

# **Polycyclic Aromatic Hydrocarbons in Bottom Sediment and Bioavailability in Streams in the New River Gorge National River and Gauley River National Recreation Area, West Virginia, 2002**

By Terence Messinger

In cooperation with the National Park Service

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## Conversion Factors and Datum

Multiply	By	To obtain
<b>Length</b>		
inch (in.)	2.54	centimeter (cm)
mile (mi)	1.609	kilometer (km)
<b>Area</b>		
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )
<b>Volume</b>		
ounce, fluid (fl. oz)	0.02957	liter (L)
<b>Mass</b>		
ounce, avoirdupois (oz)	28.35	gram (g)
ton, short (2,000 lb)	0.9072	megagram (Mg)
<b>Concentration</b>		
ounce per pound (oz/lb)	62,500,000	nanograms per gram (ng/g)
ounce per pound (oz/lb)	62,500,000	micrograms per kilogram (µg/kg)
ounce per gallon (oz/gal)	7,489,151	microgram per liter (µg/L)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).



# Polycyclic Aromatic Hydrocarbons in Bottom Sediment and Bioavailability in Streams in the New River Gorge National River and Gauley River National Recreation Area, West Virginia, 2002

By Terence Messinger

## Abstract

Polycyclic aromatic hydrocarbons (PAHs), including some on the U.S. Environmental Protection Agency's priority pollutant list, were found in bottom sediment in streams in the coal-producing region of the Kanawha River Basin in 1996-1998, and in and near the New River Gorge National River in 2002, in concentrations exceeding those thought likely to cause adverse effects to wildlife. Very low concentrations of bioavailable PAHs were measured in streams in and near the New River Gorge National River by the use of semipermeable membrane devices. The apparent contradiction between the high concentrations of total PAHs and the low concentrations of bioavailable PAHs may result from the presence of a substantial amount of particulate coal in bottom sediment.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds (Sander and Wise, 1997). Many PAHs are toxic or carcinogenic, and were the first compounds to be linked to cancer in humans, among London chimney sweeps in the 1700s (Agency for Toxic Substances and Disease Registry, 1995). PAHs are found in petroleum, coal, and as products of combustion; they are produced by humans most commonly as a byproduct of fossil fuel combustion.

PAHs were measured in bottom sediment in streams of the Kanawha River Basin in 1996-1998 in concentrations at which adverse effects to aquatic life are thought to be probable (Paybins and others, 2001). One site in the New River Gorge National River and another site in the Gauley River National Recreation Area were among those where PAH concentrations were of concern. To determine if high concentrations of PAHs in bottom sediment posed a threat to wildlife, the U.S. Geological Survey (USGS), in cooperation with the National Park Service, studied PAH concentrations in bottom sediment and bio-

availability in five streams in the New River Gorge National River and the Gauley River National Recreation Area in the summer of 2002.

## Polycyclic Aromatic Hydrocarbons

The simplest "aromatic" hydrocarbon is benzene, which has a chemical formula of  $C_6H_6$  and a molecular weight of 78 (Streitweiser and others, 1992). In benzene, six carbon atoms are bonded in a ring, or cyclic, structure and some of the electrons are distributed around the ring, so that a single hydrogen atom is bonded to each carbon atom in the ring. A "polycyclic aromatic" hydrocarbon is one in which two or more aromatic rings are bonded together. The simplest PAH is naphthalene, the structure of which is two fused benzene rings. One or more of the hydrogen atoms bonded to an aromatic or polycyclic aromatic group may be substituted with an alkyl or other functional group. Alkyl-substituted PAHs are called "alkyl homologues" of the unsubstituted or "parent" molecules. Numbering of carbon atoms begins with the uppermost ring the furthest to the right in a diagram of the molecule, with the most counterclockwise carbon atom not involved with ring fusion (Sander and Wise, 1997). For example, 1,2-dimethylnaphthalene is an alkyl homologue of the parent naphthalene molecule, in which methyl groups have been substituted for the hydrogens at the first and second carbons clockwise around the ring depicted on the right from a carbon atom shared by the two rings.

PAHs do not ionize and are only slightly soluble in water (Moore and Ramamoorthy, 1984). The solubility of PAHs in water increases three- to four-fold with an increase in temperature from 5 to 30 °C. Dissolved and colloidal organic substances also increase the solubility of PAHs. Because they are only slightly water-soluble, PAHs entering a water body have a high affinity for suspended particles. PAHs sorb to these particles, and eventually settle out of the water column onto bottom sediment. Thus, the PAH concentrations in water are usually low relative to the concentrations in bottom sediment.

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Sixteen PAHs (acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, ideno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene) are on the U.S. Environmental Protection Agency's list of priority pollutants (U.S. Environmental Protection Agency, 2003). PAHs can harm human health; the principal modes of exposure to them are by inhaling airborne PAHs or eating them in smoked food (Agency for Toxic Substances and Disease Registry, 1995). PAHs are absorbed passively by fish, but are rapidly metabolized. PAHs in aquatic systems do not accumulate in fish tissue and are not considered to pose a direct risk to humans who eat fish from water bodies contaminated with PAHs. However, PAHs in high concentrations present a threat to aquatic life. High PAH concentrations in bottom sediment of Lake Erie tributaries were correlated with liver tumors in brown bullhead (Baumann and others, 1991; Smith and others, 1994). PAHs accumulate in some invertebrates; alkylated PAHs are thought to accumulate more readily than parent PAHs (Irwin and others, 1998).

PAHs are bioavailable only if they are dissolved (Huckins and others, 1996). Solubility of PAHs depends partly on their source. Soot, smoke, petroleum, and coal are common substances that are rich in PAHs. A great deal of work has been done to develop techniques to "fingerprint" PAH sources, in particular petroleum and different combustion sources (Yunker and others, 2002). Relatively little work has been done to develop PAH fingerprints for coal, partly because PAHs from coal are thought not to be bioavailable (Chapman and others, 1996; Hostettler and others, 1999).

### Purpose and Scope

The purpose of this report is to present the findings of a study of PAH bottom sediment concentrations and bioavailability, as measured with semipermeable membrane devices, done at five stream sites in the New River Gorge National River and the Gauley River National Recreation Area during the summer of 2002. To provide a context for these findings, this report discusses the previously uninterpreted results of a 1996-1997 U.S. Geological Survey (USGS) reconnaissance study of PAH concentrations in bottom sediment of streams throughout the Kanawha River Basin (Ward and others, 1998), and previously unpublished results of a 1998 USGS study of PAH concentrations in bottom sediment of streams that drain the part of the Kanawha River Basin, in West Virginia, where mineable coal is present. The relations between land use and PAH concentrations in bottom sediment from the 1996-1998 studies are briefly discussed to provide the rationale for the 2002 study.

### Description of Study Area

The New River forms in North Carolina, and flows north to Gauley Bridge, West Virginia, where it joins the Gauley

River to form the Kanawha River (fig. 1). The Gauley River forms in the Allegheny Mountains in central West Virginia. The New River Gorge National River, Gauley River National Recreation Area, and Bluestone National Scenic River are administered as a single management unit by the National Park Service to protect scenic canyons in south-central West Virginia. The New and Gauley Rivers inside National Park lands are heavily used by whitewater kayakers and rafters, and are considered to be world-class whitewater boating destinations (American Whitewater, 2003). The New River Gorge National River is between Bluestone Dam and the upstream limits of the pool formed by Hawks Nest Dam. The Gauley River National Recreation Area is downstream from Summersville Dam and upstream from Swiss, WV. The New, Gauley, and Bluestone Rivers, and the tributaries that enter them in national parks, all form upstream from park boundaries. As a result, the National Park Service manages streams that are influenced, and often degraded in quality, by activities outside the parks.

