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# **An Exposure and Risk Assessment for Benzo[a]pyrene and Other Polycyclic Aromatic Hydrocarbons**

Volume III. Anthracene, Acenaphthene,  
Fluoranthene, FLUORENE,  
Phenanthrene, and Pyrene

**DISCLAIMER**

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<b>16. Abstract (Limit: 200 words)</b>  This report assesses the risk of exposure to polycyclic aromatic hydrocarbons (PAHs). This is Volume III of a four-volume report, analyzing 16 PAHs; it concerns six of these: anthracene, acenaphthene, fluoranthene, fluorene, phenanthrene, and pyrene. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in June of 1981.  The assessment includes an identification of releases to the environment during production, use, or disposal of the substances. In addition, the fate of PAHs in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to PAHs for various subpopulations.			<b>13. Type of Report &amp; Period Covered</b>  Final
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AN EXPOSURE AND RISK ASSESSMENT FOR BENZO[a]PYRENE AND  
OTHER POLYCYCLIC AROMATIC HYDROCARBONS:

VOLUME III. ANTHRACENE, ACENAPHTHENE, FLUORANTHENE,  
FLUORENE, PHENANTHRENE, AND PYRENE

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OFFICE OF WATER  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
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## FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

Michael W. Slimak, Chief  
Exposure Assessment Section  
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Office of Water Regulations and Standards

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AN EXPOSURE AND RISK ASSESSMENT FOR BENZO[a]PYRENE AND  
OTHER POLYCYCLIC AROMATIC HYDROCARBONS

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The Materials Balance for the PAHs in the Anthracene Group (Section 4.1) was produced by Acurex Corporation, under Contract No. 68-01-6017 to the Monitoring and Data Support Division (MDSO), Office of Water Regulations and Standards (OWRS), U.S. Environmental Protection Agency. Patricia Cruse was the task manager for Acurex, Inc.; other contributors include Robert DeRosier, Kenneth Moss and Stephen Wendt. Patricia Leslie was responsible for report production on behalf of Acurex, Inc.

John Segna and Michael Slimak were the EPA project managers for this assignment.

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## 1.0 INTRODUCTION

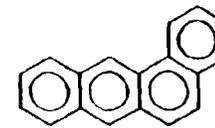
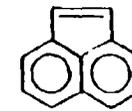
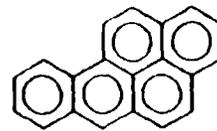
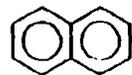
The Office of Water Regulations and Standards (OWRS), Monitoring and Data Support Division, of the U.S. Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goals of the program under which this report has been prepared are to integrate information on cultural and environmental flows of specific priority pollutants, to estimate the likelihood of receptor exposure to these substances, and to evaluate the risk resulting from such exposures. The results are intended to serve as a basis for estimating the magnitude of the potential risk and developing a suitable regulatory strategy for reducing any such risk.

This report, comprised of four separate volumes, provides a summary of the available information concerning the releases, fate, distribution, effects, exposure, and potential risks of the 16 priority pollutants that are polycyclic aromatic hydrocarbons (PAHs). The chemical structures of these compounds are shown in Figure 1-1.

The number of chemicals considered in this exposure and risk assessment is appreciable. The possibility of preparing 16 separate exposure and risk assessment documents was considered and rejected because it would lead to considerable redundancy and because so little information was available on some of the individual PAHs. As an alternative, the 16 PAHs were organized at the onset of the work into three groups, as indicated in Figure 1-1.

The rationale for the organization into these three specific groups included considerations of materials balance, chemical properties related to fate and environmental pathways, and health effects, as described briefly below.

- Naphthalene is the only one of the 16 PAHs with substantial U.S. commercial production and with a significant potential for direct exposure to consumers of a commercial product (mothballs). It is significantly more volatile and more water soluble than any other PAH. It was not anticipated to have carcinogenic effects in humans.
- Anthracene, acenaphthene, fluorene, fluoranthene, phenanthrene and pyrene are all imported in rather small quantities for special commercial uses. These compounds are three- and four-ring PAHs, with moderately low volatility and water solubility. The question of their possible carcinogenicity was expected to require careful review. Most of the information pertaining to this group is specific to anthracene.

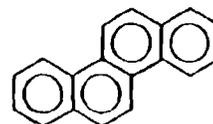


Benzo[a]pyrene

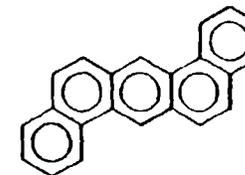
Acenaphthylene

Benzo[a]anthracene

**THE ANTHRACENE GROUP**



Chrysene



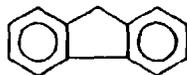
Dibenz[a,h]anthracene



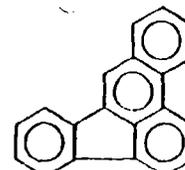
Anthracene



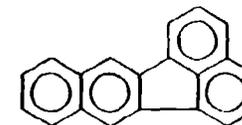
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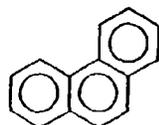
Fluorene



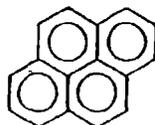
Benzo[b]fluoranthene



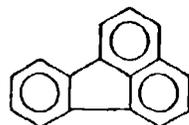
Benzo[k]fluoranthene



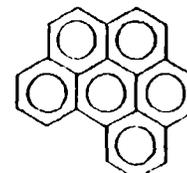
Phenanthrene



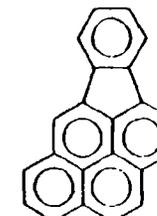
Pyrene



Fluoranthene



Benzo[g,h,i]perylene



Indeno[1,2,3-c,d]pyrene

1-2

**FIGURE 1-1 STRUCTURES OF THE PRIORITY POLLUTANT  
POLYCYCLIC AROMATIC HYDROCARBONS**

- Benzo[a]pyrene (BaP) and the eight other PAHs in the third group have no commercial production or use, except as research laboratory standards. They are released to the environment inadvertently by combustion sources. With one exception (acenaphthylene), the chemicals in this group have very low vapor pressures and water solubilities. Several of the PAHs in the BaP group had been identified as carcinogens. Much of the information regarding this group of compounds is for BaP.

The exposure and risk assessment for each of the three groups of PAHs was treated in a separate chapter of a multivolume report; Chapter 3.0 (Volume II) concerns naphthalene; Chapter 4.0 (Volume III) concerns the anthracene group PAHs; and Chapter 5.0 (Volume IV) concerns the benzo[a]pyrene group PAHs. These chapters are bound separately.

Potential waterborne routes of exposure are the primary focus of these exposure and risk assessments because of the emphasis of CWRS on aquatic and water-related pathways. Inhalation exposures are also considered, however, in order to place the water-related exposures into perspective. Each chapter contains major sections discussing the following topics:

- Information on environmental releases of the subject PAHs, including the form and amounts released and the receiving medium at the point of entry into the environment (materials balance);
- Description of the fate processes that transform and/or transport the compounds from the point of release through environmental media until exposure of humans and other receptors occurs, and a summary of reported concentrations detected in the environment, with a particular emphasis on aquatic media;
- Discussion of the available data concerning adverse health effects of the subject PAHs on humans, including (where known) the doses eliciting those effects and an assessment of the likely pathways and levels of human exposure;
- Review of available data concerning adverse effects on aquatic biota and the levels of environmental exposure; and
- Discussion of risk considerations for various subpopulations of humans and other biota.

Two comments regarding the materials balance section are appropriate. First, these sections were based in large part on draft material prepared by Acurex Corporation, under EPA Contract 68-01-6017, and provided to Arthur D. Little, Inc. by EPA. Second, the phrase "materials balance" is somewhat inappropriate when applied to chemicals such as the PAHs that are produced primarily as byproducts of combustion

processes. Since most PAH production is inadvertent rather than deliberate commercial production, the conventional approach of trying to balance production versus use and environmental release is not strictly applicable to these chemicals. Therefore, the materials balance sections of these exposure and risk assessments are focused on estimates of releases from major sources such as combustion; considerable uncertainty is associated with most of these estimates.

After an initial review of the three exposure and risk assessments covering all 16 priority pollutant PAHs, it was determined that one chemical, benzo[a]pyrene, was of appreciably greater interest to OWRS than were the other 15 compounds studied. This interest reflects the more extensive data base available for assessment of environmental fate and exposure and also the existence of some, although limited, dose-response data to which various extrapolation models can be applied for estimation of potential human carcinogenic risk from ingestion of BaP. For the other PAHs considered, data on carcinogenic or other long-term effects were generally limited, nonquantitative, and/or did not indicate statistically positive results. Table 1-1 presents a summary of the hazard of the 16 priority pollutant PAHs in terms of carcinogenicity, based on qualitative review of available information.

For these reasons, the technical summary presented in Volume I is organized somewhat differently than the rest of the report (Chapter 3.0-5.0) (Volumes II-IV). The summary is focused on benzo[a]pyrene as the PAH of greatest interest. The estimated releases to the environment, environmental fate, monitoring data, human effects and exposure, biotic effects and exposure, and risk considerations concerning BaP are presented in expanded summary form. Abbreviated summaries are then provided for naphthalene, anthracene group PAHs, and the other PAHs considered.

Included in the summary volume are critical data and references to the literature so that this volume may be read and understood by itself without reference to the separately bound Chapters 3.0-5.0. The latter volumes contain more extensive compilations of data, more detailed discussions of the available information and of the interpretations drawn, and more complete documentation of the multiple literature sources that were reviewed in the course of this work.

TABLE 1-1. SUMMARY OF EVIDENCE FOR CARCINOGENICITY OF PRIORITY POLLUTANT PAHs

<u>PAH</u> *	<u>Basis</u>
Benzo[a]pyrene	Positive oral carcinogen with other positive carcinogenic data.
Dibenz[a,h]anthracene	Positive oral carcinogen with other positive carcinogenic data.
Benz[a]anthracene	Positive oral carcinogen with other positive carcinogenic data.
Benzo[g,h,i]perylene	Not tested orally, other positive carcinogenic or co-carcinogenic data.
Benzo[b]fluoranthene	Not tested orally, other positive carcinogenic or co-carcinogenic data.
Chrysene	Not tested orally, other positive carcinogenic or co-carcinogenic data.
Indeno[1,2,3-c,d]pyrene	Co-carcinogen or initiator with negative carcinogen or <u>in vivo</u> mutagen.
Pyrene	Co-carcinogen or initiator with negative carcinogen or <u>in vivo</u> mutagen.
Fluoranthene	Co-carcinogen or initiator with negative carcinogen or <u>in vivo</u> mutagen.
Benzo[k]fluoranthene	Negative in a single carcinogenic study.
Phenanthrene	Several negative carcinogenic and mutagenic studies but not tested orally.

TABLE 1-1. SUMMARY OF EVIDENCE FOR CARCINOGENICITY OF  
PRIORITY POLLUTANT PAHs (Continued)

Anthracene	Negative studies, tested orally.
Naphthalene	Negative studies, tested orally.

\* No data for evaluation of carcinogenicity were available for acenaphthene, acenaphthylene, or fluorene.

## 4.0 ANTHRACENE, ACENAPHTHENE, FLUORANTHENE, FLUORENE, PHENANTHRENE, AND PYRENE

### 4.1 MATERIALS BALANCE

#### 4.1.1 Introduction

This section reviews both published and unpublished data concerning the production, use, and disposal of anthracene and related PAHs in the United States. Information from the available literature has been reviewed to present an overview of major sources of environmental releases of these compounds. Tables have been included to aid data evaluation. The Section is organized such that the text (Section 4.1.2) discusses the various uses, production sources, and attendant environmental releases of each of the six PAHs covered herein (anthracene, acenaphthene, fluoranthene, fluorene, phenanthrene, and pyrene), separately. Within each chemical-specific section, both major and miscellaneous sources of the compound are discussed. Sources of inadvertent releases of this group of PAHs are covered in Section 4.1.3, and PAHs in publicly-owned treatment works (POTWs) are discussed in Section 4.1.4. The tables, both in the section itself and in Appendix A, are structured to allow comparison of all of these PAHs resulting from the various sources and processes for which data were available.

#### 4.1.2 Production and Use

##### 4.1.2.1 Anthracene

###### Overview

Among the PAHs, anthracene is second in commercial importance to naphthalene. In 1979, approximately 280 kkg of anthracene were imported into the U.S. (U.S. Department of Commerce 1980, see Table 4-1). Also, more than 100 kkg were recovered domestically from creosote oil (Ritchie 1980, Hagman 1980, see Note 2, Appendix A for further details). Therefore, >380 kkg of anthracene are assumed to have been consumed in the U.S. during 1979.

Anthracene was used as an intermediate in the synthesis of various end products (see Table 4-2). It is assumed that most of the anthracene used domestically was incorporated into anthraquinone, which in turn was used to synthesize a wide variety of dyestuffs (Henley Company 1980, LaPine Scientific 1980, and Chung 1978). If one assumes that 1% is released to the environment, approximately >4 kkg of anthracene were released to the environment in 1979. This release is assumed, for lack of data, to be divided equally among the aquatic, atmospheric, and terrestrial environments.

Table 4-1. Quantities of Select PAHs Imported and Isolated Domestically in 1979 (kkg)<sup>a</sup>

	Acenaphthene	Anthracene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
Imported	250	280	100	<1	<1	90
Recovered	<1 <sup>b,d</sup>	>100 <sup>c</sup>	<1 <sup>d</sup>	<1 <sup>d</sup>	<1 <sup>d</sup>	<1 <sup>d</sup>

a) Based on the assumption that the quantities imported in 1979 were equal to those for 1978; numbers have been rounded to nearest ten metric tons.

b) Approximately 500 pounds of acenaphthene were recovered by Eastman Kodak Company (Hawryluk 1980).

c) Henley Company 1980; Hagman 1980; see Note 2, Appendix A for further details.

d) See Note 1, Appendix A for further details.

Source: US. Department of Commerce 1980.

Table 4-2. Uses of Select PAHs as Intermediates

Uses	Acenaphthene	Anthracene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
Soap <sup>a</sup>	x	x	x	x	x	x
Pharmaceuticals <sup>b</sup>	x	x	x	x	x	x
Food Processing <sup>c</sup>	x	x	x	x	x	x
Photographic Fluoras <sup>d</sup>	x <sup>i</sup>	x <sup>i</sup>	x	x	x	x
Pigments and Dyes	x <sup>e g</sup>	x <sup>e</sup>	x <sup>f</sup>	x <sup>g</sup>	x <sup>g</sup>	x <sup>h</sup>
Pyrotechnics		x <sup>i</sup>			x <sup>g</sup>	
Insecticides	x <sup>e g</sup>			x	x	
Fungicides	x <sup>e g</sup>					
Plastics	x <sup>e g</sup>					
Herbicides					x <sup>g j</sup>	
Office Copiers				x <sup>i</sup>		
Miscellaneous <sup>k</sup>	x	x	x	x	x	x

a) Based on assumption (Analabs 1980).

b) Unidentified use in pharmaceuticals industry, (Lachat Chemicals Inc 1980; Eastman Kodak Company 1980; Baker Chemical Company 1980; Columbia Organic Chemicals 1980; and Fisher Scientific 1980).

c) Unidentified use in food processing (Baker Chemical Company 1980); used as an intermediate in the manufacture of a green food dye (Henley Company 1980).

d) Based on assumption (Lachat Chemicals Inc. 1980).

e) The Merck Index 1976.

f) Used as an intermediate to make a fluorescent pigment used in leak detection, clothing and road equipment (Henley Company 1980).

g) Eastman Kodak Company 1980.

h) Hagman 1980; Chung and Farris 1979.

i) Henley Company 1980.

j) Intermediate used in herbicide manufacture, all of which is exported (Henley Company 1980).

k) To include biochemical research laboratory standards and reagents and microbiological stains (Hawryluk, 1980; Aldrich Chemical Company 1980; Analabs 1980; Baker Chemical Company 1980; and Columbia Organic Chemicals 1980).

### Pharmaceutical and Photographic Industries

Anthracene is consumed by the pharmaceutical and photographic industries, where it is assumed to be used only in select, specialized processes due to its low detection frequency and low concentration in wastewaters from those industries (EPA 1980e, EPA 1980f, see also Table 4-2). In a comprehensive pharmaceutical industry profile, only one of 212 plants reported that anthracene was used as a raw material, while one other plant responded that they used this compound in their final product (see Table A-1, Appendix A). Further, when the wastewaters (influent and effluent) of 26 plants were analyzed, with a detection limit of 10 µg/l, anthracene was found only once and at a very low concentration (14 µg/l, see Table A-2). The estimated quantity of anthracene contained in influent wastewaters generated by the pharmaceutical industries for 1979 is <1 kkg (see Table A-2). After in-plant treatment, anthracene was not detected in effluent wastewaters; and upon removal was either injected into deep wells or discharged to lagoons (EPA 1980e, see also Notes 4 and 5, Appendix A for further details). Also, anthracene was not detected in effluents of 112 plants in the photographic industry (EPA 1980f, Klobukowski 1980).

### Miscellaneous Uses

The quantities of anthracene used in the soap, food processing, and pyrotechnic industries are unknown but assumed to be small (i.e., <1 kkg). No information could be found on such uses, either in a comprehensive literature search or through contacts with 10 different anthracene distributors in the U.S. Furthermore, because anthracene is used as an intermediate in the above industries, <1 kkg is estimated to have been released from these industries combined (Henley Company 1980, Baker Chemical Company 1980).

#### 4.1.2.2 Acenaphthene

##### Overview

Approximately 250 kkg of acenaphthene were imported and used in the United States in 1979 (see Table 4-1; see also Note 1, Appendix A for further details). In all cases, acenaphthene was used as an intermediate in the synthesis of other end products (see Table 4-1). It is assumed that the majority of this compound was used in the synthesis of four pigments, since data on other uses could not be found (see Note 3, Appendix A).

Because acenaphthene is used largely as an intermediate in multistep synthesis, it appears likely that <1% of the total quantity used (i.e., <2.5 kkg/yr) is released to the environment. In the absence of specific information, any acenaphthene so released is assumed to be equally divided among the aquatic, atmospheric, and terrestrial environmental compartments.

## Pharmaceutical and Photographic Industries

Acenaphthene is consumed by the pharmaceutical and photographic industries, where it is assumed to be used only in select, specialized processes due to its low detection frequency and low concentration in wastewaters from those industries (EPA 1980f, see also Table 4-2). In a comprehensive pharmaceutical industry profile, only one of 212 plants indicated that acenaphthene was used in the final product, and only three of 26 plants generated wastewaters that contained acenaphthene (EPA 1980e, see also Tables A-1 and A-2, Appendix A). The estimated quantity of acenaphthene contained in influent wastewaters generated by the pharmaceutical industry was <1 kkg. Furthermore, after in-plant treatment, acenaphthene was not detected in effluent wastewaters; the small quantity that was removed was reportedly injected into deep wells or discharged to waste lagoons (EPA 1980e and see also Notes 4 and 5, Appendix A).

In a comprehensive study of the photographic industry (EPA 1980f), acenaphthene was not detected in effluents from 112 photographic industry facilities (Klobukowski 1980).

## Miscellaneous Uses

The quantities of acenaphthene used in the soap, food processing, insecticide, fungicide, and plastics industries are unknown but are thought to be small (i.e., <1 kkg). No information could be found on domestic use, either in a comprehensive literature search or through contacts with the eight different distributors of acenaphthene in the U.S. Furthermore, because acenaphthene is used as an intermediate, it is assumed that <1 kkg would have been released to the environment from all of these industries combined (Eastman Kodak Company 1980, Baker Chemical Company 1980).

### 4.1.2.3 Fluoranthene

#### Overview

Nearly 100 kkg of fluoranthene were imported and used in the U.S. in 1979 (see Table 4-1 and Note 1, Appendix A for further details). The only available information on fluoranthene use was obtained from its distributors (Lachet Chemical Inc., Henley Company, and Baker Chemical Company). In all cases, fluoranthene was reported to be used as an intermediate in the synthesis of other end products (see Table 4-2). One distributor indicated that the major use of fluoranthene was in the synthesis of fluorescent pigments employed for the detection of industrial leaks and for coating materials to make them glow in dim light [such as traffic directors' vests and municipal road equipment, (Henley Company 1980)]. However, the quantity of fluoranthene used in synthesis of fluorescent pigments is unknown.

### Pharmaceutical and Photographic Industries

Fluoranthene is assumed to be used by the pharmaceutical and photographic industries, but only in select, specialized processes, due to its low detection frequency and low concentration in wastewaters from those industries (see Tables A-1 and A-2, Appendix A ). In an industry profile, only one of 212 pharmaceutical plants reported that fluoranthene is used in their final products, and fluoranthene was not detected in any of the wastewaters from 26 plants surveyed (EPA 1980e, see also Appendix A).

In a comprehensive survey of the photographic industry (EPA 1980f), fluoranthene was not detected in effluents from 112 photographic industry facilities (Klobukowski 1980).

### Miscellaneous Uses

The quantity of fluoranthene used in the soap and food processing industries is unknown but is thought to be small (i.e., <1 kkg). No information could be found on domestic uses of fluoranthene, either in a comprehensive literature search or through contact with seven U.S. distributors of fluoranthene. Furthermore, because fluoranthene is used as an intermediate, it is estimated that less than 1 kkg would have been released to the environment from the two industries listed above (Analabs 1980, Henley Company 1980).

Due to the role of fluoranthene as an intermediate in the synthesis of various products, it is assumed that 99% of the fluoranthene imported and used in the U.S. (i.e., 100 kkg) is consumed/converted into end products. Therefore, approximately 1 kkg would be released to the environment; it is assumed, for lack of data, that this release is equally distributed among the aquatic, atmospheric, and terrestrial environmental compartments.

#### 4.1.2.4 Fluorene

Very small quantities of fluorene (i.e., <1 kkg) were imported into the U.S. in 1979 (U.S. Department of Commerce 1980, see also Table 4-1). Furthermore, no domestic fluorene producers could be found, and two distributors for this chemical indicated that all the fluorene used domestically for that year was imported (Henley Company 1980, McKenzie Chemical Works of Louisiana 1980).

Fluorene has diverse uses (see Table 4-2), however, because it is used as an intermediate in the synthesis of other compounds. Only about 1 kkg was used nationwide in 1979; total environmental releases to water, air and land must have been <1 kkg.

#### 4.1.2.5 Phenanthrene

Import and USITC data indicate that domestic commercial use of phenanthrene was very limited in 1979 (<1 kkg was consumed, U.S. Department of Commerce 1980, USITC 1979, and see also Table 4-1).

Phenanthrene is thought to be used by many industries in small quantities for a variety of purposes; however, because <1 kkg was used in 1979, far less than that quantity would have been released to the environment.

#### 4.1.2.6 Pyrene

According to the U.S. Department of Commerce (1980), approximately 90 kkg of pyrene were imported into the U.S. in 1979 (see Table 4-1). Also, there did not appear to be any domestic production of pyrene in 1979 (see Note 1, Appendix A).

In the absence of information concerning other uses, it is assumed that the majority of pyrene used domestically in 1979 was converted into dye intermediates (i.e., dibenzoylpyrene and pyrene-1,3,6,8-tetrasulfonic acid, see Note 6, Appendix A for further details).

Pyrene is also assumed to be used in the pharmaceutical industry (Baker Chemical Company 1980). However, pyrene was not detected in wastewater samples from 26 pharmaceutical plants (see Tables A-1 and A-2, and Note 5, Appendix A).

Pyrene has also been linked to uses as synthesis intermediates in the soap, food processing, and photographic industries (see Table 4-2). However, because no information could be found on specific uses of pyrene in these industries (either in the literature or from seven domestic pyrene distributors), the quantity of pyrene used in this manner is assumed to be small (<1 kkg). For the photographic industry, a comprehensive EPA report (1980f) does not list pyrene as a constituent of any of the effluent wastewaters collected at 112 photographic plants.

Since pyrene was used mainly as an intermediate in the multistep synthesis of the aforementioned dyes and other products (see Table 4-2), it is likely that less than 1% of the total quantity used (90 kkg) was released to the environment. Therefore, <1 kkg of pyrene may have been released to the environment, divided equally among the aquatic, atmospheric, and terrestrial environments.

#### 4.1.3 Inadvertent Sources

##### 4.1.3.1 Combustion

As is true of all PAHs, the chief source of the anthracene group PAHs is combustion. Quantities of these PAHs released from

this source are estimated in Table 4-3. Combustion of wood for residential heating generates the largest amount of PAHs. Anthracene and phenanthrene account for 75% of the total anthracene group emissions from residential wood burning. (Supplemental data concerning PAHs from combustion sources are given in Appendix A, Notes 8 through 15.)

As a byproduct of combustion, PAHs may be found in crankcase oil and may be released to either land or water if the oil is disposed of haphazardly. Table 4-4 shows estimates of the PAHs contained in these releases. (See Appendix A, Note 13 and Table A-12.)

#### 4.1.3.2 Contained Sources

This section presents information, primarily in tabular format, on amounts of anthracene group PAHs contained in coal tar and petroleum. Delineation of all such potential "inadvertent sources" of PAH release is a monumental task, since petroleum- and coal-derived oils, fuels or solvents that contain at least small amounts of PAHs are omnipresent. The major sources discussed here are summarized in two tables: Coal Tar Production and Distillation (Table 4-5) and Petroleum Sources (Table 4-6); supporting data and related information are presented in Tables A-3 to A-7, Appendix A.

