TRACE ELEMENTS AND SYNTHETIC ORGANIC COMPOUNDS IN BIOTA AND STREAMBED SEDIMENT OF THE WESTERN LAKE MICHIGAN DRAINAGES, 1992–1995

By Barbara C. Scudder, Daniel J. Sullivan, Faith A. Fitzpatrick and Stephen J. Rheaume

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
millimeter (mm)	0.0394	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square centimeter (cm^2)	0.1550	square inch
square meter (m^2)	10.76	square foot
square kilometer (km^2)	0.3861	square mile
liter (L)	33.82	ounce, fluid
cubic centimeter (cm^3)	0.06102	cubic inch
cubic meter (m^3)	35.31	cubic foot
microgram (μg)	0.0000000353	ounce, avoirdupois
gram (g)	0.03527	ounce, avoirdupois
kilogram (kg)	2.205	pound, avoirdupois

Abbreviated water-quality units used in this report: Chemical concentrations are given in micrograms per gram (mg/g) dry weight for trace elements and synthetic organic compounds in streambed sediment and for trace elements in biota. Concentrations of synthetic organic compounds in whole fish are given in micrograms per gram (mg/g) wet weight. Pore sizes of screen mesh are given in micrometers (mm) and millimeters (mm). Resistance is given in megaohms (Mohm).

MISCELLANEOUS ABBREVIATIONS

NAWQA	National Water-Quality Assessment
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
RHU	Relatively homogeneous unit
SVOC	Semi-volatile organic compound

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Trace Elements and Synthetic Organic Compounds in Biota and Streambed Sediment of the Western Lake Michigan Drainages, 1992–1995

By Barbara C. Scudder, Daniel J. Sullivan, Faith A. Fitzpatrick *and* Stephen J. Rheaume

Abstract

Sampling was conducted in 1992, 1994, and 1995 to determine the occurrence of a broad suite of trace elements and synthetic organic compounds in biota and streambed sediment in selected streams in the Western Lake Michigan Drainages—a study unit of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey. Sediment was sampled at 31 sites for trace elements and 23 sites for synthetic organic compounds; biota were collected at a subset of sites. Some of the variability in trace elements and synthetic organic compounds was related to land use, and many differences in trace element concentration by land use category were statistically significant. The spatial distribution of some trace elements was related to a combination of land use and surficial deposits and (or) bedrock type. Urban land use was likely the dominant factor influencing high sediment concentrations of Cd, Cu, Hg, and Pb. Forested land use was related to high concentrations of As in sediment and biota and high Se in sediment; however, bedrock type was an additional factor for As and surficial deposits type was a factor for Se. Land use, surficial deposits, and bedrock type appeared to influence Ni and Zn concentrations, and Cr concentrations did not directly reflect any of these factors. Most occurrences of organochlorine compounds in sediment and biota were related to urban land use. DDT and related compounds were detected at sites spanning all land uses. PCBs were detected in sediment at large-river sites and at one urban site in the Milwaukee area; the highest concentrations of PCBs in fish were found at two of four large river sites. A larger number of SVOCs were detected at urban sites and large river sites compared to agricultural and forested sites.

INTRODUCTION

The Western Lake Michigan Drainages was one of 59 basins selected nationwide as part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) program. The program was established to (1) provide a nationally consistent description of current water-quality conditions for a large part of the Nation's freshwater streams and aquifers, (2) define long-term trends (if any) in water quality, and (3) identify, describe, and explain, as possible, the major natural and anthropogenic factors that affect observed water-quality conditions and trends (Hirsch and others, 1988).

Elevated levels of various trace elements and synthetic organic compounds are of concern in the Great Lakes Region. Point and nonpoint anthropogenic sources of trace elements in the Western Lake Michigan Drainages of this region can include atmospheric deposition, urban and industrial waste, urban runoff, storm sewers, agricultural and silvicultural activities, and mining. Distinguishing between elevated trace element concentrations in streambed sediment derived from anthropogenic sources and elevated concentrations derived from geologic sources is difficult. Typical concentrations of trace elements around the world can vary widely even within similar rock types and soils (Kabata-Pendias and Pendias, 1992). Walker (1994) sampled streambed sediment from headwater streams in Wisconsin within an environmental framework of watersheds categorized according to land use, bedrock, soil type, glacial deposit, and ecoregion. A major objective of this work was to investigate the possibility of characterizing background levels of Cd, Cr, Cu, Pb and Zn in bulk and fine streambed sediment with regard to these environmental settings. Fine streambed sediment, specifically the silt/clay fraction (<63 µm), is the primary site for collection and transport of most trace elements due to the large surface-to-volume ratio of these particles (Horowitz, 1991). Use of the fraction less than 63 µm eliminates bias due to particle size differences.

Most organochlorine pesticides are no longer sold for use in the United States because of human health and environment concerns; however, these compounds and their metabolites are extremely persistent in the environment. Polychlorinated biphenyls (PCBs) are constituents of various industrial products including hydraulic fluids and electrical transformers and have many of the same chemical properties as organochlorine pesticides. Sources of semivolatile organic compounds (SVOCs) are primarily industrial, including dyes, solvents, lubricants, oil additives, and combustion. SVOCs enter rivers primarily in industrial and municipal wastewater effluent and nonpoint runoff (Moore and Ramamoorthy, 1984a). Some polycyclic aromatic hydrocarbons (PAHs) also result as by-products of natural combustion, such as forest fires, and were in historical discharges from manufactured gas plants and wood treatment facilities that used creosote.

Although determination of trace element and organic compound concentrations in sediment provides critical information as to the water-quality status of a site and exposure of existing biota, high concentrations in sediment may not translate to high biological availability or bioaccumulation. Bioaccumulation of constituents is a function not only of the contaminant concentrations in the environment, but also the interaction of physical, chemical, and biological processes that control bioavailability of trace elements and synthetic organic compounds. Uptake processes may include (1) direct uptake from solution through diffusion, active transport, or adsorption, (2) ingestion of food, sediment, or detritus and (3) adsorption of particulates onto the outside of the organism with or without subsequent absorption (Luoma, 1983; Spacie and Hamelink, 1985). The study of the concentration of trace elements and synthetic organic compounds in biota identifies those that are bioavailable and ultimately helps researchers to better understand their transport and fate in ecosystems.

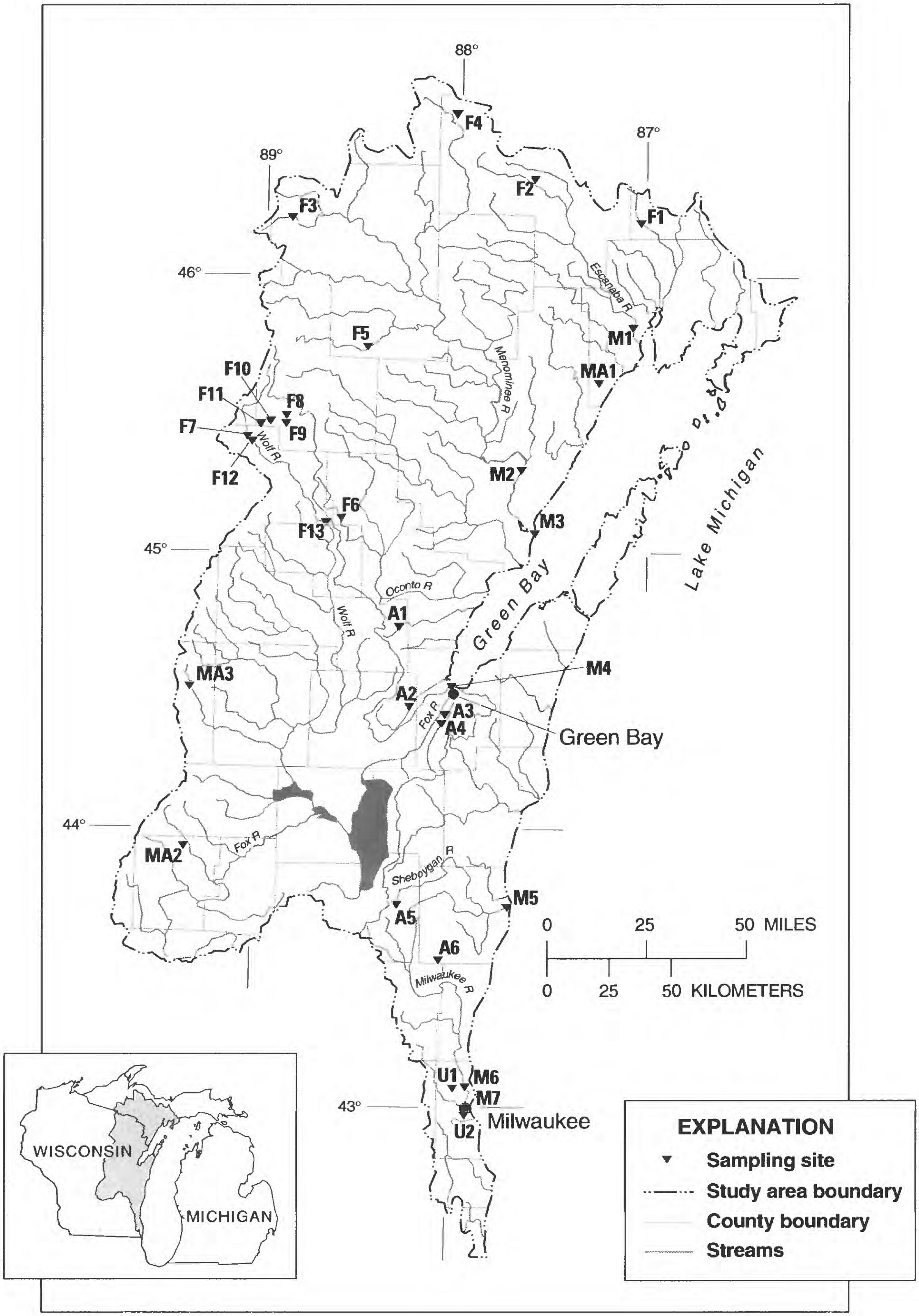
Purpose and Scope

The purposes of this report—part of the NAWQA Program—were to (1) assess the spatial occurrence of a broad suite of trace elements and several classes of synthetic organic compounds in biota and streambed sediment in tributaries to western Lake Michigan and (2) determine whether trace elements and organic compound concentrations could be related to environmental characteristics. A geographic information system (GIS) was used to delineate relatively homogeneous units (RHUs) of land use/land cover, surficial deposits, and bedrock (Robertson and Saad, 1995). Relations between concentrations of trace elements or synthetic organic compounds and these environmental factors that are used to define RHUs are discussed.

Sediment was sampled at 31 sites for trace elements and 23 sites for synthetic organic compounds; biota were collected at a subset of sites. The elements and compounds investigated in this study included trace elements, organochlorine pesticides, PCBs, and the SVOCs, including phenolic compounds, phthalates, and PAHs. The SVOCs were examined in sediment only. Biota sampled in this study were selected from a national target taxa list for NAWQA (Crawford and Luoma, 1994). Net-spinning caddisfly larvae (Order Trichoptera, Family Hydropsychidae) were selected as primary indicators for trace elements. A fish species, in most cases white sucker (Family Catostomidae: *Catostomus commersoni*), was selected as the indicator for synthetic organic compounds.

Western Lake Michigan Drainages Study Area

The study area drains approximately 51,540 square kilometers in eastern Wisconsin and the Upper Peninsula of Michigan and includes several major rivers: the Menominee, Wolf, Fox, Sheboygan, and Milwaukee Rivers (fig. 1). The major cities are Milwaukee and Green Bay. Land in the northwestern part of the study area (fig. 2) is primarily forested, and much of this land is actively used for silviculture. Wetland covers approximately 15 percent of the study area. Agriculture is the primary land use in the southern part of the study area, where dairy and dairy feed (corn and alfalfa) production are prevalent. A relatively small percentage of the study unit is represented by urban land use, with heavy industrial areas generally concentrated at Lake Michigan harbors and at the mouths of major rivers. Surficial deposits consist primarily of unconsolidated glacial, fluvial, and eolian materials. The texture of these deposits is classified as predominantly sand or sand and gravel in the north and west and as clayey in the southeast. Loam covers some north and central areas, and small peat deposits are found in the Michigan part of the study area. The bedrock of the study area consists of igneous and metamorphic rocks in the northwest, mostly carbonate rocks in the east, and sandstone in the southwest (Robertson and Saad, 1995).



Source: Seaber and others, 1986.

Figure 1. Location of sampling sites in the Western Lake Michigan Drainages study area.