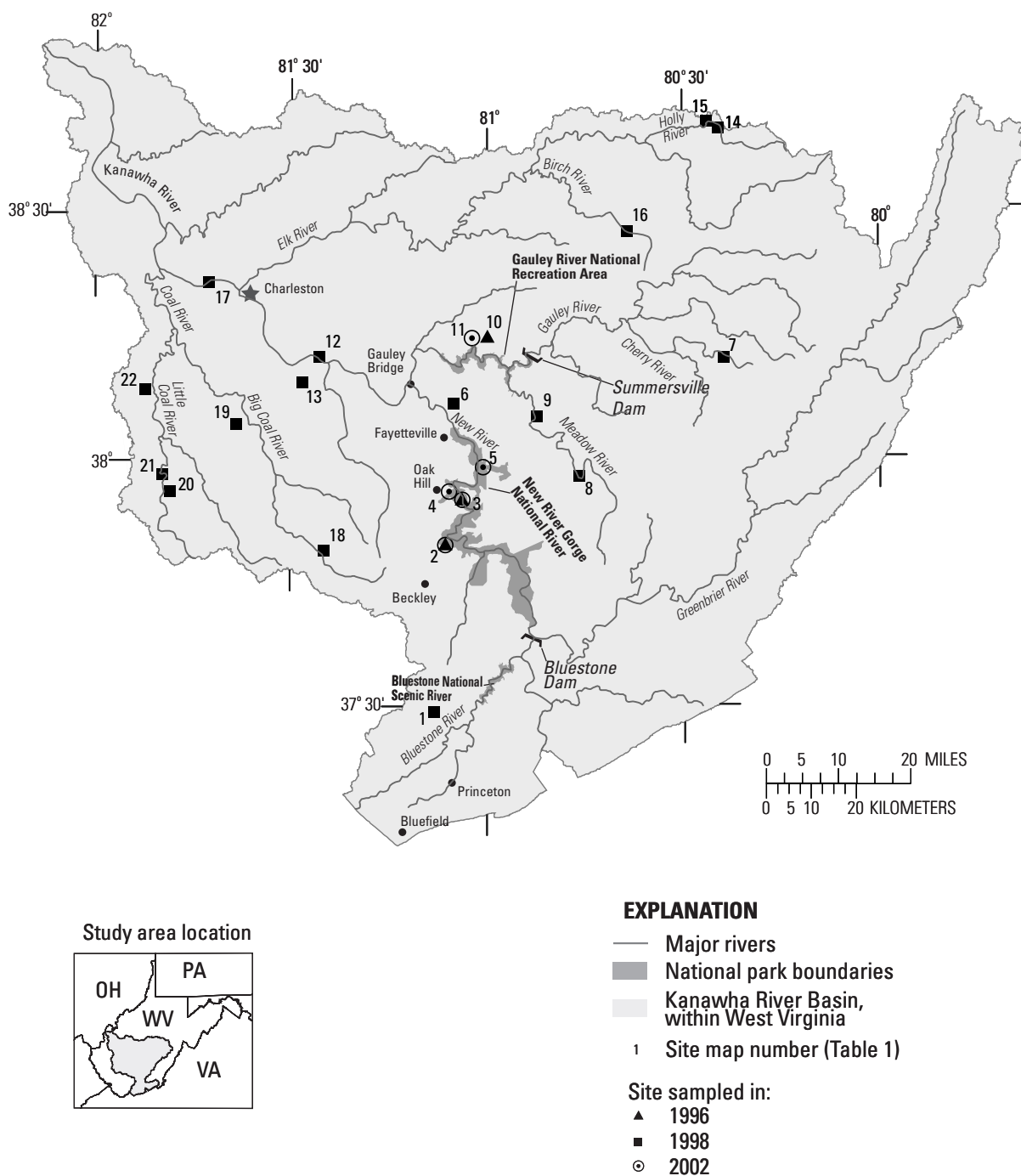
Most tributaries of the reaches of the New and Gauley Rivers managed by the National Park Service form in uplands and flow across a plateau, then plunge sharply as they approach the steep, rugged gorges. In their upstream reaches, these tributaries typically have low gradients, whereas in their lower reaches, they have steep gradients and coarse substrates associated with headwater streams.

The economy of the study area relies heavily on extractive industries such as coal mining and timbering, and historically, relied more heavily on these industries (Messinger and Hughes, 2000). Tourism, especially adventure tourism such as whitewater boating, rock climbing, and mountain biking, is now an important economic activity. Most of the population of the study area lives in rural areas, although cities and towns including Beckley, Mount Hope, Oak Hill, and Fayetteville are within basins draining to the New River Gorge.

Coal mining is an important economic activity in the study area (fig. 2). Land now managed by the National Park Service in West Virginia has an extensive history of mining, especially underground mining, that predates the creation of the parks. As a land use, coal mining is difficult to quantify (Paybins and others, 2001), for reasons including the following: (1) Unlike many other land uses, mining is three-dimensional instead of two-dimensional; seams are of different thicknesses, require different amounts of disturbance to overburden, and multiple seams may have been mined, one over the other, at different times; (2) the amount of drainage from mines differs greatly depending on factors such as mine depth, dip of the coal seams, and the mining method used; (3) both underground and surface mining may change the flow paths of water; (4) coal production may not be correlated with any measure of mining-related land disturbance; and (5) historical coal production information is limited and flawed. For these reasons, no effort was made in this report to quantify mining in the basins of the streams sampled in this study.

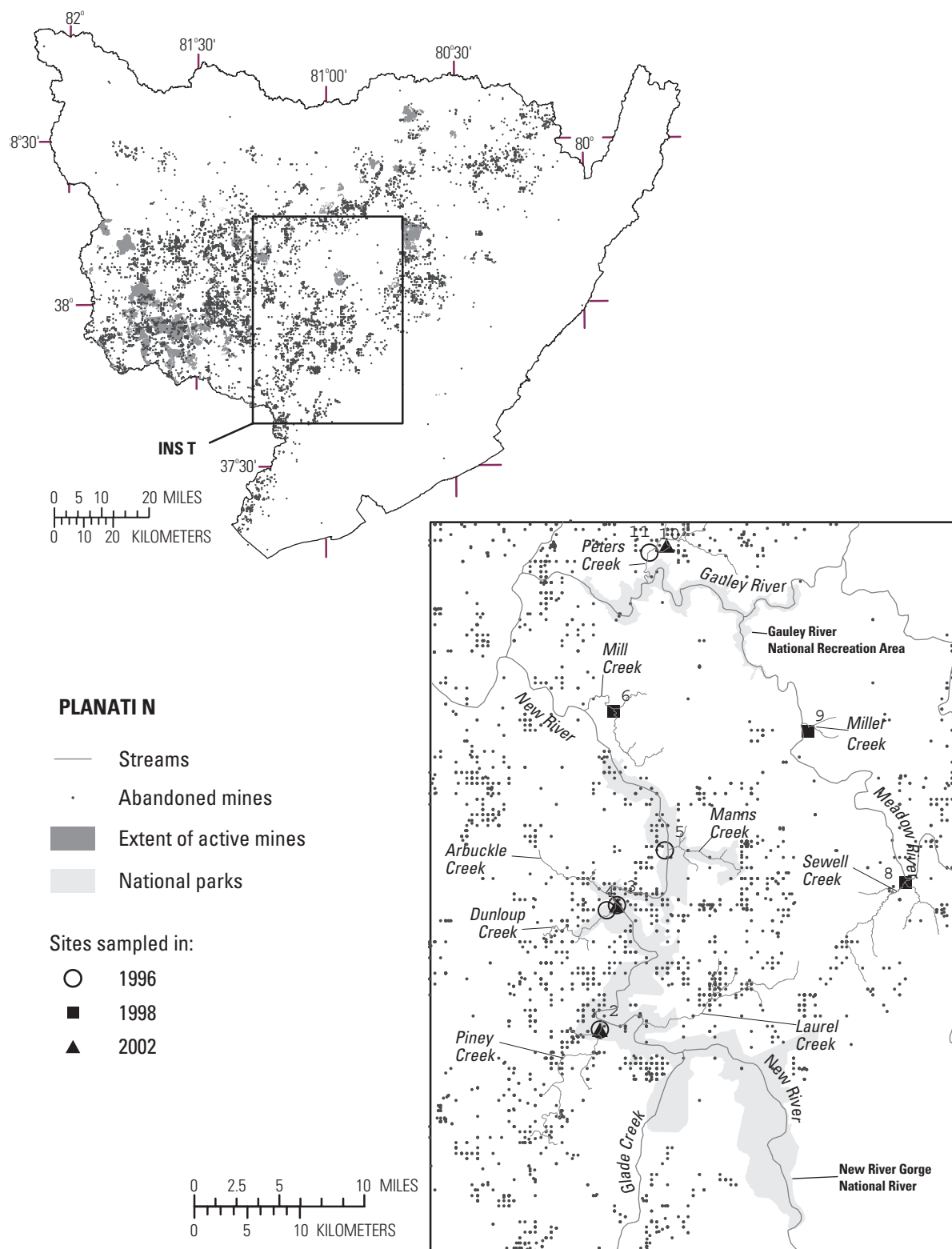
Several streams that drain to the New River Gorge were flooded in July 2001, from a series of thunderstorms that produced flows in excess of the 100-year recurrence interval in





**Figure 1.** Sampling sites, selected streams, towns, and national parks in the Kanawha River Basin, West Virginia.

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**Figure 2.** Coal mines in the Kanawha River Basin, and coal mines, selected streams, and sampling sites in and near the New River Gorge National River, West Virginia.

parts of southern West Virginia (Wiley and Brogan, 2003). Because the storm cells were extremely localized, some streams were flooded so severely that they were scoured to bedrock while flows in adjacent streams remained within the stream banks. The extreme nature of flood scouring in some New River Gorge tributaries influenced site selection in this study. In streams such as Arbuckle Creek and Laurel (Quinnimont) Creek, that were severely flooded and scoured to bedrock in 2001, the small amount of fine sediment that could be found in July 2002 was thought to be unrepresentative of fine sediment transported under normal conditions. On that basis, these streams were not sampled in favor of streams that did not flood, regardless of other basin characteristics.

## Acknowledgments

Julie A. Archer of Tango, West Virginia, volunteered her time to help with data collection during the summer 2002. Jesse Purvis, a fisheries biologist with the National Park Service at the New River Gorge National River, helped in site reconnaissance and provided helpful comments throughout the study.

## Data Collection and Study Design

Data discussed in this report were collected over several years (1996-2002) during the course of three separate studies. The initial data were collected in 1996 and 1997 as part of a reconnaissance study to determine the distribution of trace elements and organic contaminants in bottom sediment of streams, which was done as part of the USGS National Water Quality Assessment (NAWQA) Program, a broad assessment of water quality in the U.S. (Paybins and others, 2001). Stream sites sampled during this reconnaissance study were selected in the Kanawha River Basin to characterize important physiographic, geologic, and land-use characteristics. Bottom sediment was collected at 19 sites (Ward and others, 1998, 1999). At 12 of these sites, fish-community data were also collected (Messinger and Chambers, 2001). The 1996-1997 NAWQA study indicated that PAHs could be an important contaminant of bottom sediment in areas of the Appalachian Plateaus Province where coal was mined.