It is important to comment on the quality of available data in this section. Specifically, concentrations of the various PAHs in crude oils, coal, or coal and petroleum products are highly variable, depending upon the place or origin and method of processing. Furthermore, as subsequent calculations are based on these concentrations, they can be considered as rough estimates only, at the order of magnitude level of reliability.

##### Coal Tar

Coal tar is the heavy distillate fraction from the destructive distillation (coking) of coal. The distribution of coke-oven tar production in the U.S., PAH concentrations, and environmental releases (Tables 4-7, A-3, -4, and -5) have been combined to provide the information presented in Table 4-5. Naphthalene (see Section 3.1), present in the largest concentration in coal tar, is the only PAH compound warranting recovery and isolation in large amounts. Anthracene is also isolated, but to a lesser extent and usually in crystals that form during creosote oil recovery. Creosote oil is used in the wood preserving industry. Information on PAH

Table 4-3. Estimated Air Emission of PAHs by Combustion, 1978 (kg)

	Residential Coal Combustion <sup>a</sup>	Fireplaces <sup>a</sup>	Primary Residential Wood Heating <sup>a</sup>	Auxiliary Residential Wood Heating <sup>a</sup>	Cigarettes <sup>a</sup>	Coal Refuse Piles <sup>a</sup>	Prescribed Burning <sup>b</sup>	Wildfire <sup>c</sup>	Carbon Black <sup>a</sup>	Tire Wear <sup>d</sup>	Agricultural Burning <sup>e</sup>	Gasoline <sup>d</sup>	Utility Boilers Coal <sup>f</sup>	Oil <sup>f</sup>	Incinerators <sup>g</sup>	Utility and Industrial IC Engines <sup>h</sup>	Gas- and Oil- fired Residential Sources <sup>i</sup>
Acenaphthene	300	4	50	70	neg	1	90	50	1	neg	30	4					30
Anthracene	70	30	500	700	neg	neg	200	100	neg	neg	70	70	3	20	neg		7
Fluoranthene	40	5	100	200	neg	neg			neg	3							
Fluorene	200	neg	100	100	neg	1	90	50	neg	neg	30	30	1	20	neg		
Phenanthrene	70	30	500	700	neg	neg	90	50	neg	neg	30	30	1	20	neg	1	
Pyrene	40	5	100	100	neg	neg	200	100	1	10	60	100	3	8			20
Total	720	74	1,350	1,870	neg	2	580	300	2	13	190	204	7	48	neg	1	57

- a) See Appendix A Note 8 and Note 13. Blanks indicate data not available, negligible < 1 kg.  
 b) See Appendix A Note 9.  
 c) See Appendix A Note 10.  
 d) See Appendix A Note 11.  
 e) See Appendix A Note 12.  
 f) See Appendix A Note 14.  
 g) See Appendix A Note 15.  
 h) EPA 1979b.  
 i) EPA 1979c.

Table 4-4. Select PAHs Discharged in Used Crankcase Oil (kkg)

PAH	Discharge <sup>a</sup>
Anthracene	neg <sup>b</sup>
Fluoranthene	9
Fluorene	3
Phenanthrene	20
Pyrene	<u>10</u>
Total	42

a) Based upon  $2 \times 10^6$  l oil disposed of annually. Releases go presumably to POTWs and landfills. No recycling is assumed.

b) Negligible is <1 kkg.

Source: Peake and Parker 1980 and Tanacredi 1977, see Note 13, Appendix A.

Table 4-5. PAH Materials Balance: Coal Tar Production and Distillation, 1978 (kkg/yr)<sup>a</sup>

	Tar Production <sup>b</sup>	Used By Producers <sup>b</sup>		Sold for Refining <sup>b</sup>		Coal-Tar Pitch <sup>c</sup>	Coal-Tar Creosote Oil <sup>d</sup>	Environmental Releases				
		Refining/ Topping	fuel Others	Quantity	On Hand Dec. 31			Air <sup>f</sup>	Land	Water <sup>e</sup>		Total
										POTW	Surface	
Acenaphthene	26,000	6,200	4,500	400	15,000	2,200	14,000					
Anthracene	23,000	5,500	3,900	350	13,000	2,000	6,900	8				8
Fluoranthene	15,000	3,600	2,600	230	8,600	1,300	14,000	10	7	8	10	35
Fluorene	26,000	6,200	4,500	400	15,000	2,200	10,000	4	2	3	4	13
Phenathrene	77,000	18,000	13,000	1,200	44,000	6,600	35,000					
Pyrene	7,700	1,800	1,300	120	4,400	660	10,000	8	5	6	8	27
<b>Total</b>								<b>30</b>	<b>14</b>	<b>17</b>	<b>22</b>	<b>83</b>

- a) All production values rounded to two significant figures, environmental releases to one figure; blank spaces = data not available. Totals may not add due to rounding.
- b) See Tables A-3 and A-4 for tar production/distribution totals and concentrations of PAHs, respectively. Density of Coal tar = 1.223 kg/l.
- c) See Table A-4 for PAH concentrations; total based on  $790 \times 10^3$  kkg pitch produced in 1978 (USITC 1979).
- d) See Table A-4 for PAH concentrations; total based on  $3.3 \times 10^8$  l creosote oil produced in 1978 (USITC 1979). Density of creosote oil = 1.06 kg/l.
- e) See Table A-5 for coke plant effluent discharge factors. Distribution of discharge: 33% - direct, 25% - POTWs, 2% deep well, 40% quenching (20% - land, 20% - air) (EPA 1979d). All values rounded to one significant figure. See Table 4-7 for
- f) Includes emissions from coke-oven doors (see Table 4-7).

Table 4-6. PAHs in Contained Petroleum Sources, (kkg/yr)<sup>a</sup>

PAH	Input <sup>b</sup>			Environmental Releases <sup>c</sup>							
	Crude Oil <sup>d</sup>	Gasoline <sup>e</sup>	Diesel Fuel <sup>f</sup>	Oil Spills		Gasoline Spills		Petroleum Refinery Wastes			
				Water	Land	Water	Land	Air <sup>h</sup>	Water	Land	
Acenaphthene	ND			neg <sup>g</sup>	neg						
Anthracene	trace		90	neg	neg				neg		
Fluoranthene	84,000	580	20	1	neg	neg	neg	neg	neg		
Flourene	170,000			3	neg						
Phenanthrene	84,000		ND	1	neg					10	
Pyrene	84,000	420	10	1	neg	neg	neg	neg		4	

a) Blanks indicate data not available.

b) See Table A-6 for PAH concentrations.

c) See Appendix A Note 7, for derivations and Table A-6 for PAH concentrations.

d) Based on  $8.4 \times 10^8$  kkg of crude oil consumed (Guerin 1978). ND is not detected.

e) Based on  $7.4 \times 10^6$  bbl/day consumed (Oil and Gas Journal 1979); 42 gal/bbl; 0.73 kg/l.

f) Based on  $3.4 \times 10^{10}$  l/yr; 0.865 kg/l.

g) Less than one kkg.

h) Based on data in Table A-7,  $4,985 \times 10^6$  bbl/day feed for catalytic cracking,  $0.887 \times 10^6$  bbl/day for catalytic hydrocracking (Oil and Gas Journal 1979), 42 gal/bbl.

Table 4- 7. PAH Emissions: Coke-Oven Doors

	Emission Rate (mg/hr/oven) <sup>a</sup>	Yearly Emission (kkg/yr) <sup>b</sup>
Fluorene	30	2
Anthracene	120	8
Pyrene	58	4
Fluoranthene	71	4

a) EPA 1977c

b) Based on 1300 kkg coke produced per typical coke oven battery of 58 ovens; 160,000 kkg/day typical capacity for total by-product coke-making industry (resulting in a total of 123 batteries); 365 day, 24 hour operation; emission data in first column, EPA 1979d.

concentrations in creosote oil and wastewater discharges during use is presented in the previously mentioned tables and Table 4-8, respectively. Of a total of 224 wood preserving plants responding to EPA's data collection protocol, two reported direct discharge, 47 reported discharge to POTWs, and the remainder reported self-contained no-discharge operations [mostly evaporation, with some soil irrigation or treated effluent recycle (EPA 1979e)].

Besides creosote, other principal tar products containing PAHs are pitch and refined tar, used in a variety of applications ranging from road materials and electrodes to shampoos. Coal tar and tar products are also used as fuel (see Table 4-5), either by producers (e.g., iron and steel plants) or distillers.

#### Petroleum Sources

The other fossil fuel source containing appreciable amounts of PAHs is petroleum. The concentration and emissions data in Tables A-6 and A-7 have been combined for use in the summary Table 4-6.

Only spills and petroleum refinery environmental releases are presented here. As mentioned previously, the type of crude feedstock determines its chemical composition and, therefore, the composition of specific waste streams. Other variables include pollution controls, level of technology of the processes used, and operational practices and control. The air emissions listed in Table 4-6 are specifically from petroleum catalytic cracking, which accounts for over 50% of the annual oil feed to refineries (Oil and Gas Journal 1979); the remainder is used for catalytic reforming, for which emissions factors were not available.

#### 4.1.4 Publicly Owned Treatment Works (POTWs)

Input of PAHs to POTWs is largely dependent upon variations in industrial discharges feeding the POTWs and the types of industry in a particular municipality. A recent EPA study of 20 urban POTW facilities with secondary treatment and varying feed conditions produced a materials balance of PAHs shown in Table 4-9.

The materials balance in Table 4-9 was constructed using a total POTW flow of approximately  $10^{11}$  l/day (EPA 1978c) and the average concentrations of the various PAHs in influent, effluent and sludge, presented in Table 4-10. It is assumed for purposes of these calculations that influent and effluent flow rates are equal, i.e., that water losses from sludge removal and evaporation are small compared with influent flows. When these assumptions are used, 70 kkg of all PAHs were discharged from POTWs in 1978, while there was an

Table 4-8. PAH Water Discharges: Timber Products, 1978 (kkg/yr)

PAH	Input <sup>a</sup>	Raw Discharge		Treated Discharge <sup>d</sup>	
		Concentration <sup>b</sup> (mg/l)	Quantity <sup>c</sup>	Concentration <sup>b</sup> (mg/l)	Quantity <sup>c</sup>
Acenaphthene	14,000	5.03	40	2.10	20
Anthracene	6,900	3.45	20	2.07	20
Fluoranthene	14,000	3.84	30	2.13	20
Fluorene	10,000	4.35	30	1.83	10
Phenanthrene	35,000	3.45	20	2.07	20
Pyrene	10,000	2.66	20	1.21	10

a) See Table 4- 5, coal-tar creosote.

a) Source: EPA 1979e.

c) Based on 56% of 476 total plants using creosote or mixture thereof, 350 day/yr, 75,500 liters/day/plant.

d) Assumed to go to POTW (see text).

Table 4-9. PAH Materials Balance for Select PAHs: Municipal POTWs (kkg/yr)<sup>a</sup>

PAH	Input <sup>b</sup>	Environmental Releases		
		Air <sup>c</sup>	Water <sup>d</sup>	Land <sup>e</sup>
Anthracene	120	63	22	35
Phenanthrene	120	63	22	35
Pyrene	37	18	7.3	12
Fluoranthene	15	4.1	3.7	7.2
Fluorene	11	8.4	ND <sup>f</sup>	2.6
Acenaphthene	3.7	3.7	ND	3.8

- a) All values rounded to two significant figures.  
 b) Based on influent concentrations shown in Table 4-10, 1011 liters per day total POTW flow.  
 c) Difference between input and water and land.  
 d) Based on secondary effluent concentrations shown in Table 4-10, 1011 l/day total POTW flow.  
 e) Based on wet sludge concentrations shown in Table 4-10, 6x10<sup>6</sup> metric tons dry sludge generated/yr, wet sludge 95% water (by weight).  
 f) Not detected.

Table 4-10. PAH Concentrations in Municipal POTWs ( $\mu\text{g/l}$ )<sup>a</sup>

PAH	Influent	2° Effluent	Raw Sludge
Anthracene	3.3	0.6	295
Phenanthrene	3.3	0.6	295
Pyrene	1.0	0.2	101
Fluoranthene	0.4	0.1	60
Fluorene	0.3	ND	22
Acenaphthene	0.1	ND	32

a) Average values.

Source: EPA 1980d.

input of 590 kkg. Of that total, 55 kkg of anthracene group PAH were discharged to water.

PAHs discharged in sludge can be estimated from the PAH concentrations in sludge and the quantity of dry sludge produced annually,  $6.0 \times 10^6$  kkg (EPA 1970g). Wet sludge is assumed to be 95% water by weight. As ocean dumping of sludge is mandated to cease by 1981 and if more stringent air quality standards further curb incinerator use (EPA 1979h), the 150 kkg of PAHs contained in sludge may be assumed to be discharged to land. Anthracene group PAHs accounted for 96 kkg (64% of the total).

PAHs released to the atmosphere may be estimated by the difference between the loading in influent and the loading in effluent and sludge according to the following assumptions: (1) PAHs recycled within the activated sludge process will eventually be "wasted"; and (2) PAHs are lost to the atmosphere by mechanical stripping, or aeration.

These assumptions yield an estimate of 390 kkg of PAHs released to the atmosphere from POTWs in 1978. Approximately 160 kkg (41% of the total) are attributed to anthracene group PAHs.

#### 4.1.5 Summary

Table 4-11 summarizes the production and use and estimated releases for the anthracene group PAHs. Of the group, anthracene, acenaphthene, fluoranthene, and pyrene are imported, and anthracene is recovered from creosote oil. Otherwise, these compounds are produced and used in the United States only in very small quantities. The releases are primarily from inadvertent production in the combustion of wood and fossil fuels. Most of these releases are estimated to originate from household heating with wood, although both prescribed burning and wildfire appear to be important sources. Residential coal combustion is also an important source, particularly for acenaphthene and fluorene.

Table 4-12 summarizes the estimated environmental releases by media for the compounds in this group. It can be seen that releases to the atmosphere predominate. The only releases to surface waters generally identified were those from POTWs.

Table 4-11. Summary of Emissions Data for Select PAHs - 1978

	Quantity (kkg/yr)	Estimated Environmental Releases (kkg)				
		Air	Land	Water		Total
				Surface	POTW	
<u>Anthracene</u>						
Production						
Imported	280	-	-	-	-	-
Recovered from creosote oil	>100					
Uses						
Synthesis of dye stuff	most of supply	1	1	1	1	4
Pharmaceutical Industry			<1	<1		<1
Photographic Industry				<1		<1
Soap, food processing, pyrotechnic				<1		<1
Inadvertent Sources						
Combustion		1482				1482
Coal Tar Production & Distillation		8				8
Contained Petroleum Sources (Spills and Refinery Wastes)		<1	<1	<1		<1
Timber products (use of creosote)					20	20
Used Crankcase Oil			<1		<1	<1
POTW		63	35	22		120

Table 4-11. Summary of Emissions Data for Select PAHs - 1978 (Continued)

	Quantity (kg/yr)	Estimated Environmental Releases (kg)				Total
		Air	Land	Water Surface	POTW	
<u>Acenaphthene</u>						
Production						
Imported	250	-	-	-	-	-
Recovered	<1	-	-	-	-	-
Uses						
Intermediate in Synthesis of dye	Most of supply	<1	<1	<1	<1	<2.5
Pharmaceutical Industry			<1	<1		<1
Photographic Industry				<1		<1
Soap, food processing, pesticides, plastics	<1			<1		<1
Inadvertent Sources						
Combustion		455				455
Coal Tar Production & Distillation				<1		<1
Contained Petroleum Sources (Spills and Refinery Wastes)			<1	<1		<1
Timber Products (use of creosote)					20	20
Used Crankcase Oil						
POTW		4	4	<1		8

Table 4-11. Summary of Emissions Data for Select PAHs - 1978 (Continued)

	Quantity (kkg/yr)	Estimated Environmental Releases (kkg)				Total
		Air	Land	Water		
				Surface	POTW	
<u>Fluoranthene</u>						
Production						
Imported	100					
Recovered	<1					
Uses						
Intermediate in pigment						
Pharmaceutical Industry			<1	<1		<1
Photographic Industry				<1		<1
Soap, food processing industry	<1			<1		<1
Inadvertent Sources						
Combustion		811				811
Coal Tar Production & Distillation		10	7	10	8	35
Contained Petroleum Sources (Spills & Refinery Wastes)		<1	<1	1		1
Timber Products (use of creosote)					20	20
Used Crankcase Oil			4.5		4.5	9
POTW		4	7	4		15

Table 4-11. Summary of Emissions Data for Select PAHs - 1978 (Continued)

	Quantity (kg/yr)	Estimated Environmental Releases (kg)					Total
		Air	Land	Water		POTW	
				Surface			
<u>Fluorene</u>							
Production							
Imported	<1						
Recovered	<1						
Uses							
Intermediate	<1	<1	<1	<1		<1	<1
Inadvertent Sources							
Combustion		400					400
Coal Tar Production & Distillation		4	2	4		3	13
Contained Petroleum Sources (Spills and Refinery Wastes)				3			3
Timber Products (use of creosote)						10	10
Used Crankcase Oil			1.5			1.5	3
POTW		8	3	<1			11

Table 4-11. Summary of Emissions Data for Select PAHs - 1978 (Continued)

	Quantity (kg/yr)	Estimated Environmental Releases (kg)				
		Air	Land	Water		Total
				Surface	POTW	
<u>Phenanthrene</u>						
Production						
Imported	<1					
Recovered	<1					
Uses						
Miscellaneous	<1	<1	<1	<1	<1	<1
Inadvertent Sources						
Combustion		1523				1523
Coal Tar Production & Distillation						
Contained Petroleum Sources (Spills and Refinery Wastes)		10		1		11
Timber Products (use of creosote)					20	20
Used Crankcase Oil			10		10	20
POTW		63	35	22		120

Table 4-11. Summary of Emissions Data for Select PAHs - 1978 (Continued)

	Quantity (kkg/yr)	Estimated Environmental Releases (kkg)				Total
		Air	Land	Surface Water	POTW	
<u>Pyrene</u>						
Production						
Imported	90					
Recovered	<1					
Uses						
Dye Intermediate		<1	<1	<1	<1	<1
Pharmaceutical Industry			<1	<1		<1
Photographic Industry				<1		<1
Soap and Food Processing	<1			<1		<1
Inadvertent Sources						
Combustion		747				747
Coal Tar Production & Distillation		8	5	8	6	27
Contained Petroleum Services (Spills and Refinery Wastes)		4		1		5
Timber Products (use of creosote)					10	10
Used Crankcase Oil			5		5	10
POTW		18	12	7		37

Source: See text.

Table 4-12. Summary of Estimated Environmental Releases of Select PAHs - 1978

Compound	Environmental Release (kgg/year)			
	Air	Land	Surface Water	POTW
Anthracene	1560	40	20	20
Acenaphthene	460	4	<1	20
Fluoranthene	830	20	20	30
Fluorene	410	10	10	10
Phenanthrene	1600	40	20	30
Pyrene	780	20	20	20

Source: See text.

## 4.2 FATE AND DISTRIBUTION IN THE ENVIRONMENT

### 4.2.1 Introduction

This section characterizes the fate processes that determine the ultimate distribution of the anthracene group PAHs in the aquatic environment and, therefore, the opportunities for water-borne exposure of humans and other biota. Much of the information presented pertains specifically to anthracene; however, since the properties and fate characteristics of this compound are representative of those of the other compounds in the group, the behavior of anthracene in the environment is believed to be a good model for the entire group.

Section 4.2.2 presents an overview of the environmental loading of aquatic media with anthracene, from both direct releases to surface water and physical transport (deposition from the atmosphere). In Section 4.2.3, physical/chemical properties of anthracene are summarized in order to identify the processes that transform and transport the chemical upon its release to the environment (Section 4.2.3.1). Section 4.2.3.2 discusses the interplay of fate processes that determines the major pathways of anthracene in aquatic environmental media. Modelling efforts were undertaken based upon environmental loadings estimated from Section 4.1, in order to characterize the fate and distribution of anthracene in specific environmental scenarios; these are discussed in Section 4.2.3.3. Monitoring data from STORET and a limited number of other surveys are summarized in Section 4.2.4 to provide indications of concentrations of anthracene group PAHs actually detected in aquatic media. Finally, Section 4.2.5 summarizes those aspects of the fate and ultimate environmental distribution of anthracene having the greatest significance for the water-borne exposure of humans and other biota.

### 4.2.2 Input to Aquatic Media

Data presented in Section 4.1 indicate that although anthracene (as well as the other PAHs in this group) is produced and used commercially in the U.S., direct releases to surface water appear to be very low. Anthracene group PAHs are rarely observed in final industrial effluents. Direct discharges of anthracene to surface waters totalled ~2 kkg in 1978; in contrast discharges to POTWs were 20 kkg, and atmospheric emissions were almost 1560 kkg. However, anthracene may be transported indirectly from the atmosphere to aquatic systems via wet and/or dry deposition.

The air-to-surface pathway has been evaluated and that analysis is presented in Appendix B of this report. The results for anthracene are summarized in Table 4-13. Under ambient conditions typically encountered in either urban or rural areas, anthracene is expected to partition preferentially to the vapor phase. Less than 10% of the airborne anthracene is likely to be adsorbed onto ambient aerosols. However, in the plume from a combustion source smokestack, where aerosol concentrations are much greater, as much as 97% of the anthracene may be adsorbed. As a result of the preferred association with the vapor phase, dry deposition of anthracene under ambient conditions is expected to be a slow process, with a characteristic velocity of less than 0.1 cm/sec; in contrast, dry deposition velocity near a combustion source would be 1.0 cm/sec.

TABLE 4-13. EVALUATION OF AIR-TO-SURFACE  
PATHWAY FOR ANTHRACENE

	<u>Rural</u>	<u>Urban</u>	<u>Near Combustion Source</u>
Adsorbed Fraction of Airborne Mass	0.002	0.06	0.97
Dry Deposition Velocity (cm/sec)	0.02	0.08	1
Precipitation Scavenging Ratio	130	$3.6 \times 10^3$	$1.2 \times 10^5$
$\left[ \frac{\text{ng/l(water)}}{\text{ug/m}^3(\text{air})} \right]$			
Percent of Atmospheric Emissions Deposited:	<u>Rural</u>	<u>Urban</u>	
- dry deposition	1	4-19	
- wet deposition	<1	1-7	
- total	1	5-26	

Source: See Appendix B.

The vapor/aerosol partitioning also affects the precipitation scavenging ratio [rainfall concentration (ng/l) divided by air concentration ( $\mu\text{g}/\text{m}^3$ )]. The estimated scavenging ratio for anthracene is sensitive to the assumed aerosol concentration, ranging from 130 for typical rural conditions to  $1.2 \times 10^5$  for rainfall passing through the plume of a major combustion source.

Taking into account the observed concentrations of anthracene in both rural and urban areas, as well as the chemical degradation rates, it is estimated that only about 1% of emitted anthracene is deposited in rural areas. On the other hand, 5% to 26% of the anthracene emitted in major urban areas (100 square miles) is likely to be deposited there.

More than 75% of the total deposition is expected to be due to dry deposition processes, including fallout, impaction of particles with adsorbed anthracene, and dissolution of gaseous anthracene by surface moisture.

On the basis of the atmospheric emissions data given in Section 4.1 (1560 kkg/yr) and the range of percent deposition of atmospheric emissions given in Table 4-13 (5-26%), 75-400 kkg/yr can be expected to be deposited on the surface of the United States. If one assumes that approximately 2% of the total area of the continental United States is inland surface water (U.S. Bureau of Census 1980), 1.5-8.0 kkg/yr may land directly on water. The remainder of the fallout would be deposited on the surface of dry land. A fraction of that amount could be transported ultimately to aquatic systems by surface runoff. However, there are insufficient data to allow a reasonable estimate of the extent of this pathway.

The above discussion of the air-to-surface pathway clearly indicates that a significant amount of airborne anthracene near combustion sources may be removed and deposited on the land or water surfaces. A water body near a combustion source could receive large quantities of anthracene group PAHs by this pathway.

#### 4.2.3 Environmental Fate

##### 4.2.3.1 Basic Physical/Chemical Properties

The physical/chemical properties of anthracene and related PAHs (Table 4-14) suggest a number of important pathways for this chemical in the aquatic environment. Anthracene and its related compounds have relatively high octanol:water partition coefficients and low water solubilities which suggest that adsorption to sediments may be important in determining their transport and fate. The vapor pressures and Henry's Law constants for this group, although intermediate for PAHs, are still quite low; therefore, volatilization is likely to be of minimal importance as a removal mechanism in aquatic systems.

Removal pathways, as well as the chemical and biological fate processes of anthracene and the related PAHs, are discussed in the following sections.