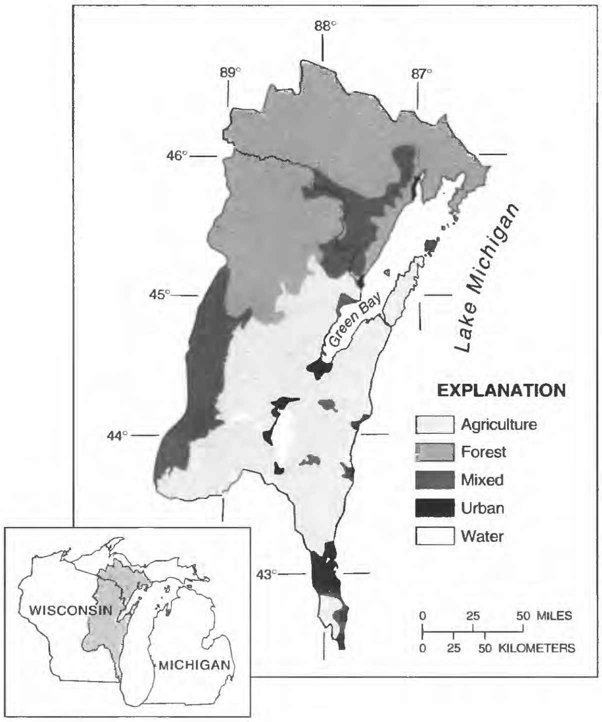


Figure 2. Generalized land use/land cover in the Western Lake Michigan Drainages study unit.

Within the study area, the International Joint Commission has named four Great Lakes Areas of Concern (AOCs) identified as severely degraded because of urban and (or) industrial contamination (International Joint Commission, 1989). The AOCs are (fig. 1): the portion of the Lower Menominee River within the cities of Menominee, Michigan and Marinette, Wisconsin (M3), Lower Fox River/southern Green Bay (M4), the lower 13 miles of the Sheboygan River and harbor (M5), and the Milwaukee Estuary (M7). Contamination of water and sediment at these locations has been associated with detrimental effects on the aquatic biota (Harris and others, 1982; Wisconsin and Michigan Departments of Natural Resources, 1990; Fox and others, 1991; Fabacher and others, 1991; Wisconsin Department of Natural Resources, 1991 and 1993; Ankley, and others, 1992).

Study Design

A total of 31 sites were sampled for trace elements and 23 sites for synthetic organic compounds in streambed sediment during low flow (table 1). The set included two sites where anthropogenic influence was minimal and one site (Green Creek in Michigan, site F2) specifically affected by a mining point source. Biota were collected at a subset of 25 sites for trace elements and 15 sites for synthetic organic compounds. Within the environmental framework of RHUs, two types of sites were chosen (table 2): sites on streams whose entire drainage was indicative of a single RHU (indicator sites), and sites on streams that integrated drainage from several RHUs (integrator sites). Three mixed-land-use indicator sites were included (surficial deposits and bedrock homogeneous). Sites were selected to obtain a broad spatial coverage of the study area.

METHODS

Sample Collection

Methods for collection and processing of sediment (Shelton and Capel, 1994) and biota (Crawford and Luoma, 1994) included use of plastic (Teflon[1], polypropylene, or polyethylene) equipment for trace element sampling; Teflon, stainless steel, aluminum, or

[1]Use of trade names in this article is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1. Sites sampled for trace elements and synthetic organic compounds in biota and streambed sediment of the Western Lake Michigan Drainages

[Land-use codes in the map numbers are: forest (F), agriculture (A), urban (U), and mixed land use (MA) indicator sites, and mixed (M) integrator sites. Components sampled were trace elements in biota (1) and streambed sediment (2) and synthetic organic compounds in biota (3) and streambed sediment (4)]

Map number	Site name	Latitude	Longitude	Component sampled
F1	West Branch Whitefish River near Diffin, Mich.	46°13'03"	87°02'58"	1, 2, 3, 4
F2	Green Creek near Palmer, Mich.	46°22'22"	87°36'21"	1, 2, 3, 4
F3	South Branch Paint River near Gibbs City, Mich.	46°13'33"	88°52'08"	1, 2, 3, 4
F4	Peshekee River near Martins Landing, Mich.	46°36'35"	88°01'20"	1, 2, 4
F5	Popple River near Fence, Wis.	45°45'50"	88°27'50"	1, 2, 3, 4
F6	Second South Branch Oconto River near Mountain, Wis.	45°08'39"	88°35'00"	1, 2, 3, 4
F7	Wolf River at Turtle Lake Road at Post Lake, Wis.	45°25'50"	89°04'29"	1, 2
F8	Swamp Creek at Keith Siding Road near Crandon, Wis.	45°30'30"	88°52'34"	1, 2
F9	Hemlock Creek near Crandon, Wis.	45°28'47"	88°52'36"	1, 2
F10	Swamp Creek above Highway 55 near Mole Lake, Wis.	45°29'17"	88°57'27"	2
F11	Swamp Creek near Mole Lake, Wis.	45°28'34"	89°00'26"	1, 2
F12	Wolf River near Post Lake, Wis.	45°24'48"	89°02'59"	1, 2
F13	Wolf River at Highway M near Langlade, Wis.	45°07'38"	88°39'45"	1, 2
A1	Pensaukee River near Krakow, Wis.	44°45'09"	88°16'35"	1, 2, 4
A2	Duck Creek at Seminary Road near Oneida, Wis.	44°27'57"	88°13'08"	1, 2, 3, 4
A3	East River at Midway Road near De Pere, Wis.	44°23'12"	88°04'47"	1, 2
A4	East River at Highway 32 in Brown County near De Pere, Wis.	44°24'21"	88°03'12"	1, 2, 3, 4
A5	Sheboygan River at Dotyville, Wis.	43°45'10"	88°15'56"	1, 2, 4
A6	North Branch Milwaukee River near Random Lake, Wis.	43°33'25"	88°03'10"	1, 2, 3, 4
MA1	Bark River near Bark River, Mich.	45°38'16"	87°15'52"	1, 2, 3, 4
MA2	Chaffee Creek at Neshkoro, Wis.	43°57'03"	89°20'50"	1, 2, 3, 4
MA3	Tomorrow River near Nelsonville, Wis.	44°31'28"	89°20'16"	1, 2, 3, 4
U1	Lincoln Creek at 47th Street at Milwaukee, Wis.	43°05'49"	87°58'20"	1, 2, 3, 4
U2	Kinnickinnic River at Chase Avenue at Milwaukee, Wis.	42°59'49"	87°54'45"	2, 4
M1	Escanaba River at Lambert, Mich.	45°50'26"	87°05'19"	2, 4
M2	Menominee River at McAllister, Wis.	45°19'20"	87°39'40"	1, 2, 3, 4
M3	Menominee River at Mouth at Marinette, Wis.	45°05'43"	87°35'22"	2, 4
M4	Fox River at Green Bay, Wis.	44°32'22"	88°00'16"	1, 2, 3, 4
M5	Sheboygan River at Mouth at Sheboygan, Wis.	43°44'50"	87°42'33"	2, 4
M6	Milwaukee River at Milwaukee, Wis.	43°06'00"	87°54'32"	1, 2, 3, 4
M7	Milwaukee River at Jones Island (at Mouth) at Milwaukee, Wis.	43°01'28"	87°53'54"	2, 4

Table 2. Environmental settings of sites sampled for trace elements and synthetic organic compounds in biota and streambed sediment of the Western Lake Michigan Drainages.

[Bedrock types are igneous/metamorphic (1), carbonate (2), shale (3), sandstone (4), or mixed (5); surficial deposits are sandy/sand and gravel (1), loamy (2), clayey (3), or mixed (4). Site F2 is a mining point source]

Map number	Drainage area (km^2)	Land cover or land use (percent)					Surficial deposits	Dominant bedrock
		Forest	Agriculture	Urban	Wetland	Water		
F1	116	71.1	3.5	0	25.4	0	2	2
F2	21.8	55.3	0	0	14.1	30.5	2	1
F3	72.0	86.2	0	0	11.8	2.0	1	1
F4	127	87.8	0	0	9.9	2.3	2	1
F5	360	61.1	3.0	0	35.1	0.6	1	1
F6	51.0	85.1	10.3	0	3.0	1.7	1	1
F7	305	60.5	5.6	0.3	28.2	5.4	1	1
F8	39.1	80.0	0.80	0	8.0	11.2	1	1
F9	8.5	72.5	0	0	3.7	23.8	1	1
F10	120	63.9	6.7	2.3	15.8	11.2	1	1
F11	148	64.8	7.1	1.9	16.8	9.3	1	1
F12	506	61.1	5.7	0.7	26.3	6.2	1	1
F13	1291	68.7	6.0	0.4	20.4	4.5	1	1
A1	92.7	4.4	86.0	0.2	9.2	0	2	2
A2	247	4.6	89.3	0.6	4.8	0	3	2
A3	122	5.1	91.5	0.83	2.5	0	3	3
A4	134	5.2	91.7	0.8	2.3	0	3	3
A5	35.7	2.3	93.1	0.8	3.5	0	1	2
A6	133	6.4	88.0	1.1	4.0	0.33	1	2
U1	24.8	0	0	100	0	0	3	2
U2	56.2	0	4.7	95.2	0	0	3	2
MA1	90.1	16.1	47.4	0.71	35.0	0.42	2	2
MA2	120	50.6	42.4	0.65	5.5	0.45	1	4
MA3	114	31.4	58.3	0.2	8.8	1.2	1	1
M1	2404	67.1	5.0	0.85	23.8	1.7	4	5
M2	10,180	74.8	6.2	0.60	15.7	2.5	4	5
M3	10,540	73.0	7.1	0.7	16.4	2.5	4	5
M4	16,400	26.4	52.0	2.76	13.0	5.6	4	5
M5	1106	6.6	80.7	3.8	7.6	0.88	4	2
M6	1803	8.3	74.6	11.2	4.5	1.1	4	2
M7	2258	7.1	66.2	21.7	3.7	1.0	4	2

glass equipment was used for synthetic organic compound sampling. Quality-control procedures for the collection and processing of biota and sediment included collection of approximately 15% replicate samples and the use of clean techniques to minimize potential contamination. Quality-control results are reported in Fitzgerald (1997) and indicate no major problems or biases in sampling and analysis of trace elements; however, a large variability between replicates and splits was found for some phthalates and PAHs in sediment. This variability may be related to the method used to split samples, or perhaps it reflects contamination, which is particularly likely in the case of phthalates because they are so ubiquitous in the environment.

Collection methods for sediment were different for wadable and nonwadable sites. For wadable sites, generally 5 to 10 samples of fine-grained sediment were collected by hand with a Teflon scoop from each of 5 to 10 depositional zones (submerged during low streamflow) along a reach of approximately 150 m. Samples were collected from the upper 2 cm (most recent, oxidized layer) and the amount collected depended on the relative size of the depositional zone. Deposits of fine-grained sediment were sought out and sampled; thus, concentrations represent conditions in depositional areas of the streams, not the average concentrations for sediment throughout the stream reach. At nonwadable sites, a stainless-steel petite Ponar dredge was used to collect the upper 2 cm sediment layer from 1 to 2 depositional zones in 1992 and from 5 zones in 1995. A Teflon scoop was used to collect a sediment subsample that had not been in contact with metal edges of the dredge. The composited trace element sample was homogenized and a bulk sediment sample (<2mm) was collected for determination of particle size. The rest of the composite sample was wet-sieved with native water through 63-µm-plastic mesh.The composite sample for synthetic organic compounds was wet-sieved through a 2-mm-mesh stainless steel sieve. Samples were placed in clean containers and shipped on ice to the laboratory.

Composite samples of single species or genera were used to determine contaminant concentrations in biota. Caddisfly larvae of the family Hydropsychidae were collected at 16 sites as the primary target organisms for trace element analysis: Caddisfly 1 (*Hydropsyche* spp.), Caddisfly 2 (*Ceratopsyche* spp.), or Caddisfly 3 (*Cheumatopsyche* spp.). *Hydropsyche* and *Ceratopsyche* were historically placed in the same genus and some taxonomists still consider these genera to be equivalent. For the purposes of this study, individuals from these genera often were combined in order to obtain adequate sample volume and spatial coverage. A study by Cain and others (1992) found variations in trace-element concentrations among species of *Hydropsyche* to be small. White sucker of approximately 15 cm total length (1-2 years old) were collected for trace elements at 5 sites and as the primary taxa for synthetic organic compounds at 13 sites. Where the primary taxa were not available, or where additional secondary taxa were desired, other species were collected, including: Caddisfly 4 (*Brachycentrus occidentalis* larvae), stonefly (*Acroneuria* sp. larvae), crayfish (*Orconectes* sp.), or damselfly (Families Coenagrionidae, 90%, and Calopterygidae, 10%), waterweed (*Elodea canadensis*), Pondweed 1 (*Potamogeton crispus*), Pondweed 2 (*Potamogeton pectinatus*), Pondweed 3 (*Potamogeton epihydrus*), rock bass (*Ambloplites rupestris*), green sunfish (*Lepomis cyanellus*), or shorthead redhorse (Family Catostomidae: *Moxostoma macrolepidotum*).

Whole caddisfly larvae were collected from rocks and woody debris. Larvae were kept in native water for a 4-6 hour depuration period, after which they were rinsed in filtered deionized water (18 Mohm), sorted by genus, counted, and frozen on dry ice. Aquatic plants were vigorously rinsed in native water to remove attached detritus and sediment, and the apical 5 cm of at least three individual plants was collected. Plant samples were given three 1-hour soaks in filtered deionized water, drained, weighed, and frozen on dry ice. Fish were collected by electrofishing. After capture, the fish were rinsed in native water, weighed, and measured for total length. A scale and spine sample was collected for age determination. For trace element analysis, fish livers were removed and frozen on dry ice. With the exception of Hg, concentrations of most trace elements do not accumulate in fish muscle to the extent that they do in fish liver (Wiener and others, 1984). For organics analysis, separate composite samples of whole fish were wrapped in clean aluminum foil and frozen on dry ice.

