The Partitioning of Polycyclic Aromatic Hydrocarbons in the Mahoning River Bottom Sediments

by

Richard W. Testa

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Signature:

Richard W. Testa 4-22-97
Student Date

Approvals:

Scott C. Martin 4/23/97
Thesis Advisor Date

Laurie S. Garton 4/23/97
Committee Member Date

Lauren Schroeder 4/24/97
Committee Member Date

Dean of Graduate Studies 4/28/97
Date

ABSTRACT

Polycyclic Aromatic Hydrocarbons occur naturally in the environment because of synthesis by some plants. The greatest amount of Polycyclic Aromatic Hydrocarbons (PAH) is produced by the combustion of fossil fuels. Several PAH are known carcinogens. The discharge of these substances into the aquatic environment at toxic concentration levels endangers aquatic life, wildlife, and human health. The Mahoning River in Northeast Ohio was heavily loaded with PAH during the industrial era.

The intent of this study was to investigate the effect of dredging the Mahoning River, specifically the release of 16 PAH compounds from the sediment into the liquid phase. Experiments were conducted to investigate three aspects of PAH behavior: partitioning; desorption; and the solids concentration effect. Mahoning River water and sediments were analyzed using High Performance Liquid Chromatography (HPLC). The results confirmed that the river sediments are very heavily polluted with PAH. The desorption experiments involved mixing PAH-free river water with river bottom sediment at water:sediment ratios of 4:1 and 12:1. The desorption of Chrysene from the Campbell sediment was 28% in the 4:1 experiment and 59% in the 12:1 experiment. Overall, the desorption of PAH compounds ranged from 5% to 71%. Dredging of river bottom sediments would result in significant desorption of PAH into the liquid phase.

To my wife, Sue, for her numerous sacrifices, support, and prayers.

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INTRODUCTION

The protection of our marine and freshwater resources has assumed national and global prominence (Adams et al., 1992). Thus, prevention of water pollution is of major concern. Pollution problems include: oil spills; medical waste dumping; ocean disposal of garbage; dredging; and pesticide and fertilizer runoff. There is an urgent need to monitor and control industrial aqueous effluents which find their way into natural and processed water supplies (Jones et al., 1978).

In 1987, the Clean Water Act (CWA) was amended to stress the need to control toxic pollutants. "Protection against toxic releases is called for under Section 101(a)(3) of the CWA which states that 'it is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited'" (Swietlik et al., 1991). Section 303(c) of the CWA requires individual states to develop water quality standards to protect public health and enhance water quality. However, while these water quality standards are of eminent importance in assuring a healthy aquatic environment, they alone have not been sufficient in protecting the environment (Swietlik et al., 1991).

Research has revealed that sediment contamination is also responsible for water quality problems (Cooke et

al.,1982; West et al.,1986; Krahn et al., 1986). "Aquatic sediments can be loosely defined as a collection of fine, medium, and coarse grain minerals and organic particles that are found at the bottom of lakes, rivers, bays, estuaries, and oceans" (Adams et al., 1992). They act as repositories for physical debris and "sinks" for a wide variety of chemicals, thus making them an important natural resource (Adams et al., 1992). "The concern associated with the chemicals sorbed to sediments is that many commercial species and food chain organisms spend a major portion of their lifecycle living in or on aquatic sediments" (Adams et al., 1992). Therefore, this provides a direct route for toxicants to be consumed by higher aquatic life, wildlife, and humans.

The need to develop sediment assessment methods originated from the recognition that sediments at many freshwater and marine sites in the United States are contaminated with varying levels of metals and organics (Adams et al., 1992). Chemicals found most often include: polycyclic aromatic hydrocarbons (PAH), chlorinated organics, and some pesticides. Assessment methods are needed to interpret the significance of these contaminant levels and the bioavailability of the toxicants from site to site (Adams et al., 1992). Suitable decisions can then be made about ecosystems and human health protection.

Section 304(a)(1) of the CWA insures the development

and publication of water quality criteria, including information on factors affecting the rates of organic and inorganic sedimentation for various types of receiving waters (Swietlik et al., 1991). The development of water quality criteria over the past several years has centered upon evaluating and developing the equilibrium partitioning approach for generating sediment criteria (Delos et al., 1984). This approach focuses on predicting the chemical interaction between sediments and contaminants (Delos et al., 1984). Understanding the principal factors of chemical/sediment interaction will allow predictions of contaminant concentrations to which benthic and other organisms will be exposed (Adams et al., 1992). Equilibrium partitioning (EqP) and sediment quality criteria (SQC) are the EPA's best recommendations of the concentrations of substances in sediment that will not unacceptably affect benthic organisms or their uses (Swietlik et al., 1991). The EPA believes that the EqP/SQC approach can provide valuable guidance for the protection of ecosystems and remedial programs.

The subject of this study is the behavior of Polycyclic Aromatic Hydrocarbons (PAH) in the Mahoning River, located in Northeast Ohio. The Mahoning River was the site of 15 major steel processing plants. The major sources of PAH in the Mahoning River ecosystem included coal tar, coal-tar pitch, and cracked mineral oil effluents from various

industrial processes, as well as sewage sludge.

"The toxic, mutagenic, and carcinogenic properties of PAH have been much studied. Many PAH are carcinogens or procarcinogens in animals and man" (Giesy et al., 1983). Because of their ability to bioconcentrate PAH, aquatic organisms are an important vector to man. Part of the hazard assessment process is to determine the amount of exposure aquatic organisms, animals, and man can endure. This requires an understanding of the fate and transport of PAH in an ecosystem (Giesy et al., 1983).

1.1 Historical Background on the Mahoning River

The Mahoning River drains an area of approximately 1,131 square miles and flows over a length of 108 miles. It originates in the vicinity of Alliance, Ohio, flows northeasterly to Newton Falls, and continues southeasterly through Warren, Niles, McDonald, Girard, Youngstown, Campbell, Struthers, and Lowellville. The Mahoning River crosses the state line into Pennsylvania for about 12 miles before it joins the Shenango River below New Castle, Pennsylvania to form the Beaver River. Six major tributaries to the river include: the West Branch of the Mahoning River, Eagle Creek, Mosquito Creek, Meander Creek, Mill Creek, and Yellow Creek (Figure 1.1).

For almost 100 years before 1952, cities and industries discharged their raw sewage and wastes into the Mahoning

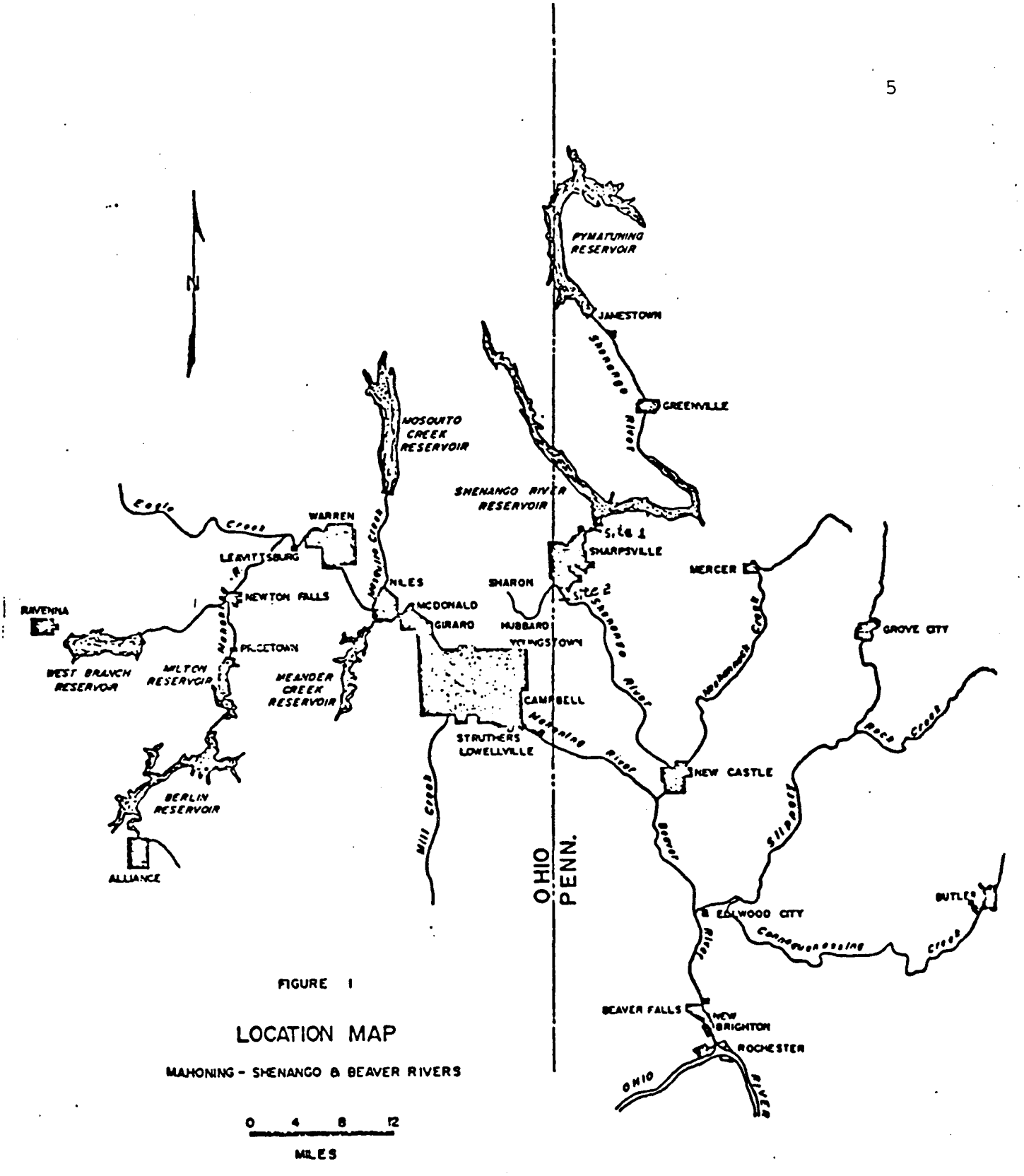

FIGURE 1

LOCATION MAP

MAHONING - SHENANGO & BEAVER RIVERS

MAHONING RIVER BASIN

(Duffy and Schroeder, 1970)

Figure 1.1

River. This was the typical practice of cities and industries throughout the United States during this era (Harnisch, 1971). Biochemical oxygen demand created by organic municipal wastes finally reached a point where the self-purification capacity of the river was exceeded. In 1952, legislation established by the Water Pollution Control Board in the Department of Health became effective and the Ohio River Valley Water Sanitation Commission (ORSANCO) was established to regulate municipal and industrial discharges. The National Environmental Policy Act was passed in 1970 and the Environmental Protection Agency was created in December of that year. A more stringent water quality program was being introduced and the steel industry became very apprehensive. They believed that the new criteria were unjustifiable and would lead to the demise of the steel industry in the Mahoning Valley (Harnisch, 1971).

In 1970, a 25 mile stretch of the Mahoning River between Warren and Lowellville, Ohio, was used for industrial purposes by 15 major plants and 9 steel companies with a total of 63 rolling mills and 3 active coke plants. The river was used by 35 other major industries that included: ceramics, plastics, food processing, glass manufacturing, tanning, chemical, and electrical industries (Harnisch, 1971). Some selected industries are listed in Table 1.1. The Mahoning Valley from Warren down to the state line was a primary center of steel production and

Table 1.1

Mahoning River Basin-Industries-May 1966

Name	Type of Industry	Receiving Stream
Allied Chemical Corp.	Plastics	Mahoning River
Copperweld Steel Co.	Rolling Mill	Mahoning River
General Electric Mahoning Glass Plant	Glass	Mosquito Creek
Jones and Laughlin Steel Corp.	Stainless Steel Rolling & Finishing	Mahoning River
Lloyd Packing Co.	Food Processing-Meat	Meander Creek
Ohio Edison Co.	Electric Power	Mahoning River
Ohio Leather Co.	Tannery	Squaw Creek
Packard Electric Co.	Electrical Parts	Mahoning River
Ravenna Arsenal, Inc.	Chemical	Eagle Creek
Ravenna Arsenal, Inc. Sewage Treatment Plant	Sewage Treatment	Mahoning River
Republic Steel	Steel, Blast Furnace, Coke Oven	Mahoning River
Union Carbide Corp.	Acetylene Production	Pond-Gibson Run
U.S. Steel Corp.	Steel, Blast Furnace	Mahoning River
Youngstown Sheet & Tube Co.	Steel, Blast Furnace, Coke Oven, Rolling Mill	Mahoning River

Source (Harnisch, 1971)

fabrication that supported over one half a million people.

The Mahoning River had a low flow of 12 to 15 million gallons per day before reservoirs were constructed to

increase its low flow capacity to over 125 million gallons per day. It furnished the water essential for the operation of steel mills that produced over 9,000,000 tons of steel each year or 7% of the nation's total steel production (Harnisch, 1971). The industries withdrew and returned over 800 million gallons of water per day (Harnisch, 1971).

The coke plants were a major source of organic pollutants, particularly PAH. The coke ovens carbonized coal to remove impurities such as coal tars and gases that were detrimental to the steel manufacturing process. This produced coke for the blast furnaces. The coke was then pushed into railroad cars which took it to a quench station for cooling and the coal tars and gases were recovered as by-product. The coke plants and steel processing plants were equipped with clean out sumps. At one site, Naphthalene would be collected in these sumps and flushed directly into the river. During coke plant modifications in the years 1959, 1960, and 1962, heavy discharges of PAH entered the river. When PAH escaped into the river in sufficient quantities, it would create taste and odor problems in the downstream water supply, particularly the Beaver Falls Water Company. In 1971, companies took measures to eliminate PAH discharges (Harnisch, 1971).

Industries also contaminated the Mahoning River's water and sediment with heavy metals; including iron, chromium, copper, nickel, and zinc. Cyanides and fluorides were also

found in the river. The water temperature in the river exceeded 95 degrees Fahrenheit over 25% of the year and reached a maximum at Lowellville of 108 degrees Fahrenheit in 1964 (Harnisch,1971; Duffy and Schroeder, 1970). The Federal Water Pollution Control Authority measured the bacterial counts for total coliform between May and June of 1971 and found it as high as 160,000 per 100 mL at a Struthers sampling location. The dissolved oxygen remained below 5 mg/L over 50% of the year in 1965 and even reached 0 mg/L in certain pool areas of organic sludge (Harnisch, 1971). The Mahoning River became a very nutrient rich body of water within 50 years. The only living organism found at a Lowellville sampling site was the pollution tolerant sludge worm. In contrast, during periods of steel mill strikes, fish were actually noted in the water at Youngstown, Struthers, and Lowellville (Duffy and Schroeder, 1971).

In 1970 the local steel industry suffered decreased profitability as production costs exceeded the price of steel. Profits hit a low in 1970 and employment in local plants shrunk from a high of 41,000 persons in 1950 to an estimated 22,000 in 1970 (Harnisch, 1971). The newly proposed water quality standards of 1970 required the installation of sophisticated treatment equipment at each point source of discharge. The steel companies believed treatment plants would be impractical economically and

technically as a number of facilities were old with little space for expansion. The total cost of complying with the proposed water quality criteria was estimated at $336 million, of which a substantial share would be borne by the steel industries (Harnisch, 1971).

