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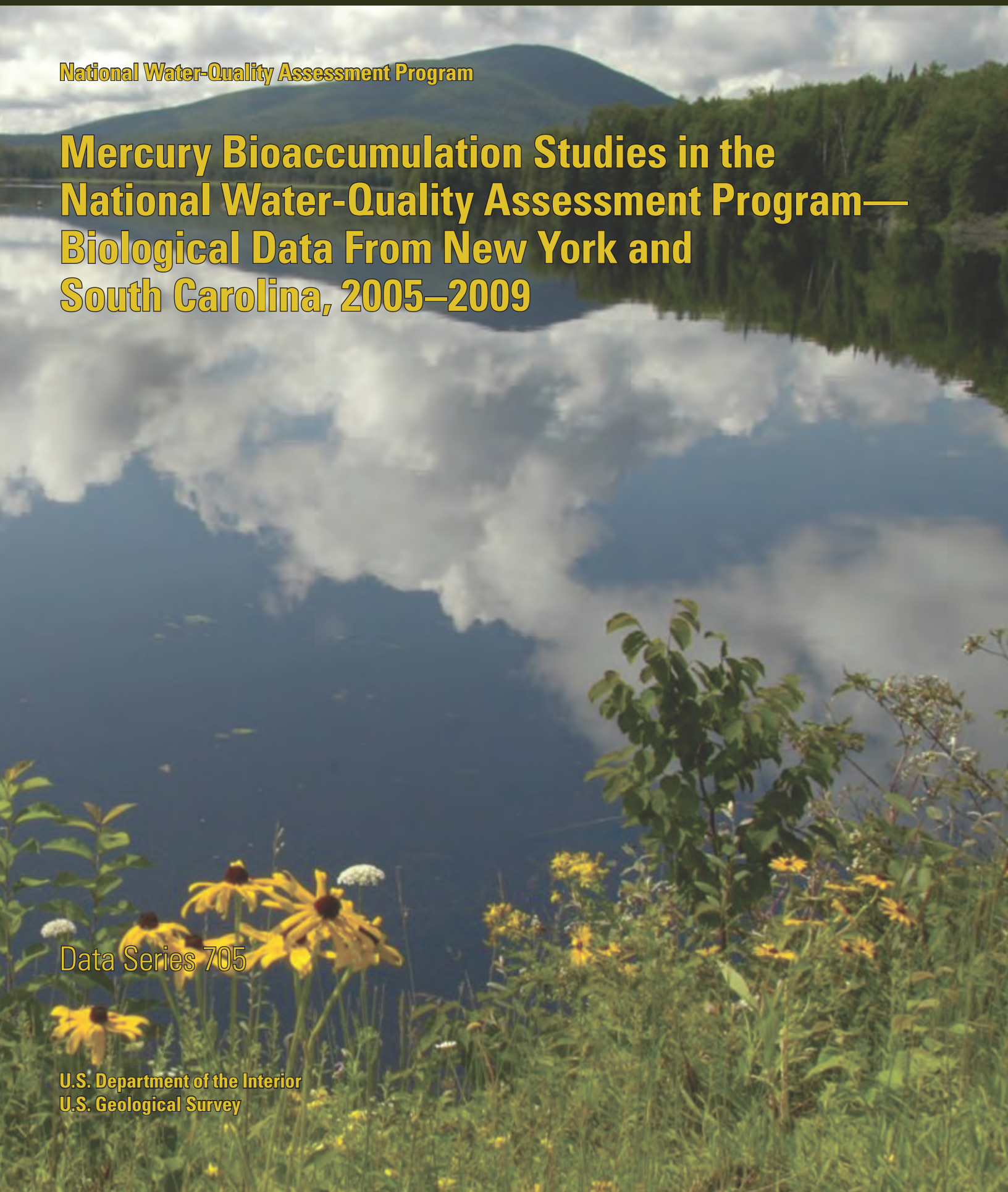
National Water-Quality Assessment Program

Mercury Bioaccumulation Studies in the National Water-Quality Assessment Program—Biological Data From New York and South Carolina, 2005–2009



Data Series 705

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

Cover. Fishing Brook (County Line Flow outlet) near Newcomb, New York. (Photograph by Dennis A. Wentz, U.S. Geological Survey)

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U.S. Department of the Interior
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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with reliable scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (http://www.usgs.gov/). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (http://water.usgs.gov/nawqa). The NAWQA Program is designed to answer: What is the quality of our Nation's streams and groundwater? How are conditions changing over time? How do natural features and human activities affect the quality of streams and groundwater, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (http://water.usgs.gov/nawqa/studies/study_units.html).

In the second decade of the Program (2001–2012), a major focus is on regional assessments of water-quality conditions and trends. These regional assessments are based on major river basins and principal aquifers, which encompass larger regions of the country than the Study Units. Regional assessments extend the findings in the Study Units by filling critical gaps in characterizing the quality of surface water and groundwater, and by determining water-quality status and trends at sites that have been consistently monitored for more than a decade. In addition, the regional assessments continue to build an understanding of how natural features and human activities affect water quality. Many of the regional assessments employ modeling and other scientific tools, developed on the basis of data collected at individual sites, to help extend knowledge of water quality to unmonitored, yet comparable areas within the regions. The models thereby enhance the value of our existing data and our understanding of the hydrologic system. In addition, the models are useful in evaluating various resource-management scenarios and in predicting how our actions, such as reducing or managing nonpoint and point sources of contamination, land conversion, and altering flow and (or) pumping regimes, are likely to affect water conditions within a region.