Laboratory Analysis

Samples were analyzed for trace elements and synthetic organic compounds at the USGS National Water-Quality Laboratory in Denver, Colorado (Faires, 1993; Fishman, 1993; Foreman and others, 1995; Leiker and others, 1995; Furlong and others, 1996; Hoffman, 1996). The sediment analyses included 46 major and trace elements (including two forms of carbon: inorganic and organic, as well as total carbon) and 32 organochlorines (including total PCBs) as well as 65 SVOCs. Biota were analyzed for a subset of these: 22 trace elements, 28 organochlorine compounds including total PCBs, and percent moisture. Concentrations of As, Cd, and Se in biota were analyzed by inductively coupled plasma-mass spectrometry; As and Se concentrations in sediment were analyzed by use of hydride-generation atomic absorption spectrophotometry and Cd was analyzed by graphite furnace atomic absorption spectrophotometry. Chromium, Cu, Ni, Pb, and Zn concentrations in biota and sediment were determined by use of inductively coupled plasma-atomic emission spectrometry. Trace-element analysis involved total digestions, and all concentrations in sediment and biota are given as micrograms per gram (µg/g) dry weight. Capillary-column gas chromatography was used to determine concentrations of organochlorine pesticides, PCBs, and SVOCs. Concentrations of synthetic organic compounds are given as µg/g dry weight for sediment and µg/g wet weight for fish. Quality-control measures at the laboratory included comparisons to standard reference materials, spikes, and duplicates. Sediment particle size was analyzed at the USGS Sediment Laboratory in Iowa City, Iowa. Age determinations of fish based on scale and spine samples were done at the USGS Great Lakes Science Center in Ann Arbor, Michigan.

Data Analysis

The SAS statistical software package (SAS Institute, 1990) was used for all statistical analyses. The data were checked for univariate normal distributions by use of Tukey modified boxplots (Tukey, 1977), stem and leaf plots (Iman and Conover, 1983), and normal probability plots (Johnson and Wichern, 1992). For trace elements, sediment data were rank transformed and analyzed by use of nonparametric statistical methods, which do not require the assumption of normal distribution. For trace elements, values less than the minimum reporting level were set equal to one-half the minimum reporting level. With respect to biota, statistical analyses were possible only for the caddisfly data, owing to the small number of sites where other types of biota were collected. At the two sites where Caddisfly 1 and 2 were collected simultaneously with Caddisfly 3, concentrations of most trace elements were more than 10% lower for Caddisfly 3. Therefore, unless noted otherwise, significant correlations for caddisfly larvae discussed in the results were observed for all caddisfly species combined (n=25), as well as for Caddisfly 1 and 2 alone (n=18). The Kruskal-Wallis test (Iman and Conover, 1983) was used to identify significant differences in trace-element concentrations in sediment and caddisfly larvae with respect to selected environmental characteristics. For this analysis, concentrations of trace elements in sediment and caddisfly larvae were grouped by land use, texture of surficial deposits, and bedrock geology. Land use was further divided into five categories that consisted of four types of indicator sites: forested (F), agricultural (A), urban (U), or mixed land use (MA), plus mixed integrator sites (M). The Tukey studentized range test (Neter and others, 1985) was used to identify which groups from the Kruskal-Wallis test were similar among the environmental characteristics at the 95 percent confidence level. Spearman rank correlation (Johnson and Wichern, 1992; Iman and Conover, 1983) — and, where possible, Pearson correlation (Iman and Conover, 1983) on log-transformed data — were used to check for relations between trace-element concentrations in sediment and biota. Significant correlations are defined as those where the probability of a Type I error is less than 5% ($p < 0.05$), and these correlations are discussed only where the absolute value of the Spearman or Pearson rho (ρ) ≥ 0.5. Principal components analysis (PCA) (Hotelling, 1933) and cluster analysis were used to examine similarities among spatial patterns of trace elements. Percentiles of element concentrations in caddisfly larvae were calculated to assess elevated concentrations.

No sediment-quality criteria currently exist for protection of benthic organisms. Potential adverse effects on certain biota may be assessed, however, by comparison to established guidelines for bulk sediment (table 3) provided by the Ontario Ministry of Environment and Energy (OMEE) (Persaud and others, 1993) and sediment effect concentrations (SECs) developed by Ingersoll and others (1996). These two guidelines were used to generally evaluate sediment concentrations of trace elements and synthetic organic compounds in our study. Both guidelines have lower and upper effect levels related to potential impacts on benthic macroinvertebrates for individual trace elements or synthetic organic compounds. Both guidelines are based entirely on freshwater data. The OMEE

Lowest Effect Level (LEL) is the concentration that 95% of the benthic biota can tolerate, and the Severe Effect Level (SEL) is the concentration at which pronounced effects can be expected for the benthic community. A recent study by Smith and others (1996) gave further support to the OMEE LELs for trace elements and most pesticides examined. The SEC Effect Range Low (ERL) is the concentration below which effects are rarely observed or predicted among sensitive life stages and (or) species of biota (Long and Morgan, 1990; Ingersoll and others, 1996). The SEC Effect Range Median (ERM) is the concentration above which effects are frequently or always observed among most species of biota. The SEC and OMEE guidelines differ for some trace elements and synthetic organic compounds; however, both guidelines are used in our evaluation to ensure that exposure of the most sensitive biota present in our study are included. Neither guideline has effect levels for Se and neither guideline accounts for interactions among elements or compounds, although the SECs were developed using only field-collected sediment in order to address potential effects of mixtures. Both guidelines are based on concentrations in bulk sediment. Therefore, comparison of the <63 μm fraction trace element concentrations in our study to these guidelines may overestimate concentrations that benthic organisms are exposed to for *in situ* bulk sediment.

In addition to concentrations reported in the literature, concentrations of synthetic organic compounds in biota were compared, where appropriate, to National Academy of Sciences/National Academy of Engineering (NAS/NAE) guidelines (1973) for the protection of fish and fish-consuming wildlife, U.S. Food and Drug Administration (FDA) action levels (1984) for the protection of human health, and Wisconsin Division of Health and Wisconsin Department of Natural Resources (WDNR) advisories (1994, 1997) for the protection of human health (table 3). Concentrations of some trace inorganic elements in fish livers were converted to wet weight and compared to elevated data levels (EDLs) for livers of freshwater fish in California's Toxic Substances Monitoring Program (TSMP). The EDL 85 and 95 values are based only on samples collected from 1978 through 1993 (Rasmussen, 1995), and do not represent established guidelines or toxic effect levels.

TRACE ELEMENTS IN BIOTA AND STREAMBED SEDIMENT

Overview of Spatial Variability

Comparisons of trace-element concentrations in sediment and biota to environmental characteristics (land use, surficial deposits, and bedrock type) revealed that the highest concentrations of certain trace elements were not always associated with urban land use or the mouths of the major rivers. Some concentrations were highest in sediment and biota from forested or forested/wetland sites. Most concentrations of Cd in biota were below minimum reporting levels and so relations to environmental characteristics could not be examined.

Effects of Land Use

Land use was found to be a significant factor in the spatial variability of some trace element concentrations in sediment and biota. For all the elements in sediment except Cr (fig. 3), and for As, Cu, Pb, and Ni in caddisfly larvae, Kruskal-Wallis tests and Tukey studentized range tests indicated that concentrations from at least one land use category were significantly different from the rest (table 4). A survey of trace elements in streambed sediment of Wisconsin (Walker, 1994) also found no relation between Cr concentration and land use.

Urban and Mixed Integrator. In comparisons among all land-use types, concentrations of Cd, Cu, Hg, Ni, Pb, and Zn were significantly higher in sediment from urban and integrator sites than in sediment from the other sites. All six elements can be associated with urban sources, especially industrial point and nonpoint sources (Winchester and Nifong, 1971; Williams and others, 1974; Förstner and Wittman, 1979; Leed and Belanger, 1981; Kelly and Hite, 1981, 1984; Moore and Ramamoorthy, 1984b; Salomons and Förstner, 1984; City of Chicago and Illinois Environmental Protection Agency, 1985; Hem, 1985; Striegel and Cowan, 1987). In PCA of element concentrations in sediment at all sites, Cd, Cu, Hg, Pb and Zn were grouped (axis 1; $\rho > 0.56$), further indicating that spatial patterns in concentrations of these elements were similar. An example for Pb concentrations in sediment, by land use, is shown in fig. 4. Many of the integrator sites were at harbors of Lake Michigan and are subject to substantial industrial discharge and nonpoint input.

Table 3. Selected guidelines for trace elements and synthetic organic compounds in bulk sediment and fish tissues

[Concentrations in sediment are in micrograms per gram dry weight; concentrations in fish tissue are in micrograms per gram wet weight; --, no guidelines. Ontario Ministry of Environment and Energy values are for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL). OMEE SEL values must be converted to bulk sediment values for the synthetic organic compounds by multiplying the table OMEE SEL value by the organic carbon concentration of the sediment expressed as a decimal weight, to a maximum of 10 percent to derive a site specific value (Persaud and others, 1993). The sediment effect criteria (SEC) are from Ingersoll and others (1996) for Effects Range Low (SEC ERL) and Effects Range Median (SEC ERM). National Academy of Sciences/National Academy of Engineering (NAS/NAE) guidelines (1973) are for whole fish; U.S. Food and Drug Administration (FDA) action levels (1984) and Wisconsin Department of Natural Resources (WDNR) advisories (1994, 1997) are only for the edible portion of the fish. Total DDT includes DDT, DDE, and DDD.]

	Sediment				Fish tissue		
	OMEE LEL	SEC ERL	OMEE SEL	SEC ERM	NAS/ NAE	FDA	WDNR
Trace Elements							
As	6	13	33	50	--	--	--
Cd	0.6	0.7	10	3.9	--	--	--
Cr	26	39	110	270	--	--	--
Cu	16	41	110	190	--	--	--
Hg	0.2	--	2	--	0.5	1.0	0.5
Ni	16	24	75	45	--	--	--
Pb	31	55	250	99	--	--	--
Zn	120	110	820	550	--	--	--
Synthetic Organic Compounds							
PCB, total[1]	0.07	50	530	730	0.5	2.0	1.9
DDD	0.008	--	6	--	--	1.0	--
DDE	0.005	--	19	--	--	1.0	--
DDT, total[2]	0.007	--	12	--	1.0	5.0	5.0
Dieldrin	0.002	--	91	--	0.1	0.3	0.3
Chlordane	0.007	--	6	--	0.1	0.3	0.3
PAH, total	4	240	10,000	2200	--	--	--

[1]The WDNR and five other Great Lakes states use five PCB levels in fish to issue advisories, beginning at > 0.05 µg/g PCB.
[2]The FDA and NAS/NAE values are for DDT + DDD + DDE or, if no DDT detected, DDD + DDE.

Table 4. Results from Tukey studentized range tests ($p \leq 0.05$) on ranked concentrations of trace elements in streambed sediment and caddisfly larvae grouped by land use, surficial deposits, and bedrock type.

[Land use codes are forested (F), agricultural (A), urban (U), and mixed (MA) land use indicator, and mixed (M) land use integrator; surficial deposit codes are sandy/sand and gravel (S), loamy (L), clayey (C), mixed (M); bedrock codes are igneous/metamorphic (I), carbonate (CA), and mixed (M); --, no significant differences among groupings. No data are available for caddisfly larvae in urban land use. An asterisk indicates that the relation is significant only for all caddisfly larvae as a group (n=25) and not Caddisfly 1 and 2 alone]

Trace element	Component	Land use	Surficial deposits	Bedrock type
As	Sediment	F>A	--	I>CA
	Caddisfly	F>A, F>MA	--	I>CA
Cd	Sediment	U>A, U>MA, M>A	--	--
	Caddisfly	--	--	--
Cr	Sediment	--	--	--
	Caddisfly	--	--	--
Cu	Sediment	M>F, M>MA	M>S	--
	Caddisfly	A>F*	--	--
Pb	Sediment	U>F, U>MA, U>A, M>F, M>MA, M>A	M>S, M>L	--
	Caddisfly	A>F	--	CA>I*
Hg	Sediment	M>A	--	--
	Caddisfly	--	--	--
Ni	Sediment	U>F, U>MA, M>F, A>F	C>S, M>S	CA>I
	Caddisfly	A>F,A>MA[1]	C>S*,L>S*	--
Se	Sediment	F>U	S>C	--
	Caddisfly	--	--	--
Zn	Sediment	U>F, U>MA, U>A, M>F, M>A, M>MA	C>S	M>I
	Caddisfly	--	--	--

[1]If site F2 (mining point source) is omitted

Concentrations of Cu, Pb, and Zn in sediment were high at the urban site Lincoln Creek (U1) compared to most other sites. Walker (1994) also found concentrations of these three elements to be high in this stream. Waterweed from U1 contained high concentrations of Cu, Pb, Ni, and Zn; these concentrations were much higher than concentrations at all other sites in our study for this aquatic plant. With the exception of Ni concentrations, which were lower, concentrations of these elements were similar to those found by Fitzpatrick and others (1995) in waterweed from the North Branch Chicago River, an urban/industrial stream in Illinois. Anomalously high Hg values in two forested sites, Hemlock Creek (F9) and Swamp Creek near Mole Lake (F11), suggest Hg enrichment (fig. 5); however, resampling of site F9 in 1997 did not find a high sediment Hg concentration.