Responding to the public demand for cleaner water, Congress passed the Water Pollution Control Act of 1972. This expanded the role of the federal government in water pollution dramatically. To address deficiencies, the Clean Water Act of 1972 was revised in 1977 (Viessman and Hammer, 1985). The Clean Water Act Amendments of 1977, the principal law governing water quality today, was implemented in the Mahoning Valley in 1977 when the U.S. EPA conducted surveys of the Mahoning River and developed a wasteload allocation report. Water quality standards developed from this report were adopted by the state of Ohio on November 14, 1977 and federally approved on February 6, 1979 (Amendola and Schregardus, 1983). During this same period the major steel companies in the area were closing. In the late 1980's municipalities were constructing secondary wastewater treatment facilities. The Clean Water Act of 1977 and the closing of the major steel mills have greatly improved the water quality of the Mahoning River. However, the bottom sediments remain badly contaminated.

1.2 Current Status

Today, most of the steel mills have been disassembled, and the Ohio Environmental Protection Agency in 1989 required all industrial and wastewater treatment plants to comply with new limitations on loadings of organic and inorganic chemicals into the Mahoning River (Ohio EPA, 1989). In the most recent revision of the State of Ohio water quality standards, total PAH must not exceed a 30 day average of 311 nanograms per liter (ng/L) in the water column based upon human health. Public water supplies must not contain more than 28 nanograms per liter (ng/L) of PAH (Ohio EPA Chapter 3745-1, 1993). Although the facilities on the river have been in compliance, there are still large amounts of PAH and heavy metals adsorbed to the bottom sediments at many sites on the river between Warren and Lowellville. Upstream from Warren the river is clean and is used for water supply and recreation just as it was during the steel era of the valley.

The U.S. EPA (1986) conducted an extensive study of PAH concentrations in the Mahoning River bottom sediments. At a particular sampling site located near a razed coke processing plant a total of 93,150 mg/kg (ppm) of PAH was detected in the river sediments. This included 38,000 mg/kg of the PAH Naphthalene and 3400 mg/kg of the carcinogen PAH Benzo(a)pyrene. A similar study by Schroeder (1993) detected a total PAH concentration of 176,813 mg/kg at a

specific Campbell sample location. In September of 1993 over 100 fish were netted in Lowellville within 24 hours by Dr. Lauren Schroeder of Youngstown State University (Schroeder, 1993). They consisted of goldfish, carp, and channel catfish. Although aquatic life has increased, the Department of Health (1989) has issued a ban on swimming, wading, and consuming fish in the Mahoning River between Warren and Lowellville because of the excessive PAH concentrations (Wildlife News, 1989). PAH deposits in the Mahoning River bottom sediments are concentrated at specific locations. In situ biodegradation of PAH has been very slow in the Mahoning River. Dredging of the river could resuspend PAH into the water column and create unsatisfactory water quality conditions downstream.

1.3 Objective of the Study

The first of four main objectives of this study was to measure the total PAH in the dried bottom sediment and pore water. The second was to simulate a dredging of the river and determine the potential for PAH release from resuspended sediments. The third objective was to study the solids concentration effect. The final objective was the calculation of the in situ partition coefficient (K'p) for PAH compounds.

CHAPTER II

LITERATURE REVIEW

2.1 Physical Properties of Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAH) are relatively non-polar, hydrophobic organic compounds of substituted and unsubstituted aromatic rings. PAH occur naturally in plants and microbes, but most PAH released into the environment result from fossil fuel combustion, oil spills, municipal sewage treatment, and industrial processes (Bowling et al., 1984). Most PAH are formed by the incomplete combustion of organic compounds with insufficient oxygen.

PAH have been detected in animal and plant tissue, sediment, soils, and surface water. A report by Shackleford and Keith (1976) indicated that PAH have been detected in surface water, well water, and ground water. PAH have been shown to be carcinogenic, teratogenic, and mutagenic in laboratory mammals and humans (Brungs et al., 1980). Exposure of humans to PAH from the aquatic ecosystem depends upon the environmental transport processes and subsequent exposure concentrations experienced by biotic components (Bowling et al., 1984).

PAH can adsorb to suspended particulates and biota and their transport is determined by the hydrogeologic condition of the aquatic system. PAH in the water column probably undergoes direct photolysis at a rapid rate. The ultimate

fate of PAH that accumulate is believed to be biodegradation and biotransformation by benthic organisms (Callahan et al., 1979). The general physical properties of several PAH are described in Table 2.1. Important properties are listed for Acenapthene, Acenapthylene, Fluorene, Naphthalene, Pyrene, Anthracene, Fluoranthene, Phenanthrene, Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chyrsene, Benzo(ghi)perylene, Benzo(a)pyrene, Dibenzo(ah)anthracene, and Ideno(123-cd)pyrene.

Table 2.1

General Physical Properties of PAH

	Acenapthene	Acenapthylene
Molecular Weight	154.21	152.21
Melting Point	96 C	92
Vapor Pressure (20 C)	10^-3 to 10^-2 torr	10^-3 to 10^-2 torr
Solubility in water (25 C)	3.42 mg/L	3.93 mg/L
Log octanol/water partition coefficient	4.33	4.07
Observed partition coefficient (K'p)	NA	NA

	Fluorene	Naphthalene
Molecular Weight	116.15	128.19
Melting Point	116-117 C	80.55
Vapor Pressure (20 C)	10^-3 to 10^-2 torr	0.0492 torr
Solubility in water (25 C)	1.69 mg/L	31.7 mg/L
Log octanol/water partition coefficient	4.18	4.337
Observed partition coefficient (K'p)	NA	NA

Table 2.1 (Continued)

	Anthracene	Fluoranthene
Molecular Weight	178.23	202.26
Melting Point	216 C	111 C
Vapor Pressure (20 C) torr	1.95x10^-4 torr	10^-6 to 10^-4
Solubility in water (25 C)	0.045-0.073 mg/L	0.26 mg/L
Log octanol/water partition coefficient	4.45	5.33
Observed partition coefficient (K'p)	25,000 organic 1600 inorganic	NA

	Phenanthrene	Pyrene
Molecular Weight	178.23	202
Melting Point	101 C	150 C
Vapor Pressure (20 C)	6.8x10^-4 torr	6.85x10^-7 torr
Solubility in water (25 C)	1.0-1.29 mg/L	0.132-0.14 mg/L
Log octanol/water partition coefficient	4.46	5.32
Observed partition coefficient (K'p)	NA	NA

	Benzo(a)anthracene	Benzo(b)fluoranthene
Molecular Weight	228.28	252.32
Melting Point	155-157 C	167-168 C
Vapor Pressure (20 C)	5x10^-9 torr	10^-6 to 10^-11 torr
Solubility in water (25 C)	0.009-0.014 mg/L	NA
Log octanol/water partition coefficient	5.61	6.57
Observed partition coefficient (K'p)	21,000 5% org.carbon	NA

Table 2.1 (Continued)

	Benzo(k)fluoranthene	Chyrsene
Molecular Weight	252.32	228.28
Melting Point	217 C	256 C
Vapor Pressure (20 C)	9.59x10^-11 torr	10^-11 to 10^-6 torr
Solubility in water (25 C)	NA	0.002 mg/L
Log octanol/water partition coefficient	6.84	5.61
Observed partition coefficient (K'p)	NA	NA

	Benzo(ghi)perylene	Benzo(a)pyrene
Molecular Weight	276	252
Melting Point	222 C	179 C
Vapor Pressure (20 C)	10^-10 torr	5x10^-9 torr
Solubility in water (25 C)	0.00026 mg/L	0.0038 mg/L
Log octanol/water partition coefficient	7.23	6.04
Observed partition coefficient (K'p)	NA	150,000 5% org.carbon 76,000 2% org.carbon 35,000 1% org.carbon 17,000 0% org.carbon

	Dibenzo(ah)anthracene	Ideno(123-cd)pyrene
Molecular Weight	278.36	276.34
Melting Point	270 C	162.5-164 C
Vapor Pressure (20 C)	10^-10 torr	10^-10 torr
Solubility in water (25 C)	0.0005 mg/L	NA
Log octanol/water partition coefficient	5.97	7.66
Observed partition coefficient (K'p)	NA	NA

NA = Not Available.

Source (Callahan et al., 1979)

Acenapthene, Acenapthylene, Fluorene, and Naphthalene are PAH with two aromatic rings and are non-carcinogenic. Anthracene, Fluoranthene, and Phenanthrene are PAH with less than four aromatic rings and are non-carcinogenic. Benzo(a)anthracene, Benzo(a)fluoranthene, Pyrene, and Benzo(k)fluoranthene, are PAH with less than four aromatic rings and are carcinogenic. Benzo(ghi)perylene, Dibenzo(a,h)anthracene, Ideno(1,2,3-cd)pyrene, and Benzo(a)pyrene contain 5 or 6 aromatic rings and are all carcinogenic except Benzo(ghi)perylene. These are relatively insoluble in water and have a high log octanol-water partition coefficient (Callahan et al., 1979).

2.2 Sources of PAH in the Aquatic Environment

Industrial facilities produce PAH through high temperature pryolysis of organic materials and low to moderate temperature pyrolysis of sedimentary organic material to form fossil fuels (Neff, 1979). PAH are contained in many industrial effluents that are ultimately discharged into surface waters. These industrial sources include: oil refineries; coke processing plants; manufacturers of chemical by-products; plastics and dye industries; and high temperature furnaces as well as many other production facilities (Neff, 1979). A selected number of industries listed in Table 2.2 produce a significant amount of PAH.

Table 2.2

Concentrations of Benzo(a)pyrene in
Industrial Wastewater Effluents (ug/L) *

Industry	Wastewater Source	Benzo(a)pyrene	Other PAH
Shale oil	after dephenolization	2-230	
Coke by-products	after biochemical treatment	12-16	At, BaA,Ch Fl, Pr, Py
	after oil separation	6.5-290	
	spent gas liquor	small quantity	
Coke or oil-gas works	before discharge to sewer	340-1000	Ac, An,Bpr, Fr, Pa
	after filtration through coke beds	20	
Oil-gas works	coking of residues after direct distillation of oil	0.48-50	
	catalytic cracking of kerosene gas oil fraction at 450 C	0.11-0.29	
	catalytic cracking	0.07-0.11	
	thermal cracking	0.09-0.23	
	pyrolysis of ethane-ethylene fractions at 700 C to 800 C	3-6	
	after settling ponds of various refineries	up to 0.22	
Acetylene	not indicated	0.015-0.1	
Ammonium sulfate	after cooling and settling	~ 10	Ap,At,BaA, Ch, Fl, Pr,Py

* Ac, Anthracene; Ap, Alkylpyrene; At, Antanthrene; An, Acenaphthylene; BaA, Benzo(a)anthracene; Bpr, Benzo(ghi)perylene; Ch, Chrysene; Fl, Fluoranthene; Fr, Fluorene; Pa, Phenanthrene; Pr, Perylene; Py, Pyrene.

Source (Neff, 1979)

Many industries and electrical generating facilities burn coal and coke. These plants create the greatest amount of PAH (Neff, 1979). Coke is an important oxygen reducing fuel used in the iron and steel industry. The process involves exposing hard coal to high temperature (approximately 1400 C) in a reducing atmosphere, which is ideal for forming PAH (Neff, 1979). Coal tar, a by-product of the coking process, contains more than 44 percent PAH by weight (Neff, 1979). In a Buffalo River, New York study (Kuzia and Black, 1985) at a major steel processing site that utilized the coking process, total PAH concentration in the water column was as high as 88,000 nanograms per liter (ng/L) and the total PAH concentration in the sediment was as high as 172,000 nanograms per gram (ng/g).

It is very difficult to estimate the amount of PAH that discharges from industrial and domestic effluents (Neff, 1979). Using average values (Borneff and Kunte, 1965; Andelman and Suess, 1970; & Harrison et al., 1975), the estimated annual PAH loading in the United States from domestic and industrial wastewater discharged into the aquatic environment is 29 tons BaP per year and 4.4 x 10^3 tons total PAH per year.

Runoff from land, fallout and rainfall from air, petroleum spillage, and biosynthesis also contribute PAH to fresh and marine waters. Table 2.3 summarizes the estimates of Benzo(a)pyrene and total PAH to the aquatic environment

TABLE 2.3

Sources of Benzo(a)pyrene and PAH in the Aquatic Environment

Sources	INPUT IN METRIC TONS/YEAR BaP	Total PAH
Biosynthesis	25	2700
Petroleum Spillage	20-30	170,000
Domestic and Industrial wastes	29	4400
Surface runoff from land	118	2940
Fallout and rainout from air	500	50,000
TOTAL INPUT	697	230,000

Source (Neff, 1979)

from various sources (Neff, 1979).

PAH remain relatively close to the point source in an aquatic environment and decrease logarithmically with distance from the point of origin. Most PAH remain localized in rivers, estuaries, and coastal marine waters. Organic and inorganic matter adsorb PAH and much of the particulate material is deposited into the bottom sediment. The relative concentration of PAH is usually highest in the sediments, followed by aquatic biota, and lowest in the water column (Neff, 1979).

2.3 Health Effects of PAH

Several studies (Baumann et al., 1982; Stegeman et al.,1981; West et al., 1986; & Krahn et al., 1986) have documented hepatomas in fish resulting from exposure to high concentrations of PAH. Baumann et al. (1982) documented that a high tumor rate in brown bullhead catfish (Ictalurus

nebulosus) correlated with high PAH concentrations in their bodies. West et al. (1986) identified PAH as genotoxic pollutants in the sediment from the Black River, Ohio, where a high incidence of hepatoma was observed in brown bullhead catfish. An Ames Assay was performed that indicated significant mutagenic activity due to compounds that contained PAH with four to six aromatic rings (West et al., 1986).

Baumann et al. (1982) analyzed two sediment samples from the Black River. The highest concentrations were found near a coke plant outfall. The level of PAH in the sediment at the coke plant site was three to four times higher than in the sediment located near a municipal discharge (Baumann et al., 1982). A wide range of PAH and other organics were present in the Black River bullheads and are listed in Table 2.4 (Baumann et al., 1982). The Black River bullhead catfish contained Benzo(a)anthracene, Benzo-fluoranthene, and Benzo(a)pyrene. These compounds have been identified as animal carcinogens by the International Agency for Research on Cancer (IARC). Benzo(a)pyrene is listed as a suspected animal carcinogen by the IARC and several of the others have caused at least benign tumors in mammalian experiments (Baumann et al., 1982).

A similar study by Krahn et al. (1986) confirmed an association between concentrations of PAH and the presence of idiopathic liver lesions in English sole from Puget

TABLE 2.4

Contaminant Residue Levels (ng/g) from Sediment and Composites of Two-year-old (2) and Three-year-old-plus (3+) Brown Bullhead Both with Tumors (T) and Normal (N)

	CONCENTRATION			
		Black River, Ohio		
Contaminant	Sediment	3+T	3+N	2N
Naphthalene	31,000	40	144	-
Acenaphthylene	40,000	775	2378	57
Acenaphthene	36,000	88	258	26
Phenanthrene	390,000	2140	5724	1669
Fluoranthene	220,000	583	1938	558
Benz(a)anthracene	51,000	4	33	3
Benzofluoranthene	75,000	1	32	-
Benzo(a)pyrene	43,000	7	18	-
Ideno(1,2,3-cd)pyrene	26,000	-	-	-
Benzo(ghi)perylene	24,000	-	-	-
Anthanthrene	13,000	-	-	-
Total PCB	NA	1900	1300	1000

(-) indicates not detected
NA: indicates not analyzed for

Source (Baumann et al., 1982)

Sound, Washington (Krahn et al., 1986). Table 2.5 supports the correlation of concentrations of PAH in bile of English sole, idiopathic lesion prevalence percentages in English sole, and the concentration of selected PAH and PCB at sampling sites.