Other activities planned during the second decade include continuing national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, trace elements, and aquatic ecology; and continuing national topical studies on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on stream ecosystems, and transport of contaminants to public-supply wells.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

William H. Werkheiser
USGS Associate Director for Water

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Conversion Factors, Datum, and Abbreviations

Multiply	By	To obtain
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
square kilometer (km^2)	247.1	acre
square centimeter (cm^2)	0.001076	square foot (ft^2)
square meter (m^2)	10.76	square foot (ft^2)
gram (g)	0.03527	ounce, avoirdupois (oz)
nanogram (ng)	0.03527×10^{-9}	ounce, avoirdupois (oz)
microgram (µg)	0.03527×10^{-6}	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)

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

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

Abbreviations

CL	confidence limit
CRM	certified reference material
$\delta^{13}C$	stable isotope ratio of carbon ($^{13}C/^{12}C$) expressed in per mil
$\delta^{15}C$	stable isotope ratio of nitrogen ($^{15}N/^{14}N$) expressed per mil
DOC	dissolved organic carbon
DTH	depositional-targeted habitat (periphyton or invertebrates)
IAEA	International Atomic Energy Agency
MeHg	methylmercury
NAWQA	National Water-Quality Assessment
NIST	National Institute of Standards and Technology
NRCC	National Research Council Canada
NWIS	National Water Information System
PVC	polyvinyl chloride
QA/QC	quality assurance and quality control
RM	reference material
RTH	richest targeted habitat (periphyton or invertebrates)
SAV	submerged aquatic vegetation
SRM	standard reference material
THg	total mercury
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Abstract

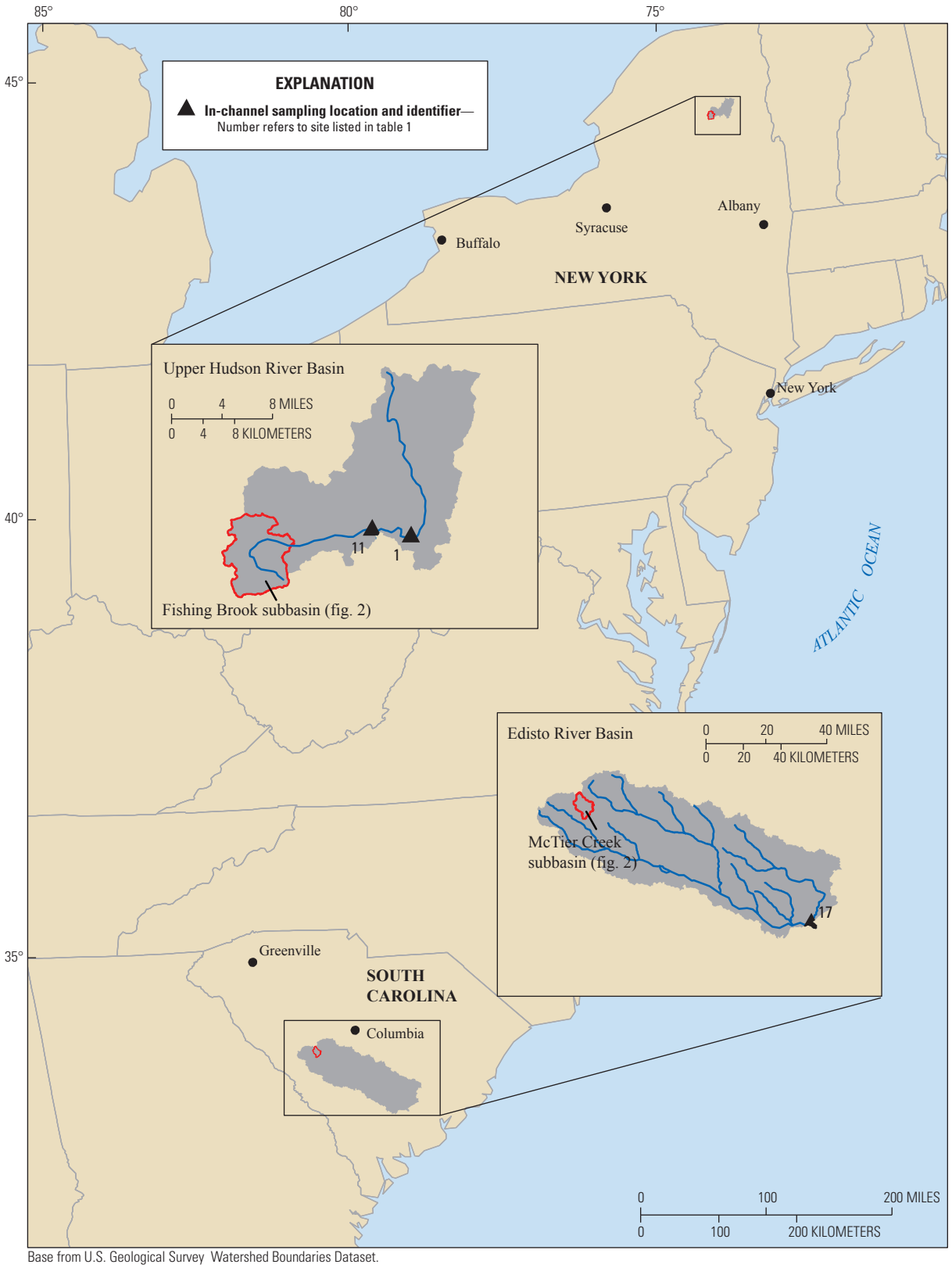
The U.S. Geological Survey National Water-Quality Assessment Program conducted a multidisciplinary study from 2005–09 to investigate the bioaccumulation of mercury in streams from two contrasting environmental settings. Study areas were located in the central Adirondack Mountains region of New York and the Inner Coastal Plain of South Carolina. Fish, macroinvertebrates, periphyton (attached algae and associated material), detritus, and terrestrial leaf litter were collected. Fish were analyzed for total mercury; macroinvertebrates, periphyton, and terrestrial leaf litter were analyzed for total mercury and methylmercury; and select samples of fish, macroinvertebrates, periphyton, detritus, and terrestrial leaf litter were analyzed for stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$). This report presents methodology and data on total mercury, methylmercury, stable isotopes, and other ecologically relevant measurements in biological tissues.