In 1998, as part of the NAWQA, parts of the Kanawha and Allegheny-Monongahela River Basins where coal is mined were studied, to characterize changes in water quality since the Coal Hydrology Program ended in 1981 (Ehlke and others, 1982; Paybins and others, 2001; Chambers and Messinger, 2001). At 16 stream sites, bottom-sediment samples were collected and analyzed for PAHs (fig. 1; table 1). At nine of these 16 sites, fish-community data were also collected (Messinger and Chambers, 2001). The PAH data from the 1998 study have not been published previously, but were an important consideration in planning the 2002 study, so they are presented and discussed here. Total 1980-1995 coal production, and other land-use characteristics, have been published for the areas drained by

all the streams sampled in this study (Chambers and Messinger, 2001).

For the current (2002) study, bottom-sediment samples were collected at five sites in the New River Gorge National River and Gauley River National Recreation Area during July and August 2002 and analyzed for PAHs. At these sites, semi-permeable membrane devices (SPMDs) were used to assess the bioavailability of PAHs in the streams during a 5-week period.

## Bottom Sediment

All bottom-sediment samples were collected from the top 2 centimeters of depositional areas that appeared to have been continuously underwater for the previous year (Shelton and Capel, 1993). At each site, a composite sediment sample was collected from ten or more depositional areas, on both sides of the stream, by dipping sediment with a teflon scoop into a glass bowl. The sample was homogenized, and sediment with a grain-size diameter smaller than 2 mm was rubbed through a pesticide-grade, methanol-rinsed stainless steel sieve into a glass jar, refrigerated, and shipped to the USGS National Water-Quality Laboratory within two days. All equipment used to collect and process sediment samples was washed and triple-rinsed in deionized water, then rinsed in methanol, and wrapped in aluminum foil until samples were collected.

Samples were analyzed for PAHs at the USGS National Water-Quality Laboratory, according to methods described by Furlong and others (1996). Surrogate compounds were added to the sample prior to extraction to verify method recoveries. Surrogate recoveries were within limits considered acceptable according to criteria cited by Furlong and others (1996).

The Method Reporting Limit (MRL), or the smallest measured concentration of a constituent that may be reliably reported using a given analytical method, was 50 g/kg for the 1996-1997 reconnaissance study, 5 g/kg for the 1998 regional coal-mining study, and varied by compound for the 2002 study. The method detection limit (MDL), the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero, was 5 g/kg for the 1996-1997 reconnaissance study, 1 g/kg for the 1998 regional coal-mining study, and varied by compound for the 2002 study. Concentrations of analytes that were less than the MRL but greater than the MDL were qualified as estimates. If a compound was not detected above the MDL, it was reported as less than the MRL. For example, a sample from 1998 with an estimated concentration of 2 g/kg of a constituent probably contained more of that constituent than a sample from 1998 with a reported concentration of <5 g/kg.

No field blanks were used in any of these studies, because sediment certified as free of organic compounds was not available. Duplicate samples were collected concurrently at two sites in the 1998 regional coal-mining study, Kellys Creek at Cedar Grove and Sewell Creek at East Rainelle. The average difference in PAH concentrations was 23 percent for the samples

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**Table 1.** Sampling sites in the Kanawha River Basin, West Virginia, and their map numbers, station numbers, and years sampled

Site	Map number (Figure 1)	Station number	Year[s] sampled
Camp Creek upstream from Mash Fork near Camp Creek	1	373017081080230	1998
Piney Creek near McCreery	2	375041081054201	1996, 2002
New River at Thurmond	3	03185400	1996, 2002
Dunloup Creek near Thurmond	4	375635081051601	2002
Manns Creek near Cunard	5	380001081013001	2002
Mill Creek near Hopewell	6	380715081045001	1998
North Fork Cherry River at Highway 39 Bridge	7	381312080234339	1998
Peters Creek near Lockwood	10	03191500	1996
Peters Creek near Lyonsville	11	381500081023101	2002
Sewell Creek at East Rainelle	8	375826080455339	1998
Miller Creek at Nallen	9	380624080521601	1998
Kellys Creek at Cedar Grove	12	381313081253739	1998
Cabin Creek at Dry Branch	13	381056081280839	1998
Davis Creek upstream from Trace Fork at Davis Creek	17	382032081423439	1998
Laurel Fork at Hacker Valley	14	384119080260139	1998
Left Fork Holly River near Replete	15	03195250	1998
Birch River at Boggs	16	382811080383339	1998
Sandlick Creek near Arnett	18	374928081245239	1998
Laurel Creek below Hopkins Fork at Hopkins Fork	19	380516081382139	1998
Spruce Laurel Fork at Clothier	20	375645081482339	1998
Hewitt Creek at Jeffrey	21	375814081493339	1998
Big Horse Creek at Altman	22	380952081520839	1998

from Kellys Creek, and 49 percent for the samples from Sewell Creek; the standard deviation among average differences in PAH concentrations was 17 percent for the samples from Kellys Creek and 12 percent for the samples from Sewell Creek. Part of the high relative difference among the duplicate samples from Sewell Creek can be explained by low concentrations of the PAHs. However, concentrations of 8 of 26 PAH compounds from the Sewell Creek site were reported as estimates because they were less than the MRL, although the average relative difference among estimated values was less (42 percent) than among measured values (52 percent).

### Semipermeable Membrane Devices

Semipermeable membrane devices (SPMDs) were obtained from Environmental Sampling Technologies (EST) Laboratories in St. Joseph, Missouri. The SPMD is composed of low-density polyethylene (LDPE) lay-flat tubing filled with high purity synthetic triolein, which represents a major portion of the lipid in fish (Huckins and others, 1990). Hydrophobic molecules that can pass through openings in the membrane are preferentially dissolved and retained in the lipid. SPMDs are not meant to estimate the approximate concentrations of organic contaminants in fish, but rather to estimate the amount of a contaminant available for uptake by animals.

The SPMDs were shipped from EST Laboratories in clean, sealed metal paint cans. When deployed, they were suspended in the water column in streams in anchored, stainless steel cages. Deployment locations were chosen to minimize visibility to passers-by. At four stream sites, SPMDs were deployed for one-week, two-week, and five-week intervals (table 2). At the fifth site, New River at Thurmond, three SPMDs were deployed and one was retrieved after one week; the other two were gone from the site at the next visit.

**Table 2.** Deployment dates and durations for semipermeable membrane devices

Site	Deployment time (in weeks)	Deployment date	Retrieval date
Piney Creek near McCreery	1	6/18/2002	6/25/2002
Piney Creek near McCreery	2	6/18/2002	7/2/2002
Piney Creek near McCreery	5	6/18/2002	7/18/2002
Dunloup Creek near Thurmond	1	6/18/2002	6/25/2002
Dunloup Creek near Thurmond	2	6/18/2002	7/2/2002
Dunloup Creek near Thurmond	5	6/18/2002	7/22/2002
New River at Thurmond	1	6/17/2002	6/24/2002
Manns Creek near Cunard	1	6/17/2002	6/24/2002
Manns Creek near Cunard	2	6/17/2002	7/1/2002
Manns Creek near Cunard	5	6/17/2002	7/19/2002
Peters Creek near Lyonsville	1	7/3/2002	7/10/2002
Peters Creek near Lyonsville	2	7/3/2002	7/18/2002
Peters Creek near Lyonsville	5	7/3/2002	8/7/2002

All SPMDs were lightly or moderately biofouled on retrieval, which probably slightly decreased the absorption of PAHs. SPMDs were returned to their cans after collection, and the cans were sealed, frozen, and stored until SPMD collection was complete. They were shipped, chilled, to EST. SPMDs

were cleaned, dialyzed in hexane, and 5 mL extracts were prepared by EST.

SPMD extracts were analyzed by the USGS National Water-Quality Laboratory. The instrumental analysis of the SPMD extracts is slightly modified from the sediment analysis procedure; parent PAHs were separated from their alkylated homologues, alkylated PAHs were identified according to the parent compound and the number of alkyl substitutions, but individual alkylated PAH homologues were not identified (Jana Iverson, U.S. Geological Survey National Water-Quality Laboratory, written commun., 2002). The MRL for the SPMD samples was 25 ng/g. As with the sediment samples, concentrations of analytes were estimated for values that were below the MRL but above the method detection limit, which was 1 ng/g, and these values are qualified as estimates. If a compound was not detected above the method detection limit, it was reported as less than the MRL.

SPMDs efficiently sequester PAHs and other organic compounds from the air, and therefore are easily contaminated by brief exposure to airborne PAHs, potentially even while an SPMD is exposed to air while being deployed. Because of this, for each SPMD deployed in the stream, a second SPMD was used as a trip blank. Each trip blank was exposed to the air while the deployed SPMD was moved from its can to the stream at deployment, from the stream to its can at retrieval, and analyzed according to the same procedure as the environmental SPMDs. One trip blank, for the SPMD deployed at Manns Creek near Cunard for two weeks, apparently was contaminated; concentrations of 31 PAHs were estimated for this blank at concentrations exceeding those estimated for the SPMD deployed in the stream. Naphthalene was measured in this blank at a concentration above the MRL. Naphthalene was also measured in the trip blank for the SPMD deployed at Dunloup Creek for five weeks; it was not measured above the MRL, however, in either of the environmental SPMDs these blanks were meant to check. The concentrations of PAHs in SPMDs discussed in this report were obtained by subtracting the concentration measured or estimated for the trip blank from the concentration measured or estimated for the environmental SPMD.