Humans are exposed to PAH through the consumption of cigarettes, drinking water, charcoaled food, and ingestion of food from the aquatic environment. Sources of drinking water in the United States are groundwater and surface waters such as rivers and lakes. Groundwater usually contains five times less PAH than surface waters unless the

TABLE 2.5

Concentrations of Metabolites of PAH (measured at BaP wavelength) in Bile of English sole; Idiopathic Lesion Prevalences (%) in Livers of English sole; and Concentrations (ng/g, dry wt.) of Selected PAH and PCB in Samples of Sediments from Four Sites:

	Eagle Harbor	Duwamish Waterway	Clinton	West Point
number of fish	22	58	16	20
BaP equilivants of metabolites (ng/g, wet wt.)	2100+-1500	1400+-2200	1300+-1700	240+-160
Idiopathic prevalences (%)				
Neo (a)	18.2	20.7	20.5	0
FCA (b)	18.2	32.8	25.0	5
MH (c)	86.4	44.8	43.8	5
Ste (d)	36.4	41.4	6.2	5
Total (e)	90.0	67.2	50.0	15.0
Concentrations (ng/g) of PAH and PCB in sediment				
Napthalenes (f)	24,000	210	<20	780
Phenanthrenes (g)	80,000	240	<11	3700
Fluoranthene	59,000	440	16	6100
Pyrene	32,000	470	19	8300
BaP	2,300	73	13	2200
Total PAH (h)	310,000	2600	120	34,000
CBD's (j)	<LOD (i)	<3.9	<LOD	0.57
PCB's (k)	<LOD	330	<LOD	13

(a) Neo = neoplasms; (b) FCA = foci of cellular alteration; (c) MH = Megalocytic hepatosis; (d) Ste Steatosis/hemosiderosis; (e) Total = Prevalences of fish livers have more than one lesion so the total is not the sum of the individual lesion prevalences; (f) Napthalenes = sum of concentrations of 5 Napthalenes; (g) Phenanthrenes = sum of 3 Phenanthrenes; (h) Total PAH = sum of concentrations of all PAH; (j) CBD's = Sum of concentrations of di-, tri-, tetra-, penta-, and hexachlorobutadiene; (i) LOD = limit of detection; (k) PCB = sum of concentrations of di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, and nonachlorobiphenyl.

Source (Krahn et al., 1986)

source is leaching polluted soil (Brungs et al., 1980). Sources of PAH in surface waters include: municipal and industrial effluent; atmospheric fallout and rainout; and runoff from polluted soils and roadways. PAH levels in surface waters used as raw sources for drinking water, and the effects of treatment of these waters, are presented in Table 2.6.

TABLE 2.6

Concentration of PAH (ug/L) in Raw and Treated Surface Water Used as Drinking Water Sources

Source	Treatment	Carcinogenic BaP	Carcinogenic PAH	Total PAH	Reference
Monongahela R. at Pittsburgh	untreated	0.04	0.14	0.60	Basu and Saxena, 1978
	treated	0.0004	0.002	0.003	
Ohio River at Huntington, W.Va.	untreated	0.006	0.020	0.058	Basu and Saxena, 1978
	treated	0.0005	0.002	0.007	
Ohio River at Wheeling, W.Va.	untreated	0.21	0.57	1.59	Basu and Saxena, 1978
	treated	0.002	0.011	0.14	
Delaware River at Philadelphia	untreated	0.04	0.16	0.35	Basu and Saxena, 1978
	treated	0.0003	0.002	0.015	

BaP = Benzo(a)pyrene
The treatment included flocculation, activated carbon addition, filtration, pH control, chlorination and fluoridation.

Source (Brungs et al., 1980)

The levels of PAH in the United States are maintained well below the World Health Organization's (1970)

recommended limit of 200 parts per trillion (ng/L), or 0.2 ug/L. In spite of the World Health Organization's recommendation, repeated exposure to PAH through drinking water is not fully understood and should be taken seriously. For the maximum protection of human health, the concentration of PAH in water should be zero; however, this is not attainable (Brungs et al., 1980). Brungs et al. (1980) recommended a total PAH level of 28 ng/L based on an estimated lifetime cancer risk of 10^-5. If these levels were based on consumption of aquatic organisms only, excluding consumption of water, the level would be 311 ng/L (Brungs et al., 1980).

The primary conveyances for PAH in foods from the aquatic environment are surface adsorption and biological accumulation. Adsorption of PAH by marine organisms is documented by Lee et al. (1972). Oysters and clams collect PAH from moderately polluted water via adsorption (Cahnmann and Kuratsune, 1957; Guerrero et al., 1976). Various other organisms have been investigated and found to contain PAH (Brungs et al., 1980). A bioconcentration factor (BCF) is used to relate the concentration of a chemical in an aquatic organism to the concentration of the chemical in the water. The BCF for tissues of various aquatic animals seem to be proportional to the percent lipid in the tissue (Brungs et al., 1980). Although PAH bioaccumulate in fish, they show little tendency for bioaccumulation in the fatty tissues of

animals or man (Lee et al., 1972; & Ahokas et al., 1975). Thus, the transfer of PAH through the food chain and its direct impact on humans is very difficult to understand.

2.4 Present Standards for PAH

Today, the U.S. EPA has standards for PAH in the water column for both aquatic life habitat and water supply. However, there are no standards for PAH in bottom sediments. Table 2.7 lists the water quality standards for the State of Ohio set by the Ohio EPA, effective September 30, 1993.

2.5 Fate and Transport of PAH in Aquatic Environment

2.5.1 Sorption

PAH are organic pollutants that tend to be relatively hydrophobic, non-polar compounds. These characteristics cause them to have a strong affinity toward aquatic particulate matter (Delos et al., 1984). The environmental fate and transport of organic chemicals are affected by the extent to which the chemicals sorb to substrates such as bottom and suspended sediments. Sorbed chemicals may be less available to the transformation processes of volatilization, biodegradation, hydrolysis, and photolysis (MacKay and Power, 1987). Two schools of thought explain the sorption process. The sorption of organics is considered by most researchers to be a true equilibrium partitioning between the water and sediments. The other

TABLE 2.7

PAH Standards of the Ohio Environmental Protection Agency

Parameter	Aquatic Life Habitat Seasonal Warmwater Habitat	Salmonid Habitat	Coldwater Habitat	Limited Resource Habitat	Water Supply Public Water Supply	Agric. Water Supply
		(a)				
Polynuclear Aromatic Hydrocarbons (PAH) (b) Human Health 30 day average	0.31 ug/L				0.028 ug/L	
Acenaphthene						
-Outside Mixing Zone						
Maximum	67 ug/L					
30 day avg.	67 ug/L					
Human Health 30 day avg.					20 ug/L	
Inside Mixing Zone Maximum	134 ug/L					
Fluoranthene						
-Outside Mixing Zone						
Maximum	200 ug/L					
30 day avg.	8.9 ug/L					
Human Health 30 day avg.	54 ug/L					42 ug/L
Inside Mixing Zone Maximum	400 ug/L					
Naphthalene						
-Outside Mixing Zone						
Maximum	160 ug/L					
30 day avg.	44 ug/L					
Inside Mixing Zone Maximum	320 ug/L					

a This aquatic life habitat use designation is in effect only during the months of October through May.

b The PAH criteria apply to the sum of anthracene, benzo(a)anthracene, benzo(k)fluoranthene, 3,4-benzofluoranthene, benzo(ghi)perylene, benzo(a)pyrene, chrysene, dibenzo(ah)anthracene, fluorene, indeno(123-cd)pyrene, naphthalene, phenanthrene, and pyrene.

Source (Ohio EPA, 1993)

principal belief is that there is a "third phase" in which part of the chemical is sorbed to colloidal or nonfilterable suspended particulate matter.

The organic toxicant is usually present at very low concentrations, therefore the sorptive sites in the dissolved phases are not saturated and the behavior follows a linear relationship (MacKay and Power, 1987). Data relating the chemical's dissolved phase concentration with its solid phase concentration are frequently expressed in terms of the Freundlich or Langmuir isotherms, which are very close to linear at low dissolved phase concentrations (Delos et al., 1984). Because of this linear relationship, the sorption of hydrophobic organics to particulate matter can be quantified, usually by a partition coefficient (K'*p*) (MacKay and Power, 1987). The partition coefficient (K'*p*) is the ratio of the sorbed particulate concentration (r) to the dissolved concentration (C*d*) (MacKay and Power, 1987).

2.5.2 Two-Phase Partitioning Model

This study utilizes the simpler two-phase partitioning model, in which PAH are considered to be either truly dissolved or sorbed to particulate matter. This model is described below.

2.5.2.1 *Partition Coefficient*

The two-phase partition coefficient is defined by

equation 2.1.

$$K'p = \frac{Cp}{m\ Cd} \qquad (2.1)$$

where:

K'*p* = <u>in situ</u> two-phase partition coefficient (L/kg)

C*p* = concentration of sorbate in particulate phase (kg/L)

m = suspended solids concentration (kg/L)

C*d* = concentration of sorbate in dissolved phase (kg/L).

2.5.2.2 *Normalized for Solid Phase*

Alternatively, this can be expressed as

$$K'p = \frac{r}{Cd} \qquad (2.2)$$

where:

r = mass of sorbate concentration in solid phase (mg/kg)

C*d* = mass of dissolved sorbate concentration (mg/L).

Because of their low solubility and hydrophobic nature, PAH tend to sorb to organic and inorganic suspended particulates in the water column rather than remain as dissolved PAH. The particulates gradually settle out of the water column carrying adsorbed PAH with them into the sediment (Neff, 1979). Once in the sediment, PAH is less susceptible to photochemical or biological oxidation, especially if the sediment is anoxic. Thus, PAH may

accumulate to high concentrations (Neff, 1979).

2.5.2.3 *Normalized for Organic Carbon*

Sorption of organic toxicants is related to chemical solubility, the organic carbon/water partition coefficient (K'*oc*), and the octanol/water partition coefficient (K'*ow*). In general, the more insoluble and hydrophobic a chemical is, the more likely it will have a large K'*p* (Delos et al., 1984). Also, when comparing the sorption of a toxicant to various types of sediments, the sediment with the highest organic content will likely adsorb the most chemical and produce the largest K'*p* (Delos et al., 1984). By dividing the measured partition coefficient (K'*p*) by the organic carbon weight fraction of the particular sediment (foc), a sediment-independent partition coefficient (K'*oc*) between the aqueous phase and the organic portion of the sediment can be obtained as shown in equation 2.3 (Delos et al., 1984).

$$K'oc = \frac{K'p}{foc} = \frac{r}{(OC)\ Cd} \qquad (2.3)$$

where:

K'*oc* = in situ two-phase organic carbon partition coefficient (L/kg)

foc = fraction of organic carbon in suspended solids (mg OC/mg SS)

OC = particulate organic carbon concentration (mg/L).

Sorption to suspended solids and sediments are an important transport process for PAH. Sorption coefficients are needed to predict the fate of PAH in the aquatic ecosystem. In recent literature, empirical correlations between the aqueous solubility, the octanol/water coefficient (Kow), the organic carbon coefficient (Koc), and the bioconcentration factor (BCF) in aquatic organisms have been developed (Delos et al., 1984). These correlations must be applied carefully since water chemistry, properties of the sediment, and adsorption/desorption kinetics are also important considerations (Delos et al., 1984).

2.5.2.4 *Two-Phase Distribution Model for Organic Sorbates*

The total concentration of organic chemical sorbate is the sum of dissolved and particulate concentrations, and can be described by equation 2.4.

$$Ct = Cd + Cp = Cd(1 + K'oc\ (OC)) \qquad (2.4)$$

where:

Ct = total concentration of sorbate (kg/L).

The fractions of sorbate in the dissolved and particulate phases are given by equations 2.5 and 2.6, respectively.

$$fd = \frac{Cd}{Ct} = \frac{1}{1 + (K'oc\ (OC))} \qquad (2.5)$$

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where:

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$$fd = \frac{Cd}{Ct} = \frac{1}{1 + (K'oc\ (OC))} \qquad (2.5)$$

where:

fd = fraction of total sorbate in dissolved phase

and,

$$fpoc = \frac{Cp}{Ct} = 1 - fd = \frac{K'oc\ (OC)}{1 + (K'oc\ (OC))} \qquad (2.6)$$

where:

fpoc = fraction of total sorbate bound to particulate organic carbon.

2.5.2.5 *Solids Concentration Effect*

The solids concentration effect on the partition coefficient (K'*p*) of organic toxicants was investigated by O'Conner and Connolly (1980) and DiToro (1985). It was observed that the partition coefficient (K'*p*) was inversely proportional to the solids concentration for high values of the weight fraction of organic carbon (OC) and the octanol/water coefficient (*Kow*) (Thomann & Mueller, 1987). This solids concentration effect has been scrutinized in many studies. Several suggestions have been conceived to explain the particle concentration effect. They include: 1) sorption by colloidal particles (Gschwend & Wu, 1985); 2) desorption induced by particle-particle interaction (DiToro, 1985); 3) failure to achieve sorption equilibrium (Karickhoff, 1984); and 4) a decrease in surface area available for sorption due to particle aggregation (Karickhoff & Morris, 1985; & Bierman et al.,1992). DiToro

(1985) suggested that the effect of particle concentration on the partition coefficient can be incorporated into the two-phase distribution model by adjustment of K'*oc* as shown in equation 2.7.

$$K''poc = \frac{foc(K'oc)}{1 + \frac{m(foc)(K'oc)}{v}} \qquad (2.7)$$

where:

K''*poc* = reversible component partition coefficient (L/kg)

K'*oc* = partition coefficient normalized to particulate organic carbon (L/kg)

foc = organic carbon weight fraction (mg OC/mg sediment)

m = suspended solids concentration (mg/L)

v = empirical constant (unitless); a value of 1.4 provides the best estimate for a wide range of organic chemicals.

