Sediment Quality and Polychlorinated Biphenyls in the Lower Neponset River, Massachusetts, and Implications for Urban River Restoration

By Robert F. Breault, Matthew G. Cooke, and Michael Merrill

Scientific Investigations Report 2004-5109

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
Charles G. Groat, Director

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Suggested citation:
Breault, R.F., Cooke, M.G., and Merrill, Michael, 2004, Sediment quality and polychlorinated biphenyls in the lower Neponset River, Massachusetts, and implications for urban river restoration: U.S. Geological Survey Scientific Investigations Report 2004-5109, 48 p.

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Conversion Factors and Abbreviations

Multiply	By	To obtain
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic yard (yd^3)	0.7646	cubic meter (m^3)
foot (ft)	0.3048	meter (m)
gallon (gal)	3.785	liter (L)
inch (in.)	25.4	millimeter (mm)
pound, avoirdupois (lb)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to
degrees Fahrenheit (°F) as follows:
$$°F = 1.8°C + 32$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

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

Concentrations of sediment-quality constituents are give in percent (%), parts per million (ppm), and parts per billion (ppb). Concentrations of water-quality constituents are given in nanograms per hexane sample (ng/hexane sample).

ACOE	Army Corps of Engineers	ng/L	nanogram per liter
BAF	bioaccumulation factor	NAQWA	National Water-Quality Assessment
BCF	bioconcentration factor		
CCC	continuous chronic criterion	NETLAB	New England Testing Laboratory
DDD	dichlorodiphenyldichloroethane	NURE	National Uranium Resource Evaluation
DDE	dichlorodiphenyldichloroethylene		
DDT	dichlorodiphenyltrichloroethane	PAH	polyaromatic hydrocarbon
MDEP	Massachusetts Department of Environmental Protection	PES	performance evaluation sample
		PCB	polychlorinated biphenyl
FCM	food-chain multiplier	PEC	probable effect concentration
FDA	Food and Drug Administration	pg/L	picogram per liter
GPS	global positioning system	RMSD	root mean square difference
GIS	geographic information system	SOP	standard operating procedure
HSSR	Hydrogeochemical and Stream Sediment Reconnaissance	TCLP	toxicity characteristic leaching procedure
IUPAC	International Union of Pure and Applied Chemistry	TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
MDC	Metropolitan District Commission	TEQ	toxic equivalency
MDL	method detection limit	TIN	triangular irregular network
μm	micrometer	USEPA	U.S. Environmental Protection Agency
mg/L	milligram per liter		
mL	milliliter	USGS	U.S. Geological Survey
MRL	minimum reporting level		

Sediment Quality and Polychlorinated Biphenyls in the Lower Neponset River, Massachusetts, and Implications for Urban River Restoration

By Robert F. Breault[1], Matthew G. Cooke[1], and Michael Merrill[2]

Abstract

Efforts to restore fish passage, habitat, and recreational use of the Neponset River, a tributary to Boston Harbor, Massachusetts, have raised concerns about the sediment, water, and biota quality of the river. Consequently, the U.S. Geological Survey, in cooperation with the Massachusetts Executive Office of Environmental Affairs Department of Fish and Game Riverways Program and the U.S. Environmental Protection Agency, studied sediment and water quality, with a specific focus on polychlorinated biphenyls, in the Neponset River.

Sediment samples were collected throughout the Neponset River and tested for elements and organic compounds including polyaromatic hydrocarbons, organochlorine pesticides, and polychlorinated biphenyls. Although enriched compared to background concentrations, sediment quality in the Neponset River was generally better than that of other urban rivers in the United States, except with respect to one constituent, polychlorinated biphenyls. Concentrations of lead, some polyaromatic hydrocarbons, and polychlorinated biphenyls in the sediment may be toxic to aquatic organisms and may pose a risk to human health. The sediment quality also fails to meet the minimum requirements set by the Commonwealth of Massachusetts for lined landfill disposal.

The locations of the source(s) of polychlorinated biphenyls to the Neponset River were determined by means of congener analysis from PISCES passive water-column samplers. The PISCES data indicate a sharp increase in polychlorinated biphenyl concentrations and a substantial shift in congener pattern downstream of one PISCES sampling location near Fairmont Avenue, Boston, Massachusetts. This result indicates that the area upstream of this sampling location may be the location of a historical source of polychlorinated biphenyls to the Neponset River. The present (2003) source to the water column may likely be PCB contaminated sediment.

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[2]Massachusetts Executive Office of Environmental Affairs Department of Fish and Game Riverways Program.

Introduction

In 1998, then Department of the Interior Secretary Bruce Babbitt reported that throughout its history America had constructed 75,000 dams. As Babbitt wrote, this number is "the equivalent of one [dam being built] every day since Jefferson wrote the Declaration of Independence" (Babbitt, 1998). These dams were built for many reasons, including flood control, power production, navigation, and water supply, but many of them no longer serve their intended purpose. As the dams have aged, many have fallen into states of disrepair. An accidental breach or catastrophic failure of a dam may represent a substantial threat to public safety and to the environment in the vicinity of the dam.

Dams also interfere with many natural processes. Blocking fish passage is perhaps the most widely recognized environmental effect of dams, but the reservoirs that dams create also inundate wetlands and terrestrial ecosystems; with dams, rivers become fragmented, and peak flows and other hydrologic characteristics are changed. Dams also change sediment regimes in a river by trapping most of the sediment in impoundments behind the dams (Heinz Center, 2002). For these and other reasons, restoring urban rivers by removing dams has gained prominence as a viable alternative to other restoration strategies within the environmental community.

The Neponset River, a tributary to Boston Harbor, has been dammed in some fashion for the past 350 years (fig. 1). Historically, the river supported abundant populations of American shad (*Alosa sapidissima*) and river herring [alewife, (*Alosa pseudoharengus*)] and blueback herring (*Alosa aestivalis*). While the estuary continues to support an important fishery of rainbow smelt (*Osmerus mordax*), dams in the lower Neponset River block passage for shad and herring. Following a habitat survey in 1995, the Massachusetts Fisheries began to stock both shad and herring upstream of the two remaining dams in anticipation of fish passage (U.S. Army Corps of Engineers, written commun., 2002).

Figure 1.   The study area, sediment-grab and sediment-core sampling locations, and the locations where PISCES polychlorinated biphenyl
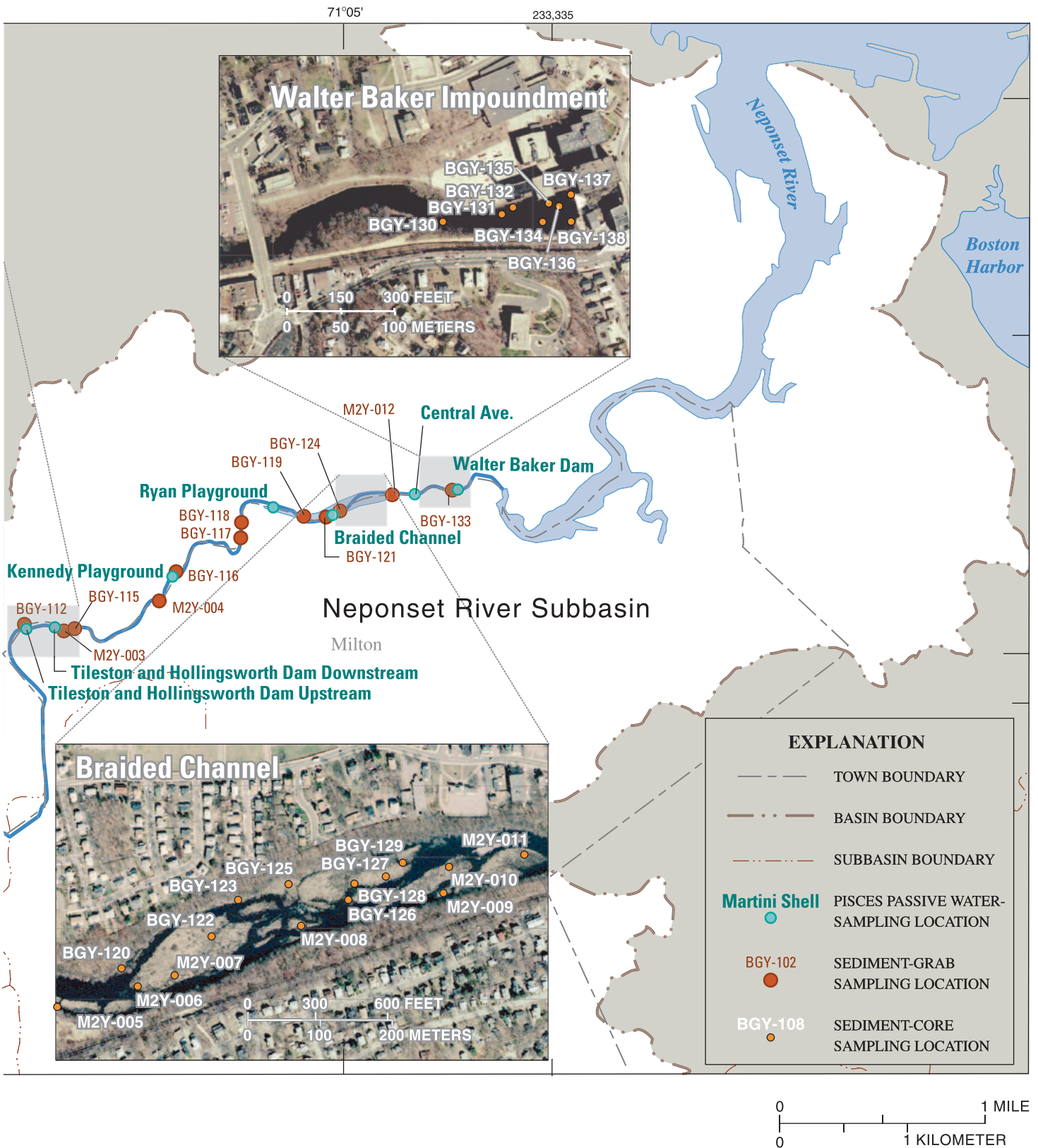
passive samplers were deployed, lower Neponset River, Massachusetts.

Environmental managers and local advocates have proposed river-restoration efforts, such as channel restoration for habitat improvements and fish-passage alternatives, including the installation of engineered fishways, dam breaching, and removal of the most downstream dams on the lower Neponset River—the Walter Baker Dam (fig. 2) and the Tileston and Hollingsworth Dam (fig. 3; U.S. Army Corps of Engineers, written commun., 2002). Fish passage at these dams would open access to more than 17 mi of riverine habitat to migratory fish and help increase recreational use of the lower Neponset River, that section of the river from Fowl Meadow to the Walter Baker Dam in Milton, MA (U.S. Army Corps of Engineers, written commun., 2002).

Like most urban rivers in the Northeast, the Neponset River has a long industrial history. Industrialization and subsequent urbanization began in the Neponset River Basin as early as 1630. By the mid 1700s, the Neponset River drained one of the most heavily industrialized drainage basins in the Nation (U.S. Army Corps of Engineers, written commun., 2002). Industrial activity continued on the Neponset River until 1965, when the last major industrial facility relocated from the lower section of the river. This industrial past, combined with the urbanization that continues in the drainage basin, has likely contaminated bottom sediment throughout the river.

The Neponset River has also been altered by flood-control measures. Most of these were implemented following the flood of 1955, which damaged many of the dams along the river and flooded much of southern New England (National Weather Service, 2002). After the flood, the Metropolitan District Commission (MDC) took ownership of the dams along the river; and by the late 1950s and early 1960s, the MDC had removed the two damaged Mattapan Dams and the Jenkins Dam. Around this same time, the MDC also rebuilt the Walter Baker and Tileston and Hollingsworth Dams. The MDC also straightened large river reaches, dredged and deepened the main channel, and armored and steepened the river banks with concrete and dredge spoils. More information concerning the history of flood control in the Neponset River Basin can be found on the World Wide Web at www.state.ma.us/dfwele/River/NeponsetFish/Neponset-Historical-Photos.htm.

Figure 2.   Walter Baker impoundment, lower Neponset River, Massachusetts.

Figure 3. Tileston and Hollingsworth Dam and impoundment, lower Neponset River, Massachusetts.

Many studies have focused on the Neponset River, but few have addressed the question of its sediment quality. In 2002, the U.S. Army Corps of Engineers (ACOE) completed a study on the environmental effects of dam removal that focused on fish passage and habitat restoration (U.S. Army Corps of Engineers, written commun., 2002). Although this study was not primarily focused on sediment quality, two bottom-sediment cores were collected—one from the Walter Baker impoundment, and one from the Tileston and Hollingsworth impoundment. These bottom-sediment cores were enriched in many contaminants, most notably polychlorinated biphenyls (PCBs).

In any river, high concentrations above background levels of any elements and organic compounds in bottom sediment are a concern. As long as the contaminated sediments stay in the river, they remain non-point sources of contaminants. Through the processes of entrainment, resuspension, or chemical and biological transformation, the contaminated sediments may directly cause adverse biological effects to benthic (bottom-dwelling) organisms, or indirectly affect pelagic (swimming) organisms (Baudo and Muntau, 1990; Sly, 1994). Consumption of these contaminated organisms can pose health risks to predatory fish, wildlife, and humans. Direct contact with or accidental ingestion of contaminated sediments may also pose health risks to humans.

Whether a river is restored through dam removal, other restoration efforts, or a combination of dam removal and other methods, data indicating the quality and quantity of bottom sediment are needed as the basis for informed sediment-management decisions. These data are especially important in the case of dam removal. Because the physical and chemical properties of most contaminants favor solid phase (or sediment) associations (Horowitz, 1991), accumulated fine-grained bottom sediment usually are associated with contaminants. These contaminants include elements and organic compounds, which can enter a river through waste disposal, urban runoff, sanitary sewers, atmospheric deposition, and inadvertent spills. As the contaminated sediments travel downstream, they commonly accumulate in the slack water behind dams.

Among the contaminants that may accumulate in sediments are PCBs, a group of organic compounds consisting of a biphenyl ring structure with 1 to 10 attached hydrogen or chlorine atoms (fig. 4). Individually, these different compounds are called congeners. These congeners are designated by an IUPAC (International Union of Pure and Applied Chemistry) number from 1 to 209 (also known as a PCB number), with 1 indicating the lowest number of attached chlorine atoms (and the highest number of hydrogen atoms) and 209 the highest number of attached chlorine atoms (and the lowest number of hydrogen atoms). Specific mixtures of congeners, called Aroclors, were commercially manufactured and sold in the past. The composition of each Aroclor depended on the intended commercial use, but consisted of 60 to 90 congeners. These mixtures were identified by four digits (for example, 1232, 1242, and 1254), which indicate the number of carbon atoms (the first two digits) and the percentage of chlorine substituted for hydrogen by weight (the second two numbers). For example, Aroclor 1254 contains 12 carbon atoms and 54 percent substituted chlorine (Wisconsin Department of Natural Resources, 2000). Over 700,000 tons (1.4 billion pounds) of PCBs were sold in North America between the 1930s and the late 1970s (North American Commission for Environmental Cooperation, 1996).

Increased public dialogue about restoration of the Neponset River, combined with extensive dam construction, the long history of industrialization and urbanization along the river, and a preliminary knowledge of the occurrence and geographic distribution of sediment contamination, including PCBs, in the lower Neponset River, prompted this study of bottom sediment quality and quantity. The U.S. Geological Survey (USGS) completed this study during 2002–03 in cooperation with the Massachusetts Executive Office of Environmental Affairs Department of Fish and Game Riverways Program, and the U.S. Environmental Protection Agency (USEPA).
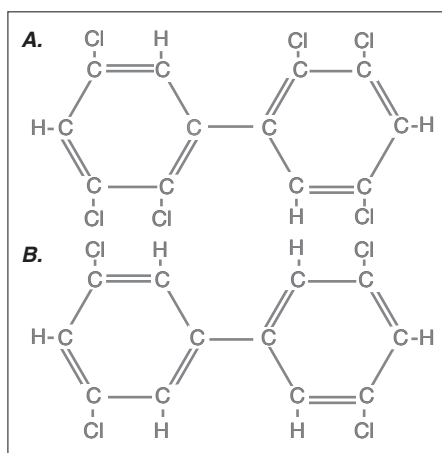
Purpose and Scope

This report presents maps of water depths (or bathymetry) and thickness of impounded (and previously impounded) bottom sediment in the study area and describes the collection of 20 sediment-grab samples (top 4 in. of sediment), 31 sediment-core samples (depth composited from 5–50 in., depending on the total depth of the sediment), and 12 measurements of PCB concentrations in the water column by means of a passive water-sampling system (PISCES). The report discusses the occurrence and geographic distribution of elements and organic compounds in the bottom sediment, as well as the potential adverse effects that these contaminants pose to aquatic organisms and humans. Throughout this report, the implications of these sediment data are discussed in terms of sediment-management options, such as sediment removal, and other river-restoration methods. Finally, this report details possible past and present source areas of polychlorinated biphenyls (PCBs) to the water, biota, and sediment of the lower Neponset River.

Study Methods

Water depths were measured in two impoundments (Walter Baker and Tileston and Hollingsworth). Sediment-thickness data were collected in these impoundments and within the former Jenkins Dam impoundment (referred to as the braided channel, fig. 5). Sediment-grab samples (top 4 in.) were collected randomly throughout the study area (table 1). Sediment cores (cores extended through the entire thickness of fine-grained sediment) were collected randomly within areas of sediment deposition just upstream of the Walter Baker and Tileston and Hollingsworth Dams and within the braided channel. All sediment samples were analyzed for elements, organic compounds, and physical properties (table 2).

Water Depths and Sediment Thickness

Water depths were measured on December 18 and 19, 2002. For these 2 days, the discharge measured at the USGS streamflow-gaging station Neponset River at Milton Village, Massachusetts (011055566), averaged about 690 ft^3/s. This amount is about four times the mean discharge (168 ft^3/s) for this station, on the basis of 6 years of record. Water depths, however, were adjusted to full pool equivalence by subtracting the difference between the height of the water measured at the time of sampling and the dam elevation (head).

An echo sounder was used to measure water depths. Water-depth data were recorded simultaneously with positional data taken with a global positioning system (GPS). A steel rod, manually pushed into the bottom sediment, was used to collect sediment-thickness data. These manual sediment-thickness measurements were made at over 200 locations.

Figure 4. Schematic of a typical polychlorinated biphenyl: *A*, more substituted; and *B*, less substituted.

Figure 5. Former Jenkins Dam impoundment, known as the braided channel, lower Neponset River, Massachusetts.

A combination of the triangular irregular network (TIN) data model and topogrid functions of ESRI's ARC/INFO geographic information systems (GIS) software (Environmental Research Institute, Inc., Version 7.11) were used to map channel morphology and bottom-sediment thickness from water-depth and sediment-thickness data. The TIN data model of ARC/INFO was used to determine water and sediment volumes (figs. 6–8).

On average, water depth in the Tileston and Hollingsworth impoundment was the deepest measured in the Neponset River (about 8.8 ft), with a maximum depth of 15 ft. Maximum water depth in the Walter Baker impoundment was 9.3 ft, with an average depth of about 7.3 ft. Where measured, sediment thickness averaged from about 1.1 to 1.4 ft. Maximum measurements of sediment thickness were 5.8, 7.6, and 9.7 ft in the braided channel, and Walter Baker, and Tileston and Hollingsworth impoundments, respectively.

The braided-channel area of the Neponset River contains about 49 percent (or about 790,000 ft^3) of the total bottom-sediment volume measured, the Tileston and Hollingsworth impoundment contains about 38 percent (or about 620,000 ft^3), and the Walter Baker impoundment contains about 13 percent (less than 210,000 ft^3). This sediment volume (about 1.6 million ft^3) is the equivalent of the volume of about 6,000 dump trucks, each containing 10 yd^3.

Sample-Collection Design

In October 2002, sediment-grab samples (from the top 4 in. of sediment) were collected (table 1; fig. 1) from 20 randomly selected locations between Fowl Meadow and the Walter Baker Dam. A subroutine within ARC/INFO GIS software (Scott, 1990) was used to select the 20 sampling locations. A GPS unit was then used to navigate to these locations in the study area. For comparison to the samples collected within the study area, one sediment-grab sample, a composite of eight randomly collected dredge samples, was collected in the estuarine part of the lower Neponset River, just downstream of the Walter Baker Dam.

Sediment-core samples were collected between December 2002 and February 2003 (table 1). A stratified random-sampling design, incorporating many of the same methods used to develop the sediment-grab sampling design, was used to collect the 31 sediment cores. Sediment-core sampling locations were limited to areas of sediment deposition just upstream of the Walter Baker and Tileston and Hollingsworth Dams and within the braided channel (fig. 1). A GPS unit was used to locate the sampling locations in the study area.

Table 1.   Sediment-grab and sediment-core sampling locations and time of sampling, from the Walter Baker impoundment, Tileston–Hollingsworth impoundment, and braided channel, lower Neponset River, Massachusetts.