Introduction

Bioaccumulation of mercury in fish and other aquatic organisms has generated increasing public concern during the past decade. Recent advances have been made in describing some of the factors that influence the transport and geochemical cycling of mercury in freshwater ecosystems. Even so, specific environmental controls and the relative importance of abiotic and biotic processes responsible for the uptake and biomagnification of mercury by aquatic organisms remain poorly characterized, especially in stream ecosystems. From 2005 through 2009, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program conducted studies of stream ecosystems across two distinct environmental settings in New York (Adirondack Mountains) and South Carolina (Inner Coastal Plain) to address this information gap. Aquatic organisms, surface water, groundwater, and streambed sediment were collected seasonally from multiple sites in each watershed. Aquatic consumers representing different trophic (feeding) levels and habits were collected, as were potential dietary sources of mercury. Consumers were fish (top predators and midlevel forage fish) and macroinvertebrates (that is, insects and other aquatic invertebrates longer than 2 millimeters (mm)). Potential dietary sources were periphyton (algae and associated inorganic and organic material attached to various substrates) and organic detritus. In addition, terrestrial leaf litter was sampled from selected locations to characterize the potential input of particulate organic matter to streams. Many physical and chemical characteristics were also characterized as part of this study. In surface water, these characteristics include dissolved and particulate forms of total mercury (THg) and methylmercury (MeHg), streamflow, pH, water temperature, dissolved organic carbon (DOC), sulfide and sulfate, major ions, and nutrients. This report presents the biological data. Geochemical data for streambed sediment, surface water, and groundwater are presented in Feaster and others (2010), Bradley and others (2011), and Nystrom and Burns (2011). Further detail regarding the environmental setting is presented in Scudder Eikenberry and others (2012). These and other reports are available from the U.S. Geological Survey (2012).

Site Selection

Sites were sampled in the upper Hudson River Basin, located in the Adirondack region of New York, and in the Edisto River Basin, located in the Coastal Plain of South Carolina (figs. 1 and 2; table 1). While the environmental characteristics differ greatly in these regions, both are “biological mercury hotspots,” having resident fish and other biota with mercury concentrations that are elevated above both human and wildlife fish consumption advisory levels and landscapes that favor the conversion of atmospherically deposited inorganic mercury to organic methylmercury and its transport to aquatic systems (Driscoll and others, 2007; Evers and others, 2007; Glover and others, 2010; New York State Department of Health, 2010; South Carolina Department of Health and Environmental Control, 2010; Bradley and others, 2011).



Base from U.S. Geological Survey Watershed Boundaries Dataset.
Albers Conical Equal Area Projection, North American Datum of 1983

Figure 1. Overview of locations of New York and South Carolina study basins.

