USGS
science for a changing world

National Water-Quality Assessment Program

Procedures for Collecting and Processing Streambed Sediment and Pore Water for Analysis of Mercury as Part of the National Water-Quality Assessment Program

Open-File Report 2008–1279

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

Cover: Sampling pore water, St Marys River, Florida (upper left); filtered pore water sample, Little Wekiva River, Florida (upper right); collecting surface streambed sediment, Oak Creek, Wisconsin (lower right); 2-cm surface streambed sediment sample, Beaverton Creek, Oregon (lower left); measuring *in situ* streambed sediment pH, Little Wekiva River, Florida (center). (All photographs by the authors.)

Procedures for Collecting and Processing Streambed Sediment and Pore Water for Analysis of Mercury as Part of the National Water-Quality Assessment Program

By Michelle A. Lutz, Mark E. Brigham, and Mark Marvin-DiPasquale

National Water-Quality Assessment Program

Open-File Report 2008–1279

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

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2008

For product and ordering information:
World Wide Web: http://www.usgs.gov/pubprod
Telephone: 1-888-ASK-USGS

For more information on the USGS--the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:
World Wide Web: http://www.usgs.gov
Telephone: 1-888-ASK-USGS

Suggested citation:
Lutz, M.A., Brigham, M.E., and Marvin-DiPasquale, M., 2008, Procedures for collecting and processing streambed sediment and pore water for analysis of mercury as part of the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 2008–1279, 68 p.

Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible 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, now 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 condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, 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 1991-2001, 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/studyu.html).

Multiple national and regional assessments are ongoing in the second decade (2001—2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and ground water. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

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.

Matthew C. Larsen
Acting Associate Director for Water

This page intentionally left blank.

Contents

Contents—Continued

Figures

Tables

Conversion Factors and Datum

Conversion Factors

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
centimeter (cm)	0.3937	inch (in.)
centimeter (cm)	0.01	meter (m)
millimeter (mm)	0.001	meter (m)
micrometer (µm)	10^{-6}	meter (m)
meter (m)	3.281	foot (ft)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Area	
square meter (m^2)	10.76	square foot (ft^2)
	Volume	
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
milliliter (mL)	0.03382	ounce, fluid (fl. oz)
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
picogram (g)	10^{-12}	gram (g)
nanogram	10^{-9}	gram (g)
microgram (µg)	10^{-6}	gram (g)
milligram (mg)	0.001	gram (g)
	Density	
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)

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

$$°F=(1.8×°C)+32$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given in micrograms per liter (µg/L), micromoles per liter (µmol/L), milligrams per liter (mg/L), or nanograms per liter (ng/L).

Concentrations of chemical constituents in streambed sediment are given in micromoles per gram dry weight (µmol/g dry wt), milligrams per gram dry weight (mg/g dry wt), or nanograms per gram dry weight (ng/g dry wt).

Datum

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

Abbreviated Streambed-Sediment- and Water-Quality Units

Abbreviations	Definition
°C	degree Celsius
µg/L	microgram per liter
µm	micrometer
µmol/g dry wt	micromole per gram, dry weight
µmol/L	micromole per liter
µS/cm at 25°C	microsiemen per centimeter at 25 degrees Celsius
%	percent
% dry wt	percent, dry weight
% wet wt	percent, wet weight
1/d	per day
cm	centimeter
cm^3	cubic centimeter
ft^3/s	cubic feet per second
g/cm^3 wet sed	gram per cubic centimeter, wet sediment
in.	inch
L	liter
L/(mg DOC*m)	liter per (milligram of dissolved organic carbon * meter)
M	molar
m	meter
m^2	square meter
mg/g dry wt	milligram per gram, dry weight
mg/L	milligram per liter
mL	milliliter
mL PW/cm^3 wet sed	milliliter of pore water per cubic centimeter, wet sediment
mm	millimeter
mV	millivolt
N	normal
ng	nanogram
ng/g dry wt	nanogram per gram, dry weight
ng/L	nanogram per liter
nm	nanometer
nmol/g dry wt/d	nanomole per gram, dry weight, per day
pg/g dry wt/d	picogram per gram, dry weight, per day
units/cm	units per centimeter
V	volt

Abbreviations and Acronyms

Abbreviation and Acronym	Definition
AVS	Acid-volatile sulfide
C	Carbon
DO	Dissolved oxygen
DOC	Dissolved organic carbon
GCU	Geomorphic channel unit
GLM	Generalized linear model
GPS	Global Positioning System
HCl	Hydrochloric acid
Hg	Mercury
Hg(II)R	Reactive mercury
LEW	Left edge of water
Log	logarithm
LOI	Loss on ignition
MCW	Mean wetted channel width
MDP	Methylmercury degradation potential
MeHg	Methylmercury
MPP	Methylmercury production potential
N	Nitrogen
NAD 83	North American Datum of 1983
NAWQA	National Water-Quality Assessment Program
NWIS	Nation Water Information System
ORP	Oxidation-reduction potential
PVC	Polyvinyl chloride
®	Registered trademark
REW	Right edge of water
SAOB	Sulfide antioxidant buffer
STAID	Station-identification number
SW	Stream water
T	Temperature
THg	Total mercury
USGS	U.S. Geological Survey
WAAS	Wide Area Augmentation System
WMRL	Wisconsin Mercury Research Laboratory

Acknowledgments

Technical Reviewers

Brent R. Topping, Hydrologist, U.S. Geological Survey, Menlo Park, Calif.
Charles N. Alpers, Research Chemist, U.S. Geological Survey, Sacramento, Calif.

Technical Support

David P. Krabbenhoft, Research Hydrologist, U.S. Geological Survey, Middleton, Wis.
George R. Aiken, Hydrologist, U.S. Geological Survey, Boulder, Colo.
John F. DeWild, Hydrologic Technician, U.S. Geological Survey, Middleton, Wis.
Margo D. Corum, U.S. Geological Survey, Reston, Va.
Mark L. Olson, Biologist, U.S. Geological Survey, Middleton, Wis.
Shane D. Olund, Chemist, Interpoll Laboratories, Incorporated, Circle Pines, Minn.
William H. Orem, U.S. Geological Survey, Reston, Va.

Editorial and Graphics

Bonnie Stich Fink, Editor, U.S. Geological Survey, Louisville, Ky.
Jennifer L. Bruce, Geographer, U.S. Geological Survey, Middleton, Wis.

Approving Official

Charles A. Peters, Wisconsin Water Science Center Director, U.S. Geological Survey, Middleton, Wis.

Procedures for Collecting and Processing Streambed Sediment and Pore Water for Analysis of Mercury as Part of the National Water-Quality Assessment Program

By Michelle A. Lutz, Mark E. Brigham, and Mark Marvin-DiPasquale

Abstract

Mercury (Hg) contamination is an issue of national concern, affecting both wildlife and human health. The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program, in association with the USGS Toxic Substances Hydrology Program and the USGS National Research Program, has initiated two levels of studies to investigate Hg contamination of the Nation's streams: reconnaissance and detailed studies. Reconnaissance studies entailed one-time sampling events at 266 stream sites across the Nation. Detailed studies entailed intensive spatial and temporal sampling of a small number of streams across the Nation in an effort to develop a more complete, process-level understanding of benthic Hg geochemistry and the underlying factors controlling it. This report summarizes the sampling methods used for the collection and processing of streambed sediment and pore water in association with both of these study levels. Bed-sediment characteristics, such as organic content and grain size, strongly influence Hg geochemistry; detailed characterization of these constituents within a stream reach will allow for the extrapolation of related Hg biogeochemical constituents to the reach scale.

Background

As of 2006, 48 States had issued fish-consumption warnings owing to mercury (Hg) contamination (U.S. Environmental Protection Agency, 2007). Hg toxicity in humans causes a variety of symptoms with primary damage affecting the central nervous system, brain, kidneys (Agency for Toxic Substances and Disease Registry, 1999), and cardiovascular system (Virtanen and others, 2005). Growth, reproductive, and behavioral effects have also been documented in wildlife (Hammerschmidt and others, 2002; Drevnick and Sandheinrich, 2003; Evers, 2005).

Current (2008) Hg levels in the environment are caused by a combination of natural and anthropogenic sources (Nriagu, 1979; Swain and others, 1992). Hg enters most ecosystems predominantly through wet and dry atmospheric deposition of primarily inorganic forms from combustion sources (U.S. Environmental Protection Agency, 1997), although some ecosystems have substantial Hg sources related to mineral deposits, mining, or industrial uses. Entry of Hg into aquatic environments occurs by direct deposition to the water body, runoff from upland sources (attached to suspended soil or organic material or complexed with dissolved organic carbon (DOC)), or influx from shallow ground-water flow (U.S. Environmental Protection Agency, 1997; Grigal, 2002). Once in an aquatic system, Hg partitions strongly to bed and suspended sediment (U.S. Environmental Protection Agency, 1997). Methylation of Hg in aquatic environments is largely mediated by sulfate-reducing bacteria (Gilmour and others, 1992) and occurs primarily in bed sediment and wetlands, although recent evidence indicates that iron-reducing bacteria can also carry out inorganic Hg methylation (Fleming and others, 2006). The resulting methylmercury (MeHg) formed from these microbial reactions is highly toxic and readily biomagnifies in aquatic food webs (Weiner and others, 2003).

Studies of Hg in Stream Ecosystems

The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program is a national program comprised of study areas throughout the country representing major river-basins and aquifer systems (Gilliom and others, 2001). The NAWQA Program, in association with the USGS Toxic Substances Hydrology Program and the USGS National Research Program, has initiated studies of Hg in streams to improve understanding of Hg cycling in stream systems. Two levels of studies have been conducted: reconnaissance studies and detailed studies (Brigham and others, 2003).

Reconnaissance Hg studies provide a "snap-shot" of Hg concentrations in various media across a wide range of stream sites throughout the country. Hg and related constituents were measured in stream water, streambed sediment (table 1), and piscivorous fish. Reconnaissance sampling was done in 1998 (Krabbenhoft and others, 1999; Brumbaugh and others, 2001), 2002, and 2004–05 at 266 stream sites across the Nation (fig. 1).

Detailed studies, designed to assess hydrologic, biogeochemical, and ecological controls on Hg transport, speciation, methylation, and bioaccumulation, focused on a smaller number of stream sites. Hg and related constituents were measured in precipitation, stream water, bed sediment and pore water (table 1), and aquatic biota. In 2002–06, eight sites were studied—two sites in Oregon, and three sites each in Wisconsin and Florida (fig. 2). Bed-sediment and pore-water samples were collected during 2003–04, and sampling was divided into three components (stream-reach characterization, spatial geochemistry, and temporal geochemistry) distinguished by variations in strategy and purpose.

This report represents an idealized version of the approach and field methods that were used to assess Hg and related constituents in bed sediment and pore waters as part of both the reconnaissance and detailed studies. It is intended for use as a protocol to guide future phases of these studies and other related studies in similar investigations of bed sediment and pore water. Explicit methodologies for sampling strategies as well as collection and processing procedures (appendix 1a–b) are intended for clarification and use during field activities.

General Guidelines

Although this report covers two studies of different focus and scope, a number of general guidelines relating to sample collection, processing, and documentation are pertinent to both.

Personnel should familiarize themselves with the clean-hands/dirty-hands sampling technique outlined by the U.S. Geological Survey (2006), as well as the cleaning and sampling methods of Shelton and Capel (1994) and Wilde (2004). Any equipment, or pieces thereof, contacting samples to be analyzed for Hg species should be made of glass, Teflon®, or other plastic. In shallow areas, sediment samples are collected directly from the streambed. However, in areas where the sediment is too deep to collect in this manner, a 9-in. square, stainless-steel Birge-Ekman grab sampler should be deployed to retrieve sediment. This grab sampler can collect fine-grained material from depth with minimal disturbance to the sediment/water interface. To minimize possible contamination, sediment samples should be collected from the center of the grab sampler, avoiding areas that are near or directly contacting metal surfaces. In addition to sediment-sampling activities, stream-water field measurements of pH, specific conductance, dissolved oxygen (DO), temperature, and streamflow also are collected at the time of sampling.

Process samples at a clean, stable workspace immediately following collection. Ideal processing sites are grassy or well-vegetated parks with picnic tables or where a portable table can be set up. Avoid workspaces within 60 m of dusty areas such as roads; workspaces should be covered with clean plastic bags or sheeting. Dedicated water-quality laboratory vans with suitable workspaces are also acceptable as long as they have never transported Hg reagents or samples with suspected high-level Hg contamination.

Proper documentation of field activities is a key component of sampling efforts. Personnel should be familiar with USGS water-quality sample coding (U.S. Geological Survey, 2006) and field forms (appendix 3); sample labels (appendix 4) and field forms should be filled out completely before leaving the stream. USGS station-identification number, mean sample time, date, and medium code together serve as the unique identifier for each sample in the National Water Information System (NWIS) database (U.S. Geological Survey, 2006). Where multiple samples of the same medium are collected from the same stream site on the same day, samples collected from different locations are distinguished from each other based on time; therefore, care should be taken when assigning times for samples, and the relationship between sample time and location should be documented on field sheets. Sketching a map of the stream reach is of particular importance. On the map, notations should include specific locations (with reference to bridge crossing/other permanent object), as well as the mean times and sediment characteristics of the areas sampled. Copies of digital orthophotos and topographic maps can be obtained on the World Wide Web (TerraServer-USA, 2008), and can aid in the drawing of stream shape and the location of sampling areas. Locational information should be supplemented with Global Positioning System (GPS) coordinates recorded at each sampling area; use of Wide Area Augmentation System (WAAS) and an external antenna provide reasonably accurate coordinates. Additional accuracy can be obtained by allowing GPS units to determine a time-averaged reading of a location.

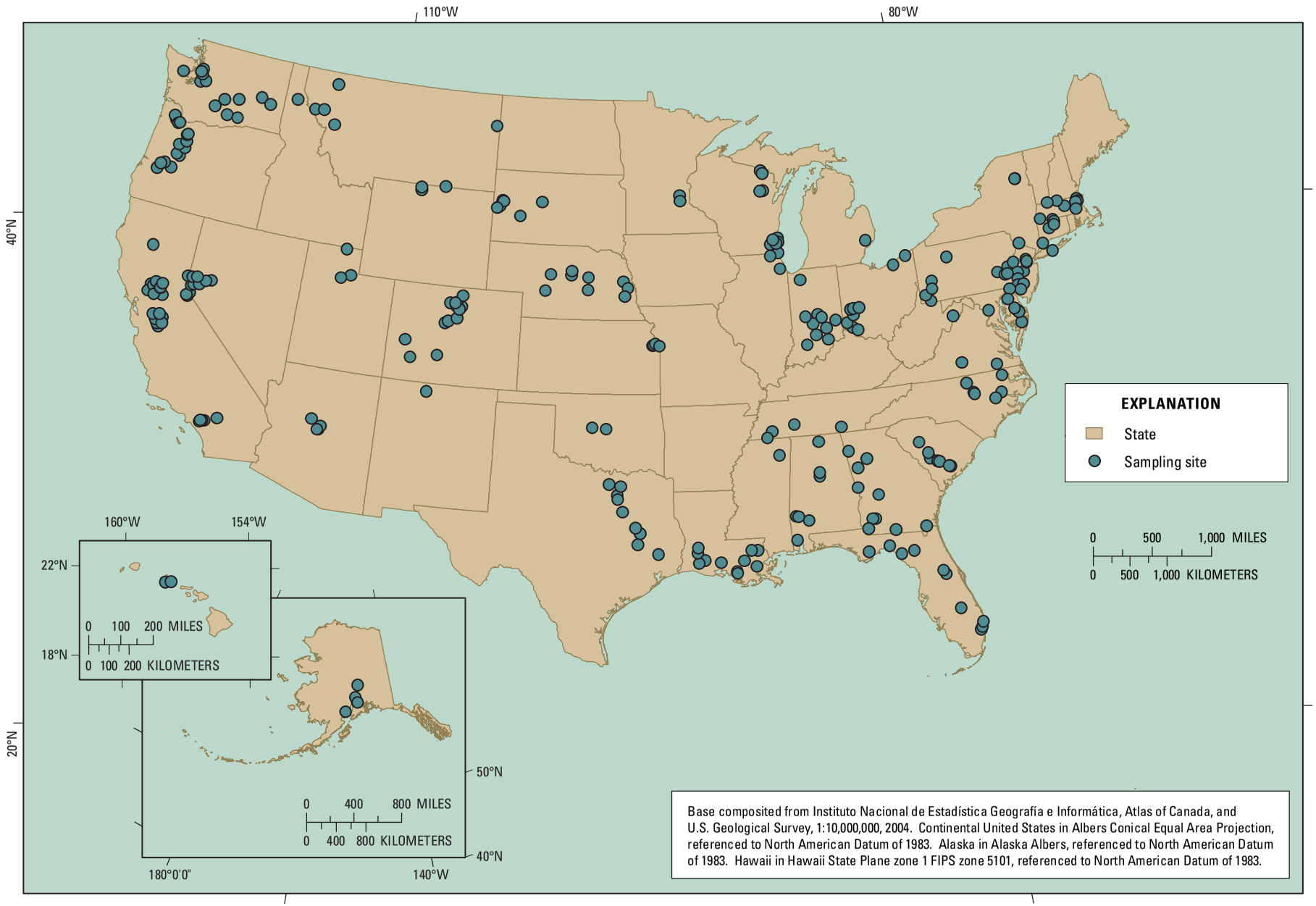


Figure 1. Locations of sites sampled for National Water-Quality Assessment (NAWQA) Program reconnaissance mercury studies.

Table 1. Overview of streambed-sediment and pore-water sampling efforts associated with National Water-Quality Assessment (NAWQA) Program reconnaissance and detailed mercury studies.

[(For a detailed list of constituents refer to appendix 2.. cm, centimeter; THg, total mercury; MeHg, methylmercury; AVS, acid-volatile sulfide; DO, dissolved oxygen; T, temperature; LOI, loss on ignition; MPP, methylmercury production potential; MDP, methylmercury degradation potential; $Hg(II)_R$, reactive mercury; DOC, dissolved organic carbon; ORP, oxidation-reduction potential]

Sampling component	Sediment sampling	Pore-water sampling	Field measurements
		Reconnaissance	
Sediment geochemistry	Surface (0–2 cm, approximately) composite sample analyzed for THg, MeHg, AVS, and percent fines.	None	Stream water pH, specific conductance, DO, T, and streamflow. None associated with sediment sampling.
		Detailed	
Stream-reach characterization	Surface (0–2 cm) grab sample analyzed for LOI and percent fines.	None	Stream water pH, specific conductance, DO, T, and streamflow. Visual and tactile assessment of grain size and organic content.
Spatial and temporal geochemistry	Surface (0–2 cm) composite sample for MPP and MDP rates, THg, MeHg, $Hg(II)_R$, AVS, percent fines, and numerous other ancillary analyses (appendix 2).	2-cm depth (nominally) composite sample analyzed for THg, MeHg, DOC, nutrients, selected major anions, and numerous other ancillary analyses (appendix 2).	Stream water pH, specific conductance, DO, T, and streamflow. Sediment ORP, pH, and T. Pore-water sulfide, ORP, and pH. Piezometric head.