Estimation of the partition coefficient requires information on the fraction organic carbon (*foc*) in total solids concentration, and is usually obtained from field studies (Thomann & Mueller, 1987). The condition of the sediment is influenced by microorganisms, sediment organic carbon dissolved in pore water, and the sediment particulate organic carbon (Thomann & Mueller, 1987). For high values of *foc* and *K'oc*, the partition coefficient is inversely proportional to solids concentration. Sediment partition coefficients are generally less than in the water column,

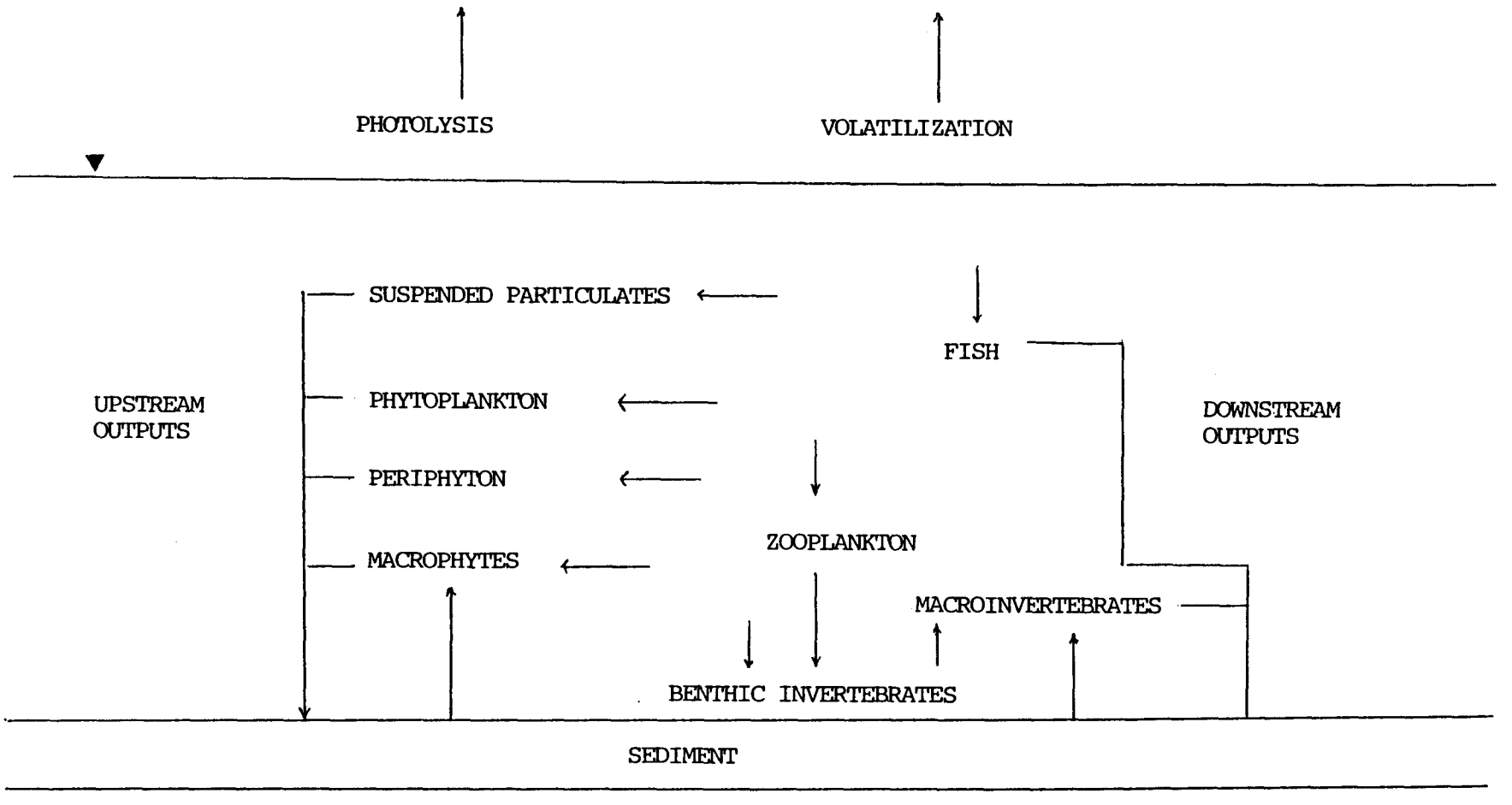
but the rate of decline apparently is reduced at the high bulk density of the sediment (Thomann & Mueller, 1987). Because of this, the partition coefficient-solids concentration relationship generally does not pertain to sediment solids concentrations. The partition coefficient is approximately independent of solids concentrations at log (foc x K'oc) of about 1 to 3 (Thomann & Mueller, 1987).

2.5.3 Transformation Processes

Various transformation processes irreversibly destroy, modify, or eliminate the toxicant from the aquatic ecosystem. Many of these processes only apply to organic chemicals. The transformation processes include: biodegradation; hydrolysis; photolysis; and volatilization (Delos et al., 1984). Figure 2.1 illustrates the transformation processes in a stream.

2.5.3.1 *Biodegradation*

Biological transformations (biolysis) are enzyme induced reactions produced by bacteria and fungi during metabolic activity. The enzymatic catalysts induce: oxidation, reduction, and hydrolysis (Delos et al., 1984). Microbes accomplish metabolism by degrading PAH compounds where energy and carbon are obtained for growth. Not all microbes are able to carry out complete oxidation of PAH, however, given a suitable growth substrate, they are able to



SIMULATION OF PAH IN STREAMS

FIGURE 2.1

SOURCE (Giesy et al., 1983)

partially metabolize them. Typically, when an organic contaminant is introduced to an aquatic community, the microbial community goes through an acclimation period in which the organisms must adapt to the organic toxicant.

Three primary factors determine the extent and rate of biological decay of PAH in the aquatic system. They include properties of the PAH such as structure, concentration, and history within the aquatic environment; the physical state of the aquatic system, such as temperature and dissolved oxygen; and the characteristics of the microbial community, such as size, diversity, and general health (Neff, 1979).

The removal of PAH by biodegradation is poorly understood. The concentrations of hydrocarboniclastic bacteria and fungi are extremely low in all but heavily polluted waters. Most species cannot use PAH as a sole carbon source. Microbial degradation of PAH in sediments is significant as long as the sediments are oxygenated (Neff, 1979). Lee et al. (1978a) showed that C-benz(a)anthracene near the surface of a marine sediment degraded rapidly, while in the deeper, presumably anoxic layers, it degraded very slowly.

2.5.3.2 *Photolysis*

There is substantial evidence that PAH in surface waters degrade by photo-induced oxidation in the aqueous phase by singlet oxygen, ozone, and other oxidizing agents

(Neff, 1979). Experimental studies (Masuda and Kuratsune, 1966; Inomata and Nagata, 1972; Pierce and Katz, 1975) demonstrated that PAH absorbs sunlight in the ultraviolet portion of the spectrum and results in photooxidation. Il'nitiskii (1971a) confirms that the sensitivity of PAH to photooxidation varies. Photooxidation of PAH adsorbed to surface particulates seems to be substantially greater than PAH dissolved in the water column (Neff, 1979).

Suess (1972a) conducted a study on the photooxidation of Benzo(a)pyrene in natural waters and concluded that degradation depended upon water depth and the varying seasons, owing to changes in solar radiation, temperature, and dissolved oxygen.

Several investigations have been performed on the efficiency of chlorination or ozonation for use in the degradation of aqueous PAH (Neff, 1979). Harrison et al. (1976a) evaluated water treatment processes for removal of PAH. At the treatment plant the water was initially pumped to a storage reservoir with an average retention of 2-4 days. It was then treated by rapid gravity filtration, followed by slow sand filtration, and finally by chlorination. Since PAH in water adsorbs to suspended solids, sedimentation of the solids in the storage reservoir caused a reduction in PAH. Filtration caused a 50 percent reduction in aqueous PAH levels and chlorination removed almost 60 percent of the remaining PAH. Because it has

been determined that chlorination of PAH produces toxic by-products alternative methods for purification must be considered (Neff, 1979).

Ozone has frequently been used as an alternative to chlorination for water purification in Europe. However, ozonation is less efficient than chlorination for the removal of PAH and the toxicity of its by-products to aquatic life has not been determined (Neff, 1979).

2.5.3.3 *Hydrolysis*

PAH do not contain favorable properties for hydrolysis, and thus, it is not an important fate process.

2.5.3.4 *Volatilization*

Volatilization is the evaporation of PAH into the atmosphere. It is not significant in the fate and transport process of PAH, except for Naphthalene. Volatilization rates decrease as vapor pressure of PAH decreases and this appears to be inversely proportional to the number of aromatic rings (Delos et al., 1984). The rate of vaporization of PAH with four or more aromatic rings is insignificant.

2.6 Review of Other Mahoning River Data

The Mahoning River bottom sediment was surveyed for PAH in 1986 by the U.S. EPA and the Ohio EPA and in 1993 by Dr.

Lauren Schroeder of Youngstown State University. Sediment samples from the Mahoning River were collected and analyzed by the Ohio EPA in 1980 and 1983 for nutrient and heavy metal contamination at RM (river mile) 46.0, RM 21.0, RM 13.5, and RM 1.5. The sediments downstream of Warren contained high concentrations of nutrients, oil and grease, cyanide, phenolic substances, and heavy metals. Total chromium, total copper, total iron, total lead, and total zinc concentrations indicated extreme contamination. Total arsenic, total cadmium, total manganese, and total mercury concentrations were also excessively high. The banks of the Mahoning River between RM 16.3 and 13.0 were oil soaked and this stretch of the river contained heavy deposits of oil in the sediment. The Ohio EPA believed that oil in the bottom sediments and bank material could be substantially eliminated in 5 to 10 years if point source loading of oil and grease could be reduced (Estenik, 1988).

Table 2.8 highlights selected results from the U.S. EPA (1986) sediment evaluation of PAH in the Mahoning River. It is of interest that the sediment sample at river mile 17.84 was in the proximity of the Briar Hill coke plant and the sediment sample at river mile 16.29 was near the Campbell coke plant. Table 2.9 summarizes the analysis of Mahoning River sediment by Schroeder (1993). Schroeder's (1993) study of the sediments indicates that high concentrations of PAH still exist in the sediment. Table 2.10 lists selected

data that compares the Mahoning River sediment PAH data levels to levels in the Black River, Ohio. The Black River PAH results are used as a basis for comparison because the lower 6 miles have a consumption advisory based on the presence of high PAH concentrations in the sediment and tumors on fish at this location (Estenik, 1988).

Table 2.8

PAH Sediment Sampling Results (U.S. EPA 1986)
(Results in mg/kg dry weight basis

Sample Location (RM)	46.02	36.24	22.99	17.84	16.29	12.36
Sample Date	6/11/86	5/28/86	6/11/86	6/10/86	6/10/86	6/11/86
Total Solids	74.3	40.8	30.8	73.7	47.5	32.1
Naphthalene	ND	21.0	1.1	3300.0	34,000.0	21.0
Acenaphthylene	ND	2.0	0.7	260.0	6200.0	ND
Acenaphthene	ND	2.9	ND	820.0	1900.0	1.5
Dibenzofluoranthene	ND	3.2	2.2	980.0	4000.0	ND
Fluorene	ND	5.4	4.8	1200.0	4100.0	ND
Phenanthrene	ND	17.0	17.0	3200.0	18,000.0	5.4
Anthracene	ND	4.2	5.6	1100.0	240.0	3.6
Fluoranthene	ND	11.0	9.7	1600.0	9500.0	8.4
Pyrene	ND	8.3	8.7	1200.0	300.0	7.1
Chyrsene	ND	8.3	8.3	870.0	1700.0	7.5
Benzo(a)anthracene	ND	6.6	6.9	850.0	2000.0	6.6
Benzo(b)fluoranthene	ND	ND	ND	150.0	900.0	3.1
Benzo(a)pyrene	ND	ND	2.6	630.0	3400.0	3.4
Ideno(123-cd)pyrene	ND	ND	ND	ND	2400.0	ND
Dibenzo(ah)anthracene	ND	ND	ND	ND	130.0	ND
Benzo(ghi)perylene	ND	ND	ND	ND	680.0	ND

RM = River Mile, ND = Not Detected.

Source (U.S. EPA, 1986)

Table 2.9
Selected Unpublished PAH Data from Schroeder(1993)
(mg/kg)

Sample Location River Mile	20	20	16	16	12	12	0
Naphthalene	0	22.4	99999.9	1859.0	5034.0	878.0	0
Acenapthylene	0	0	4107.0	0	0	0	0
Acenapthene	0	0	0	0	0	0	0
Dibenzofluoranthene	0	0	0	0	0	0	0
Fluorene	2.1	0	5476.0	92.0	118.0	0	0
Phenanthrene	1.0	0	20127.0	448.0	55.0	63.0	0
Anthracene	0.4	0	8800.0	145.0	0	0	0
Fluoranthene	0.2	0	15242.0	367.0	0	87.0	0
Pyrene	0.8	0	0	0	0	0	0
Chrysene	0	0	5257.0	0	0	0	0
Benzo(a)anthracene	1.1	6.7	5459.0	200.0	0	0	0
Benzo(b)fluoranthene	1.9	0	8123.0	168.0	0	0	0
Benzo(a)pyrene	1.0	0	4222.0	95.0	0	0	0
Ideno(123-cd)pyrene	0.8	0	0	0	0	0	0
Total PAH	9.3	29.1	176,813.9	8348.0	5207.0	1028.0	0

Source: Schroeder (unpublished, 1993)

Table 2.10

Sediment PAH Contamination in the Mahoning River
Compared to PAH Contamination in the Black River

$$\text{PAH Ratio} = \frac{\text{Total Mahoning River PAH Concentration}}{\text{Total Black River PAH Concentration}}$$

River Mile	Data Source/Year	Total PAH (ppm)	PAH Ratio
Black River	Baumann/1992	1454	1:1
Mahoning River			
16.42	U.S. EPA/1986	23,210	15.98
16.29	U.S. EPA/1986	93,150	64.16
16.14	U.S. EPA/1986	53,460	36.82
16.08	U.S. EPA/1986	3432	2.36
16.0	Schroeder/1993	8348	5.74
16.0	Schroeder/1993	3482	2.39
16.0	Schroeder/1993	176,813	121.6
12.0	Schroeder/1993	275	0.19
12.0	Schroeder/1993	5306	3.65
12.0	Schroeder/1993	1028	0.70
0.0	Schroeder/1993	924	0.64

Source (U.S. EPA, 1986; Schroeder unpublished, 1993)

CHAPTER III

METHODS AND PROCEDURES

3.1 Sample Locations

The locations chosen for two grab samplings of sediment from the Mahoning River were Campbell, Ohio and Lowellville, Ohio. The Campbell site is located at approximately river mile 16 where a coke processing plant once operated until the early 1980's. The Lowellville site is downstream from the Campbell, Ohio location at river mile 12, upstream of a dam near the Lowellville Bridge. A water sample was also collected at Newton Falls, Ohio which is situated upstream of the 33 mile stretch of the Mahoning River that is under the 1988 Health Advisory. The water sample was procured for the use as PAH-free water in desorption experiments.

3.2 Sampling Equipment and Procedures

Grab samples were taken with a 3 inch diameter steel pipe attached at a 45 degree angle to a 10 foot steel rod. This device procured approximately a three inch deep by six inch long sample of bottom sediment. The sample was removed from the river with the steel pipe parallel to the surface of the water in order to prevent the mixing of the water column with the pore water in the sediment as much as possible.

A steel hand shovel was used to place the samples in

one quart glass jars. Aluminum foil was placed over the mouth of the jars and sealed with a lid. The glass jars were covered with aluminum foil to protect the sediment samples from the possibility of photolysis. Glass and steel material were used to prevent background contamination of the sediment. The glassware was cleaned with hot water and detergent and rinsed with distilled water and acetone prior to receiving the samples. Approximately 15 pounds of sediment was collected from each Mahoning River site and stored at 4 C. Each sample jar was marked for identification.

The Lowellville, Ohio specimen was extracted from the Mahoning River on December 12, 1993. The grab sampler penetrated the bottom sediments in 10 feet of water, approximately 3 feet from the north bank of the river. The sediment consisted of silt, tar, leaves, and many decaying organics. A small oil sheen spread across the surface of the water as the sample was taken. An oil ring along the bank was observed a few hundred feet upstream of this location.

