.4	1.8	0.9	1.2	1.5	1.4
Oakland	1.8	2.0	1.4	2.4	2.5	2.3
Ontario	0.7	0.4	0.4	1.2	1.0	0.9
Riverside	1.0	0.6	0.4	1.4	1.1	1.0
Sacramento	2.0	2.9	0.5	2.0	2.5	1.9
San Bernardino	0.9	0.8	1.0	1.5	1.5	0.9
San Diego	1.8	1.7	0.6	2.1	2.1	1.8
San Francisco	2.0	2.0	1.2	1.6	2.4	2.0
Colorado						
Denver	2.0	1.9	1.7	2.9	2.8	2.7

Table 5-6 (continued). RATIOS OF BENZO [a] PYRENE TO TOTAL SUSPENDED PARTICULATES AND TO BENZENE-SOLUBLE ORGANICS AT NASN URBAN STATIONS^{4, 5}

Station	BaP/TSP ^a			BaP/BSO ^a		
	1968	1969	1970	1968	1969	1970
Connecticut Hartford New Haven	2.1 1.9	2.8 2.2	2.0 1.2	3.2 2.8	4.5 3.8	4.3 2.8
Florida Jacksonville Tampa	3.5 1.5	2.8 1.3	2.0 0.5	3.1 2.4	3.4 2.4	2.9 1.4
Georgia Atlanta	2.0	2.2	1.1	2.8	2.9	1.9
Hawaii Honolulu	1.2	1.4	0.5	2.0	2.5	1.1
Idaho Boise City	3.0	5.7	1.6	3.8	7.6	3.0
Illinois Chicago Springfield	2.5 1.6	2.7 1.6	1.6 1.0	4.2 2.9	5.3 3.1	3.5 2.5
Indiana East Chicago Hammond Indianapolis	1.2 2.0 3.2	3.6 2.6 4.4	2.8 1.3 2.0	2.8 4.0 4.7	9.6 5.3 6.2	8.9 3.4 4.6
Iowa Des Moines	1.1	0.9	0.7	2.6	2.1	1.9
Kansas Topeka Wichita	1.0 1.7	0.7 1.0	0.4 0.5	2.0 3.1	1.3 1.9	1.0 1.5
Kentucky Ashland Covington	7.1 4.0	6.0 4.1	4.4 4.5	10.2 5.7	10.6 6.2	11.5 8.1
Louisiana New Orleans	1.8	2.0	1.4	1.8	2.2	2.2
Maryland Baltimore	2.1	2.3	1.5	3.1	3.8	3.6
Massachusetts Worcester	2.0	1.5	1.4	2.8	2.5	3.0

Table 5-6 (continued). RATIOS OF BENZO [a] PYRENE TO TOTAL SUSPENDED PARTICULATES AND TO BENZENE-SOLUBLE ORGANICS AT NASN URBAN STATIONS^{4,5}

Station	BaP/TSP ^a			BaP/BSO ^a		
	1968	1969	1970	1968	1969	1970
Michigan						
Detroit	3.3	3.0	2.0	7.0	6.6	5.8
Flint	1.0	1.9	1.8	2.3	4.6	5.7
Grand Rapids	3.3	1.7	1.1	6.5	4.1	2.5
Trenton	1.2	1.6	0.8	2.8	3.8	2.6
Minnesota						
Duluth	3.2	2.6	1.5	5.7	4.8	3.6
Minneapolis	1.4	1.9	0.7	2.8	2.4	1.7
Moorhead	1.1	1.5	2.0	2.7	2.9	4.4
St. Paul	1.7	2.4	0.9	3.3	3.4	2.4
Nebraska						
Omaha	1.3	1.4	0.8	2.6	2.9	2.2
New Hampshire						
Concord	2.5	1.9	1.5	3.1	2.3	2.4
New Jersey						
Camden	1.2	1.9	1.7	2.7	3.4	3.2
Glassboro	1.7	1.6	1.7	2.7	2.7	2.6
Jersey City	2.2	3.0	4.7	3.7	4.3	8.0
Newark	2.3	2.5	1.8	3.1	3.1	2.8
Patterson	2.2	1.6	1.2	2.5	2.4	1.8
Perth Amboy	1.3	1.5	1.2	2.4	2.7	2.7
Trenton	1.6	1.9	1.3	3.3	2.8	2.6
New Mexico						
Albuquerque	1.9	1.4	1.1	2.7	2.4	2.4
North Carolina						
Charlotte	4.3	4.5	2.4	6.6	7.0	3.8
Durham	5.6	4.0	3.7	7.5	5.2	5.9
North Dakota						
Bismarck	1.0	1.2	0.5	2.5	2.4	1.4
Ohio						
Cincinnati	1.6	2.5	2.4	2.5	3.3	5.9
Cleveland	2.2	2.9	2.2	3.4	6.3	5.8
Columbus	2.3	2.6	1.6	4.2	5.4	5.2
Dayton	2.1	1.9	1.5	3.7	4.0	4.0
Toledo	2.0	2.0	1.7	3.6	3.7	4.3
Youngstown	4.5	7.5	5.3	7.2	16.2	13.0

Table 5-6 (continued). RATIOS OF BENZO [a] PYRENE TO TOTAL SUSPENDED PARTICULATES AND TO BENZENE-SOLUBLE ORGANICS AT NASN URBAN STATIONS^{4,5}

Station	BaP/TSP ^a			BaP/BSO ^a		
	1968	1969	1970	1968	1969	1970
Oklahoma						
Oklahoma City	1.4	1.0	1.2	2.1	1.5	2.8
Tulsa	1.4	0.7	1.3	2.4	1.5	2.6
Oregon						
Portland	5.2	3.1	2.2	6.7	4.0	3.1
Pennsylvania						
Allentown	1.3	1.9	2.0	2.7	3.8	4.2
Altoona	19.5	22.3	8.8	15.9	21.2	11.2
Bethlehem	2.1	2.3	2.5	4.8	4.9	6.4
Harrisburg	2.0	2.1	1.7	2.9	3.2	3.3
Philadelphia	2.3	3.1	1.7	3.4	5.0	2.9
Pittsburgh	3.5	8.3	4.3	6.9	16.8	9.8
Reading	1.8	1.8	1.3	3.4	3.7	3.1
Scranton	2.5	3.4	1.5	3.3	4.8	2.4
Wilkes Barre	1.3	1.6	1.3	2.6	3.1	2.9
York	1.7	1.8	1.2	3.0	3.3	2.8
Rhode Island						
East Providence	1.8	1.9	2.1	2.3	3.3	3.4
Providence	2.1	2.7	2.3	2.8	4.0	4.6
South Carolina						
Greenville	16.0	8.6	3.8	12.8	9.6	4.1
Tennessee						
Chattanooga	4.8	3.8	4.4	6.8	6.0	6.7
Memphis	1.7	1.0	1.6	2.9	1.5	3.4
Nashville	5.1	2.9	3.6	6.4	4.2	5.6
Texas						
San Antonio	1.4	1.2	1.6	1.9	1.4	3.0
Utah						
Ogden	1.3	0.8	2.5	2.3	1.6	3.6
Salt Lake City	1.3	0.7	1.6	2.6	1.6	3.4
Vermont						
Burlington	1.6	1.0	1.1	2.8	2.2	2.9
Virginia						
Danville	2.5	2.4	2.8	3.3	4.1	5.3
Hampton	2.3	1.8	1.8	3.6	2.8	3.7
Lynchburg	7.1	6.8	3.6	8.2	8.7	5.9
Norfolk	4.9	4.2	2.0	8.8	9.5	4.9
Portsmouth	8.3	4.1	5.0	12.1	6.7	9.9
Roanoke	8.3	5.8	6.3	9.0	8.4	9.4

Concentrations in Ambient Air

Table 5-6 (continued). RATIOS OF BENZO [a] PYRENE TO TOTAL SUSPENDED PARTICULATES AND TO BENZENE SOLUBLE ORGANICS AT NASN URBAN STATIONS^{4,5}

Station	BaP/TSP ^a			BaP/BSO ^a		
	1968	1969	1970	1968	1969	1970
Washington Seattle	2.9	2.5	2.2	3.1	2.7	3.0
West Virginia Charleston	1.5	1.2	1.2	7.5	4.2	4.7
Wisconsin Kenosha	2.0	2.2	1.8	3.4	4.0	4.4
Madison	1.8		1.4	3.1		3.2
Milwaukee	2.8	3.3	2.3	6.9	6.7	6.0
Superior	3.9	2.4	1.9	8.5	4.9	5.0
Wyoming Casper	1.5	0.9	0.7	3.3	1.7	2.2
Cheyenne	1.9	1.4	1.2	2.9	2.4	2.4

^aTo provide whole numbers for easier comparison, the BaP/TSP ratio has been multiplied by 100,000 and the BaP/BSO ratio by 10,000

Table 5-7. RATIOS OF BENZO [a] PYRENE TO TOTAL SUSPENDED PARTICULATES AND TO BENZENE-SOLUBLE ORGANICS AT NASN NONURBAN STATIONS^{4,5}

Station	BaP/TSP ^a			BaP/BSO ^a		
	1968	1969	1970	1968	1969	1970
Pennsylvania Clarion County	2.6	3.6	2.6	3.6	5.1	7.2
Texas Matagorda County	0.6	0.4	0.9	1.1	0.9	2.7
Vermont Orange County	1.0	1.0	0.5	1.5	1.8	1.5
Virginia Shenandoah Natl Park	1.0	0.9	0.6	1.7	2.1	1.9

^aTo provide whole numbers for easier comparisons, the BaP/TSP ratio has been multiplied by 100,000 and the BaP/BSO ratio by 10,000.

Table 5-8 provides a profile of the entire area with respect to each of the compounds. This example demonstrates the effect of localized sources on the immediate surroundings. The differences between the different neighborhoods were quite striking in many instances, but serve to illustrate source emission variations over the area. The seasonal data in Table 5-9 are derived from a broad data base and consequently were indicative of the types of sources contributing PPOM to Birmingham's air. The high degree of correlation among the hydrocarbon compounds shown in Table 5-10 indicated a common source for most of these pollutants and also showed that the level of one compound may be used as a fairly good index of the concentrations of the others. Obviously this generalization holds only for a given metropolitan area over a long period of time.