Forested. As a group, significantly higher sediment As concentrations were observed at forested sites compared to agricultural sites, and As was directly correlated with the percentage of forested land use ($\rho=0.56$). Arsenic concentrations in caddisfly larvae were significantly higher at forested sites than at agricultural and mixed-land-use indicator sites (fig. 6) and a correlation was found between As concentrations in caddisfly larvae and the percentage of forested land ($\rho=0.47$). Potential silvicultural sources of As might include dimethylarsinic acid (also known as cacodylic acid), a defoliant that is used in forest control (World Health Organization, 1981). Silviculture is prevalent in the forested part of the study area; however, it is not known if arsenic-containing chemicals have been used. Selenium concentrations in sediment were significantly higher ($\rho = 0.50$) at sites with a higher percentage of forested land use in their drainage basins (fig. 7), and significantly higher sediment Se concentrations were found at forested sites, as a group, compared to urban sites. No known sources of Se are associated with silviculture.

Agricultural. Although the results of Kruskal-Wallis and Tukey tests indicated that caddisfly larvae from agricultural sites had significantly higher concentrations of Cu and Pb than larvae from forested sites and higher Ni concentrations than larvae from forested or mixed-land-use indicator sites (if site F2 is omitted), urban sites were not included in the analysis because of the absence of caddisfly larvae at these sites. The concentrations of Pb in caddisfly larvae were significantly correlated with percentage of agriculture ($\rho = 0.58$). Clustering and PCA grouped Cu, Pb, and Ni in caddisfly larvae (Axis 1; $\rho > 0.68$), indicating similar spatial patterns for these elements. Concentrations of these elements were still less than those found for the same genus or species of caddisfly larvae and crayfish at urban sites by Fitzpatrick and others (1995), with the exception of Ni, and concentrations also were less than the TSMP EDLs for livers of freshwater fish.

Additional Factors That Affect Interpretation

Land use overlaps many groupings of surficial deposits and bedrock type and complicates interpretations of sources or causes. For example, 10 of the 13 forested basins have sandy/sand and gravel over igneous/metamorphic bedrock (table 2), and most of the agricultural and urban basins have loamy or clayey surficial deposits underlain by carbonate rock. In addition, texture of surficial deposits and bedrock type were directly correlated ($\rho=0.82$), sites with igneous/metamorphic rocks having sandy soils and sites with carbonate rocks having clayey or loamy soils. Other additional factors also were observed that affect interpretation of trace element concentrations in sediment and biota and these also are discussed below.

Surficial Deposits. Trace element concentrations in sediment appeared to vary with the texture of surficial deposits. Sites were grouped into four categories (sandy/sand and gravel, loamy, clayey, or mixed). Sediment concentrations of Cu, Ni, Pb, Se, and Zn differed between at least two categories (table 4). Sites with mixed surficial deposits had significantly higher Cu and Pb concentrations in sediment than sites with sandy/sand and gravel surficial deposits. Concentrations of Ni, Se, and Zn were significantly different between sandy/sand and gravel and clayey sites (data for Ni shown in fig. 8). Nickel and Zn concentrations were higher at clayey sites, whereas Se concentrations were higher at sandy/sand and gravel sites. Nickel concentrations in caddisfly larvae (n=25 only) also were significantly higher in clayey and loamy basins compared to sand/sand and gravel basins. Background concentrations of Ni are higher in clayey and loamy soils (Kabata-Pendias and Pendias, 1992). While higher background concentrations of Se are associated with

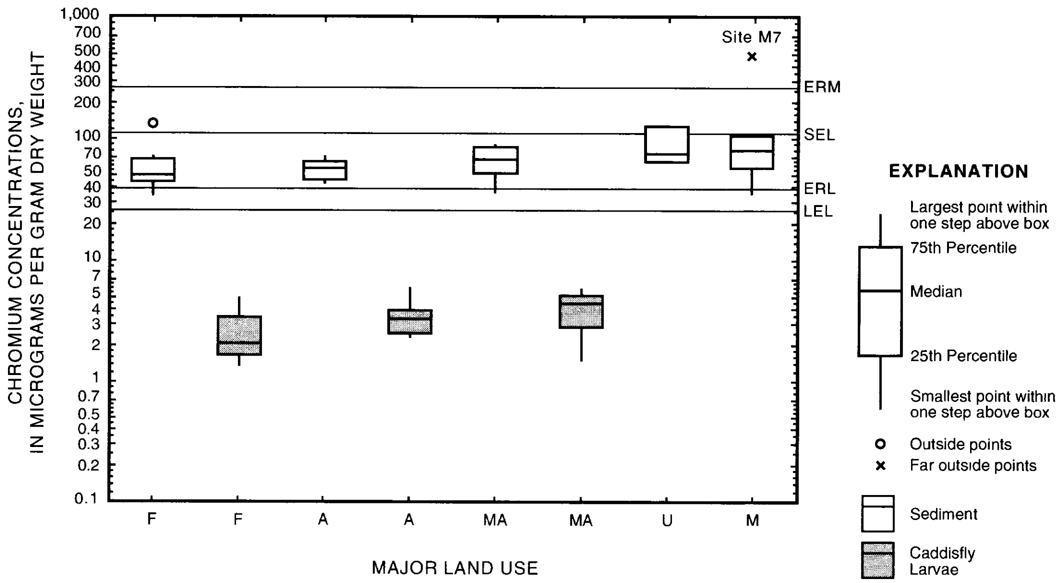


Figure 3. Chromium concentrations in sediment and caddisfly larvae of the Western Lake Michigan Drainages by major land use, 1992–1995.

[Land use codes are forested (F), agricultural (A), urban (U), and mixed (MA) land use indicator, and mixed (M) land use integrator; No data are available for caddisfly larvae in urban land use; Values below the minimum reporting level were set equal to one-half the minimum reporting level; Ontario Ministry of Environment and Energy values are shown for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL), and sediment effect criteria (SEC) from Ingersoll and others (1996) for Effects Range Low (SEC ERL) and Effects Range Median (SEC ERM) are shown].

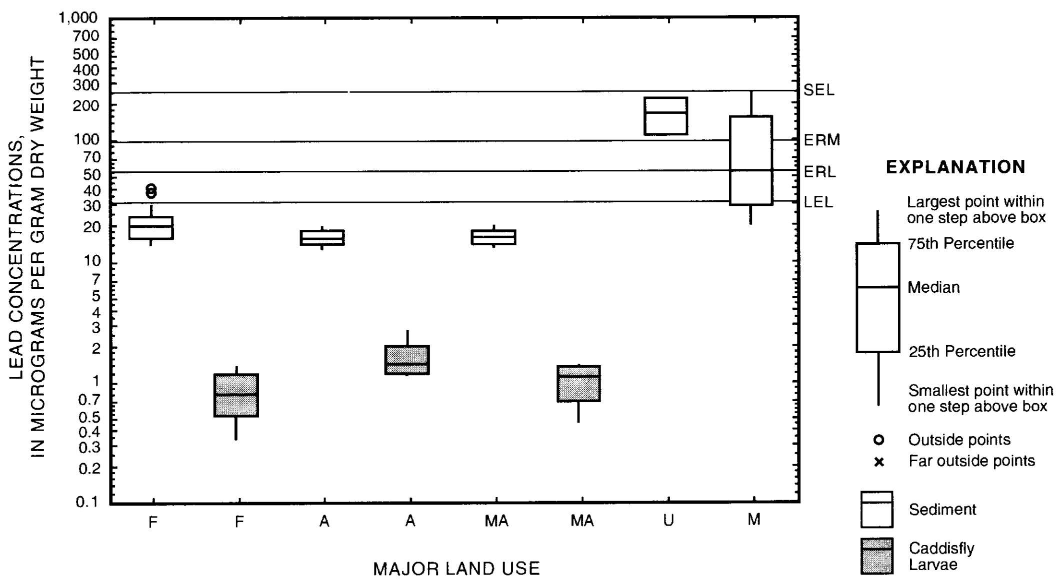


Figure 4. Lead concentrations in sediment and caddisfly larvae of the Western Lake Michigan Drainages by major land use, 1992–1995.

[Land use codes are forested (F), agricultural (A), urban (U), and mixed (MA) land use indicator, and mixed (M) land use integrator; No data are available for caddisfly larvae in urban land use; Values below the minimum reporting level were set equal to one-half the minimum reporting level; Ontario Ministry of Environment and Energy values are shown for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL), and sediment effect criteria (SEC) from Ingersoll and others (1996) for Effects Range Low (SEC ERL) and Effects Range Median (SEC ERM) are shown].

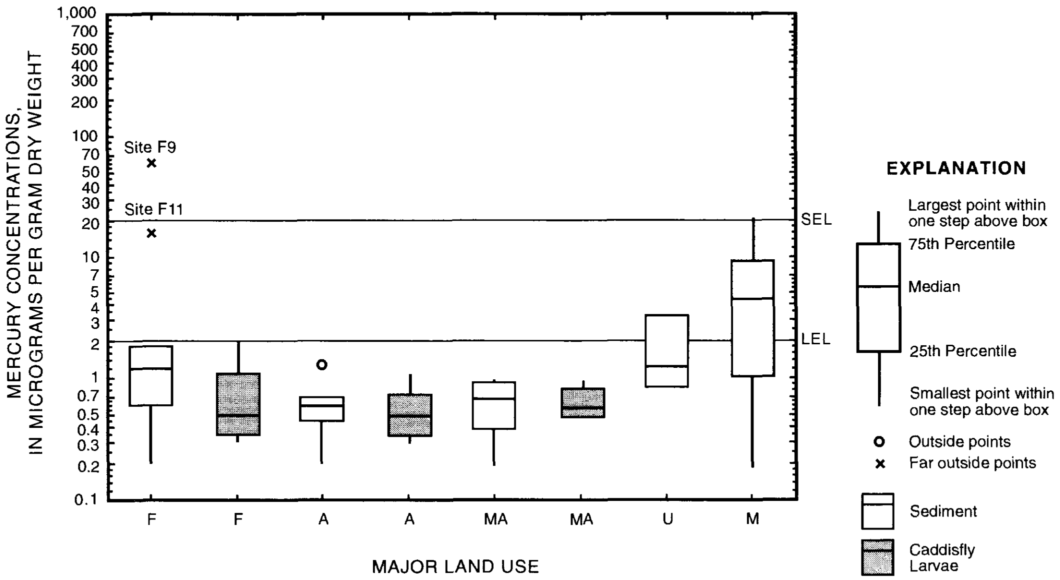


Figure 5. Mercury concentrations in sediment and caddisfly larvae of the Western Lake Michigan Drainages by major land use, 1992–1995.

[Land use codes are forested (F), agricultural (A), urban (U), and mixed (MA) land use indicator, and mixed (M) land use integrator; No data are available for caddisfly larvae in urban land use; Values below the minimum reporting level were set equal to one-half the minimum reporting level; Ontario Ministry of Environment and Energy values are shown for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL)].

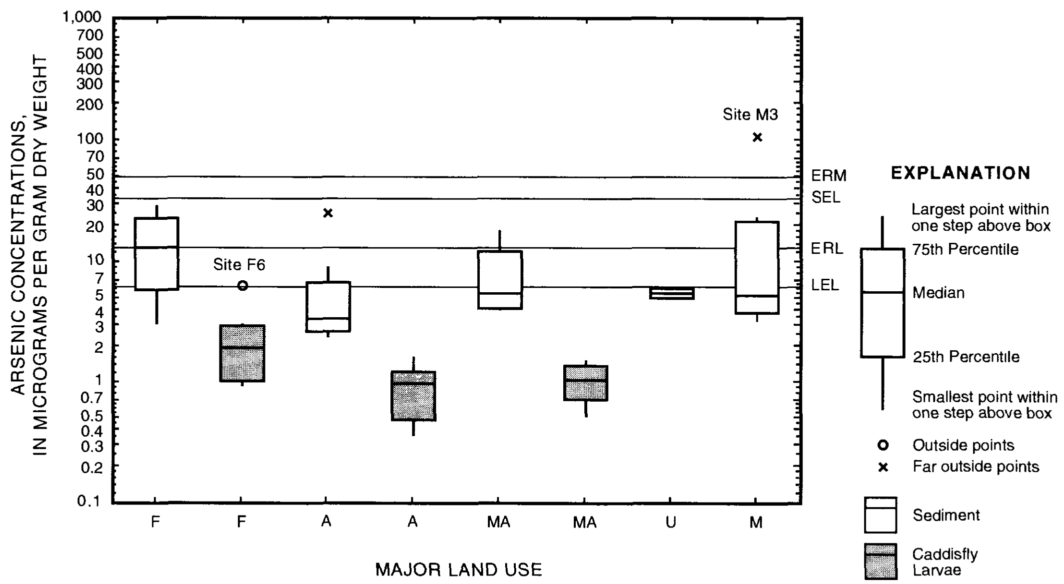


Figure 6. Arsenic concentrations in sediment and caddisfly larvae of the Western Lake Michigan Drainages by major land use, 1992–1995.