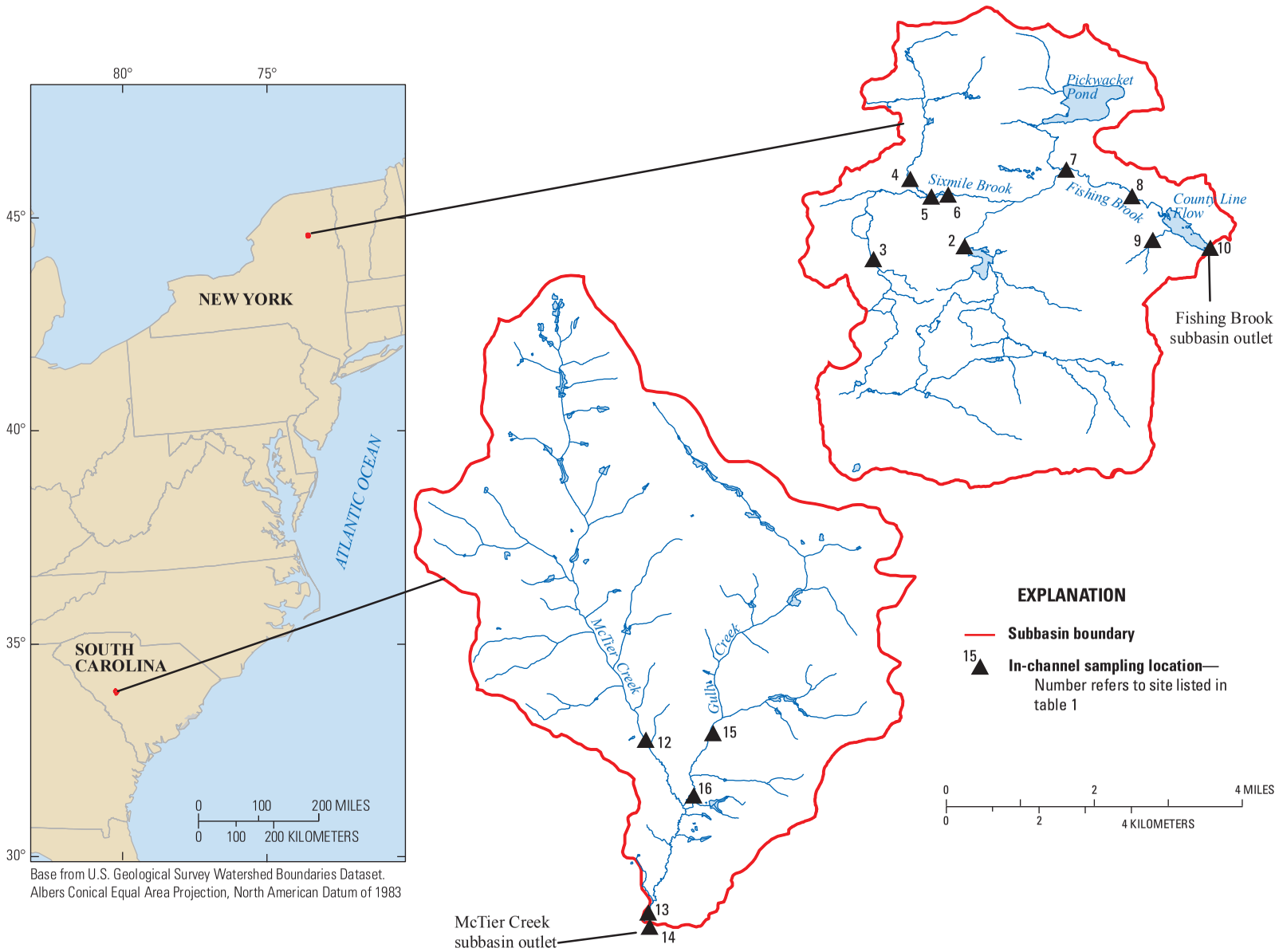


Figure 2. The Fishing Brook subbasin in New York and the McTier Creek subbasin in South Carolina.

Table 1. Sites for streams sampled in New York and South Carolina during the U.S. Geological Survey mercury studies from 2005 through 2009.

[Map code refers to USGS station ID shown in figures 1 and 2. USGS, U.S. Geological Survey; ID, identification number; km², square kilometer]

USGS station ID	USGS station name	Map code	Latitude[1]	Longitude[1]	Drainage basin area (km²)
01311951	Hudson River near Winebrook Hills, N.Y.	1	43.95841667	-74.09375000	223
01311990	Fishing Brook at 28N near Long Lake, N.Y.	2	43.97805556	-74.33666667	27.1
0131199010	Sixmile Brook at 28N near Long Lake, N.Y.	3	43.97566667	-74.36130556	4.56
0131199020	Sixmile Brook Tributary near Long Lake, N.Y.	4	43.99127778	-74.35119444	6.89
0131199021	Sixmile Brook below Sixmile Brook Tributary near Long Lake, N.Y.	5	43.98777778	-74.34555556	17.0
0131199022	Sixmile Brook near Long Lake, N.Y.	6	43.98819444	-74.34100000	17.7
0131199035	Pickwacket Pond Outlet at mouth near Long Lake, N.Y.	7	43.99284085	-74.30904714	8.42
0131199040	Fishing Brook above County Line Flow near Long Lake, N.Y.	8	43.98758333	-74.29133333	60.6
0131199045	Unnamed tributary to County Line Flow near Long Lake, N.Y.	9	43.97900000	-74.28588889	0.96
0131199050	Fishing Brook (County Line Flow outlet) near Newcomb, N.Y.	10	43.97738889	-74.27041667	65.6
01312000	Hudson River near Newcomb, N.Y.	11	43.96617378	-74.13070448	493
02172300	McTier Creek (State Highway 209) near Monetta, S.C.	12	33.75347736	-81.60177142	40.5
02172304	McTier Creek above Hunt Shed near New Holland, S.C.	13	33.74597760	-81.59704916	79.1
02172305	McTier Creek near New Holland, S.C.	14	33.71750000	-81.60750000	79.4
3345100813509	Gully Creek at Bridge on Shoals Road near Monetta, S.C.	15	33.75277778	-81.58583333	25.9
3344250813538	Gully Creek at McTier Creek near New Holland, S.C.	16	33.74027778	-81.59388889	29.9
02174175	Edisto River near Cottageville, S.C.	17	33.05461187	-80.44926614	5,341

[1]Latitude and longitude are referenced to the North American Datum 1927 (NAD27).