**Table 5-8. ANNUAL AVERAGE CONCENTRATION OF PAH COMPOUNDS IN THE
AIR OVER GREATER BIRMINGHAM, ALABAMA, 1964 and 1965⁶**
(ng/m³)

City	Site	Fluor	P	BaA	Ch	BeP	BaP	Per	BghiP	A	Cor
Bessemer	1	7.0	7.6	7.8	13.1	10.5	13.5	1.3	14.1	1.2	2.6
Birmingham	3	4.9	4.6	5.3	8.1	7.6	9.0	0.9	9.5	0.7	2.7
	4	11.2	10.8	21.2	27.9	26.1	35.8	4.1	22.4	2.2	3.8
	5	10.8	9.1	14.5	14.2	15.0	20.5	2.0	15.3	1.2	3.5
	7	2.6	2.5	3.4	4.4	5.6	6.0	0.4	7.9	0.3	2.7
Fairfield	1	10.0	8.1	13.3	11.3	13.3	18.2	1.4	11.8	1.1	2.1
Irondale	1	3.4	2.8	4.2	5.7	6.3	7.6	0.6	7.0	0.4	1.9
Mt. Brook	1	1.0	1.0	1.0	2.2	3.0	2.6	0.2	3.7	0.1	1.4
Tarrant	1	3.4	3.6	3.9	7.6	7.6	7.4	0.8	8.2	0.2	2.2
Vestavia	1	1.0	1.0	1.0	2.0	2.9	2.4	0.2	3.5	0.1	1.2
Average		5.5	5.1	7.6	9.6	9.8	12.3	1.2	10.3	0.8	2.4

**Table 5-9. SEASONAL AVERAGE CONCENTRATIONS OF PAH COMPOUNDS
IN THE AIR OVER GREATER BIRMINGHAM, ALABAMA, 1964 and 1965⁶**
(ng/m³)

Compound	Spring	Summer	Fall	Winter
Fluor	4.4	1.8	3.4	12.5
P	3.7	1.6	3.1	12.1
BaA	6.8	2.9	7.5	13.1
Ch	8.8	4.9	10.8	14.1
BeP	10.0	7.5	10.1	11.6
BaP	13.7	6.8	11.6	17.1
Per	1.3	0.8	1.2	1.5
BghiP	9.6	7.4	11.4	12.8
A	0.9	0.3	0.6	1.2
Cor	2.1	1.9	3.1	2.6

Table 5-10. INTERRELATIONSHIPS BETWEEN PAH COMPOUNDS IN THE AIR OVER
GREATER BIRMINGHAM, ALABAMA, 1964 and 1965⁶

Compound	Fluor	P	BaA	Ch	BeP	BaP	Per	BghiP	A	Cor	TSP	BSO
Fluor	1.000											
P	0.984 ^a	1.000										
BaA	0.959 ^a	0.956 ^a	1.000									
Ch	0.866	0.919 ^a	0.944 ^a	1.000								
BeP	0.902 ^a	0.927 ^a	0.980 ^a	0.986 ^a	1.000							
BaP	0.916 ^a	0.935 ^a	0.988 ^a	0.980 ^a	0.998 ^a	1.000						
Per	0.848	0.887 ^a	0.951 ^a	0.989 ^a	0.990 ^a	0.985 ^a	1.000					
BghiP	0.909 ^a	0.957 ^a	0.946 ^a	0.981 ^a	0.968 ^a	0.966 ^a	0.956 ^a	1.000				
A	0.913 ^a	0.952 ^a	0.955 ^a	0.971 ^a	0.963 ^a	0.971 ^a	0.953 ^a	0.974 ^a	1.000			
Cor	0.779	0.816	0.802	0.830	0.823	0.815	0.817	0.895 ^a	0.807	1.000		
TSP	0.668	0.730	0.742	0.842	0.823	0.789	0.830	0.839	0.716	0.856	1.000	
BSO	0.582	0.684	0.597	0.746	0.677	0.651	0.689	0.804	0.672	0.867	0.880	1.000

^aDenotes significance at $p = 0.001$ ($r \geq 0.872$). Dixon, W. J., and F. J. Massey, Jr. Introduction to Statistical Analysis (3rd ed). New York, McGraw Hill, 1969. Table A-30a, p. 549.

5.5 AZA HETEROCYCLIC ORGANIC COMPOUNDS

The aza heterocyclic organic compounds, which are characterized by the presence of nitrogen in place of carbon in one or more of the aromatic rings, have been neglected until fairly recently. This was in part due to the fact that these materials are found in the basic fraction, which constitutes a small portion of benzene-soluble organics. For many years, the emphasis centered on the aromatic hydrocarbon fraction. The recognition by Sawicki and others that potential carcinogens could be found in the basic fraction led to gathering of considerable data on levels of these compounds in the atmosphere.⁷

The approximate concentrations of six aza heterocyclics in the benzene soluble organic fraction from six large cities are given in Table 5-11. The values are only semiquantitative because at the time the work was performed the methodology had not been fully perfected. In addition to these six compounds, 13 other aza heterocyclics were qualitatively detected in the Nashville sample.

5.6 SIZE DISTRIBUTION OF BaP-CONTAINING PARTICULATE MATTER

In evaluating potential effects of PPOM, it is essential to have data relative to the particle size distribution. As of this time, very little information is available. In a study of particulates in Pittsburgh, Pa., DeMario and Corn concluded that more than 75 percent of the BaP and several other hydrocarbons was associated with aerosols less than 2.5 μm in radius.⁸ More recently Kertes-Saringer and co-workers reported that in Bucharest from 70 to 90 percent of the total BaP was associated with aerosols with a radius of 1 μm or less.⁹

**Table 5-11. APPROXIMATE CONCENTRATIONS OF AZA HETEROCYCLIC COMPOUNDS
IN BENZENE-SOLUBLE FRACTION OF SELECTED URBAN ATMOSPHERES⁶**
($\mu\text{g/g}$)

Compound	Urban Area					
	Atlanta	Cincinnati	Los Angeles	Nashville	New Orleans	Philadelphia
Benzo[f] quinoline	200	80	a	100	7	20
Benzo[h] quinoline	20	20	1	30	1	7
Benz[a] acridine	200	80	3	70	20	30
Benz[c] acridine	30	10	1	8	2	6
11H-Indeno[1,2-b] quinoline	30	40	4	20	8	10
Dibenz[a,j] acridine	8	2	a	6	0.6	6

^aUnable to detect in the amount of sample analyzed.

5.7 SUMMARY

Man is surrounded by an air environment that contains a large assortment of complex organic compounds. Many fit into the category of what is commonly called particulate polycyclics. Although the greatest emphasis in the past has been placed on the polycyclic hydrocarbons— especially BaP — it must be recognized that there are other constituent groups such as the aza heterocyclics that, although found in smaller amounts, may be of considerable significance because of their biological activity.

Five years of BaP data collected by NASN indicate definite source/concentration relationships, with highest levels occurring in those urban areas that use large amounts of coal or fuel oil both in their normal domestic activities and in industrial processes. Annual average urban concentrations range from 0.48 ng/m³ for Honolulu and 0.73 ng/m³ for Tucson to a maximum of 22.2 ng/m³ for Altoona. This represents a 1 to 50 range among urban areas. At the more remote locations, the levels are usually much lower, with a minimum annual average of 0.10 ng/m³ for Curry County, Oregon, and a maximum of 1.7 for Clarion County, Pennsylvania. The latter is an excellent example of the intrusion of urban pollutants into an otherwise unpolluted environment.

There is some question as to whether, because of year to year variability, the 1966 to 1970 data are an adequate base to determine trends. These fluctuations in annual averages could be the result of low frequency of sampling and poor precision in analysis, climate variation, as well as day to day variation in emissions. Consequently, any trend analysis would be of doubtful significance.

Typical seasonal fluctuations are shown quite clearly in Tables 5-2 and 5-9 and Figure 5-1. The Altoona data illustrate the influence of emissions from inefficient coal-burning installations.

Measurable amounts of several aza heterocyclics have been found in a number of urban atmospheres.

Relatively little effort has been expended on investigation of the particle size distribution of PPOM. The small amount of data available indicates that 75 percent more of BaP is associated with particles with less than 2.5 μ m radius, which would tend to emphasize the respirability of PPOM. This is an extremely important point to consider when investigating the biological effects of PPOM.

5.8 REFERENCES

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6. EFFECTS ON HUMAN HEALTH

6.1 TOXICOLOGICAL APPRAISAL

6.1.1 Introduction

The association between development of cancer and excessive contact with an environmental contaminant was first made in 1776 when the British physician Percival Pott noted the high incidence of cancer of the scrotum in the chimney sweeps of London. He correctly attributed the disease to their continual contact with soot.¹ The earliest laboratory investigation based on this observation was by the Japanese investigators Yamagiwa and Ichikawa in 1915.² They painted coal tar on the skin of mice and found that tumors developed after several months of repeated local applications. The first inquiry into the chemical basis of "tar cancer" was that of Bloch and Dreifuss.³ Subsequent studies by Kennaway in 1925 identified the tumorigenic material as a hydrocarbon.⁴ Chemical isolation of benzopyrene, dibenz(a,i)-anthracene, 7,12-dimethylbenz[a]anthracene, and 3-methylcholanthrene was accomplished by Cook, Hewett, and Hieger in 1933.⁵ Subsequent studies by Kennaway showed these substances to be actively carcinogenic to animals.⁶ These early studies focused attention on the carcinogenicity of polycyclic aromatic hydrocarbons and guided subsequent toxicology laboratory research in that direction.

Animal toxicologic studies have been done on many compounds that have been identified in the PPOM of ambient air. The systemic acute LD₅₀ (the lethal dose for 50 percent of animals tested) is usually so much higher than doses shown to be carcinogenic in single or multiple doses that such data are rarely mentioned.^{7,8} Recent *in vitro* toxicity studies have shown some PPOM compounds to be toxic to some human cell types but do not result in malignancy.⁹ Studies designed to evaluate noncarcinogenic effects of PPOM are rare, and studies that are designed as carcinogenesis experiments and that yield negative results usually fail to use data on noncarcinogenic effects. Little or no work has been done on the possible teratogenic or mutagenic effects of PPOM. Therefore, any appraisal of the toxicology of PPOM will be almost entirely a discussion of carcinogenicity.