[Locations shown on figure 1. USGS, U.S. Geological Survey]

USGS number	Date and time		State plane coordinates	
			Easting	Northing
Sediment-Grab Sampling Locations				
BGY-100	10-02-02	8:18	231,148.63	887,168.62
BGY-101	10-02-02	9:00	230,958.07	887,519.43
BGY-102	10-02-02	10:00	230,706.00	887,978.52
BGY-103	10-02-02	10:20	230,731.99	888,380.45
BGY-104	10-02-02	11:00	231,078.47	889,012.78
BGY-105	10-02-02	11:20	231,354.79	889,173.03
BGY-106	10-02-02	12:00	231,530.63	889,402.57
BGY-107	10-02-02	12:30	231,745.45	889,724.80
BGY-112	10-02-02	13:00	232,093.67	890,114.60
M2Y-003	10-02-02	15:30	232,401.00	890,087.87
BGY-115	10-02-02	16:00	232,487.18	890,108.19
BGY-116	10-02-02	12:30	233,296.44	890,561.52
M2Y-004	10-02-02	15:00	233,157.71	890,327.50
BGY-117	10-02-02	12:00	233,813.96	890,830.16
BGY-118	10-02-02	11:15	233,817.19	890,953.21
BGY-119	10-02-02	11:00	234,314.76	891,002.36
BGY-121	10-02-02	10:30	234,494.85	890,994.46
BGY-124	10-02-02	10:00	234,604.62	891,046.12
M2Y-012	10-02-02	9:30	235,025.07	891,176.71
BGY-133	10-02-02	9:00	235,501.41	891,208.91
Sediment-Core Sampling Locations Walter Baker Impoundment				
BGY-130	12-18-02	10:30	235,413.94	891,208.50
BGY-131	12-18-02	11:00	235,482.25	891,217.13
BGY-132	12-18-02	11:30	235,495.30	891,225.00
BGY-134	12-18-02	13:00	235,529.78	891,208.25
BGY-135	12-18-02	12:00	235,536.77	891,229.69
BGY-136	12-18-02	12:30	235,548.88	891,226.88
BGY-137	12-18-02	13:30	235,562.39	891,239.94
BGY-138	12-18-02	14:00	235,562.86	891,209.63

USGS number	Date and time		State plane coordinates	
			Easting	Northing
Sediment-Core Sampling Locations Braided Channel				
M2Y-005	1-09-03	10:00	234,365.02	890,968.13
BGY-120	1-08-03	10:45	234,429.17	891,022.19
M2Y-006	1-08-03	11:15	234,450.80	890,997.69
M2Y-007	1-08-03	12:15	234,503.42	891,012.81
BGY-122	1-08-03	12:45	234,556.05	891,066.13
BGY-123	1-09-03	10:35	234,592.81	891,117.31
BGY-125	1-09-03	11:00	234,664.19	891,139.69
M2Y-008	1-09-03	12:00	234,681.48	891,081.31
BGY-126	1-09-03	12:25	234,747.09	891,118.06
BGY-127	1-18-03	13:00	234,756.28	891,142.00
BGY-128	1-09-03	13:30	234,800.27	891,151.38
BGY-129	1-09-03	14:00	234,824.05	891,170.13
M2Y-009	2-11-03	11:45	234,880.64	891,127.25
M2Y-010	2-11-03	12:00	234,889.30	891,164.00
M2Y-011	2-11-03	11:00	234,995.98	891,181.31
Sediment-Core Sampling Locations Tileston–Hollingsworth Impoundment				
BGY-108	12-19-02	10:30	231,991.86	890,013.13
BGY-109	12-19-02	11:30	232,021.58	890,061.19
BGY-110	12-19-02	12:00	232,046.48	890,090.88
BGY-111	12-19-02	12:30	232,058.72	890,102.25
BGY-113	12-19-02	13:00	232,098.48	890,116.69
M2Y-001	12-19-02	13:15	232,120.33	890,110.13
BGY-114	12-19-02	14:15	232,129.95	890,144.19
M2Y-002	12-19-02	13:45	232,130.39	890,118.00

Table 2.   Laboratories and analytical methods used in this study.

[NETLAB, New England Testing Laboratory; TCLP, toxicity characteristic leaching procedure; USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey]

Constituent	Sample type	Laboratory	Analytical technique
Inorganic elements	Bottom sediment	XRAL	Inductively coupled plasma mass spectroscopy
TCLP trace metals	Bottom sediment	USEPA	Inductively coupled plasma mass spectroscopy
Reactive sulfides	Bottom sediment	NETLAB	Titrimetry
Polyaromatic hydrocarbons	Bottom sediment	USEPA	Gas chromatography with electron-capture detection
Hydrocarbons	Bottom sediment	USEPA	Gas chromatography with flame-ionization detection
Organochlorine pesticides	Bottom sediment	USEPA	Gas chromatography with electron-capture detection
Polychlorinated biphenyls	Bottom sediment	USEPA	Gas chromatography with electron capture
Polychlorinated biphenyls	Bottom sediment	AXYS Analytical	Low-resolution quadrupole mass selective detection
Polychlorinated biphenyls	Hexane	AXYS Analytical	Low-resolution quadrupole mass selective detection
Grain-size distribution	Bottom sediment	USGS	Gravimetry
Total solids	Bottom sediment	USEPA	Gravimetry
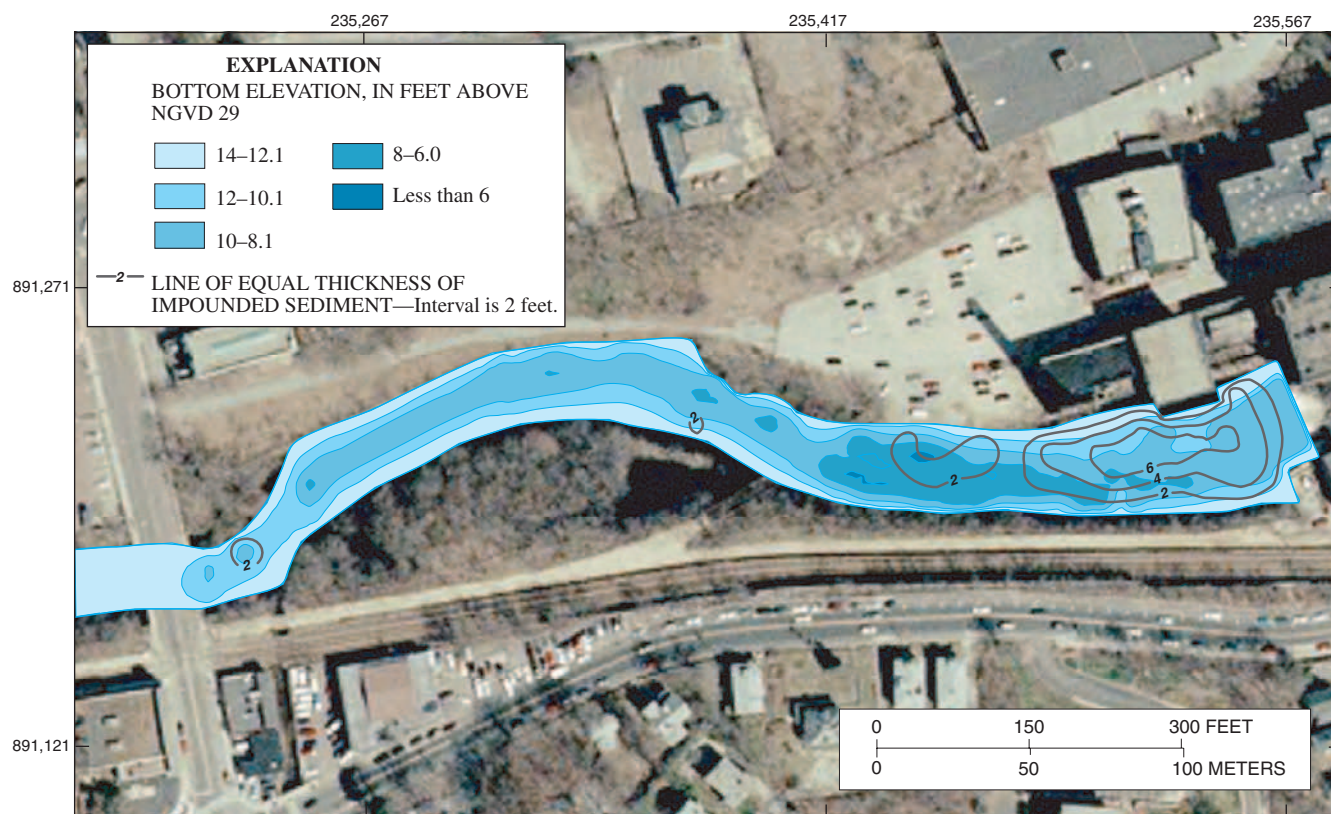
Base map from MassGIS digital orthophoto, Massachusetts coordinate system,
in meters 1:5,000, NAD 83, Zone 19

Figure 6.   Water depths and sediment thickness measured in the Walter Baker impoundment, lower Neponset River, Massachusetts.
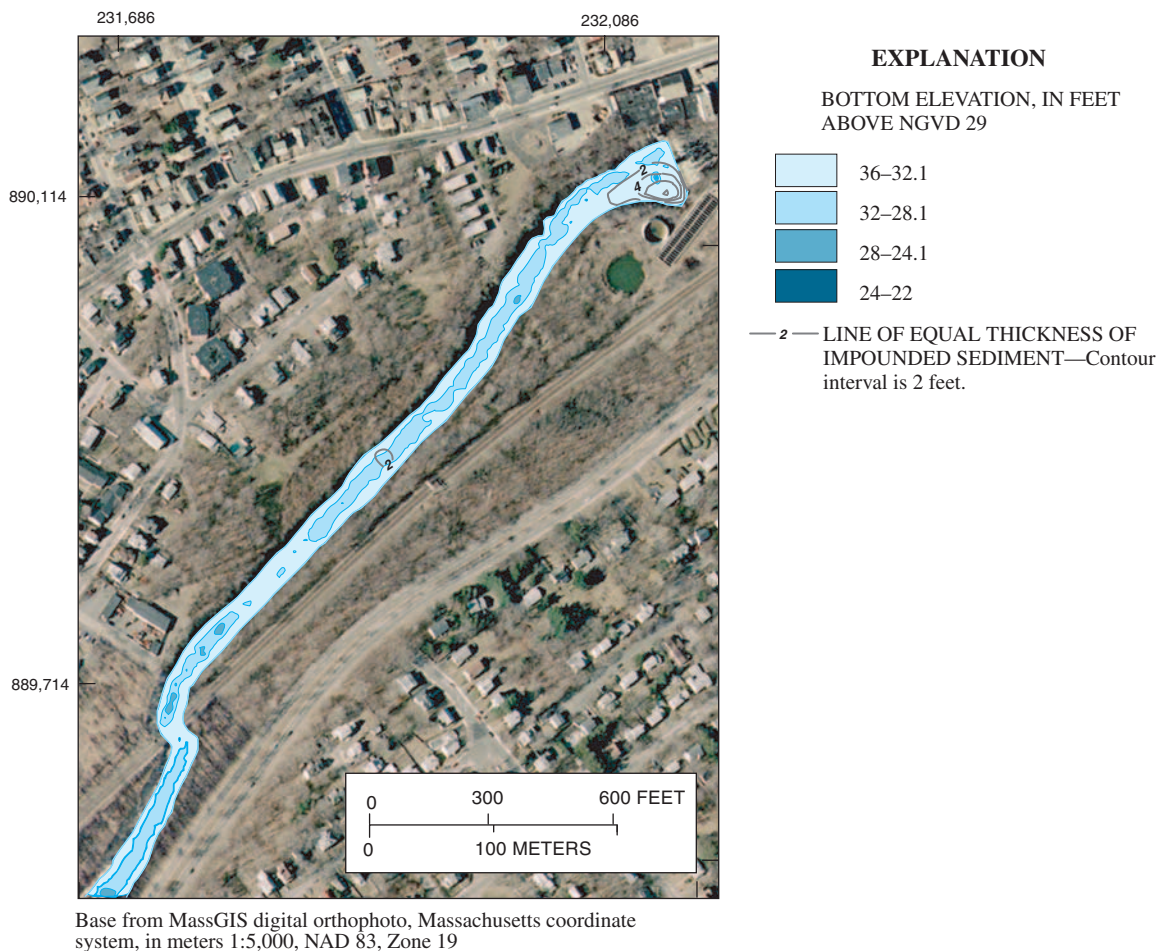
Figure 7.   Water depths and sediment thickness measured in the Tileston and Hollingsworth impoundment, lower Neponset River, Massachusetts.

In August 2002, samples for analysis of PCBs in the water column were collected according to a deterministic sampling design (fig. 1). PCB passive samplers (PISCES) were placed at 12 locations throughout the study area. Samplers were also placed upstream and downstream of Mother Brook, as well as within Mother Brook, a tributary to the Neponset River that diverts water from the Charles River and a possible source of PCBs (fig. 1).

Sample-Collection Techniques

In water deeper than about 5 ft, a stainless-steel Eckman dredge was used to collect sediment-grab samples. In water less than 5 ft deep, a stainless-steel scoop or stainless-steel spoon was used to collect sediment-grab samples. A minimum of three samples were collected at each sampling location to better characterize conditions at the site (Baudo and Mantau, 1990). Any water trapped in either the dredge, scoop, or spoon was

decanted off after most of the fines had settled. The top 4 in. (if available) of the sample was either removed from the dredge or scooped from the sediment surface and placed in a pre-cleaned stainless-steel bowl and homogenized with a stainless-steel spatula in the field, with the exception of the sediment-grab sample collected downstream of the Walter Baker Dam. This sample was scooped from the dredge by using a nylon spoon and homogenized in a pre-cleaned Teflon bag.

After homogenization, sediment-grab samples were sieved through a 6-mm sieve (the sediment-grab sample collected downstream of the Walter Baker Dam was not sieved). Sub-samples were collected, placed in pre-cleaned containers, and stored on ice for overnight delivery to the appropriate labor-atory (table 2). In the field, all sediment-sampling equipment was cleaned between samplings by scrubbing the equipment with a nylon brush and phosphate-free detergent and then copiously rinsing it with native water.

EXPLANATION

WATER

—1— LINE OF EQUAL THICKNESS OF
FORMERLY IMPOUNDED
SEDIMENT—Contour interval is 1 foot.

Base map coverages from MassGIS, NAD 83, Lambert Conformal Polyconic projection,
Massachusetts coordinate system mainland zone in meters
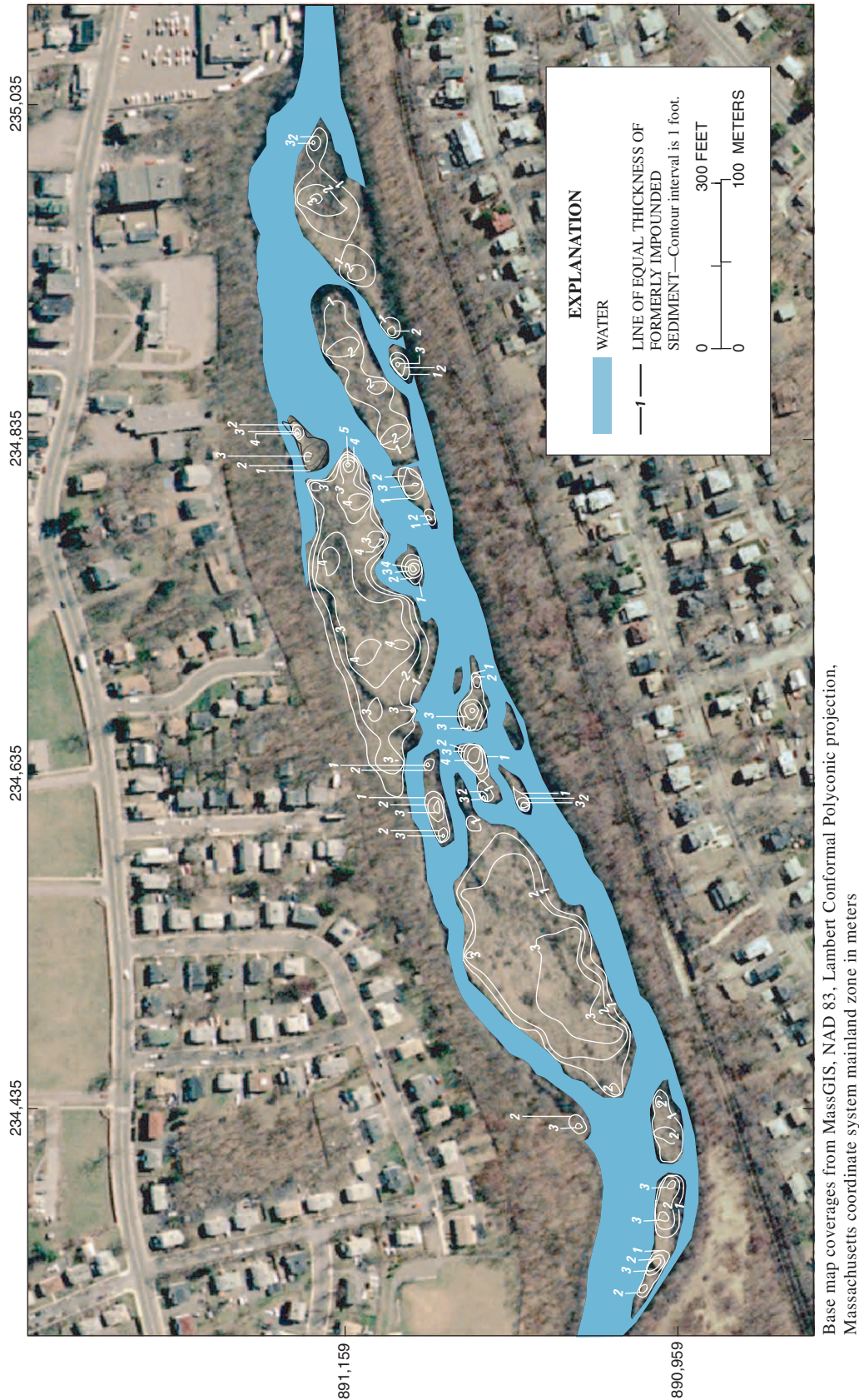
Figure 8.   Sediment thickness measured in the braided channel, lower Neponset River, Massachusetts.

Because of the large range of sediment sizes in the lower Neponset River (silt and clay to boulders), sieving was necessary. Sieving allows for more reproducible sampling results and data comparability among sampling locations (Haökanson, 1984). Use of a relatively large sieve size (6 mm) compared to other sieving procedures ensures that chemical data represent the "true" chemistry of the sample as opposed to the chemistry of a particular narrow size fraction (for example, less than 63 micrometers); secondly, ACOE has predicted that sediment of about 6 mm in size or smaller may be resuspended following dam removal (U.S. Army Corps of Engineers, written commun., 2002); and finally, because sediment-toxicity guidelines are developed on the basis of chemical data for unsieved samples, comparison with finely sieved data may be inappropriate.

A hand corer with a disposable 2.5-in. inside-diameter Lexan core barrel was used to collect sediment cores. The core barrel was pushed or hammered into the sediment until it could be driven no farther. The cores were then retrieved, capped, labeled, and transported upright to the USGS laboratory in Northborough, Massachusetts. They were visually inspected, and the lithologic characteristics (fig. 9) were logged in a notebook. The cores were then extruded into pre-cleaned Teflon bags and homogenized with a nylon spoon. Subsamples were collected and placed in pre-cleaned containers for delivery to the appropriate laboratory (table 2). Lexan core barrels were rinsed with native water before samples were taken. Teflon bags were pre-cleaned by rinsing with methanol, 5-percent hydrochloric acid, and copious amounts of deionized water.

The methods of Litten and others (1993) were used to collect PCB samples with PISCES passive water-column samplers. The samplers were filled with 0.2 L of hexane and hung from buoys that were anchored to the river bottom. After about 17 days, the samplers were collected, and their contents were poured into 250-mL amber glass bottles (table 3). Before the samplers were deployed, they were rinsed with phosphate-free detergent followed by a deionized water rinse; they then were allowed to air dry. When dry, the samplers were rinsed with acetone then rinsed three times with hexane. The polyethylene membranes were cleaned by 7-hr Soxhlet extraction (solid-liquid extraction using Soxhlet apparatus) with hexane. Once cleaned, the samplers were wrapped in hexane-rinsed aluminum foil until they were deployed.

Chemical Analysis

Sediment samples were analyzed for a suite of elements and organic compounds commonly found in rivers that drain historically industrial and urban watersheds (table 4). XRAL Laboratory of Ontario, Canada, analyzed the sediment samples by inductively coupled plasma emission spectroscopy for trace elements and by infrared spectroscopy for total organic carbon. The USEPA New England Regional Laboratory of Chelmsford, Massachusetts, also analyzed sediment samples for a suite of organic compounds, including PCBs and organochlorine pesticides; five sediment-grab samples were analyzed for polyaromatic hydrocarbons (PAHs). In addition, the USEPA also tested selected sediment cores for toxicity characteristic leaching procedure (TCLP) metals, including arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.

The New England Testing Laboratory (NETLAB) of North Providence, Rhode Island, used methods in accordance with Massachusetts methodology (Massachusetts Department of Environmental Protection, 1998) to analyze sediment-core samples for extractable petroleum hydrocarbons. The single longest cores from each impoundment and from the braided channel were selected for reactive sulfide analysis, which was completed by NETLAB. Grain-size distributions were measured by the USGS Sediment Laboratory in Louisville, Kentucky.

AXYS Analytical Services of Sydney, British Columbia, Canada, completed analysis for PCBs. PISCES passive water-column samples were analyzed for 209 individual PCB compounds or congeners. Aroclor concentrations were estimated from PCB congener data. Aroclors, mixtures of PCB congeners produced commercially and used by many industries, are the likely source of PCB congeners in the river today. Five sediment samples were also tested for PCB congeners by AXYS Analytical Services. Those samples were selected on the basis of PISCES PCB congener data and were from sample locations upstream and downstream of a suspected PCB source. Colman (2000) gives a detailed description of Aroclor and PCB congener chemical analysis.
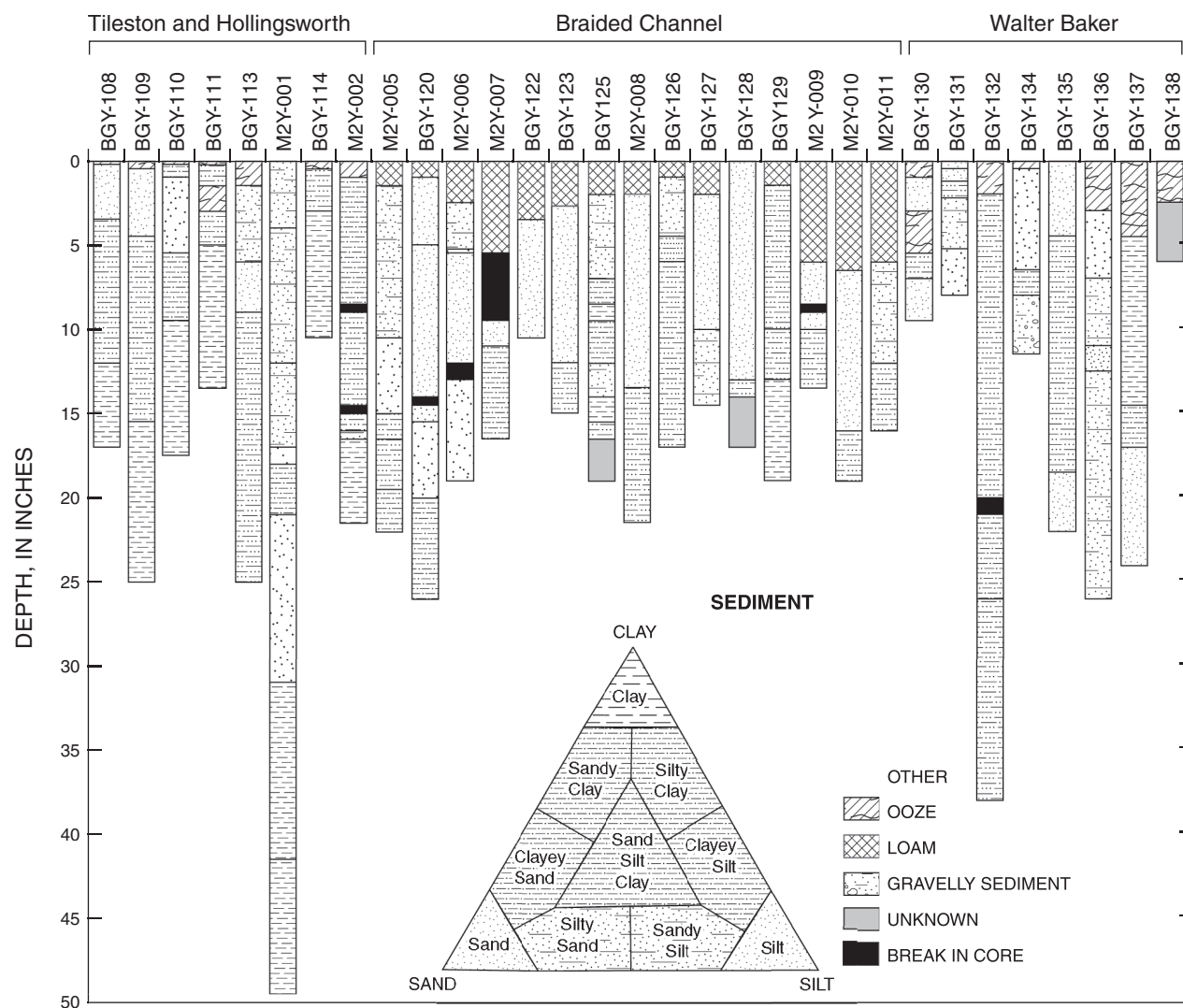
Figure 9. Sediment-core log showing visual interpretation of sediment type and length of sediment cores, collected from the lower Neponset River, Massachusetts.