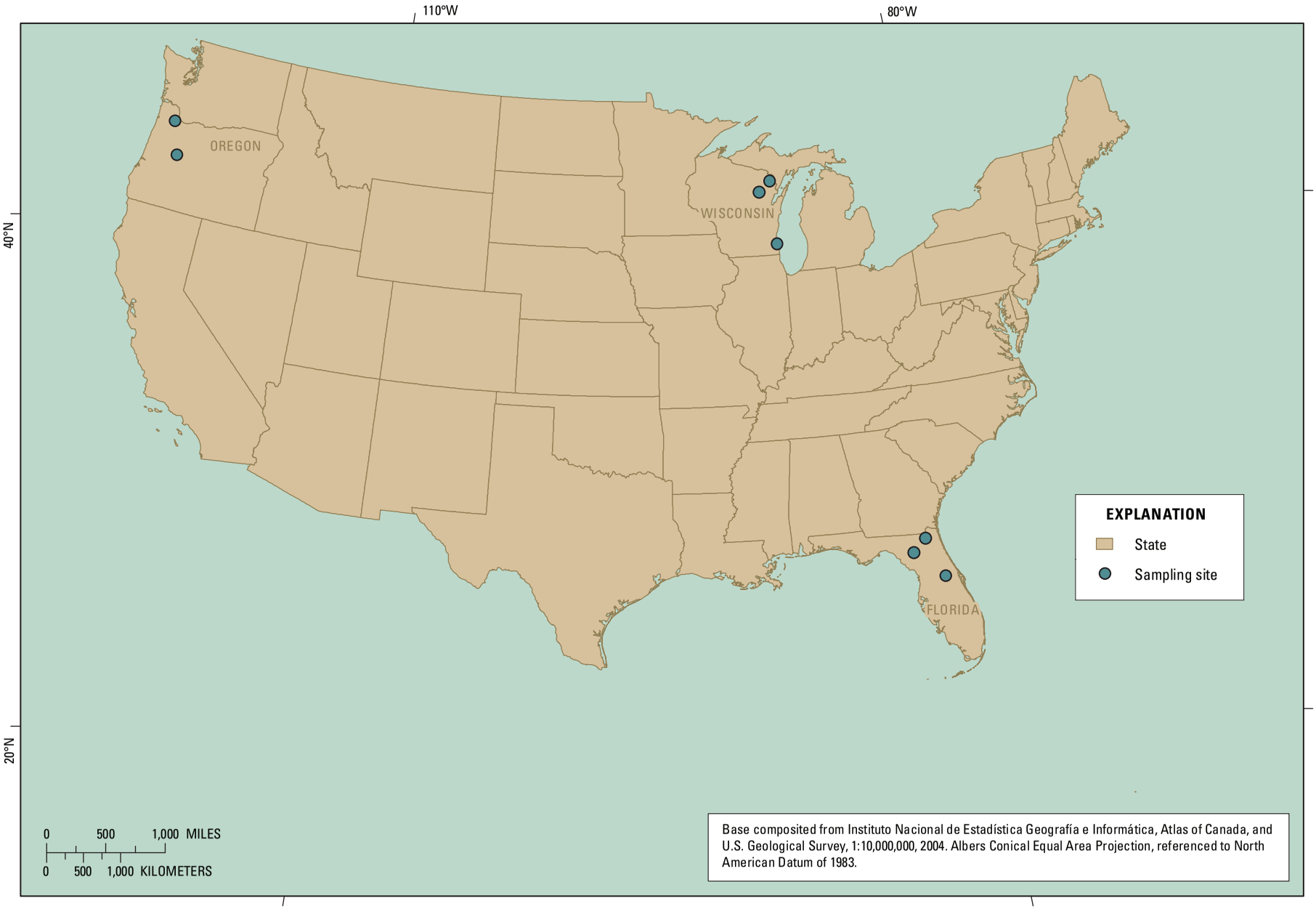


Figure 2. Locations of sites sampled for National Water-Quality Assessment (NAWQA) Program detailed mercury studies.

Reconnaissance Studies

NAWQA reconnaissance Hg studies examine Hg occurrence in stream water, bed sediment, and piscivorous fish as part of a one-time sample collection effort. The reconnaissance bed-sediment sample from each site is a composite of the sediment types present. Stream-water field measurements (table 1) are collected the same day as the sediment sample, in accordance with published methods (Wilde, variously dated; Rantz and others, 1982).

Sampling Strategy

At each stream, identify 10 discrete depositional bed-sediment zones and collect sediment from the top 2 cm (approximately) of each zone. Deposit collected sediment into a suitable container, and remove large objects such as sticks, rocks, and leafy debris. Ideal sediment volume is 120 mL, but, depending on the number of zones, considerably more sediment may be collected. Homogenize sediment to yield a single composite sample from each stream. Samples should be collected, homogenized, and processed (that is, subsampled and preserved) within 30 minutes to minimize the potential for re-oxidation of any sulfide present. Where this is not possible, reduce the number of sampled zones as needed, but use no fewer than five. Samples are analyzed for total Hg (THg), MeHg, acid-volatile sulfide (AVS), stable isotopes of carbon (C) and nitrogen (N), and percent fines (that is, percent of sediment less than 0.063 mm) (table 1). Collect quality-control samples, in the form of split replicates, at one out of every eight sites.

Sample Collection

Sample collection focuses on the surface layer (approximately the upper 0–2 cm) of sediment. Several pieces of sampling equipment are suitable, depending upon availability of equipment and local conditions such as substrate type and depth of sampling zone (appendix 5). Typically, a short (approximately 10 cm) section of Teflon® tube (1.5-in. diameter) is worked horizontally across the upper 2 cm of sediment, using gloved hands, to collect sediment. The tube is then removed from the stream, excess water is decanted, and sediment is placed in a suitable container. Other acid-cleaned plastic sampling devices, such as plastic scoops, work well in certain stream environments. A similar procedure for NAWQA sediment sampling is outlined by Shelton and Capel (1994).

Sample Processing

Process samples at a suitable workspace immediately after collection. To minimize the water-sediment partitioning of THg and MeHg, as well as the oxidation of reduced species, samples are not sieved. Stir collected sediment with a clean Teflon® policeman or plastic spoon for 30 to 60 seconds, taking care not to entrain air into the sample. Scoop (using plastic spoon) or pour sediment into jars to subsample for various analyses (THg and MeHg, AVS, stable C and N isotopes, and percent fines). Leave approximately 20 to 30% of the jar volume empty to allow room for expansion upon freezing. Preserve AVS samples with 0.3 mL of zinc acetate to minimize the oxidation of sulfide in the sample. Freeze THg and MeHg, AVS, and stable C and N isotope samples. Store samples to be analyzed for percent fines in a cool, dark location. Samples can be stored until all streams have been sampled, then submitted together to their respective laboratories (appendix 6) with the appropriate paperwork (appendix 7).

Detailed Studies

NAWQA detailed Hg studies examine Hg occurrence and cycling in precipitation, stream water, bed sediment, sediment pore water, and selected biota. Detailed bed sediment sampling is divided into three components: reach characterization, spatial biogeochemical sampling, and temporal biogeochemical sampling (table 1). The purpose and, therefore, strategy of each component differs; however, sample collection and processing methods remain the same throughout. Pore-water sampling is performed in conjunction with the spatial and temporal components of the detailed studies. Routine stream-water samples and field measurements are collected the same day as bed-sediment/pore-water sampling, in accordance with published methods (Rantz and others, 1982; U.S. Environmental Protection Agency, 1996; U.S. Geological Survey, 2006; Wilde, variously dated).

Sampling Strategy

Hg partitioning in sediment is strongly influenced by organic content and grain size. Hg has a strong affinity for organic matter (Ravichandran, 2004; Lambertsson and Nilsson, 2006), and is therefore observed in higher concentrations in organic-rich sediments. There is an inverse relation between Hg and grain size, with Hg showing greater affinity for finer sediments (Förstner and Wittmann, 1981; Horowitz and Elrick, 1987).

For the detailed Hg studies, loss on ignition (LOI) is used as a measure of sediment organic content and percent fines (that is, percent of sediment less than 0.063 mm) is used as a measure of grain size. Every sediment sample collected is analyzed for these constituents. Though not always explicitly stated, LOI is performed as an ancillary analysis on all sediment samples submitted to the USGS Wisconsin Mercury Research Laboratory (WMRL).

Reach Characterization

Reach characterization yields a quantitative description of bed-substrate type abundance in streams, thereby allowing for the extrapolation of related constituents (measured during spatial sampling) to a scale more relevant to the stream.

Establishing a Reach

The reach is considered a representative portion of the larger stream or segment that is amenable to sampling. It has relatively homogeneous physical, chemical and biological characteristics, and therefore, should not include substantial changes in streamflow, water-quality characteristics, basin characteristics, or any major hydrologic discontinuities (for example, waterfalls). Guidelines for establishing the reach are based on methods published by Fitzpatrick and others (1998). Reach location and length are determined by three factors: geomorphology (habitat type and distribution), local habitat disturbance, and wetted channel width. Wadeable reaches are preferable, if possible, for safety considerations and ease of sampling.

Habitat types, or geomorphic channel units (GCUs), are different fluvial regimes resulting from the depositional and erosional patterns of the channel. GCU type and distribution are important considerations when determining reach location and length, as they categorize the stream at a scale relevant to the majority of biota in the stream (Frissell and others, 1986). In wadeable streams, GCUs include riffles, runs, and pools (fig. 3). In unwadeable streams, GCUs include the insides and outsides of meander bends, crossovers, as well as forewater and backwater side habitats. Reach placement should aim to include two examples each of two GCUs that are representative of the overall GCU sequence in the stream (Fitzpatrick and others, 1998). If there are insufficient GCUs to fulfill this criterion, locate the reach in an area that accurately reflects the overall habitat characteristics for that stream. Areas occupying 50% or more of the stream width are considered distinct GCUs.

Locate reaches in areas outside the hydraulic effects of bridges and other man-made objects. Placement of the first reach boundary is dependent upon the types of GCUs present and their distribution in the stream. If the stream has a sequence of distinct GCUs, place the boundary one-half the mean channel width upstream or downstream of the border between two GCUs. If, however, the GCUs are not as distinct or sequential, place the boundary approximately 10 times the mean channel width from the reference location (for example, bridge or gage).

Reach length is determined by multiplying the average wetted-channel width by 20, as this typically contains 1 full meander wavelength (Leopold and others, 1964), and, therefore, should capture all GCUs present. In accordance with Fitzpatrick and others (1998), adopt minimum reach lengths of 150 m for wadeable streams and 500 m for unwadeable streams when calculated reach lengths are less than the minimum values. There is no maximum reach length.

Once the reach location and length have been established, divide the reach into 15 equidistant transects. Transects are positioned perpendicular to the flow and flagged on both sides of the stream. Transect 1 corresponds with the downstream reach boundary, and Transect 15 corresponds with the upstream reach boundary. Collect 30-minute, time-averaged GPS readings at the upstream and downstream reach boundaries, on the left and right edges of water. Include reach boundaries, transects, landmarks, distances, GCUs, and general shape of the stream on a field sketch. Record additional (instantaneous) GPS-coordinate readings at the left edge of water of each transect.

Transect Sampling

Bed-substrate zones are classified into a minimum of four basic categories for the purpose of reach characterization: fine-grained organic-rich, mixed sand and fine-grained with intermediate organic content, sandy organic-poor, and other (table 2). Substrate zones described by the first three categories are assumed to be the most likely to contribute to sediment MeHg production and are the same categories as those used for spatial sampling. Substrates larger than sand (for example, gravel and cobble) are assumed to yield negligible contributions to sediment MeHg production and, in the most basic categorization scheme, are combined into a single category to expedite sampling. The expanded category list may be used to parse these substrates into multiple categories when a more detailed assessment of the substrate is desired (table 2).

The equidistant transects are used as arbitrary lines along which reach bed substrates are characterized. Measure and record the width of each bed-substrate zone encountered along each transect. Collect point samples of surficial sediment (0–2 cm) at the midpoint of each zone assumed to be an area of MeHg production (table 2, categories 2, 2.5, and 3; fig. 4). In areas where sediment cannot be retrieved for classification, tapping substrates with polyvinyl chloride (PVC) pipe can help to estimate substrate category. Upon contact with the substrate, the PVC pipe will show varying amounts of resistance, based on the substrate type—bouncing quickly back or changing course when encountering larger substrates,

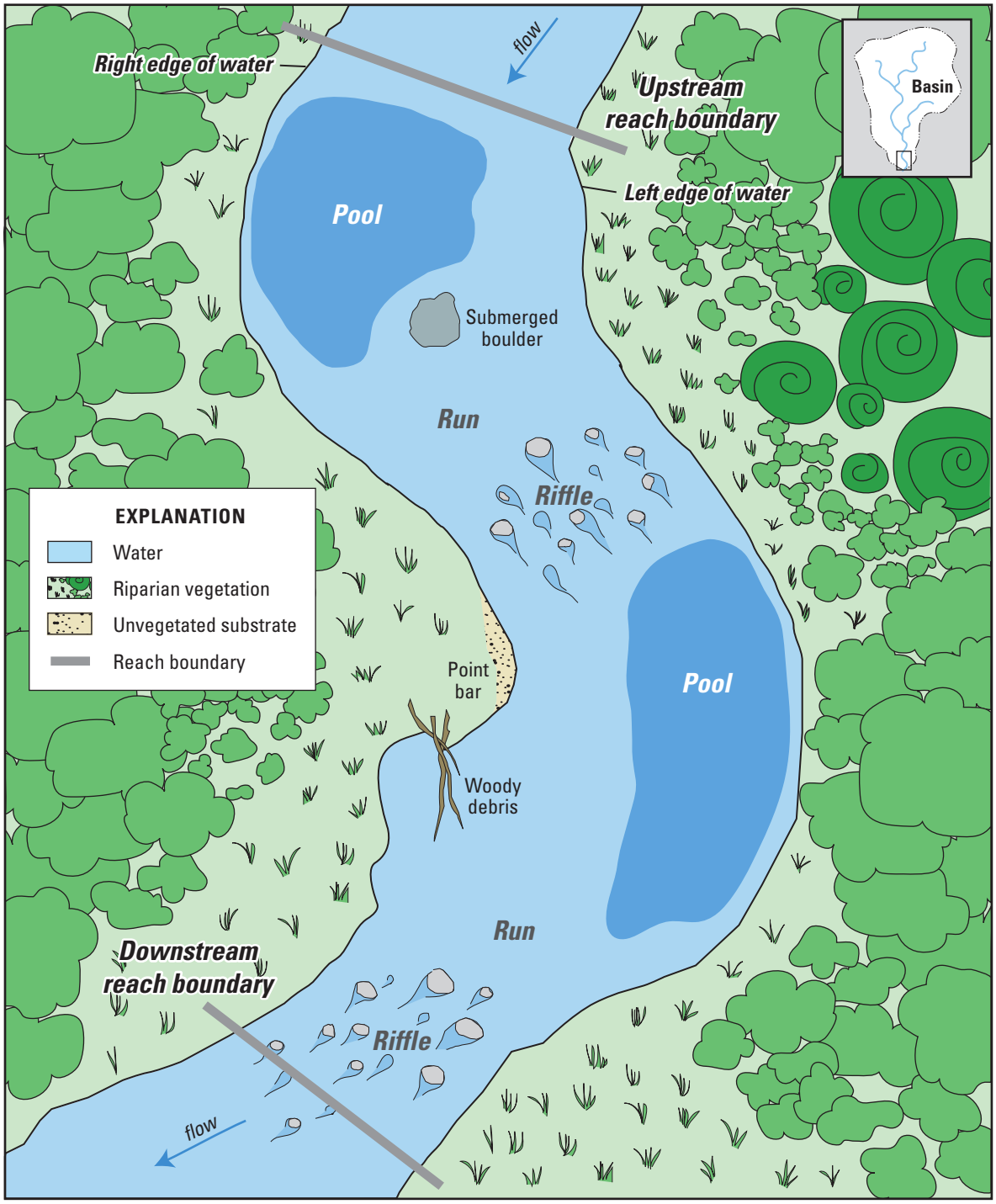


Figure 3. Diagram of simplified wadeable reach, with geomorphic channel units noted.

and slowing down or showing give when encountering finer substrates (sand and finer). Field personnel should familiarize themselves with the response of the PVC pipe to different sediment types in shallow areas where the sediment type has been classified. Where finer-scale classifications of sediment type are desired, the grab sampler can be used to obtain sediment for visual and tactile assessment. Transects are sampled in downstream to upstream order (that is, Transect 1 to Transect 15) to minimize disturbance of unsampled transects. Samples are analyzed for LOI and percent fines.

Quality-control replicate samples are collected at a minimum of 1 out of every 10 transects. Immediately following the completion of regular transect sampling, randomly choose transect numbers and resample. Characterize bed substrates and collect samples from the midpoints of zones with selected bed-sediment types, taking care to avoid disturbed sediment. Collected samples are analyzed for LOI and percent fines.

Spatial Biogeochemical Sampling

Spatial biogeochemical sampling yields a detailed characterization of sediment and pore water in different reach bed-sediment types. Select a minimum of three zone types per stream based on bed-sediment grain size and observable organic content. Potential sampling-zone types include fine-grained organic-rich zones, zones of mixed sand and fine-grained sediment with intermediate organic content, and sandy organic-poor zones (table 2). Collect an equal number of samples from each zone type present in the stream reach. Where this is not possible, give priority to more dominant zone types. If collecting multiple samples from the same type of zone, zones should be as spatially separated as possible within the reach. Once a zone has been selected, delineate an approximately 1 m^2 sampling area within each zone. Collect samples from a variety of undisturbed locations within the delineated area. If this area does not provide enough material to collect both the bed-sediment and pore-water samples, expand sampling area within the bed-sediment zone. Sampling within and among sampling areas should be done in downstream to upstream order to minimize disturbance to unsampled areas.

Each sediment sample is a composite from a variety of locations within each sampling area and is analyzed for a variety of constituents. Use a core ring to collect sediment from a 0–2 cm depth. Divide collected sediment between sieved (1 mm) MeHg production- and degradation-potential (MPP and MDP, respectively) rates fraction and whole composite fraction; continue collecting sediment until the volume is sufficient to fill all jars submitted to laboratories for analysis. Primary sediment analyses include MPP and MDP rates, THg, MeHg, and reactive Hg ($Hg(II)_R$), AVS, stable C and N isotopes, and percent fines. In addition to primary analyses, most laboratories perform additional analyses for related constituents (appendix 2). Take field measurements of oxidation-reduction potential (ORP), pH, and temperature at each sampling area after sample collection and processing is completed. After sediment field measurements have been taken, measure piezometric head at each sampling area (methods described in section, "Field Measurements").