Research on the toxicology of PPOM can be grouped under four broad headings:

- Determination of carcinogenicity
- Determination of biologic handling *in vivo* and *in vitro*
- Determination of a dose-response pattern in experimental animals that can be applied to setting an air quality standard
- Determination of teratogenesis and mutagenesis

6.1.2 Determination of Carcinogenicity

Many screening methods have been devised to evaluate carcinogenicity. They have utilized pure samples of organic compounds of the types found in the environment, as well as total PPOM and fractions collected from urban atmospheres.

Carcinogenic potential of extracts of airborne material has been undertaken on various whole animals, tissue cultures, organ cultures, and microorganisms. The methods employed on whole animals have been skin painting, subcutaneous injection, systemic inoculation, oral intake, local implantation (in lung, bladder, or other organs), intratracheal inoculation, and inhalation.

6.1.2.1 Animal Cutaneous Bioassay—Much of the early work in experimental carcinogenesis was accomplished by repeated painting of materials on the intact skin of mice. The carcinogenicity of chimney soot,¹⁰ road dust,¹¹ city airborne dust,¹²⁻¹⁸ and smoke¹³ was determined by skin painting. This method was also used in studies that suggested that the PAH fraction of urban air particulates may play an important role in carcinogenicity.^{14,15,17,19,20} A large series of experiments carried out with various extracts and fractions of airborne particulates from various sources in the United States indicated that there were geographic differences in biological activity, with the highest incidence of tumors associated with material from Birmingham and the lowest incidence with that from Los Angeles.¹⁵ Analysis of these data indicates that tumorigenicity could not be entirely related to the BaP content of these extracts. Another study showed that oxidation products of aliphatic hydrocarbons were also carcinogenic.²¹ Some N-heterocyclic hydrocarbons identified in urban air have also been shown to be carcinogens.²²⁻²⁴ The technique of applying carcinogens to mouse skin has been refined so that effects can be seen in female Ha/ICR/ml (Swiss random bred albino) mice with as little as 50 microliters (μ l) of a 0.001 to 0.002 percent acetone solution of BaP.²⁵

6.1.2.2 Animal Subcutaneous Bioassay—Subcutaneous injection of suspected chemical carcinogens or organic pollutants into mice,^{26,27} rats,²⁸ and hamsters,^{29,30} has been shown to be an effective bioassay method. The inbred hamster line developed tumors after one 0.5 milligram (mg) injection of 7,12-dimethylbenz[a]anthracene with a mean latency of 9 weeks.

6.1.2.3 Animal Oral Intake—Carcinogenesis has been reported following oral administration of PAH or aromatic amines in oil to Sprague-Dawley rats.^{31,32} Oral administration, however, is felt to be a relatively poor way of determining the carcinogenicity of PPOM, except possibly in the case of tumors of the gastrointestinal tract.²⁸

6.1.2.4 Animal Pellet Implantation Bioassay—Local implantation of pellets impregnated with carcinogen has been used in the lung^{33,34} and in the bladder.³⁵⁻³⁹ This is a technique for applying pure carcinogens directly to the target tissue. It is not likely that local implantation will gain widespread use as a screening method.²⁸

6.1.2.5 Animal Neonate Injection Bioassay—The subcutaneous and systemic inoculation of newborn animals has been shown to be a sensitive bioassay method for carcinogenicity.⁴⁰⁻⁴⁴ Cancer can be produced in these animals with a higher incidence than it can using comparable doses in adult animals.⁴⁰ A single subcutaneous injection of 0.06 mg of dibenz[a,h]anthracene and 0.1 mg of 3-methylcholanthrene into 1-day-old mice produced a high incidence of malignant tumors in 8 to 32 weeks.⁴¹ This method has also been used to assay fractions of air particulates.^{43,44} Results were similar to the previously mentioned study that used cutaneous and subcutaneous inoculation of adult animals, but with the advantage that neonatal studies use much smaller amounts of material and shorter latent periods.¹⁵

6.1.2.6 Animal Intratracheal Inoculation Bioassay—Although PPOM does come into contact with the skin, the primary concern is its action when taken into the lung. The development of intratracheal inoculation techniques allowed investigators to deposit high concentrations of potentially carcinogenic materials into the lung by a simple, inexpensive technique. Many initial experiments with this technique did not result in formation of malignant tumors in the lung.⁴⁵⁻⁴⁷ In 1949, Niskanen used repeated intratracheal injections of a suspension of dibenz[a,h]anthracene in olive oil and induced squamous cell carcinomas in six of 25 rats.⁴⁸ The intratracheal method was further refined by Della Porta, Kolb, and Shubik who injected a colloidal gelatin suspension of 7,12-dimethylbenz[a]anthracene into Syrian golden hamsters by repeated endotracheal instillations.⁴⁹ Squamous cell carcinomas of the larynx and trachea were seen in six of 17 hamsters. An appreciable incidence of lung tumors was produced by the intratracheal administration of 7,12-dimethylbenz[a]anthracene suspended in a balanced saline solution containing 4 percent casein and India ink powder.⁵⁰ In further investigations, other agents including BaP and purified carbon particles instead of India ink were used.⁵¹⁻⁵⁶ This method was very successful in producing malignancies of the lung; a 67 percent incidence of squamous cell carcinoma was produced by BaP.

The incorporation of BaP with hematite particles (Fe_2O_3) has also been extremely productive of tumors when equal parts are physically ground together, suspended in saline, and injected via the trachea of Syrian hamsters.⁵⁷⁻⁶⁴

Experimentation with the carcinogen-hematite-Syrian hamster model has been extremely successful in inducing a large number of cancers of the tracheobronchial tree and lung parenchyma that mimic those occurring naturally in human beings.⁶³ The hamster is uniquely free of inflammation and spontaneous tumors of the lung.⁶⁵ In these experiments with BaP and hematite, cancer incidences as high as 100 percent have been reported. The success of the intratracheal injection method appears to be related to addition of some other physical factors. No tumors resulted from injection of BaP alone,^{33,47} whereas addition of a cofactor such as carbon particles⁵⁰⁻⁵⁶ or hematite⁵⁷⁻⁶⁴ produced a striking effect.

In developing a model for intratracheal injection, pure compounds of known or suspected hydrocarbon carcinogens from the air were used. This model has been applied in preliminary studies of crude air particulates, organic fractions of air particulates, and combinations of these with equal amounts of BaP or hematite.⁶⁶ This model is also being widely used to screen other pure, suspected carcinogens. Sellakumar and Shubik report an 89 percent incidence of respiratory tract tumors in hamsters given a total dose of 15 mg of 7H-dibenzo[c,g]-carbazole and hematite.⁶⁷ Experiments that employ repeated intratracheal injections must be accepted with caution.⁶⁸ All such experiments are complicated by damage to the ciliated mucosa, plugging of the finer airways, introduction of infectious agents, irritation from the chemical and its carrier or solvent, and effects of repeated anesthesia (if used). In the case of rats maintained for long periods, the usual rat lung pathology interferes with interpretation of the experiment.⁶⁸

6.1.2.7 Animal Inhalation Bioassay—Exposure of animals by inhalation techniques offers the most physiologic approach to experimental carcinogenesis in the lung. Experiments of this type are most relevant to the problem of air pollution and are cogent criteria for setting air quality standards.^{6,9-71} Some studies using inhalation of pure polycyclic hydrocarbons, however, have yielded negative results.^{4,7} Only scattered success has been reported in producing lung tumors with inhalation techniques. The incidence of pulmonary adenomata in mice was reported to be increased by exposure to dust from tarred roads,^{12,72,73} chimney soot,^{74,75} and fractions of coal tars.⁷⁶ A model consisting of exposure of mice to a mixture of ozone and gasoline vapor has been employed with some success.^{77,78} Incorporation of exposure to influenza virus in this model increased the number of tumors.^{79,80} A subsequent series of experiments by other investigators employing this model produced increased evidence of pulmonary carcinomas and adenomas in C.57 strain black mice by exposure to ozonized gasoline fumes. In these experiments, however, inhibition of tumor growth resulted from influenza infection.⁸¹

A relative inhalation study was carried out using a combination of sulfur dioxide and particulate BaP.³³ For these experiments, rats were exposed to 26.2 milligrams per cubic meter (mg/m^3) SO_2 for 6 hours a day, 5 days a week. For 1 hour a day, 10 mg/m^3 BaP and 9.2 mg/m^3 SO_2 were added to the atmosphere. Exposure was for 98 weeks, and appropriate controls were used. Five of 21 rats developed lung tumors. The BaP-hematite-Syrian hamster model has not been studied by inhalation. Recently, Clark and Schmoyer developed methods to generate aerosols of respirable particles that have polycyclic organic carcinogens associated with noncarcinogenic carriers, such as hematite and carbon.⁸² It is hoped that these developments will lead to bioassay systems yielding data directly applicable as air quality criteria. (Epidemiological data question the noncarcinogenicity of hematite. See: Boyd, J.T. and R. Doll. Cancer of the Lung in Iron-Ore (Haematite) Miners. Brit. J. Prev. Med. p. 63, 1970.)

6.1.2.8 In Vitro PPOM Bioassay—In 1963, Berwald and Sachs described characteristic morphologic alterations in the growth patterns of hamsters and embryonic fibroblasts in culture with PAH.⁸³ They later demonstrated that these cells gave rise to tumors when the cells were transplanted to hamster cheek pouches.⁸⁴ A proportionality was shown between the number of transformed clones produced by a given hydrocarbon and its known carcinogenic activity.⁸⁵⁻⁸⁷ Several investigators attempted to use cultures of mouse ventral prostate for bioassay.⁸⁸⁻⁹² These studies led to the development of a quantitative system

with prostate cells in which morphologically transformed colonies were easily identified in culture; all of these colonies resulted in tumors upon transplantation to mice.⁹³ The number of transformed colonies correlated with known carcinogenic activity when nine polycyclic hydrocarbons were studied.

Huebner *et al.* also developed an *in vitro* screening technique for large numbers of possible carcinogens.^{94,95} These studies employ rodent embryonic fibroblast cell lines that are not transformed by either known carcinogens or nontransforming type-C RNA tumor virus individually. However, when these cultures are infected with virus and then exposed to a carcinogen, transformation takes place.