Nine sites were sampled across the Fishing Brook subbasin, which drains 65.6 square kilometers (km²) in the western portion of the upper Hudson River Basin, and 5 sites were sampled in the McTier Creek subbasin, which drains 79.4 km² in the northwestern portion of the Edisto River Basin. A site was located at the outlet of each of these larger basins; these were USGS station identification number (ID) 01312000 in a 493-km² drainage area on the Hudson River near Newcomb, N.Y., and USGS station ID 02174175 in a 5,341-km² drainage area on the Edisto River near Cottageville, S.C. Data are also provided for an additional site, the Hudson River near Winebrook Hills, N.Y., which was sampled only once for top predator fish in 2005 as part of a national occurrence and distribution study (Scudder and others, 2009).

Data Collection

Trace-metal clean techniques were used for all samples collected and processed for mercury analysis (U.S. Environmental Protection Agency, 1996; Cleckner and others, 1999; Olson and DeWild, 1999; Lewis and Brigham, 2004; Scudder and others, 2008). A list of the taxa collected in both study areas is provided in appendix 1. The list includes available descriptions of associated habitat, life history, and feeding strategies.

Fish and Macroinvertebrate Collection and Processing

Fish taxa were targeted to represent predatory game fish species and forage fish (appendix 2). Forage fish are generally smaller, midtrophic level species that can be consumed by predatory game fish species. Macroinvertebrate taxa were targeted to represent a range of consumer functional feeding groups and trophic positions, including shredders, scrapers, collector-gatherers, filterer-gatherers, omnivores, and predators (appendix 3).

Fish were collected by electrofishing (backpack, barge, or boat), trapping, seining, and angling. Specimens were sorted in the field and held in site water with aeration or in plastic bags of site water placed on wet ice until processing. Samples were typically processed within 4 hours of collection. Each forage fish specimen was rinsed three times in deionized water, weighed, and measured for total length. Specimens were

either processed as individual samples or as taxon-specific composites of 2 to 15 individuals of similar size. Samples were double-bagged in fresh zip-seal bags and immediately frozen on dry ice. Select game fish, typically top predators, were processed as individual samples of skin-off fillet. Fish specimens were rinsed three times in deionized water, weighed, and measured for total length. A skinless fillet was removed from one side, as described in Scudder and others (2008). The fillet was weighed, rinsed three times in deionized water, double-bagged, and immediately frozen. Samples were kept frozen until analysis. In the case of predatory game fish, the sagittal otoliths were removed from the head, cleaned, dried, and stored in plastic vials for age analysis.

Macroinvertebrates were collected by handpicking and by kick-net capture (for example, jabbing at banks, kicking substrate), using trace-metal clean techniques and equipment. Specimens were held in site water and processed generally within 4 hours of collection. Field processing involved sorting by taxon (and grouping within taxon by size, in some cases), picking clean of visible debris, and rinsing with deionized water a minimum of three times. Specimens within each taxon (and size grouping) were then divided into composites (target of three composites per taxon and size grouping), with targeted per-composite mass of at least 1 gram wet weight and targeted count of at least 15 individuals. Composite samples were stored in plastic scintillation vials, immediately frozen on dry ice, and kept frozen until analysis. Additional details regarding the collection and field processing of macroinvertebrate and fish samples can be found in Scudder and others (2008).

Age Determination of Predatory Game Fish

Age determination for fish samples collected during 2007–09 was conducted at the Florida Fish and Wildlife Conservation Commission Laboratory in Eustis, Fla., using methods described in Taubert and Tranquilli (1982), Porak and others (1986), and Hall (1991). For fish samples collected during 2005, age determination was conducted at the USGS Cooperative Wildlife Research Unit Laboratory at Clemson University in Clemson, S.C., using a standard technique described in Jearld (1983).

Periphyton Collection and Processing

Periphyton (attached algae and associated material) were collected from rocks, woody snags, unconsolidated substrates in depositional zones, and macrophytes (appendix 4). At least two of these habitats were targeted at most sites where periphyton samples were collected. These samples were referred to as (1) depositional-targeted habitat samples (DTH) of episammon or epipelon, collected from fine, unconsolidated substrates in depositional areas and (2) richest targeted habitat samples (RTH), comprising epilithon from cobbles, epidendron from woody snags, or (in a few cases) epiphyton from submerged aquatic vegetation (SAV).

Each DTH sample was a composite of algal material collected from at least five locations throughout the stream reach. DTH samples were collected by gently inserting a Teflon petri dish lid into the desired substrate, sliding a spatula under the dish, lifting the trapped material out of the water, and rinsing the material into a sample bottle. Samples were elutriated in the field to separate periphyton from sand and debris by shaking and decanting twice, adding 50 milliliters (mL) of reagent water, and shaking and decanting two more times.

RTH samples collected from cobbles or woody snags were composited from 10 locations throughout the stream reach; RTH samples collected from SAV were collected from 7 to 10 locations. RTH samples were collected by removing the desired substrate from the stream reach, then the substrate was gently scraped or brushed to dislodge periphyton into a plastic bin and lastly, the substrate was rinsed with site water. For samples collected from cobble substrate, the periphyton was scraped or brushed from a known area, delineated by a polyvinyl chloride (PVC) cylinder. For samples collected from woody snags and SAV, the area was determined by measuring the length and width of each snag and leaf. Once the periphyton was removed, subsamples were vacuum filtered on precombusted 47-mm quartz fiber filters (mercury and stable isotope analysis) or on 47-mm glass fiber filters (chlorophyll *a* and ash-free dry mass analysis). The filters were stored in petri dishes (Teflon for mercury, polystyrene for other analyses) and frozen until analysis. Additional detail regarding field protocols for collecting periphyton can be found in Bell and Scudder (2005).