## PAHs in Bottom Sediment in Kanawha River Basin Streams, 1996-2002

During 1996-1998, as part of the NAWQA Program's study of the Kanawha River Basin, the USGS did two surveys of PAHs in stream-bottom sediment (Paybins and others, 2001). The first was a reconnaissance study of streams throughout the Kanawha River Basin of North Carolina, Virginia, and West Virginia. To determine which contaminants from a broad suite of organic compounds and trace metals were present, streams representing important land uses and physiographic and geological settings were sampled throughout the study area.

The second stream-bottom sediment contaminant survey was a component of a study done in 1998 to determine status

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and trends in the effects of coal mining on water quality throughout a region in the Central Appalachians (Paybins and others, 2001). This study was done in parts of the Kanawha, Allegheny, and Monongahela River Basins, on streams draining basins where mineable coal was present. Stream basins represented a gradient of mining intensity, and included some where no coal had been mined. PAH concentrations were measured in stream-bottom sediment from some sites in the Kanawha River Basin, but not from any sites in the Allegheny or Monongahela River Basins.

### Kanawha River Basin Reconnaissance Study, 1996-1997

Bottom sediment from 19 streams in the Kanawha River Basin was sampled during 1996 and 1997 to determine the distribution of PAHs and other contaminants (Messinger and Chambers, 1998; Ward and others, 1997, 1998; Paybins and others, 2001). The study area has previously been described (Messinger and Hughes, 2000). Six of the 12 PAHs for which criteria were available were found in concentrations exceeding those at which the Canadian Council of Ministers of the Environment (1999) found harmful effects to aquatic life to be probable (the Probable Effects Level, or PEL). The other six were found in concentrations exceeding those at which harmful effects were found to be minimal (the Threshold Effects Level, or TEL) (table 3) (Paybins and others, 2001). Some of the sites where the highest PAH concentrations were measured drained some of the most heavily mined subbasins in the study unit, although not all basins that yielded high PAH concentrations were heavily mined. The highest concentrations of PAHs measured (as a sum of measured and estimated concentrations of individual compounds) during any of the three studies were found in the 1996 sample from Peters Creek near Lockwood, a site on a stream that drains into the Gauley River National Recreation Area from a heavily mined basin.

In the 1996-1997 data, log-transformed total PAH concentration in bottom sediment was significantly correlated with the proportion of fish with external anomalies ( $R^2 = 0.43$ ,  $p = 0.03$ ). The external anomalies assessed included DELT (deformities, erosion [both dermal and fin], lesions, and apparent tumors) anomalies, which can be caused by exposure to toxic contaminants (Barbour and others, 1999); external parasites are assessed as part of the NAWQA Program, but were not included in this regression analysis.

### Regional Coal-Mining Study, 1998

To further investigate these findings, bottom sediment samples were collected for PAH analysis during a regional study of stream quality in the coal region (table 4, p. 15). PAH data were collected at 16 sites in the coal region in the Kanawha

**Table 3.** Probable effects level (PEL)<sup>1</sup> and threshold effects level (TEL)<sup>1</sup> for 12 polycyclic aromatic hydrocarbons.

[PAH, polycyclic aromatic hydrocarbon; concentrations are in micrograms per kilogram]

PAH	PEL	TEL
Acenaphthene	88.9	6.71
Acenaphthylene	128	5.87
Anthracene	245	46.9
benzo[a]anthracene	385	31.7
Benzo[a]pyrene	782	31.9
Chrysene	862	57.1
Dibenzo[a,h]anthracene	135	6.22
Fluoranthene	2,355	111
Fluorene	144	21.2
Naphthalene	391	34.6
Phenanthrene	515	41.9
Pyrene	875	53

<sup>1</sup>Source—Canadian Council of Ministers of the Environment, 1999

River Basin. When PAH and fish data from nine of those sites where fish data were collected were combined with the 1996-97 data, the relation between PAH concentrations and the proportion of fish with external anomalies (excluding parasites) was weaker than the relation from the 1996-1997 data, but was significant ( $R^2 = 0.321$ ,  $p = 0.01$ , with one outlying site excluded).

Among the sites sampled in the regional coal mining study, summed PAH concentrations ranged from 360 to 36,000 g/kg. The correlation between coal production and the sum of PAH concentrations in bottom sediment was significant ( $R^2 = 0.596$ ,  $p < 0.001$ ). The five sites on streams that drained basins with coal production exceeding 20 t/mi<sup>2</sup> were among the six sites with the highest summed PAH concentrations. Field crews observed a substantial amount of sand- or finer-sized coal particles in bottom sediment and benthic invertebrate samples collected from many streams, particularly those draining heavily mined areas.

Generally, PAHs in particulate coal are thought not to be bioavailable, based principally on the results of a toxicological study in saltwater (Chapman and others, 1996). However, the high PAH concentrations and the correlation of PAH concentrations with fish anomalies were of concern. Several possible explanations might have reconciled the apparent contradictions in the correlation between PAH concentrations and fish anomalies, the correlation between PAHs and coal production, and

PAHs in coal not being bioavailable. The PAHs might not have been, or might not primarily have been, from coal. PAHs in coal might have been bioavailable in freshwater systems. The PAHs in sediments might not have caused the fish anomalies themselves, but instead have been a marker for another stressor that was not measured. The correlation between PAH concentrations and fish anomalies might have been spurious, and merely a statistical artifact. The current study is an attempt to reconcile these contradictions and narrow down possible explanations.

## New River Gorge and Gauley River National Recreation Area Study, 2002

PAH concentrations measured in 2002 were generally greater than median concentrations from the two previous studies, but less than the 75th percentile of concentrations measured in those studies (table 5, p. 18). For the 24 PAHs measured in this study, all measurements at all sites (except for six measurements from Manns Creek near Cunard) exceeded the medians from the two previous studies. The lowest concentrations measured in 2002 for 22 of the 24 PAHs were in the sample from Manns Creek near Cunard. The highest concentrations of 17 PAHs, including 11 of the 12 for which criteria were available, were measured in the sample from New River near Thurmond. The highest concentration of four PAHs, including one (naphthalene) for which criteria were available, was measured in the sample from Peters Creek near Lyonsville, and the highest concentration of three PAHs was measured in the sample from Dunloup Creek near Thurmond.

For the twelve PAHs for which criteria were available, the bottom sediment concentration of only one PAH at one site, phenanthrene at New River at Thurmond, exceeded the PEL. PAH concentrations less than the TEL were measured in the sample from Manns Creek near Cunard, for five of the twelve PAHs for which criteria were available, and in the sample from Piney Creek near McCreery, for one PAH. All other PAH measurements from 2002 were between the TEL and PEL.

Direct comparison of summed PAH concentrations between the 1996 and 2002 samples from Piney Creek near McCreery and New River at Thurmond would not have been valid because the samples were analyzed with different detection limits. Linear regression of the detected analytes in common between the two samples (non-detected PAHs were excluded from the analysis) showed a weaker correlation between the Piney Creek samples ( $R^2 = 0.726$ ,  $p < 0.001$ ) than between the samples from the New River at Thurmond ( $R^2 = 0.870$ ,  $p < 0.001$ ). The Peters Creek samples, from different sites on Peters Creek, had a weaker correlation ( $R^2 = 0.577$ ,  $p < 0.001$ ) than the Piney Creek samples. To put the strength of these correlations in context, all of the correlations among the three New River tributary sites sampled in 2002 were stronger ( $R^2$  ranging between 0.905 and 0.946;  $p < 0.001$ ) than the strongest correlation between the 1996 and the 2002 samples, than

for New River at Thurmond. The correlations between Peters Creek and the three New River tributary sites were stronger ( $R^2 = 0.808, 0.828, 0.838$ ;  $p < 0.001$ ) than the correlation between the 1996 and 2002 samples from Piney Creek near McCreery. Three of the correlations between the 2002 samples from Thurmond and the smaller stream sites were the weakest among the 2002 samples ( $R^2$  ranging between 0.732 and 0.798;  $p < 0.001$ ), although the correlation between Dunloup Creek and New River at Thurmond was stronger ( $R^2 = 0.838$ ;  $p < 0.001$ ). The sampling technique is intended to characterize the fine-grained bottom sediment that would have been transported within the previous year (Shelton and Capel, 1993), so it is not particularly surprising that samples from the same stream several years later would be more weakly correlated than samples from streams near each other collected in the same year.

## Possible Sources of PAHs in Bottom Sediment

Efforts to distinguish sources of PAHs found in sediment have often concentrated on distinguishing between PAHs from petroleum and PAHs from combustion (Yunker and others, 2002; Stark and others, 2003). Only a few times, however, have researchers attempted to distinguish coal from combustion, or coal from petroleum, as sources of PAHs in sediment (Short and others, 1999; Hostetler and others, 1999). The rationale used to develop most of the metrics for distinguishing petroleum from combustion is differential rates of persistence in the environment among different PAH parent compounds or between parent compounds and alkylated homologues (Yunker and others, 2002). It would seem to suggest that these metrics could be useful in distinguishing PAHs from any mature sources such as petroleum or coal, from PAHs from recent sources, such as combustion of wood or fossil fuels.

However, when applied to coal, these metrics give results that are at best ambiguous. Values of these metrics overlap between coal and other plausible PAH sources in these basins, including some combustion sources. Additionally, most of the available information on the PAH composition of coal is from a single study, which was limited in scope to 27 samples from representative coal seams of Washington (Barrick and others, 1984). PAH-source metrics (Yunker and others, 2002), applied to bottom-sediment data from the Kanawha River Basin, generally did not indicate a combustion source was predominant for most basins. Beyond that, they were contradictory, complex, and did not clearly indicate what the sources were of most PAHs measured in these studies, possibly because of the limited available information of the composition of the aromatic fraction of coal. Coal was probably one of the major sources of PAHs measured in bottom sediment in this study, and the most compelling evidence is that particulate coal is often visible in sediment samples or sand bars in these streams.