Table 2. Bed-substrate categories for classifying streambed sediment based on size and organic content.

[Modified from Fitzpatrick and others (1998). mm, millimeter; N/A, not applicable; >, greater than; ≤, less than or equal to; **bold** text indicates bed-sediment categories where samples will be collected]

Description	Size (mm)	Basic categories	Expanded categories
Smooth bedrock/concrete/hardpan	N/A	>3	1
Fine-grained; organic-rich	**N/A**	**2**	**2**
Mixed sand and fine-grained; intermediate organic content	**≤2**	**2.5**	**2.5**
Sand; organic-poor	**> 0.063–2**	**3**	**3**
Fine/medium gravel	> 2–16	>3	4
Coarse gravel	> 16–32	>3	5
Very coarse gravel	> 32–64	>3	6
Small cobble	> 64–128	>3	7
Large cobble	> 128–256	>3	8
Small boulder	> 265–512	>3	9
Large boulder/irregular bedrock/irregular hardpan/irregular artificial surface	> 512	>3	10

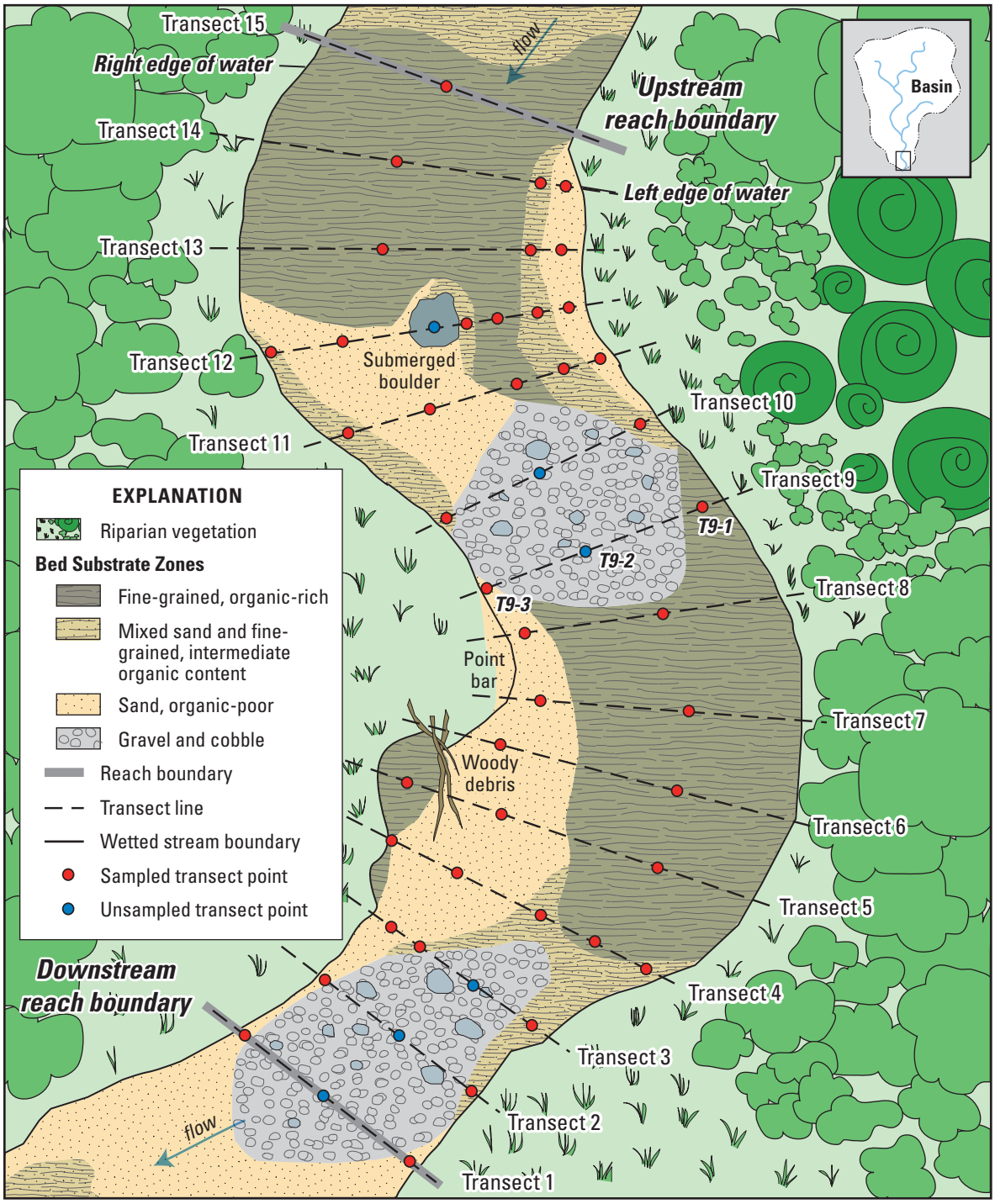


Figure 4. Diagram of simplified reach and point-sampling locations for transect sampling performed in association with reach characterization. Transect-point locations are at the cross-sectional midpoint of bed-substrate zones. Point numbering is indicated for transect 9 only; numbering strategy is identical for each transect. [T, transect number; left-most point is always 1]

Each pore-water sample is a composite from a variety of locations within each sampling area and is analyzed for a variety of constituents. Use a sipper to collect pore water in roughly equal proportions from three or more undisturbed locations within the sampling area, each at a 2 cm depth, and composite in a 500-mL Teflon® bottle. Primary pore-water analyses include THg and MeHg, DOC, nutrients, and anions. In addition to primary analyses, most laboratories perform additional analyses for related constituents (appendix 2). Immediately following sample collection, preserve water for the measurement of sulfide and take ORP measurements. Set aside additional water for pH measurements, then subsample and preserve samples for laboratory analyses. Complete measurements for pH immediately after sample preservation.

Quality-control samples are collected for both sediment and pore water during spatial sampling. One of each type of quality-control sample should be collected for every 10 regular samples collected. Sequential replicates are collected for both sediment and pore water, and are measured for all field measurements and laboratory constituents. Blanks are collected exclusively for pore water, and are measured for sulfide and all laboratory constituents.

Temporal Biogeochemical Sampling

Temporal biogeochemical sampling is performed after data from spatial sampling has been interpreted, and yields a detailed characterization of seasonal variations in sediment and pore-water constituent levels at one sampling area per stream. Select the area showing the highest MPP rate during spatial sampling and perform quarterly assessments of constituent levels for 1 year (total of five samples from each sampling area).

Use field notes from spatial sampling to locate the selected sediment-zone types, and delineate the sampling area. Note any changes that have occurred in or near the sampling area, paying particular attention to changes in sediment type. Methods for the collection of temporal sediment and pore-water samples and field measurements are the same as those used for spatial sampling.

Quality-control samples are collected for both sediment and pore water during temporal sampling. One of each type of quality-control sample should be collected for every 10 regular samples collected. Sequential replicates are collected for both sediment and pore water and are measured for all field measurements and laboratory constituents. Blanks are collected exclusively for pore water, and are measured for sulfide and all laboratory constituents. Collect blank quality-control samples during earlier sampling events, so that identified problems can be addressed.

Extrapolation of Data to the Reach Scale

Spatial sampling characterizes the geochemistry of specific zone types present in the reach, but gives little indication as to the overall abundance of a given zone type. Using transect data, biogeochemical data from specific zone types can be extrapolated to the reach scale, thereby yielding values more representative of overall stream conditions.

A variety of strategies exist for extrapolating spatial data to the reach scale; one such strategy is provided here in order to highlight details relevant to these types of calculations. To use this strategy, first develop site-specific linear regression relationships between dependent Hg variables and log-transformed LOI; for datasets containing LOI values of zero, a shift (for example, log[LOI + 1]) can be applied to allow all data to be log-transformed. For this example the Hg variables of interest will include THg and MeHg concentrations, and MPP rate. These variables can be expressed on a dry-mass basis or on a volumetric basis. Volumetric-basis Hg variables ($Y_{,vol}$) are calculated for surface (0–2 cm) sediment samples using equation 1.

$$Y_{vol} = Y \times \frac{dry\ mass}{wet\ mass} \times bulk\ density, \quad (1)$$

where

Y is the measured Hg variable in a given sample expressed on a dry-mass basis (for example, THg in ng Hg per gram, dry weight),

$dry\ mass\ /\ wet\ mass$ is mass fraction of a whole wet sediment sample that is composed of dry sediment.

For parameters containing no censored (that is, values less than the minimum detection level) values, linear regression is performed using the generalized linear model (GLM) procedure in SAS® software (release 9.1.3, SAS Institute Inc., Cary, NC). For parameters containing censored values, maximum likelihood regression is performed using the LIFEREG procedure in SAS®. For maximum likelihood regressions, r^2 values are "likelihood r^2" (Helsel, 2005). Zero-intercept regression models are used for each parameter.

Spatially-weighted THg and MeHg concentrations and MPP rates are then determined for each stream reach by applying the regression relationships to the transect LOI data collected during reach characterization. For each transect segment at which LOI is measured (that is, where material was sand or finer, including organic-rich sediment), a regression-predicted Hg variable (THg and MeHg concentration, MPP rate) is multiplied by the length of that segment. These values are then summed, and the sum is divided by the sum of all

transect lengths (equation 2). The resulting value is a spatially-weighted Hg variable, which accounts for the dependence of the Hg variable on LOI, and on the areal extent of organic matter (as measured by LOI).

$$Y = \frac{\sum Y_{pred,i} L_i}{L}, \quad (2)$$

where

Y is the spatially-weighted Hg variable,

$Y_{pred,i}$ is the Hg variable for the ith transect segment,

L_i is length of the ith transect segment, and

L is the sum of all transect lengths.

Although LOI samples are not collected from transect segments composed of material larger than sand, lengths from these segments are still included in the sum of all transect lengths; this, in effect, assigns a value of zero to Hg variables for these segments.

Standard errors of prediction, as a percentage of the spatially-weighted Hg variable (percent SE_Y), are calculated according to equation 3.

$$percent\ SE_Y = 100 \times \frac{\sum \sqrt{(L_i / L)^2 \times SE_{Y,i}{}^2}}{Y}, \quad (3)$$

where

SE_Y is the standard error of prediction of the spatially-weighted Hg variable,

$SE_{Y,i}$ is the standard error of prediction of $Y_{pred,i}$, and the remaining parameters are defined in equation 1.

Hg values also can be expressed on an areal basis. In order to do this, volumetric-basis Hg variables are used in the regression analysis, and the resulting, spatially-weighted value (Y) is multiplied by: 2 cm × 10,000 cm^2/m^2 × 0.001 µg/ng, where the interval of surface sediment sampled is 0–2 cm.

Sample Collection

Though the purpose and strategy of the components of the detailed Hg studies differ, the methodologies for sample collection are the same.

Bed Sediment

Surface sediment (0–2 cm depth) is collected during all components of the detailed Hg studies using a polycarbonate core ring that is 2 cm deep and 8 cm in diameter (fig. 5). Press the core ring into the sediment until the top edge is flush with the sediment/water interface, and then gently scoop away sediment downstream of the core ring. Insert a stiff plastic sheet under the bottom of the core ring where the downstream sediment has been removed, and gently slide it under the core ring (keeping it flush with the core-ring bottom). Slowly lift the resulting patty and transfer the sediment to appropriate containers for compositing. In situations where streamflow velocity is sufficiently fast to disturb or erode fine sediment from the core during transport through the water column, place a second plastic sheet on the core ring before lifting.

Pore Water

Pore water is sampled during both the spatial and temporal components of the detailed Hg studies. Pore water is collected by inserting a vented Teflon® probe into the sediment to the desired depth and pulling surrounding pore water through the vents (fig. 6). The attachment of an acrylic disc 2 cm from the vents minimizes the flow of stream water into the sampled area. Pore water is pulled through the probe and attached Teflon® tube using a peristaltic pump fitted with C-flex tube (Cole-Parmer). After flowing through the C-flex tube, pore water moves through a short section of Teflon® tube and into an in-line Teflon® filter cartridge with a pre-combusted quartz-fiber filter (47-mm diameter, 0.7-µm nominal pore size). The C-flex and Teflon® (short section) tube are secured together with a cable tie to prevent separation under pressure. All Teflon® and C-flex components are acid cleaned in the WMRL and double bagged in Ziploc® bags prior to use.

When collecting a pore-water sample, place the acrylic disc flat on the surface of the sediment and insert the probe perpendicular to the sediment surface. Carefully hold the probe and acrylic disc in place. Movement of the probe can introduce channels for the influx of stream water, and should be prevented.

With the probe deployed, but prior to connecting the in-line filter, pump pore water at a low flow rate; this allows an initial slug of sediment to evacuate the line. After the water runs fairly clear, attach the filter to the short section of Teflon® tube. Hold the filter cartridge upright to purge the air from the filter, and then allow it to flush with a few milliliters of water; each composite sample collected may require multiple filters, and each time a new one is used it should be conditioned in this manner. Pumping depletes pore water in the desired depth increment, inducing infiltration of both deeper pore water and stream water to the sampling zone. To minimize this effect, pump pore water through the sampling apparatus at a slow rate.

Filtered pore-water samples are collected into a clean 500-mL Teflon® bottle. Inside each 500-mL bottle is a small volume of dilute hydrochloric acid (HCl). Pour acid off into a waste acid container, and rinse the bottle three times with small aliquots of filtered pore water from the sampling area before collecting the sample. Continue collecting sample water until the 500-mL Teflon® bottle is completely full. The probe should be deployed multiple times to collect a single sample, due to the depleting effect of pumping on pore water and the large volume of pore water required for these samples. Each time the probe is deployed, remove the filter and allow the sediment plug to evacuate the line before replacing it.

Figure 5. Surficial-sediment sample collected using a core (2 centimeters deep and 8 centimeters in diameter) and a stiff plastic sheet. (Photograph by Dennis Wentz, U.S. Geological Survey, June 2003.)

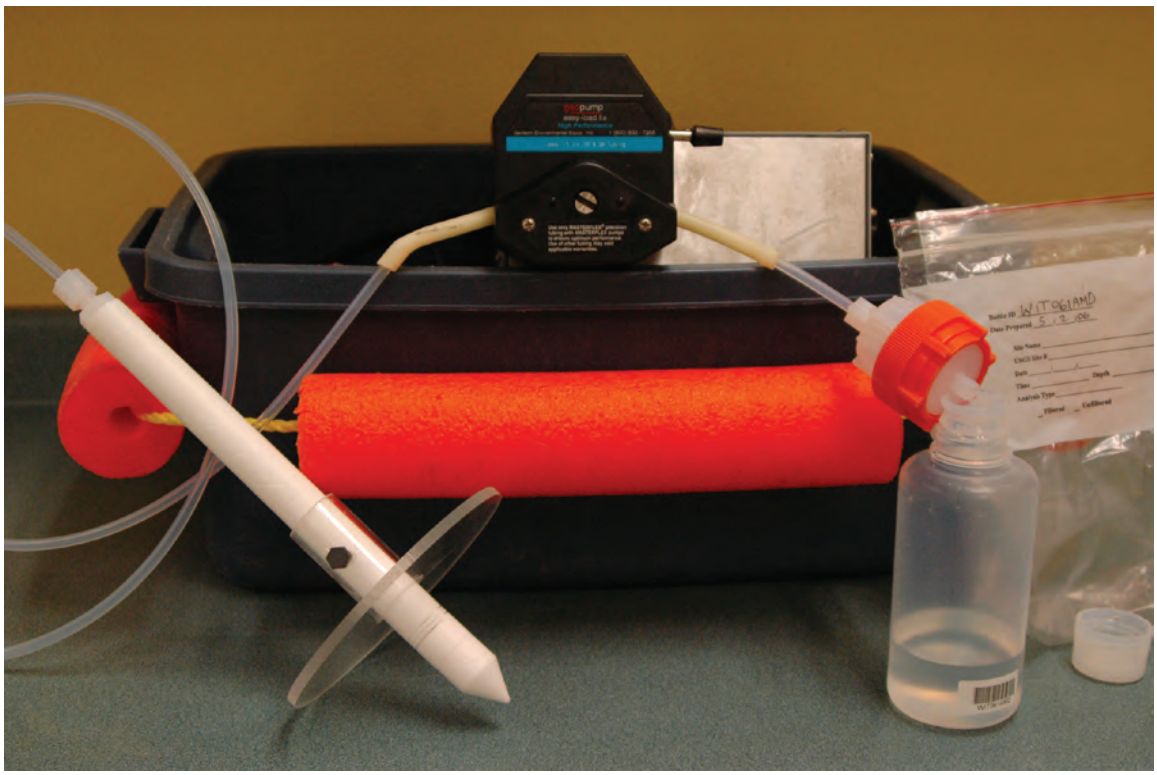


Figure 6. Pore-water sampling equipment and compositing bottle. (Photograph by Michelle Lutz, U.S. Geological Survey, May 2006.)

Most of the vials submitted for ancillary analyses are filled from this composite; the only exception is the anion vial. Fill anion samples directly from the sampling line to bypass the effects of the Teflon® bottle's recent exposure to dilute HCl.

Sample Processing

Immediately following sample collection, time-sensitive field measurements should be performed; then samples should be processed at a clean, stable workspace. Sample processing entails the subsampling and preserving of samples in preparation for laboratory analysis.

Bed Sediment

Although sample-collection methods are the same for all components, differences in purpose and strategy between components call for variations in processing methods.

Reach Characterization

During reach characterization, point samples are collected along transects at the midpoints of each substrate zone that consists of sand or finer sediment. Sediment from each collected zone is divided between two jars: one for LOI and one for percent fines. Additional sediment is discarded into the stream. LOI samples are frozen immediately. Samples to be analyzed for percent fines are stored at ambient temperature in a cool, dark location. Both LOI and percent fines samples can be held until all streams have been sampled, and then shipped to the appropriate laboratories (appendix 6).

Spatial and Temporal Biogeochemical Sampling

Bed-sediment samples collected for the spatial and temporal biogeochemical-sampling components are divided between sieved (1 mm) fractions for determination of MPP and MDP rates (approximately 7/8 of each patty) and whole composite fractions (approximately 1/8 of each patty). Bed sediment in both fractions are processed immediately after collection.