Detritus and Leaf Litter Collection and Processing

Detritus samples, consisting of conditioned leaf packs, were collected along channel margins and other depositional zones of selected stream reaches (appendix 5). Areas were targeted to include macroinvertebrate collection zones. Samples were gently and repeatedly rinsed in a clean bucket of site water to dislodge invertebrates. After dislodging invertebrates, conditioned leaf packs were rinsed with site water through a nested series of precleaned plastic sieves. The four sieves, stacked largest to smallest, allowed for four size increments of particulate organic material (very coarse (>3.4 mm), coarse (between 2 and 3.4 mm), fine (between 1 and 2 mm), and very fine (between 0.5 and 1 mm)). The contents of each sieve were placed in a bin and rinsed three times, again removing any unwanted material (invertebrates or debris). The contents of each sieve were placed in a zip-seal bag and frozen until analysis.

In the New York study area, leaf litter was collected for mercury analysis by picking up leaves immediately as they fell to the ground on a day near the time of peak fall rate (appendix 6). Deciduous leaves were separated into the two dominant species sugar maple (*Acer saccharum*) and American beech (*Fagus grandifolia*) before processing.

Samples of important shrub and ground cover were collected for mercury analysis by picking the leaves from live vegetation of speckled alder (*Alnus incana*), wood fern (*Dryopteris* sp.), and hobblebush (*Viburnum lantanoides*). Coniferous litter from balsam fir (*Abies balsamea*) was collected by stretching a piece of plastic sheet (either 25 meters (m) × 25 m or 50 m × 50 m) beneath the collection stand for a few hours, then retrieving the fallen needles. In the South Carolina study area, peach baskets were placed in a mixed coniferous tree stand and a mixed deciduous tree stand to collect leaf litter samples. Baskets were retrieved after 30 days. All litter was handled with clean nitrile gloves and placed in plastic bags. Samples were freeze-dried overnight, then pulverized to a powder with a mortar and pestle. Each sample was then placed in a glass tube for shipment for mercury analysis.

Analytical Methods

Mercury in Fish

Before analysis, fish samples were freeze dried to constant weight and ground in their entirety to a fine powder, using a stainless-steel ball mill (Retsch MM200) or an ultracentrifugal mill (Retsch ZM200). Samples were analyzed for THg by the Texas A&M University Trace Element Research Laboratory in College Station, Tex., by combustion and atomic absorption, using a direct mercury analyzer (Milestone DMA–80) following U.S. Environmental Protection Agency (USEPA) method 7473 (U.S. Environmental Protection Agency, 1998). Fish were analyzed for THg only because MeHg composes more than 90 percent of the mercury in fish tissue (Grieb and others, 1990; Bloom, 1992; Southworth and others, 1995; Hammerschmidt and others, 1999; Marrugo-Nagrete and others, 2008).

Mercury in Macroinvertebrates, Periphyton, and Leaf Litter

Before analysis, macroinvertebrates were freeze dried to constant weight and ground in their entirety to a fine powder, using a stainless-steel ball mill (Retsch MM200). Macroinvertebrates and leaf litter samples were analyzed for THg and MeHg by the USGS Wisconsin Mercury Research Laboratory in Middleton, Wisc., using a dilute nitric acid extraction and cold-vapor atomic fluorescence spectroscopy (Hammerschmidt and Fitzgerald, 2006). The same laboratory also analyzed periphyton samples for THg and MeHg using methods outlined in Olund and others (2004) and DeWild and others (2002), respectively.

Chlorophyll *a* and Ash-Free Biomass

Subsamples of the periphyton samples were analyzed for chlorophyll *a* and ash-free biomass at the National Water Quality Laboratory (NWQL) in Denver, Colorado, using a spectrofluorometric method described in USEPA method 445 (Arar and Collins, 1997).

Stable Isotopes in Biological Tissues and Plant Material

Select subsamples of fish, macroinvertebrates, periphyton, detritus, and terrestrial leaf litter were analyzed for stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) at the Stable Isotope Geochemistry Laboratory at the Florida State University National High Magnetic Field Laboratory in Tallahassee, Fla. The particulates of a sample were scraped with a stainless steel spatula from a filter and loaded into a silver cup. All the sample cups were placed in wells of a plexiglas plate. An appropriate amount of deionized water was added to moisten samples. Then the plate was placed in a desiccator overnight (approximately 20 hours), with approximately 50 mL of hydrochloric acid. After fumigation, the samples were wrapped into a tin cup and dried in an oven at 70°C. Sample capsules were stored in a desiccator if they were not analyzed the same day (Harris and others, 2001). Samples were analyzed with a Thermo Quest NC2500 elemental analyzer interfaced with a Thermo Fisher Scientific, Inc. Finnigan DELTAplus XP isotope ratio mass spectrometer.

Quality Assurance and Quality Control

Standard Reference Material and Certified Reference Material

Laboratory quality assurance and quality control (QA/QC) results for mercury and stable isotopes included the analysis of field-submitted single-blind certified reference material (CRM) and standard reference material (SRM). CRM and SRM results, along with the results for laboratory internal CRM and SRM analysis are provided in the appendix tables.