TABLE 4-14. PHYSICAL/CHEMICAL PROPERTIES OF THE ANTHRACENE GROUP PAHS

	Acenaphthene	Anthracene	Fluoranthene	Fluorene	Phenanthrene	Pyrene	References
Formula	C <sub>12</sub> H <sub>10</sub>	C <sub>14</sub> H <sub>10</sub>	C <sub>16</sub> H <sub>10</sub>	C <sub>13</sub> H <sub>10</sub>	C <sub>14</sub> H <sub>10</sub>	C <sub>16</sub> H <sub>10</sub>	
M.W.	154.21	178.24	202.26	166.23	178.24	202.26	Weast (1974)
Vapor Pressure (torr)	10 <sup>-3</sup> -10 <sup>-2</sup> (20°C) 1.6x10 <sup>-3</sup> (25°C)	1.95x10 <sup>-4</sup> (20°C) 2.4x10 <sup>-4</sup> (25°C)	10 <sup>-6</sup> -10 <sup>-4</sup> (20°C) 5x10 <sup>-6</sup> (25°C)	10 <sup>-3</sup> -10 <sup>-2</sup> (20°C) 1x10 <sup>-2</sup> (25°C)	6.8x10 <sup>-4</sup> (20°C) 9.6x10 <sup>-4</sup> (25°C)	6.85x10 <sup>-7</sup> (20°C) 2.5x10 <sup>-6</sup> (25°C)	Callahan et al. (1979) SRI (1980)
Saturated Vapor Concentration at (25°C) (g/m <sup>3</sup> )	1.3x10 <sup>-2</sup>	2.3x10 <sup>-3</sup>	5.4x10 <sup>-3</sup>	8.9x10 <sup>-2</sup>	9.2x10 <sup>-3</sup>	2.7x10 <sup>-5</sup>	Calculated PV-nRT
Water Solubility (mg/l)	3.42	0.045 0.073	0.26	1.69 1.98	1.00 1.29	0.14 0.132	Callahan et al. (1979)
Melting Pt. (°C)	96.2	216.2 216.4	111	116-117	101	156 (corrected)	Weast (1974)
Boiling Pt. (°C)	279	340 (corrected)	~375	293-295	340	393	Weast (1974)
log K <sub>ow</sub>	4.33	4.45	5.33	4.18	4.46	5.32	Callahan et al. (1979)
log K <sub>oc</sub>	3.72	4.20	4.64	3.65	4.20	4.64	SRI (1980)
Henry's Law constant $\left[ \frac{\text{atm m}^3}{\text{mole}} \right]$	9.33x10 <sup>-5</sup>	1.25x10 <sup>-3</sup>	5.12x10 <sup>-6</sup>	1.29x10 <sup>-3</sup>	2.25x10 <sup>-4</sup>	4.75x10 <sup>-6</sup>	Calculated: $\frac{\text{vapor pressure}}{\text{water solubility}}$

#### 4.2.3.2 Pathways in the Aquatic Environment

##### Introduction

This section examines the pathways of anthracene in the aquatic environment. The processes for actual removal from the water column are reviewed first, i.e., volatilization and sedimentation; the chemical transformation and degradation pathways for anthracene in solution are described; and finally, biodegradation and its role in the ultimate fate of PAHs is considered.

##### Volatilization and Atmospheric Fate

The actual rate of volatilization in the environment is dependent upon the wind velocity, temperature, and the amount of air/water mixing. Southworth (1979) measured a half-life of  $\sim 300$  hours for anthracene at a depth of 1.0 m under rapidly stirred laboratory conditions of  $\sim 0.04$  m/sec wind, and 0.1 m/sec water current. Increases in both wind and current velocity decreased the measured half-life; a four-fold decrease in half-life was observed with a ten-fold increase in both wind and current velocity. Although extrapolating these data to environmental conditions is difficult, it is likely that, except under the rare conditions of high temperature, high winds, and shallow depths, the volatilization of anthracene will be insignificant. The Henry's Law constant is a good measure of the tendency of a solute to escape from water. The values of this parameter for the other PAHs in the anthracene group indicate that volatilization will be unimportant for these compounds as well.

The portion of these PAHs that does volatilize is expected to be degraded by photooxygenation to oxygenated compounds, including quinones (Radding *et al.* 1976). Radding *et al.* (1976) estimated a half-life of 10 hours for hydroxy radical photolysis of anthracene, phenanthrene and pyrene, indicating that this process may be important in the fate of airborne PAHs. The reaction with singlet oxygen, although occurring with a shorter half-life ( $\sim 5$  hours for anthracene), is not likely to be important since the availability of singlet oxygen in air is low.

##### Adsorption and Sedimentation

Due to anthracene's limited water solubility and high octanol:water partition coefficient, as shown in Table 4-14, much of the anthracene in the aquatic system can be expected to be found adsorbed onto particulate matter. Anthracene is likely to be adsorbed onto both organic and non-organic particulate materials.

Adsorption and concentration of PAHs in the presence of various inorganic substrates such as activated carbon, calcareous material, silica, glass, soil particles, and organic particles have been cited by numerous authors as summarized in Neff (1979). From studies by Herbes (1977) on autoclaved yeast cells, it has been predicted that a significant fraction (0.15-0.65) of anthracene in the aqueous system

would be associated with both detrital and living organic matter in natural waters with only moderate amounts of suspended solids. The role of mineral particulate material may be far less significant with respect to PAH adsorption than the role of organic particulates.

The importance of organic adsorption is supported by the observation that 72% of anthracene in solution was adsorbed by yeast cells (Herbes 1977), whereas only 22% was adsorbed by bentonite clay (Meyers and Quinn 1973). In a similar experiment with autoclaved yeast cells and anthracene (Southworth 1977), a partition coefficient (solid:water) of 25,000 was observed. In another study, a partition coefficient of 1600 was reported for adsorption onto inorganic particulates (Versar 1979).

Solubilization of PAHs via micellar mechanisms involving surface active species such as detergents, biopeptides and alkaloids is discussed by several authors (Eisenbrand 1971, Elsworth *et al.* 1968). However, these laboratory-observed solubilizations may be much less important in natural waters where solubilizer concentrations are likely to be much lower than particulate concentrations (Radding *et al.* 1976).

The actual amount and rate of PAHs adsorbed onto particulates under environmental conditions seem to be governed by an equilibrium exchange between adsorbed and soluble PAHs (Smith 1978, Lewis 1975). Lewis (1975) analyzed five PAHs, including fluoranthene, in both the particulate and soluble phases from river samples. PAHs were found in both phases, with soluble PAHs accounting for 2-16 percent of the concentration of particulate PAHs. Fluoranthene, the most soluble of the PAHs analyzed in that study, was found at the highest concentration in solution. Pyrene's solubility and partition coefficients are similar to those of fluoranthene and should follow the distribution observed for fluoranthene. Anthracene has a lower solubility and higher partition coefficient than fluoranthene, and should be found in the water column at lower concentrations. The other compounds in this group, i.e., fluorene, acenaphthene, and phenanthrene, have higher solubilities and lower partition coefficients, thus should be found in the water column at somewhat higher levels than fluoranthene.

The ultimate fate of PAHs that have been adsorbed onto particulates will depend partially upon the amount of sedimentation in the environmental system. Sedimentation occurs as particulates gradually settle out of the water column; flocculation of suspended clay-sized particles (as occurs in the increasing salinity gradient of an estuary) will increase the rate of deposition (Neff 1979). Once deposited in sediment, PAHs are much less liable to be degraded photochemically; furthermore, biodegradation in sediments is not very rapid, especially under anaerobic conditions (see discussion on Biological Fate).

For anthracene, Southworth (1977) estimated the rate of removal from solution based on adsorption onto particulates and subsequent sedimentation. Using a sedimentation rate of 8.4 cm/year, a removal rate of  $7.2 \times 10^{-3}$  hours<sup>-1</sup> ( $t_{1/2} = 96$  hours) was calculated for clay particles and  $1.44 \times 10^{-3}$  hours<sup>-1</sup> ( $t_{1/2} = 481$  hours) for silt particles. Whether these rates will be competitive with other removal processes

depends upon the actual hydrologic conditions. Removal by sedimentation is expected to occur more slowly than the degradation pathway but will be competitive with volatilization in some aquatic systems.

The actual accumulation of anthracene in sediments occurs not only due to sedimentation, but also due to adsorption directly onto the sediments; so adsorption rates are expected to be higher than those calculated on the basis of sedimentation alone. In another study (Armstrong *et al.* 1977), the concentrations of PAHs in sediments and seawater were monitored in a Texas bay receiving a brine effluent. Nearly all the aromatics were found to be at much higher concentrations in sediment than in the overlying water columns. At a distance of 15 m from the dune outfall, higher weight aromatics (including anthracene) were found in the sediments, but were undetectable in the water column (detection limit 0.1 µg/l). For all but the most soluble, low molecular weight PAHs, concentrations in sediments are expected to be greater than concentrations in solution by a factor of more than 1000.

To the extent that sedimentation is controlled by flow rate, PAHs would be expected to accumulate in placid lakes and reservoirs. Much of river-borne particulate PAHs would eventually be carried to the ocean, where deltas and estuaries have been shown to be traps for suspended matter (White and Vanderslice 1980). Onshore and alongshore currents combine to restrict suspended matter in the ocean to continental shelf areas. Gross (1970) has estimated that 90% of river-borne particulates accumulate in this region of the ocean, where they are subject to resuspension and wave/current transport.

#### Chemical Degradation

PAHs have high absorptivities at wavelengths above the solar cut-off (300 nm). For this reason, direct photochemical degradation (initiated by absorption of light by the PAHs, rather than an intermediate) is expected to be a significant fate process in water despite the inefficient nature of photochemical reactions (quantum yields in the range of 0.001 to 0.01) (Smith *et al.* 1978). Table 4-15 presents the half-lives calculated for photolysis reactions and quantum yields for some of the PAHs in the anthracene group.

Anthracene and pyrene have fairly low half-lives, and quantum yields in the middle of the range for PAHs, indicating that photooxidation of these two PAHs in aquatic environments is likely to be an important process. Phenanthrene has a longer half-life (an effect usually seen in "bent" compounds, i.e., those in which the rings are not arranged linearly), and is expected to photolyze more slowly. Fluoranthene is an anomalous compound, exhibiting an unusual dependence of quantum yield on wavelength, as well as peculiar excited-state behavior. This behavior is probably related to the fact that fluoranthene, unlike the other PAHs studied, is a nonalternate aromatic hydrocarbon (i.e., contains a cyclopenta-ring and has only limited resonance) (Zepp and

TABLE 4-15. HALF-LIVES AND QUANTUM YIELDS FOR PHOTOLYSIS OF THE ANTHRACENE GROUP PAHs

<u>Compound</u>	<u>Disappearance Quantum Yield</u>	<u>Photolysis Half-Life (hours)</u>
Anthracene	0.003 (at 366 nm)	0.75
Phenanthrene	0.010 (at 313 nm)	8.4
Pyrene	0.002 (at 313 nm)	0.68
	0.0022 (at 366 nm)	0.68
Fluoranthrene	0.00120 (at 313 nm)	21
	$0.2 \times 10^{-6}$ (at 366 nm)	

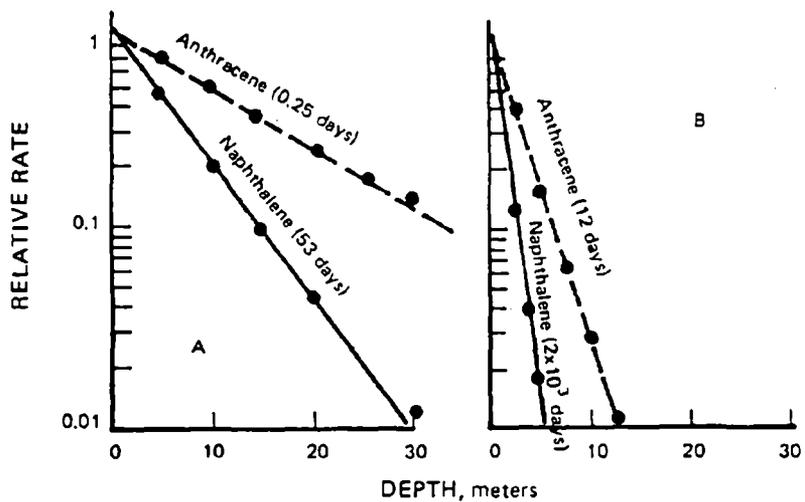
Source: Zepp and Schlotzhauer (1979)

Schlotzhauer 1979). Nagata and Kondo (1977) studied the rate of photodegradation of several PAHs in mixed acetone-water or carbon tetrachloride-water solvents. Under laboratory conditions, the PAHs do seem to be photosensitive. After 10 hours, approximately 65% of the anthracene and phenanthrene in the solution had been photodegraded; about 10% of the pyrene and fluorene had been photodegraded in the same time period.

The importance of photooxidation will vary with the actual environmental conditions and the location of the compound in the water column. In one experiment, Southworth (1977) observed a photolysis half-life of 35 minutes in distilled water under midday sun, in midsummer at 35°N latitude. Using the procedure of Southworth (1977), Zepp and Cline (1977) predict a photolytic half-life of 4.8 hours under average winter solar conditions, and 1.6 under summer conditions in shallow waters. A 19-fold increase in the photolytic half-life of anthracene in a turbid water system containing ~50 mg/l of clay suspension supports the prediction that adsorption of light by dissolved and suspended matter will greatly reduce photolysis (Southworth 1977). Zepp and Schlotzhauer (1979) further demonstrate the effect of light attenuation on PAHs. Figure 4-1 shows the depth dependence of direct photolysis for anthracene during summer. The data show photolysis half-lives for anthracene of 6 hours in mid-Gulf water, and 1.2 days in the coastal environment. The difference is primarily attributable to the greater attenuation of light in the biologically active, productive coastal zone.

An important factor limiting photolysis in the environment is the tendency for anthracene and other PAHs to partition to sediments where no light is present (Zepp and Schlotzhauer 1979). For surface PAHs (e.g., oil slicks), however, photodegradation is expected to be quite significant. Lee et al. (1978) report qualitatively from model ecosystems that photochemical oxidation seems to be an important process in the destruction of oil slicks that contain fluoranthene.

Chlorine and ozone, used in water purification processes, are strong oxidants that react with PAHs to form quinones. Several studies report various half-lives for the reaction of PAHs with chlorine, generally less than 0.5 hours. Data summarized by Radding et al. (1976) indicate that though the reactivities of the PAHs do vary, the half-lives are generally <0.5 hours when exposed to 10<sup>-5</sup>M solutions of chlorine under the standard conditions for water purification. Smith et al. (1977) identified several polychlorinated aromatics during chlorination of biphenyl and naphthalene, in addition to the quinones; some of these polychlorinated aromatics may be highly toxic and persistent in the environment.



**FIGURE 4-1** COMPUTED RELATIONSHIP BETWEEN DEPTH AND AVERAGE HALF-LIFE FOR PHOTOLYSIS OF ANTHRACENE IN THE TOP 35 M OF SEAWATER

**Note:** Data for Naphthalene (solid line) included for comparison. (A) mid-Gulf and (B) coastal water.

**Source:** Adapted from Zepp and Schlotzhauer (1979).

Ozone is also frequently used for water treatment. Radding et al. (1976) reported that PAHs generally will react with ozone. Il'natskie et al. (1968) measured the amounts of PAHs after treating 0.0067 mg/l of PAH with 40 mg/l of ozone for 1 minute at 25°C. From these data, Radding et al. (1976) calculated a half-life of 41 minutes for the reaction of pyrene with ozone. The data suggest that in urban water supplies treated with ozone, the lifetimes of PAHs would be quite short if the ozone does not evaporate or become consumed more rapidly by other organics and organisms.

## Biological Fate

### Introduction

Very little information is available on the biological fate of this PAH group except for anthracene. Bioconcentration data from laboratory studies are presented in Table 4-16. The transport, bioaccumulation and biodegradation of anthracene in aquatic ecosystems have been studied fairly extensively.

### Bioaccumulation

Bioaccumulation studies of anthracene have so far been limited to invertebrates. No measurements were available for any fish species.

Uptake by filter-feeding organisms may constitute a major pathway of entrance of PAHs to aquatic food chains. Freshwater zooplankton specifically Daphnia spp., have been shown to concentrate anthracene from both dissolved and particulate forms. Once taken up by zooplankton, it has been shown that anthracene resides in three compartments within Daphnia: (1) a rapidly-eliminated compartment that contains approximately 30% of the ingested PAHs; (2) a slowly-depurated compartment containing 60% of the PAH; and (3) a tightly-bound residue of about 8% of the PAHs. The material that is readily eliminated is believed to have been converted to metabolites, while that which is retained is unaltered anthracene. Thus anthracene and not its metabolites may be transported up the food chain.

The fate of anthracene was examined in freshwater pond microcosm studies, which simulated natural conditions. Radiolabeled anthracene was introduced, and after 12 weeks, approximately 15% of the anthracene remained in the water, with most of it accumulated in the upper 2 cm of sediment. The organisms present in the microcosm included periphyton, snails, snail eggs, zooplankton, and water mites. All organism accumulated <sup>14</sup>C-anthracene to about 10<sup>3</sup> times the levels in water. In all microcosm experiments, the highest accumulation was found in water mites and snails. These animals represent the highest levels of the grazing and detrital food chains, respectively, in this experimental system, suggesting that anthracene or its degradation products may undergo bio-magnification (Giddings et al. 1978).

TABLE 4-16. BIOACCUMULATION DATA FOR ANTHRACENE

<u>Organism</u>	<u>Compound</u>	<u>Exposure Time (hr)</u>	<u>BCF<sup>a</sup></u>	<u>Reference</u>
Cladoceran <u>Daphnia magna</u>	Anthracene	1	200	Herbes (1976)
Cladoceran <u>Daphnia pulex</u>	Anthracene	24	760	Herbes and Risi (1978)
Mayfly <u>Hexagenia sp.</u>	Anthracene	28	3500	Herbes (1976)

a) BCF = Bioconcentration factor.

The rate of PAH uptake is more rapid than the rate of metabolism in Daphnia, which results in bioaccumulation by factors of several hundred-fold. A potential exists for exposure of fish through feeding on zooplankton; therefore, water column concentration alone may not provide enough information to indicate the potential for adverse effects to fish populations. This exposure pathway to fish has not been investigated.

#### Microbial Biotransformation

The anthracene group of PAHs is subject to microbial breakdown; the rate and extent of degradation within the class of compounds is variable. Structural factors such as ring number and type of ring fusion influence biodegradation. Other environmental fate processes such as adsorption, solubility, vaporization, and other competitive transformation reactions also affect biodegradation of PAHs. Most biodegradation studies are laboratory investigations, commonly conducted in simplified systems with the goal of eliciting biodegradation. Under environmental conditions, persistence may be considerably longer than in the laboratory. This section describes the biodegradability of the anthracene group of PAHs, based upon laboratory and field studies, including rate and metabolic product data, and discusses environmental variables that influence the rate of reaction.

Microorganisms act on PAHs by removing one cyclic unit at a time (Alexander 1977). This is supported by an observed inverse relationship between ring number and degradation rate.<sup>1</sup> Tricyclics, such as anthracene, are reduced to dicyclic intermediates which, in turn, are oxidized to catechol, gentisic acids, etc. (Alexander 1977). Figure 4-2 shows this more expanded metabolic pathway.

Not all microorganisms are capable of using PAHs as sole carbon sources; thus cometabolism may play a role in degradation (Alexander 1977). Fungi, especially, may add hydroxyls to the aromatic ring but be unable to break the ring. These transformations may create a problem greater or equal to the presence of the parent compound due to the possible production of harmful intermediates rather than complete mineralization to CO<sub>2</sub> and H<sub>2</sub>O (Alexander 1977).

Presented in Table 4-17 are a number of reported biodegradation products derived from anthracene. They are primarily intermediates in the multistep pathway of reactions leading to eventual complete mineralization.

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<sup>1</sup> It must be mentioned, however, that other factors such as substituent type and size, interfere with this relationship so it is not always evident. Malaney did not find a direct relationship between ring number and biodegradability (Malaney et al. 1967).

### Rates of Biodegradation

The rate of biodegradation of PAHs is quite variable across this chemical group. Table 4-18 presents quantified rates of biodegradation reported for the anthracene group in soil and freshwater systems. Marine bacteria have also been reported capable of degrading phenanthrene, anthracene, and fluorene (Dean-Raymond 1975). One study on estuarine populations is presented. Due to the variety of test methods, analytical techniques, microbial species and data analyses used in biodegradation studies, it is difficult to compare the results from the different tests reported in Table 4-18.

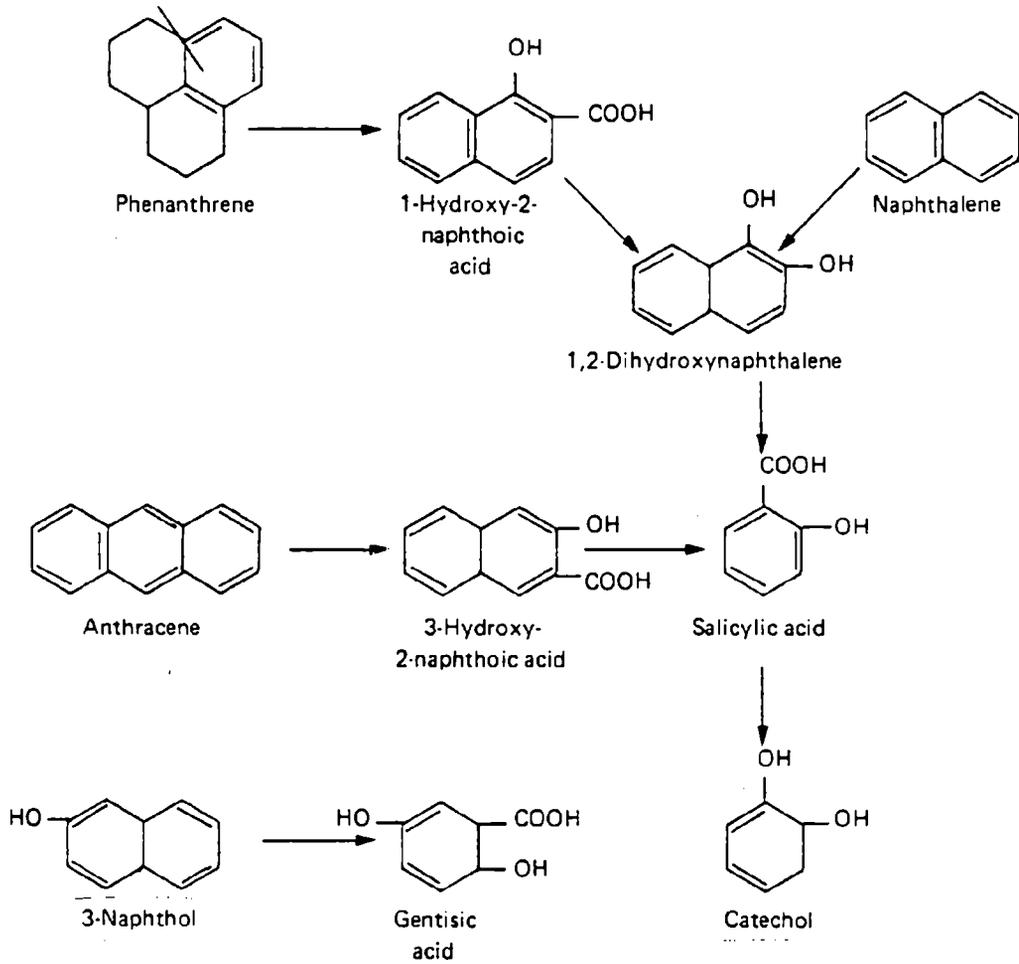
Some general trends in PAH biodegradability are illustrated by the results in Table 4-18. Anthracene, for which the most data were available, is readily degradable in acclimated cultures; however, half-lives are quite variable, ranging from on the order of hours to weeks. Degradation is slower in previously unexposed populations (Giddings et al. 1979). No data were available for acenaphthene. One study each on fluorene and fluoranthene reported significant degradation in one week at a 5 mg/l concentration of PAHs in water and a much lower percentage degraded at 10 mg/l (0% in the case of fluoranthene) (Quave et al. 1980). The results for phenanthrene seem to be contradictory. One study found the compound to be the most readily degradable of 17 PAHs tested (22-46% of theoretical oxygen demand removed) (Malaney et al. 1967); another study reported a mean degradation rate of 80% in one month (Sherrill and Saylor 1980); and a third study found 0% degradation in one week (Quave et al. 1979). The studies on pyrene generally indicated a lower rate of degradation than for anthracene and phenanthrene, with the removal of pyrene apparently enhanced by the presence of other PAHs (McKenna and Heath 1976).

The Gardner et al. (1979) study on biodegradation of anthracene and fluoranthene in estuarine sediment populations was not continued long enough to estimate a half-life for persistence. The results did indicate that the presence of polychaete worms increased the rate of degradation of fluoranthene. This may have been due to the role of the worms in sediment mixing or their own metabolism of the substances. The results for anthracene showed no difference when worms were present. Degradation was greatest in populations in large grain-size sediment and higher in the surface than in the subsurface sediment layers.

The turnover time and transformation rate of PAHs in both acclimated and unacclimated stream populations (Herbes and Schwall 1978) provide a good estimation of the environmental persistence of these compounds, as well as the importance of microbial adaptation (see Table 4-19). The turnover time in the non-acclimated populations was 167 days. How applicable these aquatic turnover times are for soil is unknown. However, the acclimated population turnover time could be comparable to a well-acclimated soil population.