[Land use codes are forested (F), agricultural (A), urban (U), and mixed (MA) and use indicator, and mixed (M) land use integrator; No data are available for caddisfly larvae in urban land use; Values below the minimum reporting level were set equal to one-half the minimum reporting level; Ontario Ministry of Environment and Energy values are shown for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL), and sediment effect criteria (SEC) from Ingersoll and others (1996) for Effects Range Low (SEC ERL) and Effects Range Median (SEC ERM) are shown].

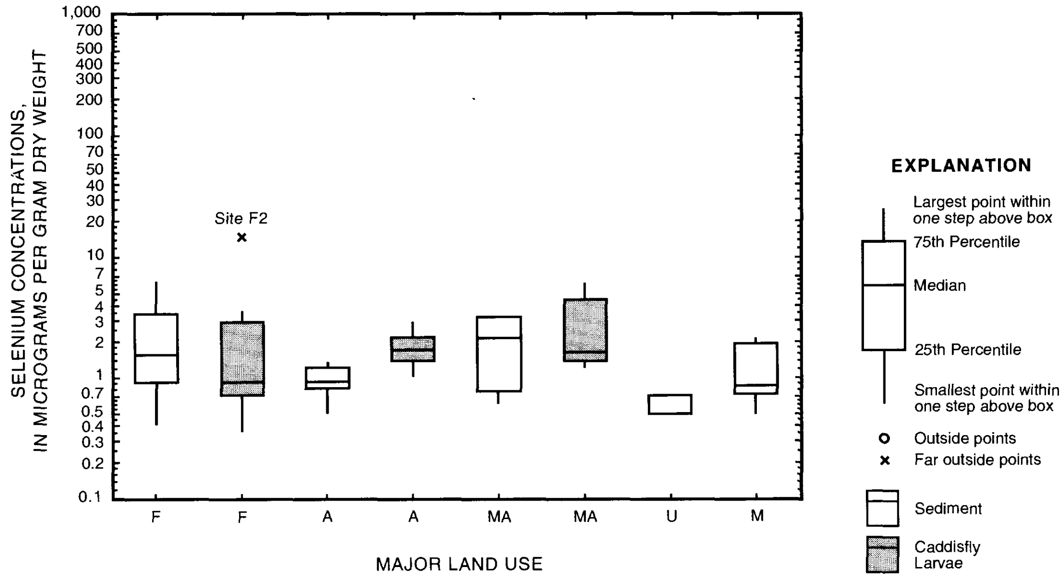


Figure 7. Selenium concentrations in sediment and caddisfly larvae of the Western Lake Michigan Drainages by major land use, 1992–1995.

[Land use codes are forested (F), agricultural (A), urban (U), and mixed (MA) land use indicator, and mixed (M) land use integrator; No data are available for caddisfly larvae in urban land use; Values below the minimum reporting level were set equal to one-half the minimum reporting level].

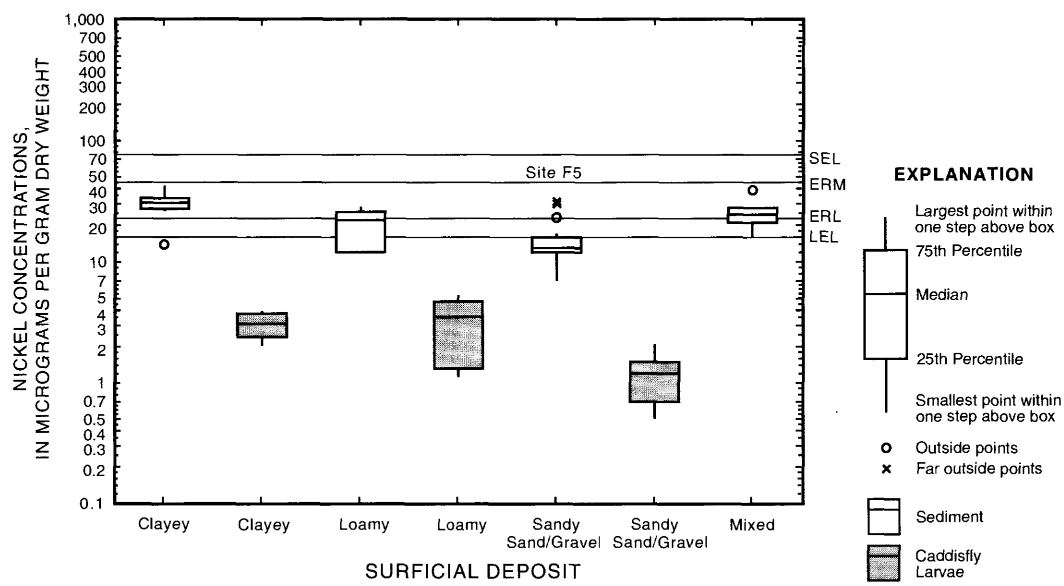


Figure 8. Nickel concentrations in sediment and caddisfly larvae of the Western Lake Michigan Drainages by surficial deposits, 1992–1995.

[Surficial deposit codes are sandy/sand and gravel (S), loamy (L), clayey (C), mixed (M); Values below the minimum reporting level were set equal to one-half the minimum reporting level; Ontario Ministry of Environment and Energy values are shown for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL), and sediment effect criteria (SEC) from Ingersoll and others (1996) for Effects Range Low (SEC ERL) and Effects Range Median (SEC ERM) are shown].

shale or clayey deposits, Se also occurs with sulfide-bearing rocks. In the United States, general concentrations of Zn in clay soils are slightly greater than in sandy soils (Kabata-Pendias and Pendias, 1992).

Bedrock Type. Sediment concentrations of As, Ni, and Zn were significantly higher between at least two categories of bedrock (table 4). Arsenic concentrations in sediment were significantly higher at sites with igneous/metamorphic bedrock than at sites with carbonate bedrock. Nickel was generally higher at sites with carbonate bedrock. Kabata-Pendias and Pendias (1992) cited similar commonly found values of As in igneous/metamorphic and carbonate rocks and, in general, high Ni concentrations are found in mafic igneous rocks.

Organic Carbon. In this study, sediment high in organic carbon contained high concentrations of Se (ρ=.85). Concentrations of Se in caddisfly larvae correlated with organic carbon concentrations in sediment (ρ=0.51) if the outlier from the mining point source site (F2) was omitted. The concentration of organic carbon in sediment is used to indicate the concentration of organic matter. The ability of organic matter in concentrating some trace elements in stream sediment is well recognized (Gibbs, 1973; Horowitz, 1991) and this ability varies with the type of organic matter. Complexation by organic matter, such as humic and fulvic acids, has generally been thought to reduce bioavailability (Spacie and Hamelink, 1985; Newman and Jagoe, 1994). Results of studies by Decho and Luoma (1994) and Winner (1985) suggest that organic carbon compounds may in some cases enhance uptake of certain trace elements. The positive relation we found between concentrations of Se in biota and sediment organic carbon may be due to Se-contaminated organic matter, such as algae or detritus, being ingested as food. Recent work suggests that uptake from food by some invertebrates is the dominant pathway for certain trace elements including Se (Hare and others, 1991; Lemly, 1996; Luoma and others, 1992; Snyder and Hendricks, 1995).

Other. The highest sediment As concentration observed in our study was at M3 on the Menominee River. A chemical company in Marinette, Wisconsin manufactured organoarsenical herbicides from 1957 until 1977, resulting in high concentrations of As in its vicinity in the Menominee River and Green Bay (Wisconsin Department of Natural Resources, 1996). Arsenicals have been developed for use in agriculture as fungicides, herbicides, and insecticides (Berg, 1976; Kelly and Hite, 1981; Sine, 1992).

High Cr concentrations in sediment and caddisfly larvae were found at the South Branch of the Paint River (F3), where concentrations in the sediment exceeded the SEL. Chromium is generally considered to be an urban-associated element. No towns are upstream of this site; however, there is an abandoned railway in the flood plain near the channel at the location sampled and an industrial logging operation upstream. In contrast to caddisfly larvae, concentrations in white sucker livers from F3 did not appear to be elevated when compared to concentrations at other sites. Chromium concentrations in these two trophic levels may be different because concentrations for caddisfly larvae are whole body and therefore also reflect metal attached to the external body parts and unassimilated metal associated with the gut (Hare and others, 1991).

The highest concentrations of Se and Hg found among all biota in this study were at one agricultural indicator site, Duck Creek (A2), where rock bass collected in 1995 contained 0.35 µg/g Hg and 17.5 µg/g Se. On the basis of a review of research on Se toxicity, Lemly (1996) suggested that 12 µg/g dry weight Se in livers of freshwater fish be considered a toxic-effects threshold for overall health and reproductive success. Concentrations of Hg and Se were not especially high in caddisfly larvae or sediment from this site. The primary route of Se accumulation in fish is through uptake by food, and so higher concentrations in the upper trophic levels might be expected. It is also possible that these mature fish migrated to the sample site from another location where concentrations of these elements were higher; this sample was composed of four mature females (3-5 years old). Mature fish may migrate long distances during spawning periods (Hall, 1972; Langhurst and Schoenike, 1990).

Relations between Concentrations in Biota and Streambed Sediment

Significant correlations between total concentrations of trace elements in sediment and biota were few, and total element concentration in sediment is not presently thought to be a good indication of bioavailable element content (Thomson and others, 1984; Newman and Jagoe, 1994). Our findings and the findings of others emphasize that both media should both be collected in order to adequately address exposure and availability of these trace elements. Other studies have found that elements extracted from sediment by certain methods better reflect the bioavailable element concentration when compared to the total element concentration as was used in our study. For example, correlations have been observed (Cain and others, 1992) between HCl-extractable element concentrations in sediment and whole caddisfly larvae (Family Hydropsychidae) for Cd, Cu, Pb, and Zn. In addition, the variety of environmental characteristics included in our study may have confounded biota-sediment relations. This hypothesis is supported by the number of correlations between trace element concentrations in biota and land use, surficial deposits, and bedrock type.

A correlation ($\rho = 0.48$) was found between concentrations of As in sediment and caddisfly larvae over all sampled sites. For example, the highest concentration of As in caddisfly larvae was found at the Second South Branch of the Oconto River (F6), whose drainage area is more than 85% forested. This concentration of As was at least twice as high as concentrations observed in caddisfly larvae from all other sampled sites, and sediment concentrations of As were high but less than predicted from the correlation. Although Cr concentrations in sediment and biota were not significantly different among land use types, spatial patterns in the Cr concentrations of sediment and caddisfly larvae were similar at many sites as shown by a significant positive correlation ($\rho = 0.51$) between these two components. A significant positive correlation ($\rho = 0.62$) also was found between Se concentrations in sediment and caddisfly larvae for all sampled sites.

Comparisons to Existing Guidelines for Trace Elements

Sediment trace-element concentrations exceeded the LEL at various sites in all land-use categories. The ERL was exceeded at fewer sites (tables 3 and 5). At sites in three AOCs (M3, M5, and M7), concentrations of one or more trace elements in sediment exceeded either the SEL or the ERM. At site M4, in the fourth AOC, no concentrations equalled or exceeded either the SEL or the ERM. At both urban sites (U1 and U2), concentrations of Pb exceeded the ERM. At U2, the concentrations of Cr and Cu exceeded the SELs, and the concentration of Zn exceeded the ERM. Even though site F2 receives discharge from iron-mine tailings, sediment from this site did not exceed the SEL or ERM for any of the trace elements; however, it had the highest Se concentration of all sampled sites for sediment (6.0 µg/g Se) and caddisfly larvae (14.4µg/g Se).

SYNTHETIC ORGANIC COMPOUNDS IN BIOTA AND STREAMBED SEDIMENT

Organochlorine Pesticides and PCBs

Concentrations of organochlorine pesticides and total PCBs were determined in fish samples from 15 sites and in sediment samples from 23 sites. Of 28 organochlorine pesticides analyzed for in fish and 32 in sediment, 11 and 10 were detected in each medium, respectively (table 6). Eight compounds were detected in both media, four were detected only in fish, and one was detected only in sediment. Only one compound, *p,p′*-DDE, the most environmentally persistent DDT-related compound, was found at sites in all the land-use categories. Overall, *p,p′*-DDE was found in fish from 9 of 15 sites and in sediment from 8 of 23 sites. In general, concentrations were higher in fish than in sediment where both media were sampled (fig. 9).