Data-Analysis Methods

A variety of statistical methods was used to summarize sediment-quality data. Particular attention was given to censored data, defined as concentrations less than the detection limit. If constituent concentrations were added to give a total concentration, censored data were set to zero, with two exceptions: (1) all of the individual values to be added are censored, and (2) the values are being added in order to calculate the probable effect concentration (PEC) quotient. In these cases, (1) the reported detection limit was substituted for the censored data, (2) censored data were set equal to one-half the reported detection limit, unless all of the constituents added were reported as less than detection, in which case detection limits were added, respectively.

The USGS Method Detection Limit (MDL) program (part of S-Plus statistical software) was used to calculate summary statistics for constituents with censored data; a minimum of three observations are required to determine summary statistics by means of the MDL program, where a log-probability method is used for determining summary statistics. Helsel and Cohn (1998) describe these statistical methods in detail. In instances where the MDL program was not appropriate (for example, if there were fewer than three observations), simple population statistics were calculated with Microsoft Excel by using the methods described previously for censored data.

Table 3.   Location and details of polychlorinated biphenyl sampling by means of PISCES passive samplers, lower Neponset River, Massachusetts.

[PCB, polychlorinated biphenyls; °C, degrees Celsius; µS/cm, microsiemens per centimeter]

Station name	Sample number	Date and time deployed		Date and time retrieved		Number of days deployed	Specific conduct-ance (µS/cm)	Temper-ature (°C)	State plane coordinates	
									Easting	Northing
Paul's Bridge	17	8-06-02	10:00	8-23-02	11:00	17.04	398	26.3	231,138.43	887,163.84
	18	8-06-02	10:00	8-23-02	11:00	17.04	398	26.3		
Martini Shell	19	8-06-02	10:30	8-23-02	11:30	17.04	567	26.6	230,732.06	888,141.67
	20	8-06-02	10:30	8-23-02	11:30	17.04	567	26.6		
Incinerator Road	23	8-06-02	11:30	8-23-02	12:20	17.03	441	29.0	227,337.28	889,542.08
	24	8-06-02	11:30	8-23-02	12:20	17.03	441	29.0		
Reservation Park	21	8-06-02	11:00	8-23-02	11:50	17.03	486	29.0	230,572.10	888,943.01
	22	8-06-02	11:00	8-23-02	11:50	17.03	486	29.0		
Fairmont Avenue	15	8-03-02	11:30	8-20-02	12:00	17.02	492	26.3	231,474.16	889,338.38
	16	8-03-02	11:30	8-20-02	12:00	17.02	492	26.3		
Tileston–Hollingsworth Dam upstream	13	8-03-02	10:55	8-20-02	11:45	17.03	503	25.9	232,116.15	890,101.56
	14	8-03-02	10:55	8-20-02	11:45	17.03	503	25.9		
Tileston–Hollingsworth Dam downstream	11	8-03-02	10:30	8-20-02	11:30	17.04	512	25.8	232,343.06	890,111.39
	12	8-03-02	10:30	8-20-02	11:30	17.04	512	25.8		
Kennedy playground	9	8-03-02	10:00	8-20-02	11:00	17.04	528	24.8	233,281.86	890,518.50
	10	8-03-02	10:00	8-20-02	11:00	17.04	528	24.8		
Ryan playground	7	8-03-02	8:30	8-20-02	10:45	17.09	540	24.1	234,089.63	891,067.10
	8	8-03-02	8:30	8-20-02	10:45	17.09	540	24.1		
Braided channel	5	8-03-02	9:05	8-20-02	10:30	17.06	538	24.3	234,555.98	891,005.87
	6	8-03-02	9:05	8-20-02	10:30	17.06	538	24.3		
Central Avenue	3	8-03-02	8:05	8-20-02	9:30	17.06	537	23.7	235,216.89	891,176.52
	4	8-03-02	8:05	8-20-02	9:30	17.06	537	23.7		
Baker Dam	1	8-03-02	7:45	8-20-02	9:00	17.05	520	24.6	235,565.80	891,213.10
	2	8-03-02	7:45	8-20-02	9:00	17.05	520	24.6		

Table 4.   Common sources and (or) uses of selected constituents typically found in rivers that drain urban and industrial drainage basins.

[BHC, 1,2,3,4,5,6-hexachlorocyclohexane; DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane]

Constituent	Common source or urban uses	Constituent	Common source or urban uses
Inorganic Elements		**Polyaromatic Hydrocarbons—Continued**	
Calcium	auto exhaust, brakes, deicers	Fluoranthene	automobile exhaust
Magnesium	.....do.	Fluorene	production of dyes, plastics, pesticides
Phosphorus	auto exhaust, fuel, lubricants, industrial and municipal runoff, wastewater	Indeno(1,2,3-cd)pyrene	automobile exhaust
		Naphthalene	coal tar, gasoline and diesel fuels
Potassium	auto exhaust, deicers	Phenanthrene	production of dyes, plastics, pesticides, explosives, and drugs
Sodium	.....do.		
Antimony	flame retardants, car batteries	Pyrene	production of dyes, plastics, pesticides
Arsenic	production of pesticides and herbicides	**Organochlorine Pesticides**	
Barium	motor vehicle brake linings		
Beryllium	ceramics, steel	4,4′-DDD	pesticide for vegetables and tobacco
Bismuth	malleable irons, medicine	4,4′-DDE	breakdown product of DDT
		4,4′-DDT	pesticide for livestock and crops
Cadmium	Ni-Cd batteries, televisions	Aldrin	termite control
Chromium	bricks, stainless steel	Alpha Chlordane	household insecticide
Cobalt	jet engines, gas turbine engines	alpha-BHC	insecticide
Copper	boats, wires		
Lanthanum	battery electrodes, lighter flints	beta-BHC	.....do.
		delta-BHC	.....do.
Lead	batteries	Dieldrin	.....do.
Lithium	.....do.	Endosulfan I	insecticide for crops
Manganese	batteries, steel	Endosulfan II	.....do.
Molybdenum	aircraft parts, electrical parts		
Nickel	electronics, automobiles	Endosulfan sulfate	.....do.
		Endrin	.....do.
Scandium	high-intensity lights	Endrin aldehyde	pesticide to control birds, rodents, insects
Silver	batteries, electronics, electrical parts	Endrin ketone	.....do.
Strontium	greases, pyrotechnics	gamma Chlordane	insecticide for fire-ant control, lawns
Tin	electronics, food packing, plumbing		
Titanium	automobiles, construction, plastics	gamma-BHC	pesticide for crops
		Heptachlor	insecticide for home, buildings, corn crops
Tungsten	electrical parts, electronics	Heptachlor epoxide	.....do.
Vanadium	batteries, electronics	Methoxychlor	insecticide for crops, livestock, household
Yittrium	television sets	Chlordane (technical)	insecticide for home lawns, gardens, crops
Zinc	paints, plastic, textiles, electronics	Toxaphene	pesticide for crops
Zirconium	production of steel, photography	**Polychlorinated Biphenyls**	
Polyaromatic Hydrocarbons			
		Aroclor (1016)	hydraulic fluids, rubber plasticizer, and adhesives
Acenaphthene	automobile exhaust		
Acenaphthylene	production of dyes, plastics, pesticides	Aroclor (1221)	.....do.
Anthracene	.....do.	Aroclor (1232)	.....do.
Benzo(a)anthracene	automobile exhaust	Aroclor (1242)	.....do.
Benzo(a)pyrene	.....do.	Aroclor (1248)	.....do.
		Aroclor (1254)	.....do.
Benzo(b)fluoranthene	automobile exhaust	Aroclor (1260)	.....do.
Benzo(ghi)perylene	.....do.	Aroclor (1262)	.....do.
Benzo(k)fluoranthene	automobile exhaust, motor oil	Aroclor (1268)	.....do.
Chrysene	combustion of coal and petroleum products		
Dibenzo(a,h)anthracene	automobile exhaust		

The statistic root mean square difference (RMSD; eq. 1) was used to compare differences in PCB congener patterns, referred to as "fingerprints" (Colman, 2000). Individual congener concentrations at a given sampling location were first divided by summed congener concentrations at that sampling location, excluding censored values, to yield a normalized concentration (Colman, 2000). The RMSD is defined as the square root of the sum of squared differences of normalized concentrations of the same congener in two different samples. The two different samples could be duplicates collected at the same site or samples collected from adjacent sites.

$$RMSD = \left[\frac{\sum (A - B)^2}{n} \right]^{0.5} \qquad (1)$$

where
- $RMSD$ is the root mean square difference;
- A and B are normalized concentrations of the same congener in two different samples; and
- n is the number of congener pairs compared.

Differences in congener patterns between sampling locations were considered important when the differences in the RMSD values for samples collected in different sampling locations (intercomparison) were greater than differences in RMSD values for duplicate samples collected at the same sampling location (intracomparison).

Bias and Variability

Water-quality and sediment-quality data are subject to bias (or systematic error) and variability (or random error) during sample collection, processing, and analysis. The nature and magnitude of bias and variability can be determined by analysis of quality-control samples including blanks, field duplicates, laboratory duplicates, matrix spikes, matrix-spike duplicates, and performance-evaluation samples (PES). With a few exceptions, bias and variability in this study were generally within acceptable limits (Charles Porfert, U.S. Environmental Protection Agency, written commun., 2002). Most notable is the potential contamination bias introduced by the equipment used for collection and processing of sediment-grab samples (stainless-steel dredge, bowl, and spoon). The analysis of PES indicates that sediment-grab samples may be enriched in chromium (values not reported here) caused by contamination bias. As a result of these findings, the standard operating procedure (SOP) for sediment-core sampling was changed to include scooping sediment from the dredge that does not come in contact with any part of the dredge, using a nylon spoon (opposed to a stainless-steel spoon), and compositing in disposable pre-cleaned Teflon bags (in place of the stainless-steel bowl). It should be noted that the amount of contamination bias was relatively low compared to the concentrations of chromium measured in the sediment cores

(processed by using the modified procedure); however, to prevent misinterpretation of the data, chromium values were not included.

The variability caused by sample collection, processing, and analysis needs particular attention when PCB congener patterns are compared. For this reason, duplicate samples were collected at each of the PISCES-sampling stations. Generally, duplicate samples were in good agreement with respect to total PCB (ΣPCB) concentrations and congener patterns, with one exception. One of the duplicate samplers (sample number 7) installed at the Ryan Playground sampling location appeared to have leaked during deployment. This problem was noted during retrieval and likely caused the observed concentration difference between the samples. The congener patterns did not appear to be affected by this problem.

Data Representativeness

Because sediment-management decisions will likely be made by regulatory agencies on the basis of data presented in this report, the data must be representative of conditions present in the river. The data collected should accurately describe the physical and chemical conditions in the river, or else more data will need to be collected before sediment-management decisions can be made.

With some simple statistics and the acceptance of a few general assumptions, equation 2 (Haökanson, 1984) can be used to test data representativeness. These assumptions include: (1) the variability of the collected data approximates the "true" variability; (2) sediment-sampling techniques and analysis were adequate (that is, bias and variability were within acceptable limits); and (3) physical and chemical data are approximately normally distributed. After accepting these assumptions, the number of sediment samples needed to calculate a representative mean value (for those properties and constituents listed in table 2) were calculated at the 90-percent confidence level, with equation 2 (table 5):

$$N_i = \left(\frac{t_c \times s_{x,i}}{y \times \bar{x}_i} \right)^2 + 1 \qquad (2)$$

where
- N_i is the number of data (or samples) for property or constituent i;
- t_c is the value of student's t for desired two-sided confidence interval c with n-1 degrees of freedom where n is the number of samples;
- $s_{x,i}$ is the measured variance for property or constituent i;
- $\bar{x}_i$ is the average concentration measured of property or constituent i; and
- y is the acceptable error, in percentage of the mean; 25 percent is considered acceptable for elements, and 50 percent is considered acceptable for organic compounds.

Table 5. Estimated number of samples needed to calculate average concentrations within a 25-percent range of acceptable error for elements, and within a 50-percent range of acceptable error for organic compounds, with 90-percent confidence for the lower Neponset River, Massachusetts.

[BHC, 1,2,3,4,5,6-hexachlorocyclohexane; DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; T&H, Tileston–Hollingsworth]

Constituent	Sediment grab	Sediment cores		
		Walter Baker	Braided channel	T&H
Total organic carbon	62	14	3	3
Inorganic Elements				
Calcium	5	4	2	2
Magnesium	7	3	2	3
Sodium	6	2	9	13
Potassium	4	4	7	11
Phosphorus	14	18	3	2
Aluminum	5	22	3	5
Antimony	1	1	14	1
Arsenic	125	30	5	5
Barium	8	9	3	5
Beryllium	4	8	4	5
Bismuth	1	1	1	1
Cadmium	42	35	6	4
Chromium	22	5	14	7
Cobalt	7	4	3	4
Copper	45	20	4	3
Iron	6	2	5	4
Lanthanum	3	4	2	3
Lead	50	23	4	3
Lithium	9	9	3	5
Manganese	30	3	11	3
Molybdenum	42	14	24	19
Nickel	10	7	181	133
Scandium	6	12	3	6
Silver	15	19	5	8
Strontium	5	7	2	3
Tin	98	143	5	3
Titanium	3	2	3	2
Tungsten	1	1	1	1
Vanadium	5	34	3	2
Yittrium	4	6	2	4
Zinc	29	31	2	3
Zirconium	5	3	5	6

Constituent	Sediment grab	Sediment cores		
		Walter Baker	Braided channel	T&H
Polyaromatic Hydrocarbons				
Acenaphthene	24	50	3	7
Acenaphthylene	12	35	19	50
Anthracene	16	116	2	3
Benzo(*a*)anthracene	13	13	3	7
Benzo(*a*)pyrene	13	20	3	14
Benzo(*b*)fluoranthene	14	13	4	2
Benzo(*ghi*)perylene	13	1	4	116
Benzo(*k*)fluoranthene	12	27	3	56
Chrysene	12	116	3	50
Dibenzo(*a,h*)anthracene	13	1	1	1
Fluoranthene	12	5	3	4
Fluorene	15	10	4	50
Indeno(1,2,3-cd)pyrene	13	1	2	1
Naphthalene	13	1	148	1
Phenanthrene	20	5	3	4
Pyrene	11	4	2	4
Organochlorine Pesticides				
4,4′-DDD	1	10	6	7
4,4′-DDE	1	8	23	6
4,4′-DDT	1	116	3	1
Aldrin	1	1	1	1
Alpha Chlordane	1	116	11	2
alpha-BHC	1	1	1	1
beta-BHC	1	1	1	1
delta-BHC	1	1	1	1
Dieldrin	1	1	1	1
Endosulfan I	1	1	1	1
Endosulfan II	1	1	1	1
Endosulfan sulfate	1	1	1	1
Endrin	1	116	1	89
Endrin aldehyde	1	1	1	1
Endrin ketone	1	1	1	1

Table 5. Estimated number of samples needed to calculate average concentrations within a 25-percent range of acceptable error for elements, and within a 50-percent range of acceptable error for organic compounds, with 90-percent confidence for the lower Neponset River, Massachusetts.—Continued

[BHC, 1,2,3,4,5,6-hexachlorocyclohexane; DDD, dichlorodiphenyldichloro-ethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltri-chloroethane; T&H, Tileston–Hollingsworth]

Constituent	Sediment grab	Sediment cores		
		Walter Baker	Braided channel	T&H
Organochlorine Pesticides—*Continued*				
gamma Chlordane	1	1	9	1
gamma-BHC	1	1	1	1
Heptachlor	1	1	1	1
Heptachlor epoxide	1	1	1	1
Methoxychlor	137	1	1	1
Polychlorinated Biphenyls				
Aroclor (1016)	1	1	1	1
Aroclor (1221)	1	1	1	1
Aroclor (1232)	1	1	1	1
Aroclor (1242)	30	17	7	2
Aroclor (1248)	1	1	1	1
Aroclor (1254)	23	16	6	3
Aroclor (1260)	18	19	5	3
Aroclor (1262)	1	1	1	1
Aroclor (1268)	1	1	1	1
Chlordane (technical)	1	1	1	1
Toxaphene	1	1	1	1

In general, enough data were collected and data were representative (the data can be used to calculate a mean value at the 90-percent confidence level) of those areas for which cores were collected. Similarly, the number of sediment-grab samples generally is appropriate, with a few notable exceptions. The combination of good (bias and variability within acceptable limits) and representative (enough or sufficient amount) sediment-quality data, combined with appropriate sampling techniques and data-analysis methods, indicate that the data interpretation will yield meaningful results that can be used to make sediment-management decisions when options for river restoration are considered.

Sediment Quality and Implications for River Restoration

Before sediment-management decisions are made and river-restoration efforts begin, it is useful to define objectives for managing and monitoring sediment quality. By determining these objectives, environmental managers can make more informed decisions about dam removal and sediment management. Sediment-quality objectives may include reducing element and organic-compound concentrations to "background" concentrations (those concentrations not affected by anthropogenic activities), or to levels equal to or below other criteria. Comparisons between measured bottom-sediment contaminant concentrations and background concentrations, concentrations from other urban rivers, and concentrations established by sediment-quality guidelines may also help decisionmakers determine the best approach to managing sediment for river restoration.

Concentrations of Elements Compared to Background Concentrations

With the concerns described above in mind, concentrations of elements measured in sediment samples from the lower Neponset River were compared to median concentrations measured in sediment collected from streams in Connecticut, Maine, Massachusetts, New Hampshire, New York, and Rhode Island. These sediment samples were collected between 1977 and 1980 as part of the National Uranium Resource Evaluation (NURE) program, specifically the Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) program (Smith, 1998) and reanalyzed by the National Geochemical Survey using modern (2000) methods (Grossman, 1998; U.S. Geological Survey, 2003). A brief history of this program, as well as tabulated data, are available on the World Wide Web (U.S. Geological Survey, 2004).

The NURE HSSR program SOP instructed researchers to collect bottom-sediment samples from small "uncontaminated" streams (Ferguson and others 1977). In other words, samples were purposely collected in areas assumed to be unaffected by humans; therefore, element concentrations measured from these sediment samples may approximate "non-urban background" concentrations of New England streams.

The samples collected by NURE HSSR and the samples collected in this study were processed by different methods (Ferguson and others 1977). The NURE HSSR samples were sieved with a 150-micrometer sieve; however, samples collected in this study were not sieved. This difference in methods could artificially bias concentrations because fine-grained sediments have much larger surface area per unit weight than coarse sediments (Horowitz, 1991); therefore, fine-grained sediments have more area for contaminants to adhere.

Enrichment factors were calculated by dividing element concentrations measured in bottom-sediment samples collected from the lower Neponset River by median background concentrations (table 6) measured as part of the NURE HSSR program. An enrichment factor greater than one indicates that the constituent concentration is greater than background concentration for that constituent; an enrichment factor less than one indicates the opposite. An enrichment factor of one indicates that the measured concentration is equal to background concentration.

There are, however, potential problems associated with the interpretation of calculated enrichment factors. Many natural factors can cause bottom sediments to be enriched with elements. Some of these factors include differential weathering (related to solubilities of individual elements), physical and chemical fractionation (for example, winnowing of fines), the mineralogy of atmospheric dust, and biogenic dust (Reimann and De Caritat, 2000); therefore, researchers may erroneously conclude that enrichment is caused by human activity, when it may actually be caused by natural processes. Nonetheless, enrichment factors might serve as a good first approximation to estimate how anthropogenic activity has affected sediment quality.

With the above discussion in mind, some element con-centrations in grab samples, which represent more recent deposition, collected from the lower Neponset River were generally (at more than one-half of the sampling sites) enriched (fig. 10). Of particular concern are nickel (nickel concentrations were greater than the background concentration for nickel at 90 percent of the grab-sampling locations), copper (85 percent), zinc (80 percent), lead (70 percent), and molybdenum (65 percent) concentrations. Of those grab-sampling stations where samples had enrichment factors greater than one, the enrichment factors for copper, lead, and zinc averaged about four. The sample collected from location BGY-121 was, on average, the most enriched. Specifically, arsenic, copper, phosphorus, lead, molybdenum, nickel, and zinc concentrations were all higher than background concentrations at this station.

Table 6. Median background concentrations of elements measured in sand, silt, and clay samples collected from Massachusetts, Connecticut, Maine, New Hampshire, New York, and Rhode Island, as part of the National Uranium Resource Evaluation Hydrogeochemical and Stream Sediment Reconnaissance Program.

[--, no data; ppm, parts per million]

Constituent	Concentration
Calcium, in percent	1.2
Magnesium, in percent	.48
Sodium, in percent	1.4
Potassium, in percent	1.4
Phosphorus, in percent	.06
Aluminum, in percent	5.1
Arsenic, in ppm	7.6
Barium, in ppm	345
Beryllium, in ppm	2
Chromium, in ppm	54
Cobalt, in ppm	8
Copper, in ppm	10
Iron, in percent	2.5
Lanthanum, in ppm	44
Lead, in ppm	30
Lithium, in ppm	15
Manganese, in ppm	815
Molybdenum, in ppm	1.2
Nickel, in ppm	12
Scandium, in ppm	9
Silver, in ppm	3
Strontium, in ppm	143
Tin, in ppm	--
Titanium, in percent	.53
Tungsten, in ppm	--
Vanadium, in ppm	53
Yittrium, in ppm	23
Zinc, in ppm	48

Figure 10.   Concentrations of *A*, elements; and *B*, organic compounds (by type) measured in grab and core samples collected from the lower Neponset River, Massachusetts (<, actual value is less than value shown).