TABLE 4-17. BIODEGRADATION PRODUCTS REPORTED FOR THE ANTHRACENE GROUP PAHS

<u>PAH</u>	<u>Degradation Products</u>	<u>Reference</u>
Anthracene	2,3-dihydroxynaphthalene via trans-1,2-dihydro-1,2-dihydroxyanthracene, 1,2-dihydroxyanthracene and 2-hydroxy-3-naphthoic acid.	Evans et al. (1965)
Phenanthrene	1-hydroxy-2-naphthoic acid, salicylic acid, catechol.	Kaneko et al. (1968, 1969)
Phenanthrene	1,2-dihydroxynaphthalene via trans-3,4-dihydro-3,4-dihydroxy-phenanthrene; 3,4-dihydroxyphenanthrene; and 1-hydroxy-2-naphthoic acid.	Colla et al. (1959)



Source: Alexander (1977).

FIGURE 4-2 MICROBIAL DECOMPOSITION OF PAH COMPOUNDS WITH TWO AND THREE RINGS

TABLE 4-18. BIODEGRADATION RATES OF ANTHRACENE GROUP PAHs

<u>Test Type/Population Origin</u>	<u>Compound Tested</u>	<u>Results</u>	<u>Source</u>
Static flask (wastewater culture)	Anthracene	92% lost at 5 mg/l and 51% at 10 mg/l at 1 week in acclimated culture.	Quave <u>et al.</u> (1980)
	Phenanthrene	0% lost at 5 and 10 mg/l at 1 week in non-acclimated culture	Quave <u>et al.</u> (1980)
	Fluorene	77% lost at 5 mg/l and 45% at 10 mg/l at 1 week in acclimated culture	Quave <u>et al.</u> (1980)
	Fluoranthene	100% lost at 5 mg/l and 0% at 10 mg/l at 1 week in acclimated culture	Quave <u>et al.</u> (1980)
	Pyrene	100% lost at 5 mg/l and 0% at 10 mg/l at 1 week in acclimated culture	Quave <u>et al.</u> (198)
Freshwater Aquatic	Anthracene	80% degraded over 12 weeks due to both photolysis and biodegradation	Giddings <u>et al.</u> (1979)
Soil population from near an oil drilling site	Anthracene	90% conversion in 90 min. (no conc.)	Giddings <u>et al.</u> (1979)
Sediment from oil-contaminated stream and uncontaminated stream	Anthracene	$t_{1/2}$ = 12 days for exposed population, $t_{1/2}$ = 120 days for unexposed	Giddings <u>et al.</u> (1979)
Freshwater populations	Anthracene	1st order rate constant of 0.055 day <sup>-1</sup> for days 0 to 15 ( $t_{1/2}$ = 13 days); 0.007 day <sup>-1</sup> for days 20 to 64 ( $t_{1/2}$ = 99 days) (tested 84 days). Not all due to biodegradation.	Giddings <u>et al.</u> (1979)

TABLE 4-18. BIODEGRADATION RATES OF ANTHRACENE GROUP PAHs (Continued)

<u>Test Type/Population Origin</u>	<u>Compound Tested</u>	<u>Results</u>	<u>Source</u>
$^{14}\text{CO}_2$ evolution from stream sediment populations from petroleum contaminated area	$^{14}\text{C}$ -anthracene	$^{14}\text{C}$ -anthracene approximately 60% of total PAH transformed at 120 hours	Schwall and Herbes (1978)
Warburg $\text{O}_2$ consumption, non-acclimated sludge population	Phenanthrene	22-46% of TOD degraded. Most degradable of 17 PAH compounds tested.	Malaney <u>et al</u> (1967)
	Anthracene	2-13% of TOD degraded.	Malaney <u>et al</u> (1967)
$^{14}\text{CO}_2$ evolution from sea water population from treated area	Anthracene	0.02 $\mu\text{g}/\text{day}$	Lee <u>et al</u> . (1978)
$^{14}\text{CO}_2$ evolution from contaminated stream sediment population	$^{14}\text{C}$ -anthracene	$2.5 \times 10^{-3}/\text{hr}$ (rate reduction occurred at $>1 \mu\text{g}/\text{g}$ )	Herbes and Schwall (1978)
Shake flasks with natural water populations	Pyrene	Negligible degradation for compound alone; with naphthalene = 36.7% remaining at 4 wks; with phenanthrene = 47.2% remaining	McKenna and Heath (1976)
Static flasks with natural water populations from contaminated and uncontaminated sites	Phenanthrene	50% to 100% degradation in 1 month over the year at different sites (80% = mean)	Sherrill and Sayler (1980)
Static flasks with natural water populations from contaminated and uncontaminated sites	Pyrene	0% to 57% degradation in 1 month over the year at different sites (15% = mean)	Sherrill and Sayler (1980)

TABLE 4-18. BIODEGRADATION RATES OF ANTHRACENE GROUP PAHs (Continued)

<u>Test Type/Population Origin</u>	<u>Compound Tested</u>	<u>Results</u>	<u>% removed in 1 week</u>		<u>Source</u> Gardner <u>et al.</u> (1979)
			<u>Anth.</u>	<u>Fluor.</u>	
Coastal estuary sediment populations (3 types) with and without presence of polychaete worm <u>Capitella capitata</u>	Anthracene Fluoranthene	<u>Experiment</u>			
		Fine sand	2.0	1.9	
		Fine sand & <u>C. capitata</u>	2.3	3.3	
		Medium sand	2.4	2.4	
		Medium sand & <u>C. capitata</u>	3.2	3.5	
		Marsh sediment	2.6	2.0	
		Marsh sediment & <u>C. capitata</u>	2.7	2.6	

In another study using microbial populations from pristine and PAH-contaminated areas, phenanthrene biodegradation was significantly greater (3 to 4 times) in the previously exposed cultures than in those from the pristine area (Sherrill and Sayler 1980).

As noted in Section 3.2.3.4, environmental factors such as availability of oxygen, soil solution pH and the presence of natural humic polymers may influence the rate of biodegradation.

A regression analysis was performed in order to determine the dependency of the phenanthrene degradation rate on numerous environmental variables (Sherrill and Sayler 1980). Approximately 46% of the total variation in the rate was attributed to environmental characteristics, the presence of acclimated bacteria, and the total viable microbial cell count. Less important were dissolved oxygen, suspended sediment levels, and nitrate-nitrogen levels, accounting each for 5% of the variability.

Phenanthrene degradation was found to be influenced significantly by incubation temperature (Sherrill and Sayler 1980). Virtually no degradation was detected at 5° and 45°C; between 15° and 37°C, the rate increased by a factor of 9 (from 10% to 90% in one month).

One study measured a very poor correlation ( $r = 0.07$ ) between suspended sediment load and phenanthrene biodegradation rate (Sherrill and Sayler 1980). This contrasts with prevailing theory and indicated that adsorption onto sediment had little effect on microbial degradation.

In conclusion, the anthracene group of PAHs is intermediate in its biodegradability when compared with higher and lower ringed class members. Half-lives were on the order of 1-2 weeks under laboratory conditions. Anthracene itself was usually readily degradable following a period of acclimation. No information was available specifically concerning the biodegradation of acenaphthene and only limited information on fluorene and fluoranthene.

TABLE 4-19. KINETIC PARAMETERS OF ANTHRACENE BIOTRANSFORMATION

<u>Compound</u>	<u>Rate Constant k (1/h)</u>		<u>Turnover Time<sup>a</sup></u>		<u>Transformation Rate (µg/g/hr)<sup>b</sup></u>	
	<u>Contaminated</u>	<u>Uncontaminated</u>	<u>Contaminated</u>	<u>Uncontaminated</u>	<u>Contaminated</u>	<u>Uncontaminated</u>
Anthracene	$2.5 \times 10^{-3}$	$2.5 \times 10^{-4}$	7 days	167 days	$8.5 \times 10^{-3}$	$<3 \times 10^{-6}$

<sup>a</sup>Turnover Time = 1/k

<sup>b</sup>Transformation Rate = k x concentration

Source: Schwall and Herbes (1978)

#### 4.2.3.3 Modeling of Environmental Distribution

##### Introduction

Very limited monitoring data are available to describe the extent of anthracene group PAH contamination in the environment. Several modeling efforts were undertaken in order to estimate the distribution of anthracene in the environment and to describe the important aspects of the behavior of anthracene in selected environmental settings. Since all of the physiochemical properties (solubility,  $K_{ow}$ , etc.) for the chemicals in this group are similar, only anthracene was modelled and the results were assumed to be representative of the behavior of all chemicals in this group.

The Mackay equilibrium model was used to predict the partitioning of anthracene among environment compartments in equilibrium (Mackay 1979). The EXAMS (Exposure Analysis Modeling System) developed by the U. S. EPA (U.S. EPA 1980a) was used to study the fate of anthracene in several environmental scenarios.

##### Mackay Equilibrium Partitioning Model

The Mackay model (described previously in Volume II) was used to predict the partitioning of anthracene among environmental compartments. The chemical-specific parameters given as input for the model are presented in Table 4-20. The total amount of anthracene in the system was taken to be 0.69 kg. Details of the calculation methods are provided elsewhere (Mackay 1979) and are not repeated here.

The results obtained for anthracene are presented in Table 4-21. The vapor pressure of anthracene is in the middle of the range of vapor pressures among the PAHs. Thus when only equilibrium processes are considered, a measurable amount of partitioning to air is expected to occur. Since anthracene's partition coefficient ( $K_{ow} = 2.8 \times 10^4$ ) is high, sorption to sediments and biota is also likely to be significant. The Mackay model confirms these expectations with the prediction that 58% of the anthracene will be found in the air and 41% in the sediment. The different fractions of material in the suspended solids and sediments are a result of the different sizes and densities of the compartments of the model; the concentrations in these compartments are the same. Within the water column (water, aquatic biota, and suspended solids), the largest mass of anthracene is dissolved in the water, although the concentrations in the other phases are much higher. Again, this result occurs because the volume of water allowed by the model is considerably larger than the volume of either aquatic biota or suspended solids.

TABLE 4-20. VALUES OF PARAMETERS USED FOR CALCULATING THE EQUILIBRIUM DISTRIBUTION OF ANTHRACENE PREDICTED BY THE MACKAY FUGACITY MODEL

CHEMICAL-SPECIFIC PARAMETERS (25°C)

Henry's Law Constant ( $m^3$ -atm/mole)  $1.25 \times 10^{-3}$

Adsorption coefficient

suspended solids ( $.01 \times K_{oc}$ )	158.50
sediment ( $.01 \times K_{oc}$ )	158.50
biota ( $.2 \times K_{ow}$ )	5640

Total Amount in System 0.69 kg

COMPARTMENT-SPECIFIC PARAMETERS (25°C)

Air:

area	$1 \times 10^4 \text{ m}^2$
depth	$3 \times 10^3 \text{ m}$

Water:

area	$1 \times 10^4 \text{ m}^2$
depth	2 m
biomass content	12.9 mg/l
suspended sediment	30 mg/l

Sediment:

area	$1 \times 10^4 \text{ m}^2$
depth	.5 m
biomass content	50.01 g/m <sup>3</sup>
wet sediment density	1.85 g/cm <sup>3</sup>
sediment dry weight	(100 x wet wt)/137

TABLE 4-21: EQUILIBRIUM PARTITIONING OF ANTHRACENE, CALCULATED BY USING THE MACKAY FUGACITY MODEL

<u>Compartment</u>	<u>Partitioning at Equilibrium</u>		
	<u>Moles</u>	<u>Concentration</u>	<u>Percent</u>
Air	2.2	0.013 mg/m <sup>3</sup>	57.88
Water	0.03	2.7x10 <sup>-4</sup> mg/l	0.770
Suspended Solids	1.4x10 <sup>-4</sup>	4.2x10 <sup>-2</sup> mg/kg	0.004
Sediment	1.6	4.2x10 <sup>-2</sup> mg/kg	41.28
Aquatic Biota	2.1x10 <sup>-4</sup>	1.5 mg/kg	0.006
Sediment Biota	2.2x10 <sup>-3</sup>	1.5 mg/kg	0.056
Total in System	3.86 moles (.690 kg)		100%

### EXAMS Model

Calculations based on EXAMS (described in Volume II) were done for anthracene. All six EXAMS environments (pond, eutrophic lake, oligotrophic lake, river, coastal plain river, and turbid river) were modelled using the ecosystem parameters that are provided with the model. The values entered for the chemical-specific parameters are given in Table 4-22. Any input variables not in the table were set to zero; the physical processes associated with these other variables (such as hydrolysis) either were not considered important for anthracene or were calculated by the model from other input data.

A loading rate of 0.1 kg/hour was initially specified for the anthracene calculations. However, in the more static systems with low volumes of water flow, a 0.1 kg/hour discharge into the input streams would exceed the maximum solubility limit. If this solubility limit is exceeded, non-equilibrium conditions (which EXAMS cannot model) occur. Thus in order to maintain equilibrium conditions, the loading rate was adjusted to 0.017 kg/hour for the lakes and 0.0007 kg/hour for the pond. The materials balance (Section 4.1) suggests that 0.1 kg/hour is representative of a maximum loading from industrial discharge.

Table 4-23 summarizes the anthracene concentrations predicted for the simulated environments under steady-state conditions. In the relatively static pond and lakes, the concentrations of anthracene dissolved in water are similar ( $2.3 \times 10^{-4}$  -  $7.2 \times 10^{-4}$  mg/l), when the anthracene is present in the input streams at close to maximum solubility levels. In the rapidly flowing rivers, the dissolved concentrations are lower due to dilution and physical transport, even though the loading rate was higher for the rivers. These aqueous concentrations are all well below the 0.045 mg/l aqueous solubility of anthracene; therefore, these results may be extrapolated for higher inputs of anthracene as long as the solubility limits of the input streams are not exceeded. Sediment concentrations are all higher than the water concentrations in the same environmental systems; biota concentrations are even higher than those of the sediments.

Table 4-24 presents the EXAMS data relative to the fate and distribution of anthracene in the same aquatic systems. Examination of the distribution data reveals the importance of environmental conditions in the partitioning of anthracene between water and sediments. In the static pond and lake systems, over 84% of the anthracene is lost by chemical transformation (photolysis). In the rapidly flowing river systems, other processes such as transport beyond the boundaries of the system account for most of the anthracene removal. In the slower coastal plain river, both transport and photolysis are important. Volatilization accounts for removal of about 8% of the anthracene in the pond, eutrophic lake, and coastal plain river. Volatilization is somewhat less important in the oligotrophic lake, because the lack of biota in the water column allows sunlight to penetrate this system and thus chemical transformation predominates. Biological transformation is significant only in the biota-rich eutrophic lake.

TABLE 4-22. INPUT PARAMETERS FOR EXAMS MODELING OF THE FATE OF ANTHRACENE IN GENERALIZED AQUATIC SYSTEMS

<u>Explanation</u>	<u>Input Value</u>	<u>Reference</u>
Molecular wt. (g/mole)	178.2	Weast (1979)
Ratio of volatilization to reareation rate	.4240	SRI (1980)
Aqueous solubility (mg/l)	.045	Callahan <u>et al.</u> (1979)
Partition coefficient biomass:water ( $\mu\text{g/g}/(\text{mg/l})$ )	4650	SRI (1980)
Henry's Law Constant ( $\text{atm m}^3 \text{ mole}^{-1}$ )	$1.25 \times 10^{-3}$	Table 4-14 (calculated)
Partition coefficient octanol:water	28,840	Callahan <u>et al.</u> (1979)
Second order bacterial degradation rate constant in water and sediment ( $\text{ml/cell/hr}$ )	$3 \times 10^{-9}$	SRI (1980)
Increase in bacterial degradation rate per $10^\circ\text{C}$ change in temperature	2	SRI (1980)
First-order photolysis rate constant ( $\text{hr}^{-1}$ )	0.924	Zepp and Schlotzhauer (1979)
Reference latitude for photolysis rate constant	35.00	Zepp and Scholtzhauer (1979)
Loading rate (kg/hr)	0.1	Section 4.1

TABLE 4-23. STEADY-STATE CONCENTRATIONS OF ANTHRACENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS RESULTING FROM CONTINUOUS DISCHARGES

System	Loading Rate (kg/hr)	Maximum Concentrations						Total Steady-State Accumulation (kg)	Total Daily Load (kg/day)
		Dissolved Water (mg/l)	Total Water (mg/l)	Pore Water (mg/l)	Sediment Deposits (µg/l)	Plankton (µg/l)	Benthos (µg/g)		
Pond	0.0007	$2.3 \times 10^{-4}$	$2.6 \times 10^{-4}$	$2.3 \times 10^{-4}$	0.43	1.1	1.1	0.29	0.017
Eutrophic Lake	0.017	$7.2 \times 10^{-4}$	$8.9 \times 10^{-4}$	$6.2 \times 10^{-4}$	0.44	3.3	2.9	3.0	0.408
Oligotrophic Lake	0.017	$7.1 \times 10^{-4}$	$8.8 \times 10^{-4}$	$3.4 \times 10^{-5}$	0.062	3.3	0.16	0.47	0.408
River	0.1	$9.4 \times 10^{-5}$	$1.0 \times 10^{-4}$	$2.1 \times 10^{-5}$	0.025	0.44	0.097	0.46	2.4
Turbid River	0.1	$8.3 \times 10^{-5}$	$1.0 \times 10^{-4}$	$4.1 \times 10^{-5}$	0.015	0.39	0.19	0.35	2.4
Coast Plain River	0.1	$8.0 \times 10^{-4}$	$8.4 \times 10^{-4}$	$2.0 \times 10^{-4}$	0.49	3.7	0.92	8.1	2.4

All data simulated by EXAMS (U.S. EPA 1980a) model (see text for further information).

TABLE 4-24. THE FATE OF ANTHRACENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS<sup>a</sup>

System	Percent Distribution		Percent Lost by Various Processes After Cessation of Loading				Time for System Self-Purification <sup>c</sup>
	Residing in Water at Steady-State	Residing in Sediment at Steady-State	Transformed by Chemical Processes	Transformed by Biological Processes	Volatilized	Lost by Other <sup>b</sup> Processes	
Pond	1.79	98.21	90.89	0.15	8.04	0.92	316 days
Eutrophic Lake	20.38	79.62	84.75	6.65	8.44	0.16	432.5 days
Oligotrophic Lake	54.46	45.54	95.70	0.00	4.27	0.02	258 days
River	19.16	80.84	5.51	0.09	1.11	93.30	73.4 days
Turbid River	25.37	74.63	3.69	0.08	0.99	95.24	62.2 days
Coastal Plain River	7.76	92.24	34.46	0.64	8.08	56.82	93.5 days

a) All data simulated by the EXAMS (U.S. EPA, SERL, Athens, Ga. 1980a) model (see text for further information).

b) Including loss through physical transport beyond system boundaries.

c) Estimate for removal of ca. 97% of the compound accumulated in system (5 apparent system half-lives). Estimated from the results of the half-lives for the compound in bottom sediment and water columns, with overall cleansing time weighted according to the pollutant's initial distribution.

In all environments, except for the oligotrophic lake, over 75% of the anthracene present at steady-state is residing in the sediments. The oligotrophic lake has very little suspended matter, and very little sedimentation; thus, the anthracene at steady-state is almost evenly divided between the sediment and the water column.

The rapidly flowing rivers, where physical transport dominates the removal processes, are the fastest systems to cleanse themselves of anthracene after loading has stopped, requiring less than 100 days for self-purification. In the lakes and ponds, where the slower process of photolysis dominates, the self-purification times are higher (250-430 days).

On the basis of the distribution and fate data, and the rates specified for the various removal and degradation processes, the persistence of anthracene can be estimated for each of the aquatic systems. These data are presented in Table 4-25. In all of the systems, the anthracene is removed more rapidly from the water column than from the sediments. This persistence in sediments occurs because of the strong adsorption of anthracene onto the sediments, and also because the major fate processes such as photolysis and volatilization do not occur to any appreciable degree in the sediments. In the rapidly moving river and turbid river where physical transport occurs, over 99% of the anthracene is lost from the water column within half a day. In the other systems, where the removal processes (photolysis, biodegradation, etc.) are slower, the anthracene will persist for longer periods. Anthracene is most persistent in the relatively static pond, where the high content of particulate matter inhibits sunlight penetration; the model predicts that after 24 days only 24% of the anthracene will have been removed from this system.

#### Comparison of Mackay and EXAMS Models

The EXAMS pond environment is the most appropriate system to compare with the Mackay models since there is very little transport across system boundaries in the pond. The Mackay model calculates partitioning between compartments, while EXAMS models the fate of pollutants within a compartment and transport out of that compartment. Since the underlying assumptions of the models are different, the quantitative results may be different. The pollutant load for the Mackay model was chosen so that the anthracene mass in the water and sediments would be equal to the total steady-state accumulation in the pond, predicted by EXAMS (0.29 kg).

Table 4-26 summarizes the concentration and distribution data from both models. The EXAMS concentrations and those predicted by Mackay for the water column agree to within an order of magnitude. Both models also predict that the highest concentrations will be in the sediments, and the lowest concentrations will be in the water. The ratios of the amount of dissolved anthracene to the amount adsorbed are also in agreement; both models predict that 50 times more anthracene will be found in the sediments than in the water column.

TABLE 4-25. THE PERSISTENCE OF ANTHRACENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS AFTER CESSATION OF LOADING

<u>System</u>	<u>Time Period (days)</u>	<u>% Lost from Water</u>	<u>% Lost from Sediment</u>	<u>% from Total System</u>
Pond	24	85.95	22.83	23.96
Eutrophic Lake	10	79.59	6.25	20.99
Oligotrophic Lake	1.5	92.89	.92	51.01
River	0.5	99.59	1.89	20.61
Turbid River	0.5	99.69	2.06	26.83
Coastal Pond	4.5	93.62	14.32	20.48

All data simulated by the EXAMS (U.S. 1980a) model. See text for further information.

TABLE 4-26. COMPARISON OF RESULTS FROM MACKAY'S EQUILIBRIUM MODEL AND EXAMS FOR ANTHRACENE IN A POND SYSTEM

EXAMS Results  
(0.0007 kg/hr loading,  
0.29 kg steady state accumulation)

Mackay Results  
(.69 kg in system)

<u>Maximum Concentration</u>		<u>Concentration</u>	
Water	2.6x10 <sup>-4</sup> mg/l	Water	2.7x10 <sup>-4</sup> mg/l
Aquatic Biota	1.1 mg/kg	Aquatic Biota	1.5 mg/kg
Sediment Biota	1.1 mg/kg	Sediment Biota	1.5 mg/kg
Sediment	.43 mg/kg	Sediment	.042 mg/kg
<u>Accumulation</u>		<u>Percent of Chemical per Compartment<sup>a</sup></u>	
% in water	1.79	% in water	0.77%
% in sediment	98.21	% in sediment	41.28%

a) 57.88% of the initial load was partitioned to the atmosphere.

#### 4.2.4 Monitoring Data

##### 4.2.4.1 STORET Data

###### Introduction

The anthracene group PAHs have been monitored in all environmental media. The highest concentrations for compounds in this group appear in urban and industrial areas.

STORET monitoring data (U.S. EPA 1980b) for PAHs in the anthracene group reflect sampling activities in thirty-one states and Puerto Rico. Over 90% of the observations for each compound are remarked, indicating that pollutant levels do not exceed a specified reporting (detection) limit. Table 4-27 presents the number and ranges of observations in ambient and effluent waters and in sediment for this compound group; Tables 4-28 and 4-29 give the distribution of concentrations in ambient and effluent waters, sediment, and tissues.

###### Ambient Water

Observations of anthracene and related PAHs in ambient waters were primarily remarked; of 2304 total observations, 64 values, or 2.8%, were unremarked and, therefore, represent concentrations actually detected. There were only two unremarked observations of anthracene reported. Of the 64 unremarked values approximately 65% were less than 100  $\mu\text{g}/\text{l}$ .

###### Effluent Water

The total number of observations for the anthracene group PAHs in effluent water was 3130; of these, 88 values, or 2.8% were unremarked. Fluoranthene was detected most often (34 observations) and acenaphthene least often (7 observations). Sixty-six of the 88 unremarked values were less than 100  $\mu\text{g}/\text{l}$ ; there were 11 observations between 100.1 and 1000  $\mu\text{g}/\text{l}$  and 11 observations greater than 1000  $\mu\text{g}/\text{l}$ .

###### Sediment

These PAHs were detected less frequently in sediment than in water, but a greater percentage of the values were unremarked. Of 738 total sediment observations, 128 or 17% were unremarked. Thirty-six percent of these, or 46 observations, were at concentrations greater than 100  $\mu\text{g}/\text{kg}$ . Phenanthrene was detected most frequently (30 observations) and fluorene least often (11 observations).

###### Fish Tissue

As shown in Table 4-29, all observations in STORET for the anthracene group PAHs in fish tissue are remarked with one exception;

TABLE 4-27. THE NUMBER AND RANGES OF OBSERVATIONS IN STORET FOR THE ANTHRACENE GROUP PAHs

	<u>Anthracene</u>	<u>Acenaphthene</u>	<u>Fluoranthene</u>	<u>Fluorene</u>	<u>Phenanthrene</u>	<u>Pyrene</u>
<u>Ambient Water (µg/ℓ)</u>						
Total Observations	254	417	414	424	382	413
Unremarked	2	10	17	8	12	15
Remarkd	252	407	397	416	370	398
Maximum Detection Limit	50	560	400	400	600	400
Range of Unremarked Observations	1-27	0.1-880	0.4-1100	0.3-390	1-630	0.3-960
<u>Effluent Water<sup>a</sup> (µg/ℓ)</u>						
Total Observations	341	567	685	577	394	566
Unremarked	8	7	34	11	14	14
Remarkd	333	560	651	566	380	552
Maximum Detection Limit	2500	2500	2500	2500	2500	2500
Range of Unremarked Observations	0.4-6200	1.5-3600	0.01-2500	0.6-6400	0.5-36000	0.5-11000
<u>Sediment (µg/kg-dry wt.)</u>						
Total Observations	121	131	125	129	116	116
Unremarked	27	13	26	11	30	21
Remarkd	94	118	99	118	86	95
Maximum Detection Limit	10000	10000	10000	1000	5000	10000
Range of Unremarked Observations	0.7-2000	2.3-97	0.1-1150	3.6-145	2.9-1100	0.03-2500

SOURCE: STORET Water Quality System (U.S. EPA 1980b) as of November 20, 1980.