Organ culture has also been used for bioassay. Respiratory^{96,97} and prostatic^{89,98} tissues undergo morphologic changes in proportion to the established *in vivo*-animal activity of many known carcinogens. Using suckling rat tracheas, Crocker and his associates established the similarity between early *in vivo* and *in vitro* morphologic changes in this system with air particulate extracts and pure known carcinogens.^{96,99-101} *In vitro* methods for screening effects of PPOM have the advantage that dose-response analysis of relative biologic activity can be easily accomplished, concentration and duration of exposure can be better controlled, and human tissues can be exposed directly to compounds that could not be used safely *in vivo* in human studies. One investigator¹⁰² has reported epithelial hyperplasia of human epithelial tissue *in vitro* as a result of BaP activity, and one group⁹ has reported toxic effects at 1 µg per milliliter levels of hydrocarbon in culture. The use of human cells *in vitro* should be further explored as a test system for screening and determining relative carcinogenicity of PPOM.

6.1.2.9 Indirect Tests Used for PPOM Bioassay—The suppression of sebaceous glands of mouse skin¹⁰³⁻¹⁰⁸ and the photodynamic assay of *Paramecium caudatum*¹⁰⁹⁻¹¹⁴ have been found to correlate with carcinogenicity of some substances. None of these tests have had goals of carcinogenicity, but because they have shown a correlation in cases of known carcinogens, they may have some value as screening tests.

6.1.2.10 Testing for Carcinogenicity in Primates—Experimental carcinogenesis caused by PAH has been achieved in prosimian primates.¹¹⁵⁻¹¹⁹ Administering methylcholanthrene, dibenzanthracene, and BaP by many routes, Pfeiffer and Allen failed to produce cancer in simians.¹²⁰ This raised questions of resistance due to metabolic or immune characteristics that may also be present in man. Primates of the suborder Prosimii appear more susceptible to carcinogenesis by PAH.¹¹⁹ Pulmonary carcinoma in simians has been produced by administration of particles of beryllium salt,¹²¹ and hepatic carcinoma has been produced by oral administration of nitrosamines.¹²² Domestically bred simian primates should be tested with methods identical to those which succeeded in prosimian primates and rodents in order to provide data on the relative susceptibility to systemic, skin, and bronchial carcinogenesis by PAH in the primate suborder that includes man.²⁸

6.1.2.11 Discussion—Extensive research has been done on methods to be used in bioassay of carcinogens. Most of these methods have used the same known carcinogens to ensure that the assay is accurate. Similarly, methods have been applied to assay of chemical fractions of air particulates. In no case have all the compounds in these fractions been characterized. Nevertheless, these studies have identified many carcinogens in the air as noted in Table 5-1 but others remain to be evaluated.

None of the toxicological data presented thus far can be extrapolated for the determination of an air quality standard unless that standard attempts to completely eliminate all carcinogens from the atmosphere.

6.1.3 Determination of Biologic Handling In Vivo and In Vitro

Much information has been gained on the interaction of PPOM and animal systems. Information is available on: deposition of PPOM in the lung, the role of other factors in potentiating PPOM activity, clearance of PPOM from the lung, metabolism and distribution of PPOM, enzyme systems that change these carcinogens *in vivo*, chemical carcinogenesis at the molecular level in the cell, modification of PPOM interaction by modification of host factors, and diagnosis of results of PPOM inhalation. Although many of these factors

do not appear to be directly involved in the task of establishing air quality criteria for PPOM, their discussion is included here because all play an important role in understanding the biologic effects of these compounds.

6.1.3.1 Deposition, Potentiation, and Clearance—Airborne particles range from 0.001 to 10,000 μm in diameter, with the majority ranging from 0.1 to 10 μm in diameter.¹² Particles 0.25 to 5 μm in diameter are retained in the lung, with a maximal retention of 80 percent of 1 μm particles and less than 5 percent retention of particles smaller than 0.1 μm or larger than 5 μm .¹²³ Particles greater than 5 μm are trapped in the upper respiratory tract.¹²³ PPOM in the air appears to be adsorbed on particles with a size range of 0.1 to 10 μm and should therefore be deposited throughout the respiratory tract.²⁸ Falk and co-workers demonstrated that BaP was present in soot samples of respirable particle size, but that when soot was recovered from human lungs at autopsy, BaP could not be detected.¹²⁴

The BaP-hematite-Syrian hamster model has been used to elucidate information on the role of carrier particulate and on the elution of hydrocarbon carcinogens from the particle. Clearance studies have shown that retention of intratracheally injected BaP is proportional to the amount of hematite employed and that the rate of elimination is skewed with time, suggesting a prolonged retention due to the presence of the particle.⁵⁹ The elimination of BaP has also been related to the size of the particle to which it is adsorbed, since it is eliminated more slowly from smaller particles.⁵⁴ In experiments employing tritiated BaP in hamsters, clearance of radioactivity from the lung after a 14-day period was significantly slower when the BaP was incorporated on carbon or asbestos than when BaP was used alone.¹²⁵ It appears that the carrier particle prolongs the residence time of the carcinogen in the lung. It is not clear exactly how this is accomplished, nor is it known to what degree this takes place in nature.

The role of macrophage, surfactant, mucus, cilia, blood, and lymphatic clearance mechanisms of the carcinogen and particle should be clearly defined because it is possible that the level, or size distribution, of total particulate in the atmosphere may be more important in carcinogenesis than the percentage of that total that is carcinogenic hydrocarbon.

Hilding has proposed that changes in ciliary movement and mucus viscosity are caused by nonspecific airborne irritants, and that these changes are most important in failure to clear carcinogens.¹²⁶ Laskin's³³ demonstration of enhanced tumor production with SO_2 and BaP may be an example of the nonspecific irritant effects proposed by Hilding,¹²⁶ or it may be due to another mechanism. Palmer and associates have shown that ozone decreased the amount of BaP hydroxylase enzyme in lung¹²⁷ and tracheal mucosa.¹²⁸

6.1.3.2 Distribution, Excretion, and Metabolism of PAH—In 1936, Peacock injected colloidal suspensions of anthracene, dibenz[a,h]anthracene, and BaP intravenously into animals and found that the compounds were rapidly cleared from the blood and excreted into the bile.¹²⁹ The use of radioactive tracer techniques has confirmed this observation¹³⁰ and established that biliary excretion also follows intratracheal injection.¹³¹ Maly has evaluated the content of dibenzo[a,1]pyrene (1,2-3,4-dibenzpyrene) in the urine of smokers, nonsmokers forced to smoke, and nonsmokers.¹³² He found that levels of this metabolite were 0.0 $\mu\text{g/liter}$ in nonsmokers, 0.3 $\mu\text{g/liter}$ in smoking nonsmokers, and 1.1 $\mu\text{g/liter}$ in active smokers. The identification of this metabolite in urine may lead to a useful screening test for hydrocarbon exposure. It also indicates that higher metabolite levels are seen in people who have had repeated previous exposures and probably have higher levels of an enzyme that converts contaminants in cigarette smoke to this metabolite.

Most work on POM metabolism has been done in animals or *in vitro* systems, but in no case have all the metabolites of any hydrocarbon been identified.²⁸ Sims has identified the following metabolites of BaP: the monophenols (3- and 6-hydroxy), the diphenols (3,6- and 1,6-dihydroxy), quinones (1,3-dione and 1,6-dione), and two dihydrodiols (1,2- and 9,10)¹³³ None of these metabolites is carcinogenic. It is postulated, however, that metabolic activation is probably necessary to induce cancer. It has been proposed that epoxides are formed from hydrocarbons and that these are the carcinogenic form.¹³⁴ Recently Sims has synthesized benz[a]anthracene 8,9-oxide, an epoxide; when this was added to rat liver homogenates, a dihydrodiol was formed, as when benz[a]anthracene was metabolized in this system.¹³⁵ Similarly,

synthesized K-region epoxides are more active in malignant *in vitro* transformation than are the parent hydrocarbon, its dihydrodiols, or its phenols.¹³⁶

The primary enzyme system for metabolism of PAH is the microsomal aryl hydrocarbon hydroxylase.¹³⁷⁻¹³⁹ It converts these compounds to the derivatives just discussed. This system is inducible with PAH and with a variety of other materials.¹³⁷⁻¹⁴⁰ The level of enzyme and inducibility are genetically determined,²⁸ and can also be induced transplacentally.¹⁴⁰⁻¹⁴² It has also been shown that tumorigenesis is decreased by preinduction of this enzyme.^{143,144} This enzyme can be inhibited with 7,8-benzoflavone²⁸ and with ozone.^{127,128} Obviously, this enzyme system plays a very important role in biologic handling of PPOM.

6.1.3.3 Chemical Carcinogenesis at Molecular Level—Chemical carcinogens transform normal cells into cancer cells.^{145,146} Mondal and Heidelberger have very efficiently transformed individual normal cells into malignant cells with 3-methylcholanthrene.¹⁴⁷ It has also been postulated that all chemical carcinogens can act through intermediary oncogenic viruses.¹⁴⁸ Some examples of this have been found.^{94,95} When viruses have not been detected, however, their participation is not definitely disproved. Nevertheless, whether viruses are involved or not, it is still the chemical that triggers the process.

If chemical carcinogens themselves produce cancer directly, then the mechanism is by mutation or nonmutation (derepression of genetic information already contained in the cell). Mutation requires interaction with DNA, change in the primary sequence, and perpetuation of that change. Chemical carcinogens (or derivatives of these carcinogens) have been found to bind covalently with DNA, RNA, and protein of target tissues.¹⁴⁹ Binding of PAH to mouse skin DNA and RNA has been studied, but the chemistry of this binding is not yet known.¹⁵⁰⁻¹⁵² The binding of PAH to proteins also has been studied.^{153,154} It is postulated that this binding may depress an oncogene which results in carcinogenesis by a nonmutational mechanism.¹⁴⁹ The finding of fetal antigens in several human tumors is evidence in support of this theory;^{155,156} however, that theory is by no means universally accepted. Hydrocarbon-induced tumors have been shown to acquire new transplantation antigens.^{157,159} The significance of these antigens to the process of carcinogenesis remains unexplained.

6.1.3.4 Modification of Host Factors in Relation to PPOM Exposure—The immune system may be involved in two aspects of chemical carcinogenesis—immunity to chemical carcinogens and immunity to transformed cells. Peck and Peck showed a tumor inhibition of over 50 percent when rats were first sensitized with a carcinogen-protein conjugate and then given a chemical carcinogen.¹⁶⁰ Earlier studies of this type were done with similar but less spectacular results.^{161,162}

The role of age in carcinogenesis testing has been investigated using screening studies in neonates, but few studies have been done in aged animals. One study suggested that aged animals were more susceptible to skin carcinogenesis.¹⁶³ Others have seen no differences between young adult and aged animals,¹⁶⁴ and still another study showed a decline in carcinogenesis in aged animals.¹⁶⁵ Neonates have been shown to be an effective screening bioassay for carcinogens, and studies are needed into the mechanism of their increased susceptibility.