Sieve samples for assays of MPP and MDP rates using a 10×10 cm piece of 1-mm nylon mesh sieve. Attach the sieve to the top of a half-pint mason jar with the brass lid-ring; a 250-mL plastic beaker with the bottom removed is secured upside-down to the top of the mason jar (fig. 7). Deposit a small amount of sediment in this enclosure, and tamp with a flat-bottomed acid-cleaned plastic bottle to sieve the sediment less than 1 mm into the mason jar. To minimize entrainment of air and unwanted changes in reduction-oxidation conditions, fill the half-pint jar to the top with sieved sediment and pore water. Remove brass lid-ring and mesh, and remove sediment from the threads of the jar using a Kimwipe®; then cap with the mason lid and secure with the cleaned brass lid-ring. Wrap Parafilm M® around the lid to seal it. Label the jar, place it into a foam sleeve, and seal it inside a Ziploc® bag. Samples for determination of MPP and MDP rates are stored on wet ice or in a refrigerator and should be shipped to the laboratory as soon as possible (optimally within 24 hours) after sampling.

Composite the unsieved portion of the sample into a 120-mL polypropylene jar and briefly stir with a clean Teflon®, plastic, or glass device, taking care not to entrain excessive air into the sample. Subsample sediment (using a clean plastic spoon, a 10 cm^3 plastic syringe with the barrel end cut off, or by pouring) into four jars for (1) THg, MeHg, and $Hg(II)_R$; (2) AVS; (3) stable C and N isotopes; and (4) percent fines analysis. Leave approximately 20 to 30% of total volume of the jars as headspace to allow room for expansion upon freezing. Both Hg and AVS samples are frozen immediately (preferably by placing in a cooler containing dry ice). Stable C and N isotope samples are stored on wet ice or in a refrigerator. Samples to be analyzed for percent fines are stored in a cool, dark location. All samples are considered preserved at this point, and are shipped to respective laboratories once all streams have been sampled (appendix 6).

Pore Water

Pore-water samples are collected from a 2-cm depth and composited in a 500-mL Teflon® bottle. Once the Teflon® bottle is completely full, rinse the anion vial and fill it with filtered pore water taken directly from the sampling line. Decant pore water from the Teflon® bottle into vials for all field measurements; preserve water for sulfide measurements and measure ORP immediately after sample collection. Set aside water for pH measurements. Decant pore water into vials for DOC and nutrient analyses; the DOC vial is filled without rinsing, and the nutrient vial is rinsed with small aliquots of composite water prior to filling. Preserve remaining composite water to a final volume of 1% HCl to preserve for THg and MeHg analysis. Store DOC and anion samples on wet ice, the nutrient sample on dry ice, and the preserved THg and MeHg sample in a cool, dark location. Complete measurements for pH immediately after sample preservation, and submit samples to respective laboratories once all streams have been sampled (appendix 6).

Field Measurements

Field measurements taken at the time of sampling provide ancillary data that describe general media conditions (table 1). Prior to each day's sampling, perform calibrations and checks for all instrumentation used, and record on field sheets. Techniques for calibration are outlined in the USGS National Field Manual (Wilde, variously dated), and manufacturer documentation.

Figure 7. Surficial-sediment core being deposited into the methylmercury production- and degradation-potential-rates sampling apparatus. (Photograph by Dennis Wentz, U.S. Geological Survey, June 2003.)

Stream Water

Stream-water field measurements are collected each day that samples are collected (table 1). Measure pH, specific conductance, dissolved oxygen, and temperature as outlined in the USGS National Field Manual (Wilde, variously dated). Obtain streamflow measurements from a nearby USGS gaging station, or determine manually, in accordance with Rantz and others (1982).

Bed Sediment

Bed-sediment field measurements are taken for each composite sample collected for the spatial and temporal geochemistry components of the detailed studies (table 1). Measurements of interest are ORP, pH, and temperature; each measurement should be performed in replicate.

Oxidation-Reduction Potential

The electrode used in the measurement of ORP is a refillable electrode (Orion® model 9180BN), and is therefore not amenable to submersion. Calibration of ORP instrumentation is performed in the laboratory, and is checked using the standard solution provided with the electrode, according to manufacturer instructions. If the ORP reading is outside of the allowable range (determined by the manufacturer) in the field, maintain the electrode according to manufacturer instructions or replace with a working electrode. Take measurements by retrieving a patty of sediment from the sampling area (using the same method as was used in sample collection) and inserting the electrode to the desired depth. Alternatively, to minimize exposure to oxygen, fill scintillation vial 2/3 of the way full with sediment from the patty, insert the electrode and wrap intersection with Parafilm M®. Readings likely will not completely stabilize; regardless of the method, record values quickly after insertion, as the ORP of the sediment changes quickly once exposed to air.

pH and Temperature

The instrumentation used in the measurement of pH and temperature is a low-maintenance pH triode (Orion® model 9107BN) with an automatic temperature compensator. Calibrate for pH according to manufacturer instructions. Temperature is calibrated by laboratory personnel and need not be verified in the field. The low-maintenance triode is sealed, which allows it to be submerged for the collection of *in situ* measurements. Alternatively, measurements may be taken by retrieving a patty of sediment from the sampling area (using the same method as was used in sample collection). If the temperature is measured in a sediment patty, rather than *in situ*, measure the temperature immediately while shielding the sample from direct sunlight to minimize heating. Regardless of the method used, insert the electrode to the desired depth and allow it to equilibrate until stable readings are obtained.

Pore Water

Pore-water field measurements are collected for each pore-water sample collected (table 1). Measurements of interest are sulfide, ORP, and pH.

Sulfide

Sulfide is measured using a refillable, silver/sulfide combination electrode (Orion® model 9616BN). It is shipped from the laboratory evacuated of filling solution. Approximately 12 hours before sampling, fill the electrode with the solution provided, then replace tape over the filling hole and cap the end for storage. Before each day's sampling, pour the premeasured ascorbic acid into the premeasured sulfide antioxidant buffer (SAOB) (Brouwer and Murphy, 1994), cap, and mix; then pour the mixture into the ascorbic acid vial, cap and mix. Finally, pour the mixture back into the SAOB container and let it sit for 10 minutes before using. The SAOB solution stabilizes sulfide in the samples for up to 24 hours, although measuring the samples as soon after collection as possible is recommended. Sulfide calibrations are done in the sulfur geochemistry laboratory, Reston, Va., before and after each field trip. Calibrations are conducted using serial dilutions of a sodium sulfide stock solution. The exact concentration of the sodium sulfide stock solution is determined by titration with a lead nitrate standard. Experience has demonstrated that the calibrations remain stable for at least several weeks, and changes in calibration curves for a given electrode vary only slightly over a year (W. Orem, U.S. Geological Survey, written commun., 2006).

Using the provided syringe, prepare scintillation vials (20-mL) containing 3 mL of the SAOB-ascorbic acid mixture. The number of scintillation vials prepared should equal the number of pore-water samples to be collected. Store the electrode in the remaining solution while not in use, including overnight.

Sulfide is unstable until it is placed in the SAOB-ascorbic acid mixture. Therefore, immediately after sample collection, deposit 3 mL of pore water into a scintillation vial containing the premeasured SAOB-ascorbic acid mixture, cover, and shake briefly to mix. The preserved sulfide sample should be labeled, stored in a dark place, and measured within 24 hours of collection.

To measure sulfide, remove the electrode from the SAOB-ascorbic acid mixture, rinse it with deionized (DI) water, dry, and uncover the filling hole. Stir the preserved sample gently using a Teflon®-coated magnetic stir bar (12.7-mm length). Lower the electrode into the sample. If the sample is below detection limit (-700 mV), the reading will not stabilize, and the electrode should be kept in the sample for 5 to 10 minutes. If the sample is above detection limit, the value will become stable much faster. Record the meter response in millivolts. Between samples, rinse the electrode with DI water and blot dry.

Once all sampling has been completed, rinse the electrode inside and out with DI water, drain, cover the filling hole with tape, replace the cap, and ship back to the sulfur geochemistry laboratory in Reston, Va.

ORP

Pore-water ORP is measured using a refillable glass microelectrode (Microelectrodes, Inc. model MI-800/710). The microelectrode is stored in a glass sheath containing a sponge moistened with DI water. Each day that field measurements are collected, move the sleeve away from the filling hole and check the calibration using the standard solution provided with the electrode, per manufacturer instructions. If the instrumentation reads outside of the allowable error (determined by the manufacturer), clean the metal tip of the electrode with a Kimwipe®. If it continues to read outside of the allowable error, a different electrode should be used.

ORP is unstable and should be measured immediately after preserving the sulfide sample. To measure, pour a small amount of water from the composite sample into a clean scintillation vial. From the vial, draw water into a clean syringe that has been fitted with a short piece (approximately 5 cm) of plastic tube, then expel air slowly from the syringe and tube, and place the electrode partially into the tube. Taking care not to get the filling hole wet, expel the water from the syringe past the electrode, noting mV readings. Readings will jump around as water pushes past the electrode; record the approximate median reading, paying particular attention to the readings from the last milliliter in the syringe. ORP readings should be taken in replicate.

Equipment used for ORP readings can be reused. Between samples, remove sample water; there is no need to rinse equipment or electrode. Blot the electrode dry, replace the stopper, and return to the glass sheath.

pH

The electrode used to measure pore-water pH is the same low-maintenance triode (Orion® model 9107BN) that is used in the collection of sediment field measurements. To collect the pH measurement, pour a small amount of pore water from the composite bottle into the same scintillation vial used for the ORP readings, and set aside; measurements should be taken immediately following sample processing. To measure, place the electrode in the water and record the value when stabilized. Readings should be taken in replicate.

Piezometric Head

Piezometric-head measurements can be used to indicate whether the stream is potentially gaining or losing water to the hyporheic zone in the sampling area. Piezometric head is measured using a transparent (clear plastic) minipiezometer fitted to a stainless steel point; this apparatus is driven vertically into the sediment at a number of points in the sampling area. Insert the minipiezometer properly to the appropriate depth, then remove the metal sheath and apply a slight vacuum to the plastic tube. Leave open to the atmosphere. The water level in the tube equilibrates to a level corresponding to the pressure (head) in the hyporheic zone. Using a metric ruler, measure the difference (in millimeters) between the stream-water surface and the water surface in the tube and record value. If the water in the tube is above the stream-water surface, record the value as a positive number. If the water in the tube is below the stream-water surface, record the value as a negative number.

References Cited

Agency for Toxic Substances and Disease Registry, 1999, Toxicological profile for mercury (update): Atlanta, Ga., U.S. Department of Health and Human Services, Public Health Service, [656] p.

Brigham, M.E., Krabbenhoft, D.P., and Hamilton, P.A., 2003, Mercury in stream ecosystems—New studies initiated by the U.S. Geological Survey: U.S. Geological Survey Fact Sheet 016–03, 4 p.

Brouwer, H., and Murphy T.P., 1994, Diffusion method for the determination of acid-volatile sulfides (AVS) in sediment: Environmental Toxicology and Chemistry, v. 13, p. 1273–1275.

Brumbaugh, W.G, Krabbenhoft, D.P., Helsel, D.R., Weiner, J.G., and Echols, K.R., 2001, A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients—bioaccumulation in fish: U.S. Geological Survey Biological Science Report 2001–0009, 25 p.

Drevnick, P.E., and Sandheinrich, M.B., 2003, Effects of dietary methylmercury on reproductive endocrinology of fathead minnows: Environmental Science and Technology, v. 37, no. 19, p. 4390–4396.

Evers, D.C., 2005, Mercury connections—The extent and effects of mercury pollution in Northeastern North America: Biodiversity Research Institute, Gorham, Maine, 28 p.

Fitzpatrick, F.A., Waite, I.R., D'Arconte, P.J., Meador, M.R., Maupin, M.A., and Gurtz, M.E., 1998, Revised methods for characterizing stream habitat in the National Water-Quality Assessment Program: U.S. Geological Survey Water Resources Investigations Report 98–4052, 67 p.

Fleming, E.J., Mack, E.E., Green, P.G., and Nelson, D.C., 2006, Mercury methylation from unexpected sources—Molybdate-inhibited freshwater sediments and iron-reducing bacterium: Applied and Environmental Microbiology, v. 72, no. 1, p. 457–464.

Förstner, U., and Wittmann, G.T.W., 1981, Metal pollution in the aquatic environment: New York, Springer-Verlag, 486 p.

Frissell, C.A., Liss, W.J., Warren, C.E., and Hurley, M.D., 1986, A hierarchical framework for stream habitat classification—Viewing streams in a watershed context: Environmental Management, v. 10, p. 199–214.

Gilliom, R.J., Hamilton, P.A., and Miller, T.L., 2001, The National Water-Quality Assessment Program—Entering a new decade of investigations: U.S. Geological Survey Fact Sheet 071–01, 6 p.

Gilmour, C.C., Henry, E.A., and Mitchell, R., 1992, Sulfate stimulation of mercury methylation in freshwater sediments: Environmental Science and Technology, v. 26, p. 2281–2287.

Grigal, D.F., 2002, Inputs and outputs of mercury from terrestrial watersheds—A review: Environmental Reviews, v. 10, no. 1, p. 1–39.

Hammerschmidt, C.R., Sandheinrich, M.B., Wiener, J.G., and Rada, R.G., 2002, Effects of dietary methylmercury on reproduction of fathead minnows: Environmental Science and Technology, v. 36, no. 5, p. 877–883.

Helsel, D.R., 2005, Nondetects and data analysis—Statistics for censored environmental data: New York, John Wiley & Sons, 266 p.

Horowitz, A.J., and Elrick, K.A., 1987, The relation of stream sediment surface area, grain size, and composition to trace element chemistry: Applied Geochemistry, v. 2, p. 437–451.

Krabbenhoft, D.P., Weiner, J.G., Brumbaugh, W.G., Olson, M.L., DeWild, J.F., and Sabin, T.J., 1999, A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—proceedings of the technical meeting, Charleston, S.C., March 8–12, 1999: U.S. Geological Survey Water-Resources Investigations Report 99–4018B, p. 147–159.

Lambertsson, L., and Nilsson, M., 2006, Organic material—the primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments: Environmental Science and Technology, v. 40, p. 1822–1829.

Leopold, L.B., Wolman, M.G, and Miller, J.P., 1964, Fluvial processes in geomorphology: San Francisco, W.H. Freeman and Company, 522 p.

Nriagu, J.O., 1979, The biogeochemistry of mercury in the environment: Elsevier/North Holland, Biomedical Press, 696 p.

Rantz, S.E., and others, 1982, Measurement and computation of streamflow—Volume 1—Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.

Ravichandran, M., 2004, Interactions between mercury and dissolved organic matter—A review: Chemosphere, v. 55, p. 319–331.

Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–458, 20 p.

Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A., and Brezonik, P.L., 1992, Increasing rates of atmospheric mercury deposition in midcontinental North America: Science, v. 257, p. 784–787.

Terraserver-USA, 2008, Orthophotos: accessed August 1, 2008, at http://www.terraserver-usa.com/

U.S. Environmental Protection Agency, 1996, Method 1669—Sampling ambient water for trace metals at EPA water quality criteria levels: EPA–821/R–96–008, 36 p.

U.S. Environmental Protection Agency, 1997, Mercury study report to Congress volume III—fate and transport of mercury in the environment: EPA–452/R–97–005, [359] p.

U.S. Environmental Protection Agency, 2002, Method 1631, Revision E—Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry: EPA–821–R–02–019, 38 p.

U.S. Environmental Protection Agency, 2007, 2005/2006 National listing of fish advisories: U.S. Environmental Protection Agency Fact Sheet EPA–823–F–07–003, 7 p.

U.S. Geological Survey, 2006, User's manual for the National Water Information System of the U.S. Geological Survey Water-Quality System (ver. 4.4): U.S. Geological Survey Open-File Report 2006–1145, 372 p.

Virtanen, J.K., Voutilainen, S., Rissanen, T.H., Mursu, J., Tuomainen, T.-P., Korhonen, M.J., Valkonen, V.-P., Seppänen, K., Laukkanen, J.A., and Salonen, J.T., 2005, Mercury, fish oils, and risk of acute coronary events and cardiovascular disease, coronary heart disease, and all-cause mortality in men in eastern Finland: Arteriosclerosis, Thrombosis, and Vascular Biology, v. 25, p. 228–233.

Weiner, J.G., Krabbenhoft, D.P., Heinz, G.H., and Scheuhammer, A.M., 2003, Ecotoxicology of mercury, *in* Hoffman, D.J., and others, eds., Handbook of ecotoxicology (2d ed.): Boca Raton, Fla., CRC Press, p. 407–461.

Wilde, F.D., ed., variously dated, Field measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, accessed August 1, 2008, at http://pubs.water.usgs.gov/twri9A6

Wilde, F.D., ed., April 2004, Cleaning of Equipment for water sampling (version 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A3, accessed August 1, 2008, at http://pubs.water.usgs.gov/twri9A3

U.S. Geological Survey, September 2006, Collection of water samples (version 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed August 1, 2008, at http://pubs.water.usgs.gov/twri9A4

Appendix 1. Method Summary Sheets

Appendix 1a. Method summary sheets: reconnaissance studies.

Sampling strategy

1. **Advanced preparation for sampling**
    a. Personnel familiarize themselves with sampling techniques presented by Shelton and Capel (1994)
    b. Procure proper sampling equipment
        - Acceptable streambed-sediment collection devices
            - Guillotine sampler (Shelton and Capel, 1994)
            - An approximately 10-cm section of 1.5-in.-diameter Teflon® tube (modified piece of the guillotine sampler) (Shelton and Capel, 1994)
            - Teflon® spoon, scoop, or spatula sampler (Shelton and Capel, 1994)
            - Other plastic spoons/scoops are suitable
                - Plastic scoops can be formed by cutting a plastic sample bottle
        - Additional equipment required for unwadeable streams
            - Birge-Ekman grab sampler (9-in. square)
        - Acceptable bed sediment compositing containers include glass, Teflon®, or other plastic bowl, tub, or pail
    c. Clean glass, Teflon® and plastic equipment according to trace-element cleaning methods (Shelton and Capel, 1994; Wilde, 2004)
2. **Prepare for field measurements**
    a. Before each day's sampling prepare equipment for field measurements
        - Record all calibrations on field sheets
        - SW field measurements
            - pH, specific conductance, dissolved oxygen (DO), and temperature
                - Calibrate multiparameter meter according to manufacturer instructions
            - Streamflow
                - Either
                    – Verify rated gage is working properly
                    – Verify proper operation of equipment used for direct measurement, according to Rantz and others (1982) and manufacturer instructions
    b. Collect SW field measurements the same day as bed-sediment sample collection
3. **Sampling overview**
    a. Target time
        - 30 minutes for collection and processing (that is, subsampling and preserving) of bed-sediment samples
    b. Collect and process each sample as quickly as possible to minimize oxidation of sulfide in sediment samples
4. **Bed-sediment sampling**
    a. Regular samples
        - Depth: top 2 cm (approximately)
        - Sample type: composite
        - Analyses:
            - Total mercury (THg) and methylmercury (MeHg)
            - Acid-volatile sulfide (AVS)
            - Percent fines
        - Collection strategy
            - Identify depositional zones for sampling
                - Number of zones should be between 5 (minimum) and 10 (optimal)
                    – Collect sediment from as many zones as possible, keeping target time in mind
                - Spatially separated throughout the stretch of stream sampled

Appendix 1. Method summary sheets—Continued

Appendix 1a. Method summary sheets: reconnaissance studies—Continued.