## PAH Bioavailability in New River Gorge National River and Gauley River National Recreation Area streams, 2002

Only 3 PAHs were measured in SPMDs in only 4 of 13 SPMDs at concentrations high enough to report without qualifiers (exceeding the MRL, 25 g/g) (table 6, p. 20). Fluoranthene and pyrene were measured at concentrations less than twice the MRL in the 5-week SPMDs from Dunloup Creek near Thurmond and Piney Creek near McCreery. Naphthalene was measured at a concentration slightly greater than the MRL in the 1-week SPMD from New River at Thurmond.

Some PAHs were detected at concentrations less than the MRL for all SPMDs, and estimated concentrations were reported for these. The 5-week SPMD from Piney Creek near McCreery had the largest sum of estimated and measured PAH concentrations of any SPMD. The 1-week SPMD from New River at Thurmond, the only SPMD that was retrieved from that site, had the largest sum of PAHs of any 1-week SPMD, which indicates that New River at Thurmond may have had more bioavailable PAHs than any of the other sites. No SPMD from Manns Creek near Cunard had a concentration of PAHs exceeding that from any of the other SPMDs from this study. The ranks of sites in the sum of PAH concentrations in SPMDs was not the same as their ranks in total PAHs in sediment. The relative error

in these measurements was high as a result of the low PAH concentrations in the SPMDs relative to the MRL—most measurements were reported as estimated concentrations—which might affect the ranks.

SPMDs have the capacity to take up large amounts of PAHs if dissolved PAHs are present (Huckins and others, 1996, 1999). On the basis of uptake rate constants determined by Luellen and Shea (2002), estimates of PAH concentrations in SPMDs exposed for seven days to the lowest dissolved concentrations of selected PAHs that had been shown to have significant adverse biological effects (Germain and others, 1993) ranged between four and six orders of magnitude greater than the PAH concentrations measured in this study (table 7). Sustained dissolved PAH concentrations in streams were therefore much lower than concentrations that have significant biological effects.

SPMDs effectively detect episodic increases in organic contaminants, although a particular SPMD concentration of a compound could be the result of a brief exposure to a relatively high concentration of the compound, a prolonged exposure to a relatively low concentration of the compound, or an intermediate exposure to an intermediate concentration of the compound (Huckins and others, 1990). One way to assess the potential for significant episodic exposure of SPMDs to contaminants is to determine the time that an SPMD under ideal conditions for uptake might have been exposed to a biologically important

**Table 7.** Maximum polycyclic aromatic hydrocarbon (PAH) concentrations measured in semipermeable membrane devices (SPMDs) in streams managed by the National Park Service in West Virginia in 2002, with the lowest dissolved concentrations at which the PAHs had significant adverse biological effects, and estimates of the concentrations those PAHs would reach in SPMDs under exposure to the stated dissolved concentration at 20°C for the time the SPMD was deployed

[SPMD, semipermeable membrane device; g/L, microgram per liter; ng/g, nanograms per gram]

Compound	Threshold dissolved concentration <sup>1</sup> (g/L)	Estimated SPMD concentration at threshold <sup>2</sup> (ng/g)	Maximum observed SPMD concentration <sup>1</sup> (ng/g)	Deployment time <sup>2</sup> (weeks)
Acenaphthene	60	1,000	5.6	1
Anthracene	6.6	1,100	2.6	5
Benzo[a]anthracene	5.0	850	5.4	5
Benzo[a]pyrene	5.0	540	3.2	5
Benzo[k]fluoranthene	0.2	21.5	3.3	5
Fluoranthene	38	7,300	39.5	5
Fluorene	125	8,000	4.7	2
Naphthalene	10	480	54.2	2
Phenanthrene	8.0	560	17.2	2
Pyrene	91	20,000	43.8	5

<sup>1</sup>From Germain and others (1993)

<sup>2</sup>Determined using uptake rates from Luellen and Shea (2002)



contaminant concentration. Germain and others (1993) published concentrations of several PAHs at which acute toxic effects (effects caused by exposure to a contaminant for less than four days) were observed for some aquatic organisms. Exposure for about 80 seconds of an SPMD under ideal uptake conditions to benzo[a]pyrene at 1 g/L, a concentration at which acute toxic effects were observed in aquatic vertebrates, would have resulted in the maximum concentration of benzo[a]pyrene estimated in this study (table 8). For the other five PAHs for which data on acute toxic effects were available, the maximum exposure time under ideal uptake conditions at the lowest concentration for which acute toxic effects to aquatic vertebrates were reported ranged from less than 1 second to about 7 seconds. PAH concentrations reported to cause acute toxic effects to aquatic invertebrates were generally lower than those for aquatic vertebrates. Exposure for about 8 minutes of an SPMD under ideal uptake conditions to benzo[k]fluoranthene at 0.2 g/L, a concentration at which acute toxic effects were observed to aquatic invertebrates, would have resulted in the maximum concentration of benzo[k]fluoranthene estimated in this study (table 8). For the other seven PAHs for which data on acute toxic effects were available, the maximum exposure time under ideal uptake conditions at the lowest concentration for which acute toxic effects to aquatic invertebrates were reported ranged from less than 1 second to about 18 seconds.

This comparison of observed PAH concentrations in SPMDs to estimated concentrations and exposure times has limitations. Four of the possible problems include the following: (1) All the SPMDs that were deployed for this study were affected by moderate biofouling. Biofouling decreases PAH uptake by SPMDs, but moderate biofouling only decreases uptake moderately (Huckins and others, 1996). (2) The uptake rate constants published by Luellen and Shea (2002) included error terms as high as 21 percent of the rates. (3) The most recent review that compiled threshold and acute toxicity concentrations was published in 1993 (Germain and others, 1993). That study attempted to be as comprehensive as possible, and as a result, included some inconsistencies such as publishing a concentration at which acute lethal effects were observed that was lower than the concentration of the same compound at which acute sublethal effects were observed. Such inconsistencies suggest, and Germain and others (1993) point out, that the best available information on PAH toxicity is limited and may not be relevant to common environmental conditions. (4) The available toxicity data were obtained by exposing organisms to extremely high concentrations of single PAHs (Germain and others, 1993). Effects of low concentrations of PAHs, or of mixtures of PAHs, could be greatly different. Nevertheless, the differences are large between the observed PAH concentrations in SPMDs, and the concentrations estimated for SPMDs

**Table 8.** Maximum observed polycyclic aromatic hydrocarbon (PAH) concentration in semipermeable membrane devices (SPMDs), threshold concentration at which acute toxic effects were observed in aquatic vertebrates and invertebrates, and maximum exposure times under ideal uptake conditions for the observed concentrations in the SPMDs to be reached in a solution at the threshold concentration of the PAH

[ng/g, nanograms per gram; ng/L, nanograms per liter; min:sec, time in minutes and seconds]

PAH	Maximum observed concentration in SPMD (ng/g)	Lowest concentration producing acute effects, vertebrates <sup>1</sup> (ng/L)	Exposure time at acute threshold, vertebrates <sup>2</sup> (min:sec)	Lowest concentration producing acute effects, invertebrates <sup>1</sup> (ng/L)	Exposure time at acute threshold, invertebrates <sup>2</sup> (min:sec)
Acenaphthene	5.6	580,000	<0:01	60,000	0:02
Anthracene	2.6	6,600	:07	10,000	:05
Benz[a]anthracene	5.4	--	--	10,000	:10
Benzo[a]pyrene	3.2	1,000	1:29	5,000	:18
Benzo[k]fluoranthene	3.3	--	--	200	7:45
Fluoranthene	39.5	--	--	45,000	:14
Fluorene	4.7	820,000	<:01	212,000	<:01
Naphthalene	54.2	1,600,000	:01	1,000,000	:01
Phenanthrene	17.2	234,000	:01	96,000	:03
Pyrene	43.8	--	--	91,000	:07

<sup>1</sup>From Germain and others (1993)

<sup>2</sup>Determined using uptake rates from Luellen and Shea (2002)

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exposed to aquatic concentrations of PAHs known to be harmful to aquatic life, and indicate that the concentration of bioavailable PAHs was low in the streams that were studied in 2002.

The bioavailable portion of PAHs in streams in and near the New River Gorge appears to have been small during the summer of 2002. This is consistent with the idea that fine coal particles are the source of much of the PAH in bottom sediment of streams in this area. This suggests that the apparent relation between external fish anomalies and bottom-sediment PAHs in the mining region of the Kanawha River Basin may be spurious, or that PAHs are a marker for other stressors. Further investigation into the causes of external fish anomalies in this area could concentrate on other possible stressors.

### Summary and Conclusions

Polycyclic aromatic hydrocarbons, or PAHs, are a group of organic compounds, many of which are toxic or carcinogenic. PAHs do not ionize and are only slightly soluble in water. PAHs in aquatic systems do not accumulate in fish tissue and are not considered to pose a direct risk to humans who eat fish from water bodies contaminated with PAHs. However, PAHs in high concentrations present a threat to aquatic life. PAHs were measured in bottom sediment in streams of the Kanawha River Basin in 1996-1998 in concentrations at which adverse effects to aquatic life are thought to be likely. One site in the New River Gorge National River and another site in the Gauley River National Recreation Area were among those where PAH concentrations were of concern.