The role of nutrition in chemical carcinogenesis has had some study especially with regard to the role of vitamin A, which appears to have some protective effect on epithelial tissues.¹⁶⁶ It has also been observed that obesity may be coincident with greater susceptibility to develop cancer.^{167,168} Another association of diet and chemical carcinogenesis involves the dietary induction of aryl hydrocarbon hydroxylase enzyme.²⁸ However, it does not appear that diet will be among the most significant factors involved in chemical carcinogenesis.

The role of infection in respiratory carcinogenesis has been studied, with conflicting results. Campbell found a reduction in the incidence of tar-induced lung tumors after viral infection, but the number of mice in the study was small.¹⁶⁹ Nettesheim *et al.* found that influenza virus decreased the incidence of lung tumors induced by gasoline.⁸¹ Steiner and Loosli found that the virus decreased the incidence of

spontaneous lung tumors.¹⁷⁰ In contrast, Kotin and co-workers found that viral infection increased the incidence of lung tumors induced by gasoline fumes,^{79,80} and Imagawa *et al.* found the same to be true with urethane.¹⁷¹ Despite the conflicting results, the possibility of infection playing a role in carcinogenesis is an attractive hypothesis. The alteration of clearance mechanisms, the effects of infection on the trachea-bronchial lining cells, and the interactions involved in the immune status during infection are poorly understood in relationship to *in vivo* handling of PPOM.

The role of radiation in chemical carcinogenesis has been investigated experimentally and epidemiologically. Epidemiologic studies on uranium miners have shown a higher incidence of cancer in miners who are smokers; a synergistic effect between exposure to alpha radiation and components of cigarette smoke was implied.^{172,173} However, experimental studies using BaP or 7,12-dimethylbenz[a]anthracene and either external irradiation^{174,175} or polonium-210^{28,176} have shown additive effects of this combination. Further studies on the interaction of alpha radiation particles and PAH compounds would provide data to help assess any adverse health effects resulting from the exposure to a combination of these materials.

6.1.3.5 Summary of PPOM Interaction—Although some work has been done on every level of PPOM interaction with biologic materials, definitive work remains to be accomplished in most of these areas. Safe exposure levels in the presence of “inert” particles, irritants, metabolic inhibitors, infection, immunosuppression, and irradiation are not known.

6.1.4 Determination of Dose-Response Patterns in Animals

Saffiotti *et al.* have recently evaluated respiratory tract carcinogenesis induced in hamsters by different numbers of administrations of BaP and hematite.^{177,178} A positive dose-response relationship was demonstrated. A total dose of as low as 15 mg produced a 15 percent tumor incidence, with high doses yielding higher incidences. On this basis, it was felt that valid results could be obtained with lower doses and larger numbers of animals. However, the usefulness of such data is limited relative to problems of air pollution, because intratracheal injections are not physiologic, and unequal distribution in the lung is common.¹⁷⁹ No attempts to equate dose and response have been carried out by inhalation studies which would avoid distribution problems. Several investigators have attempted to extrapolate a conservative safe dosage of an agent whether or not carcinogenic activity was found.^{180,181} This extrapolation based in statistics is at best a poor guess of the actual situation, but at present is the best extrapolation available.

The question of whether a threshold concentration exists in the environment below which no adverse health effects are produced is very important. The National Academy of Sciences document considered this question only briefly since experimental approaches are at present very expensive and complex.²⁸ However, the alternatives in setting air quality standards are: (1) recommending these standards on the basis of epidemiologic studies alone, which will require extensive investigation; (2) recommending arbitrary standards based on no biologic investigation; (3) recommending a level of zero for any carcinogen in the air, based on screening studies; and (4) setting no standard at all until adequate information is available.

6.1.5 Teratogenesis and Mutagenesis

A very limited amount of work has been done on the teratogenic and mutagenic effects of pollutant compounds found in the ambient atmosphere. The following material extracted from the NAS report²⁸ reflects the current state of knowledge regarding these subjects.

There are no known data on teratogenicity testing, by any route, of air pollutant PPOM.

A method of detecting point mutations in mammalian somatic cells is to use *in vitro* tissue-culture systems. The potential of using mammalian somatic cells *in vitro* for genetic studies has long been recognized, but substantial progress was not made until improved and simplified techniques for mammalian cells were

developed by Puck and associates.^{182,183} These methods made possible quantitative analysis of genetic variations in cell populations via the plating technique for mammalian cells.

It was demonstrated that gene mutations are induced by treatment of Chinese hamster cells in cultures with alkylating agents.^{184,185} In addition, physical agents (such as x-rays and ultraviolet radiation) and chemical agents (such as carcinogens) have been shown to induce forward and back mutations at several genetic loci in these cells.¹⁸⁶⁻¹⁹⁰ Thus, *in vitro* cell culture offers a new system for testing the mutagenicity of chemicals in human environment. Whether somatic mutation may cause cancer can now be reexamined more critically, because both carcinogenesis and mutagenesis have been shown to occur experimentally in the same target cell system *in vitro*. Furthermore, human somatic cells from normal and neoplastic tissues can also be tested directly.

Chu and co-workers have tested the mutagenicity in Chinese hamster cell cultures of a few selected groups of chemical carcinogens and their related compounds and derivatives.¹⁸⁹ Table 6-1 lists the compounds tested and their relative carcinogenicity (based on animal studies) and mutagenicity. The genetic marker assayed in the hamster cells was the change from 8-azaguanine sensitivity to resistance. The results obtained thus far indicated that there was direct relation between the degree of carcinogenicity and mutagenicity and that metabolically activated derivatives of the test compounds often played important roles in mutagenic action. It was recently demonstrated that epoxides of PAH are much more mutagenic to mammalian cells than are the corresponding hydrocarbons, dihydrodiols, and phenols.¹⁹¹

Parallel results have been obtained in the induction of mutations with the same series of compounds at the adenine-3 region of *Neurospora*.¹⁹² Similarly, N-acetoxy-2-acetylaminofluorene has been shown to be mutagenic in T₄ bacteriophage,¹⁹³ *Bacillus subtilis*,¹⁹⁴ and *Escherichia coli*.¹⁹⁵

Clearly, these results are promising, but more data using more representative compounds and additional genetic loci will be needed before a more definitive conclusion may be drawn. The use of mammalian cells *in vitro* for a combined and coordinated test for chemical mutagenesis and carcinogenesis may be expected to yield significant information on cellular mechanisms of cancer. However, data on mutagenesis derived from somatic cells *in vitro* are limited by present inability to identify factors involved by conventional genetic techniques. There are no published data on mutagenicity testing of air pollutants by inhalation.

Table 6-1. RELATIVE CARCINOGENICITY AND MUTAGENICITY OF SELECTED COMPOUNDS^{28,189}

Test compound	Carcinogenicity ^a	Mutagenicity
Benzo[e] pyrene	—	—
Benzo[a] pyrene (BaP)	+	—
3-Hydroxybenzo[a] pyrene	—	±
Dibenz[a,c] anthracene	—	—
Dibenz[a,h] anthracene	±	±
7,12-Dimethylbenz[a] anthracene	+++	+++
2-Acetylaminofluorene	+	—
N-Hydroxy-2-acetylaminofluorene	+	—
N-Acetoxy-2-acetylaminofluorene	+++	+++

- ^a—: not carcinogenic (or mutagenic)
 ±: uncertain or weakly carcinogenic (or mutagenic)
 +: carcinogenic (or mutagenic)
 +++: strongly carcinogenic (or mutagenic)

6.2 EPIDEMIOLOGICAL APPRAISAL

6.2.1 Introduction

Some components of PPOM can be deleterious to human health, but considerable doubt surrounds such questions as: Which specific PPOM compounds are most harmful? What concentrations of PPOM are harmful? How long must one be exposed to PPOM before his health is endangered? Can PPOM alone affect health? Epidemiology is an essential instrument for answering these questions, but it alone cannot answer them completely. Firm answers will be found only through the joint efforts of the epidemiologist, the toxicologist, the clinician, and the environmental engineer.

6.2.2 Epidemiologic Findings

The illnesses usually related to exposure to PPOM are cancer of the skin and lung. Nearly all the findings have been made in studies of occupational exposure to the combustion products of carboniferous material. In all these studies, PPOM concentrations have been very high and exposures prolonged. In most cases, the actual concentrations to which the subjects were exposed were not known, nor could the chemical compounds of the occupational exposure environment be characterized with a high degree of certainty.

Of course, in occupational exposure, the dose of PPOM is far greater than in ambient air. In gas works, the concentration of BaP has been estimated at $3 \mu\text{g}/\text{m}^3$; above coke ovens, it may reach levels of $216 \mu\text{g}/\text{m}^3$. In even the most polluted ambient air, the annual average BaP concentration rarely exceeds $0.01 \mu\text{g}/\text{m}^3$.

PPOM is produced mainly by the combustion or volatilization of fossil fuels. Most of the industry-related cancer experiences have been cases involving combustion or distillation of coal products. In gas-works retort houses in England, BaP concentrations of 3 to $216 \mu\text{g}/\text{m}^3$ were measured. These concentrations were 100 to 10,000 times higher than the normal BaP level in London.²⁸

In one study, British gas workers employed for at least 5 years were divided into a high-exposure and a low-exposure group. The lung cancer incidence in the high-exposure group was 69 percent greater than in the control group. Coke oven workers also have experienced an increase in the incidence of lung cancer.¹⁹⁶⁻¹⁹⁸

For two centuries, it has been recognized that soot may cause scrotal cancer. Despite this knowledge, chimney sweeps were shown to experience excess scrotal cancer as recently as 1964.¹⁹⁹ Wax pressers with prolonged exposure to crude wax have been shown to have increased scrotal cancer rates.²⁰⁰ Other substances associated with excess skin cancer include tars, shale oil, and cutting oil.²⁰¹⁻²⁰³

In addition to cancer, other cutaneous disorders have been linked to PPOM. Among these are nonallergic and allergic dermatitis, phototoxic inflammatory reactions, pilosebaceous responses, and pigmentation disorders.²⁰⁴⁻²⁰⁶ No skin disorder has yet been demonstrated to result from exposure to PPOM in ambient air.