Sampling strategy (continued)

- Sampling location
  - Undisturbed sediment
  - Collect sediment from several locations within each zone
- Collect sediment (top 2 cm depth, approximately)
  - Directly from streambed
  - Where stream is too deep to collect sediment directly from streambed, use a 9-in. Birge-Ekman grab sampler
    - Retrieve sediment
    - Collect sediment for sample from the surface (top 2 cm, approximately) of the retrieved sediment
    - Avoid areas near/in contact with metal surfaces
- Deposit collected sediment into composite container
  - Target volume: 120 mL
  - Remove woody debris, rocks, and other large items from the sample
  - Process sample immediately after collection to minimize oxidation of sulfide

b. Quality-control samples

- Replicates
  - Type: split
  - Frequency: 1 replicate for every 8 sites sampled
  - Analyses: all laboratory analyses performed for regular samples

Sample collection

1. **Bed-sediment-sample collection**

a. Variety of equipment (and therefore techniques) are acceptable

- Work an approximately 10-cm section of Teflon® tube (1.5-in.-diameter) horizontally across the upper 2 cm of sediment
- Scoop up the top 2 cm of sediment using a spatula or scoop

b. Decant water

c. Deposit into container (bowl, tub, or pail) for compositing

Sample processing

1. **Bed-sediment-sample processing**

a. Mix sediment by stirring the sample

- 30 to 60 seconds
- Try not to entrain air into sample

Appendix 1. Method summary sheets—Continued.

Appendix 1a. Method summary sheets: reconnaissance studies—Continued.

Sample processing (continued)

b. Place sediment in jars using a plastic spoon or Teflon® policeman
- Leave headspace of approximately 20 to 30 percent of container volume (for expansion upon freezing)
- Fill jars for analyses:
  - Total mercury (THg) and methylmercury (MeHg)
    - 30-mL polypropylene jar (acid-rinsed)
    - Store on dry ice/in freezer
    - Ship
      - Timing: once all streams have been sampled
      - To: Wisconsin Mercury Research Laboratory (WMRL)
      - Conditions: dry ice
  - Acid-volatile sulfide (AVS)
    - 30-mL polypropylene jar (not acid-rinsed)
    - Preserve immediately
      - Add 0.3 mL of zinc-acetate solution to the sediment using a disposable pipet
        - Pipets are graduated at 0.1-mL increments
      - Stir sample well with disposable pipet
    - Store on dry ice/in freezer
    - Ship
      - Timing: once all streams have been sampled
      - To: Sulfur geochemistry laboratory
      - Conditions: dry ice
  - Percent fines
    - 30-mL polypropylene jar (not acid-rinsed)
    - Store at ambient temperature in a cool, dark location (don't freeze)
    - Ship
      - Timing: once all streams have been sampled
      - To: Sediment laboratory
      - Conditions: ambient temperature (cool, dark location)

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies.

Sampling strategy

Reach characterization: establishing a reach

1. **Prepare for field measurements**
    a. Before each day's sampling prepare equipment for field measurements
        - Record all calibrations on field sheets
        - Stream-water (SW) field measurements
            - pH, specific conductance, dissolved oxygen (DO), and temperature
                - Calibrate multiparameter meter according to manufacturer instructions
            - Streamflow
                - Either
                    – Verify rated gage is working properly
                    – Verify proper operation of equipment used for direct measurement, according to Rantz and others (1982) and manufacturer instructions
2. **Collect SW sample and field measurements**
    a. Collect routine SW sample and field measurements the same day as streambed-sediment sample collection
        - SW samples are collected before any other personnel have entered the stream to minimize sample bias caused by disturbance/suspension of sediment
3. **Determine reach length**
    a. Use measuring tape or rangefinder to determine wetted-channel width in three representative locations
    b. Calculate mean wetted-channel width (MCW)
    c. Multiply MCW by 20 to determine reach length
        - Wadeable reaches must be ≥ 150 m in length
        - Unwadeable reaches must be ≥ 500 m in length
4. **Determine reach boundary locations**
    a. Reaches are relatively homogenous lengths of stream and should not contain
        - Substantial changes in
            - Streamflow
            - Water quality characteristics
            - Basin characteristics
        - Major hydrologic discontinuities (for example, waterfalls)
    b. Determine reach location
        - Locate reach in an area that includes two examples each of two geomorphic channel units (GCUs) that are representative of the overall GCU sequence in the stream (distinct GCUs occupy 50% or more of the stream width)
            - Where abundance of GCUs is insufficient, locate reach in area where GCU sequence reflects overall stream characteristics
        - Locate reach upstream or adequately downstream of hydraulic effects resulting from man-made disturbances
    c. Place first reach boundary:
        - If stream has distinct, sequential GCUs
            - 0.5 × (MCW) from border between two GCUs
        - If stream has no distinct, sequential GCUs
            - 10 × (MCW) from reference location (for example, bridge or gage)
5. **Determine, flag, and georeference transect locations**
    a. Measure distance from reference location (for example, bridge or gage) to closest reach boundary and mark with appropriate flag (that is, Transect 1 for downstream boundary, Transect 15 for upstream boundary)

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

b. Determine distance between transects:
Reach length/14 = distance between each of the 15 transects
c. Flag transects on both sides of stream with numbered stake flags
    - Orient transects perpendicular to the flow
    - When flagging, try to avoid being in the water/disturbing the sediment
    - Flag from upstream to downstream (Transect 15 to Transect 1)
        - This positions personnel to begin sampling from downstream to upstream
d. Georeference reach boundary transects using Global Positioning System (GPS) unit
    - Locations to reference (directionality is assigned while facing downstream)
        - Upstream reach boundary transect (Transect 15)
            - Left edge of water (LEW)
            - Right edge of water (REW)
        - Downstream reach boundary transect (Transect 1)
            - LEW
            - REW
    - Engage features
        - Wide Area Augmentation System (WAAS)
        - Time-averaging
        - External antenna
    - Allow unit to average for 30 minutes in each location
    - Record
        - Location in degrees/minutes/seconds
        - Datum (North American Datum of 1983 (NAD 83) preferred)
        - Accuracy (with units)
e. Georeference remaining transects using GPS unit
    - Location to reference at each transect
        - LEW
    - Engage features
        - WAAS
        - External antenna
    - Take instantaneous reading
    - Record
        - Location in degrees/minutes/ seconds
        - Datum (NAD 83 preferred)
        - Accuracy (with units)

Reach characterization: transect sampling strategy

1. **Mapping and sampling overview**
    a. Target time
        - No specific time limit
    b. Map bed-substrate zones and collect samples from downstream to upstream, by transect
    c. Samples are processed (that is, subsampled and stored at appropriate temperatures) as they are collected; no additional processing is required

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

2. **Map bed-substrate zones**
    a. Decide whether to use basic or expanded substrate categories (table 2)
        - Basic is recommended
    b. Extend measuring tape across stream at transect location
        - Distance along tape should increase from LEW to REW
        - Anchor each end of the measuring tape with a stake
    c. Classify substrate zones into defined categories
        - Start at the LEW and proceed across stream
        - Basic categories for classification (table 2)
            - Fine-grained, organic-rich (category 2)
            - Mixed sand and fine-grained, intermediate organic content (category 2.5)
            - Sand, organic-poor (category 3)
            - Other (category >3)
        - Categorize substrates
            - Obtain sediment directly from streambed for assessment
                - Visual assessment
                - Tactile assessment
                - Partitioning through 0.063-mm sieve
                - (For expanded categories, use meterstick for additional size assessments)
            - Alternatives for where stream is too deep to collect sediment directly from streambed for assessment
                - Tap a polyvinyl chloride (PVC) pipe against the substrate to estimate substrate category
                    – To prepare
                        - In shallow areas where substrates are easily classified, note characteristic responses of the pipe to different bed substrates
                    – Pipe responds differently to different substrates
                        - Larger substrates (table 2, category >3)
                            - Bounce back quickly
                            - Change course
                        - Finer substrates (table 2, categories 2, 2.5, and 3)
                            - Pipe will stop slowly/show resistance
                - Retrieve sediment using a 9-in. Birge-Ekman grab sampler
                    – Visual assessment
                    – Tactile assessment
                    – Partitioning through 0.063-mm sieve
    d. Record boundaries of bed substrate zones
        - Record position of the LEW on measuring tape
        - Proceed along transect toward the REW
            - For each bed substrate zone
                - Record position of right edge of zone on measuring tape
                - Determine width of zone
                - Collect bed-sediment samples, where appropriate
        - Record position of the REW on measuring tape
        - Determine wetted width of stream (that is, the distance between the LEW and the REW)

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

3. **Collect transect samples**
    a. Regular samples
        - Sample type
            - Surface sediment
                - Depth: 0–2 cm
                - Sample type: grab
                - Analyses: loss on ignition (LOI) and percent fines
        - Sampling location
            - Bed-substrate zones in categories 2, 2.5, and 3 (table 2)
            - Position at the midpoint of that zone
            - Undisturbed sediment
            - Record position of sampling location on measuring tape
        - Sampling strategy
            - Collect sediment sample (0–2 cm depth), as patty
                - Directly from streambed
                - Where stream is too deep to collect sediment directly from streambed, use a 9-in. Birge-Ekman grab sampler
                    - Retrieve sediment
                    - Take a 0–2 cm patty from the surface of the retrieved sediment
                    - Avoid areas near/in contact with metal surfaces
            - Divide each patty between jars for analysis
                - LOI
                - Percent fines
            - Store jars at appropriate temperatures immediately
            - Discard remaining sediment into stream
    b. Quality-control samples
        - Replicates
            - Type: sequential
            - Frequency: 1 replicate transect for every 10 transects sampled
            - Analyses: LOI and percent fines
            - Details:
                - After completion of transect sampling, randomly select transects for replicate sampling (for example, by selecting numbers out of a hat)
                - Note widths of bed-substrate zones, as was done during collection of regular sampling
                - Collect sediment at the midpoints of bed-substrate zones in categories 2, 2.5, and 3
                    - Undisturbed sediment
                    - If sediment is disturbed (likely), shift sampling location slightly within zone

4. **Document sample information**
    a. Key sample identification information
        - Station-identification number (STAID)

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Date
- Mean sample time
  - Samples of the same medium collected from the same stream site on the same day are distinguished from each other on the basis of mean sample time in the National Water Information System (NWIS) database
- Medium code
  - "H" for regular samples
  - "W" for replicate samples

b. Fill out all sample labels

c. Fill out forms
- Field forms
  - Fill out all field forms completely in the field
  - Draw map of stream reach
    - Use orthophotos and topographic maps to assist in drawing stream
      - http://www.terraserver-usa.com/
    - Draw and label each transect
    - Record stream and riparian features
    - Indicate position of reference location (for example, bridge/gage)
      - Record distance from nearest reach boundary to reference location
    - Indicate flow direction
    - Draw any other distinguishing features that will assist in reestablishing that same reach again
- Shipping forms
  - Shipping forms may be filled out in the office, prior to shipping samples

d. Verify that all labels and forms are in agreement regarding key sample-identification information

Spatial biogeochemical sampling: preparation and sampling area selection

1. **Prepare for field measurements**

a. Approximately 12 hours before sample collection
- Fill sulfide electrode with filling solution provided
- Replace tape over filling hole
- Cap the end

b. Before each day's sampling prepare equipment for field measurements
- Record all calibrations and calibration checks on field sheets
- SW field measurements
  - pH, specific conductance, dissolved oxygen (DO), and temperature
    - Calibrate multiparameter meter according to manufacturer instructions
  - Streamflow
    - Either
      - Verify rated gage is working properly
      - Verify proper operation of equipment used for direct measurement, according to Rantz and others (1982) and manufacturer instructions

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Sulfide
  - Sulfide is calibrated by laboratory personnel and need not be verified in the field
  - Prepare sulfide antioxidant buffer (SAOB)-ascorbic acid mixture
    - Pour premeasured ascorbic acid into the premeasured SAOB, cap, and mix
    - Pour mixture into the ascorbic acid vial, cap, and mix
    - Pour mixture back into the SAOB container
    - Let mixture sit 10 minutes
    - Use syringe to distribute 3 mL of the mixture to each of a number of 20-mL scintillation vials
      - Number of scintillation vials should equal the number of pore-water samples to be collected
    - Store electrode in mixture when not in use
- Oxidation-reduction potential (ORP) calibration checks
  - Sediment
    - Remove plug from filling hole
      - Verify levels of filling solution in electrode, and if low, replenish with provided filling solution
    - Check calibration against standard solution provided by the manufacturer
      - If reading is outside the error allowed by the manufacturer, maintain according to manufacturer instructions
      - If electrode continues to read outside of allowable error, do not use electrode
      - Check calibration of secondary electrode
  - Pore water
    - Remove microelectrode from glass sheath
    - Move sleeve away from filling hole
      - Verify levels of filling solution in electrode, and if low, replenish with provided filling solution
    - Check calibration against standard solution provided by the manufacturer
      - If reading is outside the error allowed by the manufacturer, clean metal tip with Kimwipe®
      - If electrode continues to read outside of allowable error, do not use electrode
      - Check calibration of secondary electrode
- pH calibration
  - Calibrate according to manufacturer instructions
  - Sediment and pore-water pH measurements are collected using the same electrode
- Temperature
  - Temperature is calibrated by laboratory personnel and need not be verified in the field

2. Collect SW sample and field measurements

a. Collect routine SW sample and field measurements the same day as sediment- and pore-water-sample collection

- SW samples are collected before any other personnel have entered the stream to minimize sample bias caused by disturbance/suspension of sediment

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

3. **Locate and characterize substrate zones**
    a. Locate zones in reach having bed substrates of sand or fine-grained sediment
        - Take care not to disturb zones until sample has been collected
            - Walk along shore
            - Walk on coarse substrates in-stream
    b. Classify substrate zones of sand or fine-grained sediment into defined categories
        - Categories for classification (table 2)
            - Fine-grained, organic-rich
            - Mixed sand and fine-grained, with intermediate organic content
            - Sand, organic-poor
        - Categorize substrates
            - Obtain sediment directly from streambed for assessment
                - Visual assessment
                - Tactile assessment
                - Partitioning through 0.063-mm sieve
            - Where stream is too deep to collect sediment directly from streambed, use a 9-in. Birge-Ekman grab sampler
                - Visual assessment
                - Tactile assessment
                - Partitioning through 0.063-mm sieve
    c. Note relative abundance of substrate zones in each category
4. **Select bed-sediment zones for sampling**
    a. Sampling-area selection criteria (in order of priority)
        - Undisturbed sediment
        - Grain size and organic content
            - Obtain at least one sample from each of the three zone types of interest (table 2) present in the reach
            - Where this is not possible, obtain a minimum of 3 samples from different zones in as many categories as possible
        - Representativeness of zones
            - Collect an equal number of samples from each of the represented categories
            - Where this is not possible, give priority to categories that are more dominant in the stream reach
        - Spatial separation between zones
            - Zones of similar classification that are being sampled should be as spatially separated as possible
    b. Delineate sampling area within each zone
        - 1 m^2
        - Mark edges with stake flags

Spatial biogeochemical sampling: sample collection strategy

1. **Sampling overview**

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

a. Target time
   - No specific time limit

b. Collect samples from downstream zones first, then work upstream

c. Collect and process each sample as quickly as possible to minimize oxidation of sulfide in sediment and pore-water samples

2. Bed-sediment sampling

a. Regular samples
   - Depth: 0–2 cm
   - Sample type: composite
   - Analyses:
     - MeHg production- and degradation-potential (MPP and MDP, respectively) rates
     - THg, MeHg, and reactive mercury ($Hg(II)_R$)
     - AVS
     - Percent fines
   - Take care not to disturb any additional sediment in the sampling area
   - Collection strategy
     - Sampling location
       - Undisturbed sediment
       - In (or adjacent to) the delineated sampling area
       - Spatially separated throughout the sampling area
       - Downstream to upstream
     - Collect sediment sample (0–2 cm depth), as patty
       - Directly from streambed
       - Where stream is too deep to collect sediment directly from streambed, use a 9-in. Birge-Ekman grab sampler
         - Retrieve sediment
         - Take a 0–2 cm patty from the surface of the retrieved sediment
         - Avoid areas near/in contact with metal surfaces
     - Divide each patty between fractions
       - Sieved MPP- and MDP-rates fraction
         - 7/8 of each patty
       - Whole composite fraction
         - 1/8 of each patty
     - Collect sufficient patties to fill all jars for analysis
     - Process sample immediately
     - Perform field measurements in replicate
       - ORP
         - Collect patty of sediment (0–2 cm depth) and use one of the following methods
           - Insert electrode into patty
           - Fill scintillation vial 2/3 full, insert electrode, wrap top with Parafilm M®
         - Readings likely will not completely stabilize
         - Record values quickly, as ORP of sediment changes rapidly with exposure to air
         - Repeat

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- pH and temperature
  - Use one of the following methods
    - Insert electrode directly into sediment to a depth of 2 cm
      - Allow electrode to remain in sediment until readings stabilize
    - Collect patty of sediment (0–2 cm depth)
      - Minimize changes in sediment being measured
        - → Work quickly
        - → Shield patty from sunlight to minimize heating
      - Insert electrode into sediment patty
  - Allow electrode to remain in sediment until readings stabilize
  - Record readings for pH and temperature
  - Repeat

b. Quality-control samples
- Replicates
  - Type: sequential
  - Frequency: 1 replicate for every 10 regular samples
  - Analyses: all field measurements and laboratory analyses performed for regular samples

3. Pore-water sampling

a. Regular samples
- Depth: 2 cm
- Sample type: composite
- Analyses:
  - THg and MeHg
  - Dissolved organic carbon (DOC)
  - Nutrients
  - Anions
- Take care not to disturb any additional sediment in the sampling area
- Collection strategy
  - Deploy probe to 2 cm depth in at least three locations
  - Sampling location
    - Undisturbed sediment
    - In (or adjacent to) the delineated sampling area
    - Spatially separated throughout the sampling area
    - Downstream to upstream
  - Collect pore water into 500-mL Teflon® bottle
  - Collect roughly equal volumes from each location
  - Fill anion vial directly from sampling line (not part of composite)
  - Reserve water for field measurements
    - Sulfide – preserve water
      - Decant water from 500-mL Teflon® bottle into an empty 20-mL scintillation vial
      - Use syringe to transfer 3 mL to scintillation vial containing 3 mL of SAOB-ascorbic acid mixture
      - Cap and shake briefly to mix

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Label vial
- Store at ambient temperature in a cool, dark location
- Measure within 24 hours