Data discussed in this report were collected over several years (1996-2002) by the U.S. Geological Survey in three studies. The initial data were collected in 1996 and 1997 as part of a reconnaissance study of the distribution of trace elements and organic contaminants in bottom sediment of streams, which was done as part of the National Water Quality Assessment (NAWQA) Program, a broad assessment of water quality in the United States. Six of the 12 PAHs for which criteria were available were found in concentrations exceeding those at which the Canadian Council of Ministers of the Environment (1999) found harmful effects to aquatic life to be probable (the Probable Effects Level, or PEL), and the other six were found in concentrations exceeding those at which harmful effects were found to be minimal (the Threshold Effects Level, or TEL). Some of the sites where the greatest PAH concentrations were measured drained some of the most heavily mined subbasins in the study unit, although not all basins yielding high PAH concentrations were heavily mined. The highest concentrations of summed PAHs measured during any of the three studies were found in the 1996 sample from Peters Creek near Lockwood, a site on a stream that drains into Gauley River National Recreation Area from a heavily mined basin.

In 1998, also as part of NAWQA, a study was done in parts of the Kanawha and Allegheny-Monongahela River Basins where coal is mined, to characterize changes in water quality

since the Coal Hydrology Program ended in 1981. The relation between the sum of PAH concentrations and the proportion of fish with external anomalies (excluding parasites) was weak but significant ( $R^2 = 0.321$ ,  $p = 0.01$ , with one outlying site excluded) among all sites where fish communities and bottom sediment were sampled. The correlation between coal production and the sum of PAH concentrations in bottom sediment was significant ( $R^2 = 0.596$ ,  $p < 0.001$ ), and the five sites on streams that drained basins with coal production exceeding 20 tons per square mile were among the six sites with the highest summed PAH concentrations. Field crews observed a substantial amount of sand- or finer-sized coal particles in bottom sediment and benthic invertebrate samples collected from streams, particularly those draining heavily mined areas. Generally, PAHs in particulate coal are thought not to be bioavailable. However, the high PAH concentrations, and the correlation of PAH concentrations and fish anomalies, were of concern.

Bottom sediment samples were collected at five sites in the New River Gorge National River and Gauley River National Recreation Area in July-August 2002 and analyzed for PAHs. At these sites, semipermeable membrane devices (SPMDs) were used to assess the bioavailability of PAHs in the stream during a 5-week period. PAH concentrations measured in 2002 were generally greater than median concentrations from the two previous studies, but less than the 75th percentile of concentrations measured in those studies. For the twelve PAHs for which criteria were available, the bottom sediment concentration of only one PAH at one site, phenanthrene at New River at Thurmond, exceeded the Probable Effects Level (PEL). PAH concentrations less than the Threshold Effects Level (TEL) were measured in the sample from Manns Creek near Cunard, for five of the twelve PAHs for which criteria were available, and in the sample from Piney Creek near McCreery, for one PAH. All other PAH measurements from 2002 were between the TEL and PEL.

Three PAHs were measured at concentrations greater than the Method Reporting Limit (MRL) (25 g/g) in only 3 of 13 SPMDs. Some PAHs were detected at concentrations less than the MRL for all SPMDs, and estimated concentrations were reported for these. The 5-week SPMD from Piney Creek near McCreery had the largest sum of estimated and measured PAH concentrations of any SPMD. The 1-week SPMD from New River at Thurmond, the only SPMD that was retrieved from that site, had the largest sum of PAHs of any 1-week SPMD, which indicates that New River at Thurmond may have had more bioavailable PAHs than any of the other sites. No SPMD from Manns Creek near Cunard had a concentration of PAHs exceeding that from any of the other SPMDs from this study. Estimates of PAH concentrations in SPMDs that would have been exposed in a laboratory for seven days to the lowest dissolved concentrations of selected PAHs that had been shown to have significant adverse biological effects ranged between two and four orders of magnitude greater than the PAH concentrations measured in this study. The low concentration of bioavailable PAHs measured suggests that coal may be the primary source of PAHs in the study area, and indicates that the apparent rela-

tion between external fish anomalies and bottom-sediment PAHs in the mining region of the Kanawha River Basin may be spurious, or that PAHs may be a marker for other stressors.

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**Table 4. Polycyclic aromatic hydrocarbon concentrations measured in fine bottom sediment at selected sites in coal-mining areas in the Kanawha River Basin in West Virginia, in July 1998**[All concentrations are in g/kg; E, estimated; <, less than; **bold type**, exceeding the Probable Effects Level<sup>1</sup>; *italic type*, between the Threshold Effects Level<sup>1</sup> and Probable Effects Level<sup>1</sup>]

Site	Sampling date	Acenaphthene	Acenaphthylene	Anthracene	Benz[a]anthracene	Benz[a]pyrene	Chrysene	Dibenz[a,h]anthracene	Fluoranthene
Camp Creek upstream from Mash Fork near Camp Creek	7/20/98	E0.84	E1.5	E3.2	10	10	19	E2.3	22
Mill Creek near Hopewell	7/28/98	E1.2	11	19	54	45	54	7.5	74
North Fork Cherry River at Highway 39 Bridge	7/23/98	5.0	E1.6	E1.9	6.5	6.3	14	E1.5	9.7
Sewell Creek at East Rainelle	7/22/98	E3.4	E4.1	13	38	35	58	6.7	98
Miller Creek at Nallen	7/23/98	E2.3	E1.4	5.0	6.1	6.5	20	E3.1	7.2
Kellys Creek at Cedar Grove	7/13/98	12	25	64	190	195	284	57	243
Cabin Creek at Dry Branch	7/13/98	27	46	108	242	198	400	56	278
Davis Creek upstream from Trace Fork at Davis Creek	7/13/98	E1.6	E3.6	7.2	32	33	42	5.6	80
Laurel Fork at Hacker Valley	7/14/98	E2.1	14	12	44	53	62	11	70
Left Fork Holly River near Replete	7/14/98	5.0	E1.7	E2	6.5	6.0	16	E1.5	11
Birch River at Boggs	7/16/98	E1.6	E3.7	5.6	31	26	64	7.6	44
Sandlick Creek near Arnett	7/23/98	E4.5	24	43	163	100	239	31	306
Laurel Creek below Hopkins Fork at Hopkins Fork	7/21/98	15	24	32	131	148	188	30	192
Spruce Laurel Fork at Clothier	7/29/98	5.8	5.0	8.9	56	38	118	13	48
Hewitt Creek at Jeffrey	7/14/98	5.2	11	25	82	93	119	29	130
Big Horse Creek at Altman	7/14/98	E0.82	5.0	5.0	19	22	20	E4	25

<sup>1</sup>Canadian Council of Ministers of the Environment (1999)

**Table 4.** Polycyclic aromatic hydrocarbon concentrations measured in fine bottom sediment at selected sites in coal-mining areas in the Kanawha River Basin in West Virginia, in July 1998

[All concentrations are in g/kg; E, estimated; &lt;, less than; bold type, exceeding the Probable Effects Level; italic type, between the Threshold Effects Level and Probable Effects Level]

Site	Fluorene	Naphthalene	Phenanthrene	Pyrene	1,2-dimethylnaphthalene	1,6-dimethylnaphthalene	1-methyl-9H-fluorene	1-methylphenanthrene	1-methylpyrene	2,3,6-trimethylnaphthalene
Camp Creek upstream from Mash Fork near Camp Creek	E2.8	E3.1	26	19	5.0	E2.3	5.0	E3.6	E1.6	E1.5
Mill Creek near Hopewell	E4.8	E3.7	51	58	E0.94	E2.9	E3.1	5.9	E3	E3.0
North Fork Cherry River at Highway 39 Bridge	E0.87	E3.4	19	9.4	E0.7	E3.0	E2.0	6.9	E1.3	E2.3
Sewell Creek at East Rainelle	7.0	9.8	65	75	E1.1	5.0	E3.4	7.8	E3.8	E3.2
Miller Creek at Nallen	7.6	63	56	12	16	54	10	27	9.4	24
Kellys Creek at Cedar Grove	51	<b>633</b>	<b>701</b>	252	146	479	75	182	69	206
Cabin Creek at Dry Branch	105	<b>432</b>	<b>836</b>	300	202	606	155	302	89	291
Davis Creek upstream from Trace Fork at Davis Creek	E3.3	20	43	67	E4.2	11	E2.6	7.9	5.1	E4.6
Laurel Fork at Hacker Valley	E4.3	18	71	76	8.7	11	E3	17	8.2	6.5
Left Fork Holly River near Replete	E2.2	8.1	23	14	E2.5	8.9	E2.6	9.3	E2.8	5.4
Birch River at Boggs	11	71	134	44	22	77	16	50	11	36
Sandlick Creek near Arnett	19	15	181	252	5.9	37	21	66	22	21
Laurel Creek below Hopkins Fork at Hopkins Fork	36	385	<b>575</b>	155	118	329	67	167	90	152
Spruce Laurel Fork at Clothier	27	173	278	63	64	253	48	105	45	94
Hewitt Creek at Jeffrey	19	199	280	116	56	157	29	87	29	61
Big Horse Creek at Altman	E1.9	19	28	23	E4.9	12	E1.9	6.2	E3.0	5.4