<sup>a</sup>Effluent data as of April 9, 1981.

TABLE 4-28. DISTRIBUTION OF OBSERVED AMBIENT AND EFFLUENT CONCENTRATIONS OF ANTHRACENE GROUP PAHs IN STORET

Compound	No. Ambient Observations										
	Remarked					Unremarked					
	Total	Conc. (µg/l)				Total	Conc. (µg/l)				
	≤1	1.1-10	10.1-100	100.1-1000		≤1	1.1-10	10.1-100	100.1-1000	>1000	
Anthracene	252	48	179	25		2	1		1		
Acenaphthene	407	36	308	56	7	10	3	3	1	3	
Fluoranthene	397	40	325	32		17	1	7	1	6	2
Fluorene	416	39	318	55	4	8	1	1	4	2	
Phenanthrene	370	37	307	22	4	12	1	2	4	5	
Pyrene	398	9	82	9		15	3	5	2	5	

STORET data as of November 20, 1980.

Compound	No. Effluent Observations										
	Remarked					Unremarked					
	Total	Conc. (µg/l)				Total	Conc. (µg/l)				
	≤1	1.1-10	10.1-100	100.1-1000	>1000		≤1	1.1-10	10.1-100	100.1-1000	>1000
Anthracene	333	186	137	10		8	2	2		3	1
Acenaphthene	560	185	358	17		7		5		1	1
Fluoranthene	651	276	335	40		34	25	3	2	3	1
Fluorene	566	187	362	17		11	3	3	2	1	2
Phenanthrene	380	194	171	15		14	6	1	1	3	3
Pyrene	552	186	340	26		14	3	5	3		3

STORET data as of April 9, 1981.

TABLE 4-29. DISTRIBUTION OF OBSERVED SEDIMENT AND TISSUE CONCENTRATIONS OF ANTHRACENE GROUP PAHS IN STORET

Compound	No. of Sediment Observations											
	Total	Remarked					Total	Unremarked				
		≤1	1.1-10	10.1-100	100.1-1000	>1000		≤1	1.1-10	10.1-100	100.1-1000	>1000
Anthracene	94	19		1	17	57	27	1	5	10	9	2
Acenaphthene	118	33	1	2	17	65	13		5	7		
Fluoranthene	99	20	1	2	11	65	26	2	3	10	8	3
Fluorene	118	32	2	2	17	65	11		6	3	2	
Phenanthrene	86	15		1	16	54	30		2	15	10	3
Pyrene	95	17	2	1	16	59	21	1	2	9	9	

Compound	No. of Fish Tissue Observations											
	Total	Remarked					Total	Unremarked				
		<1	1.1-10	10.1-100	100.1-1000	>1000		<1	1.1-10	10.1-100	100.1-1000	>1000
Anthracene	73	10	63				0					
Acenaphthene	73	10	63				0					
Fluoranthene	68	7	61				0					
Fluorene	73	10	62		1		1	1				
Phenanthrene	72	10	62				0					
Pyrene	72	20	52				0					

SOURCE: STORET data as of November 20, 1980.

there is one unremarked observation of fluorene no higher than 1 mg/kg. The distribution indicates that roughly 10% to 15% of the samples were analyzed with detection limits not exceeding 1 mg/kg, and about 85% of the detection limits are between 1.1 and 10 mg/kg.

#### 4.2.4.2 Data from Other Sources

##### Drinking Water

Kim and Stone (1979) have analyzed public water system wells for levels of organic chemicals. Thirty-nine wells were tested for anthracene/phenanthrene levels; of these 7 (18%) were positive. The maximum level of anthracene/phenanthrene detected was 21  $\mu\text{g}/\text{l}$ .

Levins *et al.* (1980) reported that none of the anthracene group PAHs were found (at 10  $\mu\text{g}/\text{l}$  reporting limits) in tap water samples from Cincinnati, St. Louis, Atlanta, and Hartford.

##### Municipal Wastewater

The U. S. EPA (1980d) has measured levels of fluoranthene in sewage water and found that concentrations were elevated after heavy precipitation. On a dry day, sewage water concentration of fluoranthene was 0.352  $\mu\text{g}/\text{l}$ ; a concentration measured after a heavy rain was 16.3  $\mu\text{g}/\text{l}$ , approximately 50 times greater. Levins *et al.* (1980) found that anthracene group PAHs were absent (at 10  $\mu\text{g}/\text{l}$  reporting limits) in municipal wastewater from Cincinnati, St. Louis, Atlanta, and Hartford.

##### Industrial Effluents

Water samples from industrial effluents and industrial sewage effluents, in particular, indicate that industrial input will raise the level of fluoranthene found in the surrounding water (U.S. EPA 1980d). Fluoranthene concentrations in industrial sewage effluents ranged from 2.6  $\mu\text{g}/\text{l}$  to 3.4  $\mu\text{g}/\text{l}$ . Other results reported for fluoranthene levels in industrial and domestic effluents are given in Table 4-30.

##### Soils and Sediment

White and Vanderslice (1980) have reported levels of pyrene and fluoranthene in urban soils. Concentrations of both compounds ranged from 5000-120,000  $\mu\text{g}/\text{kg}$  in urban soils. Levels in marine sediments have also been reported by White and Vanderslice (1980). The maximum pyrene concentration in marine soil was 1000  $\mu\text{g}/\text{kg}$ ; fluoranthene levels reached a maximum of 900  $\mu\text{g}/\text{kg}$ . These results were found at Buzzard's Bay, Massachusetts. The average ranges for pyrene and fluoranthene were 9-90  $\mu\text{g}/\text{kg}$  and 10-100  $\mu\text{g}/\text{kg}$ , respectively.

TABLE 4-30, FLUORANTHENE LEVELS DETECTED IN WASTEWATER  
AND EFFLUENTS

<u>Type of Sample</u>	<u>Concentration (µg/l)</u>	<u>Comment</u>
Domestic Effluent	2.4	From runoff and atmospheric washout
Domestic Effluent	0.273	
Factory Effluent	2.2	Man-made sources
Sewage		
Industry	2.6-3.4	From natural and industrial sources (i.e., detergents, atmospheric washout)
Domestic	0.35	
Domestic (heavy rains)	16.3	

SOURCE: U.S. EPA 1980d.

## Food

Pancirov and Brown (1977) have studied concentrations of pyrene in edible marine tissue. These measurements, which were taken at a variety of locations, reported levels ranging from  $<0.2 \mu\text{g}/\text{kg}$  (crab) to  $58 \mu\text{g}/\text{kg}$  (oyster). The highest level ( $58 \mu\text{g}/\text{kg}$ ) was taken from a polluted harbor area on Long Island Sound. Table 4-31 provides a complete listing of the pyrene levels reported by Pancirov and Brown. No other data were found concerning the levels of anthracene group PAHs in food.

## Air

The anthracene group PAHs have been detected in the air of urban and industrial areas (U.S. EPA 1980c, 1980d). Table 4-32 presents concentrations of fluoranthene found in automotive air samples in Los Angeles. An average fluoranthene concentration from four sites was  $1.6 \text{ ng}/\text{m}^3$  (0.18 ppt). Table 4-32 also summarizes fluoranthene concentrations taken from air samples near a coking source in Birmingham, Alabama. The average of four site readings was  $7.4 \text{ ng}/\text{m}^3$  (0.822 ppt) (U.S. EPA 1980d). Other air levels of fluoranthene have been measured by Fox and Staley (1976) and Hoffman and Wynder (1977) (Table 4-33). An average concentration range found in U. S. cities was  $0.10\text{--}4.1 \text{ ng}/\text{m}^3$  (0.01-0.45 ppt). Phenanthrene levels in Providence, Rhode Island, have been measured by Krstulovic *et al.* (1977). The concentration range for this compound, which can be found in Table 4-33, is  $0.011\text{--}0.340 \text{ ng}/\text{m}^3$  (0.001-0.04 ppt). Table 4-33 also presents the concentration range of pyrene levels found in urban air. These levels ranged from  $0.18\text{--}5.2 \text{ ng}/\text{m}^3$  (0.02-0.57 ppt) (Fox and Staley 1976, Gordon and Bryan 1973). The U. S. EPA (1980c) has reported concentrations of pyrene in urban air samples over a summer-winter period (Table 4-34). The average pyrene concentration of the seven cities reported was  $7.6 \text{ ng}/\text{m}^3$  (0.84 ppt). Anthracene levels detected in this study were lower than those of pyrene, as shown in Table 4-34. The average concentration from the seven urban areas sampled was  $0.6 \text{ ng}/\text{m}^3$  (0.07 ppt). Table 4-34 shows that the range of pyrene concentrations found was  $1.0\text{--}19.4 \text{ ng}/\text{m}^3$ ; the lowest concentration was measured in San Francisco and the highest in Detroit, a more industrialized city. The anthracene concentration ranges follow a similar pattern; they range from  $0.1 \text{ ng}/\text{m}^3$  to  $1.3 \text{ ng}/\text{m}^3$ .

### 4.2.5 Summary of Fate and Distribution

The environmental release data indicate that most of the discharges of the PAHs in the anthracene group are to the atmosphere. Atmospheric deposition (from both wet and dry processes) may remove 5-26% of the atmospheric load of anthracene in urban areas, accounting for 75-400 kkg/yr of anthracene fallout. It is estimated that about 2% will fall directly on inland surface waters, representing 1.5-8.0 kkg/yr anthracene. The upper limit on this range corresponds to deposition in areas near combustion sources, where the anthracene will be primarily adsorbed onto particulates. The percentage of these PAHs that remains in the atmosphere will be degraded by photolysis to oxygenated compounds, including quinones.

TABLE 4-31. CONCENTRATIONS OF PYRENE IN TISSUES OF EDIBLE  
MARINE SPECIES

<u>Location of Sample</u>	<u>Marine Tissue</u>	<u>Concentrations of Pyrene (<math>\mu\text{g}/\text{kg}</math> wet wt.)</u>
Long Island Sound	Oyster	58
Chincoteague, VA		
Black Point	Oyster	0.5
Little Toms Cove	Clam	1.0
Darien, CN, Scotts Cove	Clam	12
Fish Market, Linden, NJ	Clam	<1
Chesapeake Bay	Crab	<0.2
Raritan Bay	Crab	<0.2
	Menhaden	<0.6
Atlantic Ocean		
Long Branch, NJ	Flounder	<0.6
South of Long Island	Flounder	0.5
Falmouth, MA		
Little Sippewissett	Mussel	2
Wild Harbor	Mussel	4
Palacios, TX	Shrimp	<0.3
Atlantic Ocean		
25 mi. off Toms River, NJ	Codfish	<0.5

SOURCE: Pancirov and Brown (1977).

TABLE 4-32. AUTOMOTIVE AND COKING SOURCE CONCENTRATIONS OF  
FLUORANTHENE IN AIR

<u>Location/Source</u>	<u>Concentration (ng/m<sup>3</sup>)</u>				
	<u>Site 1</u>	<u>Site 2</u>	<u>Site 3</u>	<u>Site 4</u>	<u>Average</u>
Los Angeles (automotive)	1.9	0.8	3.4	0.12	1.6
Birmingham, AL. (coking sources)	4.9	11.2	10.8	2.6	7.4

SOURCE: U.S. EPA (1980d).

TABLE 4-33. CONCENTRATIONS OF ANTHRACENE GROUP PAHs DETECTED  
IN THE URBAN ATMOSPHERE

<u>Compound</u>	<u>Sampling Location</u>	<u>Concentration</u>	<u>Reference</u>	<u>Comment</u>
Fluoranthene	Various U.S. cities	0.10 ng/m <sup>3</sup> - 4.1 ng/m <sup>3</sup> (0.01 - 0.45 ppt)	Fox and Staley (1976) Hoffman and Wynder (1977)	average range
Phenanthrene	Providence, RI	0.011 ng/m <sup>3</sup> - 0.34 ng/m <sup>3</sup> (0.001 - 0.04 ppt)	Krstulovic <u>et al.</u> (1977)	urban range
Pyrene	Urban air	0.18 ng/m <sup>3</sup> - 5.2 ng/m <sup>3</sup> (0.02 - 0.57 ppt)	Fox and Staley (1976) Gordon and Bryan (1973)	urban range

TABLE 4-34. AVERAGE CONCENTRATIONS OF PYRENE AND ANTHRACENE IN THE AIR OF SELECTED U.S. CITIES

<u>City</u>	<u>Concentration (ng/m<sup>3</sup>)<sup>a</sup></u>	
	<u>Pyrene</u>	<u>Anthracene</u>
Atlanta	3.4	0.4
Birmingham	9.6	1.3
Detroit	19.4	1.2
Los Angeles	3.2	0.1
Nashville	15.3	1.0
New Orleans	1.3	0.1
San Francisco	1.0	0.1

a) The report values (U.S. EPA 1980c) were average of summer and winter concentrations.

Since the water solubilities of the anthracene group PAHs are relatively low and the octanol:water partition coefficients are fairly high, adsorption onto both organic and inorganic matter is a primary removal pathway for these compounds in the water column. The particulate matter will ultimately be transported to the sediment where these PAHs will accumulate; biodegradation and photo-oxidation in sediments are expected to be quite slow. The fraction of these PAHs that remain in the water column is expected to be degraded photolytically; however, the extent of this removal pathway will be affected by the turbidity and light penetration in the actual system. Volatilization from water is not expected to be a major fate process, but the relative importance of this pathway differs among aquatic systems. Bioconcentration factors for anthracene are on the order of several hundred; half-lives for biodegradation have been determined to be 1-2 weeks in acclimated cultures.

EXAMS calculations for anthracene indicate that in all model systems, except the oligotrophic lake where sedimentation rates are low, more than 75% of the anthracene resides in the sediment compartment when the system is at steady state. Rapid photolysis is predicted by EXAMS for the anthracene remaining in the water column of clear, quiescent systems; volatilization is important only in the pond and eutrophic lake systems where light penetration is reduced by suspended matter. Biological degradation is important only in the highly productive eutrophic lake. In the more dynamic river systems, physical transport (downstream) accounts for most of the anthracene removal.

Anthracene and the related PAHs have been detected in all environmental media. Monitoring data support the predictions that significant amounts of anthracene and related PAHs will reside in the sediments. The majority of the STORET surface water concentrations of these PAHs are less than 100  $\mu\text{g}/\text{l}$ ; STORET effluent data include concentrations ranging from  $<1 \mu\text{g}/\text{l}$  to  $>1,000 \mu\text{g}/\text{l}$  for these PAHs. Various other sources report effluent and sewage concentrations of fluoranthene from 2  $\mu\text{g}/\text{l}$  to 20  $\mu\text{g}/\text{l}$ . Levels of pyrene and fluoranthene in soil were high, up to 120,000  $\mu\text{g}/\text{kg}$ . Concentrations of pyrene in several edible marine species were reported to range from less than 0.6  $\mu\text{g}/\text{kg}$  to 58  $\mu\text{g}/\text{kg}$  (wet weight). PAH levels in air from a variety of urban locations were generally less than 20  $\text{ng}/\text{m}^3$ .

A schematic drawing of the major inputs of anthracene to the aquatic environment, as well as the major fate and transformation processes, is given in Figure 4-3. Since the half-lives shown were determined by various methods, care should be taken in drawing conclusions based on the absolute rather than the relative rates.

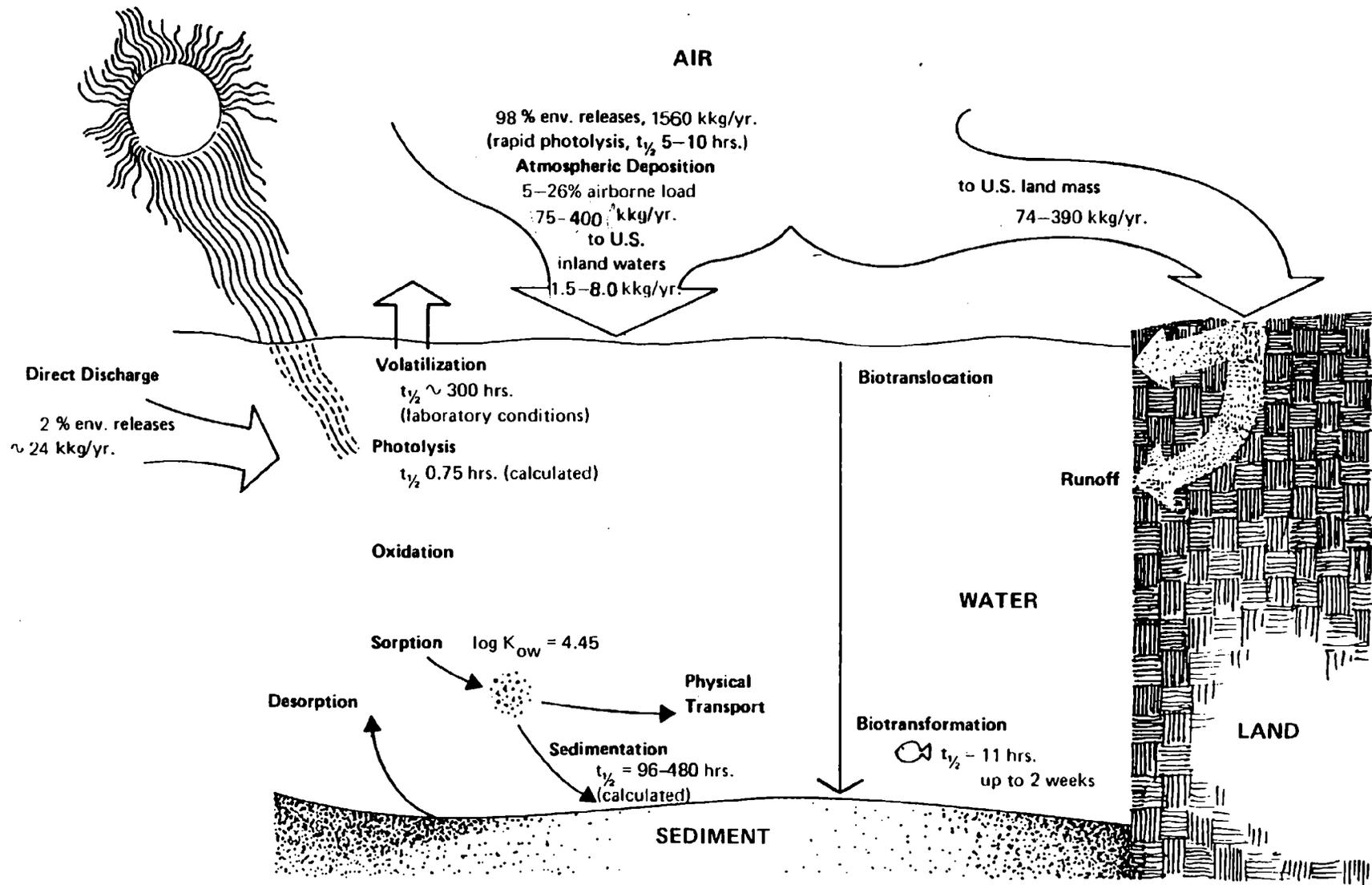


FIGURE 4-3 SOURCES AND FATE OF ANTHRACENE IN THE AQUATIC ENVIRONMENT

### 4.3 HUMAN EFFECTS AND EXPOSURE

#### 4.3.1 Human Toxicity

##### 4.3.1.1 Introduction

There is a scarcity of data concerning human health effects of the six PAHs designated as the anthracene group. The discussion of these compounds as a group should not be construed to mean necessarily that they have similar toxic effects either qualitatively or quantitatively. Available data for each compound have been discussed under the various subsections below.

##### 4.3.1.2 Pharmacokinetics

All of the compounds in the group are lipid soluble, which would permit absorption and distribution throughout the body. Demonstrated toxicity orally and by dermal application supports the notion of ready absorption. For the most part, detailed studies of the pharmacokinetics and metabolism of most of the compounds in this group have not been conducted. However, it is presumed that these compounds are metabolized via the mixed-function oxidase system, as are naphthalene and other PAHs. Subsequently, possibly toxic metabolites, as well as presumably non-toxic water-soluble conjugates are formed.

Studies in rats and rabbits suggest that phenanthrene is converted to phenols, possible 1- and 9-phenanthrols and to a mercapturic acid. Anthracene appears to be converted to 1,2-dihydroanthracene-1,2-diols and their glucuronides. A hydroxydihydroanthracene, 1-anthrylmercapturic acid, and possibly anthraquinone have also been found in the urine of these animals. The main urinary metabolite of fluorene in rabbits is the glucuronide of 2-hydroxyfluorene; small amounts of the free phenol have also been found (Williams 1959).

Mitchell and Tu (1979) recently reported that pyrene was rapidly cleared from the respiratory tract of rats exposed to a pyrene aerosol (500 mg/l; 0.3-0.5  $\mu$ m particles) for 60 minutes and eliminated primarily via the liver and bile to the feces. Significant amounts of pyrene (measured as pyrene fluorescence) were detected in trachea, nasal turbinates, and lungs 30 minutes post-exposure; these levels dropped to between 5 and 20% of post-exposure values by 48 hours. The highest tissue concentrations were noted in the GI tract at 24 hours (4-fold increase above 30 min. value), which returned to pre-exposure levels within 4 days.

In a separate experiment, Mitchell and Tu (1979) administered 50  $\mu$ g pyrene in a gelatin-saline suspension to two rats by stomach tube. At 24 hours, approximately half of the administered pyrene was present in the GI tract; the remainder was apparently absorbed and was either below detection limits in the various tissues and/or was excreted.

#### 4.3.1.3 Human and Animal Studies

##### Carcinogenicity

None of the compounds in this group is considered carcinogenic by the oral route. Anthracene has been considered as a cause of skin cancer in anthracene-exposed workers (Hueper 1972); however, it would appear that these workers had been exposed to undefined mixtures (e.g., anthracene oil) in the manufacture and use of anthracene rather than to the pure substance. Virtually, no data appear to exist on the human carcinogenicity of the other compounds in this group.

Carcinogenicity results in experimental animal studies are summarized in Tables 4-35, -36, -37, and -38. Anthracene (Table 4-35) was not carcinogenic in rats by the oral route (Schmähl 1955). An increased incidence of injection-site tumors was reported by Schmähl (1955); however, the relevance of injection site tumors is disputed, because the response is generally too non-specific. A study by Innes et al. (1969) indicated that a possible metabolite of anthracene, anthraquinone, was not carcinogenic by the oral route.

Fluoranthene was inactive as a complete carcinogen or tumor initiator in several skin-painting experiments with mice (Table 4-36). However, both fluoranthene and pyrene are reported to be co-carcinogens; repeated application to mouse skin, along with low doses of a complete carcinogen such as benzo[a]pyrene, produced a considerable enhancement of carcinogenic effect (Van Duuren et al. 1973, 1976; U.S. EPA 1980b,c). The mechanism of co-carcinogenesis is not clear, and can only be surmised at this time. In addition, specific chemical entities involved, such as the duration of exposure, as well as the dose and dose rate, may influence the final outcome. Until these divergent points are worked out in sufficient detail, estimations of human risk based on co-carcinogenic results would appear to be premature.

Buening and co-workers (1979) reported significant tumorigenic activity with a phenanthrene derivative, phenanthrene H<sub>4</sub>-3,4-epoxide, but not phenanthrene itself in newborn Swiss mice injected intraperitoneally with 0.8 μmol of either substance on days 1, 8 and 15 of life.

Tables 4-37 and 4-38 present the results of two studies on the ability of anthracene, pyrene, and phenanthrene to act as initiators in the mouse skin carcinogenesis model. In both studies, phenanthrene was apparently a more potent initiator than pyrene, while anthracene was apparently without activity. Results of Scribner (1973) show that phenanthrene is far less active than benz[a]anthracene in terms of potency, latency and incidence. At this time, it is difficult to assess the importance to human health of the classification of a compound as an initiator in the mouse skin carcinogenicity model, without evidence of its direct carcinogenicity.