The Campbell, Ohio sample was more difficult to acquire as the sediment was very rocky. The sediment grab sample was obtained at about a foot below the surface of the water and about a foot away from the south bank of the river, where the sediment was more silty. A large oil sheen spread across the width of the river during the sampling. The

sediment smelled like moth balls and portions of it contained tar and white crystals. This sample was procured on January 11, 1994.

3.3 PAH Analysis

Method 610-Polynuclear Aromatic Hydrocarbons in Volume 49, No. 209 of the Federal Register was utilized to determine polynuclear aromatic hydrocarbons (PAH). This method included: 1) Soxhlet Extraction; 2) Kuderna-Danish Concentration; 3) Florisil Cleanup; 4) Nitrogen Cleaning; and 5) High Performance Liquid Chromotography. The following PAH can be detected by this method:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(ghi)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene.

(Federal Register Vol.49. No. 209, 1984)

Method 610 provides for both high performance liquid chromatography (HPLC) and gas chromatography (GC) techniques to determine PAH. Method 3540A (Soxhlet Extraction) was used to extract and concentrate PAH from sediment samples in preparation for HPLC.

3.3.1 Overview of Method

The sediment sample is prepared by placement in an extraction thimble and mixed with anhydrous sodium sulfate. It is then extracted in a Soxhlet extractor using hexane. The extract is dried, concentrated, and cleaned up for HPLC analysis.

3.3.2 Apparatus and Materials

Soxhlet Extractor, with 500 ml flask.
Drying Column.
Kuderna-Danish (K-D) apparatus
- Concentrator tube, 10 ml.
- Evaporation Flask, 500 ml.
Snyder Column.
Springs.
Boiling Chips.
Water bath - Hot plate apparatus used in a hood.
Vials - Glass, 2 ml.
Paper thimble.
Heating mantle - Rheostat controlled.
Disposable glass pipet and bulb.
Freeze Dryer.
Oven - Drying.
Desiccant.
Crucibles.
Grinding apparatus.
Balance.
Sillitherm hotplate.
Nitrogen.

3.3.3 Extraction and Exchange Solvents

Hexane - HPLC grade.
Acetone - HPLC grade.
Acetonitrile - HPLC grade.
Methylene chloride - HPLC grade.
2-Propanol - HPLC grade.
Methanol - HPLC grade.
Distilled non-organic water.
Anhydrous sodium sulfate.

3.4 Sample Handling

Water was decanted off the top of the sample jar and the sediment was mixed thoroughly. Leaves, twigs, and rocks were discarded from the specimen. Several sediment portions were placed on aluminum dishes and weighed. The sediment was freeze dried for 48 hours to remove all moisture. The samples were again weighed after freeze drying and the percent moisture was calculated. The formula used to determine percent moisture in the sample is as follows:

$$\% \textit{ moisture} = \frac{\textit{Wet Weight - Dry Weight}}{\textit{Wet Weight}} \textit{ x } 100 \qquad (3.1)$$

3.5 Soxhlet Extraction

1) The freeze dried sediment was ground up into very fine particles in a crucible. A subsample of sediment was placed in a tared thimble and weighed, and the sediment weight was recorded. At least 10 grams of sediment was used on the initial Soxhlet extractions. The Campbell sediment weight had to be reduced to approximately 100 milligrams as the PAH concentrations were so high the HPLC detection range was exceeded. Six grams of anhydrous sodium sulfate was placed on the surface of the sediment in the thimble.

2) A Soxhlet flask was filled with 250 mL of hexane and a boiling chip was placed in the Soxhlet flask.

3) The thimble with the subsample was placed into the Soxhlet column.

4) The Soxhlet column was placed into the Soxhlet flask.

5) The Soxhlet flask and column was placed onto a heating tray and a condensing water hose was connected to the Soxhlet column.

6) The condensing water to the Soxhlet column was opened and the flow was adjusted. The heating tray was turned on and the rheostat adjusted to a setting just above the boiling point of hexane.

7) The Soxhlet flask was covered with aluminum foil to prevent photolysis of PAH.

8) The hexane boiled, evaporated, and recondensed in the Soxhlet column. The hexane filled the thimble, extracted the PAH from the sediment and flowed back to the Soxhlet flask by means of the vacuum created from the condensing process. Thus, the hexane along with the PAH collected in the Soxhlet flask.

9) The Soxhlet extraction was performed between 16 and 24 hours. An indication that the Soxhlet extraction was complete was when the hexane in the Soxhlet column and thimble became clear *after* the sixteenth hour of extraction.

10) The Soxhlet apparatus was removed from the heating tray and allowed to cool. The thimble was removed from the Soxhlet column. The Soxhlet extraction step was executed with little difficulty. Sediments with *very high* PAH concentrations would bake the hexane and PAH deposits onto the Soxhlet flask. The Soxhlet flask clean up and hexane

transfer into the Kuderna-Danish (K-D) could not be accomplished. If high concentrations of PAH were suspected (e.g. moth ball smell, white crystals, and high tar sediment), the sediment weight in the thimble was reduced. In this study it was reduced to 100 milligrams. This provided easier Soxhlet apparatus clean up and improved HPLC detection results.

3.6 Kuderna-Danish (K-D) Concentration

1) A clean and dry Kuderna-Danish (K-D) concentrator was assembled by attaching a 10 mL concentrator tube with springs to a 500 mL evaporation flask. Two boiling chips were added to the K-D concentrator tube-flask assembly.

2) The hexane/PAH extract was emptied from the Soxhlet device into the K-D concentrator tube-flask. The Soxhlet flask and column were rinsed with hexane three times using a clean pipette. The hexane rinse was placed into the K-D concentrator.

3) A Snyder column was placed into the K-D concentrator and prewet with 1 mL of hexane.

4) The K-D apparatus was placed on a hot water bath just above the boiling point of hexane. The concentrator tube was partially immersed in the hot water and the flask was just above the water level where it was heated by the hot vapor. The hot water bath temperature was adjusted so that the Snyder column did not flood. The proper distillation

rate was achieved when the column balls actively chatter.

5) When the volume of the liquid reached 1-2 mL in the concentrator tube, the K-D apparatus was removed and allowed to drain and cool.

6) The hexane/PAH extract was removed from the K-D concentrator and transferred to a clean sample vial with a pipette. The K-D concentrator was rinsed three times with approximately 1 mL of hexane. Each sample vial was properly labeled with the appropriate location of the study.

3.7 Florisil Standardization

The Florisil adsorbent capacity must first be determined and a standardization procedure accomplished. The method used in this study is from Mills (1968).

3.7.1 *Apparatus and Reagents*

1) 25 mL Buret.

2) 125 mL and 25 mL Erlenmeyer flasks.

3) 500 mL volumetric flasks.

5) 10 mL and 20 ml pipets.

6) A lauric acid solution was created by dissolving 10.000 grams lauric acid into 500 mL hexane in an Erlenmeyer flask, yielding a solution where 1 mL = 20 mg.

7) Phenolphthalein indicator was produced by dissolving 1 gram of phenolphthalein in ethyl alcohol and diluting to 100 mL. The ethyl alcohol used in this procedure was USP or

absolute, neutralized to the phenolphthalein endpoint.

8) The hexane used was HPLC quality.

9) Sodium hydroxide was produced by dissolving 20 grams of NaOH in water and diluting to 500 mL (1N). This was diluted to 0.05N by bringing 25 mL of 1N NaOH to a volume of 500 mL with water (0.05N).

10) A standardization to calculate the ratio of mg lauric acid per mL of 0.05N NaOH was performed. 200 mg of lauric acid was weighed and dissolved in 50 mL neutralized ethyl alcohol. 3 drops of phenolphthalein indicator was added to this solution and titrated with 0.05N NaOH to permanent endpoint. The 200 mg lauric acid/50 mL ethyl alcohol solution was titrated to a permanent endpoint using 23.2 mL of 0.05N NaOH. The ratio of mg lauric acid / mL 0.05N NaOH was calculated as follows:

$$\frac{200\ mg\ lauric\ acid}{23.2\ mL\ 0.05\ NaOH} = \frac{8.62\ mg\ lauric\ acid}{mL\ 0.05\ NaOH}$$

3.7.2 Procedure

2.000 grams of Florisil was transferred to a 25 mL Erlenmeyer flask. The flask was covered loosely with aluminum foil and heated overnight at 130 degrees centigrade. The flask was stoppered and then cooled to room temperature. 20.0 mL lauric acid solution (400 mg) was

added and the flask was stoppered, and shaken occasionally for 15 minutes. After allowing the adsorbent to settle, 10.0 mL of supernatant was pipetted into a 125 mL Erlenmeyer flask, avoiding the inclusion of Florisil. Then, 50 mL of neutral alcohol and 3 drops of phenolphthalein indicator solution were added. This was titrated with 0.05N NAOH to a permanent end point. The titration was performed 4 separate times and the mean titrant volume of 10.7 mL was used for calculation of lauric acid adsorption on Florisil.

The calculation of the amount of lauric acid (L.A.) adsorbed on Florisil was performed as follows:

mg L.A./g Florisil = 200 - [(mL 0.05N NaOH titrant) x (L.A. : 0.05N NaOH ratio)]

mg/g Florisil = 200 - (10.7 mL x 8.62 mg/mL) = 107.766 mg/g

A lauric acid value of 110 mg/g was selected as the desired adsorptive capacity of a Florisil. According to the Floridin Co. (Mills et al., 1963), 20 grams of Florisil would fill a column 22 mm i.d. to a depth (after settling) of 100 mm if its nominal or apparent density (60-100 mesh) is about 30 lb/cubic foot.

The minimum amount of Florisil placed into the column was calculated as:

$$\frac{110 mg/g}{107.766\ mg/g \times 20\ g} = 20.41\ grams\ of\ Florisil$$

3.8 Packing the Florisil Column

1) Florisil was activated overnight at 130 C.

2) Solid Sodium sulfate was activated overnight at 400 C.

3) 20.5 grams of Florisil was measured out on a plastic tray and poured into a 50 mL beaker. Hexane was added to the Florisil. The hexane and Florisil were stirred continuously with a clean pipette to remove all air bubbles.

4) The Florisil and hexane mixture was poured into the column with the column needle valve open until the Florisil was completely in the column. 2 centimeters of anhydrous sodium sulfate was poured over the top of the Florisil. The Florisil column was rinsed with 60 mL of hexane, leaving the hexane just covering the column of Florisil and sodium sulfate.

3.9 Florisil Clean Up of PAH Extract

1) The hexane/PAH extract was pipetted from the sample vial into the Florisil column. The sample vial was rinsed three times with hexane and pipetted from the vial into the column.

2) The Kuderna-Danish apparatus was placed under the Florisil column and the column needle valve was opened to start a steady drip. A 6% ether/hexane was pipetted in the

column in order not to disturb the hexane/PAH extract as the column continuously dripped. When 10 cm of solution remained above the column, the rest of the 200 mL of 6% ether/hexane was poured into the column. A new Florisil column was made for each hexane/PAH extract sample, as the columns accumulated many impurities.

3.10 Kuderna-Danish Concentration

1) The Kuderna-Danish concentration procedure previously described in section 3.6 was repeated to concentrate the PAH extract to 1-2 mL again. Samples were placed in appropriately marked vials.

3.11 Nitrogen Cleaning

A Sillitherm hotplate was used to maintain a temperature of 55-59 C. (Hexane boils at 60 C). The glass sample vials were placed onto the hot plate and nitrogen gas was applied to each vial. The gas was maintained at a flow that was barely blowing into the sample. The PAH extract was reduced to 1 mL in the sample vial. The sample vial was now prepared for High Performance Liquid Chromatography (HPLC).

On January 20, 1994 two subsamples of sediment from the Lowellville, Ohio bottom sediment, two subsamples of sediment from the Campbell, Ohio bottom sediment, and a blank (no sediment) were prepared for HPLC analysis using

the above procedures. They were analyzed for PAH on February 11, 1994.

3.12 Analysis of PAH in the Dissolved Phase

A procedure by J.T. Baker Inc. (1991) was used to analyze PAH in the Mahoning River sediment pore water and water column after many failed attempts using C-18 extraction columns from the Youngstown State University Biology Lab. This procedure uses Empore Extraction Disks to provide a rapid, efficient alternative to liquid / liquid extraction for sample preparation. The advantages of Empore Extraction Disks include reduced solvent usage, rapid sample throughput, and reduced analytical interferences. The following procedure was used to analyze PAH in water.

3.12.1 Removal and Pretreatment of Pore Water

The Campbell, Ohio and Lowellville, Ohio sediment samples were centrifuged to obtain pore water samples. Approximately 12 pounds of sediment from each site was centrifuged at 12,000 x G to obtain 1000 mL of pore water.

The pH of each water sample was reduced to 2 using 6N HCl in order to retard microbiological growth. The Lowellville, Ohio pore water sample was filtered through 20-25 micron filter paper and refiltered with 8 micron filter paper. This pore water sample took over 12 hours to extract as the water was not filtered sufficiently. Particulate

matter collected on the C-18 disks and increased amounts of PAH were detected in the extract. The PAH concentrations of the Lowellville water filtered through an 8 micron filter was later compared with PAH levels in water that was filtered through a 0.45 microns filter.

All other pore water and desorption water samples were prefiltered in 4 steps with a 20-25 microns filter, an 8 micron filter, a 1 micron filter, and a 0.45 micron filter. Following the collection of 1000 mL of sample water, 5 mL of methanol was added to the sample and mixed well.

3.12.2 Disk Conditioning

Disk conditioning with methanol is a critical step for successful extraction. Disk conditioning provides for good interaction between the non-polar bonded phase and the polar sample matrix. *Failure to condition properly will result in erratic and low recoveries*.

* An Empore C-18 extraction disk was placed in a disk holder, making sure the disk covered the frit.
* 10 mL methylene chloride/ethyl acetate (1:1) was added to the disk. With the vacuum off, this was allowed to stand for three minutes. The solvent was then drawn through the disk, and dried under vacuum for one minute. With the vacuum off, 10 mL of methanol was added and allowed to stand for three minutes. The vacuum was applied to draw most of the methanol through the disk, and released before the disk

ran dry. A meniscus of methanol remained just above the top of the disk. *The disk must not be allowed to run dry.*

3.12.3 Sample Extraction

Initially, a sample was added to the disk by pipette and a vacuum applied. The remaining sample was poured into the apparatus. This was drawn through the disk at the maximum possible flow rate. Then the vacuum was released. Recoveries are not significantly affected by the flow rate. Flow rate can be adjusted across a broad range from 5 to 45 minutes for a 1 liter sample. Processing time is dependent on vacuum source and particulate matter content. The rate of flow through individual extraction disks may vary (J.T. Baker Inc., 1991).

3.12.4 Sample Elution

Air was drawn through the disk for 15 minutes with a vacuum to remove residual water from the disk. An appropriate collection vessel was placed below the disk. The collection vessel was rinsed with 10 mL of ethyl acetate. 10 mL of ethyl acetate was added to the disk and allowed to stand for 3 minutes. 5 mL of ethyl acetate was drawn through under vacuum. The remaining ethyl acetate was allowed to stand for 3 minutes. The last of the ethyl acetate was drawn through. 10 mL of methylene chloride was then added to the disk. This was allowed to stand for 3

minutes and 5 mL was drawn through. The remaining methylene chloride was allowed to stand for 3 minutes and drawn through. The eluent were combined and dried by pouring over 3 grams of anhydrous sodium sulfate. The mixture was concentrated by a nitrogen cleanup to 1 mL. The sample was then ready for HPLC analysis (J.T. Baker Inc., 1991).