Fish Tissue

Samples submitted for fish QA/QC were sent to the Texas A&M University Trace Element Research Lab. Reference material included various forms of biological tissue inoculated with known quantities of THg (National Research Council Canada, 1993, 1994, 2003; National Institute of Standards and Technology, 2008). Tissue types included mussel tissue in the form of marine bivalve mollusk tissue (National Institute

of Standards and Technology standard (NIST 2976), dogfish liver (National Research Council Canada standard (NRCC) DOLT–3), lobster hepatopancreas (NRCC TORT–2), and dogfish muscle (DORM–2). The target values for CRM and SRM analysis, individual results, percentage recovery, and comparison to target confidence limits (CLs) for THg are found in appendix 7.

Summary statistics for THg in fish are provided in appendix 8. The median recovery for THg in CRM and SRM submitted samples was 94.6, 99.4, and 107.4 percent for NIST 2976, NRCC DOLT–3, and NRCC TORT–2, respectively. The mean measured value for NIST 2976 was less than the lower 95 percent of the CL of the target value, while all others were within the range of the confidence limits. For the combined CRM and SRM samples, 47.4 percent of the samples were within 95 percent of the CL of the target value, and 89.5 percent were within 25 percent of the target value. For internal laboratory reference samples, 84.7 percent were within 95 percent of the CL of the target value, and all samples were within 25 percent of the target value. The median recovery for laboratory internal reference samples was 100.4 percent for NRCC DOLT–3 and 96.8 percent for NRCC DORM–2.

Macroinvertebrates

Samples submitted for macroinvertebrate QA/QC included reference material with known quantities of THg and MeHg (National Research Council Canada, 1994, 2003; National Institute of Standards and Technology, 2008) and were sent to the USGS Wisconsin Mercury Research Laboratory for analysis. The target values for CRM/SRM analysis, individual results, percentage recovery, and comparison to target CL are found in appendix 9 for THg and appendix 10 for MeHg.

Summary statistics for THg and MeHg in macroinvertebrates are provided in appendix 11. The median recovery for THg in the CRM and SRM samples was 94.9, 92.0, and 100 percent for NIST 2976, NRCC DOLT–3, and NRCC TORT–2, respectively, and 48.8 percent of the samples were within 95 percent of the CL of the target value, and 92.7 percent were within 25 percent of the target value. Internal laboratory analysis of macroinvertebrate tissue for THg used an SRM (IAEA–407) from the International Atomic Energy Agency (2003); 12.2 percent of samples were within 95 percent of the CL of the target value, and 95.1 percent were within 25 percent of the target value. The median recovery for MeHg analysis was 93.6, 81.1, and 97.7 percent for NIST 2976, NRCC DOLT–3, and NRCC TORT–2, respectively. For the combined CRM and SRM samples, 26.0 percent of the measured MeHg values were within 95 percent of the CL of the target value, and 78.0 percent were within 25 percent of the target value. Internal laboratory analysis of MeHg for macroinvertebrate tissue also used IAEA–407; 46.2 percent of the samples were within 95 percent of the CL of the target value, and 94.2 percent were within 25 percent of the target value. The median recovery for laboratory internal reference samples was 89.0 percent for THg and 98.2 percent for MeHg.

Stable Isotopes

Stable isotope ratios were measured relative to reference gases and calibrated to known carbon and nitrogen standards [$\delta^{13}C$ and $\delta^{15}N$, ranging from -12.7 to -32.1 per mil (per thousand) and -5.3 and 2.5 per mil, respectively]. Twenty reference material (RM) single-blind samples of USGS40 L-glutamic acid (National Institute of Standards and Technology, 2007) were submitted to the Florida State University Stable Isotope Laboratory. RM samples accounted for approximately 1 of every 10 regular samples submitted (appendix 12). The range between the target value and measured value differences was 0.47 and 0.046 per mil for $\delta^{13}C$ and 0.69 and 0.028 per mil for $\delta^{15}N$. Recoveries ranged from 98.22 to 101.15 percent for $\delta^{13}C$ and 90.72 and 115.25 percent for $\delta^{15}N$.

Summary results are presented in appendix 13. Of the samples submitted, the results for three $\delta^{13}C$ samples and five $\delta^{15}N$ samples were within 95 percent of the CL of the standards. Results for all $\delta^{13}C$ samples and 11 $\delta^{15}N$ samples were within 10 percent of the target value. The mean measured value for $\delta^{13}C$ was -26.33 per mil (target value: -26.39), and the mean measured value for $\delta^{15}N$ was -4.64 per mil (target value: -4.52). Appendix 13 also provides a summary of internal laboratory results for RM. The laboratory uses a variety of internally created RM and those received from other stable isotope labs (Biasatti, 2009; Y. Wang, Stable Isotope Geochemistry Laboratory at the Florida State University National High Magnetic Field Laboratory in Tallahassee, Fla., oral commun., January 27, 2012). The laboratory does not use USGS40 L-glutamic acid. Therefore, samples are not directly comparable with submitted samples. Over the study period, 81 internal RM samples were analyzed for $\delta^{13}C$ and 69 were analyzed for $\delta^{15}N$. Overall, for the five RM types, median percent recovery ranged from 99.4 to 101.1 for $\delta^{13}C$ and 80.1 to 100.8 for $\delta^{15}N$. For the combined lab internal $\delta^{13}C$ results, 65.4 percent of samples were within 95 percent of the CL of the target values, and all were within 10 percent of the target value. For $\delta^{15}N$, 60.9 percent of samples were within 95 percent of the CL of the target values, and 66.7 percent were within 10 percent of the target value.