Sediment collected at two sites in the Milwaukee metropolitan area (U1 and M6) accounted for 68 percent (13 of 19) of all organochlorine pesticide detections in sediment. Similarly, of 12 organochlorines detected in fish tissues, 5 were detected only at U1; 3 others were detected only at U1 and M6. M6 is downstream of U1 and thus receives contributions from many of the same point and nonpoint pollution sources. However, a different fish species, green sunfish *(Lepomis cyanellus)*, was collected at U1, and thus this sample is not directly comparable to the other samples, although it does indicate a relatively high level of contamination.

PCBs were detected only in areas of known contamination. Sediment samples with detectable PCBs were collected in urban areas at four integrator sites (M3, M4, M5, and M6) and an indicator site (U2). PCBs were detected in whole fish from all three integrator sites where fish were collected (M2, M4, and M6), at the urban site at which fish were collected (U1), and an agricultural site (A2, 1995 sample). PCBs were not detected in sediment samples from either U1 or A2. These data suggest that fish collected at these sites may have migrated from areas where concentrations of these compounds were higher. This is supported by data on trace elements, which also were elevated in fish but not sediment collected at A2.

Table 5. Number of observations from the Western Lake Michigan Drainages that equalled or exceeded available guidelines for trace element concentrations in sediment

[Ontario Ministry of Environment and Energy values (Persaud and others, 1993) are for the Lowest Effect Level (OMEE LEL) and Severe Effect Level (OMEE SEL). The sediment effect criteria (SEC) are from Ingersoll and others (1996) for Effects Range Low (SEC ERL) and Effects Range Median (SEC ERM); --, no guidelines]

Trace element	Number of observations	OMEE LEL	SEC ERL	OMEE SEL	SEC ERM
As	40	18	12	1	1
Cd	41	25	19	0	2
Cr	42	42	38	3	1
Cu	42	30	9	3	0
Hg	42	8	--	2	--
Ni	42	25	16	0	0
Pb	42	12	10	1	5
Zn	42	17	17	1	3

Table 6. Number of organochlorine compound detections in streambed sediment (<2 mm) and whole fish of the Western Lake Michigan Drainages by land use

{Land use codes are forested (F), agricultural (A), urban (U), mixed (MA) land use indicator sites, and mixed (M) land use integrator sites}

Compound	Detections in streambed sediment					Detections in whole fish				
	F	A	U	MA	M	F	A	U	MA	M
Total no. samples	**6**	**5**	**2**	**3**	**7**	**5**	**4**	**1**	**3**	**3**
cis-Nonachlor			1							
trans-Nonachlor			1		1			1		
Oxychlordane					1			1		1
cis-Chlordane			1		1			1		1
trans-Chlordane			1					1		
o,p'-DDD										1
p,p'-DDD					1			1		1
p,p'-DDE	1	1	2	2	2	1	2	1	2	3
p,p'-DDT					1			1	1	1
Dieldrin			1		1			1		
Heptachlor epoxide								1		
Hexachlorobenzene								1		
PCB, total			1		4		1	1		3

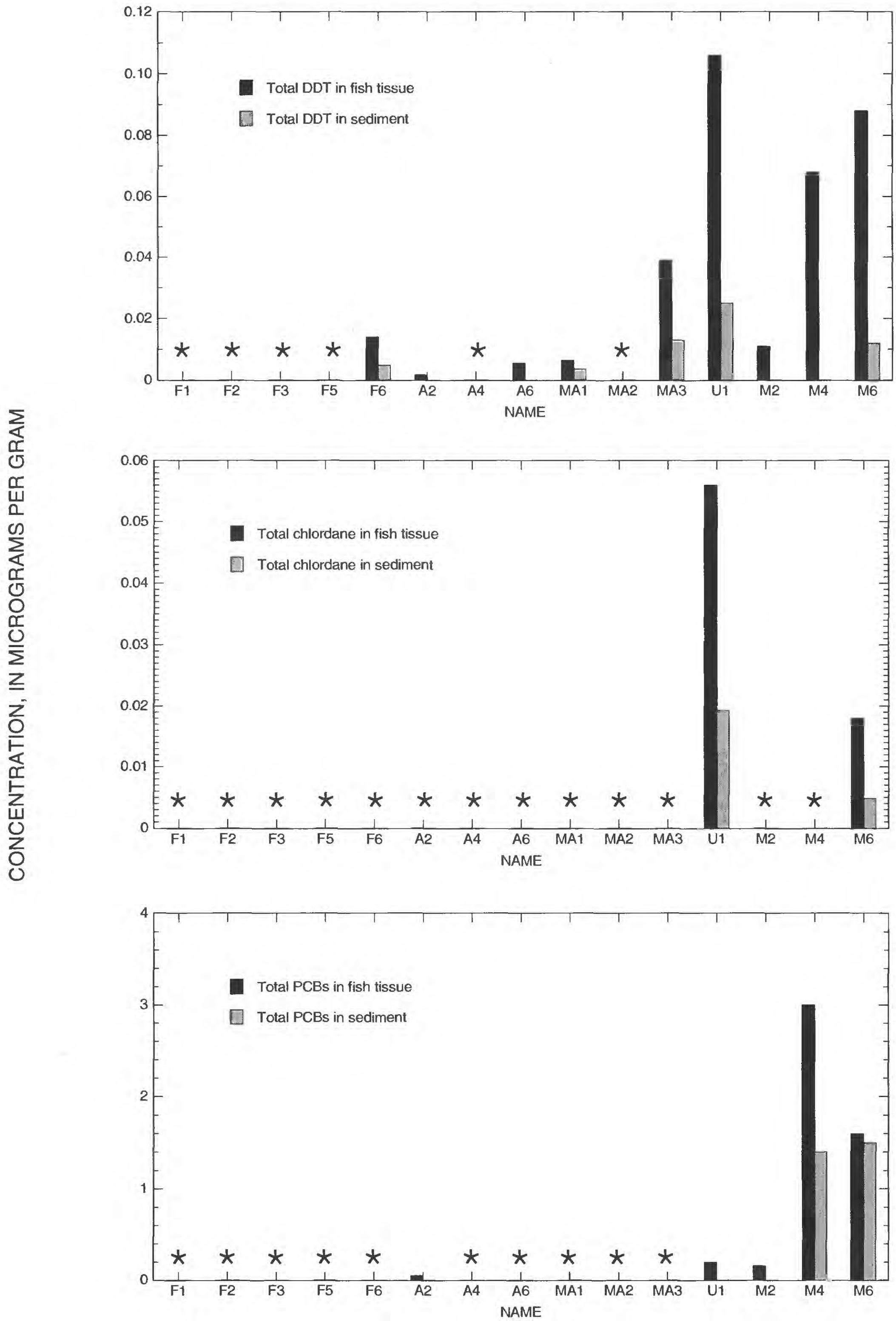


Figure 9. Concentrations of selected synthetic organic compounds and groups in whole fish and streambed sediment of the Western Lake Michigan Drainages, 1992 and 1995. [Fish tissues are wet weight, streambed sediments are dry weight. An asterisk indicates that the compound or group was not detected. Only sites with both media collected are shown.]

Semivolatile Organic Compounds

Because they do not bioaccumulate in most fish species, SVOCs were analyzed for only in sediment. For this report, the SVOCs have been grouped into three general types: the polycyclic aromatic hydrocarbons (PAHs, 52 individual compounds); the phenols (6); and the phthalates (6). A total of 41 of the 52 PAHs were detected in at least one sample, four of the phenols were detected in at least one sample, and all six phthalates were detected in at least one sample. The PAHs and phthalates were detected more frequently and at higher concentrations at urban-affected sites, while the phenols do not show as strong an urban influence (fig. 10). The sites with the most SVOCs detected were Milwaukee-area sites U2 and M7, where 41 SVOCs were detected at each.

The maximum concentrations found for 50 of the 51 SVOCs detected were from river mouth and urban sites. Of these, 45 were from sites in the Milwaukee metropolitan area. Pyrene, a PAH, was detected at the highest concentration (21 µg/g) of all SVOCs, at site M7, the mouth of the Milwaukee River. The highest concentrations of five SVOCs were in sediments from the mouth of the Fox River at Green Bay (M4). The remaining SVOC detected, 4-chloro-3-methylphenol, was detected only at a forested site (F4). However, the concentration was relatively low (.021 µg/g). The source of this phenolic compound may be a nearby railroad grade. At this same site, high Cr concentrations were observed in sediment and biota.

Comparisons to Existing Guidelines for Synthetic Organic Compounds

Concentrations of synthetic organic compounds in sediment exceeded only one guideline, the LEL. Total PCB concentrations exceeded the LEL most frequently, at a total of 5 sites (U2, M3, M4, M5, M6), all of which have known PCB contamination. DDE concentrations were in exceedance at four sites (U1, U2, M3, M6), as were total DDT concentrations (U1, U2, MA3, M6). Dieldrin (U1), DDD (M6), and total chlordane (U1) concentrations were in exceedance at one site each. Elevated levels of synthetic organic compounds from sources in the Milwaukee urban area are evident as 11 of the 16 total exceedances were from three sites located in the Milwaukee metropolitan area.

The concentrations of PCBs in fish at M4 and M6 were 3.0 and 1.6 µg/g, respectively, both exceeding NAS/NAE guidelines for whole fish that are in place to protect fish and fish-consuming wildlife (table 3). No other exceedances of NAS/NAE guidelines for synthetic organic compounds were found. PCB concentrations in whole fish from M4 exceeded FDA guidelines for human health; however, whole-fish concentrations of synthetic organic compounds are not directly comparable to FDA guidelines or WDNR advisories for human consumption because the guidelines are based on the edible (fillet) portion of fish. The concentrations of lipophilic organics are generally lower in fillets than in whole-body samples because fillets contain proportionally less lipids. However, fish-consumption advisories are in place for numerous fish species if taken from the lower reaches of many Wisconsin rivers flowing to Green Bay and Lake Michigan, including sites M2, lower reaches of many Wisconsin rivers flowing to Green Bay and Lake Michigan, including sites M2, M3, M4, M5, M6, and M7 (Wisconsin Division of Health and Wisconsin Department of Natural Resources, 1997).

Concentrations of synthetic organic compounds found in whole fish by the U.S. Fish and Wildlife Service's National Contaminant Biomonitoring Program (NCBP) (Schmitt and others, 1990) are listed with findings from the Western Lake Michigan Drainages (table 7). The NCBP program targeted mouths of rivers and other sites with a history of contamination, whereas our study targeted not only contaminated but also relatively pristine sites. The mean concentrations for the two studies are similar for DDT and metabolites. Unfortunately, minimum reporting levels for total PCBs, oxychlordane, and cis-chlordane in our study exceed the NCBP means for these compounds. The NCBP mean for trans-nonachlor is higher than our mean but similar to the maximum concentration for our study.

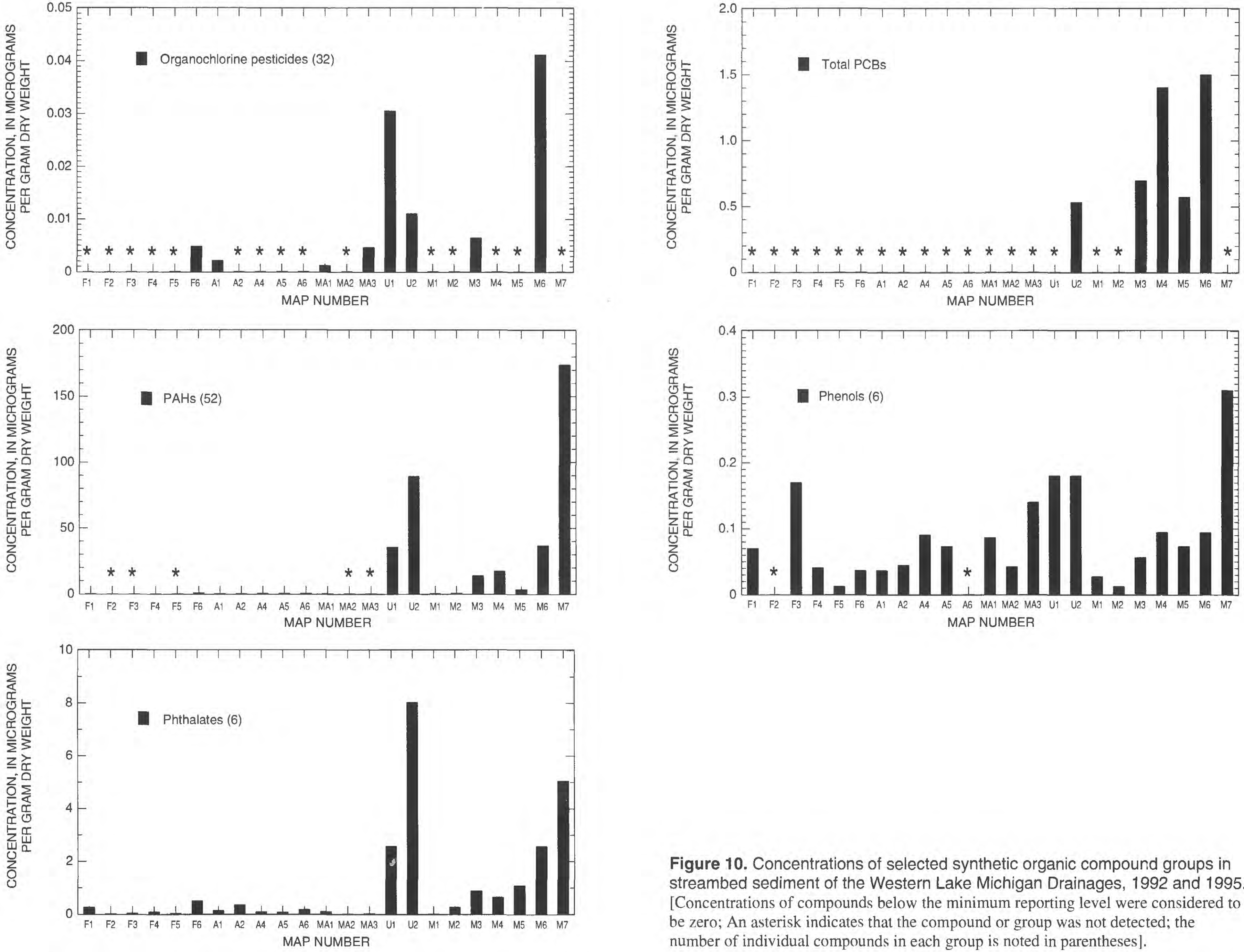


Figure 10. Concentrations of selected synthetic organic compound groups in streambed sediment of the Western Lake Michigan Drainages, 1992 and 1995. [Concentrations of compounds below the minimum reporting level were considered to be zero; An asterisk indicates that the compound or group was not detected; the number of individual compounds in each group is noted in parentheses].