TABLE 4-35. RESULTS OF CARCINOGENICITY STUDIES WITH ANTHRACENE

Species	Route: Dosage	Findings	Reference
Rat (BD I & III)	<p>Oral: 5-15 mg/day, 6d/wk, 550 days (total dose 4.5 g/rat)</p> <p>Intraperitoneal: 20 mg/wk x 33 wks</p> <p>Subcutaneous: 20 mg/wk x 33 wks</p>	<p>Tumors in 2/28; one associated with a liver parasite cyst, the other an adenocarcinoma of the uterus.</p> <p>Control incidence, 0.5%. Both above tumors were not attributed to anthracene.</p> <p>0/10 tumors</p> <p>5/9 injection site sarcomas</p> <p>0/10 injection site sarcomas in naphthalene treated group with oil vehicle.</p>	Schmähl (1955)
Mice (cc 57)	Subcutaneous: 2.5 mg in 0.5 ml peach oil	0/25 tumors up to 260 days	Bergol'ts and Il'yina (1951)
Mice (C 57BL/6 x C3H/An <sub>f</sub> )	Oral(Anthraquinone): 464 mg/kg in gelatin gavage, 7-28 days of age; then, 1206 ppm diet	No significant elevation in tumor incidence in 72 mice (male and female) after 18 months	Innes et al. (1969)



TABLE 4-37. RESULTS OF THE SCREENING OF ANTHRACENE, PHENANTHRENE, AND PYRENE FOR TUMOR-INITIATING ACTIVITY

Compound	Total Dose (mg)	No. of Mice	Test Substance Application <sup>a</sup>	Croton Oil Application <sup>b</sup>	Tumor Incidence at End of Croton Oil Treatment <sup>c</sup>		Survivors
					Tumor-Bearing Mice	Total Tumors	
Anthracene	30	20	5%; 2 applications with interval of 30 minutes, repeated 3x/wk for 20 applications	18 weekly applications of 0.3 ml sol'n in acetone (0.17% wk 1; 0.085% wk 2,3; 0.17% wk 4-18)	3	4	17
Phenanthrene	540	20	18%, 3x/wk for 10 applications	as above	5	12 <sup>d</sup>	20
Pyrene	250	20	8.3%, 3x/wk for 10 applications	as above	6	9	20
Controls	---	20	----	as above	4	4	19

<sup>a</sup>Each application was 0.3 ml of solution in acetone at concentration shown (w/v for solids, v/v for liquids).

<sup>b</sup>Croton oil treatment began 25 days after last test substance application.

<sup>c</sup>All tumors recorded were benign papillomata.

<sup>d</sup>p < 0.05; chi-square test, one-tailed.

Source: Salaman and Roe (1956).

TABLE 4-38. TUMOR INITIATION BY APPARENTLY NONCARCINOGENIC  
POLYCYCLIC AROMATIC HYDROCARBONS

Compound	Dose ( $\mu$ mole)	Dose of TPA ( $\mu$ mole) <sup>a</sup>	Animals per Group	No. of papillomas/mouse <sup>b</sup> (% tumor-bearing mice)						Survivors 35 wk.
				10 wk.	15 wk.	20 wk.	25 wk.	30 wk.	35 wk.	
Anthracene	10	5	30	0 (0)	0 (0)	0.07 (7)	0.10 (10)	0.14 (14)	0.14 (14)	28
Pyrene	10	5	30	0 (0)	0 (0)	0.07 (7)	0.07 (7)	0.17 (17)	0.21 (17)	29
Phenanthrene	10	5	30	0 (0)	0.10 (10)	0.27 (20)	0.37 (23)	0.50 (30)	0.60 (40)	30
Benz [a]anthracene	2.2	10	30	0.4 (30)	1.83 (57)	1.50 (50)	1.60 (53)	1.86 (69)	2.00 (62)	29
None	---	10	30	0 (0)	0 (0)	0 (0)	0.03 (3)	0 (0)	0 (0)	30

<sup>a</sup>12-0-tetradecanoylphorbol-13-acetate - applied 2x/wk one week after initiation with hydrocarbon

<sup>b</sup>%  $\leq$  17.  $p < .05$ :  $\chi^2$  test, one-tailed.

Source: Scribner (1973).

Pfeiffer (1973, 1977) tested ten non-carcinogens and two carcinogens in combination by subcutaneous injection in NMRI mice. The ten "non-carcinogens" were benzo[e]pyrene (2-70 µg); benz[a]anthracene (3-100 µg); phenanthrene (125-4000 µg); anthracene (31-1000 µg); pyrene (62-2100 µg); chrysene (3-100 µg); perylene (0.2-7.0 µg); benz[g,h,i]perylene (12.8-400 µg); coronene (3-100 µg) and fluoranthene (28-900 µg). Benzo[a]pyrene (3-100 µg) and dibenz[a,h]anthracene (2-70 µg) were the two carcinogens in the mixture. The carcinogenic effect of the mixture was attributed to the presence of the two carcinogens; neither an inhibitory or stimulating effect was attributed to the ten non-carcinogens of the mixture.

In summation, none of the compounds in this group of PAHs has been shown to be carcinogenic by the oral route. Phenanthrene, and possibly pyrene, have been shown to possess weak tumor-initiation activity in the mouse skin carcinogenesis model; anthracene and fluoranthene appear inactive. Augmentation of carcinogenic action has been demonstrated with both fluoranthene and pyrene, but an assessment of human risk based on co-carcinogenic results would appear to be premature at this time. No studies were found for acenaphthene or fluorene alone; tests with complex mixtures of PAHs suggest no carcinogenic activity, but do not allow firm conclusions to be drawn.

#### Teratogenicity

No data have been found.

#### Mutagenicity

Various mutagenicity studies conducted with anthracene, phenanthrene, fluorene, and pyrene have produced essentially negative responses (see Table 4-39). A single experiment with acenaphthene produced positive findings in one strain of Salmonella typhimurium in the presence of rat liver activation, but only at concentrations that were toxic to the bacteria. No other data were available for this compound. Data for fluoranthene are mixed. Kaden et al. (1979) reported that fluoranthene induced a significantly greater number of mutations in Salmonella typhimurium TM 677 than an equimolar concentration of benzo[a]pyrene, the positive control. However, negative results have been reported for four other strains of Salmonella (Salamone et al. 1979), as well as in a mouse embryo cell assay (Kamei 1980).

#### Other Toxic Effects

Little is known concerning other toxic effects associated with exposure to compounds designated as the anthracene group.

Relatively low acute toxicity has been reported for fluoranthene; i.e., an oral LD<sub>50</sub> of 2g/kg in the rat and a dermal LD<sub>50</sub> of 3.18g/kg in the rabbit (USEPA 1980b).



Limited data on acenaphthene indicate loss of body weight, changes in peripheral blood, increased aminotransferase levels in blood and mild morphological damage to both liver and kidney in rats administered 2g/kg/day orally for 32 days (Knobloch et al. 1969). Another study noted toxic effects on blood, lungs and glandular constituents in rats inhaling 12 mg/m<sup>3</sup> 4 hours/day, 6 days/week for 5 months. The bronchial epithelium showed hyperplasia and metaplasia, but this appears to be related to pneumonia which killed a large portion of the study population. There were no controls (Reshetyuk et al. 1970).

#### 4.3.1.4 Overview

##### Ambient Water Quality Criteria - Human Health

The U.S. EPA (1980a) determined that sufficient data were not available to derive an ambient water quality criterion that would protect against potential toxicity of acenaphthene. The mammalian and human health effects of acenaphthene are virtually unknown. The level for controlling undesirable taste and odor quality of ambient water was estimated at 0.02 mg/l.

A criterion has been established for fluoranthene (USEPA 1980b). Based on a no-effect level for mortality (6.1 mg/kg/day) in a chronic mouse skin-painting study (Hoffmann et al. 1972), an assumption of 100% absorption of the applied dose, and an uncertainty factor of 1000, an acceptable human daily intake of 0.4 mg is calculated, which corresponds to an ambient water quality criterion of 42 µg/L.

No specific criteria have been established for the remaining compounds in this group, none of which is a carcinogen by ingestion.

##### Other Considerations

None of the compounds in this group (anthracene, acenaphthene, fluoranthene, fluorene, phenanthrene, pyrene) is carcinogenic by the oral route; however, most of these compounds have not been extensively studied. An increased incidence of injection site tumors was noted with anthracene, but this type of oncogenic effect is generally regarded as irrelevant to human exposure. Phenanthrene, and possibly pyrene, are weak initiators in the mouse skin carcinogenesis model, although considerably less active than benzo[a]anthracene. It is difficult to assess the relevance of these findings to human health in the absence of direct carcinogenic effects. Fluoranthene and pyrene have been shown to be co-carcinogens with benzo[a]pyrene. Current understanding of the co-carcinogenesis process, however, is not sufficiently adequate to allow estimation of human risk.

Mutagenicity studies for most of these compounds are essentially negative; mixed data were obtained for fluoranthene. Additional data are needed to resolve this issue. No reproductive data were found for these compounds, and virtually no toxicological data are available.

#### 4.3.2 HUMAN EXPOSURE

##### 4.3.2.1 Introduction

This section examines human exposure to the anthracene group PAHs via ingestion (food and drinking water), inhalation, and dermal contact. As is apparent from Section 4.2.4, monitoring data for these compounds are very limited.

##### 4.3.2.2 Ingestion

###### Drinking Water

Basu and Saxena (1977, 1978) sampled 16 water samples in New York, Pennsylvania, and West Virginia. Fluoranthene was detected in four samples at levels of 2.4-94.5 ng/l. Removal efficiencies ranged from 98.9-100%; treatment plants at which removal efficiencies were measured utilized activated carbon treatment. Harrison *et al.* (1976) showed a 70% reduction with settling, filtration and chlorination. These concentrations are considered to be low, and thus in areas where these treatment methods are used, drinking water levels of PAHs will be low.

Fluoranthene was also detected in the National Organic Monitoring Survey (NOMS) in 20 of 110 samples at a detection limit of 10 ng/l. The mean of the positive samples was 20 ng/l and the range was 10-80 ng/l (U.S. EPA 1978). The U.S. EPA (1980b) estimated an average concentration of 8.6 ng/l in drinking water, utilizing the data of Basu and Saxena (1977, 1978) and by assigning the detection limit to those samples in which none was detected. These assumptions appear to be reasonable in view of the limited data available.

Anthracene/phenanthrene was detected in 7 of 39 public water system wells; the maximum concentration was reported to be 21 µg/l (Kim and Stone 1979). No data on drinking water levels were found for the other chemicals in this group (acenaphthene, fluorene, and pyrene). Furthermore, they are rarely detected in ambient water (see Section 4.2.4). Anthracene was reported only twice in STORET as levels above the detection limit: 1 µg/l, 27 µg/l.

Table 4-40 contains estimated daily exposures via drinking water. Typical estimates are only shown for fluoranthene because sufficient data on drinking water levels are lacking for the other PAHs in this group.

### Food

Levels of PAHs in raw foods appear to be generally low. However, vegetables or fruits grown in the vicinity of releases to air may contain higher levels (U.S. EPA 1980c). The highest levels of PAHs in food appear to result from the cooking process, especially charcoal broiling and smoking.

Table 4-41 estimates the exposure to PAHs via ingestion of such foods, as well as the various assumptions made. The data on contamination levels were taken from U.S. EPA (1980 a,b,c) and White and Vanderslice (1980); data are very limited for many of these chemicals. Columns in the table were not always totaled since the exposure shown represents an unknown portion of the actual exposure.

Considering all of the uncertainties, typical daily intakes for fluoranthene have been estimated to be 0.3 µg/day; pyrene, 0.1 µg/day, and anthracene, 0.02 µg/day. Data were too fragmentary for the other compounds for making an estimate of total daily exposure. The maximum intakes shown represent a maximum level of contamination in the food and maximum daily consumption. The total is meant to represent a worst case. It is apparent that charcoal broiling represents the major source of exposure. However, consumption of fruits and vegetables from contaminated locations may also contribute significantly to exposure in some cases.

#### 4.3.2.3 Inhalation

The U.S. EPA (1980 c,d) has summarized the available monitoring data for PAHs in air, mostly for urban areas. These limited data, including data from Section 4.2.4, were utilized to develop exposure estimates for an assumed respiratory flow of 20 m<sup>3</sup>/day (ICRP 1975). The results are shown in Table 4-42. As is the case for exposure due to food and drinking water, fluoranthene appears to represent the largest exposure of chemicals in this group.

In addition to ambient air, smoking can contribute to inhalation of PAHs. For comparison, Hoffman *et al.* (1972) have estimated that smoking one cigarette may contribute up to 0.26 µg fluoranthene to the lungs; thus a person smoking one pack per day could receive 5.2 µg/day via mainstream smoke from this source. Similarly, mainstream smoke from one cigarette was found to contain 0.42 µg of fluorene, resulting in an exposure of 8.4 µg/day from smoking one pack per day.

#### 4.3.2.4 Dermal Contact

No direct information is available regarding the dermal exposure of humans to PAHs in water. However, due to the low levels found in water, any dermal exposure is expected to be low.

TABLE 4-40. ESTIMATED HUMAN EXPOSURE TO THE ANTHRACENE GROUP PAHs VIA DRINKING WATER

<u>Compound</u>	<u>Concentration (ng/l)</u>		<u>Estimated Daily Exposure (µg/day)<sup>b</sup></u>	
	<u>Typical</u>	<u>Maximum</u>	<u>Typical</u>	<u>Maximum</u>
Anthracene	NA <sup>a</sup>	21,000 <sup>e</sup>	NA	40 <sup>f</sup>
Acenaphthene	NA	NA	NA	NA
Fluoranthene	8.6 <sup>c</sup>	94.5 <sup>d</sup>	0.02	0.2
Fluorene	NA	NA	NA	NA
Phenanthrene	NA	21,000 <sup>e</sup>	NA	40 <sup>f</sup>
Pyrene	NA	NA	NA	NA

<sup>a</sup>Not available.

<sup>b</sup>Based on a 2-liter per day consumption of drinking water (ICRP 1975).

<sup>c</sup>U.S. EPA (1980b).

<sup>d</sup>Basu and Saxena (1977, 1978).

<sup>e</sup>

Reported as undifferentiated data for anthracene/phenanthrene (Kim and Stone 1979).

<sup>f</sup>Calculated from maximum reported for unresolved anthracene/phenanthrene.

TABLE 4-41. LEVELS OF ANTHRACENE GROUP PAHs IN FOOD AND ESTIMATED EXPOSURE VIA INGESTION OF FOOD

FOOD CATEGORY		CONSUMPTION		ANTHRACENE				FLUORANTHENE			
		(g/day)		CONTAMINATION		INTAKE (µg/day)		CONTAMINATION		INTAKE (µg/day)	
		Typical <sup>e</sup>	Max.								
Charcoal- broiled beef <sup>a</sup>	Hamburger	10		NA	NA	NA	NA	5	15	0.05	
	Steak	3	86	4.5	NA	0.01	NA	30	50	0.09	4.3
Charcoal broiled pork <sup>b</sup>		1	27	7.1	NA	0.007	NA	10	49	0.02	1.3
Smoked pork <sup>b</sup>		1	27	NA	NA	NA	NA	3	NA	0.003	NA
Smoked sausage <sup>c</sup>		1.5	30	NA	NA	NA	NA	15	40	0.02	1.2
Smoked fish <sup>d</sup>		0.1	14	2	26	0.0002	0.4	3	12	0.0003	0.2
Oil		18	NA	NA	36	NA	0.6	5	450	0.09	8.1
Leafy Vegetables		40	NA	NA	12	NA	0.5	NA	180	NA	7.2
Total ...						0.02				0.27	

<sup>a</sup> Consumption of beef - 86 g/day, 15% charcoal broiled - 80% hamburger, 20% steak. Worst case maximum: 86 g consumption of charcoal-broiled steak.

<sup>b</sup> Consumption of pork - 27 g/day, 5% smoked, 5% charcoal-broiled. Worst case maximum: 27 g/day charcoal-broiled.

<sup>c</sup> Consumption of sausage - 30 g/day, 5% smoked. Worst case maximum: 30 g/day smoked.

<sup>d</sup> Consumption of fish - 14 g/day, 1% smoked. Worst case maximum: 14 g/day smoked.

<sup>e</sup> "Typical" may be defined here as a qualitative estimate based on average consumption of the range of concentrations. The available contamination data did not lend themselves to statistical treatment.

Source: USDA (1978, 1980), U.S. EPA (1980 a,b,c), White and Vanderslice (1980).

TABLE 4-41. LEVELS OF ANTHRACENE GROUP PAHs IN FOOD AND ESTIMATED EXPOSURE VIA INGESTION OF FOOD  
(Continued)

FOOD CATEGORY	CONSUMPTION (g/day)		FLUORENE				PYRENE				PHENANTHRENE			
			CONTAMINATION (µg/kg)		INTAKE (µg/day)		CONTAMINATION (µg/kg)		INTAKE (µg/day)		CONTAMINATION (µg/kg)		INTAKE (µg/day)	
			Typical <sup>e</sup>	Max.	Typical <sup>e</sup>	Max.	Typical <sup>e</sup>	Max.	Typical <sup>e</sup>	Max.	Typical <sup>e</sup>	Max.	Typical <sup>e</sup>	Max.
Charcoal- broiled beef <sup>a</sup>	Hamburger	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Steak	3 86	NA	NA	NA	NA	20	35	0.06	3	NA	21	NA	1.8
Charcoal broiled pork <sup>b</sup>		1 27	NA	NA	NA	NA	NA	42	NA	1.1	NA	58	NA	1.6
Smoked pork <sup>b</sup>		1 27	NA	NA	NA	NA	5	161	0.005	4.3	NA	NA	NA	NA
Smoked sausage <sup>c</sup>		1.5 30	NA	NA	NA	NA	1.5	NA	0.002	NA	NA	NA	NA	NA
Smoked fish <sup>d</sup>		0.1 14	5	67	0.0005	0.9	3	6	0.0003	0.08	10	52	0.001	0.7
Oil		18 NA	NA	NA	NA	NA	2	15	0.04	0.03	NA	51	NA	0.9
Leafy vegetables		40 NA	NA	NA	NA	NA	NA	109	NA	4.4	NA	88	NA	3.5
Total ...										0.11				

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<sup>a</sup>Consumption of beef - 86 g/day, 15% charcoal broiled - 80% hamburger, 20% steak. Worst case maximum: 86 g consumption of charcoal-broiled steak.

<sup>b</sup>Consumption of pork - 27 g/day, 5% smoked, 5% charcoal-broiled. Worst case maximum: 27 g/day charcoal-broiled.

<sup>c</sup>Consumption of sausage - 30 g/day, 5% smoked. Worst case maximum: 30 g/day smoked.

<sup>d</sup>Consumption of fish - 14 g/day, 1% smoked. Worst case maximum: 14 g/day smoked.

<sup>e</sup>"Typical" may be defined here as a qualitative estimate based on average consumption of the range of concentrations. The available contamination did not lend themselves to statistical treatment.

TABLE 4-42. ESTIMATED EXPOSURE TO ANTHRACENE GROUP PAHs  
DUE TO INHALATION OF AMBIENT AIR

<u>Chemical</u>	<u>Ambient Concentration (ng/m<sup>3</sup>)<sup>a</sup></u>			<u>Intake (µg/day)<sup>b</sup></u>		
	<u>Urban</u>	<u>Rural</u>	<u>Max.</u>	<u>Urban</u>	<u>Rural</u>	<u>Max.</u>
Anthracene	0.1-1.3	NA	NA	0.003-0.03	NA	NA
Acenaphthene	0.7	NA	NA	0.014	NA	NA
Fluoranthene	4	NA	40	0.08	NA	0.8
Fluorene	NA <sup>c</sup>	NA	NA	NA	NA	NA
Phenanthrene	0.011-0.34	NA	NA	0.0002-0.007	NA	NA
Pyrene	1.0-19.4	NA	NA	0.02-0.4	NA	NA

<sup>a</sup>U.S. EPA (1980 a,b,c).

<sup>b</sup>Based on respiratory flow of 20 m<sup>3</sup>/day (ICRP 1975).

<sup>c</sup>NA = Not available.

#### 4.3.2.5 Overview

Very little information is available regarding the exposure of humans to anthracene and the other chemicals in this group. These compounds have rarely been detected in drinking water, surface water, or air. Monitoring and detection in food appears to be more frequent, especially for charcoal-broiled and smoked foods.

Table 4-43 summarizes the exposure estimates previously discussed. Food appears to be the major exposure medium, although exposure due to inhalation may be comparable in some urban areas. Smoking could dominate all of these routes, however, since intakes from this source of 5.2  $\mu\text{g}/\text{day}$  and 8.4  $\mu\text{g}/\text{day}$  have been estimated for fluoranthene and fluorene, respectively. Of the chemicals in this group, fluoranthene appears to represent the greatest exposure of humans. The presence of anthracene contamination in drinking water supplies could possibly result in a high exposure level. The exposure calculated for ingestion of drinking water containing the maximum reported concentration of anthracene/phenanthrene was 40  $\mu\text{g}/\text{day}$ .

TABLE 4-43. ESTIMATED HUMAN EXPOSURE TO ANTHRACENE GROUP PAHs

<u>Compound</u>	<u>"Typical"<sup>a</sup> Exposure (ug/day)</u>			
	<u>Drinking Water</u>	<u>Food</u>	<u>Inhalation in Urban Areas</u>	<u>Smoking</u>
Anthracene	NA <sup>b</sup>	0.02	0.003-0.03	NA
Acenaphthene	NA	NA	0.01	NA
Fluoranthene	0.02	0.3	0.08	5.2
Fluorene	NA	>0.0005 <sup>c</sup>	NA	8.4
Phenanthrene	NA	>0.001 <sup>c</sup>	0.0002-0.007	NA
Pyrene	NA	0.1	0.02-0.4	NA

<sup>a</sup> "Typical" may be defined here as a qualitative estimate based on average consumption of the range of concentrations. The available contamination data did not lend themselves to statistical treatment.

<sup>b</sup> NA = Not available.

<sup>c</sup> Insufficient data available.

Source: Estimates derived in Section 4.3.2.

#### 4.4 EFFECTS AND EXPOSURE--AQUATIC BIOTA

##### 4.4.1 Effects on Aquatic Organisms

###### 4.4.1.1 Introduction

The acute toxicity data for this group of manufactured PAHs were not extensive and were available for only four of the six compounds under consideration. Some limited information on the toxicity of anthracene was available from general studies and through personal communication with investigators presently conducting toxicity studies.

###### 4.4.1.2 Acute Toxicity

Limited data for freshwater fish and invertebrates are presented in Table 4-44. The acute toxicity of acenaphthene and fluoranthene was measured for the bluegill sunfish and cladoceran; LC<sub>50</sub> data ranged from 1700 µg/l to 325,000 µg/l.

The acute toxicity data for marine fish and invertebrates (Table 4-45) are more extensive. The range in values is quite broad, from 40 µg/l (fluoranthene, juvenile mysid shrimp) to 2230 µg/l (acenaphthene, sheepshead minnow). For all of the four compounds tested, invertebrates are generally more sensitive (range 40-1090 µg/l) than fish (range 150-2230 µg/l), but the data for fish are somewhat limited. The most sensitive fish species was the mosquito fish (Gambusia affinis) with an LC<sub>50</sub> of 150 µg/l phenanthrene. Among the invertebrates, there are some data indicating differences in the toxicity of different PAHs to the same species. Acenaphthene was 24 times more toxic to mysid shrimp (Mysidopsis bahia) than was fluoranthene to juveniles of the same species. Data from one study on the marine polychaete worm (Neanthes arenaceodentata) indicate that for three PAHs tested, toxicity increased with increasing molecular weight. The order of toxicity was fluoranthene > phenanthrene > fluorene (Table 4-45). The opposite trend was seen with both freshwater and marine algae species tested (Table 4-46), as acenaphthene was significantly more toxic than fluoranthene.

###### 4.4.1.3 Chronic Toxicity

This group of PAHs has been tested for chronic effects to marine species only. Chronic effects levels (Table 4-47) ranged from 12 µg/l (fluoranthene in mysid shrimp) to > 500 (acenaphthene in sheepshead minnow). This limited data set suggests that chronic toxicity may increase with greater molecular weight.

TABLE 4-44. ACUTE TOXICITY OF ANTHRACENE GROUP  
PAHs FOR FRESHWATER SPECIES

<u>Species</u>	<u>Compound</u>	LC 50 ( <u>ug/l</u> )	<u>Reference</u>
Cladoceran <u>Daphnia magna</u>	Acenaphthene	41,200	U.S. EPA (1978)
Bluegill <u>Lepomis macrochirus</u>	Acenaphthene	1,700	U.S. EPA (1978)
Cladoceran <u>Daphnia magna</u>	Fluoranthene	325,000	U.S. EPA (1978)
Bluegill <u>Lepomis macrochirus</u>	Fluoranthene	3,980	U.S. EPA (1978)

TABLE 4-45. ACUTE TOXICITY OF ANTHRACENE GROUP  
PAHs FOR MARINE INVERTEBRATES AND FISH

<u>Species</u>	<u>Compound</u>	<u>LC<sub>50</sub></u> <u>(ug/l)</u>	<u>Reference</u>
<u>Invertebrates</u>			
Mysid shrimp <u>Mysidopsis bahia</u>	Acenaphthene	970	U.S. EPA (1978)
Mysid shrimp (juvenile)	Fluoranthene	40	U.S. EPA (1978)
Grass Shrimp <u>Palaemonetes pugio</u>	Phenanthrene	370 (24 hr.)	Young (1977)
Grass shrimp	Fluorene	320	Wofford and Neff (1978)
Polychaete <u>Neanthis arenaceodenta</u>	Fluorene	1,090	Rossi and Neff (1978)
Polychaete	Phenanthrene	600	Rossi and Neff (1978)
Polychaete	Fluoranthene	500	Rossi and Neff (1978)
<u>Fish</u>			
Sheepshead minnow <u>Cyprinodon variegatus</u>	Fluorene	1,680	Wofford and Neff (1978)
Sheepshead minnow <u>Cyprinodon variegatus</u>	Acenaphthene	2,230	U.S. EPA (1978)
Mosquito fish <u>Gambusia affinis</u>	Phenanthrene	150	U.S. EPA (1978)

TABLE 4-46. TOXICITY OF ANTHRACENE GROUP  
PAHs FOR FRESHWATER AND MARINE PLANTS

<u>Species</u>	<u>Compound</u>	96-Hour <u>EC<sub>50</sub> (µg/l)<sup>a</sup></u>	<u>Reference</u>
<u>Freshwater Species</u>			
Alga <u>Selenastrum capricornutum</u>	Acenaphthene	530 Chlorophyll a	U.S. EPA (1978)
Alga	Acenaphthene	520 Cell numbers	U.S. EPA (1978)
Alga	Fluoranthene	54,400 Cell numbers	U.S. EPA (1978)
Alga	Fluoranthene	54,600 Chlorophyll a	U.S. EPA (1978)
<u>Saltwater Species</u>			
Alga <u>Skeletonema costatum</u>	Acenaphthene	500 Chlorophyll a	U.S. EPA (1978)
Alga	Acenaphthene	500 Chlorophyll a	U.S. EPA (1978)
Alga	Fluoranthene	45,000 Chlorophyll a	U.S. EPA (1978)
Alga	Fluoranthene	45,600 Cell numbers	U.S. EPA (1978)

<sup>a</sup> EC<sub>50</sub> = concentration causing effect on 50% of test organisms.