A.—Continued

Figure 10—Continued.   Concentrations of *A*, elements; and *B*, organic compounds (by type) measured in grab and core samples collected from the lower Neponset River, Massachusetts (<, actual value is less than value shown).
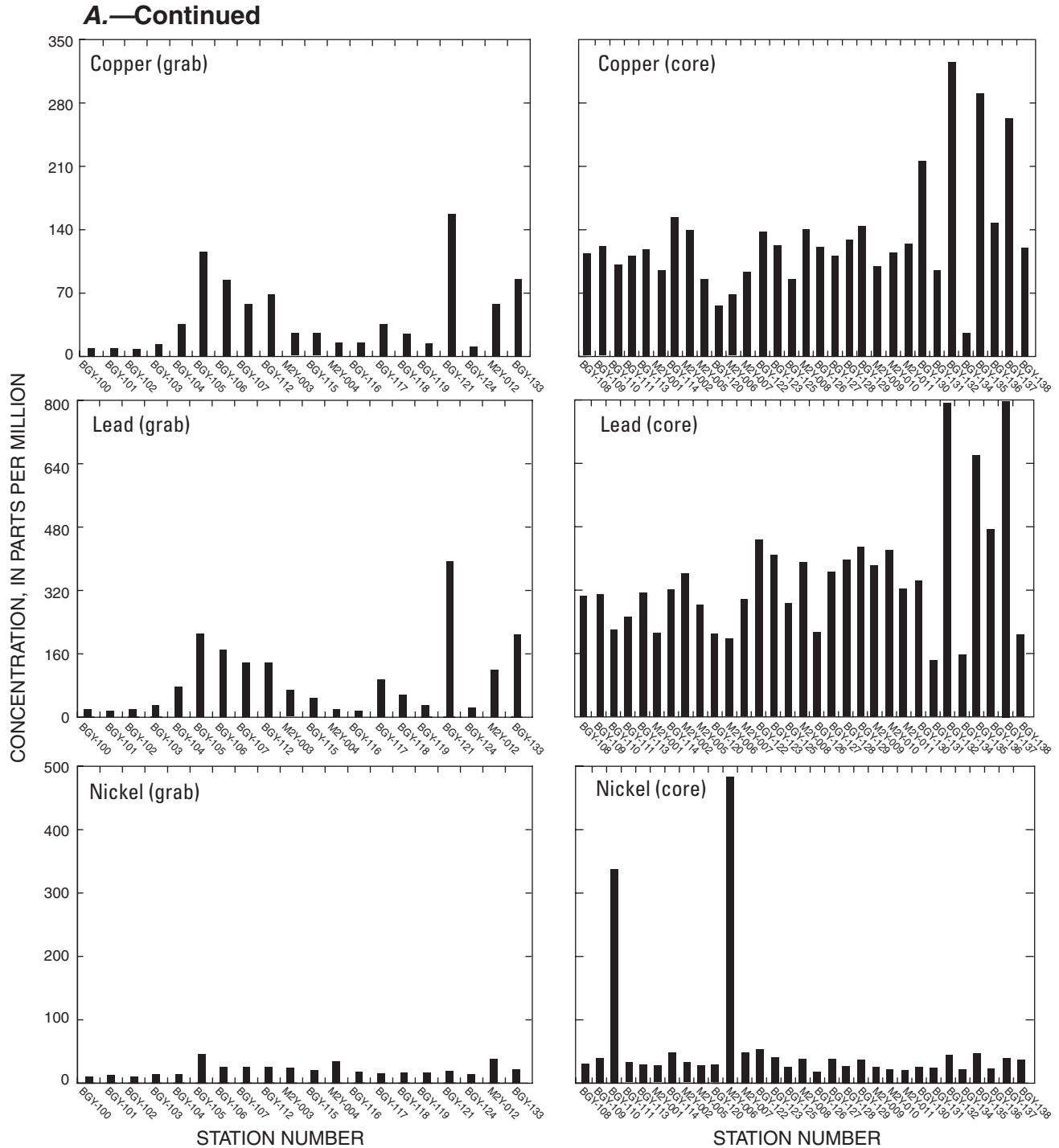
A.—Continued

Figure 10—Continued.   Concentrations of *A*, elements; and *B*, organic compounds (by type) measured in grab and core samples collected from the lower Neponset River, Massachusetts (<, actual value is less than value shown).
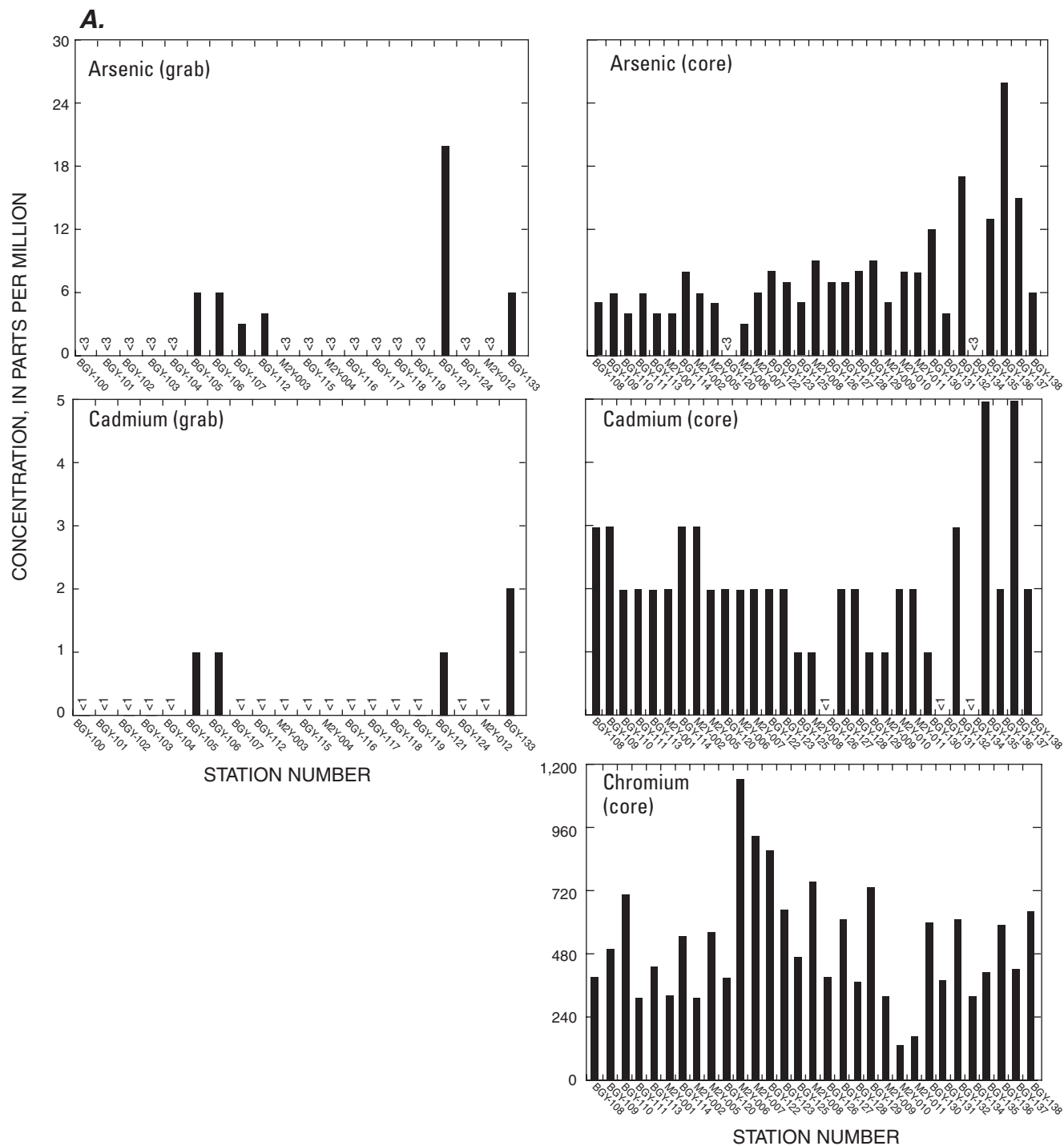
Figure 10—Continued.   Concentrations of *A*, elements; and *B*, organic compounds (by type) measured in grab and core samples collected from the lower Neponset River, Massachusetts (<, actual value is less than value shown).
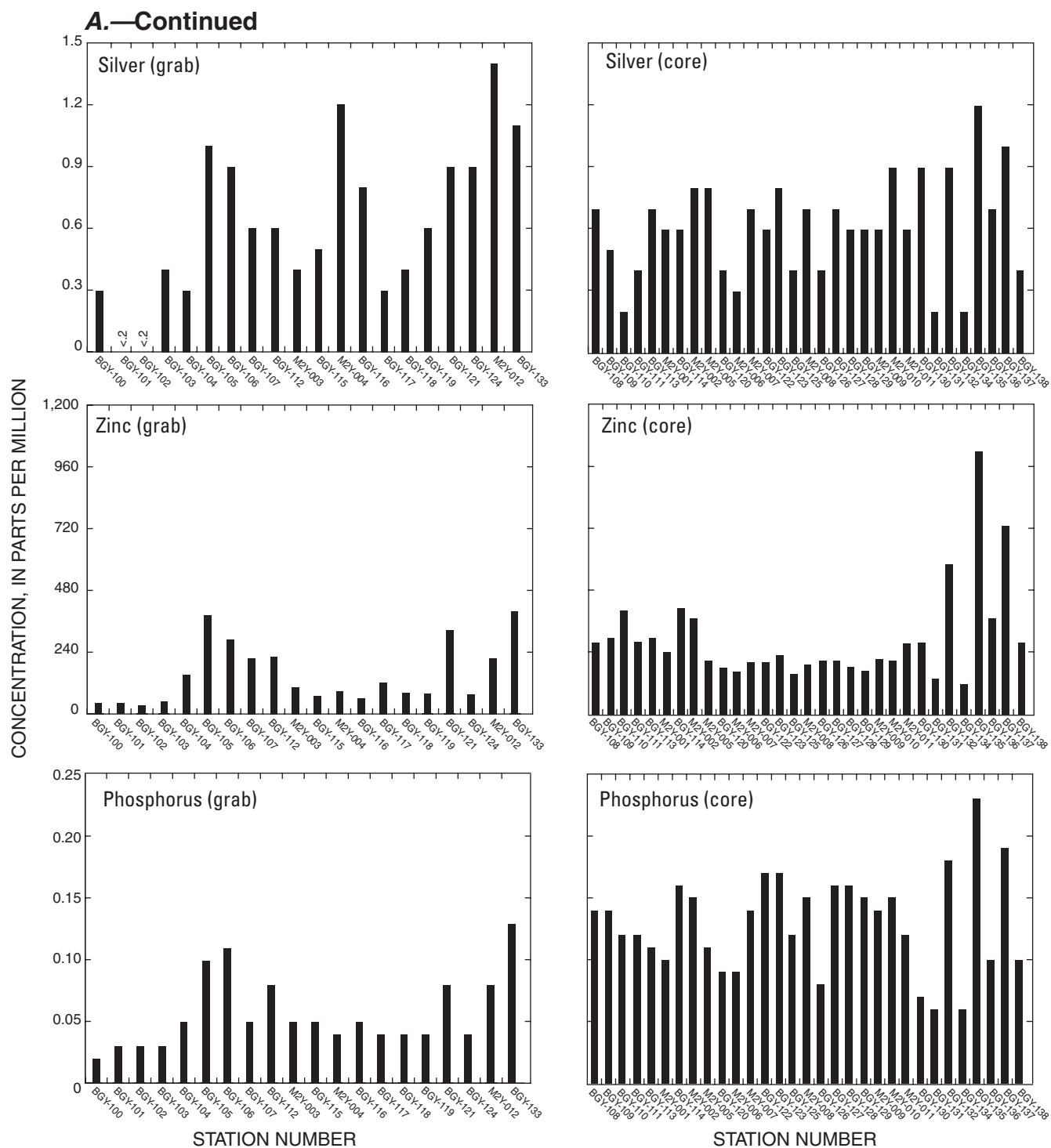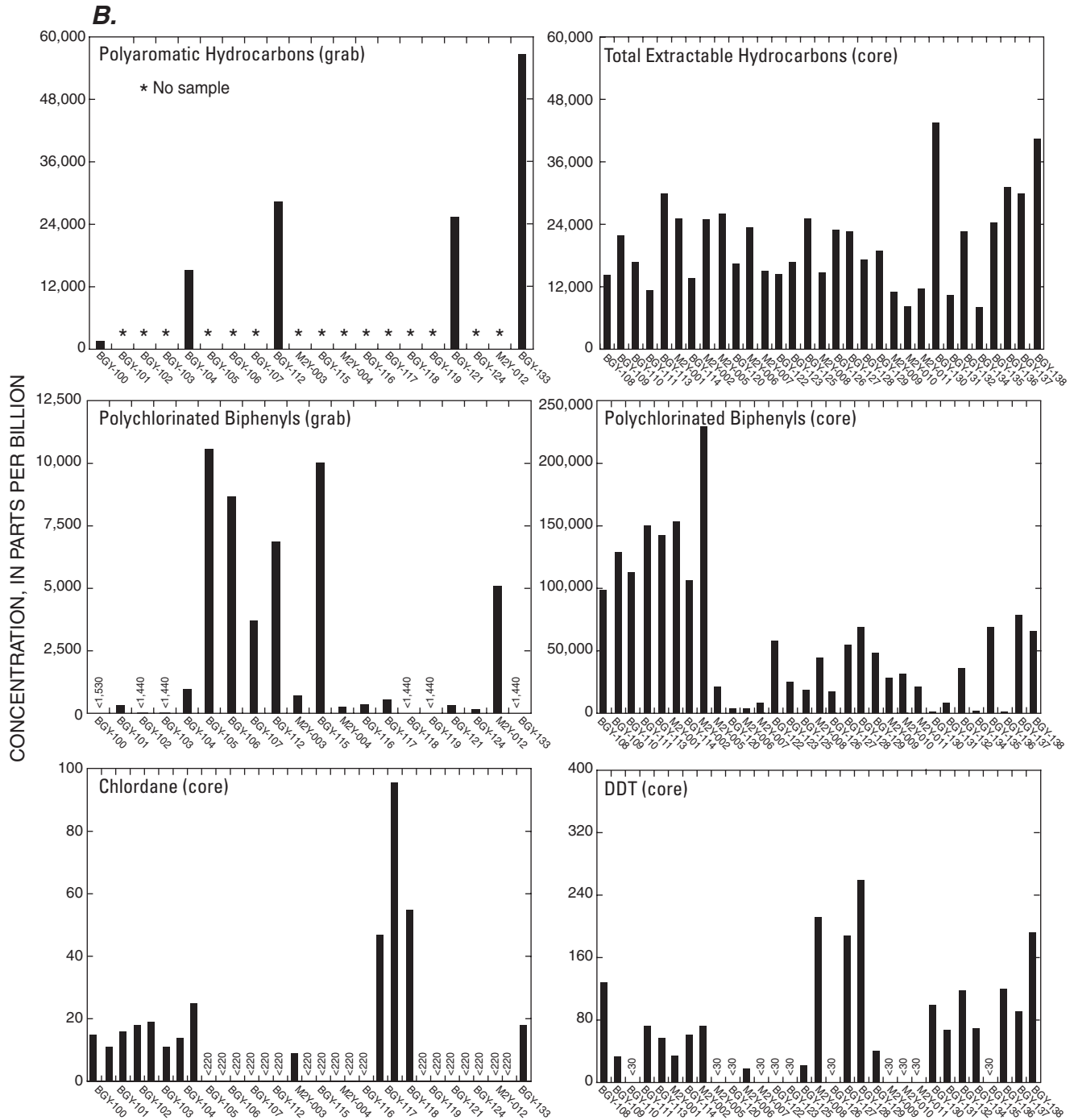
Similar to the grab samples, core samples, which represent both recent and historical deposition, are enriched with elements. Cobalt, iron, lithium, magnesium, molybdenum, and potassium, whose concentrations in the core samples were similar to their concentrations in the grab samples, and all other elements in core samples with calculated enrichment factors greater than one were more enriched in core samples than they were in grab samples. In addition to potentially toxic chemicals that were enriched at more than one-half of the grab-sampling sites [nickel (100 percent of the sites), copper (100 percent), lead (100 percent), and zinc (100 percent)], chromium (100 percent), cobalt (84 percent), molybdenum (100 percent), phosphorus (90 percent), and vanadium (68 percent) concentrations were enriched at more than one-half of the core-sampling sites. In the core samples, copper, on average, had the greatest degree of enrichment (average enrichment factor 13), followed by lead (12), and chromium (9.5).

Sediment cores collected from the Walter Baker impoundment were, on average, more enriched than sediment cores collected from the Tileston and Hollingsworth impoundment and the braided channel area. Of all samples from coring locations, the sample collected from location M2Y-006 (braided channel) was the most enriched. Specifically, chromium, cobalt, copper, phosphorus, molybdenum, nickel, lead, and zinc concentrations were all higher than background concentrations at this station.

Enrichment factors calculated for core samples were expected to be greater than those calculated for grab samples. Sediment cores were not collected throughout the study area. Instead, they were collected specifically from current and former impoundments where contaminants may have accumulated in fine-grained sediment. Additionally, because sediment cores indicate contamination that has accumulated over the history of an impoundment, the sediment cores collected from the lower Neponset River represent historical input of contaminants to the river, which may have been substantially greater than current (2003) inputs.

Simply comparing enrichment factors between grab samples and core samples, however, allows only generalizations about sediment quality in the study area. The comparison does not definitively indicate whether sediment quality is improving, getting worse, or remaining constant. If more definitive information about the history of sediment quality in the lower Neponset River is needed, then it would be necessary to complete a detailed paleolimnological study, which would include the collection, analysis, and dating of sediment cores; such work was beyond the scope of this study.

Organic Compounds

In contrast to the natural occurrence of elements in bottom sediments, many organic compounds in bottom sediment can originate only as a result of human activities. A clear understanding of detection rates, however, requires an understanding of the implications of the detection or non-detection of a chemical. Essentially, a detection indicates only that the constituent concentration is greater than the minimum reporting level (MRL) for a given analytical method. A non-detection, however, can indicate two possibilities: (1) the chemical is not present in the sample, or (2) the chemical is present in the sample at a concentration less than the MRL. Non-detection of a constituent, therefore, does not unequivocally demonstrate the absence of that constituent. Knowing this fact is particularly important when analyzing organic compound data. Because of interferences from coeluting compounds (compounds that cannot be separated from the analyte during the sample analysis), the MRLs for organic compounds can differ among some samples (even when the same method is used). This aspect of the MRLs can create a situation in which a constituent is undetected in one sample but detected in another. In this section, constituent concentrations reported as "less than detection" were considered to be absent from the sample. It is important to note that this assumption can substantially affect data interpretation.

With this in mind, a few of the PAHs for which analysis was completed were detected in all of the sediment samples (fig. 10). Similarly, PCBs[3] were also detected in all but six grab samples. Of the PCB Aroclors tested, only three were detected: 1242, 1254, and 1260. The other Aroclors were not detected in any of the samples. Except for two detections of Methoxychlor from grab samples collected at the most downstream part of the study area (stations BGY-124 and BGY-133), there were almost no detections of organochlorine pesticides in the grab samples. There were, however, many detections of these pesticides in the core samples. Most notably, Chlordane, DDT (dichlorodiphenyltrichloroethane), and its isomers DDD (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyl-dichloroethylene), were detected in many samples.

Concentrations of PAHs and PCBs in grab samples indicated great spatial variability. Among locations where organic compounds were detected in the grab samples, the Walter Baker impoundment yielded sediment with the highest concentrations of ΣPAHs (sum of 16 PAHs); high ΣPAHs in the Walter Baker impoundment may result because of the railroad bridge that spans the river just upstream of the impoundment. Interestingly, the ΣPCB concentration (sum of Aroclors 1242, 1254, and 1260) measured in the grab samples collected at sampling location BGY-105 was the highest from all of the sampling locations (Breault and Cooke, 2004). The PISCES water-column data collected from this stretch of the river also indicated a major source of PCBs.

Organic compound concentrations measured in core samples were generally much higher than concentrations measured in grab samples, the only exception being PAH concentrations, which were similar in core and grab samples.

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[3]Discussions about PCB Aroclors or ΣPCB concentrations (sum of Aroclors 1242, 1254, and 1260) in sediment samples refer to those PCBs analyzed by the U.S. Environmental Protection Agency, unless otherwise noted.

Similar PAH concentrations were expected because combustion sources continue to enrich the upper layers of sediment with PAHs (VanMetre and others, 2000).

On average, the sediment cores collected from the Tileston and Hollingsworth impoundment had the highest concentrations of ΣDDT (sum of DDT, DDE, and DDD) and ΣPCBs. Sediment cores collected from the braided channel, on average, had the highest concentrations of ΣChlordane (sum of alpha-Chlordane, gamma-Chlordane, and Chlordane-technical); however, sediment collected from the Walter Baker impoundment may have an average ΣChlordane concentration of equal or greater magnitude (estimated ΣChlordane concentration equal to less than 220 ppb).

Of all the core-sampling locations, location M2Y-010 (braided channel) yielded sediment samples with the highest concentrations (about four times the average) of ΣDDT and ΣChlordane. The highest concentration of ΣPCBs (about four times the average) was detected in the sample from location M2Y-002 (Tileston and Hollingsworth impoundment).

As with the elements, the greater number of detections and higher concentrations of some organic compounds in core samples than in grab samples was expected. More detections were expected in cores because the cores were specifically collected from the impoundments, or former impoundments (for example, braided channel), which are depositional areas. In contrast, many of the surficial grab samples were collected from the higher velocity, free-flowing reaches, which tended to have particles of a coarser grain size. Also, the use and disposal of some organic compounds was more prevalent in the past than in recent years. In fact, general use of DDT was banned in the United States in 1972 (U.S. Environmental Protection Agency, 1972). In 1988, the USEPA banned all uses of Chlordane (Agency for Toxic Substances and Disease Registry, 1995a).

It is important to note that the history of sediment distribution in the Neponset River has been changed by dredging and channelization that took place in the 1950s and 1960s. Although beyond the scope of this study, it is likely that much of the early contamination (before the 1960s) is present in the banks and upland soils that surround the river, where the dredged sediment was disposed.

Comparison of Sediment Chemistry in the Lower Neponset River to that in Other Urban Rivers

One goal of river restoration is to restore a river to its "natural" state, the condition present before human activities affected the river. For this goal to be achieved, metal concentrations, for example, might be reduced to background levels, or all synthetic organic compounds might be removed from the river. This goal, however, is often unrealistic for rivers that drain heavily urban and industrial areas, such as the area drained by the Neponset River. In these cases, it may be important to define alternative goals for urban-river restoration.

For example, the sediment quality of a particular river might be improved enough to match that of rivers in other similarly urban areas.