Table 7. Summary of selected organochlorine concentrations in whole fish of the Western Lake Michigan Drainages and a nationwide mean for whole fish from the U.S. Fish and Wildlife Service's National Contaminant Biomonitoring Program (NCBP) (Schmitt and others, 1990).

[Total DDT includes DDT, DDE, and DDD. Concentrations are in micrograms per gram wet weight]

Organic Compound	Western Lake Michigan Drainages			NCBP Mean
	Max (map #)	Mean	Median	
p,p′-DDE	0.068 (M4)	0.017	0.005	0.019
p,p′-DDT	.027 (U1)	<.005	<.005	.003
Total DDT	.106 (U1)	.023	.006	.026
Total PCB	3.0 (M4)	<.050	<.05	.039
Oxychlordane	.011 (M6)	<.005	<.005	.001
trans-Nonachlor	.019 (U1)	<.005	<.005	.017
cis-Chlordane	.016 (U1)	<.005	<.005	.002

CONCLUSIONS

It is important to examine concentrations of trace elements and synthetic organic compounds in sediment and biota with regard to environmental characteristics such as land use, surficial deposits, and bedrock type to provide insight on effects of natural versus anthropogenic factors. In our study, most of the variability in concentrations of trace elements and synthetic organic compounds was related to land use. However, variability of four trace elements in biota and sediment also were correlated with the type of surficial deposits and (or) bedrock, and this complicates interpretation of primary causative factors. The dominant factor influencing sediment concentrations of Cd and Hg is land use, specifically urban land use, as evidenced by correlations between concentrations of these elements in sediment and urban land use together with the lack of correlations with either surficial deposits or bedrock type. Urban land use also is likely the dominant factor influencing Cu and Pb because the highest concentrations were found at urban and integrator sites. High Ni concentrations at urban and agricultural sites indicates the influences of another factor besides land use. Distinguishing the primary factors for As, Se, and Zn is more complicated. Forested land use and igneous/metamorphic bedrock together seem to be equally important for As, whereas forested land use and sandy/sand and gravel surficial deposits appear equally important for Se. Influencing factors on Ni and Zn concentrations are the most complex, with apparent influences from land use, surficial deposits, and bedrock type. Chromium concentrations, on the other hand, do not directly reflect any of the three influences examined in this study.

PCBs were detected only in areas of urban land use and other areas of known contamination. PCBs were detected in sediment in urban areas at four integrator sites and one indicator site. The highest concentrations of PCBs in fish were found at the Fox and Milwaukee Rivers; these concentrations in fish and concentrations in sediment from these sites were above NAS/NAE guidelines for the protection of fish and fish-consuming wildlife. DDT and related compounds were detected at a variety of sites spanning all land uses. The most environmentally persistent DDT-related compound, *p,p′*-DDE, was found in fish and sediment from sites in all the land-use categories. Two sites in the Milwaukee metropolitan area accounted for most of all organochlorine pesticide detections in sediment. The maximum SVOC concentrations found for most of the SVOCs detected were from large river sites and urban sites, and most of these high concentrations were found in the Milwaukee area.

These results show the complexity involved in trying to distinguish between anthropogenically- and naturally-occurring trace element concentrations in sediment and provide insight for the need to collect and analyze trace element data within the most detailed environmental framework possible. Data from this study will provide baseline information for long-term trend analysis by future NAWQA sampling in the Western Lake Michigan Drainages. Intensive data collection in this area will be repeated beginning in the year 2002. Concentrations from many of our sites reflect background conditions for trace elements from a variety of physical settings commonly found in Wisconsin and the Upper Peninsula of Michigan, and the data provide a basis for assessing the current and future status of water quality in the Western Lake Michigan Drainages.

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APPENDIX A

APPENDIX A. TRACE ELEMENTS AND SYNTHETIC ORGANIC COMPOUNDS IN BIOTA AND STREAMBED SEDIMENT OF THE WESTERN LAKE MICHIGAN DRAINAGES

Tables in this section list selected concentrations of trace elements and synthetic organic compounds by site and biota type. Included are the following:

TABLES

Table A1. Concentrations of trace elements in aquatic biota of the Western Lake Michigan Drainages

[Biota type: Caddisfly 1 = *Hydropsyche* spp., Caddisfly 2 = *Ceratopsyche* spp., Caddisfly 3 = *Cheumatopsyche* spp., Caddisfly 4 = *Brachycentrus occidentalis*, Stonefly = *Acroneuria* spp., Damselfly = Families Coenagrionidae (90%) and Calopterygidae (10%), Pondweed 1 = *Potamogeton crispus*, Pondweed 2 = *Potamogeton pectinatus*, Pondweed 3 = *Potamogeton epihydrus*, Waterweed = *Elodea canadensis*, Crayfish = *Orconectes* sp., Rock bass = *Ambloplites rupestris*, White sucker = *Catostomus commersoni*, Shorthead redhorse = *Moxostoma macrolepidotum*; n= number of individuals per composite sample; nd = not determined]

Map #	Date	Biota Type	n	Water	Element concentration (μg/g dry weight)								
				(%)	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
F1	27 Aug 92	Caddisfly 1/2	250	87.3	.91	<0.57	2.7	13.5	.06	1.5	1.4	3.4	139
	27 Aug 92	Stonefly	60	79.0	.43	<0.19	0.75	17.9	.12	0.39	<0.19	1.1	156
F2	26 Aug 92	Caddisfly 1/2	400	85.0	2.9	<0.44	3.3	16.9	.11	4.1	0.54	14	109
F3	26 Aug 92	Caddisfly 1/2	400	84.0	1.9	<0.36	4.6	11.5	.04	0.74	0.82	2.2	104
	26 Aug 92	White sucker	8	78.4	<0.20	<0.20	0.60	6.60	<.10	<0.20	<0.20	2.9	51.5
F4	20 Sep 94	Caddisfly 2	378	93.0	1.0	1.2	2.0	15.8	.20	3.5	1.4	0.80	231
	20 Sep 94	Stonefly	46	85.3	.40	0.40	0.90	25.5	.23	1.4	<0.30	2.0	245
	20 Sep 94	Pondweed 1	nd	92.2	1.5	<0.70	1.7	4.70	<.07	4.5	1.3	0.8	54.5
F5	25 Aug 92	Caddisfly 1/2/3	400	83.3	2.1	<0.27	1.7	9.16	.03	0.55	0.34	1.6	102
	25 Aug 92	Stonefly	40	87.6	1.0	<0.25	1.4	24.8	.12	0.44	<0.25	2.5	233
	19 Sep 94	Stonefly	30	85.8	<0.40	<0.40	0.90	22.5	.14	1.3	<0.40	0.80	246
	19 Sep 94	Waterweed	nd	95.8	8.4	<1.0	2.8	5.70	<.10	4.8	1.2	<1.0	98.6
	15 Aug 95	Caddisfly 1	452	86.1	3.0	<0.70	1.6	10.4	<.07	0.90	<0.70	<0.70	133
	15 Aug 95	Stonefly	55	79.7	1.4	<0.50	1.0	13.9	.08	0.60	<0.50	1.6	187
F6	26 Aug 92	Caddisfly 4	379	87.2	6.7	<0.47	2.4	8.37	.11	0.76	0.89	2.8	239
F7	13 Sep 95	Caddisfly 1/2	344	83.1	1.0	<0.30	1.5	8.40	.05	1.2	1.2	0.60	76.2
	13 Sep 95	Waterweed	nd	95.0	1.6	<0.90	2.1	2.80	<.10	1.3	1.4	<0.90	26.4
F8	11 Sep 95	Pondweed 3	nd	91.0	2.8	<0.50	0.70	0.60	.08	0.70	<0.50	<0.50	67.9
F9	14 Sep 95	Waterweed	nd	95.9	<1.0	<1.0	2.1	1.40	<.10	<1.0	<1.0	<1.0	44.7
F11	15 Sep 95	Waterweed	nd	95.2	1.4	<0.80	1.5	1.40	<.08	<0.80	<0.8	<0.80	28.0
	15 Sep 95	Pondweed 1	nd	94.2	1.3	<0.80	1.5	1.90	<.08	1.1	<0.8	1.0	37.2
F12	12 Sep 95	White sucker	9	77.6	0.40	<0.20	0.60	30.1	.15	<0.20	<0.20	3.8	84.3
	12 Sep 95	Caddisfly 1/2	317	82.7	1.9	<0.30	4.8	12.3	.06	3.9	1.1	0.70	101
	12 Sep 95	Caddisfly 3	157	81.8	1.6	<0.20	1.3	11.3	.07	0.70	0.60	0.70	113
F13	25 Oct 95	Caddisfly 1/2	340	82.3	1.7	<0.30	1.8	9.90	<.10	0.60	0.80	0.9	88.3
	25 Oct 95	White sucker	15	76.4	0.40	<0.20	0.70	25.7	<.10	<0.20	<0.20	3.5	71.7
A1	21 Sep 94	Pondweed 2	nd	84.5	0.70	<0.50	2.9	4.80	<.05	4.9	1.3	0.7	29.3
	21 Sep 94	Caddisfly 3	389	91.4	1.6	<0.40	5.7	14.2	.05	5.3	2.8	1.0	131
A2	28 Aug 92	Caddisfly 1/2	275	81.1	.96	<.25	3.2	14.7	.06	2.8	1.2	1.9	112
	28 Aug 92	Caddisfly 3	300	81.4	.82	<.23	2.3	11.2	.04	2.0	1.5	1.4	71.4

Table A1. Concentration of trace elements in aquatic biota from the Western Lake Michigan Drainages—Continued

Map #	Date	Biota Type	n	Water (%)	Element concentration (µg/g dry weight)								
					As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
A2	22 Sep 94	Caddisfly 3	250	81.8	1.3	.40	3.8	16.0	.07	3.9	1.7	1.3	121
	16 Aug 95	Caddisfly 3	508	81.6	1.1	<.50	3.2	18.4	.08	3.6	1.2	2.0	103
	02 Aug 95	Rock bass	4	87.5	<.50	.70	1.0	6.30	.35	<0.50	<0.50	17.5	89.4
A3	22 Sep 94	Crayfish	47	77.3	.90	<.20	1.0	88.1	.09	12	<.20	1.0	50.5
A4	28 Aug 92	Caddisfly 1/2	300	81.0	.54	<.36	3.6	15.1	.11	3.1	1.2	2.2	109
A5	29 Aug 92	Caddisfly 1/2	300	80.6	.98	<.28	2.5	13.3	.03	1.4	1.4	1.7	104
A6	23 Sep 94	Pondweed 2	nd	92.2	<1.0	<1.0	1.2	4.90	<.10	5.4	<1.0	1.6	36.8
	23 Sep 94	Caddisfly 1/2	370	85.9	.40	<.30	2.2	15.1	.04	2.1	2.5	1.4	136
	02 Aug 95	White sucker	18	80.9	<.40	<.40	0.70	44.2	.08	<0.40	<0.40	4.3	109
	15 Aug 95	Caddisfly 1	306	84.9	<.70	<.70	2.4	17.6	<.06	1.4	1.6	2.8	139
	15 Aug 95	Pondweed 2	nd	91.1	<.50	<.50	1.2	2.50	<.05	1.9	0.7	0.60	15.9
MA1	27 Aug 92	Caddisfly 1/2	400	81.6	1.0	<.30	1.4	11.1	.10	1.1	1.0	1.6	94.9
MA2	24 Aug 92	Caddisfly 1/2	203	90.0	<1.0	<1.0	3.9	13.2	<.10	<1.0	<1.0	6.0	120
MA3	24 Aug 92	Caddisfly 1/2	250	85.2	1.5	<.38	5.5	13.0	.06	1.3	1.5	2.8	110
	21 Sep 94	Caddisfly 3	293	89.6	.90	<.30	4.3	13.4	.07	1.5	1.2	1.2	129
	21 Sep 94	Pondweed 1	nd	90.8	1.7	<.60	4.8	4.40	<.05	2.4	1.0	.6	59.0
	14 Aug 95	Caddisfly 2	300	87.8	1.2	<.90	4.2	13.8	<.10	1.7	1.4	1.5	132
U1	23 Sep 94	Damselfly	324	87.1	1.2	.90	1.1	22.4	.06	1.3	1.8	2.3	101
	23 Sep 94	Waterweed	nd	95.7	<1.4	<1.4	2.2	49.6	<.10	14	7.6	<1.4	195
M2	31 Jul 95	Shorthead redhorse	7	74.4	.60	.30	<.50	22.9	.20	<.20	<0.20	3.9	73.3
M4	01 Aug 95	Shorthead redhorse	5	73.9	<.20	<.20	.50	17.6	.14	<.20	<0.20	4.2	72.7
M6	06 Sep 95	White sucker	8	79.4	.50	<.40	.6	45.2	.05	.60	<.40	3.9	100