The procedures described in Sections 3.4 to 3.12 were used to prepare sediment, pore water, and desorption water samples for HPLC analysis.

The Lowellville, Ohio pore water was extracted on December 15, 1993 and analyzed for PAH using HPLC on December 17, 1993. The Campbell, Ohio pore water was extracted on January 20, 1994 and analyzed for PAH using HPLC on February 11, 1994.

3.13 PAH Desorption Analysis

On February 13, 1994 desorption research was conducted to simulate an actual dredging of the Mahoning River and to study the solids concentration effect. The sediments used in this research were subsamples from Lowellville, Ohio and Campbell, Ohio. The water used in the desorption experiments was collected from the Mahoning River at Newton Falls, Ohio. Approximately 10 liters of Newton Falls water was acquired and refrigerated at 4 C. The Newton Falls, Ohio water was analyzed for PAH using the J.T. Baker water analysis method and HPLC. It was determined to be PAH-free.

The desorption experiment was conducted using a laboratory shaker device that was capable of holding a 1500 mL Erlenmeyer flask. In the desorption experiment, the Newton Falls, Ohio water and sediment subsamples from Lowellville, Ohio and Campbell, Ohio were mixed at a 4 to 1 ratio to simulate a dredging.

The Campbell and Lowellville sediments were first freeze dried. Then, 300 grams of each sediment sample were mixed with 1200 mL of Newton Falls water and shaken for 24 hours. The water/sediment solutions were allowed to settle for 8 hours. No particulate matter was visible in the water column of the Erlenmeyer flask. The water was decanted off the top of the sediment and poured into a labeled amber jar. After shaking, the sediment was centrifuged and the sediment pore water was collected and poured into the same marked amber jar. The pH of the resulting water samples was reduced from 6.97 to 2.00 by adding 6N HCl. The sediments were freeze dried and placed in a properly labeled amber jar.

The sediments were prepared using the sediment analysis procedures described in sections 3.5-3.11. The supernatant samples were prepared using the method described in section 3.12. These desorption experiment samples were analyzed for PAH using HPLC on March 13, 1994.

3.14 Solids Concentration Effect

The solids concentration effect was studied by conducting the above desorption experiment at a 12 to 1 water to sediment ratio. 100 grams of Campbell, Ohio and 100 grams of Lowellville, Ohio sediment were mixed individually with 1200 mL of Newton Falls, Ohio water. Both sediment and supernatant water from this experiment were analyzed for PAH using HPLC on March 13, 1994.

3.15 Analysis of PAH using HPLC

Sixteen PAH were analyzed using High Performance Liquid Chromatography (HPLC) at the Youngstown State University Biology Laboratory. The sixteen PAH analyzed include:

Naphthalene	Acenaphthylene
Acenapthene	Fluorene
Phenanthrene	Anthracene
Fluoranthene	Pyrene
Chrysene	Benzo(a)anthracene
Benzo(b)fluoranthene	Benzo(k)fluoranthene
Benzo(a)pyrene	Dibenz(a)anthracene
Benzo(ghi)perylene	Ideno(1,2,3-cd)pyrene.

The HPLC was standardized by running a known factory PAH standard separately in a 1 mg/L sample and a 10 mg/L sample. The external PAH standard amount was plotted against the area under the curve of the chromatograph using the HPLC apparatus. Calculations of the slope and intercept were performed. The PAH concentrations in the field samples were determined by the linear equation:

$$y = mx + b \qquad (3.2)$$

where:

y = area of chromatograph factory for factory PAH standard

m = slope of line of area of chromatograph vs. concentration of factory standard PAH

x = concentration of field PAH sample (ppm)

b = intercept of chromatograph vs. concentration of factory standard PAH.

Rearranging the reciprocal of this linear relationship results in the equation:

$$x = \frac{1}{m}(y - b) \qquad (3.3)$$

or, field PAH concentration (ppm) = [reciprocal of the slope] x ([area of the chromatograph] - [intercept of chromatograph vs. concentration of factory standard PAH]).

The concentration of Mahoning River PAH (ppm) was calculated using the original standards set by the Youngstown State University Biology Laboratory on October 18, 1993. Subsequent improvements of these standards have been produced since that date. The following equations were used to calculate PAH concentrations (ppm):

concentration of Naphthalene = [1.4577*10^-4 * area] + 0.1021

concentration of Acenaphthylene = [3.4169*10^-4 * area] + 0.15119

concentration of Acenapthene = [2.1742*10^-4 * area] + 0.17979

concentration of Fluorene = [4.2839*10^-4 * area] + 0.50947

concentration of Phenanthrene = [3.3194*10^-4 * area] + 0.25729

concentration of Anthracene = [1.5441*10^-4 * area] + 0.30047

concentration of Fluoranthene = [4.4783*10^-4 * area] + 0.19232

concentration of Pyrene = [1.7785*10^-4 * area] + 0.15237

concentration of Chrysene = [2.5953*10^-4 * area] + 0.21645

concentration of Benzo(a)anthracene = [3.3801*10^-4 * area]+ 0.19814

concentration of Benzo(b)fluoranthene = [9.3227*10^-4 * area]+ 0.17207

concentration of Benzo(k)fluoranthene = [5.0516*10^-4 * area]+ 0.4051

concentration of Benzo(a)pyrene = [6.7951*10^-4 * area] + 0.28663

concentration of Dibenz(a)anthracene = [2.4325*10^-4 * area]- 1.7353

concentration of Benzo(ghi)perylene = [4.9043*10^-4 * area]+ 0.23058

concentration of Ideno(1,2,3-cd)pyrene = [4.7808*10^-4 * area]+0.23306

(Youngstown State University Biology Laboratory unpublished, 1993)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 PAH Concentrations in Mahoning River Sediment

The results of PAH concentrations in Mahoning River bottom sediment samples from Lowellville, Ohio and Campbell, Ohio are presented in the Table 4.1. The Ohio Environmental Protection Agency water standards for PAH concentrations are 28 nanograms per liter (ng/L) for drinking water and 311 nanograms per liter (ng/L) for aquatic life habitat (Ohio EPA, 1993). The Ohio Environmental Protection Agency has no standards for aquatic bottom sediment.

The sediment PAH concentrations recorded at Mahoning River miles of approximately 16 and 12 by the U.S. EPA (1986), unpublished data from Schroeder (1993), and the results of this study (1993-1994) are all within similar ranges.

Table 4.2 compares the PAH results of this study with previous studies. As explained in Chapter II, a PAH ratio (column 4 of Table 2.13) greater than 1 indicates a sediment PAH concentration greater than that reported for the Black River sediment, which is under a fish consumption advisory. Based on this data, the Campbell sediment at river mile 16 and the Lowellville site at river mile 12 were more contaminated than the Black River. Although this evaluation is limited because not all PAH detected were common to both

Table 4.1

PAH Analysis of Mahoning River Bottom Sediments
Sediment Concentration (mg/kg)

PAH	Lowellville	Campbell
Naphthalene	6.4	7.16
Anthracene	ND	8.14
Phenanthrene	ND	12.12
Benzo(ghi)perylene	38.0	163.52
Benzo(k)fluoranthene	307.89	550.82
Benzo(b)fluoranthene	202.04	561.17
Benzo(a)pyrene	255.62	882.02
Benzo(a)anthracene	31.15	76.11
Dibenzo(a)anthracene	25.71	89.74
Chrysene	98.67	426.31
Ideno(123-cd)pyrene	85.82	225.33
Fluoranthene	124.8	ND
Total PAH	1178.1	3002.44

ND = Not Detected.

sites, and only some PAH are carcinogenic, the table does emphasize the extremely high level of PAH contamination in the Mahoning River.

The difficulty in assessing the natural degradation of PAH in the Mahoning River is that the deposits are highly localized in nature. An illustration of this is provided by U.S. EPA data (1986). The U.S. EPA (1986) recovered three distinct sediment samples at the Mahoning River 16.08 mile location and three different total PAH concentrations were detected. The total PAH concentrations for the samples were 3432 mg/kg, 126.5 mg/kg, and 168.2 mg/kg. The study by Schroeder (1993) and this research proves that the PAH concentration in the Mahoning River sediment is still excessive eight years later.

Table 4.2

Sediment PAH Contamination in the Mahoning River

River Mile	Data Source/Year	Total PAH ppm	PAH Ratio
Black River	Baumann/1982	1454	1.1
Mahoning River			
16.42	U.S. EPA/1986	23,210	15.98
16.29	U.S. EPA/1986	93,150	64.16
16.14	U.S. EPA/1986	53,460	36.82
16.08	U.S. EPA/1986	3432	2.36
16.08	U.S. EPA/1986	126.5	0.08
16.08	U.S. EPA/1986	168.2	0.11
12.36	U.S. EPA/1986	70.5	0.04
16.0	Schroeder/1993	8348	5.74
16.0	Schroeder/1993	3482	2.39
16.0	Schroeder/1993	176,813	121.6
12.0	Schroeder/1993	275	0.19
12.0	Schroeder/1993	5306	3.65
12.0	Schroeder/1993	962	0.66
12.0	Schroeder/1993	1028	0.70
0.0	Schroeder/1993	0	0.0
0.0	Schroeder/1993	924	0.64
16.0	Testa/1994	3002	2.06
12.0	Testa/1993	1178	0.81

(Estenik, 1988; Schroeder unpublished, 1993)

4.2 PAH Concentrations in Mahoning River Sediment Pore Water

The results of PAH measurements on the pore water at the Lowellville and Campbell sites are presented in Table 4.3. The Lowellville pore water was prepared with less filtration than the Campbell pore water, therefore direct comparison of PAH concentrations in the pore water of the two sites should not be attempted. The Lowellville pore water was filtered through 20 micron and 8 micron filters,

Table 4.3

Concentration of PAH in Mahoning River Pore Water at Campbell, Ohio and Lowellville, Ohio (ng/L)

PAH	Lowellville Pore Water *	Campbell Pore Water**	Comments
Naphthalene	170	ND	
Fluoranthene	2400	ND	
Phenanthrene	2700	1600	
Anthracene	960	ND	
Benzo(k)fluoranthene	4300	ND	Carcinogen
Benzo(b)fluoranthene	6000	12,000	Carcinogen
Benzo(a)pyrene	3400	ND	Carcinogen
Benzo(a)anthracene	3200	ND	Carcinogen
Chrysene	1200	3000	Carcinogen
Benzo(ghi)perylene	1500	ND	Carcinogen
Total PAH	25,830	16,600	
Total Carcinogenic PAH	19,600	15,000	

*Lowellville pore water filtered through 8 micron filter.

**Campbell pore water filtered through 0.45 micron filter.

U.S. EPA standards for total PAH: 28 ng/L for drinking water; 311 ng/L for aquatic life.

while the Campbell pore water was filtered through 20 micron, 8 micron, 1 micron, and 0.45 micron filters. Therefore, greater amounts of fine particulate matter passed onto the C-18 extraction disk from the Lowellville pore water than from the Campbell sample.

Although the only Ohio EPA standards for PAH are for drinking water (28 ng/L) and water for aquatic life (311 ng/L), no prior information of PAH concentration in the Mahoning River water column or pore water is available.

The PAH concentrations detected in the Mahoning River pore water at river miles 16 and 12 significantly exceed the Ohio EPA standards. PAH detected in the dissolved phase (filtered to 0.45 microns) of the Mahoning River pore water at the Campbell, Ohio sampling site exceeded 16,000 ng/L. PAH observed in the pore water at the Lowellville, Ohio location exceeded 25,000 ng/L. However, the latter included greater amounts of colloidal and fine suspended matter.

If dredging of the Mahoning River took place, the pore water PAH would be initially released into dredge slurry or the water column in dissolved form. The fate of particulate PAH would depend on the time period that sediments remain in the water column, as well as the desorption behavior of the sediment-bound PAH.

4.3 Partition Coefficient (K'*p*) Analysis and Solids Concentration Effect

PAH have a strong affinity for aquatic particulates. The partition coefficient is a relationship that describes the distribution of PAH at equilibrium between the particulate and dissolved phases. This assists in predicting the fate and transport of PAH (Delos, et al., 1984). The higher the partition coefficient, the more total PAH concentration is in the particulate phase.

In situ partition coefficients (K'*p*) were calculated for individual PAH when detectable concentrations were

obtained in both sediment and pore water. These coefficients are shown in Table 4.4.

Table 4.4

In Situ Partition Coefficient (K'p) for PAH in Campbell, Ohio Bottom Sediments (L/Kg)

PAH	Campbell Sediment/ Pore Water
Phenanthrene	7575
Benzo(b)fluoranthene	46,764
Benzo(a)anthracene	8737
Chrysene	142,103

In Situ Partition Coefficient (K'p) for PAH in Lowellville, Ohio Bottom Sediments (L/Kg)

PAH	Lowellville Sediment/ Pore Water
Naphthalene	37,647
Benzo(ghi)perylene	25,333
Benzo(k)fluoranthene	71,602
Benzo(b)fluoranthene	33,673
Benzo(a)pyrene	75,182
Benzo(a)anthracene	9734
Chrysene	82,225

- Campbell pore water filtered through 0.45 micron filter.
- Lowellville pore water filtered through 8 micron filter.

The in situ partition coefficients (K'p) of the Mahoning River were comparable to the in situ partition coefficients (K'p) of the Australian Brisbane River in a study by Kayal and Connell (1990). Table 4.5 compares these values of the Mahoning and Brisbane Rivers.

Table 4.5

In Situ Partition Coefficients (K'p) of the Mahoning River Bottom Sediments and Brisbane River Suspended Particulate Matter (L/Kg)

PAH	Campbell	Lowellville*	Site No.	Brisbane R.
Phenanthrene	7575	-	1	7142
			2	16,667
			3	40,769
			4	22,500
			5	13,846
			mean	20,147
Benzo(a)anthracene	8737	9737	1	13,333
			2	22,000
			3	66,000
			4	33,333
			5	20,000
			mean	30,000
Chrysene	142,103	82,225	1	14,286
			2	24,286
			3	107,500
			4	36,000
			5	22,500
			mean	41,750
Naphthalene	-	37,647	1	10,526
			2	12,273
			3	39,615
			4	10,000
			5	8400
			mean	17,054
Benzo(k)fluoranthene	-	71,602	3	60,000
			4	48,333
			5	68,000
			mean	42,000
Benzo(a)pyrene	-	75,182	1	21,667
			2	28,571
			3	53,750
			4	31,111
			5	30,000
			mean	33,684

* Lowellville pore water filtered through 8 microns.
\- Insufficient Data.

The differences in partition coefficients (K'p) are possibly due to: 1) the difference in organic content in the sediment compared to the literature; 2) the solids concentration effect; and 3) the low particulate phase concentration and high dissolved phase concentration of PAH for Lowellville due to 8 micron filtration.

4.4 Desorption Analysis

The dominant aquatic fate processes for PAH are the adsorption to and desorption from suspended particulate matter. PAH have a strong tendency to sorb to organic particulates. This provides the basis for the strong argument that the sorption of PAH to sediment is a function of the organic carbon content of the sediment (OC) and the octanol/water partition coefficient (Kow) of the compound. This study did not include analysis of the sediment for organic carbon, however, organics were very visible in each sample (tar, leaves, twigs, etc.). The Mahoning River at the Campbell, Ohio and Lowellville, Ohio sites had very silty, organic sediment near the banks of the river and very rocky sediment in the middle of the channel.