- ORP – measure
  - Decant water from 500-mL Teflon® bottle into an empty 20-mL scintillation vial
  - Place short piece (approximately 5 cm) of plastic tube on syringe
  - Draw water from scintillation vial into syringe
  - Move sleeve away from filling hole in the electrode
  - Place electrode partially into tube
  - Expel water past electrode
    - Take care not to get the filling hole wet
  - Note mV readings, and record approximate median
    - Pay particular attention to the last 1 mL of water
  - Repeat
- pH – set aside water
  - Decant water from 500-mL Teflon® bottle into an empty 20-mL scintillation vial
  - Set aside and measure immediately after sample processing

- Process sample immediately
- Perform remaining field measurements
  - pH
    - Timing: immediately after sample processing
    - Measure pH
      - Lower electrode into sample
      - Allow reading to stabilize
      - Record value
      - Repeat
  - Sulfide
    - Timing: within 24 hours of sample collection
    - Prepare electrode
      - Remove from SAOB-ascorbic acid mixture
      - Rinse with deionized water
      - Blot dry with Kimwipe®
      - Uncover filling hole
    - Measure sulfide
      - Stir preserved sample with 12.7-mm Teflon®-coated, magnetic stir bar
      - Lower electrode into sample
      - Allow readings to stabilize
        - Record value in mV
      - If sample is below detection limit (-700 mV), readings will not stabilize
        - Keep electrode in sample for 5 to 10 minutes, then record value in mV
      - Repeat
    - Between samples, rinse electrode with deionized water, and blot dry with Kimwipe®
    - Store electrode in SAOB-ascorbic acid mixture (prepared fresh daily) when not in use
    - After sampling is completed,

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Prepare electrode for shipment back to laboratory
  - Remove filling solution
  - Rinse inside and outside with deionized water
- Convert mV readings to concentrations

b. Quality-control samples
- Blanks
  - Frequency: 1 blank for every 10 regular samples
  - Analyses: sulfide field measurement and all laboratory analyses performed for regular samples
  - Blank waters to be used
    - Sulfide
      - Inorganic blank water
    - THg and MeHg
      - Milli-Q® water obtained from the WMRL
    - DOC
      - Certified organic-free water
    - Nutrients and anions
      - Inorganic blank water
- Replicates
  - Type: sequential
  - Frequency: 1 replicate for every 10 regular samples
  - Analyses: all field measurements and laboratory analyses performed for regular samples

4. Piezometric-head measurements

a. Measure after sediment- and pore-water sample collection

b. Making measurements
- Collect at multiple depths
  - 10 cm
  - 20 cm
  - 30 cm
- Collect in each area sampled for sediment and pore water

5. Georeference each sampling area using a GPS unit

a. Engage features
- WAAS
- External antenna

b. Record
- Location in degrees/minutes/seconds
- Datum (NAD 83 preferred)
- Accuracy (with units)

6. Document sample information

a. Key sample identification information
- Station-identification number (STAID)
- Date
- Mean sample time
  - Samples of the same medium collected from the same stream site on the same day are distinguished from each other on the basis of mean sample time in the NWIS database

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Medium code
  - Sediment
    - "H" for regular samples
    - "W" for replicate samples
  - Pore water
    - "F" for regular samples
    - "Z" for replicate samples
    - "Q" for blank samples

b. Fill out all sample labels

c. Fill out forms
- Field forms
  - Fill out all field forms completely in the field
  - Draw map of stream reach
    - Use orthophotos and topographic maps to assist in drawing stream
      - http://www.terraserver-usa.com/
    - Record stream and riparian features
    - Draw, label, and classify each zone and sampling area
      - Assign a letter-number combination name to each sampling area
        - The letter should be based on sediment grain size and observable organic content (table 2)
          - F = Fine-grained, organic-rich
          - M = Mixed sand and fine-grained, intermediate organic content
          - S = Sand, organic-poor
        - The number should be based on the sample order by sediment type
          - For example, F2 was collected from a fine-grained, organic-rich sediment zone, and that zone was the second zone of this type sampled at that stream
      - Briefly describe additional sediment characteristics
      - Indicate distance to reference location (for example, bridge/gage)
      - Indicate flow direction
      - Draw any other distinguishing features that will assist in finding sampling area locations again
  - Record relationship between sampling-area name and key sample-identification information for NWIS on MPP- and MDP-rates field form
- Shipping forms
  - Fill out Wisconsin Mercury Research Laboratory (WMRL) analytical services request form
    - Use a new sheet for each sample collected
  - Remaining shipping forms may be filled out in the office, prior to shipping samples

d. Verify that all labels and forms are in agreement regarding sampling-area names and key sample-identification information

Temporal biogeochemical sampling: preparation and sampling area selection

1. **Prepare for field measurements**

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

a. Approximately 12 hours before sample collection
   - Fill sulfide electrode with filling solution provided
   - Replace tape over filling hole
   - Cap the end

b. Before each day's sampling prepare equipment for field measurements
   - Record all calibrations and calibration checks on field sheets
   - SW field measurements
     - pH, specific conductance, dissolved oxygen (DO), and temperature
       - Calibrate multiparameter meter according to manufacturer instructions
     - Streamflow
       - Either
         - Verify rated gage is working properly
         - Verify proper operation of equipment used for direct measurement, according to Rantz and others (1982) and manufacturer instructions
   - Sulfide
     - Sulfide is calibrated by laboratory personnel and need not be verified in the field
     - SAOB-ascorbic acid mixture
       - Pour premeasured ascorbic acid into the premeasured SAOB, cap, and mix
       - Pour mixture into the ascorbic acid vial, cap, and mix
       - Pour mixture back into the SAOB container
       - Let mixture sit 10 minutes
       - Use syringe to distribute 3 mL of the mixture to each of a number of 20-mL scintillation vials
         - Number of scintillation vials should equal the number of pore-water samples to be collected
       - Store electrode in mixture when not in use
   - ORP calibration checks
     - Sediment
       - Remove plug from filling hole
         - Verify levels of filling solution in electrode, and if low, replenish with provided filling solution
       - Check calibration against standard solution provided by the manufacturer
         - If reading is outside the error allowed by the manufacturer, maintain according to manufacturer instructions
         - If electrode continues to read outside of allowable error, do not use electrode
         - Check calibration of secondary electrode
     - Pore water
       - Remove microelectrode from glass sheath
       - Move sleeve away from filling hole
         - Verify levels of filling solution in electrode, and if low, replenish with provided filling solution
       - Check calibration against standard solution provided by the manufacturer
         - If reading is outside the error allowed by the manufacturer, clean metal tip with Kimwipe®
         - If electrode continues to read outside of allowable error, do not use electrode
         - Check calibration of secondary electrode

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- pH calibration
  - Calibrate according to manufacturer instructions
  - Sediment and pore-water pH measurements are collected using the same electrode
- Temperature
  - Temperature is calibrated by laboratory personnel and need not be verified in the field

2. Collect SW sample and field measurements

a. Collect routine SW sample and field measurements the same day as sediment- and pore-water-sample collection
   - SW samples are collected before any other personnel have entered the stream to minimize sample bias caused by disturbance/suspension of sediment

3. Locate temporal sampling area (spatial sampling area with highest measured MPP rate)

a. Consult field notes
   - GPS coordinates
   - Maps
   - Field descriptions

b. Do not disturb bed-sediment-sampling zone

c. Delineate sampling area within each zone
   - 1 m2
   - Mark edges with stake flags

Temporal biogeochemical sampling: sample collection strategy

1. Sampling overview

a. Target time
   - No specific time limit

b. Collect and process samples as quickly as possible to minimize oxidation of sulfide in sediment and pore-water samples

2. Bed-sediment sampling

a. Regular samples
   - Depth: 0–2 cm
   - Sample type: composite
   - Analyses:
     - MPP and MDP rates
     - THg, MeHg, and $Hg(II)_R$
     - AVS
     - Percent fines
   - Take care not to disturb any additional sediment in the sampling area
   - Collection strategy
     - Sampling location
       - Undisturbed sediment
       - In (or adjacent to) the delineated sampling area
       - Downstream to upstream

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Collect sediment sample (0–2 cm depth), as patty
  - Directly from streambed
  - Where stream is too deep to collect sediment directly from streambed, use a 9-in. Birge-Ekman grab sampler
    - Retrieve sediment
    - Take a 0–2 cm patty from the surface of the retrieved sediment
    - Avoid areas near/in contact with metal surfaces
- Divide each patty between fractions
  - Sieved MPP- and MDP-rates fraction
    - 7/8 of each patty
  - Whole composite fraction
    - 1/8 of each patty
- Collect sufficient patties to fill all jars for analysis
- Process sample immediately
- Perform field measurements in replicate
  - ORP
    - Collect patty of sediment (0–2 cm depth) and use one of the following methods
      - Insert electrode into patty
      - Fill scintillation vial 2/3 full, insert electrode, wrap top with Parafilm M®
    - Readings likely will not completely stabilize
    - Record values quickly, as ORP of sediment changes rapidly with exposure to air
    - Repeat
  - pH and temperature
    - Use one of the following methods
      - Insert electrode directly into sediment to a depth of 2 cm
        - Allow electrode to remain in sediment until readings stabilize
      - Collect patty of sediment (0–2 cm depth)
        - Minimize changes in sediment being measured
          - → Work quickly
          - → Shield patty from sunlight to minimize heating
        - Insert electrode into sediment patty
    - Allow electrode to remain in sediment until readings stabilize
    - Record readings for pH and temperature
    - Repeat

b. Quality-control samples

- Replicates
  - Type: sequential
  - Frequency: 1 replicate for every 10 regular samples
  - Analyses: all field measurements and laboratory analyses performed for regular samples

3. Pore-water sampling

a. Regular samples

- Depth: 2 cm
- Sample type: composite
- Analyses:
  - THg and MeHg

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- DOC
- Nutrients
- Anions

- Take care not to disturb any additional sediment in the sampling area
- Collection strategy
  - Deploy probe to 2-cm depth in at least three locations
  - Sampling location
    - Undisturbed sediment
    - In (or adjacent to) the delineated sampling area
    - Spatially separated throughout the sampling area
    - Downstream to upstream
  - Collect pore water into 500-mL Teflon® bottle
  - Collect roughly equal volumes from each location
  - Fill anion vial directly from sampling line (not part of composite)
  - Reserve water for field measurements
    - Sulfide – preserve water
      - Decant water from 500-mL Teflon® bottle into an empty 20-mL scintillation vial
      - Use syringe to transfer 3 mL to scintillation vial containing 3 mL of SAOB-ascorbic acid mixture
      - Cap and shake briefly to mix
      - Label vial
      - Store at ambient temperature in a cool, dark location
      - Measure within 24 hours
    - ORP – measure
      - Decant water from 500-mL Teflon® bottle into an empty 20-mL scintillation vial
      - Place short piece (approximately 5 cm) of plastic tube on syringe
      - Draw water from scintillation vial into syringe
      - Move sleeve away from filling hole in the electrode
      - Place electrode partially into tube
      - Expel water past electrode
        - Take care not to get the filling hole wet
      - Note mV readings, and record approximate median
        - Pay particular attention to the last 1 mL of water
      - Repeat
    - pH – set aside water
      - Decant water from 500-mL Teflon® bottle into an empty 20-mL scintillation vial
      - Set aside and measure immediately after sample processing
  - Process sample immediately
  - Perform remaining field measurements
    - pH
      - Timing: immediately after sample processing
      - Measure pH
        - Lower electrode into sample
        - Allow reading to stabilize
        - Record value
        - Repeat

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Sulfide
  - Timing: within 24 hours of sample collection
  - Prepare electrode
    - Remove from SAOB-ascorbic acid mixture
    - Rinse with deionized water
    - Blot dry with Kimwipe®
    - Uncover filling hole
  - Measure sulfide
    - Stir preserved sample with 12.7-mm Teflon®-coated, magnetic stir bar
    - Lower electrode into sample
    - Allow readings to stabilize
      - Record value in mV
    - If sample is below detection limit (-700 mV), readings will not stabilize
      - Keep electrode in sample for 5 to 10 minutes, then record value in mV
    - Repeat
  - Between samples, rinse electrode with deionized water, and blot dry with Kimwipe®
  - Store electrode in SAOB-ascorbic acid mixture (prepared fresh daily) when not in use
  - After sampling is completed
    - Prepare electrode for shipment back to laboratory
      - Remove filling solution
      - Rinse inside and outside with deionized water
    - Convert mV readings to concentrations

b. Quality-control samples
- Blanks
  - Frequency: 1 blank for every 10 regular samples (during early sampling events)
  - Analyses: sulfide field measurement and all laboratory analyses performed for regular samples
  - Blank waters to be used
    - Sulfide
      - Inorganic blank water
    - THg and MeHg
      - Milli-Q® water obtained from the WMRL
    - DOC
      - Certified organic-free water
    - Nutrients and anions
      - Inorganic blank water
- Replicates
  - Type: sequential
  - Frequency: 1 replicate for every 10 regular samples
  - Analyses: all field measurements and laboratory analyses performed for regular samples

4. Piezometric-head measurements

a. Measure after sediment- and pore-water-sample collection

b. Making measurements
- Collect at multiple depths
  - 10 cm
  - 20 cm
  - 30 cm

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Collect in the area sampled for sediment and pore water

5. Document sample information

a. Key sample identification information
   - Station-identification number (STAID)
   - Date
   - Mean sample time
     - Samples of the same medium collected from the same stream site on the same day are distinguished from each other on the basis of mean sample time in the NWIS database
   - Medium code
     - Sediment
       - "H" for regular samples
       - "W" for replicate samples
     - Pore water
       - "F" for regular samples
       - "Z" for replicate samples
       - "Q" for blank samples

b. Fill out all sample labels

c. Fill out forms
   - Field forms
     - Fill out all field forms completely in the field
     - Draw map of stream reach
       - Use orthophotos and topographic maps to assist in drawing stream
         - http://www.terraserver-usa.com/
       - Record stream and riparian features
       - Draw, label, and classify the zone and sampling area
         - Label it using the same sampling-area name (that is, letter-number combination) assigned to it during spatial sampling
         - Briefly describe additional sediment characteristics
         - Record any changes that have occurred in/near the sampling area
           - Riparian area
           - Grain size
           - Observable organic content
           - Other
         - Indicate distance to reference location (for example, bridge/gage)
         - Indicate flow direction
         - Draw any other distinguishing features that will assist in finding sampling area location again
     - Record relationship between sampling-area name and key sample-identification information for NWIS on MPP- and MDP-rates field form
   - Shipping forms
     - Fill out Wisconsin Mercury Research Laboratory (WMRL) analytical services request form
       - Use a new sheet for each sample collected

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sampling strategy (continued)

- Remaining shipping forms may be filled out in the office, prior to shipping samples

d. Verify that all labels and forms are in agreement regarding sampling-area names and key sample-identification information

Sample collection

1. **Bed-sediment-sample collection**
   a. Insert 2-cm-deep polycarbonate core (8-cm diameter) into the sediment until top edge is flush with sediment/water interface
   b. Gently scoop away sediment downstream of the core ring
   c. Insert stiff plastic sheet under the bottom of the core ring (where sediment has been scooped away)
   d. Slide sheet under the core ring, keeping it flush with the core ring bottom
   e. Slowly lift the resulting patty from the stream bottom
      - Where flows are sufficiently fast to remove top layer of sediment, place a second plastic sheet on the core ring before lifting
   f. Divide patty for analysis
      - Hold plastic sheet containing core ring and patty horizontal
      - Lift core ring straight up, leaving sediment patty on plastic sheet
      - Use core ring to parse patty for sample processing
2. **Pore-water-sample collection**
   a. Sampling equipment preparation
      - Attach acrylic disc to probe, 2 cm above vents
      - Secure the C-flex and short Teflon® tubes together with cable tie
      - Insert probe perpendicular to the sediment surface
        - Acrylic disc should rest on top of sediment
        - Avoid moving probe, as this can cause stream-water influx
      - Pump water at a low flow rate to minimize depletion of pore water in the area
      - Allow sediment slug to evacuate the line
      - Once water runs fairly clear, attach cartridge filter (quartz fiber, 47-mm diameter, 0.7-µm nominal pore size)
      - Hold filter upright to purge air from it
      - Allow a few milliliters of water to flush it
   b. Sample collection
      - Pour acid (dilute hydrochloric acid (HCl)) from 500-mL Teflon® bottle into an acid-waste container
      - Rinse three times with small aliquots of filtered pore water
      - Deploy probe to a minimum of three, spatially separated locations in the sample area
        - Each time probe is deployed, remove filter from line and allow sediment plug to evacuate before replacing
      - Rinse anion vial three times and fill directly from line
      - Fill 500-mL Teflon® bottle to the top

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sample processing

Bed sediment: reach characterization

1. **Use core ring to parse patty directly into sample jars (no compositing)**
    a. Leave headspace of approximately 20 to 30 percent of container volume (for expansion upon freezing)
    b. Discard remaining sediment into stream
    c. Fill jars for analyses:
        - LOI
            - 30-mL polypropylene jar (not acid-rinsed)
            - Store on dry ice/in freezer
            - Ship
                - Timing: once all streams have been sampled
                - To: WMRL
                - Conditions: dry ice
        - Percent fines
            - 30-mL polypropylene jar (not acid-rinsed)
            - Store at ambient temperature in a cool, dark location (don't freeze)
            - Ship
                - Timing: once all streams have been sampled
                - To: Sediment laboratory
                - Conditions: ambient temperature (cool, dark location)

Bed sediment: spatial and temporal biogeochemical sampling

1. **Bed-sediment-sample processing**
    a. Sieved MPP- and MDP-rates fraction
        - Constitutes 7/8 of each patty collected in a sampling area
        - Construct apparatus (fig. 5)
            - Use brass lid-ring to secure 1-mm nylon mesh to a half-pint mason jar
            - Cap mason jar with an upside-down, 250-mL beaker (with bottom cut out)
                - This fits snugly over the lid-ring (overlapping it by ~1 cm) and forms an enclosure to contain sediment during sieving
        - Sieve sample
            - Add small amount of sediment (~1/4 of patty) to the enclosure formed by the upside-down beaker
            - Tamp down on sediment using plastic bottle
            - Remove larger pieces stuck on mesh and repeat with another small amount of sediment
        - Continue collecting patties until the mason jar is filled to the top with sieved sediment and pore water
        - Prepare sample for storage and shipment
            - Remove mesh sieve and lid-ring
            - Clean threads with Kimwipe®
            - Secure lid on mason jar using lid-ring
            - Wrap lid with Parafilm M®, to seal
            - Place mason jar in foam sleeve

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sample processing (continued)

- Place wrapped jar in sealed Ziploc® bag
- Store on wet ice
- Ship
  - Timing: as soon as possible (optimally within 24 hours of sampling)
  - To: MPP- and MDP-rates laboratory
  - Conditions: wet ice

b. Whole-sediment fraction

- Constitutes 1/8 of each patty collected in a sampling area
- Deposit sediment into a 120-mL polypropylene jar for compositing
- Mix sediment by stirring the sample
  - Use a clean Teflon®, plastic, or glass device
  - 30 to 60 seconds
  - Try not to entrain air into sample
- Remove sediment for jars using an acid-cleaned plastic spoon or Teflon® policeman
  - Leave headspace of approximately 20 to 30 percent of container volume (for expansion upon freezing)
  - Fill jars for analyses:
    - THg, MeHg, and $Hg(II)_R$
      - 20-mL Teflon® jar
        - Alternatively an acid-cleaned, DI-rinsed 30-mL polypropylene jar may be used
      - Store on dry ice/in freezer
      - Ship
        - Timing: once all streams have been sampled
        - To: WMRL
        - Conditions: dry ice
    - AVS
      - 30-mL polypropylene jar (not acid-rinsed)
      - (Do not add zinc acetate)
      - Store on dry ice/in freezer
      - Ship
        - Timing: once all streams have been sampled
        - To: Sulfur geochemistry laboratory
        - Conditions: dry ice
    - Percent fines
      - 30-mL polypropylene jar (not acid-rinsed)
      - Store at ambient temperature in a cool, dark location (don't freeze)
      - Ship
        - Timing: once all streams have been sampled
        - To: Sediment laboratory
        - Conditions: ambient temperature (cool, dark location)

Pore water: spatial and temporal biogeochemical sampling

1. Pore-water-sample processing

a. Fill vial directly from sampling line

- Anions

Appendix 1. Method summary sheets—Continued.