Table A2. Concentrations of trace elements in streambed sediment of the Western Lake Michigan Drainages

[Trace element and carbon concentrations are for the < 63 μm (wet-sieved) sample; percent (%) sand and silt are for the bulk (unsieved) sample]

Map #	Date	Element concentration (μg/g dry weight)									Organic Carbon (%)	Inorganic Carbon (%)	Total Carbon (%)	Sand (%)	Silt (%)
		As	Cd	Cr	Cu	Pb	Hg	Ni	Se	Zn					
F1	27 Aug 92	5	1.5	43	16	38	0.18	12	1.5	170	16.2	0.32	16.5	60.4	39.6
F2	26 Aug 92	28	0.6	49	23	17	.10	23	6.0	77	7.90	.39	8.29	75.7	24.3
F3	26 Aug 92	12	1.5	130	23	17	.13	14	3.1	120	15.8	.02	15.8	34.4	65.6
F4	20 Sep 94	13	1	66	41	22	.12	28	0.9	120	--	--	8.23	79.7	20.3
F5	25 Aug 92	3	.3	70	28	20	.05	31	.4	77	3.07	1.35	4.42	72.0	28.0
	19 Sep 94	29	.9	47	9	16	.09	13	1.0	150	--	--	--	59.5	40.5
	15 Aug 95	14	.4	50	17	14	<.02	30	.8	99	2.02	4.02	6.04	61.0	39.0
F6	25 Aug 92	25	.7	61	13	24	.13	10	3.2	86	21.2	.05	21.3	57.7	42.3
F7	13 Sep 95	6	.5	40	13	30	.06	12	.9	68	--	--	--	84.5	15.5
F8	11 Sep 95	20	.9	66	18	40	.18	11	5.3	120	19.5	.07	19.6	78.9	21.1
	5 May 97	15	--	--	--	--	.20	--	3.2	--	22.2	.08	22.3	--	--
F9	14 Sep 95	--	--	34	23	16	6.1	7	--	72	--	--	--	16.4	83.6
	8 May 97	7.7	--	--	--	--	.13	--	1.8		22.3	.06	22.4	--	--
F10	14 Sep 95	19	.9	50	22	24	.14	12	3.4	130	--	--	--	10.1	89.9
F11	15 Sep 95	--	.4	33	14	18	1.6	8	--	55	--	--	--	30.4	69.6
F12	13 Sep 95	5.6	.4	45	13	16	.04	14	1.2	61	--	--	--	72.6	27.4
F13	26 Oct 95	6.5	.7	49	13	22	.10	12	1.9	99	13.7	.1	13.8	16.8	83.2
A1	21 Sep 94	3.2	.6	52	23	16	.06	22	.9	100	--	--	--	55.4	44.6
A2	28 Aug 92	3.7	.5	61	23	17	.05	26	.9	87	5.21	1.05	6.26	77.3	22.7
	22 Sep 94	4.4	.4	64	31	19	.06	30	.8	96	3.67	.88	4.55	44.4	55.6
	16 Aug 95	8.9	.3	55	19	14	<.02	31	.8	96	1.70	4.70	6.40	37.4	62.6
A3	22 Sep 94	3.3	.2	69	30	16	.04	34	.5	78	2.05	.93	2.98	59.2	40.8
A4	28 Aug 92	26	1.1	57	11	18	.13	14	1.2	150	10.4	.05	10.4	61.7	38.3
A5	29 Aug 92	2.7	.4	44	19	20	.07	17	.8	69	4.86	2.71	7.57	68.3	31.7
A6	23 Sep 94	2.3	<.9	44	22	15	.07	16	1.2	80	--	--	--	42.3	57.7
	17 Aug 95	2.5	.6	41	14	13	.06	15	1.3	80	5.13	2.03	7.16	39.0	61.0
U1	31 Aug 92	5.4	2	71	72	240	.13	30	.7	430	3.98	5.04	9.02	81.2	18.8
	23 Sep 94	4.9	1	61	<1	120	.09	31	.5	280	2.03	4.77	6.80	4.8	95.2
U2	31 Aug 92	5.9	2.2	120	120	180	.34	42	.7	840	4.62	4.88	9.50	80.4	19.6
MA1	27 Aug 92	3.9	.6	34	12	14	.06	12	.9	89	7.96	1.45	9.41	75.7	24.3
MA2	24 Aug 92	6	.4	84	16	16	.07	13	3.1	70	14.2	0.24	14.4	89.2	10.8
MA3	24 Aug 92	5.4	.5	77	18	21	.09	14	3.1	83	16.9	0.19	17.1	50.0	50.0
	21 Sep 94	4.2	.6	64	20	17	.10	12	2.1	73	--	--	--	75.4	24.6
	14 Aug 95	18	.2	64	14	17	<.02	23	.6	92	1.20	1.73	2.93	69.9	30.1
M1	2 Oct 92	6	1.1	33	40	22	.14	16	2.1	100	20.2	0.41	20.6	31.2	68.8
M2	15 Aug 95	23	.2	74	15	24	<.02	25	.5	97	1.11	0.64	1.75	72.8	27.2
M3	03 Oct 92	110	3.9	77	110	200	2.3	21	1.9	560	16.1	0.94	17.0	12.4	87.6
M4	07 Oct 92	3.8	1.3	99	64	66	1.0	28	.8	180	6.74	2.20	8.94	14.1	85.9
	17 Aug 95	4.4	1.3	100	62	84	1.0	27	.8	190	--	--	7.39	46.2	53.8
M5	06 Oct 92	3.2	.6	62	42	57	.12	24	.7	170	3.84	3.60	7.44	21.2	78.8
M6	18 Aug 95	3.7	1.4	51	36	57	.11	21	.9	200	3.74	5.13	8.87	20.9	79.1
M7	06 Oct 92	16	6.8	460	130	280	.82	39	1.9	650	5.66	4.02	9.68	13.9	86.1

Table A3. Concentrations of selected synthetic organic compounds in whole fish from the Western Lake Michigan Drainages

[Concentrations are in micrograms per gram wet weight; nd = not detected]

Map #	Date	Fish species	Aldrin	total Chlordane	*p,p′*-DDE	*p,p′*-DDT	total DDT	Dieldrin	Hepta-chlor epoxide	total PCB
F1	27 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
F2	26 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
F3	26 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
F5	25 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
F6	25 Aug 92	White sucker	nd	nd	0.014	nd	0.0014	nd	nd	nd
A2	28 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
A2	2 Aug 95	White sucker	nd	nd	.0051	nd	.0051	nd	nd	.050
A4	28 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
A6	17 Aug 95	White sucker	nd	nd	.0055	nd	.0055	nd	nd	nd
MA1	27 Aug 92	White sucker[1]	nd	nd	.0064	nd	.0064	nd	nd	nd
MA2	24 Aug 92	White sucker	nd	nd	nd	nd	nd	nd	nd	nd
MA3	24 Aug 92	White sucker	nd	nd	.035	.0049	.040	nd	nd	nd
U1	6 Sep 95	Green sunfish	nd	.0559	.056	.027	.116	.0072	.0053	.200
M2	31 Jul 95	Shorthead redhorse	nd	nd	.011	nd	.011	nd	nd	.160
M4	1 Aug 95	Shorthead redhorse	nd	nd	.068	nd	.068	nd	nd	3.0
M6	6 Sep 95	White sucker	nd	.0184	.046	.0058	.0883	nd	nd	1.6

[1]Concentrations shown are averages of 3 composited samples submitted from this site.

Table A4. Concentrations of selected synthetic organic compounds and groups in streambed sediment from the Western Lake Michigan Drainages
[concentrations are micrograms per gram dry weight; nd = not detected]

		EPA Group 1 Priority Pollutants: Organochlorines and semi-volatile organics									
Map #	Date	Benzo (a) pyrene	Benzo (b) fluoran-thene	bis (2-Ethyl hexyl) phthalate	Chrysene	Dibenzo (a,h) anthracene	1,4-Dichloro-benzene	Dieldrin	Hep-tachlor/ H. epoxide	n-Nitroso-diphenyl-amine	PCBs
F1	27 Aug 92	nd	nd	0.160	nd	nd	nd	nd	nd	nd	nd
F2	26 Aug 92	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
F3	26 Aug 92	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
F4	11 Aug 95	nd	nd	.032	nd	nd	nd	nd	nd	nd	nd
F5	25 Aug 92	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
F6	25 Aug 92	0.078	0.097	.170	nd	nd	nd	nd	nd	nd	nd
A1	16 Aug 95	nd	nd	.055	nd	nd	nd	nd	nd	nd	nd
A2	28 Aug 92	nd	nd	.210	nd	nd	nd	nd	nd	nd	nd
A4	28 Aug 92	.057	.024	.022	0.013	nd	nd	nd	nd	nd	nd
A5	29 Aug 92	nd	nd	.058	nd	nd	nd	nd	nd	nd	nd
A6	17 Aug 95	nd	.058	.092	.028	nd	nd	nd	nd	nd	nd
MA1	27 Aug 92	nd	nd	.047	nd	nd	nd	nd	nd	nd	nd
MA2	24 Aug 92	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
MA3	24 Aug 92	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
U1	31 Aug 92	2.2	2.60	1.90	3.10	0.670	nd	0.0044	nd	nd	nd
U2	31 Aug 92	5.6	6.60	**6.70**	7.40	1.90	0.044	nd	nd	nd	0.53
M1	02 Oct 92	nd	.016	nd	.017	nd	nd	nd	nd	nd	nd
M2	15 Aug 95	.04	.046	.086	.034	nd	nd	nd	nd	nd	nd
M3	03 Oct 92	.52	.850	.80	1.20	.170	.120	nd	nd	nd	.690
M4	07 Oct 92	.16	.200	.250	.300	.045	.036	nd	nd	nd	.260
M4	17 Aug 95	1.7	.840	.640	1.20	nd	.069	nd	nd	nd	1.40
M5	06 Oct 92	.23	.270	.770	.310	.049	nd	nd	nd	nd	.570
M6	18 Aug 95	3.3	3.20	2.10	2.90	.680	nd	.0014	nd	**0.047**	**1.50**
M7	06 Oct 92	**9.9**	**12.0**	4.80	**16.0**	**4.40**	**.140**	nd	nd	nd	nd

Table A4. Concentrations of selected synthetic organic compounds and groups in streambed sediment from the Western Lake Michigan Drainages—Continued

Map #	Group of organic compounds					
	Total DDT	Total chlordane	Total organo-chlorine pesticides	Total PAH's	Total phenols	Total phthalates
F1	nd	nd	nd	0.130	0.070	0.259
F2	nd	nd	nd	nd	nd	.014
F3	nd	nd	nd	nd	.170	.034
F4	nd	nd	nd	.082	.041	.085
F5	nd	nd	nd	nd	.012	.018
F6	0.0048	nd	0.0048	.822	.036	.492
A1	.0021	nd	.0021	.184	.036	.134
A2	nd	nd	nd	.047	.044	.339
A4	nd	nd	nd	.210	.090	.078
A5	nd	nd	nd	.250	.073	.067
A6	nd	nd	nd	.377	nd	.172
MA1	.0012	nd	nd	.150	.086	.091
MA2	nd	nd	nd	nd	.042	nd
MA3	.0046	nd	nd	nd	.140	.013
U1	.0068	**0.019**	.0305	35.4	.180	2.56
U2	.0110	nd	.0110	89.1	.180	**8.02**
M1	nd	nd	nd	.193	.027	.005
M2	nd	nd	nd	.604	.012	.258
M3	.0064	nd	.0064	13.7	.056	.869
M4	nd	nd	nd	4.02	.057	.250
M4	nd	nd	nd	17.2	.094	.640
M5	nd	nd	nd	3.69	.051	1.08
M6	**.0350**	.005	**.0412**	36.7	.094	2.56
M7	nd	nd	nd	**174.0**	**.310**	5.05