To help define the effort needed to restore the sediment quality of the lower Neponset River to that of other urban rivers, concentrations of elements and organic compounds measured in grab samples collected from the Neponset River were compared with those collected from other urban rivers throughout the conterminous United States as part of the National Water-Quality Assessment (NAQWA) Program of the USGS (Rice, 1999; fig. 11). Element concentrations in grab samples from the Neponset River are generally less than or equal to element concentrations in sediment collected from other urbanized, free-flowing rivers, with the exception of molybdenum and silver. Of the organic compound concentrations tested, concentrations of PAHs and PCBs were much higher in the samples from the Neponset River. In fact, median PCB concentrations measured in grab samples from the Neponset River are over 120 times greater than those collected from the NAQWA urban rivers.

Although a comparison of contaminant concentrations from the Neponset River to those of other urban rivers from across the United States is valuable, a better comparison might be that of concentrations from the Neponset River to those of other urban rivers in Massachusetts. Better yet, a comparison of concentrations with those from the other two dammed rivers tributary to Boston Harbor would be the most valuable comparison (Breault and others, 2000). The element and organic compound concentrations in bottom sediment in the Neponset, upper Mystic, and lower Charles Rivers are shown in figure 12. Generally, element concentrations are lower in the Neponset River than in the lower Charles and upper Mystic Rivers. Organic compound concentrations in the Neponset are generally lower than in the lower Charles River and upper Mystic River, which has concentrations higher than the Charles River, although PCB concentrations are similar in the Charles and Neponset Rivers. No PCBs were detected in the upper Mystic River.

These comparisons are useful, but different sampling methods, sample preparation, and laboratory analytical methods also may contribute to the observed differences in concentrations, particularly in the case of the NAQWA samples. Sediment samples collected by the NAQWA Program for trace metal and organic compound analysis were sieved through a 63-mm sieve and a 2-mm sieve, respectively. Knowledge of this sieving is important because contaminants are often associated with the "finer" fraction; therefore, constituent concentrations measured by the NAQWA Program may be biased high relative to the Neponset River sediment samples. In addition, the chemical-analysis methodology used by the NAQWA Program includes a more robust digestion than that used in this study. A comparatively stronger digestion may also bias the NAQWA Program data high relative to the Neponset River sediment samples.
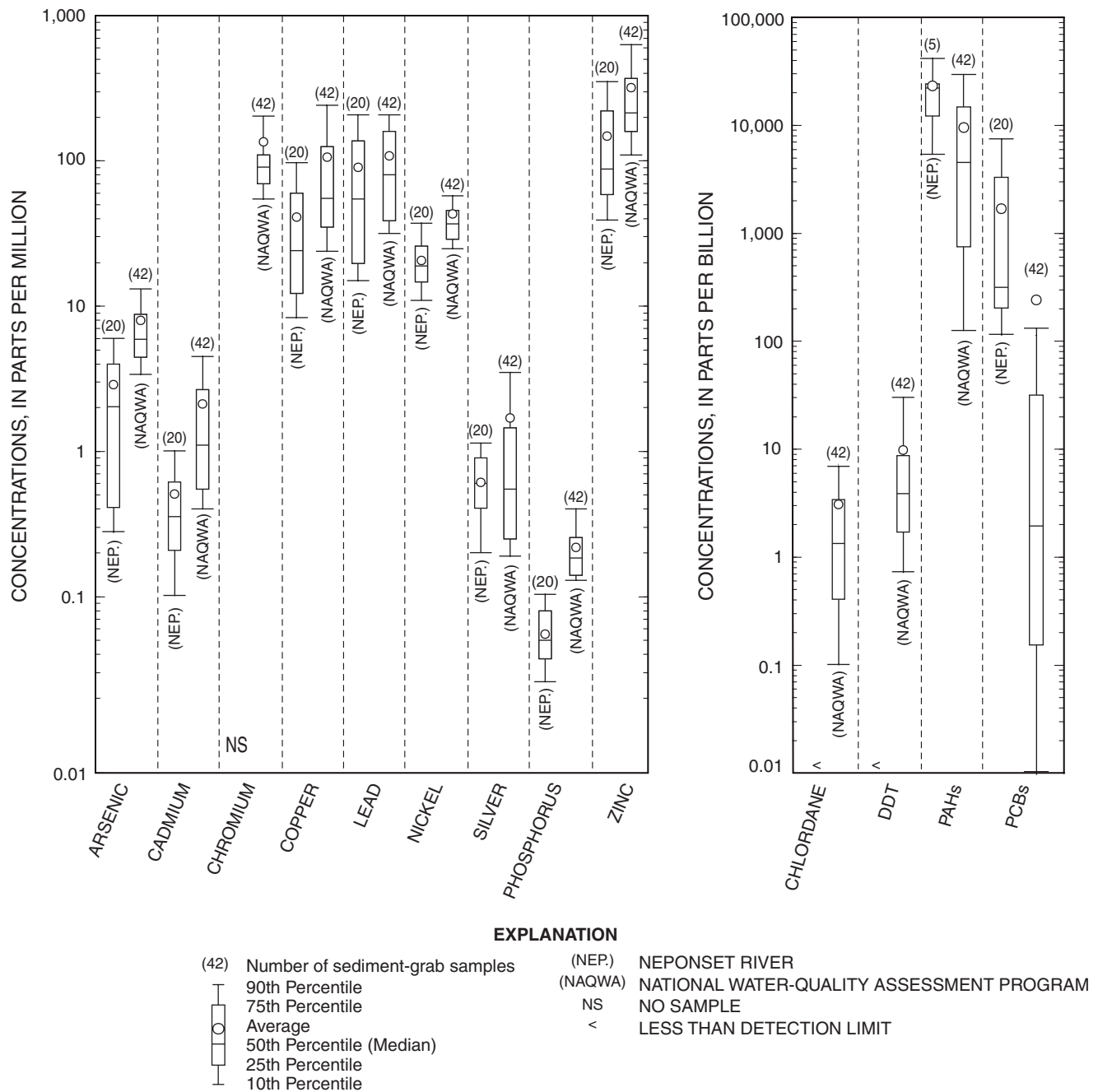
Figure 11. Population statistics for element and organic compound concentrations measured in grab samples collected from the lower Neponset River, Massachusetts, in comparison to other urban rivers in the United States.
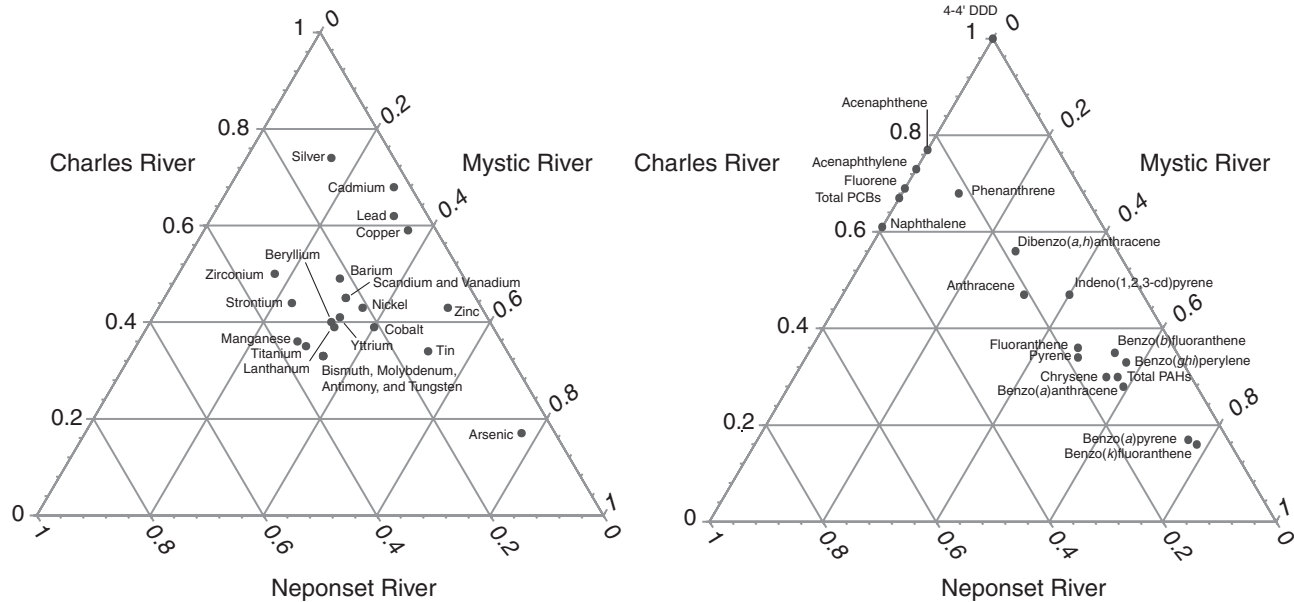
Figure 12.   Relative amount of enrichment of elements and organic compounds from three urban rivers tributary to Boston Harbor—the lower Neponset River, the upper Mystic River, and the lower Charles River, Massachusetts.

Comparisons of data from grab samples collected from throughout the lower Neponset River (Paul's Bridge to the Walter Baker Dam) and other urban rivers, including those tributary to Boston Harbor, give insight into the overall sediment quality of the Neponset River. Some parts of the river, however, are highly contaminated with PCBs, in particular the impounded and formerly impounded reaches. It may be useful, therefore, to compare PCB concentrations measured in the Neponset River sediment to concentrations in sediment from other rivers with known PCB contamination. One such river is the Housatonic River, in western Massachusetts. From 1932 to 1977, at least 10,000 kilograms of PCBs were discharged to the Housatonic River (Gay and Frimpter, 1984). In the most heavily contaminated sections of the Housatonic River, PCB concentrations average about 1,500,000 ppb, with a maximum of 54,000,000 ppb (U.S. Environmental Protection Agency, 2002). Although these concentrations are higher than those in the Neponset River, concentrations downstream of the most heavily contaminated section of the Housatonic River are comparable to those in the Neponset River. In Woods Pond, the first impoundment downstream of the heavily contaminated area on the Housatonic River, sediment PCB concentrations

ranged from less than the detection limit to 220,000 ppb (U.S. Environmental Protection Agency, 2003a). In the Neponset River, PCB concentrations are of similar magnitude; these concentrations averaged about 140,000, 30,000, and 32,000 ppb in cores from the Tileston and Hollingsworth impoundment, braided channel, and Walter Baker impoundment, respectively.

Contaminated Bottom-Sediment Toxicity

Water-resource managers and environmental constituencies often use the terms "fishable" and "swimmable" to describe the goals of river restoration. In practice, for a river to be fishable and swimmable, the water and sediment quality must (1) allow for a healthy and diverse fish population, and (2) be safe enough for humans to swim in the river. If achieving a fishable and swimmable Neponset River is the goal of river restoration, then sediment quality must be quantified in terms of potential adverse effects to aquatic organisms and humans, particularly if environmental managers choose the "no-action" sediment-management option, in which sediment is allowed to remain and is not removed, contained, remediated, or released.

Benthic Organisms

One way to assess whether a river can support a healthy and diverse population of fish is to test the health of their food source, particularly benthic organisms. Benthic organisms (for example, amphipods, mussels, and worms), upon which some fish feed, are those organisms that live and feed on the river bottom, where they come in direct contact with contaminated sediment. Contaminants can accumulate in the tissues of these organisms as they ingest sediment contaminated with elements and organic compounds or sorb these containments directly from sediment and water (Forstner and Whittman, 1983). Eventually, the accumulation of these constituents in benthic organisms can cause physiological problems and death. Subsequent ingestion of contaminated benthic organisms by other organisms higher in the food chain (for example, fish) can cause similar health effects.

The potential toxicity of Neponset River sediment to benthic organisms can be estimated by comparing measured contaminant concentrations to a set of sediment-quality guidelines known as PECs. Concentrations greater than the PECs are known to cause toxicity because of their effect on the survival or growth of laboratory test organisms, such as the amphipod *Hyalella azteca*, and the insect larva *Chironomus* spp. The predicted potential for toxicity depends on the organism and the test conditions. First, a measured contaminant concentration is divided by its corresponding PEC to yield a PEC quotient. In this study, the PEC quotients for up to three types of contaminants (trace metals, ΣPAHs, and ΣPCBs) were computed and then averaged for each sample according to equation 3:

$$\overline{Q}_x = \frac{\sum \dfrac{C_{x,y}}{PEC_y}}{n_x}, \qquad (3)$$

where
$\overline{Q}_x$ is equal to the average *PEC* quotient for sample *x*;
$C_{x,y}$ is equal to the concentration of contaminant type *y* in sample *x*. Contaminant types are the PAHs, PCBs, or the trace elements arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn);
PEC_y is equal to the *PEC* for contaminant y (Ingersoll and others, 2000); and
n is equal to the number of contaminant types available for sample *x*.

Finally, the average PEC quotients are compared to PEC-quotient ranges associated with different toxicity potentials (Ingersoll and others, 2000).

The potential for toxicity was determined for the top 2–4 in. of bottom sediment, which can be considered the biologically active sediment layer (Baudo and Muntau, 1990). The potential for toxicity by test organisms (*Hyalella azteca*

and *Chironomus* spp.) and test conditions (10- to 14-day test and 28- to 42-day test) at each site is shown in figure 13. The potential for toxicity in figure 13 refers to the potential for toxicity compared to a control or reference sediment (Ingersoll and others, 2000). For example, a sediment sample with an estimated potential toxicity of 20 percent means that 20 out of 100 toxicity tests are likely to show some level of toxicity for the concentration of contaminants measured in that sediment sample for a particular organism and a particular set of test conditions.

The predicted potential of toxicity ranged from about 13 percent to 100 percent among the sampling locations (fig. 13). Trace elements and the PAHs accounted for some level of toxicity at every sediment-sampling location for which they were tested; however, PCBs were most responsible for predicted toxicity, on average. The largest PEC quotient was calculated for sediment-sampling location BGY-105. In fact, PCBs accounted for most (96 percent) of the PEC quotient at this location.

This evaluation of potential toxicity is an informal screening to distinguish groups of chemicals, and locations, that are likely to be associated with adverse biological effects. This treatment of the data is intended to supplement, not substitute, direct measures of sediment toxicity.

Humans

River-restoration efforts often focus on bringing people and river together. When a river is restored, access to it improves, recreational opportunities increase, and more people fish and swim in the river. As people interact with the river, they will likely come in contact with sediment. Consequently, information about human health risks associated with direct contact or incidental ingestion of contaminated sediment is important for water-resources management.

Potential human-health effects caused by direct contact with or incidental ingestion of contaminated sediment can be indirectly assessed by comparing sediment-contaminant concentrations with exposure-based guidelines. Such guide-lines, however, do not exist for aquatic sediment, but they do exist for contaminated upland soil. In the absence of aquatic-sediment guidelines, comparison with direct-contact, exposure-based soil standards may suffice (Massachusetts Department of Environmental Protection, 1996; method 2, soil category S-1).

Soil standards exist for many of the constituents tested; but in the sediment samples (grabs and cores), only a few of the constituents were detected at concentrations equal to or greater than the soil standards. Of the elements, beryllium, chromium, lead, and nickel had concentrations closest to the soil standards. Beryllium and lead concentrations measured at about 40 percent of the sites were greater than the soil standards (fig. 14).
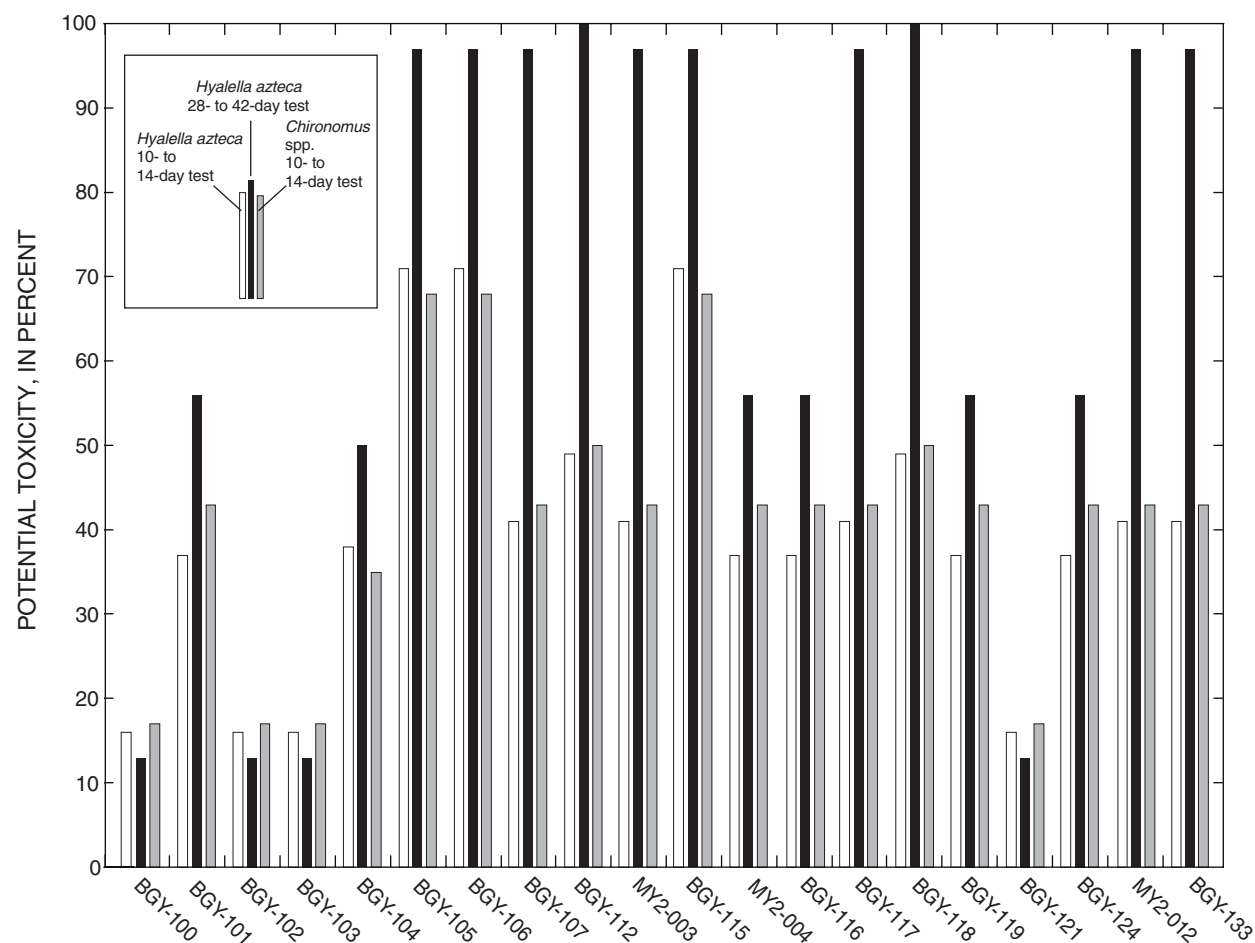
Figure 13.   Estimated sediment toxicity to *Hyalella azteca* and *Chironomus* spp. with respect to consensus-based freshwater sediment-quality guidelines from samples collected from the lower Neponset River, Massachusetts.

Measurements of organic compound concentrations are more important in terms of (1) the number of constituents, and (2) the magnitude of concentrations greater than the soil standards. Of particular importance are PCBs (PCB concentrations measured at about 67 percent of the sites were greater than the soil standard) and some of the PAHs listed by the Department of Health and Human Services as known animal carcinogens: benzo(*a*)anthracene (55 percent of the sites), benzo(*b*)fluoranthene (59 percent), and benzo(*a*)pyrene (57 percent) (Agency for Toxic Substances and Disease Registry, 1995b) (fig. 14).

Comparing sediment concentrations to soil-based, human-health standards likely overestimates the potential human-health risk. As people wade or swim near contaminated sediment, the sediment is washed quickly from their skin. On the other hand, people exposed to contaminated soils have extended contact time with the soil; therefore, the contaminant is more likely to enter the body (Clifford Opdyke, U.S. Army Corps of Engineers, written commun., 2004). Nonetheless, the comparison can provide a sense of the risk associated with contacting the sediment. These comparisons, however, are not intended to replace direct measures of the health risk.
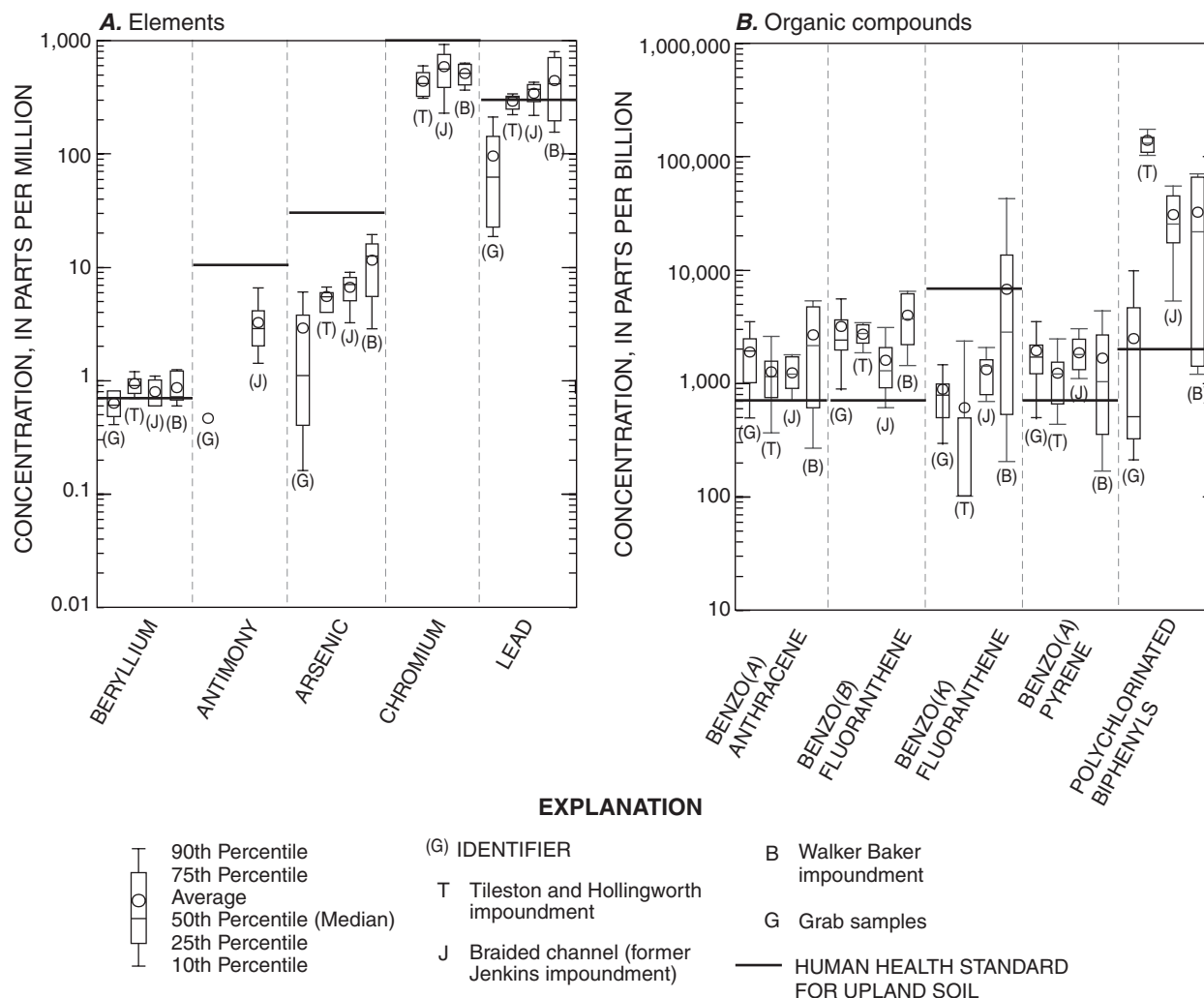
Figure 14. Comparison of concentrations of selected *A*, elements; and *B*, organic compounds in sediment collected from the lower Neponset River, Massachusetts, with human health guidelines for direct contact with and incident ingestion of contaminated soils.