Appendix 1b. Method summary sheets: detailed studies—Continued.

Sample processing (continued)

- 6-mL high-density polyethylene vial
- Filtered sample, but not part of composite
- Store on wet ice/refrigerator
- Ship
  - Timing: once all streams have been sampled
  - To: Sulfur geochemistry laboratory
  - Conditions: wet ice

b. Field measurements
- Decant water from the composite pore water bottle (500-mL Teflon®) for all measurements

c. Fill vials from the composite pore water collected in the 500-mL Teflon® bottle
- DOC
  - 40-mL amber glass vial
  - Do not rinse vial
  - Fill vial
  - Store on wet ice/refrigerator
  - Ship
    - Timing: once all streams have been sampled
    - To: Carbon geochemistry laboratory
    - Conditions: wet ice
- Nutrients
  - 60-mL plastic vial
  - Rinse vial three times
  - Fill vial, but leave 20 to 30 percent of vial volume as headspace for expansion upon freezing
  - Store on dry ice/in freezer
  - Ship
    - Timing: once all streams have been sampled
    - To: Sulfur geochemistry laboratory
    - Conditions: dry ice
- THg and MeHg
  - 500-mL Teflon® bottle
    - Minimum submission volume is 250 mL
  - After water has been poured off for other analyses, preserve sample
    - Final volume of 1-percent HCl
      - 10 mL of 6-normal (50-percent) HCl for ~500 mL of sample
      - 5 mL of 6-normal (50-percent) HCl for ~250 mL of sample
    - Mix
    - Store at ambient temperature in a cool, dark location
    - Ship
      - Timing: once all streams have been sampled
      - To: WMRL
      - Conditions: ambient temperature (cool, dark location)

Appendix 2. Primary and Ancillary Constituents Analyzed for in Bed Sediment and Pore Water Collected for the National Water-Quality Assessment (NAWQA) Program Detailed Mercury Studies.

[NWIS, National Water Information System; --, constituent is incompatible with storage in the National Water Information System database; MeHg, methylmercury; MPP, methylmercury production potential; MDP, methylmercury degradation potential; Fe(II), ferrous iron; Fe(III), ferric iron; THg, total mercury; $Hg(II)_R$, reactive mercury; nm, nanometer; S, sulfur; C, carbon; N, nitrogen; P, phosphorus]

Medium	Parameters	Units (abbreviated)	Units (full)	NWIS database parameter code
		Field		
Stream water	pH	standard units	standard units	00400
	Specific conductance	µS/cm at 25°C	microsiemen per centimeter at 25 degrees Celsius	00095
	Dissolved oxygen (DO)	mg/L	milligram per liter	00300
	Temperature	°C	degree Celsius	00010
	Streamflow, instantaneous	ft^3/s	cubic feet per second	00061
Sediment	Oxidation-reduction potential (ORP), relative to the standard hydrogen electrode	mV	millivolt	63002
	pH	standard units	standard units	70310
	Temperature	°C	degree Celsius	--
Pore water	Sulfide	mg/L	milligram per liter	--
	Oxidation-reduction potential (ORP), relative to the standard hydrogen electrode	mV	millivolt	63002
	pH	standard units	standard units	--
Hyporheic zone	Piezometric head	mm	millimeter	--
		Methylmercury production- and degradation-potential-rates laboratory		
Sediment	MeHg production-potential (MPP) rate	pg/g dry wt/d	picogram per gram, dry weight, per day	--
	MeHg degradation-potential (MDP) rate	pg/g dry wt/d	picogram per gram, dry weight, per day	--
	MPP rate:MDP rate ratio	(unitless)	(unitless)	--
	MeHg production rate constant	1/d	per day	--
	MeHg degradation rate constant	1/d	per day	--
	Microbial sulfate reduction	nmol/g dry wt/d	nanomole per gram, dry weight, per day	--
	Dry weight	% wet wt	percent, wet weight	--
	Loss on ignition (LOI)	%	percent	--
	Bulk density	g/cm^3 wet sed	gram per cubic centimeter, wet sediment	--
	Porosity	mL PW/cm^3 wet sed	milliliter of pore water per cubic centimeter, wet sediment	--
	Acid-volatile sulfur	µmol/g dry wt	micromole per gram, dry weight	--

Appendix 2. Primary and ancillary constituents analyzed for in bed sediment and pore water collected for the National Water-Quality Assessment (NAWQA) Program detailed mercury studies—Continued.

[NWIS, National Water Information System; --, constituent is incompatible with storage in the National Water Information System database; MeHg, methylmercury; MPP, methylmercury production potential; MDP, methylmercury degradation potential; Fe(II), ferrous iron; Fe(III), ferric iron; THg, total mercury; $Hg(II)_R$, reactive mercury; nm, nanometer; S, sulfur; C, carbon; N, nitrogen; P, phosphorus]

Medium	Parameters	Units (abbreviated)	Units (full)	NWIS database parameter code
		Methylmercury production- and degradation-potential-rates laboratory (cont.)		
Sediment (cont.)	Total-reduced sulfur	µmol/g dry wt	micromole per gram, dry weight	--
	Acid-extractable Fe(II)	mg/g dry wt	milligram per gram, dry weight	--
	Amorphous Fe(III)	mg/g dry wt	milligram per gram, dry weight	--
	Crystalline Fe(III)	mg/g dry wt	milligram per gram, dry weight	--
	Sediment oxidation-reduction potential (ORP) at time of incubation	mV	millivolt	--
	Sediment pH at time of incubation	standard units	standard units	--
	Incubation temperature	°C	degree Celsius	--
Pore water[1]	Fe(II)	mg/L	milligram per liter	--
	Sulfate	µmol/L	micromole per liter	--
	Chloride	µmol/L	micromole per liter	--
	Acetate	µmol/L	micromole per liter	--
		Wisconsin Mercury Research Laboratory (WMRL)		
Sediment	THg	ng/g dry wt	nanogram per gram, dry weight	62978
	MeHg	ng/g dry wt	nanogram per gram, dry weight	62979
	$Hg(II)_R$	ng/g dry wt	nanogram per gram, dry weight	--
	Loss on ignition (LOI)	%	percent	64178
	Dry weight	% wet wt	percent, wet weight	64177
Pore water	THg, filtered water	ng/L	nanogram per liter	50287
	MeHg, filtered water	ng/L	nanogram per liter	50285
		Carbon geochemistry laboratory		
Pore water	Dissolved organic carbon (DOC)	mg/L	milligram per liter	00681
	Ultraviolet (UV) absorbance at 254 nm	units/cm	units per centimeter	50624
	Specific ultraviolet absorbance (SUVA) at 254 nm	L/(mg DOC*m)	liter per (milligram of dissolved organic carbon * meter)	63162

Appendix 2. Primary and ancillary constituents analyzed for in bed sediment and pore water collected for the National Water-Quality Assessment (NAWQA) Program detailed mercury studies—Continued.

[NWIS, National Water Information System; --, constituent is incompatible with storage in the National Water Information System database; MeHg, methylmercury; MPP, methylmercury production potential; MDP, methylmercury degradation potential; Fe(II), ferrous iron; Fe(III), ferric iron; THg, total mercury; $Hg(II)_R$, reactive mercury; nm, nanometer; S, sulfur; C, carbon; N, nitrogen; P, phosphorus]

Medium	Parameters	Units (abbreviated)	Units (full)	NWIS database parameter code
		Sulfur geochemistry laboratory		
Sediment	Acid-volatile sulfide (AVS)	% wet wt	percent, wet weight	--
	Disulfides	% wet wt	percent, wet weight	--
	Organic S	% wet wt	percent, wet weight	--
	Sulfate	% wet wt	percent, wet weight	--
	Total C	% dry wt	percent, dry weight	--
	Organic C	% dry wt	percent, dry weight	--
	Inorganic C	% dry wt	percent, dry weight	--
	Total N	% dry wt	percent, dry weight	--
	Total P	% dry wt	percent, dry weight	--
	Total S	% dry wt	percent, dry weight	--
Pore water	Specific conductance	µS/cm at 25°C	microsiemen per centimeter at 25 degrees Celsius	--
	Total dissolved solids (TDS)	mg/L	milligram per liter	--
	Sulfate	mg/L	milligram per liter	--
	Chloride	mg/L	milligram per liter	--
	Fluoride	mg/L	milligram per liter	--
	Bromide	mg/L	milligram per liter	--
	Nitrate	mg/L	milligram per liter	--
	Ammonium	µg/L	microgram per liter	--
	Phosphate	µg/L	microgram per liter	--
		Sediment laboratory		
Sediment	Percent fines, percent of sediment less than 0.063 millimeters	%	percent	80164

[1] Pore water used for analyses in the Methylmercury production- and degradation-potential-rates laboratory was derived by centrifuging sediment collected for microbial rate assays.

Appendix 3. Field Forms

Appendix 3a. Field forms common to reconnaissance and detailed studies.

3a–1. Stream water (not included in this report)

3a–2. General sampling form
This form is available for download at http://pubs.usgs.gov/ofr/2008/1279/

General sampling form

Field Data Sheet			
SAMPLE HEADER			
Station:		Date (MM/DD/YYY):	
Waterbody:			
Station description:			
Station ID:	Reach:	Start time:	h
Collector (leader):		End time:	h
Streambed-sediment temperature:	°C		
Sample and photographic notes:			

RELATED SAMPLING ACTIVITIES (Circle all that apply)			
Water chemistry	Streamflow	Habitat	Tissues
Invertebrate survey	Algae survey	Other (specify):	

SKETCHES AND ADDITIONAL NOTES

Appendix 3. Field forms—Continued.

Appendix 3b. Field forms specifically for detailed studies.

3b–1. Reach establishment

This form can be accessed at http://pubs.usgs.gov/ofr/2008/1279/

Collectors: _____
Station Name: _____
STAID: _____
Date: _____

Reach type (circle one): wadeable unwadeable
Representative wetted channel widths:

1. _____ m ft
2. _____ m ft
3. _____ m ft

Mean: Mean wetted channel width (MCW) = _____ m ft

Ideal reach length: MCW x 20 = _____ m ft

Actual reach length: _____ m ft
[wadeable reaches must be ≥150 m (492 ft)]
[unwadeable reaches must be between ≥500 m (1,640 ft)]

Distance between transects: Actual reach length / 14 = distance between transects
_____ m ft / 14 = _____ m ft

Reference location:
Description (circle one): gage bridge other _____
Location: latitude ____ ____ ____ longitude ____ ____ ____
Datum: NAD 83 NAD 27 Other _____
(can be obtained from site header file, reference location for the STAID;
all NWIS information is in NAD 27)

Location of reach:
Distance from reference location to nearest reach boundary: _____ m ft
Boundary nearest reference location (circle one): upstream downstream
Descriptors of reach-boundary locations
Upstream:
LEW:
Latitude (DMS):_____ Longitude (DMS): _____
Datum:_____ (NAD 83 preferred) Accuracy: _____ m ft
Landmarks/reference points:_____
REW:
Latitude (DMS):_____ Longitude (DMS): _____
Datum:_____ (NAD 83 preferred) Accuracy: _____ m ft
Landmarks/reference points:_____
Downstream:
LEW:
Latitude (DMS):_____ Longitude (DMS): _____
Datum:_____ (NAD 83 preferred) Accuracy: _____ m ft
Landmarks/reference points:_____
REW:
Latitude (DMS):_____ Longitude (DMS): _____
Datum:_____ (NAD 83 preferred) Accuracy: _____ m ft
Landmarks/reference points:_____

Comments: _____

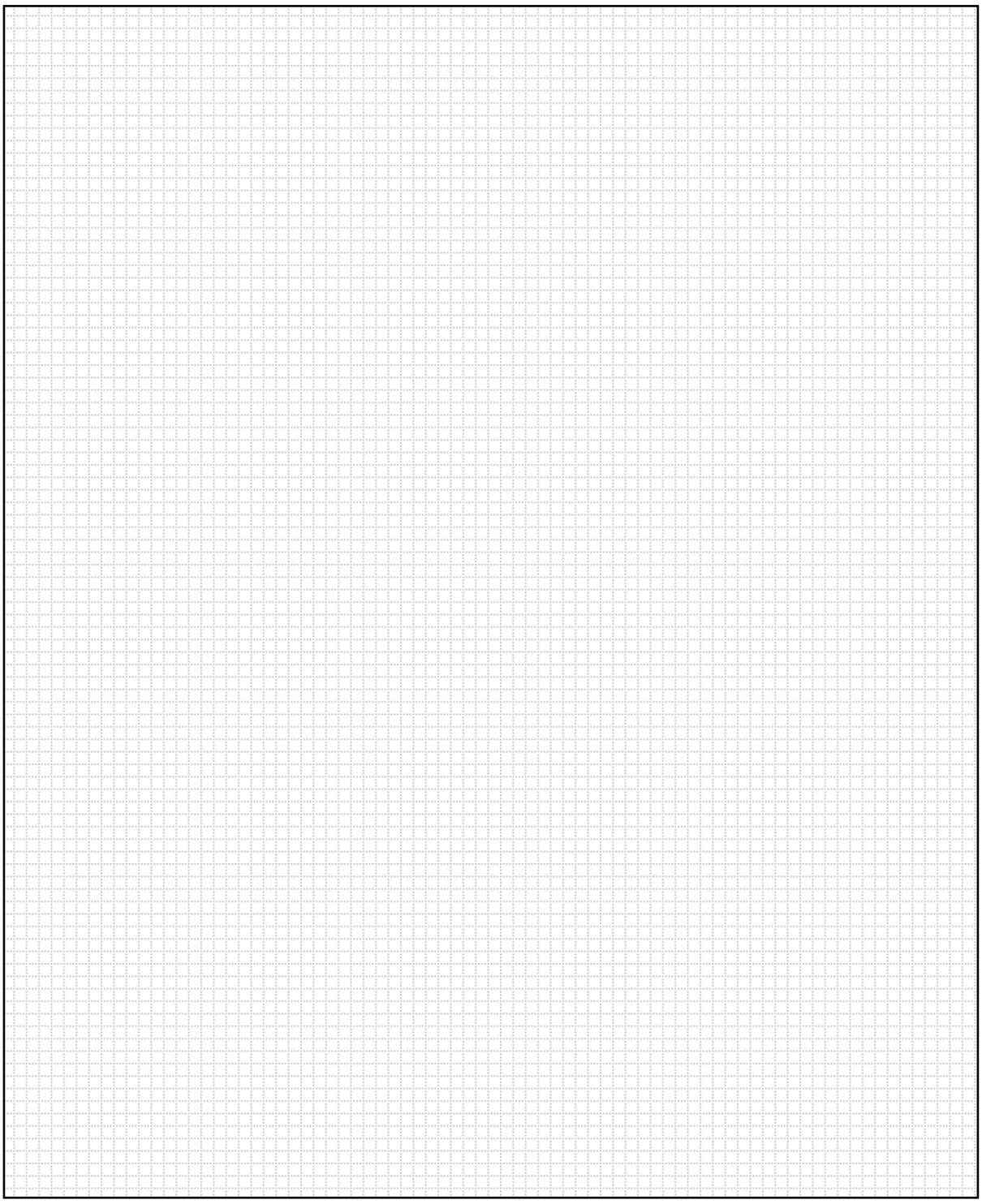
Appendix 3. Field forms—Continued.

Appendix 3b. Field forms specifically for detailed studies.

3b–2. Reach diagram

This form can be accessed at http://pubs.usgs.gov/ofr/2008/1279/

Station Name: _____ STAID:_____ Date:_____



(**include:** reference location, habitat types, flow direction, important features in area, substrate zones)

Appendix 3. Field forms—Continued.

Appendix 3b. Field forms specifically for detailed studies.

3b–3. Transect sampling

This form can be accessed at http://pubs.usgs.gov/ofr/2008/1279/

Transect sampling

Station Name: _____ **Collectors:** _____

STAID: _____

Date: _____ **Transect:** _____

Bed-Substrate Characterization

Description	Size (mm)	Basic categories	Expanded categories
Smooth bedrock/concrete/hardpan	N/A	>3	1
Fine-grained; organic-rich	**N/A**	**2**	**2**
Mixed sand and fine-grained; intermediate organic content	**≤ 2**	**2.5**	**2.5**
Sand; organic-poor	**> 0.063–2**	**3**	**3**
Fine/medium gravel	> 2–16	>3	4
Coarse gravel	> 16–32	>3	5
Very coarse gravel	> 32–64	>3	6
Small cobble	> 64–128	>3	7
Large cobble	> 128–256	>3	8
Small boulder	> 265–512	>3	9
Large boulder/irregular bedrock/irregular hardpan/irregular artificial surface	> 512	>3	10

Method used for measurements (circle one):

rangefinder measuring tape other: _____

Units of measurement (circle one): ft m

Substrate zone	Position of right-most boundary *	Width of zone	Position of zone midpoint **	Bed-substrate category (see table above)	Core collected? (Y/N)	Time of sample collection	Method of core collection (circle)
LEW		--	--	--	--	--	--
T__-1							Core Grab None
T__-2							Core Grab None
T__-3							Core Grab None
T__-4							Core Grab None
T__-5							Core Grab None
T__-6							Core Grab None
T__-7							Core Grab None
T__-8							Core Grab None
T__-9							Core Grab None
T__-10							Core Grab None
T__-11							Core Grab None
T__-12							Core Grab None
T__-13							Core Grab None
T__-14							Core Grab None
T__-15							Core Grab None
REW* **		--	--	--	--		--

* "Position of right-most boundary" refers to the location of the right-most (when facing downstream) boundary of the substrate zone on the tape or rangefinder. With a tape, the left edge of water may not be positioned at the zero point marked on the tape; record the measurement on the tape at the left edge of water (LEW) or at the boundary of the substrate zone. With a rangefinder, all measurements should be taken from the LEW; the LEW should be zero.