A number of epidemiologic studies have linked PPOM to nonoccupational neoplastic pulmonary disease.²⁸ Most of them generally agree that, in American males, the urban lung cancer death rate is about twice the rural rate, even after adjustment for differences in smoking habits. These studies have attributed at least part of the excess mortality to urban air pollution. In the United Kingdom, Stocks found increasing standardized mortality ratios for lung cancer with increasing density of dwelling units.²⁰⁷ In an area near Osaka, Hitosugi made a detailed study of the differences in lung cancer death rates between people living in high industrially polluted-sections and people living in relatively low-polluted sections.²⁸ The results listed in Table 6-2 indicate that lung cancer death rates among male smokers of comparable smoking habits were higher in sections of high industrial pollution. The largest urban-rural difference in lung cancer deaths was found among the lightest smokers.

Table 6-2. LUNG CANCER DEATH RATES FOR MALES AND FEMALES, AGE 35-74, BY SMOKING CATEGORY AND AIR POLLUTION LEVEL

Smoking category	Lung cancer death rate per 100,000 persons ^a			
	Low pollution	Intermediate pollution	High pollution	Total
Males				
Nonsmoker	11.5 (5)	3.8 (1)	4.9 (1)	7.9 (7)
Exsmoker	26.2 (11)	42.6 (7)	61.7 (7)	36.0 (25)
Smoker (ciga- rettes/day)				
1 to 14	10.6 (9)	14.2 (10)	23.5 (14)	15.3 (33)
15 to 24	14.7 (18)	19.1 (17)	27.0 (17)	19.1 (52)
≥ 25	36.3 (19)	15.8 (4)	46.4 (6)	44.0 (32)
Females				
Nonsmoker	4.6 (15)	6.9 (12)	3.8 (6)	4.9 (33)
Exsmoker	12.4 (2)	52.6 (2)	124.0 (3)	13.3 (6)
Smoker (ciga- rettes/day)				
1 to 14	19.7 (13)	16.5 (6)	15.3 (5)	17.6 (24)
15 to 24	12.4 (1)	23.1 (2)	24.0 (1)	19.7 (4)
≥ 25	--- (0)	--- (0)	--- (0)	--- (0)

^aNumbers in parentheses are numbers of deaths.

Stocks and Campbell performed a similar study in the Liverpool area. Table 6-3 lists their results. The conclusions from their study agreed with those reached by Hitosugi—that lung cancer death rates were higher in the urban areas than in the rural areas for each smoking category. Stocks and Campbell, along with Hitosugi, pointed out that the most prominent urban-rural difference in lung cancer death rates was in the group of lightest smokers. The urban-rural difference among the heavier smokers was less pronounced.

Table 6-3. LUNG CANCER DEATH RATES FROM MID-1952 TO MID-1954 BY AGE, SMOKING CATEGORY, AND POPULATION AREA^a

Smoking category	Lung cancer death rates per 100,000 persons												Percent difference ^c	Percent difference per BaP unit ^d
	Age 45-54			Age 55-64			Age 65-74			SDR ^b Age 14-74				
	Rural	Mixed	Urban	Rural	Mixed	Urban	Rural	Mixed	Urban	Rural	Mixed	Urban		
Nonsmoker	0	0	31	0	0	147	70	0	336	14	0	131	89.3	12.8
Pipe smoker	0	0	104	30	59	143	145	26	232	41	25	143	71.3	10.2
Cigarette smoker														
Light	69	57	112	70	224	376	154	259	592	87	153	297	70.7	10.1
Moderate	90	83	138	205	285	386	362	435	473	183	132	287	36.2	5.2
Heavy	117	214	205	626	362	543	506	412	588	363	303	394	7.9	1.1
Number of deaths	16	26	124	26	56	230	27	36	183	68	118	539		

^aDerived from Stocks and Campbell.²⁸

^bStandardized death rate.

^cEquals $100 \times \frac{(\text{urban SDR}) - (\text{rural SDR})}{\text{urban SDR}}$

^dEquals $\frac{\text{Percent difference}}{7.0 (\mu\text{g BaP per } 1000 \text{ m}^3)}$

In a study of U.S. residents, Haenszel categorized subjects by similarities in smoking habits, age, sex, location, and duration of residence.^{2,8} His results (see Table 6-4) indicate that lung cancer death rates among males, adjusted for age and smoking habit, were higher in urban areas than in rural areas. In contrast to previous studies, Haenszel pointed out that the greatest urban-rural difference in lung cancer death rates in males was among the heaviest smokers. The controversy here is over the degrees of difference and not over the fact that differences existed among comparable smokers located in different areas. Table 6-4 also shows that lung cancer death rates for lifetime urban residents was twice that of lifetime rural residents—in close agreement with conclusions from previous studies. Nevertheless, most urban-rural comparison surveys have not carefully considered differences in smoking habits and other environmental covariates. Occupational exposure is probably an extremely important factor. The necessity for caution against overstating the effect of ambient pollution is exemplified by the Nashville study, which did not show a high correlation between lung cancer and air pollution.^{2,8} In a study in Buffalo, Winkelstein *et al.* also failed to find a consistent relation between air pollution and lung cancer deaths.^{2,9}

Though urban air often contains PPOM, there is as yet no clear evidence that urban levels of PPOM are carcinogenic to man. In many instances, BaP has been used as a practical index of air pollution because it: (1) is a solid in air, and thus it can be adsorbed on particles and collected for assay; (2) can be correlated with other polycyclic compounds; and (3) is a known carcinogen in animals and a suspected one in man. However, one must be cautious in drawing conclusions about the health effects of BaP. It may be shown that a certain rise in BaP levels is associated with a certain rise in mortality. When BaP levels are high, however, several other pollutants also tend to be abundant—notably hydrocarbons, total suspended particulates, and sulfur dioxide. All of these substances are present in coal smoke.

Caution is further warranted by the fact that the correlation of BaP to other urban pollutants varies among cities. BaP and other PPOM are formed in highest concentration in reducing atmospheres. Sulfur dioxide is a combustion product of high-sulfur fossil fuels. Thus, the BaP/sulfur dioxide ratio will be very high with combustion of low-sulfur coal and very low with complete combustion of high-sulfur coal. In either situation, lung cancer mortality might be affected, but one cannot necessarily ascribe the excess mortality to the same pollution components in both cases.

Several human cancers involving organs other than skin and lung have been associated with particulate air pollution. In the Nashville study, some correlation was demonstrated between the soiling index and cancers of the bladder, esophagus, and prostate. There was also a relationship between dustfall and stomach cancer. It would be most premature to ascribe these tumors to a specific pollutant such as BaP or another polycyclic compound.

Table 6-4. STANDARD LUNG CANCER MORTALITY RATIOS IN WHITE MALES IN URBAN AND RURAL AREAS, ADJUSTED FOR AGE AND SMOKING HISTORY^a

Current residence	Standard mortality ratio by duration of residence ^b (years)					
	All durations	Less than 1	1-9	10-39	Over 40	Lifetime
Urban	113	166	107	117	177	100
Rural	79	154	88	83	75	50

^aDerived from Haenzel *et al.*^{2,8}

^bLung cancer base death rate = 78.2.

Although little evidence relates to nonneoplastic diseases, some provocative findings have been made. For example, English coal gas workers exposed to high levels of PPOM—especially BaP—had an even greater excess of chronic bronchitis than of lung cancer.²⁰⁷ BaP did not appear to have much bearing on the incidence of pneumonia, and it was concluded that BaP is not an important contributor to chronic bronchitis mortality.

6.2.3 Discussion

To date, epidemiologic findings implicate PPOM in the production of skin and lung cancers. Although most authors cite BaP as the primary human carcinogen, this conclusion is probably premature. A great deal of work remains in defining more completely the roles of specific polycyclic compounds in producing human disease. For example 7,12-dimethylbenz[a]anthracene has been implicated as an animal carcinogen, but its role as a human carcinogen has not been determined.

Studies to date have suffered from the inability to define the individual components of local air pollution. A symptom of this inability has been the tendency to ascribe the total air pollution effect to BaP alone. In some cases, it may be reasonable to use BaP as an index of PPOM pollution, but it must be borne in mind that PPOM has never been shown to cause human lung cancer, *per se*, and has never even been associated with skin cancers of any kind. Many current studies, such as those of EPA's CHESSE program (The Community Health and Environmental Surveillance Study) are making a concerted effort to characterize local air pollution profiles. For the present, the epidemiologist is not justified in making broad generalizations about local findings.

The problem of defining the role of PPOM is complicated by the phenomenon of cocarcinogenesis.²¹⁰ It has often been found that even a potent carcinogen is relatively inactive unless coupled with one or more other substances (cocarcinogens). Furthermore, cocarcinogens can greatly shorten the latent period of carcinogenesis. Known cocarcinogens include ultraviolet radiation, epoxides, lactones, asbestos, and aromatic hydrocarbons; suspected cocarcinogens include sulfur dioxide or sulfates, nitrogen oxides, and ozone. Clearly, present data do not warrant well-founded long-range conclusions. The whole spectrum of airborne hydrocarbons has not been assessed for possible interactions with polycyclic hydrocarbons. The degree to which a particular concentration ratio of sulfur dioxide (or other gaseous or particulate pollutants) to PPOM is conducive to tumor formation is not known. It may be that an atmosphere with fairly low concentrations of both PPOM and sulfur dioxide may result in adverse health effects.

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7. OTHER (WELFARE) EFFECTS

7.1 ECOLOGICAL

Ecosystems are affected by higher concentrations of POM, such as occur near urban centers, petrochemical industries, and fossil-fuel-utilizing sources. The effects of POM are evaluated in the general ecological context, including the effects on soil, water, biological components, and their relationship within environmental systems.

Naturally functioning ecosystems may contribute PPOM either as solids or liquid aerosols. Generally, the contribution from natural sources enters the atmosphere in amounts that do not cause major air pollution problems.¹ However, the total POM produced by natural sources is unknown. Since POM may exist in relatively pure form on particles, it can be readily absorbed—especially when animals may be receptors—through ingestion, inhalation, or direct skin contact.

In whatever form POM reaches the soil, water, or the biological receptors, its deposition and eventual fate will affect the receptor.