Comparison between Upstream and Downstream Sediment Chemistry

With comparisons between sediment-quality data and background concentrations, concentrations from other urban rivers, and concentrations set forth in aquatic life guidelines, water-resources managers can begin to make informed decisions about sediment management. One possible management option is natural sediment redistribution. With this option, the deltaic deposits trapped behind a dam would be released partially and slowly after dam deconstruction or breaching and allowed to naturally redistribute downstream. A decision to redistribute the sediment, however, would have to be based on information about sediment quality downstream of the dam that traps the contaminated sediment. To meet this need, eight grab samples were collected from the estuarine portion of the river downstream of the Walter Baker Dam, where any released sediment would initially be deposited and from which tidal action could then distribute the sediment farther downstream. Detailed sediment-transport models would be needed to determine the ultimate distribution of these sediments, but that work was beyond the scope of this study. The detailed grain-size distribution data collected in this study (fig. 15), however, could serve as the basis for any future modeling of sediment transport.
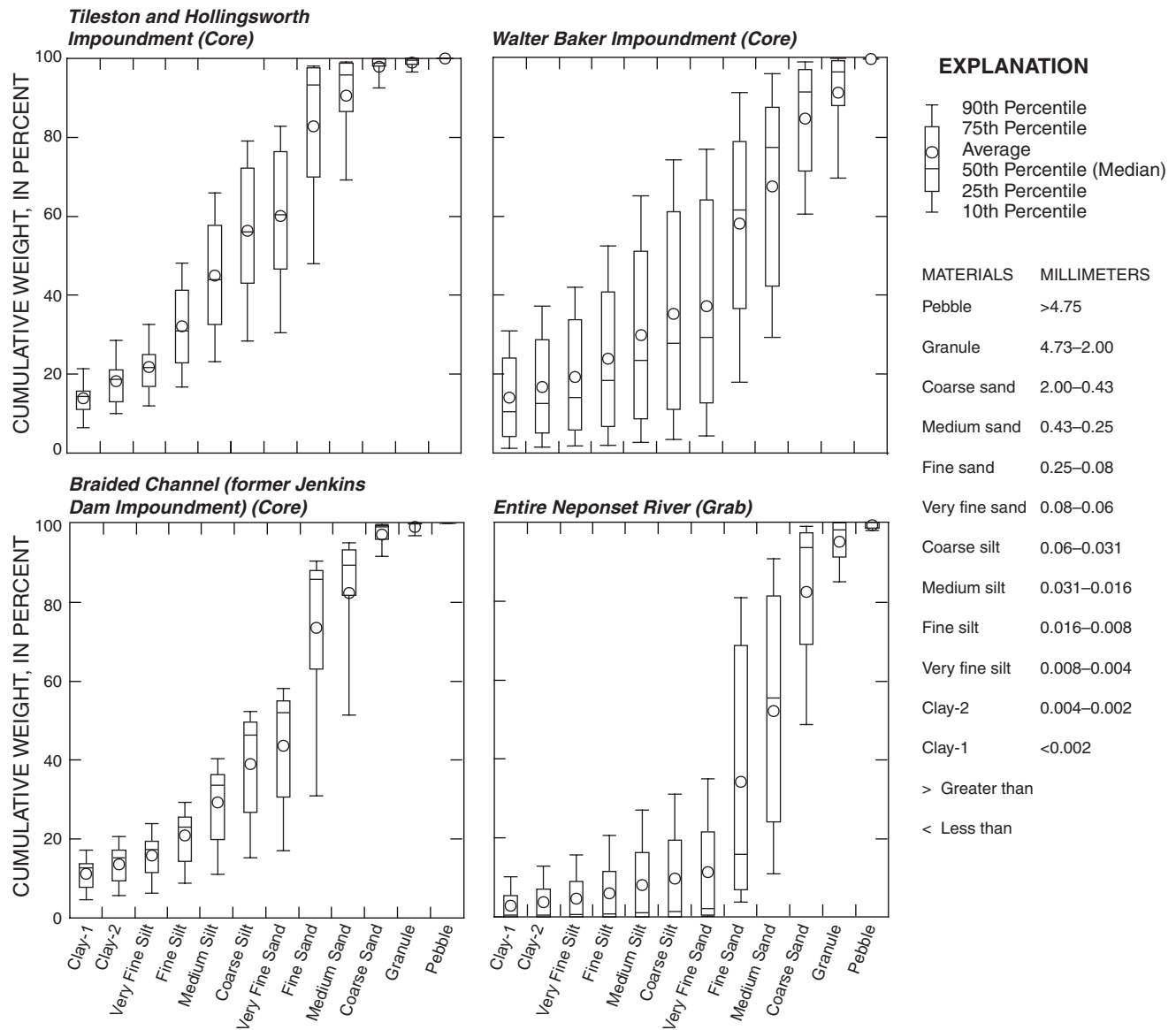
Figure 15.   Sediment-type summary statistics for grab and core samples collected from the lower Neponset River, Massachusetts.

The eight samples were composited into one and analyzed for a suite of elements and organic compounds (these data are published in a companion report by Breault and Cooke, 2004). As the data indicate, the sediment quality downstream of the Walter Baker Dam was generally better than that of the sediment quality upstream of the dam, in the braided channel, and behind the Tileston and Hollingsworth Dam. The likely reason for this difference in sediment quality is that much of the past and present contamination is trapped upstream of the dam.

Additionally, any contaminated sediment that does make it into the estuary may be flushed by tidal action or diluted by cleaner sediment brought in with the tides.

If the sediments upstream of the Walter Baker Dam were purposefully or accidentally released, the sediment quality just downstream of the dam might be severely affected. Ultimately, the release of large volumes of contaminated sediment may adversely affect sediment quality in the downstream estuarine part of the river and in Boston Harbor (fig. 1).

Implications of Sediment Contamination for Waste Disposal

Contaminated sediment may also be completely or partially removed from a river, but this managment option is often the most costly. The costs associated with sediment removal often increase exponentially with the type and amount of contamination. The relation between cost and contamination mostly results because of costs associated with sediment disposal, rather than with sediment removal. For example, uncontaminated sediment may be reused as capping material at lined landfills. Contaminated sediment cannot be used for similar purposes, so it must be disposed of so that it does not re-enter the environment.

The Massachusetts Department of Environmental Protection (MDEP) has set maximum allowable contaminant concentrations of some chemicals in sediments to be disposed of as capping material at lined landfills. By comparing the measured concentration to this maximum concentration, the appropriate disposal option of the sediment can be determined (Massachusetts Department of Environmental Protection, 1997). Sediment with contaminant concentrations greater than these values usually requires special disposal, but sediment with concentrations below these values may not.

Generally, contaminant concentrations measured in sediment cores collected from the Neponset River were less than concentrations required for disposal of sediment in a lined landfill, with one exception (fig. 16). The PCB concentrations measured in sediment cores from the Walter Baker and Tileston and Hollingsworth impoundments and from the braided channel were greater than the allowable concentrations for PCBs. In fact, PCB concentrations were, on average, about 30 times greater than the concentration prescribed by the MDEP.

Although it is helpful to compare contaminant concentrations to those values set by the MDEP, other methods can help predict the consequences of different modes of sediment disposal. Specifically, the TCLP and reactive sulfide test can be used to determine the likelihood of sediment contamination entering the environment from a landfill. In the TCLP, sediment samples are subjected to conditions similar to those found in landfills. By doing this test, researchers determine the concentration of chemicals, if any, that may leach to the environment under those conditions. Reactive sulfide testing determines if exposure of sediment to slightly acidic precipitation causes a release of hydrogen sulfide gas (H_2S).

TCLP results of selected sediment cores from the Neponset River indicate that some trace metals (barium and lead) are likely to leach from these sediments (laboratory blanks showed a bias for barium; however, this bias was about three times less than the measured concentrations). In contrast, it appears that under normal environmental conditions, no H_2S would be released from these sediments.

Polychlorinated Biphenyls in Water, Sediment, and Fish

For many years, environmental managers have suspected that the Neponset River was contaminated with PCBs. Consequently, the ACOE collected sediment samples from the Neponset River and tested them for PCBs (U.S. Army Corps of Engineers, written commun., 2002). The data from these tests indicated that sediment in the Neponset River, at least in the areas tested, is contaminated with PCBs.

One method of successfully sampling for PCBs in the water column is to use PISCES passive-water-column samplers (Litten and others 1993; Colman, 2002). These samplers, which are deployed in the river, absorb PCBs from the water column across a semipermeable membrane; therefore, these samplers collect a time-integrated sample (over the time of deployment) of the PCBs dissolved in the water that passes the sampling point.

Using passive-water-column sampler methodology to detect PCBs has many advantages that other methods (for example, sampling sediment and fish tissue) lack. These include: (1) water-column samples generally have lower detection limits because of fewer chemical interferences; (2) dissolved PCB concentrations are an indirect measure of bioavailable PCBs in the aquatic environment; and (3) PCB concentration variability measured in water-column samples is not affected by external factors such as grain size or organic carbon content (in sediment samples), or weight, age, sex, and lipid content (in fish-tissue samples) (Colman, 2002).

Two techniques can be used to analyze PCB data: Aroclor or congener analysis. Aroclors are analyzed by testing for characteristic congeners, and then by using a mathematical algorithm to estimate the concentrations of other congeners. These data are reported in terms of Aroclor concentration. The problem with measuring PCBs by testing for Aroclors arises when congener patterns deviate from those of the original Aroclor (fig. 17). For example, once an Aroclor enters the environment, individual congeners can be preferentially (1) degraded by microbial action, (2) chemically weathered, or (3) physically changed in such a way that the original congener pattern for that Aroclor is lost (Butcher and others, 1997). In contrast, a congener analysis tests for the presence of individual congeners.

Because the advantages of using congener analysis usually outweigh those of Aroclor analysis, congener analysis of the PISCES passive-water-column samples was used. All of the sediment samples were analyzed for PCBs by Aroclor analysis, but a few sediment samples were also analyzed for PCB congeners.

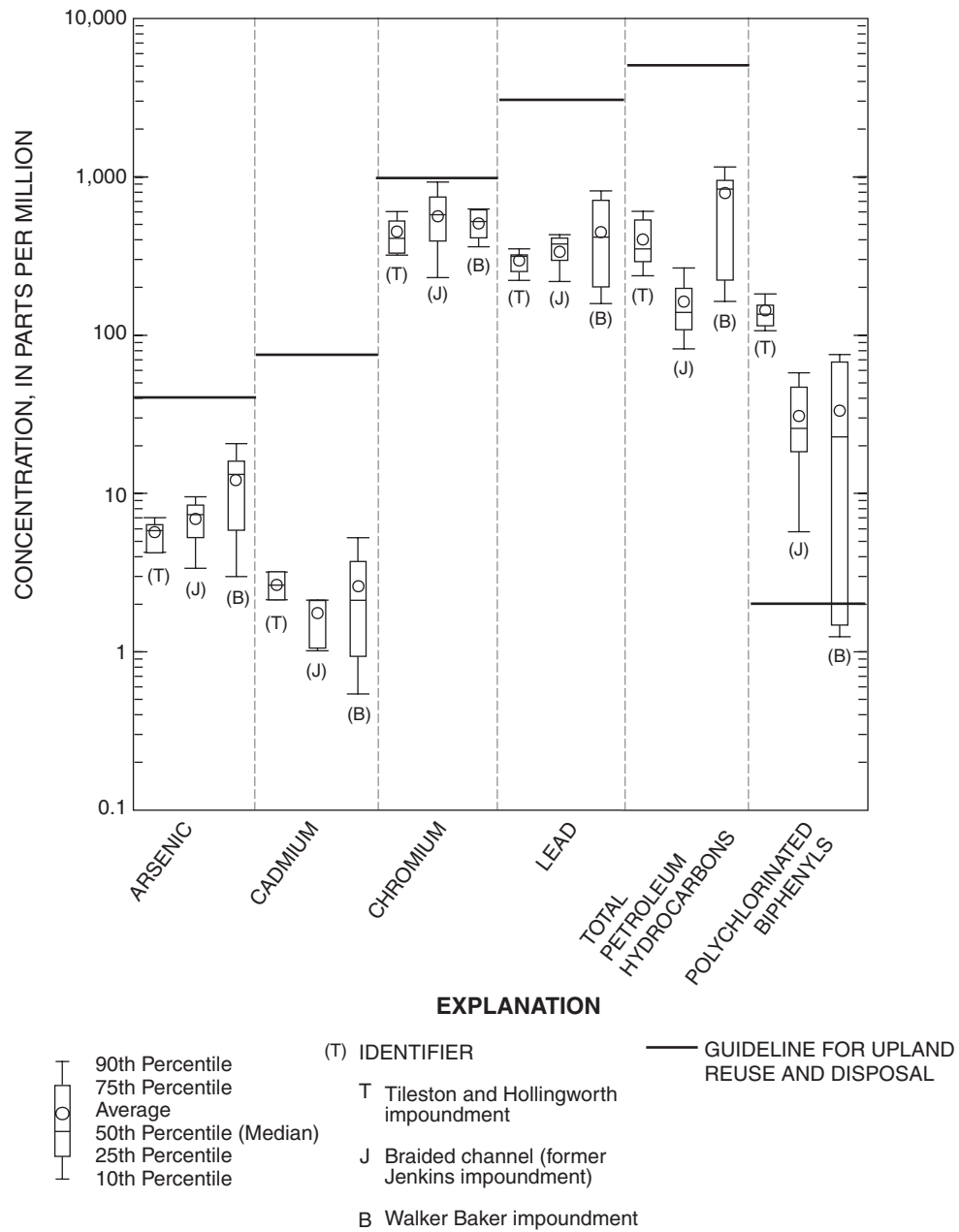**Figure 16.**   Comparison of elements and organic compound concentrations in sediment collected from the lower Neponset River, Massachusetts, with Commonwealth of Massachusetts guidelines for the reuse and disposal of contaminated soil.

Figure 17.   Polychlorinated biphenyl congener patterns of commercially available Aroclors by International Union of Pure and Applied Chemistry number (IUPAC).

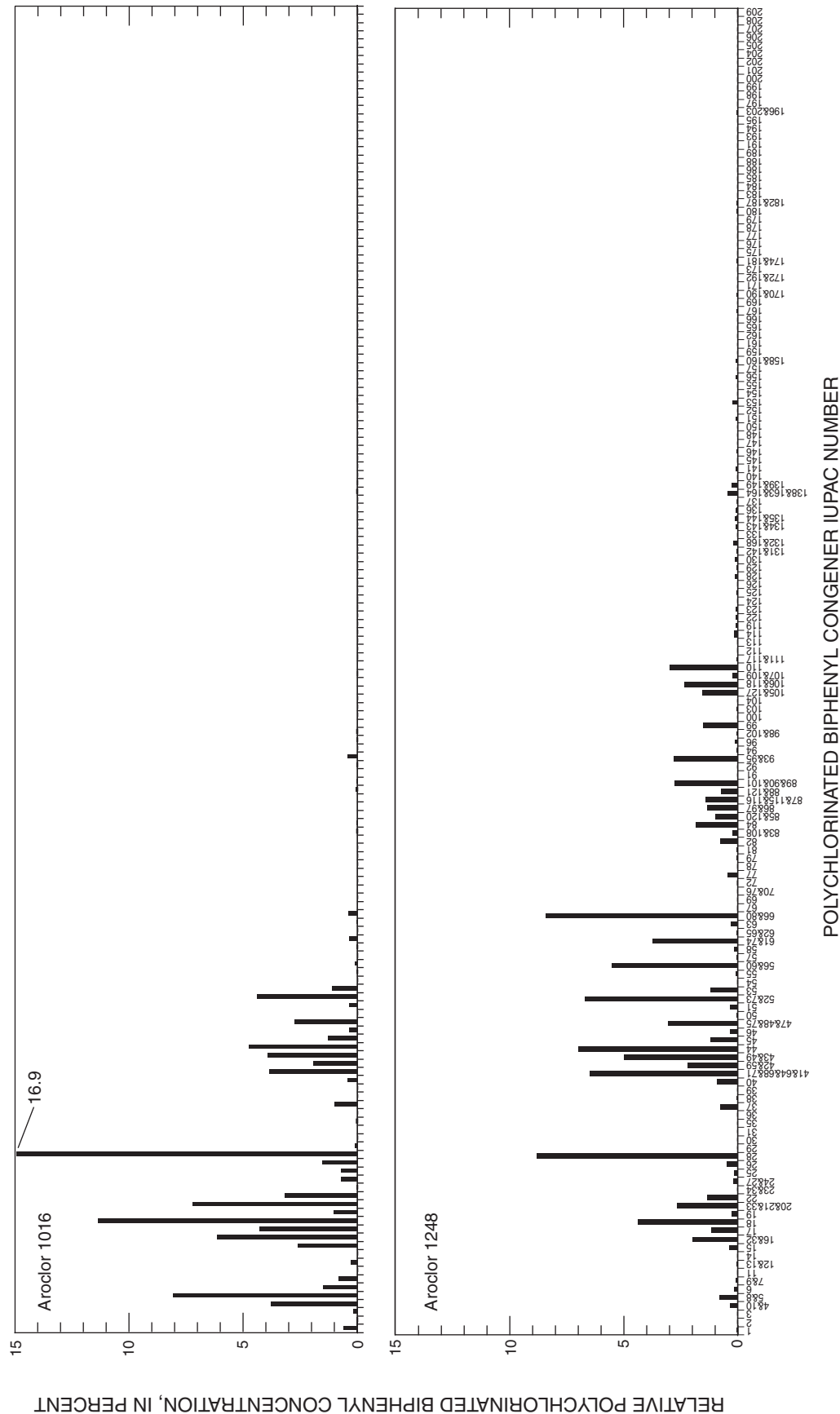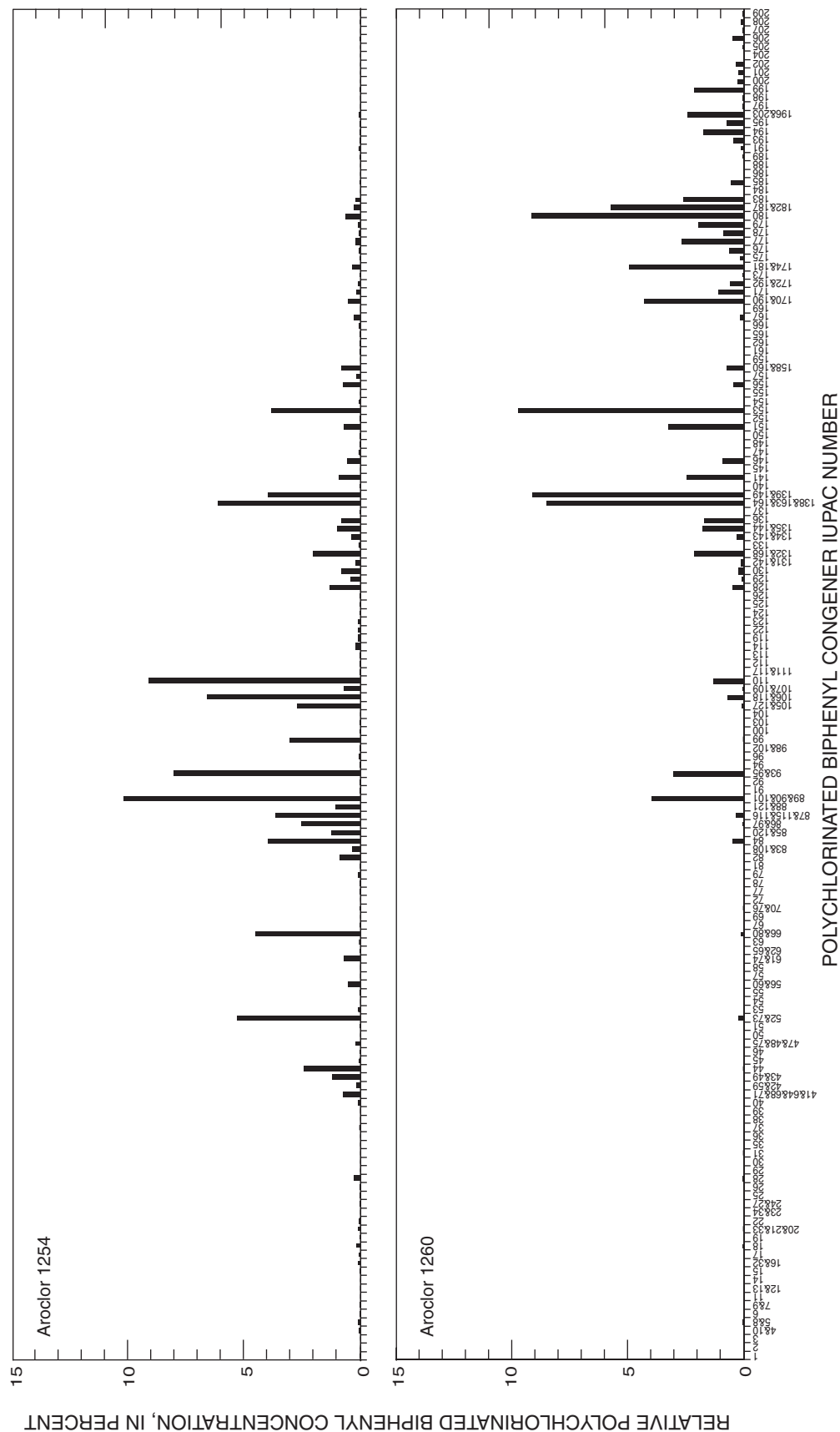**Figure 17—Continued.** Polychlorinated biphenyl congener patterns of commercially available Aroclors by International Union of Pure and Applied Chemistry number (IUPAC).