**Table 4.** Polycyclic aromatic hydrocarbon concentrations measured in fine bottom sediment at selected sites in coal-mining areas in the Kanawha River Basin in West Virginia, in July 1998—Continued[All concentrations are in g/kg; E, estimated; <, less than; **bold type**, exceeding the Probable Effects Level; *italic type*, between the Threshold Effects Level and Probable Effects Level]

Site	2,6-dimethyl- naphthalene	2-methyl- anthracene	4,5-methylene- phenanthrene	Benzol[b]- fluoranthene	Benzo[g,h,i]- perylene	Benzo[k]- fluoranthene	Coronene	Indeno- [1,2,3-c,d]- pyrene
Camp Creek upstream from Mash Fork near Camp Creek	6.0	E1.2	E2.2	13	5.9	8.4	E1.5	7.4
Mill Creek near Hopewell	5.8	5.1	9.6	38	21	34	E3.1	28
North Fork Cherry River at Highway 39 Bridge	E4.3	5.0	5.0	8.6	E4.7	5.1	<5	E4.4
Sewell Creek at East Rainelle	8.8	E3.4	7.7	40	20	32	E2.2	26
Miller Creek at Nallen	58	E1.6	5.0	8.5	12	E2.7	E2.8	E2.8
Kellys Creek at Cedar Grove	385	42	60	186	337	123	E74.6	119
Cabin Creek at Dry Branch	567	45	5.0	235	180	132	E38.0	127
Davis Creek upstream from Trace Fork at Davis Creek	15	E2.9	5.7	32	22	28	E3.0	25
Laurel Fork at Hacker Valley	13	E4.1	9.6	44	37	35	E7.7	39
Left Fork Holly River near Replete	9.8	E1.1	E2.5	7.9	6.6	E4.8	E2.3	E4.1
Birch River at Boggs	75	E4.2	5.0	32	31	13	E7.8	17
Sandlick Creek near Arnett	58	14	33	114	86	93	E11.4	96
Laurel Creek below Hopkins Fork at Hop- kins Fork	281	31	35	173	132	102	E23.9	68
Spruce Laurel Fork at Clothier	191	26	5.0	43	77	18	25	18
Hewitt Creek at Jeffrey	137	18	50	84	228	55	E56.0	66
Big Horse Creek at Altman	13	E2.1	E2.8	20	20	14	E2.8	15

**Table 5.** Polycyclic aromatic hydrocarbon concentrations in fine stream-bottom sediment at selected sites in the New River Gorge National River and Gauley River National Recreation Area, West Virginia, in 1996 and July 2002[All concentrations are in g/kg; <, less than; E, estimated; --, not measured; **bold type**, exceeding the Probable Effects Level<sup>1</sup>; *italic type*, between the Threshold Effects Level<sup>1</sup> and the Probable Effects Level]

Site	Sampling date	Acenaphthene	Acenaphthylene	Anthracene	Benz[a]-Anthracene	Benz[a]-pyrene	Chrysene	Dibenz[a,h]-anthracene	Fluoranthene
Piney Creek near McCreery	9/24/96	<50	<50	E17.2	64.3	51.6	210	<50	136
Piney Creek near McCreery	7/18/02	28.9	12.0	25.3	74.8	66.2	124	13	129
New River at Thurmond	10/4/96	<50	E45	74.0	200	160	240	56	370
New River at Thurmond	7/22/02	50.2	82.2	190	334	252	336	50.6	820
Dunloup Creek near Thurmond	7/22/02	35.6	54.6	76.7	169	138	276	35.8	332
Manns Creek near Cunard	7/19/02	15.0	11.3	15.5	44.2	37.4	89.2	8.5	110
Peters Creek near Lockwood	9/25/96	<b>100</b>	39.7	<b>371</b>	<b>822</b>	<b>754</b>	<b>1,570</b>	<50	<b>1,630</b>
Peters Creek near Lyonsville	8/7/02	14.4	39.8	55	268	166	249	26	282

<sup>1</sup> Canadian Council of Ministers of the Environment (1999)

Site	Fluorene	Naphthalene	Phenanthrene	Pyrene	1,2-dimethyl-naphthalene	1,6-dimethyl-naphthalene	1-methyl-9H-Fluorene	1-methyl-phenanthrene	1-methyl-pyrene
Piney Creek near McCreery	E37.4	85	320	137	<50	E45.6	E47.8	114	E24.9
Piney Creek near McCreery	37.7	72	242	114	10.3	87.3	62.1	55.7	11.9
New River at Thurmond	57.0	74	290	310	E18	78	59	84	64
New River at Thurmond	101	111	<b>764</b>	603	23.9	102	65.5	101	45.9
Dunloup Creek near Thurmond	50.5	93.8	420	282	25.6	107	74.4	130	39.4
Manns Creek near Cunard	19.4	35	144	87.4	12.2	80	37.2	54.8	11
Peters Creek near Lockwood	120	<b>419</b>	<b>2,270</b>	<b>1,570</b>	E41.5	188	73.2	684	206
Peters Creek near Lyonsville	23	140	242	316	62.3	214	40.3	99.8	52.1



**Table 5.** Polycyclic aromatic hydrocarbon concentrations in fine stream-bottom sediment at selected sites in the New River Gorge National River and Gauley River National Recreation Area, West Virginia, in 1996 and July 2002 —Continued

[All concentrations are in g/kg; <, less than; E, estimated; --, not measured; bold type, exceeding the Probable Effects Level; italic type, between the Threshold Effects Level and the Probable Effects Level]

Site	2,3,6-trimethyl-naphthalene	2,6-dimethyl-naphthalene	2-methyl-anthracene	4,5-methylene-phenanthrene	Benzo[b]-fluoranthene	Benzo[g,h,i]-perylene	Benzo[k]-fluoranthene	Coronene	Indeno-[1,2,3-c,d]-pyrene
Piney Creek near McCreery	E47.2	123	<50	<50	79.4	60.7	61	--	E43
Piney Creek near McCreery	49.8	168	8	10.3	110	48.9	57.9	E16.2	56.8
New River at Thurmond	62	140	59	E44	190	97	150	--	170
New River at Thurmond	83.5	156	55	109	338	140	150	E36.2	191
Dunloup Creek near Thurmond	87.7	169	27.6	29.8	199	90.7	109	E33.5	115
Manns Creek near Cunard	46.4	102	6.2	9.4	60.8	27.9	28	E10.4	29.9
Peters Creek near Lockwood	75.3	206	66.8	400	564	238	451	--	176
Peters Creek near Lyonsville	79.3	154	21.3	10.7	260	98.2	121	E26.3	99.4

## 20 PAHs in Bottom Sediment and Bioavailability in Streams in the New River Gorge National River

**Table 6.** Polycyclic aromatic hydrocarbon concentrations measured in semipermeable membrane devices in streams in the New River Gorge National River and Gauley River National Recreation Area, 2002

[wk, week; E, estimated; <, less than]

Site	Deployment time	Naphthalene	2-ethyl-naphthalene	2,6-dimethyl-naphthalene	1,6-dimethyl-naphthalene	Acenaphthylene
Piney Creek near McCreery	1 wk	E3.2	E1.1	E1.6	E1.7	<25
Piney Creek near McCreery	1 wk blank	<25	<25	<25	<25	<25
Piney Creek near McCreery	2wk	54.2	E1.8	E1.7	E1.6	E4.3
Piney Creek near McCreery	2wk blank	<25	<25	<25	<25	<25
Piney Creek near McCreery	5 wk	E1.9	E1.0	E1.6	E1.6	E1.2
Piney Creek near McCreery	5 wk blank	<25	<25	<25	<25	<25
New River at Thurmond	1 wk	31.9	E1.5	E1.5	E1.3	E2.4
New River at Thurmond	1 wk blank	E9.6	<25	E1.4	E1.3	<25
Dunloup Creek near Thurmond	1 wk	E3.2	E1.0	E1.9	E2.1	<25
Dunloup Creek near Thurmond	1 wk blank	E9.8	E1.2	E1.4	E1.3	<25
Dunloup Creek near Thurmond	2wk	E2.5	E1.1	E1.7	E1.8	E1.2
Dunloup Creek near Thurmond	2wk blank	E6.3	<25	E1.3	E1.2	<25
Dunloup Creek near Thurmond	5 wk	E2.4	E1.1	E1.7	E1.7	E1.2
Dunloup Creek near Thurmond	5 wk blank	97.5	E1.7	E1.7	E1.4	E8.3
Manns Creek near Cunard	1 wk	E1.9	E1.1	E1.3	E1.2	<25
Manns Creek near Cunard	1 wk blank	E10.1	E1.1	E1.4	E1.4	<25
Manns Creek near Cunard	2wk	E1.3	E1.0	E1.3	E1.1	<25
Manns Creek near Cunard	2wk blank	102	E1.8	E1.5	E1.1	E23.7
Manns Creek near Cunard	5 wk	E1.0	<25	E1.2	E1.3	<25
Manns Creek near Cunard	5 wk blank	E8.5	<25	E1.2	E1.2	<25
Peters Creek near Lyonsville	1 wk	E2.1	E1.1	E1.5	E1.4	<25
Peters Creek near Lyonsville	1 wk blank	E11.4	E1.1	E1.4	E1.4	<25
Peters Creek near Lyonsville	2wk	E0.96	E1.1	E1.5	E1.6	<25
Peters Creek near Lyonsville	2wk blank	E12.8	E1.2	E1.4	E1.4	<25
Peters Creek near Lyonsville	5 wk	E0.96	<25	E1.5	E1.6	<25
Peters Creek near Lyonsville	5 wk blank	E11.6	E1.2	E1.4	E1.4	<25