Synergistic reactions, the ramifications of which are virtually unknown, are possible between POM and other agents. It has been shown in hamsters and other test animals that ionizing radiation along with some chemical carcinogens will increase the incidence of lung cancer.²

There is voluminous literature on the fate of PAH in experimental animals. A large number of PAH compounds are capable of being metabolized by animals.¹ The majority of the carcinogens of the PAH type are derivatives of phenanthrene, but not all derivatives of phenanthrene are carcinogenic.³

POM has not been shown to produce tumor-like reactions in plant tissues; however, it is a suspect in the case of cultivated mushrooms.⁴

No information was found to indicate that carcinogenic PAH affect vegetation. Other PAH, however, are produced by plants. Evidence suggests that some individual PAH compounds may behave as plant hormones.⁵

POM has been reported in many plant and plant products such as tobacco smoke; snuff; peat; wood soot; pulp mill stack gases; roasted coffee beans; plant tissues; pyrolyzed cellulose, lignin, and pectin; wood-smoked foods; incinerator effluents; and marine flora and fauna.² It may also be produced when foods are heated during preparation.

Plants may also synthesize POM, thus contributing to biological intake through food chains.² However, uptake of polycyclic compounds from the soil is a greater source of POM. The incidence of human gastric cancer and intestinal neoplastic disease correlates with ingestion of plants bearing POM.² Most atmospheric hydrocarbons from vegetation are thought to be terpenes.

Benzopyrenes have been found in remote rural soils, in tree leaves, and in roots and shoots of some cereal crops. They also have been detected in decaying litter and other similar organic matter and have been shown to be in soil solutions, where they are subject to uptake by plants.²

In addition to the POM from industrial processes, pesticides and derivatives thereof applied to crops contribute POM to the environment; the greatest impact is on food chains or on soil microbiota.²

POM can have a direct effect upon soil microorganisms. It is well documented that the microbial populations of soil can be altered by the deposition of hydrocarbons. The response from a particular soil type, whether rural or urban, depends on the types of microorganisms present. Successional changes in microbial populations occur over a period of time after the soil has been enriched with POM.^{2,6}

Many PAH compounds which are carcinogenic to man can be utilized by a variety of microorganisms common in polluted soil and water.¹ Both bacteria and yeasts may utilize BaP, and Shabad and coworkers noted an enrichment effect in soils contaminated with BaP.⁷ Some strains of soil bacteria are capable of absorbing and concentrating BaP, whereas others destroy it, i.e., transform it into derivatives. BaP in soil may therefore be taken up by plants or utilized or transformed by microorganisms.

Similar types of problems have been found in aquatic ecosystems concerning sediment deposition and POM distribution and actions within the biological components.⁸

It is possible that attenuation of light or visibility may either interfere with the normal photosynthetic processes of vegetation or will affect other metabolic processes. The impact of PPOM will depend on ambient atmospheric conditions, particle size, and the differential ability of receptors to accumulate this matter. For example, Neuberger and coworkers suggest that conifers are better natural filters than deciduous trees.⁹ It is also known that vegetation in general adsorbs more particles of 20 μm or less in size than of those above that size.¹⁰ The size range of PPOM is from a few tens of Angstroms to hundreds of micrometers.²

7.2 MATERIALS

No evidence has been found of effects of ambient levels of PPOM on materials. Based on the nature of this type of pollutant, two possible effects are suspected:

1. POM may cause inorganic particulate matter to adhere to material surfaces and so contribute to soiling; or
2. Polymeric material such as vinyl paints may become susceptible to solvent-actions of POM.

Given ambient concentrations of PPOM, these are expected to be relatively minor effects.

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8. CONTROL TECHNOLOGY

8.1 INTRODUCTION

Very little specific test information is available on the effectiveness of techniques to control POM emissions. Control techniques are based largely on considerations of the mode of formation and physical and chemical characteristics of these materials.

Theoretical considerations suggest that much of the POM will be associated with particulates. Therefore, the use of conventional particulate collection equipment may remove much of this pollutant. Because most POM is thought to be associated with the submicron sized particles, however, preference should be given to equipment capable of removing such particles—for example, electrostatic precipitators, high energy scrubbers, or bag filters. Because of their relatively inefficient collection of particles smaller than 5 μm , cyclones do not appear to be highly applicable to removal of POM; they may have value upstream of an electrostatic precipitator, however.

Electrostatic precipitators appear to offer considerable promise because of their ability to remove small particles. Dry precipitators have difficulty handling sooty and tarry particulates. Wet precipitators, however, have been developed to remove such particles and have been used extensively on larger utility boilers. Considerable research is still needed to improve these devices so they will be uniformly effective in the fine-particle range.

Wet scrubbers appear to offer considerable advantages in the removal of POM. Because of their relatively long residence times, low-energy devices such as spray towers may be used as condensers for VPOM. Following this with a high energy device such as a venturi scrubber should be highly efficient in removing fine particulates.

Fabric filter bag collectors possess unequalled ability to remove submicron particles, but they may suffer from binding problems when handling the sooty, tarry particulates often associated with high organic loads. The efficiency of these devices for collecting PPOM will depend upon the particle size distribution of the PPOM itself and/or the particle size distribution of other particles upon which the POM is adsorbed.

In the absence of adequate information on size distribution of PPOM, it can only be said that the more efficient the gas-cleaning equipment is in removing the entire size range of all particulates, the more efficient it will be in collecting PPOM. It is suspected, however, that PPOM is associated with incomplete combustion. The size range for tobacco smoke, resin smoke, carbon black, and combustion nuclei is from 0.01 to 1 μm . Thus, it is anticipated that the PPOM will be mainly in this size range.

In selecting a technique or combination of techniques for any given application, and in selecting the equipment type within each technique, three broad factors must be considered:

- The characteristics of the cleaning equipment required to remove POM.
- The effects of tarry and viscous material on the gas-cleaning equipment.
- The effects of other components in the flue gas stream on the gas-cleaning equipment.

In summary, POM associated with gross particulates may be removed by conventional particulate removal equipment designed in accord with conventional design procedures. The extent of this removal will depend upon both the ratio of total POM to total particulates, and also upon the distribution of POM among the size fractions of total particulate matter. At present, adequate control technology does not exist for fine particulates. So, if as anticipated, PPOM lies mainly in the fine range, control technology has not been fully developed.

8.2 STATIONARY COMBUSTION EMISSIONS

Techniques that will control emissions of POM from stationary combustion sources may be broadly categorized as follows:

- Good design
- Good practice
- Process modification
- Energy substitution
- Clean fuels
- Gas cleaning
- Source shutdown
- Energy conservation

Good design, good practice, process modification, and energy substitution are all techniques aimed at improving combustion in stationary fuel combustion sources and thus preventing the formation of POM. In evaluating possible control techniques for a particular combustion source or group of sources, these techniques merit special consideration. Not only will they make the most economical use of fuel, but they will also help reduce the emission of other pollutants such as carbon monoxide and gaseous hydrocarbons that result from incomplete combustion. It must be borne in mind, however, that over-application of techniques to promote good combustion—high flame temperatures and excessive amounts of air—may, for example, result in increased emissions of nitrogen oxides.

Clean fuels offer a unique control possibility. Considerable interest has developed in the “hydrogen fuel system” in which hydrogen would become a major substitute for presently used fossil fuels. Hydrogen combustion yields only water. Carbon monoxide may also produce no particulate matter in combustion. If so, “low-Btu gas,” a mixture of carbon monoxide and hydrogen, may have as much potential as natural gas as a *minimum-PPOM* source of energy.

The sixth technique, gas cleaning, may find application where, for any reason, the first five techniques cannot be applied or cannot achieve the reduction needed in PPOM. Gas-cleaning equipment will probably be installed in conjunction with one or more of the first four techniques. Since gas-cleaning equipment will also remove other pollutants, the benefits derived must be taken into consideration in evaluating gas cleaning as a technique for the reduction of POM emissions.

The seventh technique, source shutdown, is a drastic control technique, but it should not be completely disregarded. Source shutdown is useful for control of particulate emissions when air pollution levels threaten the public health in emergency episodes and for control of emissions when lawful orders to abate are ignored.

The eighth technique, energy conservation, limits POM emissions by reducing the amount of fuel burned for a given energy output. It differs from the first technique, good design, in that it is concerned not with the efficiency of the combustion process itself, but with the subsequent process steps used in converting the heat released by the combustion process into the form of energy required. This technique does not appear to have application in the reduction of emissions from a particular source at a particular time since, at present, the technology of energy conversion is being improved only slowly.

8.3 INCINERATION EMISSIONS

As with fuel-burning installations, the proper design of incinerators has been the subject of a great deal of study. It is not appropriate to deal with this complex subject in detail in this document. The publication, *Interim Guide of Good Practice for Incineration at Federal Facilities*,¹ provides guidance as to good design practice. It must be emphasized again that although theoretical considerations indicate any design technique that will improve combustion will reduce emissions of POM, no quantitative information has been found to show the actual reduction to be expected by good combustion as now conventionally defined.

In view of the heterogeneous nature of refuse and the often erratic feed rates, good operation is of the utmost importance in ensuring good combustion. At present, there appear to be no automatic control systems that can fully control all the important variables of an incinerator—grate speed, over-fire air, under-fire air, and furnace draft—to avoid smoky operation. Almost always the skill and vigilance of the operating crew must be relied upon. For example, if the crane operator mixes various kinds of refuse in the bin to give a furnace feed reasonably uniform in calorific value and moisture content, then it will be much easier for the furnace operators to maintain good combustion.

The use of conventional gas-cleaning equipment to remove POM from incinerator effluent streams may be considered along the general lines discussed for fuel-burning equipment. As in that case, removal of particulates and incineration of organic vapors by conventional gas-cleaning techniques will reduce POM emissions. However, conventional criteria for selection and design of gas-cleaning equipment for incinerators are not exactly the same as for fuel-burning equipment because incinerator effluent streams are subject to wide fluctuations in flow-rate, temperature, physical and chemical composition, and corrosive properties.

8.4 OPEN-BURNING EMISSIONS

Vegetation such as forest debris, crop residues, scrub, brush, weeds, and grass are burned in controlled fires to:

- Control vegetation, insects, and other organisms harmful to desired plant life.
- Reduce waste volume.
- Improve land.
- Minimize fire hazards.