TABLE 4-47. CHRONIC TOXICITY OF ANTHRACENE  
GROUP PAHs FOR MARINE SPECIES

<u>Species</u>	<u>Compound</u>	<u>Effects Level (<math>\mu\text{g}/\text{l}</math>)</u>	<u>Reference</u>
Sheepshead minnow <u>Cyprinodon variegatus</u>	Acenaphthene	520-970 embryo-larval test	U.S. EPA (1978)
Mysid shrimp <u>Mysidopsis bahia</u>	Fluoranthene	12-22 life-cycle	U.S. EPA (1978)
Mud Crab <u>Rithropanopeus harrisi</u>	Phenanthrene	200 decreased growth	Neff (1979)
Grass shrimp <u>Palaemonetus pugio</u>	Phenanthrene	100 @ 30 days decreased growth	Young (1977)

#### 4.4.1.4 Other Toxicity Studies

No bioassay toxicity data were available for anthracene, but the compound is believed to be acutely toxic to freshwater organisms in the low  $\mu\text{g}/\text{l}$  range. In microcosm stream model studies at the Savannah River Ecology Laboratory, anthracene in concentrations of 1-10  $\mu\text{g}/\text{l}$  killed all fish (bluegill sunfish) and insects (chironomids) in the system in 8 hours. Photolysis is an important degradation process for anthracene (and other PAHs). The toxicity of anthracene appeared to be increased by sunlight since the results were not reproduced in the laboratory or outside at night (personal communication, P. Landrum et al., Savannah River Ecology Laboratory, 1980).

#### 4.4.1.5 Factors Affecting Toxicity

In order to study the effect of salinity on the toxicity of various concentrations of phenanthrene to larvae of the mud crab Rithropanopeus harrisi, Laughlin and Neff (1979) tested concentrations of 0, 100, 150, and 200  $\mu\text{g}/\text{l}$  at salinities of 5, 15, and 25<sup>o</sup>/oo. Concentrations of 200  $\mu\text{g}/\text{l}$  were acutely toxic to these crabs, and mean survival was lowest at the low salinity values. The threshold of acute toxicity was at 150  $\mu\text{g}/\text{l}$ , and survival was  $\leq 30\%$  at 5<sup>o</sup>/oo salinity. At 15 and 25<sup>o</sup>/oo salinity, survival was higher, as was the case at 200  $\mu\text{g}/\text{l}$  phenanthrene. These studies show that variations in environmental factors such as salinity, even when well within the normal tolerance range of the species, may create slightly stressful environmental conditions which in turn may significantly increase organisms' sensitivity to PAHs (Laughlin and Neff 1979).

#### 4.4.1.6 U.S. EPA Ambient Water Quality Criteria

No ambient water quality criteria for protection of freshwater or saltwater life from these PAHs have been proposed at this time. This is due to a lack of sufficient data on the toxicity of this group of PAHs to aquatic life.

#### 4.4.1.7 Conclusions

From the limited data available for this group of PAHs, some generalizations can be made about the toxic effects of these compounds.

- Acute effect levels for freshwater invertebrates and fish range from 1700  $\mu\text{g}/\text{l}$  (acenaphthene/bluegill) to 325,000  $\mu\text{g}/\text{l}$  (fluoranthene/Daphnia).
- Marine fish and invertebrates are somewhat more sensitive than freshwater species with acute values ranging from 40  $\mu\text{g}/\text{l}$  (fluoranthene/mysid shrimp) to 2230  $\mu\text{g}/\text{l}$  (acenaphthene/sheepshead minnow).

- Data for marine invertebrates indicate that toxicity increases with increasing molecular weight, but this trend is not similarly demonstrated with all other organisms. Therefore, nothing definitive can be concluded regarding the relative toxicity of these PAHs.
- Chronic toxicity values range from 12 µg/l to greater than 500 µg/l. However, data were available for only four marine species and for no freshwater species.

Aquatic organisms appear to be fairly resistant to anthracene group PAHs in laboratory experiments, and overall these PAHs are similar in their toxicity to biota. However, the results of microcosm studies, which simulate natural environmental conditions, indicate that anthracene is acutely toxic to stream biota at relatively low levels (1-10 µg/l) and warrant further in situ studies of the toxicity of anthracene, particularly since photodegradation is a significant environmental fate process for anthracene.

#### 4.4.2 Exposure of Aquatic Biota

##### 4.4.2.1 Introduction

PAHs are universal components of the aquatic and terrestrial environment, and, as discussed in Section 4.1, originate from direct input of petroleum-related processes, urban runoff, industrial effluents, and air to water deposition.

The anthracene group PAHs are all commercially produced. This is reflected in the monitoring data and numerous studies which reveal higher concentrations of anthracene group PAHs near industrialized areas, major ports, and areas of petroleum-related activity. Higher levels of these PAHs are also found in sediment, as opposed to water at the same location.

##### 4.4.2.2 Monitoring Data

Summary descriptions and percentage distributions of STORET observations for the PAHs in the anthracene group were given previously in Section 4.2.4. Nearly all (>75%) of the STORET observations for ambient and effluent water, and sediment were remarked, i.e., they represent detection limits of the analytic procedure and not concentrations actually detected. Of the few unremarked values reported (64 for ambient water, 88 for effluent water, and 128 for sediment), a majority (~70%) of the levels in water were below 100 µg/l (µg/kg).

More of the unremarked sediment values (36%, or 46 observations) were in the range of 100 µg/l to >1000 µg/l; this would support the modeling predictions discussed in Section 4.2 that anthracene will accumulate in the sediments. The highest levels observed (eight values) were in the range of 1-10 mg/kg, and occurred consistently in several places, including Puget Sound and the Washington State coast, the Oregon coast, San Francisco Bay and North Coastal California, a hazardous waste site in North Carolina, and the Houston ship channel. It is apparent that PAHs tend to accumulate in the sediments near industrialized or major port areas. Levels in soil have also been found to be as high as 5,000-120,000 µg/kg.

Other monitoring data (Section 4.2.2.5) indicate that PAH levels in (industrial and domestic) wastewater are in the low µg/l range, indicating that overall the levels in surface waters are not high, even those in the vicinity of effluent discharges.

##### 4.4.2.3 Aquatic Fate

Environmental conditions have a significant influence on the disposition of the anthracene group PAHs in aquatic systems. The results of the EXAMS modeling indicate that in five of the six generalized

aquatic environments examined, greater than 70% of the anthracene accumulated in the sediments, as opposed to that remaining in the water column (see Section 4.2.3.3). Anthracene is persistent in sediment, and for all six environments the amount of anthracene lost from the sediments is at least five times less than that lost from the water in the same time period. Photolysis is a significant and rapid fate process for anthracene in the water column. Anthracene (and/or its metabolites) from the sediments is available to deposit-feeding organisms, and may also be reintroduced, but apparently in small amounts, into the water column. Regarding exposure of biota to anthracene from sediments as compared with the water column, one study has shown that uptake from water is greater than from sediment (Giddings et al. 1978).

#### 4.4.2.4 Biosynthesis

Biosynthesis of PAHs in the environment from naturally occurring quinones is believed to take place, particularly under conditions of high sediment organic content. It has been postulated, however, that direct biosynthesis probably contributes little to the global PAH burden, but may represent a significant localized source of PAHs (Neff 1979). Evidence against biosynthesis as a source of substantial amounts of PAH in sediments has been suggested in that the PAHs formed by biosynthesis would be expected to be much simpler in composition than the complex PAH assemblages found in environmental samples (Youngblood and Blumer 1975). Thus biosynthesis would not be assumed to contribute to the exposure of biota to the anthracene-group PAHs.

#### 4.4.2.5 Conclusions

For all of the anthracene group PAHs, most of the levels detected in water were remarked values in the 10-500 µg/l range. Although no water quality criteria for these PAHs have been established due to insufficient data, the concentrations reported are below the range of toxic effects seen in the laboratory for those compounds for which effects data are available.

It should be noted, that in experiments at the Savannah River Ecology Laboratory, concentrations of 10 µg/l anthracene killed all organisms present in a pond microcosm experiment exposed to sunlight, whereas in the laboratory outside at night, acute effects did not occur at this low concentration (personal communication, P. Landrum 1980). This suggests that laboratory data may not reflect toxicity of the compounds under actual environmental conditions.

Although some sediment levels have been found in the range of levels causing acute toxic effects in aquatic organisms, the complex processes affecting the bioavailability of anthracene would probably result in biota being exposed to lower concentrations than those sampled. However, the direct

toxicity of sediments has not yet been tested. A greater concern than toxicity is that high levels of these compounds may be available chronically for bioaccumulation by organisms and biomagnification in the food chain.

## 4.5 RISK CONSIDERATIONS

### 4.5.1 Introduction

The purpose of this section is to evaluate potential risks to humans and aquatic biota resulting from exposure to the commercially produced PAHs in this group (anthracene, acenaphthene, fluoranthene, fluorene, phenanthrene, and pyrene). This risk analysis is hampered greatly by the lack of quantitative data on the levels that may produce health effects, and by the very limited amount of monitoring data available to indicate the extent of environmental exposure.

### 4.5.2 Humans

#### 4.5.2.1 Statement of Risk

The human effects data for this group of compounds are inadequate to allow a quantitative extrapolation of the human risk associated with environmental exposure to these compounds. The few studies of long-term exposure that were found did not indicate carcinogenic or mutagenic activity. Pyrene and fluoranthene act as co-carcinogens when applied to mouse skin in combination with other, carcinogenic compounds, but the significance of this finding to human health is unknown at this time. The dose levels of concern for acute or sublethal toxic effects have not been evaluated. The levels of environmental exposure estimated for these PAHs are low. Fluoranthene and pyrene are the two PAHs in this group with the highest potential exposure levels, reaching maximum daily intake levels on the order of 10-20 µg/day for the general population. Smokers could receive additional exposures on the order of 5.2 µg/day fluoranthene and 8.4 µg/day fluorene.

#### 4.5.2.2 Discussion

All of the compounds in the anthracene group are lipid soluble, a characteristic that would suggest that they may be absorbed and distributed throughout the body following ingestion or inhalation.

None of the six compounds in this group is considered carcinogenic by the oral route. An increased incidence of injection-site tumors was noted with anthracene, but this type of oncogenic effect is generally not regarded as relevant to human exposure. Phenanthrene, and possibly pyrene, show weak tumor-initiation activity in the mouse skin carcinogenicity model. However, it is difficult to assess the significance to human health of classifying these compounds as tumor-initiators in the absence of their direct carcinogenicity. Fluoranthene and pyrene were both shown to be co-carcinogens in the mouse skin carcinogenesis model; however, the mechanism of co-carcinogenesis is not clear and can only be surmised at this time. An assessment of human risk based on co-carcinogenic results would thus appear to be premature.

Mutagenicity studies with this group of PAHs have produced essentially negative results, and no data on adverse reproductive effects were found. Since virtually no toxicological data are available for these compounds,

considerable uncertainty exists with respect to the relative risk associated with human exposure to these materials.

There is also very little information quantifying the human environmental exposure to the PAHs in the anthracene group. These compounds are rarely detected in drinking water, and the levels reported in ambient air are very low. The available monitoring data indicate that fluoranthene exposure from ingestion of drinking water could reach a maximum of 0.2  $\mu\text{g}/\text{day}$ . On the basis of urban air concentrations, inhalation exposure to each of the compounds in this group, except pyrene, is estimated to be considerably less than 0.1  $\mu\text{g}/\text{day}$ ; daily intake levels of pyrene in urban air could reach 0.4  $\mu\text{g}/\text{day}$ .

For the general population, the primary route of environmental exposure to these compounds is oral intake of contaminated foodstuffs, especially cooking oil, smoked or charcoal-broiled meats, and fruits or vegetables from contaminated areas. The exposure estimates in Section 4.3.2 indicate that fluoranthene and pyrene are the most prevalent of these PAHs in food. Estimated daily intake levels range from typical levels of 0.3  $\mu\text{g}/\text{day}$  and 0.1  $\mu\text{g}/\text{day}$  to maximum levels of about 20  $\mu\text{g}/\text{day}$  and 10  $\mu\text{g}/\text{day}$  for fluoranthene and pyrene, respectively; a typical daily anthracene exposure from food was estimated to be 0.02  $\mu\text{g}/\text{day}$ . Data for the other compounds were insufficient to permit estimates of daily exposure via this route.

Cigarette smokers may be exposed to 5.2  $\mu\text{g}/\text{day}$  of fluoranthene and 8.4  $\mu\text{g}/\text{day}$  of fluorene in the mainstream smoke of one pack of cigarettes (20 cigarettes). One-third of all U.S. adults smoke cigarettes and 25-30% of the smokers smoke more than 25 cigarettes per day. The risk to this subpopulation due to smoking may be significantly higher than the total risk to the general population from all of the typical exposures estimated for the six PAHs in this group.

#### 4.5.3 Aquatic Biota

Risk to aquatic biota exposed to ambient concentrations of these PAHs is expected to be low. The U.S. EPA has not established ambient water quality criteria for these compounds for the protection of aquatic life. However, all ambient concentrations in the STORET data base were below the levels that were reported to be acutely toxic to freshwater organisms. The STORET concentration data for surface water do overlap the range of chronic and acute toxic effects levels for marine organisms, which appear to be more sensitive to these PAHs; however, there are no monitoring data specifically for marine systems. Since the potential does exist for bioaccumulation of these PAHs in zooplankton and subsequent biomagnification by fish, direct comparison of ambient concentrations with effects levels may not adequately describe the risk to aquatic organisms.

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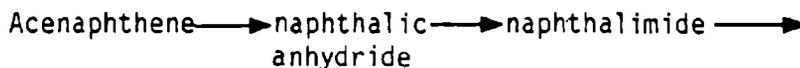
U.S. Environmental Protection Agency (U.S. EPA). Ambient water quality criteria for fluoranthene. EPA 440/5-80-049. Washington, DC: Criteria and Standards Division, Office of Water Regulations and Standards, U.S. EPA; 1980b.

APPENDIX A

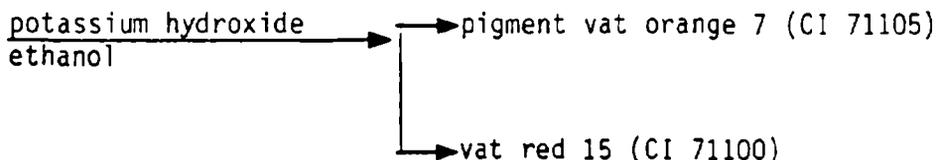
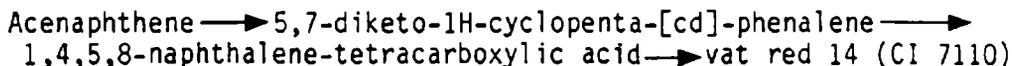
NOTE 1: Acenaphthene, fluoranthene, fluorene, phenanthrene, and pyrene are not listed in the 1979 edition of the U.S. International Trade Commissions' Synthetic Organic Chemicals Production and Sales Publication (USITC, 1979). Consequently, according to a spokesperson for that Commission (Edmund Cappuccilli), these chemicals most likely were not produced domestically; and any plants producing them would have made <1 kkg (i.e., <2,200 pounds).

NOTE 2: According to an Allied Chemical Corporation spokesperson (Dick Ritchie), Allied sells all of the anthracene they recover from coal tar to Toms River Chemical Corporation. A spokesperson (William Hagman) from that corporation confirmed that statement and said they receive the anthracene from Allied via alcarri; each holds 40 tons. More than 100 kkg of anthracene were produced and shipped to Toms River Chemical Corporation in 1979.

NOTE 3: Acenaphthene is used as a starting material in the production of four pigments:



pigment brown 26 (CI 71129);



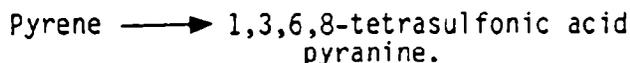
Source: EPA, 1977d; USITC, 1979.

NOTE 4: Acenaphthene was found in influent wastewaters from 3 of 26 pharmaceutical plants in the following concentrations: 135, 2, and 92 µg/ℓ. The flow rates of the wastewaters for those plants were 378,500, 189,250, and 37,850 ℓ/day, respectively. These plants were assumed to operate 360 days/year. Therefore, with an average concentration of 76 µg/ℓ and annual flow rate of 72,670,000 ℓ, 5 kg of acenaphthene were contained in influent wastewaters generated by three pharmaceutical plants. If the ratio of 3 plants of the 26 plants sampled represents the entire industry (464 plants), then 54 plants possibly generated wastewaters (influent) that contained 270 kg or <1

kg of acenaphthene. Furthermore, because these wastewaters were treated to remove this compound, acenaphthene was probably not discharged to water (EPA 1980e).

NOTE 5: Of all the PAHs shown in Table A-2, acenaphthene was contained in pharmaceutical influent wastewaters at the highest concentration (i.e., 270 kg, derived in Note 4). If acenaphthene represents a worst case scenario, then <1 kkg each of anthracene, fluoranthene, fluorene, phenanthrene, and pyrene was contained in pharmaceutical industry influent wastewaters. Furthermore, because these compounds were not found in pharmaceutical effluent wastewaters, it is assumed that these chemicals are not released to aquatic environments. Also, because pharmaceutical wastewater treatment facilities usually remove chemicals and deep well inject or lagoon them, the <1 kkg of each chemical removed is assumed to be disposed to land.

NOTE 6: Pyranthrone (CI Vat Orange 9), a commercially important dye, can be prepared by condensation of pyrene with benzoyl chloride and aluminum chloride to give dibenzoyl-pyrene, which upon heating with aluminum chloride provides pyranthrone (Chung and Farris 1979). Pyranine (CI 59040, Ext. D+C Green 1) is another dye in which pyrene is used as a starting material:



Source: EPA 1977d.

NOTE 7:

a. Oil:

Water figure based on  $3.6 \times 10^7$  g of various oils - crude (36%), diesel (18%), fuel (42%), waste (2%), lube (0.3%) other (1.7%) - spilled in navigable waters in 1978 (U.S. Coast Guard, 1980).

Land figure based on  $5.1 \times 10^5$  g of crude oil spilled in 1978 by common carrier (23%), private carrier (22%), rail (6%), and "other" (49%) (U.S. Dept. of Transportation, 1980). Average oil Density = 0.85.

Gasoline:

Water -  $1.1 \times 10^7$  g spilled: aviation/automobile gasoline (98%) and natural (Casinghead) Gasoline (2%) (U.S. Coast Guard, 1980).

Land -  $3.7 \times 10^6$  g spilled: common carrier (53%), private carrier (47%), rail (0.8%), "other" (<0.01%) U.S. Dept. of Transportation, 1980). Gasoline density: 0.73.

NOTE 8:

Residential Coal Combustion

Emissions were calculated from the emission factors in Table A-8 (EPA 1977a) and the value  $8,688 \times 10^3$  kkg of coal consumed for residential combustion (DOE 1980.)

Fireplaces

Emissions were calculated from emission factors (see Table A-8) that represented the average of three tests (EPA 1980b). The total mass of wood burned in fireplaces in 1976,  $2.7 \times 10^6$  kkg (EPA 1980a) was extrapolated to 1977, based upon the number of housing units in each region of the country, the percentage of those housing units with fireplaces (see Table A-10), an average consumption of 98.3 kg/housing unit (EPA 1980a). These assumptions led to the estimate that  $3.0 \times 10^6$  kkg of wood were burned in 1977.

Residential Primary and Auxiliary Heat from Wood

Emissions from these sources were calculated using the emission factors presented in Table A-9 and 1977 wood consumption of  $6.9 \times 10^6$  kkg and  $9.2 \times 10^6$  kkg for primary and auxiliary heating, respectively. The emission factors presented in Table A-8 are averages of those for baffled and nonbaffled wood stoves (EPA 1980a). Total 1977 wood consumption for primary heating was obtained from the number of housing units that used wood for primary heat in 1976 and 1977 (912,000 and 1,239,000) a proportional extrapolation of the estimated  $5.1 \times 10^6$  kkg of wood burned in 1976 to  $6.9 \times 10^6$  kkg for 1977 (EPA 1980a and Census 1979). Total 1977 wood consumption for auxiliary heating ( $9.2 \times 10^6$  kkg) was extrapolated from the 1976 estimate of  $8.5 \times 10^6$  kkg (EPA 1980a) on the basis of the increase in the number of houses with fireplaces (see Fireplaces).

Cigarettes

The emission factors for cigarette smoking shown in Table A-8 were used along with the number of cigarettes produced ( $616 \times 10^9$ ) (USDA 1979). The emission factors are all from Neff (1979), except that for naphthalene, which is from Schmeitz, et al. (1978).

### Coal Refuse Piles

Using the composition of the particulate polycyclic organic matter (POM) shown in Table A-8, emissions were calculated based upon a refuse pile volume of  $190 \times 10^6 \text{ m}^3$  (21% of which is estimated to be burning), a density of  $1.5 \text{ kkg/m}^3$ , and a POM emission rate of  $1.3 \times 10^{-8} \text{ kg/kkg-hr}$  (EPA 1978a). Only particulate emissions were analyzed here, and only preliminary sampling data are presented.

### Carbon Black

An estimated  $1.0 \times 10^6 \text{ kkg}$  of carbon black were produced in 1977 (SRI 1979). The emission factors in Table A-8 (Serth and Hughes 1980) were used to estimate PAH emissions, although the resulting estimates are limited by the fact that testing was performed upstream of an emissions control device (burner).

An estimate of PAH production associated with carbon black manufacture is presented in Table A-10.

#### NOTE 9:

### Prescribed Burning

The emission factors in Table A-8 (EPA 1978a) and an estimated  $36 \times 10^6 \text{ kkg}$  (dry weight) of fuel burned by prescribed burning (Pierovich 1978) were used to estimate emissions. Note that this does not include agricultural burning.

#### NOTE 10:

### Wildfire

The emission factors in Table A-8 (McMahon and Tsoukalas 1977) are averages obtained from six tests on pine needles with differing fuel densities used for heading and backing fires; hence these factors cannot provide an accurate basis for nationwide emissions estimates. The total amount of fuel burned was estimated by assuming that  $10^{10} \text{ m}^2$  ( $3 \times 10^6$  acres) of land were burned on the average (Dahl 1980), and that the fuel loading was  $2 \text{ kg dry weight consumed/m}^2$  (based upon estimates by EPA 1978b).

NOTE 11:

Tire Wear

A crude estimate of PAH emission from tire wear associated with carbon black (see Table A-11) was developed from the following data:

- 365 da/yr.
- $7.4 \times 10^6$  bbl/da gasoline consumption (Oil and Gas Journal 1979).
- 14.7 miles/gal average (EPA 1975).
- 42 gal/bbl.
- 0.34 g/vehicle-mile weight loss from tires of which 0.19 g/vehicle-mile is airborne particulates and 0.15 g/vehicle-mile is deposited on road surface (EPA 1979a).
- Rubber composed of 33% carbon black (SRI 1979).
- Average PAH composition of carbon black in Table A-12 (Locati et al. 1979).

NOTE 12:

Agricultural Open Burning

Emissions were calculated on the basis of the forest fire emission factors in Table A-8 and an estimated  $13 \times 10^6$  kkg (dry weight) of material burned. (EPA 1977b).

NOTE 13:

Motor Vehicles

Motor vehicle PAH emissions were calculated by using the emission factors in Table A-8 (Hangebrauck 1977), an estimated  $2.7 \times 10^{15}$  meters/yr travelled (see note on tire wear for estimation of vehicle miles travelled), and an assumed emission reduction of two thirds. This emission reduction was based upon the following information:

Fraction of Automobile

<u>Population</u>	<u>Control</u>	<u>Present Reduction</u>
0.32	catalytic Converter	99
0.58	Engine Modification	65
0.10	None	0

The automobile population is from EPA (1978b), and the percent reductions are based on ranges given in that document.