**Table 6.** Polycyclic aromatic hydrocarbon concentrations measured in semipermeable membrane devices in streams in the New River Gorge National River and Gauley River National Recreation Area, 2002—Continued

[wk, week; E, estimated; &lt;, less than]

Site	1,2-dimethyl-naphthalene	Acenaphthene	2,3,6-trimethyl-naphthalene	Fluorene	1-methyl-9H-Fluorene	Phenanthrene
Piney Creek near McCreery	<25	E3.8	E1.4	E3.5	E1.8	E9.2
Piney Creek near McCreery	<25	<25	<25	E1.0	E1.4	E1.8
Piney Creek near McCreery	E1.0	E4.3	E1.5	E4.7	E2.0	E19.2
Piney Creek near McCreery	<25	<25	<25	<25	E1.5	E2.0
Piney Creek near McCreery	E1.0	E3.6	E1.6	E4.0	E2.0	E17.9
Piney Creek near McCreery	<25	<25	<25	<25	E1.4	E1.8
New River at Thurmond	E0.9	E2.1	E1.3	E3.0	E1.7	E10.2
New River at Thurmond	E0.8	E0.5	E1.2	E1.1	<25	E1.9
Dunloup Creek near Thurmond	E0.8	E6.2	E1.4	E4.9	E1.9	E15.9
Dunloup Creek near Thurmond	<25	E0.6	E1.2	E1.2	E1.5	E2.0
Dunloup Creek near Thurmond	<25	E5.8	E1.5	E4.5	E1.8	E18.3
Dunloup Creek near Thurmond	<25	E0.5	E1.2	E1.2	E1.8	E2.2
Dunloup Creek near Thurmond	E0.9	E5.2	E1.6	E4.2	E2.0	E24.0
Dunloup Creek near Thurmond	E0.9	E1.5	E1.2	E3.5	E1.7	E13.4
Manns Creek near Cunard	E0.9	E0.6	E1.2	E1.2	E1.5	E2.5
Manns Creek near Cunard	E1.0	<25	E1.2	E1.1	E1.5	E1.9
Manns Creek near Cunard	E1.0	E0.7	E1.3	E1.2	E1.5	E2.9
Manns Creek near Cunard	<25	E1.4	E1.2	E4.1	E1.7	E18.5
Manns Creek near Cunard	<25	E0.7	E1.3	E1.4	E1.6	E4.2
Manns Creek near Cunard	<25	<25	E1.2	E1.1	E1.4	E1.6
Peters Creek near Lyonsville	<25	E2.3	E1.4	E2.2	E1.6	E6.9
Peters Creek near Lyonsville	<25	<25	<25	E1.1	E1.4	E1.7
Peters Creek near Lyonsville	<25	E1.8	E1.7	E2.1	E1.9	E7.9
Peters Creek near Lyonsville	E0.8	E0.5	E1.2	E1.2	E1.5	E1.9
Peters Creek near Lyonsville	<25	E2.2	E1.8	E2.4	E2.0	E10.7
Peters Creek near Lyonsville	<25	<25	E1.2	E1.2	E1.6	E2.2

## 22 PAHs in Bottom Sediment and Bioavailability in Streams in the New River Gorge National River

**Table 6.** Polycyclic aromatic hydrocarbon concentrations measured in semipermeable membrane devices in streams in the New River Gorge National River and Gauley River National Recreation Area, 2002—Continued

[wk, week; E, estimated; <, less than]

Site	Anthracene	2-methyl-anthracene	4,5-methylene-phenanthrene	1-methyl-phenanthrene	Fluoranthene	Pyrene
Piney Creek near McCreery	E1.6	<25	E2.3	E1.8	E8.4	E8.0
Piney Creek near McCreery	<25	<25	<25	E1.6	E1.8	E1.7
Piney Creek near McCreery	E2.4	E2.3	E4.0	E2.4	E21.8	E22.3
Piney Creek near McCreery	<25	<25	<25	E1.6	E1.8	E1.6
Piney Creek near McCreery	E2.6	E6.1	E5.6	E2.9	41.3	45.5
Piney Creek near McCreery	<25	<25	<25	E1.5	E1.8	E1.7
New River at Thurmond	E1.7	<25	E2.5	E1.9	E11.2	E5.9
New River at Thurmond	<25	<25	<25	E1.5	E1.7	E1.6
Dunloup Creek near Thurmond	E2.2	<25	E2.9	E2.2	E12.4	E8.6
Dunloup Creek near Thurmond	<25	<25	<25	<25	E1.7	E1.6
Dunloup Creek near Thurmond	E2.1	<25	E3.7	E2.5	E19.7	E14.3
Dunloup Creek near Thurmond	<25	<25	<25	E1.6	E1.7	E1.7
Dunloup Creek near Thurmond	E2.2	<25	E5.5	E3.2	43.1	31.9
Dunloup Creek near Thurmond	E2.3	<25	E2.0	E1.8	E4.6	E4.4
Manns Creek near Cunard	<25	<25	<25	E1.6	E2.9	E2.1
Manns Creek near Cunard	<25	<25	<25	E1.6	E1.6	E1.6
Manns Creek near Cunard	<25	<25	<25	E1.6	E3.7	E2.6
Manns Creek near Cunard	E2.7	<25	E3.8	E1.8	E11.8	E12.9
Manns Creek near Cunard	<25	<25	E1.9	E1.8	E6.3	E4.1
Manns Creek near Cunard	<25	<25	<25	E1.5	E1.6	E1.5
Peters Creek near Lyonsville	E1.5	<25	E2.1	E1.8	E5.8	E4.3
Peters Creek near Lyonsville	<25	<25	<25	E1.5	E1.7	E1.6
Peters Creek near Lyonsville	E1.6	<25	E2.4	E2.4	E9.1	E7.5
Peters Creek near Lyonsville	<25	<25	<25	E1.6	E1.8	E1.6
Peters Creek near Lyonsville	E1.7	<25	E3.0	E3.0	E17.3	E14.5
Peters Creek near Lyonsville	<25	<25	<25	E1.6	E1.7	E1.6

**Table 6.** Polycyclic aromatic hydrocarbon concentrations measured in semipermeable membrane devices in streams in the New River Gorge National River and Gauley River National Recreation Area, 2002—Continued

[wk, week; E, estimated; &lt;, less than]

Site	1-methyl-pyrene	Benz[a]-anthracene	Chrysene	Benzo[b]-fluoranthene	Benzo[k]-fluoranthene	Benzo[e]-pyrene
Piney Creek near McCreery	E1.6	E2.0	E2.4	E2.5	E1.7	E1.6
Piney Creek near McCreery	<25	<25	<25	<25	<25	<25
Piney Creek near McCreery	E2.0	E3.2	E6.5	E4.2	E2.9	E2.8
Piney Creek near McCreery	<25	<25	<25	<25	<25	<25
Piney Creek near McCreery	E2.8	E5.4	E13.6	E7.4	E3.3	E4.8
Piney Creek near McCreery	<25	<25	<25	<25	<25	<25
New River at Thurmond	E1.5	E2.9	E1.7	E2.1	E1.5	E1.3
New River at Thurmond	<25	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	E1.5	<25	E2.0	E2.1	E1.5	E1.4
Dunloup Creek near Thurmond	<25	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	E1.7	E2.2	E3.3	E2.8	E1.9	E1.7
Dunloup Creek near Thurmond	<25	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	E2.1	E3.4	E8.2	E4.5	E2.5	E2.9
Dunloup Creek near Thurmond	E1.6	E2.2	E1.1	E2.0	E1.7	E1.3
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	E1.8	E2.5	E1.7	E2.9	E2.2	E2.1
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	E1.5	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	E1.8	E2.0	E1.6	E2.1	E1.5	E1.4
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	E2.8	E2.8	E3.4	E2.9	E1.8	E1.9
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25

## 24 PAHs in Bottom Sediment and Bioavailability in Streams in the New River Gorge National River

**Table 6.** Polycyclic aromatic hydrocarbon concentrations measured in semipermeable membrane devices in streams in the New River Gorge National River and Gauley River National Recreation Area, 2002—Continued

[wk, week; E, estimated; <, less than]

Site	Benzo[a]-pyrene	Perylene	Benzo[g,h,i]-perylene	Indeno [1,2,3-c,d] pyrene	Dibenzo[a,h] anthracene	Coronene
Piney Creek near McCreery	E2.4	<25	<25	<25	<25	E0.76
Piney Creek near McCreery	<25	<25	<25	<25	<25	<25
Piney Creek near McCreery	E2.7	E1.2	E1.2	E2.4	<25	E0.86
Piney Creek near McCreery	<25	<25	<25	<25	<25	<25
Piney Creek near McCreery	E3.2	E1.5	E1.7	E2.7	E1.6	E0.59
Piney Creek near McCreery	<25	<25	<25	<25	<25	<25
New River at Thurmond	E2.4	<25	<25	<25	<25	E0.97
New River at Thurmond	<25	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	E2.3	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	<25	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	E2.4	<25	E1.0	E2.2	<25	<25
Dunloup Creek near Thurmond	<25	<25	<25	<25	<25	<25
Dunloup Creek near Thurmond	E2.7	<25	E1.2	E2.4	<25	<25
Dunloup Creek near Thurmond	E2.4	<25	E0.98	E2.2	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	E3.7	E1.2	E2.9	E3.5	<25	E1.2
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Manns Creek near Cunard	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	E2.4	<25	<25	<25	<25	<25
Peters Creek near Lyonsville	<25	<25	<25	<25	<25	<25