Polychlorinated Biphenyl Source Identification

To determine the causes of a change in congener pattern, it is necessary to examine the changes in patterns in the PISCES data and in the sediment data, and to examine the changes from one location to another. Because changes in congener patterns could be caused by slight variations in the positioning of PISCES samplers in the water column (Colman, 2000), or by sediment heterogeniety, it is first necessary to determine congener-pattern variability, if any, between duplicate samples collected at a single location.

Differences in congener patterns between duplicate samples were quantified by comparing the RMSDs of normalized congener concentrations. The RMSD values for PISCES duplicate pairs ranged from 0.06 to 0.3 percent (fig. 18). Colman (2000) reports a similar range of RMSDs for similar total (Σ) PCB concentrations in the Millers River of central Massachusetts. The RMSD values for sediment-sample duplicate pairs averaged about 0.2 percent.

The second step in determining the locations of potential PCB sources to a river is to compare RMSD values from adjacent PISCES sampling stations. RMSD values are plotted in downstream order in figure 19. RMSD values from adjacent PISCES sampling stations were determined to be statistically different (α=0.05) by using the student's t-test function of S-Plus 2000 statistical software (for two samples, assuming equal variance). The means for the t-test were from pooled RMSD values of the duplicate pairs (n=12) and RMSD values calculated for adjacent PISCES sampling stations (n=2); sample 1 at one station was compared to sample 1 of another station and sample 2 of the first station was compared to sample 2 of the second station.

In this case, the PISCES data show a substantial change in congener pattern, as measured by the RMSD, between the Fairmont Avenue and the two upstream sampling locations, Reservation Park on Mother Brook, and Martini Shell on the Neponset River (fig. 19). Two scenarios could account for the congener-pattern change measured in the PISCES samples in this location: (1) a historic PCB source is between the Fairmont Avenue and the Martini Shell or Reservation Park locations and the original congener pattern has not been altered; or (2) a historic PCB source was upstream of Martini Shell or Reservation Park. PCBs from this source were transported in the water column downstream to Fairmont Avenue, and ultimately settled there in the sediment. Once deposited, microbial action may have degraded the historic PCB pattern, thereby causing the observed pattern change. Because anaerobic degradation by
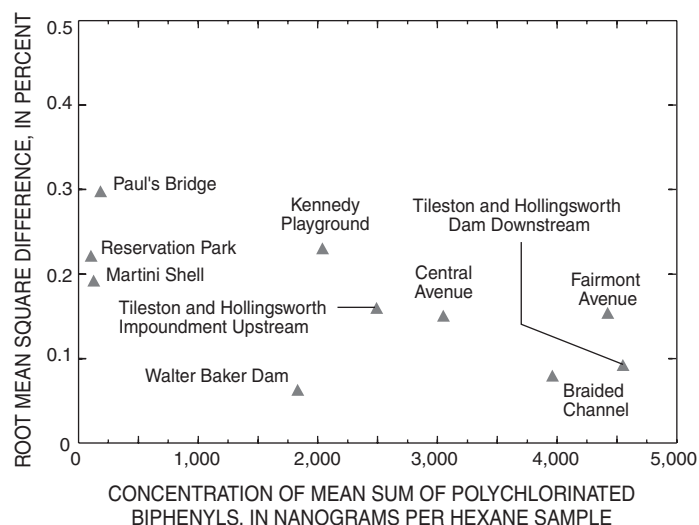

Figure 18.   Differences in polychlorinated biphenyl congener patterns between duplicate samples collected from the lower Neponset River, Massachusetts.

microbial processes favors substitution of chlorine atoms by hydrogen atoms (Wisconsin Department of Natural Resources, 2000), this process would explain the preeminence of mono- and dichlorobiphenyls in PISCES samples downstream of Fairmont Avenue (fig. 20).

Analysis of the sediment data, however, suggests a third possibility. The change in congener pattern may be caused by both a change in PCB source and anerobic degradation of that source. The congener pattern from the sediment sample collected at site BGY-104, just upstream of Fairmont Avenue, is distinctly different than the pattern observed in the sample collected at site BGY-105, between site BGY-104 and Fairmont Avenue (figs. 21 and 22). This difference cannot be explained by microbial degradation; therefore, the congener pattern in the sample from site BGY-105 may be indicative of a major source of PCBs to the river. In contrast, the congener-pattern change observed in some sediment samples downstream of BGY-105 can be explained by the process of anaerobic degradation. However, the samples collected from stations M2Y-012, BGY-133, and BGY-128 complicate this interpretation, because the congener patterns in these samples most closely resemble that from BGY-105. It is likely that conditions at these stations (including the ΣPCB concentration) are not conducive to anaerobic degradation, and that sediment in these samples was contaminated by the same PCB source as the sample from BGY-105. It is also possible that PCBs consisting mostly of a single congener may have been directly released into the Neponset River. More detailed studies are required for positive identification of the historical source(s) of PCBs to this part of the river.
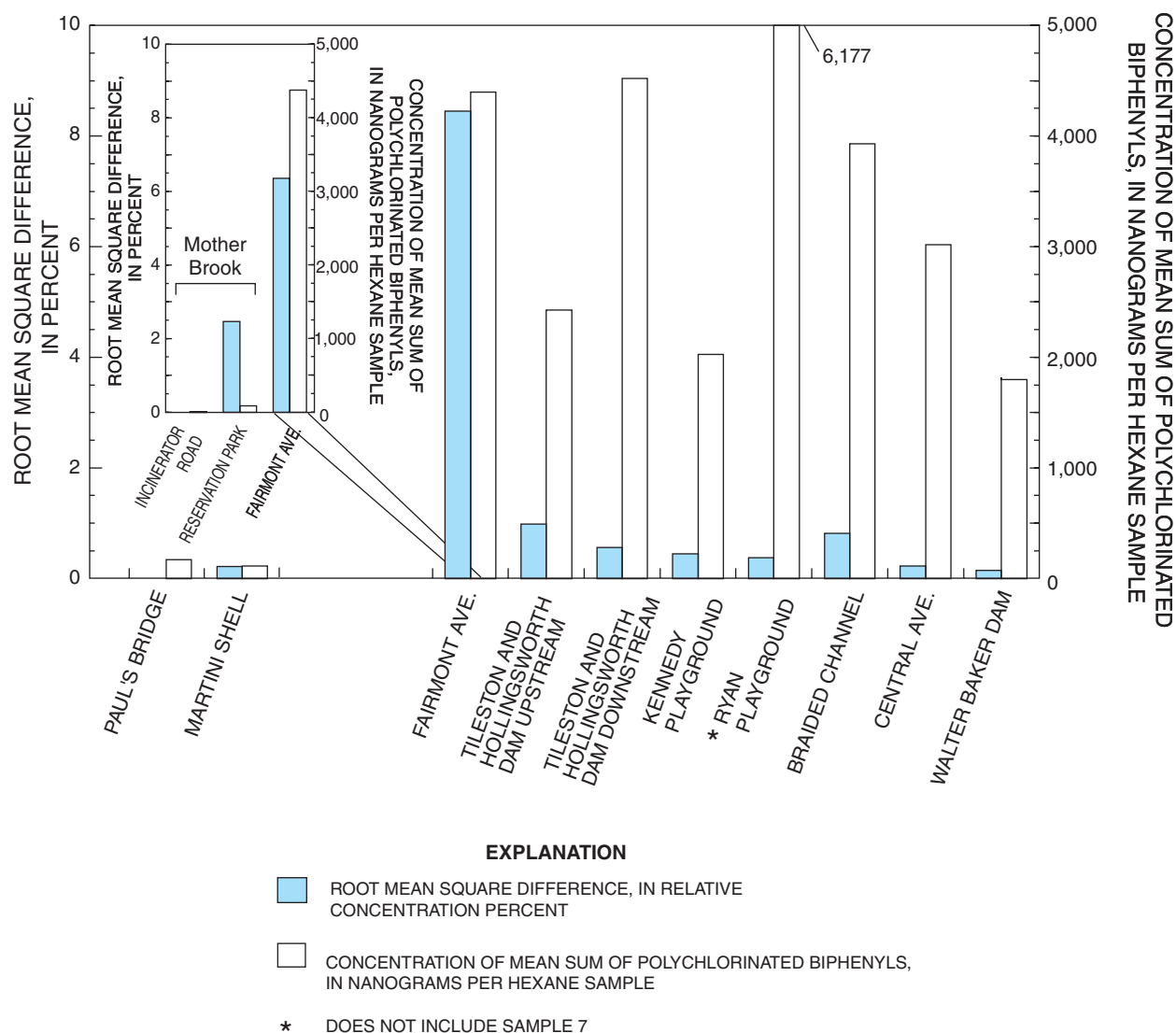
Figure 19. Polychlorinated biphenyl concentrations and between-station root mean square differences of congener patterns measured in PISCES passive samplers, Mother Brook and the lower Neponset River, Massachusetts.

Whatever the case, it appears that presently (2003) the majority of dissolved PCBs in the Neponset River continue to be released into the river from the existing sediment downstream of Fairmont Avenue. This is demonstrated by the fact that congener patterns from PISCES samples and from sediment samples are similar in this reach of the river. As PCBs enter a river, they attach to fine-grained sediment suspended in the water column. These particles move downstream in the

flowing water and ultimately settle in slack pools. The PCBs that accumulate in the sediment eventually move from the sediment back into the water column (Chambers, 1999). Although some sediment samples were analyzed for PCB congener data (table 8), more detailed studies are required to identify the present-day source(s) and their importance to water-column PCBs contamination.

Table 7.   Measured total polychlorinated biphenyl (ΣPCB) concentrations, by congener analysis in PISCES samplers, estimated ΣPCB water-column concentrations, and estimated ΣPCB concentrations in fish tissue, lower Neponset River, Massachusetts.

[Because the food chain multiplier for primary consumers equals 1, bioconcentration values are identical to primary consumer values. ΣPCBs, sum of the 209 polychlorinated biphenyls; mg/kg/kg lipid, milligram per kilogram per kilogram lipid; ng, nanogram; ng/L, nanogram per liter; --, no data]

| Station	Sample number	ΣPCB by congener (ng/hexane sample)	Water-column estimated concentration (ng/L)	Bioaccumulation (mg/kg/kg lipid)		
				Primary consumers	Secondary consumers	Predators
Paul's Bridge	17	112	2.0	4.0	52.3	91.2
	18	257	4.7	8.6	110.8	192.3
Martini Shell	19	142	2.5	4.8	61.3	106.6
	20	115	2.0	3.5	44.5	77.1
Incinerator Road	23	--	--	--	--	--
	24	29	.4	.8	10.5	18.0
Reservation Park	21	102	1.5	2.0	24.2	41.1
	22	108	1.6	2.1	25.5	43.3
Fairmont	15	5,253	95	27.3	264.2	405.8
	16	3,595	65	18.8	179.6	272.2
Tileston–Hollingsworth Dam upstream	13	2,330	43	14.9	147.3	230.2
	14	2,652	49	18.9	198.3	320.6
Tileston–Hollingsworth Dam downstream	11	4,719	89	32.8	341.0	544.5
	12	4,382	82	29.6	309.1	499.4
Kennedy playground	9	2,373	48	16.8	170.7	271.9
	10	1,706	34	11.0	107.6	168.4
Ryan playground	7	1,304	28	8.7	82.8	127.6
	8	6,177	131	44.4	434.6	677.1
Braided channel	5	3,381	71	27.1	264.0	406.6
	6	4,541	95	37.1	363.6	561.7
Central Avenue	3	2,956	65	29.2	297.3	466.2
	4	3,144	69	30.0	302.4	472.4
Baker Dam	1	1,790	37	16.0	161.3	251.8
	2	1,874	38	17.0	172.3	270.4
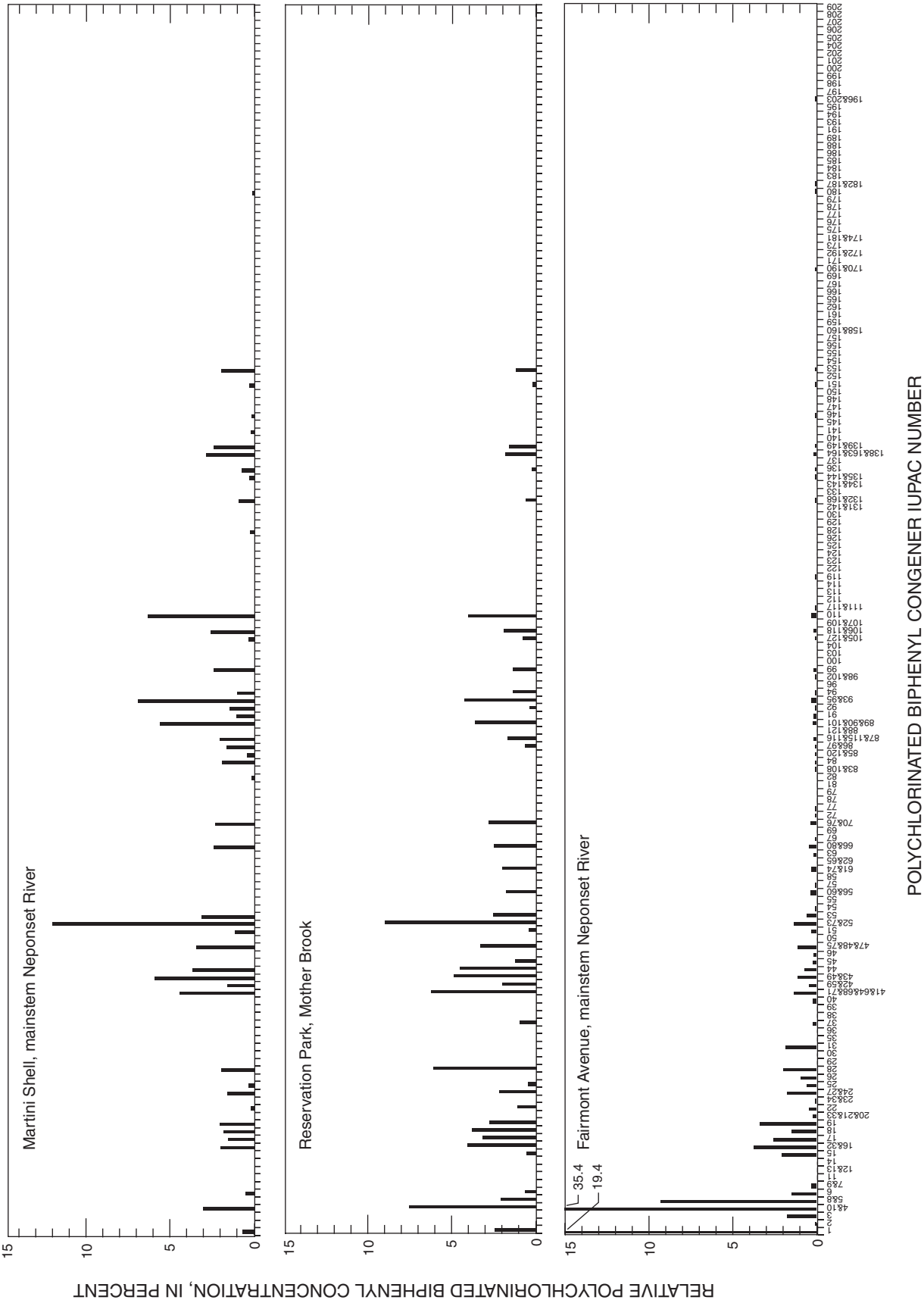
Figure 20. Average relative polychlorinated biphenyl congener concentrations in selected PISCES samples collected from the lower Neponset River, Massachusetts, by International Union of Pure and Applied Chemistry (IUPAC) number.

Table 8.   Total polychlorinated biphenyl concentrations by congener analysis in selected grab and core samples, lower Neponset River, Massachusetts.

[dup, duplicate; ΣPCBs, total polychlorinated biphenyls; ppb, parts per billion]

USGS number	ΣPCB (ppb)	USGS number	ΣPCB (ppb)
BGY-102	29	M2Y-002	230,845
BGY-104	1,054	BGY-128	66,053
BGY-105	13,843	M2Y-012	4,670
BGY-106	16,293	BGY-133	5,841
BGY-112	16,458	BGY-137	79,182
BGY-102-dup	28	BGY-128-dup	59,660

Polychlorinated Biphenyl Toxicity

Numerous studies have shown that PCBs pose a risk to fish, wildlife, and humans, by causing a variety of health effects, including cancer (U.S. Environmental Protection Agency, 1996). Numerical standards for aquatic-life protection (aquatic-life criteria) and human health (toxic equivalency factors) can help determine the health risks associated with PCB exposure. These aquatic-life criteria and human-health guidelines are available for dissolved PCB concentrations. Because PISCES passive-water-column samplers concentrate PCBs from the dissolved phase, data from the samples can be used to estimate dissolved PCB concentrations (table 7; Colman, 2000). These data can then be used to estimate exposure-based health risks.

The relation between PCB concentrations in the samples from PISCES passive-water samplers and the concentrations of dissolved PCBs in the water column is as follows (John Hassett, State University of New York–Syracuse, written commun., 2000; equation 4):

$$C_w = \frac{M_s}{A \times e^{\left(\frac{-6.591}{T} + 19.269\right)} \times t} \qquad (4)$$

where
  C_w is the concentration of the congener in water, in nanograms per liter;
  M_s is the mass of the congener measured in the PISCES sample, in nanograms per hexane sample;
  A is the surface area of the semipermeable membrane, in square centimeters;
  T is water temperature, in degrees Kelvin; and,
  t is the exposure time, in days.

Estimated ΣPCB dissolved concentrations ranged from less than 0.5 ng/L at Incinerator Road in Mother Brook to a maximum concentration of 131 ng/L in the Neponset River at the Ryan Playground PISCES sampling location (sample number 8 in table 7) (fig. 23). On average, ΣPCB water-column concentrations were about 1.17 ng/L on Mother Brook. On the Neponset River, upstream and downstream of the Fairmont Avenue sampling location, concentrations were about 2.8 and 66 ng/L, respectively (excluding sample number 7).
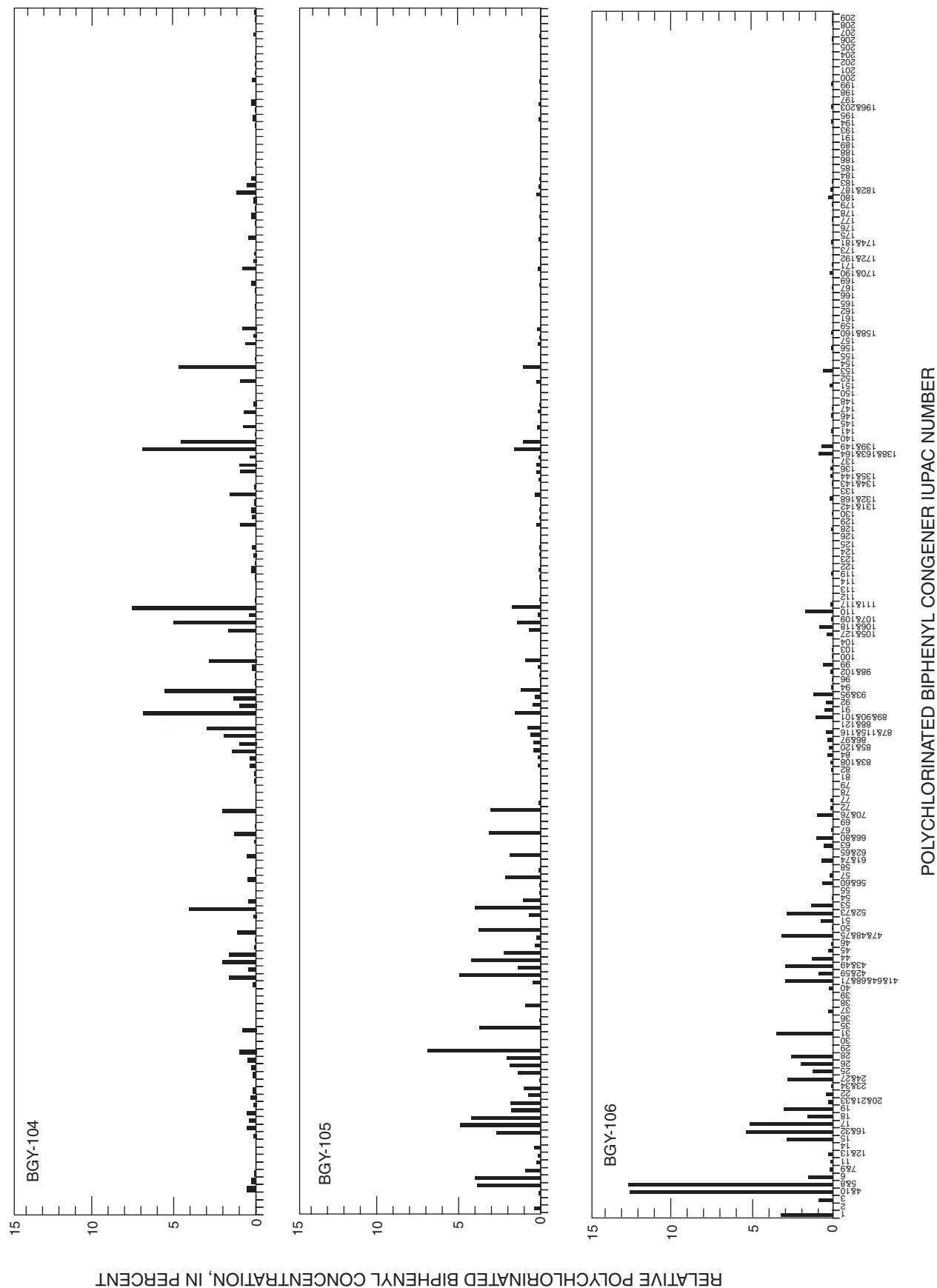
Aquatic-Life Criteria

As aquatic organisms, for example, predatory fish, eat other aquatic organisms, such as smaller fish or benthic organisms that feed and live on bottom sediments contaminated with PCBs, the predatory organism can become contaminated (Oliver and Niimi, 1985). Aquatic organisms may also become contaminated directly from the water column by absorbing dissolved PCBs through gill membranes (Björk and Gilek, 1999). Through this process, PCBs can become more concentrated in fish tissue (bioaccumulation) than in the water or sediment. As of December 1998, bioaccumulation of PCBs in fish tissue was responsible, at least in part, for the 679 fish-consumption advisories that were issued in the United States. Only one other constituent, mercury, accounts for more fish-consumption advisories than PCBs (U.S. Environmental Protection Agency, 1999).

The USEPA publishes numerical standards that relate chronic toxicity to concentrations of PCBs dissolved in the water column. Presently (2003), the freshwater continuous chronic criterion (CCC) for aquatic organisms is 14.0 ng/L (U.S. Environmental Protection Agency, 2003b). The USEPA defines the CCC as the highest constituent concentration to which an aquatic organism can be exposed indefinitely without causing adverse biological effects. Aquatic organisms exposed for any length of time to PCB levels greater than the CCC may develop impaired reproductive-, endocrine-, and immune-system function, increased lesions and tumors, or they may die (U.S. Environmental Protection Agency, 1999).