Table 4.6 displays the results of the desorption analysis on Lowellville, Ohio sediment and Table 4.7 summarizes the results of the desorpton evaluation on Campbell, Ohio sediment. The tables present the original concentration of PAH in the sediment, the final

Table 4.6
PAH Desorption Analysis of Mahoning River Bottom Sediments
at Lowellville, Ohio (mg/kg)

PAH	Sediment	4:1 Water/ Sediment	4:1 Percent Desorbed	12:1 Water/ Sediment	12:1 Percent Desorbed
Naphthalene	6.4	6.1	5%	ND	-
Anthracene	ND	3.38	-	2.62	-
Benzo(ghi)perylene	38.0	31.69	17%	13.97	63%
Benzo(k)fluoranthene	307.89	252.69	18%	179.11	41%
Benzo(b)fluoranthene	202.04	ND	-	114.93	43%
Benzo(a)pyrene	255.62	210.76	18%	142.58	45%
Benzo(a)anthracene	31.15	23.58	25%	17.15	45%
Dibenzo(a)anthracene	25.71	16.27	37%	9.32	64%
Chrysene	98.67	80.74	18%	49.77	50%
Ideno(123-cd)pyrene	85.82	71.67	16%	52.87	38%
Fluoranthene	124.8	ND	-	ND	-
Total PAH	1178.1	696.88	40%	582.32	51%

ND = Not Detected.

Table 4.7

PAH Desorption Analysis of Mahoning River Bottom Sediments
at Campbell, Ohio (mg/kg)

PAH	Sediment	4:1 Water/ Sediment	4:1 Percent Desorbed	12:1 Water/ Sediment	12:1 Percent Desorbed
Naphthalene	7.16	6.37	11%	4.03	44%
Anthracene	8.14	ND	-	6.21	23%
Phenanthrene	12.12	11.31	7%	6.39	47%
Benzo(ghi)perylene	163.52	110.61	32%	50.68	69%
Benzo(k)fluoranthene	550.82	454.61	18%	406.18	26%
Benzo(b)fluoranthene	561.17	ND	-	316.02	44%
Benzo(a)pyrene	882.02	790.79	10%	442.52	50%
Benzo(a)anthracene	76.11	57.89	24%	32.33	58%
Dibenzo(a)anthracene	89.74	64.99	28%	26.41	71%
Chrysene	426.31	306.23	28%	174.42	59%
Ideno(123-cd)pyrene	225.33	160.71	29%	113.97	49%
Total PAH	3002.44	1963.11	34%	1579.16	47%

ND = Not Detected.

concentrations of PAH in the sediment after desorption at both 4:1 and 12:1 water/sediment ratios, and the percent of the PAH desorbed from the sediment at each ratio.

The desorption study included HPLC analysis of PAH in the dissolved phase after equilibration with the Lowellville and Campbell sediments at the 4:1 and 12:1 sediment/water ratios. The results of the dissolved phase measurements were very low and a mass balance could not be accomplished due to analytical error. Further discussion of dissolved (or liquid) phase PAH is presented in Section 4.5.

The 4:1 water/sediment ratio desorption experiments were performed to simulate an actual dredging of the Mahoning River. The 4:1 ratio is a standard for dredging operations. Subsamples of Lowellville and Campbell freeze dried sediment were each mixed with Newton Falls PAH-free water at a 4:1 water/sediment ratio, shaken for 24 hours, then separated and analyzed.

The results of this experiment confirmed that PAH would desorb from the sediment and resuspend in the dissolved and colloidal phases. In the Lowellville 4:1 ratio experiment, approximately 40% (481 mg/kg) of the original total PAH concentration was desorbed from the sediment. Sediment phase concentrations of every PAH compound decreased during the desorption study. Naphthalene decreased by 5% (0.3 mg/kg), while 37% (8.83 mg/kg) of Dibenzo(a)anthracene was desorbed.

The concentration of total sediment PAH decreased by 34% (1039 mg/kg) in the Campbell 4:1 water/sediment ratio experiment. The sediment phase concentration of Phenanthrene was reduced by 7% (0.81 mg/kg) while Benzo(ghi)perylene decreased by 32% (52.91 mg/kg).

A subsample of Lowellville freeze dried sediment and Newton Falls PAH-free water were mixed at a 12:1 water/sediment ratio, shaken for 24 hours, then separated and analyzed. The concentration of total PAH in the Lowellville sediment was reduced by approximately 596 mg/kg or 51%, which is more than the amount desorbed (40%, or 481 mg/kg) from the sediment in the Lowellville 4:1 investigation. This illustrates that desorption increases as suspended solids concentration decreases. The total percent desorption was calculated using individual PAH compounds detected in the experiment.

The total PAH could not be compared accurately between the Lowellville 12:1 ratio and 4:1 ratio studies, since not every PAH compound was detected. However, the desorption of PAH compounds can be compared individually. For example, the concentration of the carcinogen Chrysene decreased by 49 mg/kg in the 12:1 ratio study, while it decreased by only 18 mg/kg in the 4:1 experiment. This also demonstrated that more PAH desorb at lower suspended solids concentrations.

A subsample from the original freeze dried Campbell sediment sample and PAH-free Newton Falls water were mixed

in the Campbell solids concentration effect experiment. Again, the concentration of total PAH desorbed (1423 mg/kg or 47%) from the Campbell sediment during the 12:1 ratio study was more than the amount (1039 mg/kg or 34%) of PAH desorbed in the 4:1 ratio investigation.

The Campbell 4:1 ratio and 12:1 ratio experiments were compared using individual PAH compounds. For example, the sediment phase concentration of the carcinogen Benzo(a)pyrene in the 4:1 ratio experiment decreased by 91.23 mg/kg, while the concentration of Benzo(a)pyrene was reduced by 439.5 mg/kg in the 12:1 ratio study. Thus, 4 times more Benzo(a)pyrene was desorbed in the 12:1 ratio study than in the 4:1 ratio experiment.

Sediment PAH analyse typically show high analytical variability. While the trend observed in this study seems reasonable, estimates of percent desorption probably have a high degree of uncertainty associated with them.

4.5 Analysis of Dissolved Phase PAH

The partition coefficient (K'p) for the desorption experiments could not be calculated. Although five PAH were detected in the supernatant from the desorption experiment, the concentrations were much too low to give a correct mass balance. The low concentrations are may be due to analytical error that caused a low extraction efficiency

using the C-18 disks. The lag time of about 1 month between extraction and analysis of desorption water may also have been a factor.

In an effort to estimate dissolved phase PAH concentrations in the desorption water, calculations were performed using the following equations and data from Tables 4.6 and 4.7.

The dissolved phase PAH for the 4:1 desorption experiment is calculated using equation 4.1.

$$Cw = \frac{Cs,i - Cs,f \ [\frac{mg\ PAH}{Kg\ sed.}]}{4 \qquad [\frac{Kg\ water}{Kg\ sed.}]} \qquad (4.1)$$

The dissolved phase PAH for the 12:1 desorption experiment is calculated using equation 4.2.

$$Cw = \frac{Cs,i - Cs,f \ [\frac{mg\ PAH}{Kg\ sed.}]}{12 \qquad [\frac{Kg\ water}{Kg\ sed.}]} \qquad (4.2)$$

where:

Cw = calculated dissolved PAH concentration (mg/L)

Cs,i = initial PAH concentration in sediment (mg/Kg)

Cs,f = final PAH concentration in sediment (mg/Kg).

The calculated dissolved phase concentrations are listed in Table 4.8.

Table 4.8

Results of Dissolved Phase PAH Calculations Following Desorption Experiments (mg/L)

A. Experiment with Lowellville Sediment

PAH	4:1 Water: Sediment Ratio	12:1 Water: Sediment Ratio
Naphthalene	0.08	-
Benzo(ghi)perylene	1.58	2.0
Benzo(k)fluoranthene	13.8	10.73
Benzo(b)fluoranthene	-	7.26
Benzo(a)pyrene	11.22	9.42
Benzo(a)anthracene	1.89	1.17
Dibenzo(a)anthracene	2.36	1.37
Chrysene	4.48	4.08
Ideno(123-cd)pyrene	3.54	2.75

B. Experiment with Campbell Sediment

PAH	4:1 Water: Sediment Ratio	12:1 Water: Sediment Ratio
Naphthalene	0.20	0.26
Anthracene	-	0.16
Phenanthrene	0.20	0.48
Benzo(ghi)perylene	13.23	9.4
Benzo(k)fluoranthene	24.05	12.05
Benzo(b)fluoranthene	-	20.43
Benzo(a)pyrene	22.81	36.63
Benzo(a)anthracene	4.56	3.65
Dibenzo(a)anthracene	6.19	5.28
Chrysene	30.02	20.99
Ideno(123-cd)pyrene	16.16	9.28

- Insufficient Data.

Except for Naphthalene and Phenanthrene, all of the dissolved phase PAH calculations exceed the solubility limits. Because of this, calculated partition coefficients

(K'p) are generally very low. For example, the partition coefficient (K'p) at Lowellville for Benzo(a)pyrene at the 4:1 water/sediment ratio was 18.8 L/Kg and the partition coefficient (K'p) for Benz(a)pyrene at the 12:1 water/sediment ratio was 15.1 L/Kg. It is possible that calculated liquid phase concentrations in Table 4.6 include PAH associated with collodial material. This PAH would not be truly dissolved.

Bockelen and Niessner (1993) state that the determination of PAH dissolved in aqueous media is often difficult. Results are influenced by losses in the sampling and enrichment steps or during storage. Pinto et al. (1994) assert that PAH losses are caused by sorption onto sample containers and dissolved organics. A preconcentration step using micelle-mediated methodology is used to prevent this and increase PAH recoveries. This study used the J.T. Baker PAH extraction method (1991) that did not include the micelle-mediated method.

The PAH concentrations detected in the supernatant of this study were much too low to calculate the proper partition coefficient (K'p) in the desorption experiments, which is needed to analyze the solids concentration effect. The low concentrations are most likely due to analytical error that caused a low extraction efficiency using the C-18 disks. The micelle mediated extraction step may yield better analytical results for dissolved PAH.

4.6 Overview

This Mahoning River study demonstrates that the PAH levels in the bottom sediment pore water are well above Ohio EPA standards. Also, there has been no noticeable decline in sediment PAH levels in the Mahoning River over the last eight years. Although PAH are known to be biodegradable (Varanasi, 1989), natural biodegradation does not appear to be occurring at any appreciable rate in the Mahoning River bottom sediments. The desorption experiments illustrate that a simple dredging of the river will resuspend PAH into the dredge slurry or water column in both dissolved and suspended particulate forms. A technique that minimizes "leakage" of sediment into the water column during dredging would be needed to avoid significant elevation of dissolved or colloidal PAH concentrations in the river.

CHAPTER V

SUMMARY AND CONCLUSIONS

5.1 PAH Concentrations in Mahoning River Bottom Sediments

The PAH concentration of the Mahoning River bottom sediments was above the PAH concentration of the Black River sediments, which is under a fish consumption advisory. The Mahoning River PAH deposits were highly localized in nature. The bottom sediments at approximate river mile 12 (Lowellville, Ohio) had a total PAH concentration of 1178.1 mg/kg. The total PAH concentration at river mile 16 (Campbell, Ohio) was 3002.44 mg/kg.

5.2 PAH Concentrations in the Mahoning River Pore Water

The Mahoning River pore water PAH concentration was above the Ohio Environmental Protection Agency standards for drinking water (28 ng/L) and water for aquatic life (311 ng/L). The pore water from river mile 16 was filtered to 0.45 microns and contained total PAH of over 16,000 ng/L. The pore water from river mile 12 was filtered to 8 microns and contained total PAH of about 26,000 ng/L. A greater amount of particulate matter was collected on the extraction disk for the river mile 12 sample.

5.3 The Partition Coefficient (K'*p*) and Solids Concentration Effect

The partition coefficient is a relationship that describes the distribution of PAH between the particulate and dissolved phases. The higher the partition coefficient, the more total PAH concentration is in the particulate phase, whereas the lower the partition coefficient, the more PAH is in the dissolved form.

The in situ partition coefficient (K'*p*) of seven PAH compounds in the Lowellville bottom sediments were calculated: Naphthalene-37,647 L/Kg; Benzo(ghi)perylene-25,333 L/Kg; Benzo(k)fluoranthene-71,602 L/Kg; Benzo(b)fluoranthene-33,673 L/Kg; Benzo(a)pyrene-75,182 L/Kg; Benzo(a)anthracene-9734 L/Kg; and Chrysene-142,103 L/Kg.

The in situ partition coefficients (K'*p*) of 3 PAH in the Campbell sediment were calculated: Phenanthrene-7575 L/Kg; Benzo(b)fluoranthene-46,764 L/Kg; and Chrysene-142,103 L/Kg.

These in situ partition coefficients (K'*p*) were comparable to in situ partition coefficients (K'*p*) of an Australian Brisbane River study (1990) and partition coefficient (K'p) values of the U.S. EPA (1979). The differences between the in situ partition coefficients (K'*p*) of this study and in situ partition coefficients (K'*p*) of other studies are possibly due to: 1) the organic content in

the sediment; 2) the solids concentration effect; and 3) the low particulate phase concentration and high dissolved phase concentration of PAH at Lowellville due to less filtration.

5.4 Desorption Analysis

The desorption analysis was conducted at a 4:1 water/sediment ratio, which simulated an actual dredging of the Mahoning River. In the Lowellville 4:1 ratio experiment, approximately 40% (481 mg/kg) of original PAH was desorbed from the bottom sediments. The concentration of individual PAH compounds in the Lowellville sediment decreased by 5% - 37%. The concentration of total sediment PAH decreased by 34% (1039 mg/kg) in the Campbell 4:1 water/sediment ratio experiment. The concentration of individual PAH compounds in the Campbell sediment decreased by 7% - 32%.

From the desorption experiment, it was concluded that dredging the Mahoning River would resuspend PAH into dredge slurry and possible water column above the Ohio EPA standards of 28 ng/L for drinking water and 311 ng/L for aquatic life. This study did not determine the length of time the PAH will remain in the water column.

The 12:1 water/sediment ratio experiment provided a method to study the solids concentration effect. This investigation was designed to test the theory that partition coefficient (K'p) decreases as suspended solids

concentration increases.

The concentration of PAH in the Lowellville sediment was reduced by 47% (596 mg/kg) in the 12:1 water sediment experiment compared to 34% (481 mg/kg) in the 4:1 water/sediment ratio. The concentration of PAH in the Campbell sediment decreased by over 51% (1423 mg/kg) in the 12:1 water/sediment ratio experiment compared to 40% (1039 mg/kg) in the 4:1 water/sediment ratio experiment. Desorption of PAH increased with less suspended solids.

5.5 Overview

There has been no noticeable decline in PAH levels in the Mahoning River in the past eight years. Natural biodegradation will apparently be a lengthy process. Dredging the Mahoning River would release dissolved PAH in the dredge slurry at concentrations greatly exceeding the Ohio EPA standards of 28 ng/L for drinking water and 311 ng/L for aquatic life. Dredging will create an environmental risk in the short term, however, it may be very beneficial for the river in the long run. Further studies are needed to determine the length of time that PAH will remain in the water column and the concentrations that will settle in the bottom sediments. Procedures for handling and disposal of dredged sediments must also receive careful consideration.