The emissions from open burning cannot be controlled directly. It has been found that burning agricultural wastes in single-chamber incinerators without employing special emission control techniques and equipment will not significantly reduce emissions of POM below that for open burning.

Other alternatives to incineration are to abandon or bury the materials at the site, to dispose of them in remote areas, or to use them.

Coal refuse is piled near mining operations and coal cleaning and preparation plants. It typically consists of less than 25 percent combustible matter. The principal materials in coal refuse are coal, slate, shale, bone, calcite, gypsum, clay, pyrite, or marcasite. These culm piles are more likely to ignite if they contain extraneous organic material such as wood or garbage. Camp fires or brush fires often furnish the ignition. Spontaneous firing occurs by slow oxidation of the coal. Water may contribute to ignition by the heat of wetting, depending on the physical nature of the coal and on humidity and precipitation.

Extinguishing or preventing such fires are the techniques used to eliminate emissions from coal refuse fires. These methods involve locating the piles away from brush and other sources of ignition, cooling and

repiling the refuse, sealing refuse with impervious material, injecting slurries of noncombustibles into the refuse, minimizing the quantity of combustibles in the refuse, and extinguishing fires by such techniques as digging them out.

8.5 INDUSTRIAL PROCESS EMISSIONS

There have been a very limited number of studies on emissions of POM or individual compounds such as BaP from industrial processes. In addition to the problems of sampling and analysis common to all sources of POM, industrial processes tend to be highly variable, making representative sampling difficult and increasing the error of extrapolation to other sources even in the same industrial category. Also, for many important processes such as coke production and roofing operations, pollutants are not discharged from a definable point or stack but occur sporadically and from diffuse surfaces. Two general situations have the most potential for emission of POM. Processes that involve incomplete combustion of carbonaceous material may produce large quantities of POM. In the handling, processing, and utilization of aromatic compounds, a common raw material in the chemical and light metal industries, POM may also be formed and released.

The most important process emissions result because coal can contain significant quantities of POM. Some is released when coal is heated as in the manufacture of coke, and much POM remains in the coal chemicals. POM may be released in subsequent heating and use of other coking by-products such as coal tar pitch or carbon electrodes in aluminum plants. The other industrial operations of potential importance are the partial combustion of carbon such as in catalyst regeneration, or quenching operations used in the manufacture of carbon black.

From the wide range of potential sources of POM, the following industrial processes seem most important based on the available test data: petroleum refineries, coke ovens, use of coal-tar pitch, and asphalt hot-road-mix manufacture.

8.5.1 Refinery Emissions

Although nearly every process and piece of equipment in a refinery can emit hydrocarbons, only those that handle or process the heavy fractions at elevated temperatures will be significant emitters of POM.

Typical refinery processes likely to emit POM include: catalytic cracking and catalyst regeneration, air-blowing of asphalt or other heavy oils, waste gas disposal system, oil-water effluent system, and boilers and process heaters.

Boilers and process heaters are simply combustion operations, not unique to refineries, and were covered in the section on stationary combustion sources. Of the remaining sources, only catalytic regeneration and air-blowing have been tested specifically for POM emissions. The others must be considered potential, but as yet unproven, emission sources.

POM is produced in the catalyst bed and in the regeneration system, in both the fluid- and moving-bed systems. The regenerators can be considered inefficient combustion systems utilizing petroleum coke as a fuel. The emissions will be a function of a variety of design and operational factors, including type of feedstock, temperature, excess air available, throughput time, and type of afterburner used.

8.5.2 Coke Oven Emissions

Control of particulates from coking—through modified charging or pushing or through continuous coking—are being investigated. The efficiency of POM control is a part of those studies. Since, however, particulate emissions are expected to be reduced by 90 percent by particulate air standards, it is anticipated that POM will also be significantly reduced.

8.5.3 By-Product Plant Emissions

A study of a coal tar pitch plant has resulted in some specific recommendations for controlling gas and steam emissions. The major sources of emissions were leaks in the equipment and the venting of waste gases into the atmosphere through a washer sprayed with liquor from the gas-cooling cycle. Burning the waste gases in a special afterburner failed because it was difficult to provide a sufficiently large contact surface area at the 1,250 to 1,350°C temperatures required to decompose POM.

The first source of emissions, leaks in the equipment, was controlled by installing airtight doors. The second source, the waste gas outlet, was controlled by venting the waste gases into the gas pipe for raw coal tar pitch. These gases were then either collected in special apparatus or burned in furnaces at elevated temperatures after mixing with coke-oven gases. The pitch preparation flow sheet was greatly simplified by excluding the afterburner, trap, air washers, fans, and pump. The liquor from the gas washer cycle was no longer needed, and its removal improved the cooling and washing of the coke-oven gas.

There are no sources of information on emission control techniques specifically for POM from coal tar pitch at point of use.

8.5.4 Emissions from Hot Asphalt Batching and Airblowing

Hot asphalt batching plants are potential sources of heavy particulate emissions, and for this reason have been subject to control procedures. Cyclones, scrubbers, and bag filters have all been used.

On the basis of the theoretical considerations, the gas-cleaning equipment installed for particulate removal should be effective in reducing POM emissions, although a higher degree of performance may be required to reduce them to acceptable levels.

Airblowing of asphalts generates oil and tar mists and malodorous gaseous pollutants. It is common practice to scrub the oils and tars from the hot (150 to 200° C) gas stream. Sea water is sometimes used for this purpose. In any case, separators are necessary to reclaim the oil and prevent contamination of effluent water. Afterburners are used to incinerate the uncondensed gases and vapors, which are odorous.

8.6 MOBILE SOURCES

8.6.1 Mechanism of POM Emission

Detailed evidence is lacking for a single, dominant reaction mechanism for the formation of POM in combustion systems. Nevertheless, it has long been recognized that their formation in rich flames parallels carbon formation.² Thus, a wide variety of POM can be formed in sooting flames when C₂-C₅ hydrocarbons are used as fuels.³ There is strong evidence that soot forms in flames through polymerization (or oligomerization) of C₂H fragments in the post-flame gases, with subsequent cross-linking of polyacetylene chains.⁴ It seems likely that POM is formed in a similar way.²

Soot (and probably POM as well) persist in postflame gases from rich flames because of a deficiency of OH radicals, a necessary reactant for the principal carbon burnout mechanism.⁵ Alkaline earth oxides are known to suppress carbon formation; their principal mode of action has recently been shown to be catalysis of OH radical formation.⁶ Thus, POM formation may well be tied to these features of carbon formation, and POM emission may be influenced by local fuel-air ratio in the combustion zone, by persistence of OH radicals in the postflame gases, and by the use of smoke suppressant additives.

Pyrolysis of oil or diesel fuel droplets could occur in locally oxygen-poor patches of combustion gas, producing the case discussed in the NAS document. It is believed, however, that gas phase formation of carbon dominates in real systems.⁵ Therefore, this mechanism cannot be ignored in discussion of POM formation.

8.6.2 Control Technology for Mobile Sources

There are no elements of control hardware directed principally at POM emissions from mobile sources. Most investigators seem to feel that hydrocarbon control devices and engine modifications will also control POM. Thus, decreasing fuel-air ratios in passenger cars has resulted in decreased POM emissions. Given the

85 percent reduction figure in the NAS report, the relative importance of diesel emissions has increased considerably.⁷ Thus, diesel- and gasoline-powered trucks must now be the leading mobile source of POM.

Opinions conflict on the potentiality for control of POM from cars by control of gasoline composition. Thus, the work of Colucci and Begeman indicates a dramatic effect of lubricating oil consumption on BaP emissions.⁸ By analogy, it might be expected that higher-molecular-weight hydrocarbons in the fuel might increase POM emissions as well. Yet, recent work suggests that gasoline end-point or aromatics content have minimal influences on POM.⁹ All these conclusions are now clouded by uncertainties in analytical results. Thus, in recent studies it is believed that at least half the BaP and benz[a]anthracene were lost in the sample-trapping procedure.⁹ It now appears important to develop a reliable, quick POM analytical procedure and to resurvey prototype and in-use vehicles if the current and future picture of passenger car POM emissions are to be reliably assessed.

Thus far, there has been very little work on diesels. The NAS report indicates correctly that the POM emissions from diesels are a function of load.⁷ Whether variation in diesel fuel molecular weight, physical properties, or use of carbon suppressant additives influence POM emissions is not known.

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APPENDIX

The information presented below became available as this report went to press; therefore, it is not considered in discussions in this report but the reader should consider these data in evaluating annual emissions.

**Table A-1 ESTIMATED BENZO[a]PYRENE EMISSIONS
IN UNITED STATES, 1972^a**

Source Type	Emissions, MT/yr
Stationary sources	
Coal, hand-stoked and underfeed-stoked residual furnaces	270
Coal, intermediate-size furnaces	6
Coal, steam power plants	<1
Oil, residential through steam power type	2
Gas, residential through steam power type	2
Wood, home fireplaces	23
Enclosed incineration, apartment through municipal type	3
Open burning, coal refuse	281
Open burning, vehicle disposal	5
Open burning, forest and agriculture	10
Open burning, other	9
Petroleum catalytic cracking	6
Coke production	0.05 to 153
Asphalt air-blowing	<1
Mobile sources	
Gasoline-powered, automobiles and trucks	10
Diesel-powered, trucks and buses	<1
Rubber tire degradation	10

^aFrom: Preferred Standards Path Report for Polycyclic Organic Matter. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Durham, N.C. October 1974. p. 27-36.

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16. ABSTRACT This report is a review and evaluation of the current knowledge of particulate polycyclic organic matter in the environment as related to possible deleterious effects on human health and welfare. Sources, distribution, measurement, and control technology are also considered. Results of an extensive literature search are presented. Experiments have shown a number of polycyclic organic compounds to be carcinogenic in animals. Although these same compounds have not been proven to be carcinogenic in humans, evidence strongly suggests that they may contribute to the "urban factor." In American males, the urban lung cancer death rate is about twice the rural rate, even after adjustment for differences in smoking habits. Evidence suggests significant differences between specific urban areas across the United States. The bulk of the available data is in terms of Benzo[a]pyrene; so this compound has been used as an index on particulate polycyclic organic matter. Average seasonal concentrations of BaP in the ambient atmosphere range from less than 1 ng/m ³ in nonurban areas to a maximum of 50 ng/m ³ in rural areas.		
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