Generally, estimated dissolved ΣPCB concentrations in Mother Brook and upstream of the Fairmont Avenue station on the Neponset River were less than the CCC for PCBs (fig. 23). Downstream of the Fairmont Avenue sampling station, estimated dissolved ΣPCB concentrations were greater than the CCC for PCBs. Therefore, PCBs would not be expected to cause adverse biological effects in Mother Brook or in the Neponset River upstream of the Fairmont Avenue sampling station, but exposure to PCBs downstream of that station may cause adverse biological effects to aquatic organisms or wildlife.

Although PCBs in aquatic organisms were not directly measured, bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) can be used to estimate order-of-magnitude concentrations expected in tissue samples. These factors represent ratios that might be expected between contaminant concentrations in tissue and contaminant concentrations in water. The mode of exposure determines which ratio (BCF or BAF) is most appropriate to use. A BCF is used to estimate contaminant concentrations in tissue that result from contaminated water in equilibrium with gill membranes and skin (U.S. Environmental Protection Agency, 1993). Direct ingestion and the uptake of contaminants through the food chain is accounted for in the BAF (U.S. Environmental Protection Agency, 1995).
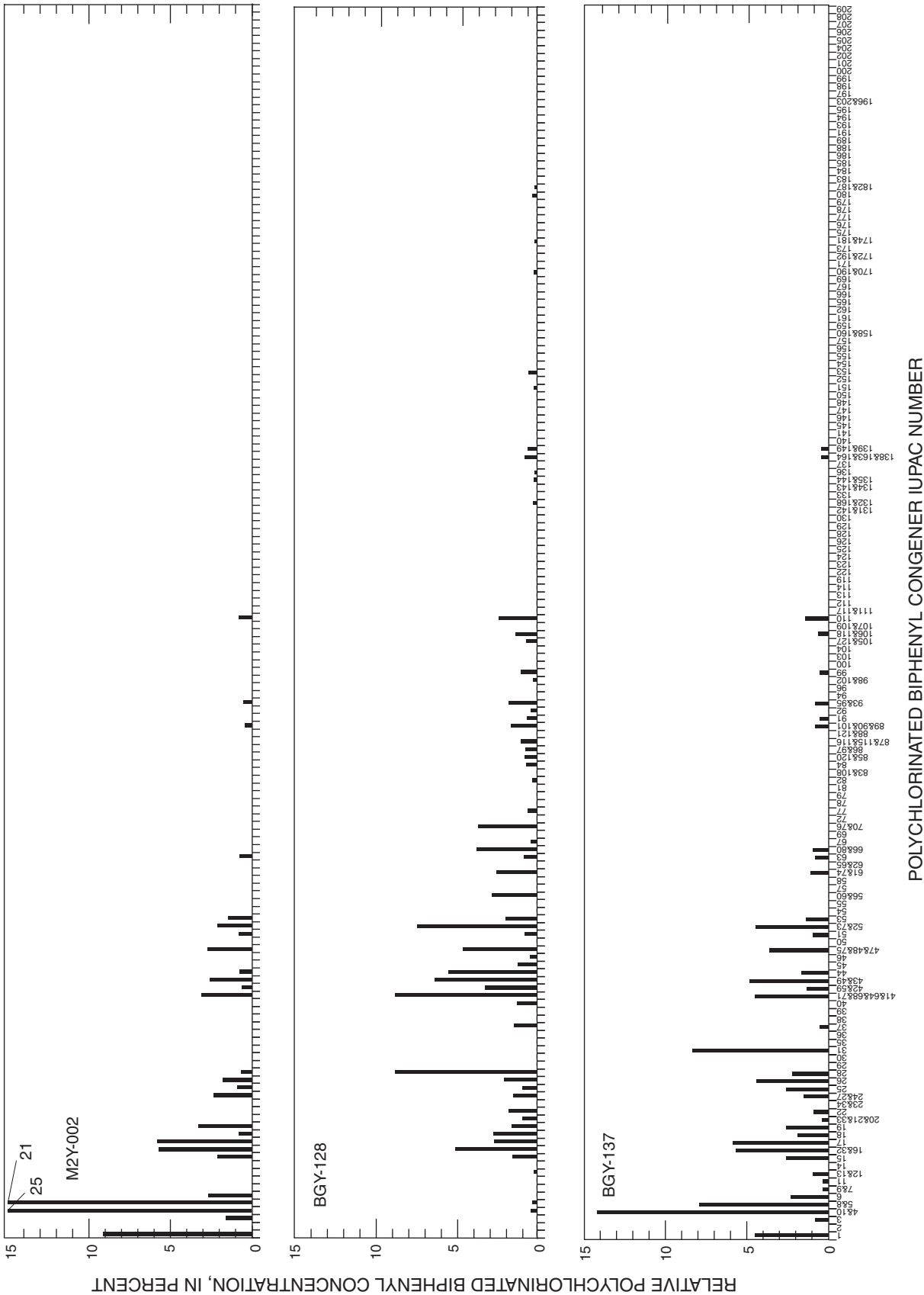
POLYCHLORINATED BIPHENYL CONGENER IUPAC NUMBER

Figure 21. Average relative polychlorinated biphenyl congener concentrations in selected grab samples collected from the lower Neponset River, Massachusetts, by International Union of Pure and Applied Chemistry (IUPAC) number.

RELATIVE POLYCHLORINATED BIPHENYL CONCENTRATION, IN PERCENT

Figure 22.   Average relative polychlorinated biphenyl congener concentrations in selected core samples collected from the lower Neponset River, Massachusetts, by International Union of Pure and Applied Chemistry (IUPAC) number.
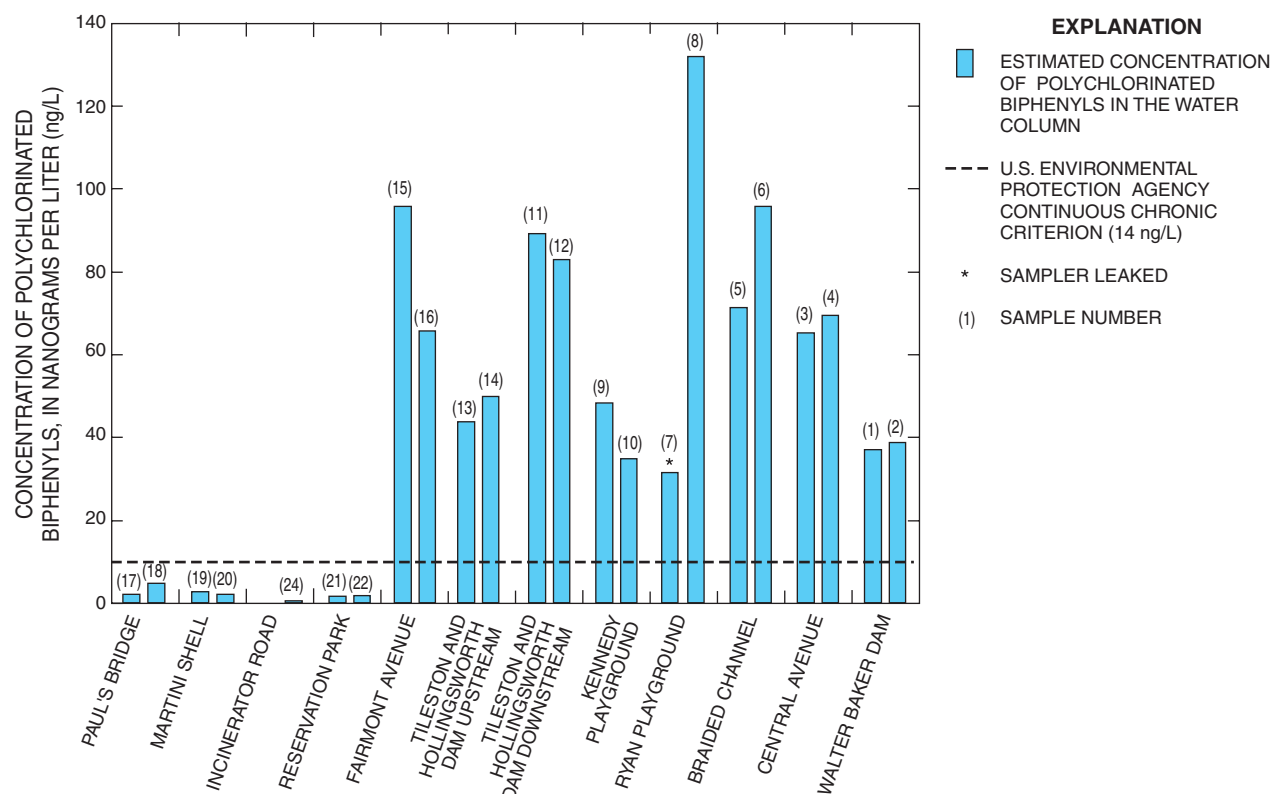
Figure 23. Estimated water-column concentrations of total polychlorinated biphenyls (ΣPCBs) collected from the lower Neponset River, Massachusetts, in comparison to the U.S. Environmental Protection Agency freshwater continuous chronic criterion for ΣPCBs.

Octanol-water partition coefficients (K_{ow}), which are measures of the tendency for a chemical to partition to a substance other than water (for example, tissue), can be used to estimate lipid-normalized BCFs as

$$BCF_i \approx K_{ow, i} \tag{5}$$

where

BCF_i is the lipid-normalized BCF for congener i, in microgram congener per kilogram lipid per microgram per liter congener concentration in water; and,

$K_{ow, i}$ is the octanol-water partition coefficient for congener i.

Congener-specific K_{ow} values estimated by Hawker and Connell (1988) were used to calculate BCFs for each congener. In the case of coeluting congeners, an average K_{ow} value was used.

Unlike BCFs, the biomagnification of a contaminant as it moves through the food chain is accounted for in the BAF. For example, largemouth bass (*Micropterus salmoides*), a predator, is expected to have higher ΣPCB concentrations in its tissues than those found in the fish eaten by the largemouth bass. To account for this increase, PCB congener concentrations are multiplied by a food-chain multiplier (FCM) as

$$BAF_i = FCM \times K_{ow, i} \tag{6}$$

where

BAF_i is the BAF for congener i, in microgram congener per kilogram lipid per microgram per liter congener concentration in water; and,

FCM is the food-chain multiplier for a given feeding level.

In this calculation, USEPA-derived FCMs for three feeding levels were used: (1) primary consumers (herbivores and suspension feeders), (2) secondary consumers (small fish), and (3) predators (fish) (U.S. Environmental Protection Agency, 1993). These FCMs generally increase with feeding level and congener K_{ow} values; however, some superlipophilic congeners (K_{ow} greater than 6.5) have slightly lower FCM values. Because large molecules cannot readily pass through gill membranes, these congeners biomagnify to a lesser degree through the food chain (Oliver and Niimi, 1985).

With equation 7, BCFs and BAFs were used to estimate lipid-normalized ΣPCB in primary consumers, secondary consumers, and predators (table 7):

$$\Sigma PCB = \frac{\dfrac{C_i}{1{,}000} \times Y_i}{1{,}000} \qquad (7)$$

where
ΣPCB is the estimated concentration of PCBs, in milligrams per kilogram (or parts per million) per kilogram lipid;
C_i is the estimated concentration of PCB congener i in the water, in nanograms per liter;
Y_i is either the BCF or BAF for congener i, in microgram congener per kilogram lipid per microgram per liter congener concentration in water.

A previous study of fish fillets (edible fish parts) contaminant concentrations completed by the MDEP and other State agencies measured ΣPCB concentrations of about 1.4 ppm (average 4.0 g lipid or 0.56 percent lipid) in a composite of brown bullhead (*Ameiurus nebulosus*), a secondary consumer (Massachusetts Department of Environmental Protection, 1994). These fish were collected far upstream of the study area, but were said also to represent the upper part of the study area (Paul's Bridge to the Tileston and Hollingsworth Dam). Largemouth bass (*Micropterus salmoides*), a predator, were also collected and analyzed. A concentration of 0.17 ppm was measured in a composite of largemouth bass fillets (average 2.2 g lipid or 0.18 percent lipid).

The Massachusetts Department of Public Health issues fish-consumption advisories for fish with measured PCB concentrations in their tissue of about 2 ppm, the U.S. Food and Drug Administration (FDA) and USEPA "action level" for PCBs (U.S Food and Drug Administration, 2001). Consequently, a fish advisory was issued for the consumption of brown bullhead collected from the Neponset River between the Hollingsworth and Vose Dam (Walpole, MA) to the Tileston and Hollingsworth Dam (Hyde Park, MA).

Estimated average ΣPCB concentrations (calculated by using an average lipid mass of 4.0 g) in secondary consumers ranged from about 0.1 ppm in Mother Brook and 0.3 ppm upstream of Fairmont Avenue to about 1.0 ppm downstream of Fairmont Avenue on the Neponset River. Similar concentrations were estimated for predatory fish in Mother Brook (0.1 ppm), and upstream (0.3 ppm) and downstream (0.8 ppm) of Fairmont Avenue on the Neponset River (average lipid mass of 2.2 g). Estimated ΣPCB concentrations in the river reach from Paul's Bridge to the Tileston and Hollingsworth Dam were similar to those measured, and averaged about 0.4 ppm for both secondary consumers and predatory fish. Estimates of ΣPCB concentrations (lipid normalized) in tissue samples for other feeding levels and modes of exposure by PISCES sampling station are given in table 7.

Another comparison can be made with fish-tissue ΣPCB concentrations measured in fish from the Housatonic River. White suckers (*Catostomus commersoni*), a bottom-feeding fish, were collected as part of the NAQWA Program and analyzed for PCBs. The average of the whole-body (entire fish) ΣPCB concentrations measured in white suckers from the Housatonic River ranged from 12 to 72 ppm (Coles, 1998). This range is higher than the whole-body concentrations estimated for small fish in the PCB contaminated area of the Neponset River (9.0 ppm, based on a lipid mass of 35 g or 5.3 percent lipid). This concentration range is not surprising, because PCB contamination in the Housatonic River is greater and more widespread than the Neponset River.

Many factors affect PCB concentrations in aquatic organisms, particularly fish, including the character of the river, temperature, and organic carbon concentrations (Cook and Burkhard, 1998). A study that involves the collection and analysis of aquatic organisms would help to determine definitively how PCB contaminated sediment and water affect biota in the lower Neponset River.

Human Health

Dioxin and "dioxin-like" compounds are a group of structurally similar organic compounds that act by a similar cellular mechanism to cause comparable biological and toxic effects (U.S. Environmental Protection Agency, 2001). Of the 30 dioxin or dioxin-like compounds in the environment, the most toxic is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (often referred to as 2,3,7,8-TCDD, TCDD, or dioxin; Murphy, 1986). Human exposure to high levels of TCDD causes a variety of ailments, including chloracne, porphyria (skin and nerve damage), liver damage, and psychiatric disturbances (International Agency for Research on Cancer, 1997).

Of the 209 PCB congeners, 13 are considered dioxin-like; that is, they cause toxic effects similar to TCDD. Because of this similarity, the USEPA has developed an approach in which PCB toxicity can be estimated relative to TCDD to produce a "toxic equivalency" (fig. 24). Equation 8 was used to calculate the toxic equivalency (TEQ) for dissolved PCB congener concentrations (calculated by equation 4):

$$TEQ_i = \sum_{i=1}^{k} C_i \times TEF_i \qquad (8)$$

where
TEQ_i is the toxic equivalency of congener i, in picograms per liter (pg/L);
C_i is the concentration of congener i, in water, in pg/L;
TEF_i is the toxic equivalency factor for congener i.

The toxic equivalency factors were derived by the World Health Organization in 1997, and are considered applicable for human and wildlife species (Van den Berg and others, 1998).
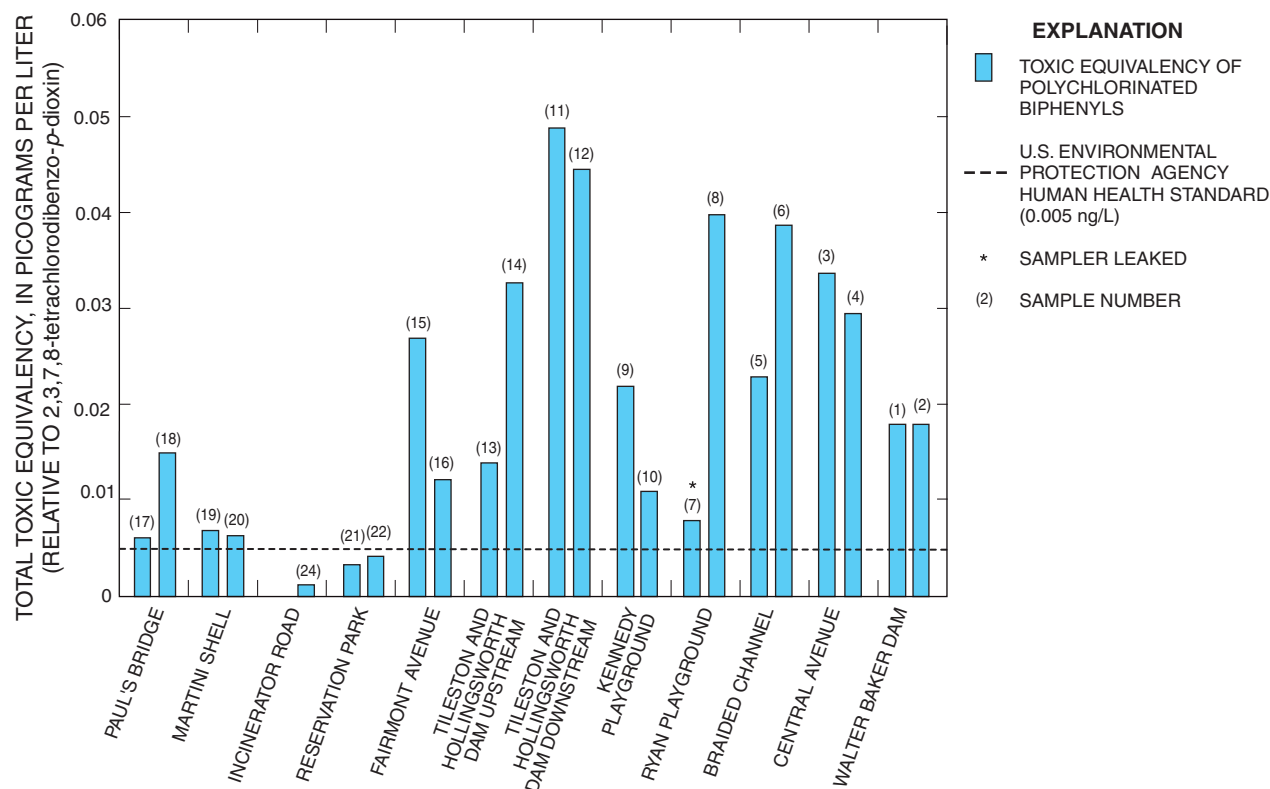
Figure 24. Toxic equivalency of total polychlorinated biphenyls relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) collected from the lower Neponset River, Massachusetts.

Estimated water-column PCB concentrations, expressed as TCDD, were greater than the USEPA human-health standard (0.005 pg/L), with the exception of the sample from the Incinerator Road location. The largest total TEQ was calculated for PCB congener concentrations measured just downstream of the Tileston and Hollingsworth Dam. At this station, the TEQ was about 10 times greater than the standard. This assessment of PCB toxicity does not include any toxicity caused by "nondioxin-like" PCB congeners. Moreover, analysis used by this study may underestimate some "dioxin-like" congener concentrations.

Interestingly, TEQs normalized by ΣPCB concentrations indicate that PCBs from upstream of Fairmont Avenue are much more toxic than PCBs downstream of Fairmont Avenue. This finding indicates that either the major source of PCB contamination near Fairmont Avenue was relatively non-toxic, compared to PCBs from upstream sources, or that dechlorination has reduced the toxicity of the original PCB source.

Summary

Evaluation of fish-passage alternatives, including dam removal or breaching for the purposes of increasing fish passage and river restoration of the Neponset River in Massachusetts has raised concerns about the quality and quantity of bottom sediment. Of particular concern is the well-known presence of elevated concentrations of polychlorinated biphenyls (PCBs) in the bottom sediment of the river. In response to these concerns, the U.S. Geological Survey, in cooperation with the Massachusetts Executive Office of Environmental Affairs Riverways Program, and the U.S. Environmental Protection Agency, tested sediment and water quality in the lower Neponset River.

Bottom-sediment quality was measured by collecting sediment-grab samples (top 4 in.) from the outlet of Fowl Meadow, Canton, MA, to the Walter Baker Dam, Milton, MA, and sediment cores (extending the length of impounded sediment) from two impoundments (Walter Baker and Tileston and Hollingsworth), and from within the former Jenkins Dam impoundment, known as the braided channel. Sediment samples were analyzed for elements and organic compounds (including PAHs and PCBs) and for physical properties such as grain-size distribution. Bottom-sediment quantity was measured by manual measurements of sediment thickness. Data on bottom-sediment quality and quantity will help water-resources managers make informed decisions regarding dam removal and other river-restoration efforts.

The source of PCB contamination was determined by comparing PCB concentrations and PCB congener patterns (or "fingerprinting") analyzed from samples collected with PISCES passive-water-column samplers. PISCES passive-water-column samplers were deployed at 12 locations along the Neponset River, retrieved about 2 weeks later, and their contents were analyzed for 209 PCB congeners. Congener patterns, in combination with PCB concentrations measured in sediment-grab samples, may provide insight into past and present PCB source(s).

Bottom-sediment samples (grab and core) collected from the Neponset River are generally enriched in elements and organic compounds when compared to "nonurban-background" concentrations. Although enriched relative to background, most constituent concentrations were equal to or less than those found in other urban rivers, with the notable exception of PCBs. Some chemicals, particularly PCBs, are in sufficiently high concentrations in sediment samples collected from the Neponset River to pose a threat to benthic organisms and potentially to cause human health risks if humans come in contact with the sediment.

PCB fingerprinting techniques indicate a significant change in congener pattern between two sampling locations. These data may possibly be used to locate the original source of PCB contamination to the river. Presently (2003), it appears that PCBs in the Neponset River are from PCB contaminated sediment from Fairmont Avenue downstream. PCB concentrations in the water column downstream of this area persist at potentially toxic levels to fish, wildlife, and humans.

The data and analysis presented in this report will help water-resources managers evaluate the advantages and limitations of various sediment-management options. Sediment removal or redistribution may increase the risk of introducing buried contaminants back into the environment. On the other hand, the contaminated sediment left in place may serve as a continuing future source of contaminants to the water column and biota living in and around the river. In either case, contaminated sediment and water in settings like the Neponset River have substantial implications for the restoration of urban rivers and dam deconstruction.

Acknowledgments

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