References

Adams, William J., James W. Barnett, and Richard A. Kimerle. 1992. Sediment Quality and Aquatic Life Assessment. Environmental Science and Technology, Vol. 20, No. 10, pp. 1865-1875.

Ahokas, J.T., et al. 1975. Metabolism of Polycyclic Hydrocarbons by a Highly Active Aryl Hydrocarbon Hydroxylase System in the Liver of a Trout Species. Biochem. Biophys. Res. Comm.,63:635.

Amendola, Gary A. and Donald R. Schregardus. 1983. Mahoning River Wasteload Allocation Study. U.S. EPA. Region V. Environmental Services Division. Eastern District Office. Westlake, Ohio.

Andelman, J.B. and M.J. Suess. 1970. Polynuclear Aromatic Hydrocarbons in the Water Environment. Bull. World Health Organization, 43:479-508.

Baker, J.T. 1991. *Extraction of PAHs from Water*, Bakerbond Application Note, (Phillipsburg, N.J.), p. EMP - 002.

Baumann, P.C., W.D. Smith, and Ribick, M. 1982. Hepatic tumor rates and polynuclear aromatic hydrocarbon levels in two populations of brown bullhead (Ictalurus Nebulosus). In: Cooke, M., Dennis, A.J., Fisher, G.L. (eds.) In: Polynuclear Aromatic Hydrocarbons, Sixth International Symposium on Physical and Biological Chemistry. Edited by M. W. Cooke, A.J. Dennis and G.I. Fisher. Battelle Press, Columbus, Ohio. pp. 93-102.

Bierman, Jr., V.J., J.V. DePinto, S.C. Martin, R. Raghunathan, P.W. Rodgers, and T.C. Young. Analysis of Organic Carbon Sediment-Water Exchange in Green Bay, Lake Michigan, USA. Wat. Sci. Tech. Vol. 28, No. 8-9, pp. 149-159, 1993.

Bockelen, Achim and R. Niessner. 1993. Combination of Micellar Extraction of Polycyclic Aromatic Hydrocarbons from Aqueous Media with Detection by Synchronous Fluorescence. Fresenius Journal of Analytical Chemistry. 346: 435-440.

Borneff, J. and H. Kunte. 1965. Carcinogenic Substances in Water and Soil. Arch. Hyg. (Berlin), 149: 226-243. *(German)*

Bowling, Haddock, and Allred. 1984. "Disposition of Anthracene in the Water and Aufwuchs Matrices of a Large Outdoor Channel Microcosm : A Data Set for Mathemathematical Simulation Models." Project Summary. U.S. EPA, Environmental Research Laboratory. Athens, Georgia, EPA-600/S-3-84-036.

Brungs, William A., et al. U.S. EPA. 1980. Ambient Water Quality Criteria for Polynuclear Aromatic Hydrocarbons. Office of Water Regulations and Standards Criteria and Standards Division. Washington D.C. EPA 440/5-80-069.

Cahnmaman, H.J. and M. Kuratsune. 1957. Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Waters. Anal. Chem., 29: 1312.

Callahan, Michael A., et al. U.S. EPA 1979. Water Related Environmental Fate of 129 Priority Pollutants, Volume II. Office of Water Regulations and Standards Monitoring and Data Support Division, Washington, D.C. EPA/440-79-029B.

Cooke, Marcus, Anthony J. Dennis, and Gerald L. Fisher. 1982. Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry. Sixth International Symposium Sponsored by: U.S. Environmental Protection Agency, Battelle's Columbus Laboratories, and the American Petroleum Institute. pp. 872-883. Battelle Press. Columbus, Ohio.

Delos, Charles G., et al. U.S. EPA. 1984. "Book II Streams and Rivers Chapter 3 Toxic Substances." Technical Guidance Manual for Performing Waste Load Allocations. Office of Water Regulations and Standards Monitoring and Data Support Division, Washington, D.C. EPA/440/4-84-022.

DiToro, D. M. 1985. A Particle Interaction Model of Reversible Organic Chemical Sorption. Chemosphere, 14: 1503-1538.

Division of Wildlife. 1989. "Swimming, Wading, Fish Consumption Advisory for Mahoning River." Wildlife News, ODNR. Division of Wildlife, District One, Dublin, Ohio.

Duffy, Robert and Dr. Lauren Schroeder. 1970. A Survey of Water Pollution in the Mahoning and Shenango Rivers, Unpublished manuscript, Youngstown State University, Youngstown, Ohio.

Estenik, John F., Toxics Advisor. Ohio EPA. 1988. Fish Tissue and Sediment Organic Chemical Evaluation Lower Mahoning River. Water Quality Monitoring and Assessment, June, 24, 1988.

Federal Register Part VIII. EPA 40 CFR Part 136. U.S. EPA. 1984. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Federal Register, Vol. 49 No. 209, Friday, October 26, 1984.

Brungs, William A., et al. U.S. EPA. 1980. Ambient Water Quality Criteria for Polynuclear Aromatic Hydrocarbons. Office of Water Regulations and Standards Criteria and Standards Division. Washington D.C. EPA 440/5-80-069.

Cahnmaman, H.J. and M. Kuratsune. 1957. Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Waters. Anal. Chem., 29: 1312.

Callahan, Michael A., et al. U.S. EPA 1979. Water Related Environmental Fate of 129 Priority Pollutants, Volume II. Office of Water Regulations and Standards Monitoring and Data Support Division, Washington, D.C. EPA/440-79-029B.

Cooke, Marcus, Anthony J. Dennis, and Gerald L. Fisher. 1982. Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry. Sixth International Symposium Sponsored by: U.S. Environmental Protection Agency, Battelle's Columbus Laboratories, and the American Petroleum Institute. pp. 872-883. Battelle Press. Columbus, Ohio.

Delos, Charles G., et al. U.S. EPA. 1984. "Book II Streams and Rivers Chapter 3 Toxic Substances." Technical Guidance Manual for Performing Waste Load Allocations. Office of Water Regulations and Standards Monitoring and Data Support Division, Washington, D.C. EPA/440/4-84-022.

DiToro, D. M. 1985. A Particle Interaction Model of Reversible Organic Chemical Sorption. Chemosphere, 14: 1503-1538.

Division of Wildlife. 1989. "Swimming, Wading, Fish Consumption Advisory for Mahoning River." Wildlife News, ODNR. Division of Wildlife, District One, Dublin, Ohio.

Duffy, Robert and Dr. Lauren Schroeder. 1970. A Survey of Water Pollution in the Mahoning and Shenango Rivers, Unpublished manuscript, Youngstown State University, Youngstown, Ohio.

Estenik, John F., Toxics Advisor. Ohio EPA. 1988. Fish Tissue and Sediment Organic Chemical Evaluation Lower Mahoning River. Water Quality Monitoring and Assessment, June, 24, 1988.

Federal Register Part VIII. EPA 40 CFR Part 136. U.S. EPA. 1984. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Federal Register, Vol. 49 No. 209, Friday, October 26, 1984.

Giesy, John P., S.M. Bartell, P.F. Landrum, G.J. Leversee, and J.W. Bowling. U.S. EPA. 1983. "Fates and Biological Effects of Polycyclic Aromatic Hydrocarbons in Aquatic Systems." Project Summary. Research and Development Agency, Athens, Georgia. EPA 600/53-83-053.

Guerrero, H., et al. 1976. High-pressure Liquid Chromatography of Benzo(a)pyrene and Benzo(g,h,i)perylene in Oil-contaminated Shellfish. Jour. Assoc. Off. Anal. Chem., 59: 989.

Gschwend, P.M., and S. Wu. 1985. On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants. Environmental Sci. Technology., 19:90-96.

Harnisch, William J., 1971. Statement of the Steel Companies on the Mahoning River Before the Ohio Water Pollution Control Board Youngstown, Ohio. Unpublished manuscript, Youngstown State University, Youngstown, Ohio.

Harrison, R.M., R. Perry, & R.A. Wellings. 1975. Polynuclear Aromatic Hydrocarbons in Raw & Potable Waters & Wastewaters. Water Res., 9:331-346.

Harrison, R.M., R. Perry, and R.A. Wellings. 1976a. Effects of Water Chlorination Upon Levels of Some Polynuclear Aromatic Hydrocarbons in Water. Environmental Science Technology, 10: 1151-1156.

Il'nitiskii, A.P., K.P. Ershova, A.Y. Khesina, L.G. Rozhkova, V.G. Klubkov, and A.A. Korolev. 1971a. Stability of Carcinogens in Water and Efficacy of Methods of Decontamination. Hyg. Sanit. 36:9-13 *(Russian)*.

Inomata, M., and C. Nagata. 1972. Photoinduced Phenoxy Radical of 3,4-benzopyrene. Gann 63: 119-130.

Jones, Peter W., Paul E. Strup, and Joann E. Wilkinson. 1978. Trace Analysis of Polycyclic Aromatic Hydrocarbons in Aqueous Systems Using XAD-2 Resin and Capillary Column Gas Chromatography-Mass Spectrometry Analysis. Battelle Columbus Laboratories. Columbus, Ohio.

Karickhoff, S.W. 1984. Organic Pollutant Sorption in Aquatic Systems. J. Hydraulic Eng., 110:707-735.

Karickhoff, S.W., and K.R. Morris. 1985. Sorption Dynamics of Hydrophobic Pollutants on Natural Sediments. Water Res., 13: 241-248.

Kayal, Serhan I., and Des W. Connell. 1990. Partitioning of Unsubstituted Polycyclic Aromatic Hydrocarbons Between Surface Sediments and the Water Column in the Brisbane River Estuary. Australian Journal of Marine and Freshwater Research., 41, pp. 443-56.

Krahn, M.M., L.D. Rhodes, M.S. Myers, L.K. Moore, W.D. Macleod, Jr., D.C. Malins. 1986. Association Between Metabolites of Aromatic Compounds in Bile and the Occurrence of Hepatic Lesions in English Sole from Puget Sound, Washington. Archives of Environmental Contamination and Toxicology, 15, pp. 61-67.

Kuzia, Edward J. and John J. Black. U.S. EPA. 1985. Investigation of Polycyclic Aromatic Hydrocarbon Discharges to Water in the Vicinity of Buffalo, New York. Great Lakes National Program Office, Chicago, Illinois. EPA-905/4-85-002.

Lee, R.F. et al. 1972. Uptake, metabolism, and discharge of polycyclic aromatic hydrocarbons by marine fish. Marine Biology, 17:201.

Lee, R.F., W.S. Gardner J.W. Anderson, JW. Blaylock, and J. Barwell-Clarke. 1978a. Fate of Polycyclic Aromatic Hydrocarbons in Controlled Ecosystem Enclosures. Environmental Science Technology, 12:832-838.

Mackay, Donald and Powers, Bruce. 1987. Sorption of Hydrophobic Chemicals From Water: A Hypothesis for the Mechanism of the Particle Concentration Effect. Chemosphere, Vol. 16, No. 4, pp. 745-757.

Masuda, Y., and M. Kuratsune. 1975. Photochemical Oxidation of Benzopyrene. Int. J. Air Wat. Pollut. 10: 805-811.

Mills, Paul A. "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the A.O.A.C., Vol. 51, No. 1, pp. 20-32, 1968.

Mowrey, Tammy. Youngstown State University Biology Laboratory. 1994. Unpublished raw data.

Neff, Jerry M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment; Sources, Fate, and Biological Effects. Applied Science Publishers LTD, London.

O'Connor, D.J., and J.P. Connolly. 1980. The Effects of Concentration of Adsorbing Solids on the Partition Coefficient. Water Res., 14: 1517-1523.

Ohio Department of Health. 1983. Black River Fish Advisory and Technical Support Document.

Ohio EPA. 1986. Lower Mahoning River Basin Water Quality Technical Support Document. Final Draft. May 28, 1984 (Revised July 15, 1986). pp. 3-42 to 3-47.

Ohio EPA. 1989. "Wasteload Allocation for selected Mahoning River Dischargers." Division of Water Quality Monitoring and Assessment, Columbus, Ohio.

Ohio EPA. 1993. "State of Ohio Water Quality Standards." Chapter 3745-1 of Administrative Code. Division of Surface Water Standards and Toxic Section, Columbus, Ohio.

Pierce, R.C., and M. Katz. 1975. Dependency of Polynuclear Aromatic Hydrocarbon Content on Size Distribution of Atmospheric Aerosols. Environmental Science Technology, 9:347-353.

Pinto, Carmelo Garcia, J.L.P. Pavon, and B.M. Cordero. 1994. Cloud Point Preconcentration and High-Performance Liquid Chromatographic Determination of Polycyclic Aromatic Hydrocarbons with Fluorescence Detection. Analytical Chemistry, 66, pp. 874-881.

Schroeder, L.A. 1993. Polycyclic Aromatic Hydrocarbons in Mahoning River Sediment. Unpublished raw data.

Shackelford, W. and L.H. Keith.. 1976. Frequency of Organic Compounds Identified in Water. U.S. EPA, Office of Research and Development. Athens, Georgia, EPA-600/4-76-062.

Stegeman, J.J., B.R. Woodin, and R.L. Winder. 1981. Patterns of Benzo(a)pyrene Metabolism by Varied Species, Organs, & Developmental Stages in Fish. National Cancer Institute, Monograph No. 65. Woods Hole, Massachusetts.

Suess, M.J. 1972a. Laboratory Experimentation with 3,4-benzpyrene in Aqueous Systems and Environmental Consequences. Zblt. Bakt. Hyg. 155: 541-546.

Swietlik et. al. 1991. "Water Quality Criteria and Standards." Technical Support Document For Water Quality-based Toxic Control. U.S. EPA Office of Water, Washington, D.C. EPA/505/2-90-001.

Thomann, Robert V. and Mueller, John A. 1987. Principles of Surface Water Quality Modeling and Control. Harper Collins Publishers, New York, New York.

U.S. EPA. 1986. Polynuclear Aromatic Hydrocarbon Sediment Investigation. LTV Steel Corporation. Campbell, Ohio. U.S. EPA, Region 5. Environmental Services Division. Eastern District Office. Westlake, Ohio. p.11.

U.S. EPA. 1986. Polynuclear Aromatic Hydrocarbon Sediment Investigation. LTV Steel Corporation. Youngstown, Ohio and LTV Steel Corporation. Brier Hill, Ohio. U.S. EPA, Region 5. Environmental Services Division. Eastern District Office. Westlake, Ohio. pp.13.

U.S. EPA. 1986. Polynuclear Aromatic Hydrocarbon Sediment Investigation. LTV Steel Corporation. Warren, Ohio. U.S. EPA, Region 5. Environmental Services Division. Eastern District Office. Westlake, Ohio. pp.13.

U.S. EPA. 1990. Revision 3540A-6. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Proposed Rule," October 26, 1984.

Varanasi, Usha. 1989. Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. CRC Press Inc., Baco Raton, Florida.

Viessman, Jr. Warren and Mark J. Hammer. 1985. Water Supply and Pollution Control. Harper Collins Publishers. New York, New York.

West, W.R., P.A. Smith, G.M. Booth, S.A. Wise, M.L. Lee. 1986. Determination of Genotoxic Polycyclic Aromatic Hydrocarbons in a Sediment from the Black River (Ohio). Archives of Environmental Contamination and Toxicology, 15, pp. 241-249.