The concentrations of PAHs in used crankcase oil are shown in Table A-12. Releases to sewers and landfills were assumed to account totally for  $2 \times 10^9$  % of oil disposed of by the public (Tanacredi 1977); however, this figure does not take into account used oil that is recycled.

NOTE 14:

Coal- and Oil-fired Utility Boilers

The estimates of total PAHs released to the environment are based upon the emission factors averaged from Table A-14 and a total coal and oil consumption for electricity generation of  $4.8 \times 10^8$  and  $7.8 \times 10^7$  kkg per year, respectively (Monthly Energy Review 1980).

These emissions are uncontrolled releases calculated from 1967 emissions factors and are probably lower today with the use of baghouses or electrostatic precipitator units. Further, the emission factors for oil are for small- or intermediate-sized units, and thus serve as an upper limit of the PAH releases from higher capacity plants.

NOTE 15:

Municipal Incinerators

Releases were calculated from the release factors in Table A-13 (Davies 1976) for 104 plants with an average capacity of 385 kkg/day operating at full capacity (EPA 1978b).

Commercial Incinerators

Releases were assumed to be similar to those from municipal incinerators. Even using the higher emission factors in Table A-13, emission of any given PAH was negligible without controls. The population was assumed to be 100,000 units, firing 3 hours/day, 260 days/yr at an average capacity of 0.1 kkg/hr (EPA 1978b).

Table A-1. Frequency of Select PAHs in the Pharmaceutical Industry<sup>a</sup>

Pollutant	Usage <sup>b</sup>	
	As raw Material	In Final Product
Acenaphthene		1
Anthracene	1	1
Fluoranthene		1
Fluroene		1
Phenanthrene		1
Pyrene		1

- a) Four-hundred and sixty-four U.S. pharmaceutical plants existed at the time the data was collected where 212 plants responded to the questionnaire.
- b) Number of positive responses obtained from 212 U.S. pharmaceutical plants.

Source: EPA 1980e.

Table A-2. Quantities of Select PAHs Released from US Pharmaceutical Industries in 1979 (kkg)<sup>a</sup>

Pollutant	Detection Frequency <sup>b</sup>	Quantity Contained (kkg) <sup>c</sup>		Environmental Releases (kkg) <sup>c</sup>			
		Influent	Effluent	Water		Land	Air
				Surface	POTW		
Acenaphthene	3/26	<1	ND			<1	
Anthracene	1/26	<1	ND			<1	
Fluoranthene	0/26	<1	ND			<1	
Fluorene	2/26	<1	ND			<1	
Phenanthrene	1/26	<1	ND			<1	
Pyrene	0/26	<1	ND			<1	

a) Based on screening/verification data of wastewater samples from 26 of the 464 US pharmaceutical plants. EPA 1980e.

b) Number of times the pollutant was detected in samples from 26 plants.

c) See Notes 4 and 5, Appendix 4 for calculations; ND = not detected with a detection limit of 10 µg/l.

Table A-3. Coke-Oven Tar Produced in the United States, Used by Producers, and Sold in 1978, By State  
(Thousand Liters)

State	Produced		Used by Producers			Sold for Refining into Tar Products			
	Total	L/kg of Coal Coked	For Refinery or Topping	As Fuel	Other	Quantity	Value Thousand Dollars	Average Per Liter	On-hand Dec. 31
Alabama-----	130,000	27	a	-	-	130,000	\$ 11,970	\$ 0.09	9,700
Calif., Colo., Utah-----	130,000	35	-	-	-	130,000	11,905	0.09	13,000
Illinois-----	59,000	25	-	-	-	60,000	5,593	0.09	5,700
Indiana-----	350,000	33	a	a	a	120,000	12,840	0.11	21,000
Ken., Mo., Tenn., Tex.----	34,000	25	-	a	-	31,000	3,021	0.10	2,700
Maryland, New York-----	170,000	32	-	a	-	120,000	12,911	0.11	25,000
Michigan-----	a	a	-	-	-	a	a	a	a
Minnesota, Wisconsin-----	20,000	23	-	a	-	19,000	1,938	0.10	a
Ohio-----	330,000	31	-	170,000	a	180,000	17,529	0.10	27,000
Pennsylvania-----	580,000	35	a	a	a	280,000	29,425	0.11	55,000
Virginia, West Virginia---	a	a	a	-	-	a	a	a	5,700
Undistributed-----	240,000	30	500,000	190,000	32,000	150,000	12,904	0.09	14,000
<b>Total (1978) <sup>b</sup></b>	<b>2,100,000</b>	<b>44</b>	<b>500,000</b>	<b>360,000</b>	<b>32,000</b>	<b>1,200,000</b>	<b>120,036</b>	<b>0.10</b>	<b>180,000</b>
At Merchant Plants	89,000	34	c	-	-	89,000	8,986	0.10	4,900
At Furnace Plants	2,000,000	44	500,000	360,000	32,000	1,100,000	111,050	0.10	170,000
<b>Total (1977) <sup>b</sup></b>	<b>2,200,000</b>	<b>32</b>	<b>570,000</b>	<b>550,000</b>	<b>38,000</b>	<b>1,100,000</b>	<b>106,728</b>	<b>0.10</b>	<b>160,000</b>

- a) Included with "Undistributed" to avoid disclosing individual company data.  
b) Data may not add to totals shown due to independent rounding.  
c) Included with "Furnace Plants" to avoid disclosing individual company data.

Source: DOE 1979.

Table A-4. Concentrations of Various PAHs in Coal and Coal Tar Derivatives (mg/kg)<sup>a</sup>

	Coal	Coal Tar	Coal Tar Pitch	Creosote Oil
Acenaphthene		10,000 <sup>b</sup>		40,000 <sup>c</sup>
Anthracene		9,000 <sup>b</sup>		20,000 <sup>c</sup>
Phenanthrene		30,000 <sup>d</sup>		100,000 <sup>c</sup>
Benzo[a]anthracene		<0.007 <sup>d</sup>	<10 <sup>d</sup>	<3 <sup>d</sup>
Benzo[a]pyrene	0.7	30 <sup>d</sup>	10 <sup>d</sup>	neg <sup>d,e</sup>
Chrysene		4,000 <sup>d</sup>	<10 <sup>d</sup>	<1 <sup>d</sup>
Fluoranthene		6,000 <sup>b</sup>		40,000 <sup>c</sup>
Fluorene		10,000 <sup>b</sup>		30,000 <sup>c</sup>
Naphthalene		90,000 <sup>f</sup>		200,000 <sup>c</sup>
Pyrene		3,000 <sup>g</sup>		30,000 <sup>c</sup>

a) All numbers rounded to one significant figure; blank spaces = data not available.

b) Sources: Rhodes 1954; Lowry 1945 (averaging of data).

c) Source: Stasse 1954; as cited in Weiler 1963.

d) Source: IARC 1973.

e) Less than 0.01 ppm.

f) Source: Rhodes 1954; and Lowry 1945.

g) Source: Rhodes, 1954.

Table A-5. PAH Wastewater Discharge: By-Product Cokemaking<sup>a</sup>

	Discharge Factors (kg/kg coke)			(kg) Total Discharge
	Ammonia Liquor	Cooler Blowdown	Benzol Plant	
Acenaphthylene	0.00073	0.000097	0.000129	40
Benzo[a]anthracene	0.000006	0.000032	0.000125	7
Benzo[a]pyrene	0.000032	0.000024	ND	3
Chrysene	0.000045	0.000018	0.000155	10
Fluoranthene	0.000196	0.000323	0.000189	30
Fluorene	0.000145	0.000048	0.000049	10
Naphthalene	0.00395	0.0115	0.00341	800
Pyrene	0.000393	0.000026	0.000109	20

a) Based on the total of three factors and a 1978 coke production of  $44.5 \times 10^6$  kkg (DOE 1979). Distribution: 33%-direct, 25%-POTWs, 2%-deep well, 40% quenching (20% land, 20% air) (EPA 1979d).

Source: EPA 1979d.

Table A-6. Concentration of Select PAHs in Petroleum Products, mg/kg

	Crude Oil	Gasoline	Kerosene	Petroleum Asphalt	Diesel Fuel	Number 2 Heating Oil
Acenaphthene	ND <sup>a</sup>					
Acenaphthylene	400					
Anthracene	trace	3	0.4		3	4
Benzo(a)anthracene	trace	3	<0.1	0.04	0.1	0.04
Benzo(b)fluoranthene	<5					
Benzo(k)fluoranthene	<5					
Benzo(ghi)perylene	.02	2	<0.1		0.03	0.03
Benzo(a)pyrene	1	2	0.01	0.01	0.07	0.03
Chrysene	<100	2	ND	0.02	0.5	0.6
Dibenzo(a,b)anthracene						
Fluoranthene	100	7	0.09		0.5	2
Fluorene	200					
Indeno[1,2,3-cd]pyrene						
Naphthalene	1,000					
Phenanthrene	100		ND		ND	ND
Pyrene	100	5	0.2		0.4	1

a) ND means not detected.

Source: Guerin 1978; Guerin *et al.* 1978; EPA 1979f

Table A-7. Emissions of PAHs from Catalyst Regeneration in Petroleum Cracking,  $\mu\text{g}/\text{m}^3$  Oil Charges

Type of Unit	Benzo(a) pyrene	Pyrene	Benzo(ghi)- perylene	Anthra- cene	Phenan- threne	Fluoran- thene
FCC: <sup>a</sup>						
Regenerator outlet	0.7 - 73	6.4 - 4,450	24 - 67		63,560	7.0 - 3,180
Carbon monoxide boiler outlet	1.7 - 3.4	3.9 - 26	8.8	330		3.2 - 13
HCC: <sup>b</sup>						
Regenerator outlet	32,600 - 36,700	20,700 - 20,800	47,700 - 60,400	146 - 318	3,340 - 4,600	1,320 - 1,810
TCC: <sup>c</sup>						
Air lift, regenerator outlet	8,900 - 19,100	21,000 - 41,300	7,000 - 11,450	1,640 - 1,685	52,500 - 56,000	1,685 - 4,610
TCC:						
Brucket lift, regen- erator outlet	5	46 - 57				9.17

NOTE: Blanks indicate data not available. Emission factors used are arithmetic averages over the four types of units listed.

a) Fluid catalytic cracking.

b) Houdriflow catalytic cracking.

c) Thermoform catalytic cracking.

Source: Hangebrauck, et al. 1967.

Table A-8. Emission Factors

	Residential Coal Combustion (g/kg)	Fireplaces (g/kg)	Primary and Auxiliary Wood Heating (g/kg)	Cigarettes (µg/cig)	Coal Refuse Piles (kg/kg) POM	Forest Fire(g) (ng/g) (dry fuel)	Carbon Black µg/g	Gasoline (ng/m)
Acenaphthene	0.039	0.0012	0.0076					
Acenaphthylene		0.010	0.057				800	
Anthracene <sup>a</sup>	0.008	0.010	0.076	0.17	0.1	2,500	35	4.3
Benzo[a]anthracene	0.002	0.0008	0.0071	0.02		3,100	4.5	
Benzo[b]fluoranthene <sup>c</sup>	0.002	0.0008	0.0058		0.01	1,300	15	
Benzo[k]fluoranthene	0.002	0.0008	0.0058		0.01	1,300	15	
Benzo[ghi]perylene		0.0009	0.0053			2,500	12	47
Benzo[a]pyrene <sup>d</sup>	0.0015	0.0008	0.0040	0.01	0.005	740		11.5
Chrysene <sup>b</sup>	0.002	0.008	0.0071	0.02		3,100	4.5	
Dibenzo[a,h]anthracene <sup>e</sup>	0.003	0.0001	0.0007		<0.001			
Fluoranthene	0.005	0.0028	0.019	0.01	0.05	5,500	60	75
Fluorene	0.026	0.0047	0.016					
Indeno[1,2,3-cd]pyrene	0.002	ND	ND	0.006	<0.001	1,700	<2	
Naphthalene	0.15	0.0403	0.25	3				
Phenanthrene	0.008	0.010	0.076	0.36	0.1	2,500	35	30
Pyrene	0.005	0.0028	0.016	0.16	0.05	4,600	500	110

a) Reported as anthracene/phenanthrene, assumed equal division between them.

b) Reported as chrysene/benzo[a]anthracene, assumed equal division between them.

c) Reported as benzo fluoranthenes, assumed divided solely between benzo[b]fluoranthene and benzo[k]fluoranthene.

d) Reported as benzopyrene(s) and perylene, assumed to be 50% benzo[a]pyrene.

e) Reported as dibenzanthracene, assumed to be solely dibenzo[a,h]anthracene.

Sources listed in Appendix 4 text.

Table A-9. Fireplace Population

Region	Number of Housing Units (1977)	Percentage w/Fireplace	Fireplaces
Northeast	17,707,000	47	8,300,000
North Central	21,181,000	33	7,000,000
South	26,422,000	29	7,700,000
West	15,406,000	46	<u>7,100,000</u>
Total			30,100,000

Sources: Census 1979 and EPA 1980a

Table A-10. PAH Associated with Carbon Black ( $\mu\text{g/g}$ )<sup>a</sup>

Carbon PAH Black Type	Vulcan J	Regal 300	330 HAF	660 GPF	339	Avg	Contained in Carbon Black (kkg)
Anthracene <sup>b</sup>	0.5	ND	0.05	ND	1	0.3	0.5
Benzo[fluoranthenes	10	ND	<0.9	4	7	4	6
Benzo[ghi]perylene	166	16	25	41	164	82	100
Benzopyrenes	20	1	3	8	32	17	30
Fluoranthene <sup>c</sup>	68	9	10	13	52	30	50
Indenopyrene	24	1	0.3	7	35	13	20
Phenanthrene	0.5	ND	0.05	ND	1	0.3	0.5
Pyrene	314	58	47	52	207	140	200

a) Based  $1.6 \times 10^6$  kkg carbon black production (SRI 1979).

b) Reported as anthracene/phenanthrene, assumed equal division among them.

c) Excluding benzo[ghi]fluoranthene, reported separately.

Source: Locati et al. 1979

Table A-11. PAH Releases From Tire Wear (kkg)<sup>a</sup>

	Airborne		Sedimentary or directly trans- ferred to Roadway	Total
	Initial	Reentrained		
Anthracene				
Benzofluoranthenes				
Benzo[ghi]perylene	1	7	7	20
Benzopyrenes	0.3	1	1	3
Fluoranthene	0.5	3	2	6
Indenopyrene	0.2	1	1	2
Phenanthrene				
Pyrene	2	10	10	20

See Appendix text for calculations and sources

a) Blanks indicate <1 kkg/yr. For all entires, totals may not add due to rounding.

Table A-12. Concentrations of PAHs in Used Crankcase Oils (mg/l)

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Anthracene	0.3
Benzo[a]anthracene	0.9
Benzo[k]fluoranthene	1.4
Benzo[ghi]perylene	1.7
Benzo[a]pyrene	0.4
Chrysene	1.2
Fluoranthene	4.4
Fluorene	1.5
Phenanthrene	7.8
Pyrene	6.7

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Source: Peake and Parker 1980.

Table A-13. Municipal Incinerators Release Factors ( $\mu\text{g}/\text{kg}$  refuse)

	Environmental Release Factors ( $\mu\text{g}/\text{kg}$ refuse)		
	Air <sup>a</sup>	Land	Water <sup>b</sup>
Benzo[a]anthracene <sup>c</sup>	1.5	18	0.08
Benzo[b]fluoranthene <sup>d</sup>	0.5	21	0.01
Benzo[k]fluoranthene <sup>d</sup>	0.5	21	0.01
Benzo[ghi]perylene	1.8	10	0.007
Benzo[a]pyrene <sup>e</sup>	0.04	16	0.016
Chrysene <sup>c</sup>	1.5	18	0.08
Fluoranthene	2.5	12	0.14
Indeno[1,2,3-cd]pyrene	0.77	<2.1	<0.002

a) After scrubber.

b) Taken as one half reported benzo[a]anthracene + chrysene emissions.

c) Taken as one third of benzo[b+k+j]fluoranthene emissions.

d) Taken as one half of benzo[a+e]pyrene emissions.

e) Scrubber water.

Source: Davies 1976.

Table A-14. Emissions of PAHs from Coal-Fired Plants and Intermediate/Small Oil-Fired Units  
( $\mu\text{g}/10^9 \text{ J Fuel}$ )

Type of Unit	Benzo[a]- pyrene	Pyrene	Benzo[ghi]- perylene	Phenan- threne	Fluoran- thene
Pulverized coal (vertically-fired, dry-bottom furnace)	18 - 123	70 - 218	79		80 - 389
Pulverized coal (front-wall-fired, dry-bottom furnace)	16 - 20	152 - 190	13	190	12 - 152
Pulverized coal (tangentially-fired, dry-bottom furnace)	123	133	142	30	370
Pulverized coal (opposed-, downward inclined burners; wet bottom furnace)	20 - 133	37 - 114	142 - 1,042		52 - 199
Crushed coal (cyclone-fired, wet-bottom furnace)	72 - 351	237 - 1,706	34 - 341		42 - 104
Spreader stoker (traveling grate)	<14 - 23	20 - 56			20 - 56
<u>Oil-fired:</u>					
Steam atomized	<19 - 45	46 - 284		1,700	53 - 256
Low pressure air atomized	853	5,780	285	3,320	1,800
Pressure atomized	<38 - <57	14 - 1,700		8,440	72 - 4,470
Vaporized	<95	1,140			14,200

NOTE: Blanks indicate data not available.

Source: Hangebrauck et al. 1967.

APPENDIX B. APPLICATION OF THE AIR-TO-SURFACE PATHWAY EVALUATION  
METHOD FOR POLYNUCLEAR AROMATIC HYDROCARBONS

A method has been developed for estimating airborne toxicant deposition rates (air-to-surface pathway evaluation method, Arthur D. Little, Inc., 1981). The method accounts for both wet and dry deposition to land and water surfaces. When deposition to a watershed or other land area is estimated, this can be interpreted as an upper bound on the chemical loading to an associated surface water body resulting from air deposition, since only a fraction of the mass deposited on land surfaces will be delivered to the water body. The air-to-surface pathway evaluation method accounts for the partitioning of an airborne contaminant between adsorbed and vapor phases, with differing deposition rates inferred for the separate phases. It relies on fundamental physicochemical properties and is designed to use available data, while filling in data gaps with estimated values of various parameters. The evaluation method has been applied to naphthalene, anthracene, and benzo[a]pyrene. Each of the three PAHs modeled has an atmospheric chemical degradation of roughly  $0.1 \text{ hr.}^{-1}$  leading to half-lives of 5-10 hours (Radding et al. 1976). Under typical meteorologic conditions this corresponds roughly to the travel time across major urban areas. Since urban areas also would be expected to have much greater emission densities than rural areas, significant urban/rural differences in air concentrations of PAHs are expected, and indeed observed. These factors suggest that deposition rates under urban and rural conditions should be considered separately.

One of the most important chemical properties influencing air-to-surface transfer is the vapor pressure. The vapor pressure affects the partitioning of airborne contaminants between vapor and adsorbed phases. The deposition rate is typically much greater for the adsorbed fraction of the airborne contaminant. The effect of vapor pressure is expressed by equation (5) of the Arthur D. Little report (1981):

$$\phi = \frac{.165\theta}{p_0 + .165}$$

where

$\phi$  is the adsorbed fraction of the total airborne mass,

$\theta$  is the available aerosol surface area  $\frac{\text{cm}^2}{\text{cm}^3}$  and

$p_0$  is the saturation vapor pressure of the contaminant at ambient temperature (torr)

The available aerosol surface area is typically greater in urban areas where concentrations of total suspended particulates are higher

than in rural areas. In the plume from a combustion source, the aerosol surface area is even higher than typically found in urban air. Application of the above equation results in aerosol partitioning for the three PAHs as shown below:

PAH	Adsorbed Fraction of Total Airborne Mass		
	Rural	Urban	Near Combustion Sources
Naphthalene	$7 \times 10^{-6}$	$3 \times 10^{-4}$	0.02
Anthracene	0.002	0.06	0.97
Benzo[a]pyrene	.99	1.00	1.00

Benzo[a]pyrene is strongly partitioned with the aerosol phase, regardless of ambient conditions, while at the other extreme naphthalene exists primarily as a vapor in the atmosphere. Anthracene exhibits intermediate properties, and the adsorbed fraction is sensitive to ambient conditions.

The dry deposition flux is proportional to the dry deposition velocity,  $V_d$ , i.e.,

$$\text{Dry Flux} = V_d C_{\text{air}}$$

where

$C_{\text{air}}$  is the ground-level air concentration.

The dry deposition velocity with respect to the total airborne contaminant is calculated as the (mass) weighted average of the deposition velocity for the vapor and sorbed fractions, i.e.,:

$$V_d = V_{d,s} \phi + V_{d,v} (1-\phi) \quad (\text{Eq. 6 of Arthur D. Little 1981})$$

According to the air-to-surface pathway method (Arthur D. Little 1981), the respective dry deposition velocities are given below:

PAH	Dry Deposition Velocity				Combustion Source
	$V_{d,v}$ (cm/sec)	$V_{d,s}$ (cm/sec)	Rural	Urban	
Naphthalene	0.04	1	0.04	0.04	0.06
Anthracene	0.02	1	0.02	0.08	1.00
Benzo[a]pyrene	0.02	1	1.00	1.00	1.00

Wet deposition is controlled by the precipitation scavenging ratio,  $r$ , which expresses the ratio of pollutant concentration in precipitation (ng/l) to pollutant concentration in air ( $\mu\text{g}/\text{m}^3$ ). The scavenging ratio is calculated by contributions from the vapor and sorbed fractions, i.e.:

$$r = r_s (\phi) + r_v (1-\phi)$$

where  $r$ ,  $r_s$  and  $r_v$  are scavenging ratios for the total airborne mass, the sorbed contaminant, and the vapor phase, respectively. Once the scavenging ratio is known, the wet deposition flux is given by wet flux =  $rRC_{\text{air}}$ , where  $R$  is the rainfall rate. These parameter values have been estimated, as shown below:

PAH	Precipitation Scavenging Ratios				
	$r_s^*$	$r_v$	$r$		
			Rural	Urban	Combustion Sources
Naphthalene	$6 \times 10^4$	53	53	71	$2.5 \times 10^3$
Anthracene	$6 \times 10^4$	14	130	$3.6 \times 10^3$	$1.2 \times 10^5$
Benzo[a]pyrene	$6 \times 10^4$	$5.4 \times 10^4$	$6 \times 10^4$	$6 \times 10^4$	$1.2 \times 10^5$

For the purpose of further analysis a generic urban environment has been modeled on the basis of characteristics of Philadelphia and Cleveland. The average wind speed is 10.25 kts (5.3 m/s) and the annual rainfall is 1.0 m/yr. The urban area is  $100 \text{ mi}^2$  ( $2.6 \times 10^8 \text{ m}^2$ ).

The generic rural area is defined as a volume of air within which an associated urban source would contribute to rural concentrations. The size of the area is constrained by the half-life in air, such that the concentration is typical of an area significantly affected by the urban source. At a half-life of 5 hours, and typical wind speed of 5.3 m/sec., naphthalene contamination from an urban area could be significant over an area of  $10^{10} \text{ m}^2$  (roughly 40,000 square miles).

Median observed ambient concentrations for three PAHs in urban and rural areas are presented below (White and Vanderslice 1980):

\*Tabulated  $r_s$  values apply for rural and urban conditions. Near a combustion source the adsorbed phase is expected to be associated with larger particles resulting in a scavenging ratio,  $r_s = 1.2 \times 10^5$ .

PAH	Median Observed Concentration ( $\mu\text{g}/\text{m}^3$ )	
	Rural	Urban
Naphthalene	$7 \times 10^{-5}$	$5 \times 10^{-4}$
Anthracene	$1 \times 10^{-3}$	$8 \times 10^{-3}$
Benzo[a]pyrene	$1 \times 10^{-3}$	$1 \times 10^{-2}$

Using the pathway evaluation method we have estimated the emission that would result in a specific ambient concentration, given the degradation rate, deposition velocity, rainfall rate, and precipitation scavenging ratio. Applying the equation for wet flux and dry flux we also estimated the amount deposited in the generic rural and urban study areas. Then, by comparison of the deposition rates with emission rates, we estimated the fraction of total atmospheric emissions of each of the three PAHs which would be deposited within the urban and rural study areas. These results are shown below:

PAH	Deposition Rate					
	% of Emissions Dry Deposited		% of Emissions Wet Deposited		% Deposited	
	Rural	Urban*	Rural	Urban	Rural	Urban
Naphthalene	2	2-3	<1	<1	2	2-3
Anthracene	1	4-19	<1	1-7	1	5-26
Benzo[a]pyrene	22	19	4	4-7	26	23-26

From the results above, it is apparent that a very small fraction of atmospheric emissions of naphthalene are deposited on land or water surfaces. The fraction of air emitted anthracene that is eventually deposited is uncertain, but could be fairly large percentage. Approximately one-fourth of all benzo[a]pyrene emitted into the atmosphere will eventually be deposited on land and water surfaces, where it would contribute to the contamination of surface runoff and surface water bodies.

\*The range for urban areas reflects alternative assumptions that the chemical has equilibrated with ambient aerosol or remains associated with particulates in the plume from the combustion zone.

APPENDIX  
REFERENCES

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