Summary

Bioaccumulation of mercury in fish and other aquatic organisms has generated increasing public concern during the past decade. Recent advances have been made in describing some of the factors that influence the transport and geochemical cycling of mercury in freshwater ecosystems. The U.S. Geological Survey National Water-Quality Assessment Program conducted a multidisciplinary study in 2005–09 to investigate the bioaccumulation of mercury in streams from

two contrasting environmental settings. Study areas were located in the central Adirondack Mountains region of New York and the Inner Coastal Plain of South Carolina. Fish, macroinvertebrates, periphyton (attached algae and associated material), detritus, and terrestrial leaf litter were collected. Fish were analyzed for total mercury; macroinvertebrates, periphyton, detritus, and terrestrial leaf litter were analyzed for total mercury and methylmercury; and select samples of fish, macroinvertebrates, periphyton, detritus, and terrestrial leaf litter were analyzed for stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$).

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Glossary

benthic Associated with (living on or near) the bottom of an aquatic habitat (Thorp and Covich, 2001; Wehr and Sheath, 2003).

bioaccumulation Gradual increase in the amount of a substance in the tissue(s) of an organism that occurs when the rate of intake (through respiration, ingestion, dermal contact, and other mechanisms) exceeds removal (International Union of Pure and Applied Chemistry, 1993).

confidence limits (95 percent) Upper and lower limits of the 95-percent confidence level. This is an estimate of the interval that contains the true mean value with a 95-percent degree of certainty and is defined as follows:

$$X \pm \frac{t\left(\frac{\alpha}{2}, N-1\right)s}{\sqrt{N}} \qquad (1)$$

where

X is the sample mean,
t is the critical value of the t-distribution,
α is the significance level (for example, for 95-percent confidence level, $\alpha = 0.05$),
N is the number of samples, and
s is the standard deviation.

depositional-targeted habitat A habitat where fine sediment, such as sand and silt, is deposited (Moulton and others, 2002).

ecosystem The collective term describing biota (all biological organisms) and their associated abiotic environment.

epidendron Benthic habitat that consists of woody substrates on which organisms are attached or loosely associated.

epilithon Benthic habitat that consists of natural, coarse-grained substrates (for example, gravels, cobbles, or boulders) or bedrocks or artificial, hard substrates (such as submerged concrete) on which organisms are attached or loosely associated.

epipelon Benthic habitat that consists of silt-sized (less than 0.064-millimeter (mm) diameter) streambed sediments on which organisms are loosely associated. This habitat is commonly found in areas of low flow velocities, such as pools and side-channel areas, where silt can deposit.

epiphyton Benthic habitat hat consists of plants on which organisms are attached or loosely associated.

epipsammon Benthic habitat that consists of sand-sized (between 0.064- and 2-mm diameter) particles on which organisms are attached or loosely associated.

forage fish Primary (herbivores) and secondary consumers (omnivores or carnivores) that are generally smaller fecund species that are forage (prey) for larger predaceous fish.

macroinvertebrate Invertebrates (organisms without a spinal column) larger than microinvertebrates; that is, organisms larger than 2-mm diameter retained on a sieve (Thorp and Covich, 2001).

periphyton Commonly used to indicate algal cells; however, periphyton collectively refers to fungi, bacteria, algae, and detritus attached to any substrate in an aquatic system (Wehr and Sheath, 2003).

predatory game fish The predaceous fish species that occupy the highest trophic level in a given community or ecosystem.

richest targeted habitat Usually riffles or woody snags; this is the habitat type where the taxonomically richest (greatest number of species) algal or invertebrate community is located in a given stream (Moulton and others, 2002).

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Appendixes 1–13

The following data files are included as part of the U.S. Geological Survey (USGS) Data Series 705 and are available for download from http://pubs.usgs.gov/ds/705/.

Appendix 1. Ecological information for fish and macroinvertebrate taxa collected in New York and South Carolina.

Appendix 2. Fish results and field measurements for samples collected in New York and South Carolina.

Appendix 3. Macroinvertebrate results and field measurements for samples collected in New York and South Carolina.

Appendix 4. Periphyton results for samples collected in New York and South Carolina.

Appendix 5. Detritus results for samples collected in New York and South Carolina.

Appendix 6. Leaf litter results for samples collected in New York and South Carolina.

Appendix 7. Quality assurance and quality control results of reference material for the assessment of mercury in fish.

Appendix 8. Summary of results for reference material submitted in assessment of mercury in fish.

Appendix 9. Quality assurance and quality control results of reference material for the assessment of mercury in macroinvertebrates.

Appendix 10. Quality assurance and quality control results of reference material for the assessment of methylmercury in macroinvertebrates.

Appendix 11. Summary of results for reference material submitted in assessment of mercury and methylmercury in macroinvertebrates.

Appendix 12. Quality assurance and quality control results of reference material for the assessment of stable isotopes in tissue.

Appendix 13. Summary of results for reference material submitted in assessment of stable isotopes in tissue.

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