** "Position of zone midpoint" refers to the location of the zone's midpoint on the tape/rangefinder.

*** REW: right edge of water

Wetted Width (circle units): REW – LEW = _____ ft m

Comments: _____

_____

_____

_____

Appendix 3. Field forms—Continued.

Appendix 3b. Field forms specifically for detailed studies.

3b–4. Methylmercury production- and degradation-potential rates

This form can be accessed at http://pubs.usgs.gov/ofr/2008/1279/

Methylmercury production- and degradation-potential rates

Collected by: _____

NAWQA Mercury Detailed Studies
Field Data Sheet

Full date (dd/mm/yy): _____

I. LOCATION

Site (full name): _____ Site/Station ID: _____
Latitude: _____ Longitude: _____ Datum: _____ Accuracy: _____

II. SEDIMENT SAMPLING

Begin time: _____ End time: _____ Median time: _____ SW Temp (ºC): _____
Mason jars filled (#): _____ mason jar size (#): _____
Depth interval (for example, 0–2 cm)
D1 (cm): _____ D2 (cm): _____ D3 (cm): _____ D4 (cm): _____

Site description:_____
_____
_____
_____

Sample collection:_____
_____
_____
_____

Sample physical description (color, texture, smell, etc.):_____
_____
_____
_____
_____

III. Analysis To Be Conducted (Check)

_____ 203Hg-Methylation
_____ 14C-MeHg Degradation
_____ 35S-Sulfate reduction
_____ TRS/AVS
_____ PW-SU
_____ PW-SO_4, Ac
_____ LOI
_____ Eh/pH
_____ BS/PW-Fe
_____ PW-DOC
_____ other (specify): _____
_____ other (specify): _____

IV. Electrode checks and calibrations

	Reading (mV)
ORP electrode calibration	
Std. Used	
Zobell's	
quinhydrone @ pH 4	
quinhydrone @ pH 7	
Orion® ORP std (bed-sediment electrode)	
Orion® ORP std (pore-water electrode)	

pH electrode calibration (If auto-calibration, circle buffers used)	Reading	Temp. (ºC)
4.0		
7.0		
10.0		

V. Minipiezometer measurements

	R1	R2
Depth of penetration (cm) _____		
Head difference (+/-)(mm)		
Depth of penetration (cm) _____		
Head difference (+/-)(mm)		
Depth of penetration (cm) _____		
Head difference (+/-)(mm)		

VI. On-Site Measurements

	R1	R2	*in situ* or patty
Bed-sediment ORP (mV)			
Bed-sediment pH			
Bed-sediment temperature (ºC)			

	R1	R2
Pore-water ORP (mV)		
Pore-water pH		
Pore water S^{2-} (circle 1º or 2º) (mV)		

Appendix 3. Field forms—Continued.

Appendix 3b. Field forms specifically for detailed studies.

3b–5. Pore-water sulfide

This form can be accessed at http://pubs.usgs.gov/ofr/2008/1279/

Pore-water sulfide

Pore-water sulfide collection sheet

Site Name: _____ Site Number: _____

Project Name: _____ Date: _____

Detection Limit of Electrode: -700 mV Electrode Used: _____

Sample ID	Sulfide Reading (mV)

Appendix 4. Sample Labels

All labels are 1 in. by 2-5/8 in., and designed to fit Avery© weather-proof mailing labels (Avery© label number 5520). All labels are available online as pre-formatted Microsoft© Word templates at: http://pubs.usgs.gov/ofr/2008/1279/ Please note that Avery© labels 5520 use the same Microsoft© Word template as Avery© label number 5160.

Appendix 4a. Sample labels: reconnaissance studies.

WMIC – 05 **04070720**
South Branch Oconto R. nr. Breed, WI
Medium Code: H
Sample Type: 9
Date: _____ Time: _____
Hg (THg and MeHg) – 30-mL Jar

WMIC – 05 **04070720**
South Branch Oconto R. nr. Breed, WI
Medium Code: H
Sample Type: 9
Date: _____ Time: _____
AVS – 30-mL Jar

WMIC – 05 **04070720**
South Branch Oconto R. nr. Breed, WI
Medium Code: H
Sample Type: 9
Date: _____ Time: _____
Sand/Fine – 30-mL Jar Acct. No.: XXXXX

Appendix 4. Sample labels—Continued.

All labels are 1 in. by 2-5/8 in., and designed to fit Avery© weather-proof mailing labels (Avery© label number 5520). All labels are available online as pre-formatted Microsoft© Word templates at: http://pubs.usgs.gov/ofr/2008/1279/ Please note that Avery© labels 5520 use the same Microsoft© Word template as Avery© label number 5160.

Appendix 4b. Sample labels: detailed studies.

Bed sediment for LOI **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Pore water for Hg **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Bed sediment for percent fines **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Pore water for DOC **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Bed sed. for MeHg prod/degrad. **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Pore water for anions **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Bed sediment sample for Hg **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Pore water for nutrients **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Bed sediment for AVS **04075365**
Evergreen River near Langlade, WI
Date: _____ Time: _____
Medium: _____ Sample Type: _____
Depth: _____ Site: _____
Contact: <Contact name> (XXX/XXX-XXXX)

Appendix 5. Equipment Required for Bed-Sediment and Pore-Water Sampling in Association with the National Water-Quality Assessment (NAWQA) Program Reconnaissance and Detailed Mercury Studies.

[cm, centimeter; *M*, molar; HCl, hydrochloric acid; mm, millimeter; mL, milliliter; WMRL, Wisconsin Mercury Research Laboratory; ®, registered trademark; THg, total mercury; MeHg, methylmercury; $Hg(II)_R$, reactive mercury; USEPA, U.S. Environmental Protection Agency; AVS, acid-volatile sulfide; LOI, loss on ignition; n/a, not applicable; SW, stream water; PW, pore water; QFF, quartz fiber filter; µm, micrometer; N, normal; L, liter; DOC, dissolved organic carbon; HDPE, high-density polyethylene; ORP, oxidation-reduction potential; SAOB, sulfide antioxidant buffer; cm^3, cubic centimeter; MPP, methylmercury production potential; MDP, methylmercury degradation potential; V, volt; m, meter; PVC, polyvinyl chloride; DI, deionized; %, percent; GPS, Global Positioning System; WAAS, wide area augmentation system; sample (to which quantities are related to) refers to all sediment and pore water (where applicable) collected from the same sampling area within a stream; study area (to which quantities are related to) refers to the NAWQA study area (for example, the Willamette Basin)]

Equipment	Cleaning procedure	Quantity per study				Quantity relates to each…
		Reconnaissance	Detailed			
			Reach characterization[1]	Spatial	Temporal	
Methylmercury production- and degradation-potential-rates laboratory						
2-cm sections of polycarbonate core tube (8-cm diameter)	Laboratory method[2]	0	1	1	1	Stream
Flexible solid plastic sheets	Laboratory method[2]	0	2	2	2	Stream
Half-pint mason jars	Laboratory method[2]	0	0	1	1	Sample
Lids (for half-pint mason jars)	New	0	0	1	1	Sample
Nylon 1-mm mesh (10 cm x 10 cm)	New	0	0	1	1	Stream
Plastic beakers with bottom cut off (250-mL)	Laboratory method[2]	0	0	1	1	Stream
Plastic bottle that fits through small end of cut-off beaker	Laboratory method[2]	0	0	1	1	Stream
Wisconsin Mercury Research Laboratory (WMRL)						
20-mL Teflon® jar (acid rinsed) (for sediment THg/MeHg/$Hg(II)_R$)	USEPA, 2002	1	0	1	1	Sample
30-mL polypropylene jar (not acid-rinsed) (for sediment AVS, percent fines, and LOI)	New	2	2	2	2	Sample
Zinc-acetate solution (for preserving AVS samples)	n/a	1	0	0	0	Trip
Disposable pipets (graduated at 0.1-mL increments) (for delivering zinc-acetate solution to AVS samples)	New	1	0	0	0	Sample
Pore-water probe	USEPA, 2002	0	0	1	1	Trip
Acrylic disc (for minimizing the flow of SW into the PW-sampling area)	Laboratory method[3]	0	0	1	1	Trip
Long Teflon® sampling line (1/4-inch outside diameter)	USEPA, 2002	0	0	1	1	Stream
Short C-flex pump-head tube	Laboratory method[4]	0	0	1	1	Stream
Short Teflon® sampling line (1/4-inch outside diameter)	USEPA, 2002	0	0	1	1	Stream
Loaded filter cartridges (QFF: 47-mm diameter, 0.7-µm nominal pore size)	USEPA, 2002	0	0	3	3	Sample

Appendix 5. Equipment required for bed-sediment and pore-water sampling in association with the National Water-Quality Assessment (NAWQA) Program reconnaissance and detailed mercury studies—Continued.

[cm, centimeter; *M*, molar; HCl, hydrochloric acid; mm, millimeter; mL, milliliter; WMRL, Wisconsin Mercury Research Laboratory; ®, registered trademark; THg, total mercury; MeHg, methylmercury; $Hg(II)_R$, reactive mercury; USEPA, U.S. Environmental Protection Agency; AVS, acid-volatile sulfide; LOI, loss on ignition; n/a, not applicable; SW, stream water; PW, pore water; QFF, quartz fiber filter; µm, micrometer; N, normal; L, liter; DOC, dissolved organic carbon; HDPE, high-density polyethylene; ORP, oxidation-reduction potential; SAOB, sulfide antioxidant buffer; cm^3, cubic centimeter; MPP, methylmercury production potential; MDP, methylmercury degradation potential; V, volt; m, meter; PVC, polyvinyl chloride; DI, deionized; %, percent; GPS, Global Positioning System; WAAS, wide area augmentation system; sample (to which quantities are related to) refers to all sediment and pore water (where applicable) collected from the same sampling area within a stream; study area (to which quantities are related to) refers to the NAWQA study area (for example, the Willamette Basin)]

Equipment	Cleaning procedure	Quantity per study				Quantity relates to each…
		Reconnaissance	Detailed			
			Reach characterization[1]	Spatial	Temporal	
Zip ties	New	0	0	1	1	Sample
500-mL coded Teflon® sample bottle (for filtered THg and MeHg)	USEPA, 2002	0	0	1	1	Sample
Spare filters (QFF: 47-mm diameter, 0.7-µm nominal pore size)	Laboratory method[5]	0	0	5	5	Sample
Tweezers (for loading spare filters into cartridges)	USEPA, 2002	0	0	2	2	Trip
Cartridge wrench	n/a	0	0	2	2	Trip
Bottle of 6*N*-HCl with jar (for filtered THg and MeHg preservation)	n/a	0	0	1	1	Study area
1-L bottle of Milli-Q® water (for pore water THg and MeHg blanks)	n/a	0	0	Varies	Varies	Trip
Carbon geochemistry laboratory						
40-mL amber baked glass bottles with Teflon®-lined lids (for DOC)	New or baked using laboratory method[6]	0	0	1	1	Sample
Sulfur geochemistry laboratory						
Anion vials	New	0	0	1	1	Sample
Nutrient vials	New	0	0	1	1	Sample
20-mL HDPE scintillation vials (for pore-water sulfide, ORP, and pH)	New	0	0	2	2	Sample
SAOB in vials (pre-measured)	n/a	0	0	1	1	Day
Ascorbic acid in vials (pre-measured)	n/a	0	0	1	1	Day
5-cm^3 syringe (for pore-water ORP and sulfide)	New	0	0	2	2	Sample
C-flex tube (for ORP)	New	0	0	1	1	Sample
Sulfide electrode (Orion® model 9616BN)	n/a	0	0	1	1	Kit
Filling solution A (for sulfide electrode)	n/a	0	0	1	1	Kit
Sediment-ORP electrode (Orion® model 9180BN)	n/a	0	0	1	1	Kit
Pore-water-ORP electrode (Microelectrodes, Inc. model MI-800/710)	n/a	0	0	1	1	Kit

Appendix 5. Equipment required for bed-sediment and pore-water sampling in association with the National Water-Quality Assessment (NAWQA) Program reconnaissance and detailed mercury studies—Continued.

[cm, centimeter; *M*, molar; HCl, hydrochloric acid; mm, millimeter; mL, milliliter; WMRL, Wisconsin Mercury Research Laboratory; ®, registered trademark; THg, total mercury; MeHg, methylmercury; $Hg(II)_R$, reactive mercury; USEPA, U.S. Environmental Protection Agency; AVS, acid-volatile sulfide; LOI, loss on ignition; n/a, not applicable; SW, stream water; PW, pore water; QFF, quartz fiber filter; µm, micrometer; N, normal; L, liter; DOC, dissolved organic carbon; HDPE, high-density polyethylene; ORP, oxidation-reduction potential; SAOB, sulfide antioxidant buffer; cm^3, cubic centimeter; MPP, methylmercury production potential; MDP, methylmercury degradation potential; V, volt; m, meter; PVC, polyvinyl chloride; DI, deionized; %, percent; GPS, Global Positioning System; WAAS, wide area augmentation system; sample (to which quantities are related to) refers to all sediment and pore water (where applicable) collected from the same sampling area within a stream; study area (to which quantities are related to) refers to the NAWQA study area (for example, the Willamette Basin)]

Equipment	Cleaning procedure	Quantity per study				Quantity relates to each…
		Reconnaissance	Detailed			
			Reach characterization[1]	Spatial	Temporal	
Orion® ORP standard	n/a	0	0	1	1	Kit
ORP filling solution	n/a	0	0	1	1	Kit
Low-maintenance pH/temperature triode (Orion® model 9107BN)	n/a	0	0	1	1	Kit
pH calibration standards	n/a	0	0	1	1	Kit
Magnetic stir plate	n/a	0	0	1	1	Kit
Stir bars (12.7-mm length)	n/a	0	0	1	1	Kit
Orion® meter model 250 A+	n/a	0	0	1	1	Kit
Study area						
Guillotine sampler/10-cm section of 1.5-inch diameter Teflon® tube/Teflon® spoon, scoop or spatula/plastic spoon or scoop (can be made by cutting plastic sample bottle)	Shelton and Capel, 1994; Wilde, 2004	1	0	0	0	Sample
Glass/Teflon®/plastic bowl (for compositing samples)	Shelton and Capel, 1994; Wilde, 2004	1	0	0	0	Sample
120-mL polypropylene jar (for compositing samples)	Shelton and Capel, 1994; Wilde, 2004	0	0	1	1	Sample
Plastic spoon/Teflon® policeman (WMRL) (for mixing sediment)	Shelton and Capel, 1994; Wilde, 2004	1	0	1	1	Sample
Grab sampler (Birge-Ekman, 9-inch square)	Shelton and Capel, 1994; Wilde, 2004	1	1	1	1	Trip
Soft rope (in meters) (for grab sampler, clipboards, and float boats)	n/a	6	15–30	6	6	Trip
Sieve (0.063-mm pore size) (for assisting in categorizing substrate zones)	n/a	0	1	1	1	Trip
Parafilm M® roll (for sealing mason jars)	n/a	0	0	1	1	Study area
Foam sleeves (for protecting the MPP- and MDP-rates samples in storage and shipment)	New	0	0	1	1	Sample
Floating cooler/tub boats for equipment towing on stream	n/a	0	0	2	2	Trip
Peristaltic pump	n/a	0	0	1	1	Trip
12-V battery	n/a	0	0	1	1	Trip

Appendix 5. Equipment required for bed-sediment and pore-water sampling in association with the National Water-Quality Assessment (NAWQA) Program reconnaissance and detailed mercury studies—Continued.

[cm, centimeter; *M*, molar; HCl, hydrochloric acid; mm, millimeter; mL, milliliter; WMRL, Wisconsin Mercury Research Laboratory; ®, registered trademark; THg, total mercury; MeHg, methylmercury; $Hg(II)_R$, reactive mercury; USEPA, U.S. Environmental Protection Agency; AVS, acid-volatile sulfide; LOI, loss on ignition; n/a, not applicable; SW, stream water; PW, pore water; QFF, quartz fiber filter; µm, micrometer; N, normal; L, liter; DOC, dissolved organic carbon; HDPE, high-density polyethylene; ORP, oxidation-reduction potential; SAOB, sulfide antioxidant buffer; cm^3, cubic centimeter; MPP, methylmercury production potential; MDP, methylmercury degradation potential; V, volt; m, meter; PVC, polyvinyl chloride; DI, deionized; %, percent; GPS, Global Positioning System; WAAS, wide area augmentation system; sample (to which quantities are related to) refers to all sediment and pore water (where applicable) collected from the same sampling area within a stream; study area (to which quantities are related to) refers to the NAWQA study area (for example, the Willamette Basin)]

Equipment	Cleaning procedure	Quantity per study				Quantity relates to each…
		Reconnaissance	Detailed			
			Reach characterization[1]	Spatial	Temporal	
Lead for 12-V battery (for connection to the peristaltic pump)	n/a	0	0	1	1	Trip
Clear zip ties (for attaching C-flex tube to short Teflon® tube)	New	0	0	1	1	Sample
Rangefinder (for measuring reach length, distance from reference location, distance between transects; best if has at least a 10-m minimum range)	n/a	1	1	1	1	Trip
Stream measuring tape [metric preferred] (for measuring stream width, point locations)	n/a	0	1	0	0	Trip
Stakes for measuring tape	n/a	0	2	0	0	Trip
Stake flags (for marking transects on both sides of stream)	n/a	0	30	Varies	Varies	Stream
Flagging tape roll (in case stake flag is hard to see)	n/a	0	1	1	1	Trip
4-person inflatable raft (for carrying transect-sampling equipment)	n/a	0	1	0	0	Trip
Inflators (for inflating raft(s))	n/a	0	1	0	0	Trip
Small, inexpensive calculator	n/a	0	1	0	0	Trip
PVC Pipe (1-inch inside diameter or larger)	New	0	1	0	0	Trip
Cooler with wet ice (for storing and shipping sediment samples for MPP and MDP rates; for storing PW samples for DOC and anions)	n/a	0	0	2	2	Trip
Cooler with dry ice (for storing sediment THg, MeHg, $Hg(II)_R$, AVS, and LOI samples; for storing PW-nutrient samples)	n/a	1	3	1	1	Trip
Empty cooler/box (for storing sediment percent fines, and PW THg and MeHg samples)	n/a	1	2	1	1	Trip
Minipiezometers	n/a	0	0	1	1	Stream
Shovel (for retrieving the minipiezometer tip, if needed)	n/a	0	0	1	1	Trip
Hand vacuum pump	n/a	0	0	1	1	Trip
C-flex tube (for connecting hand vacuum pump to minipiezometer tubes)	n/a	0	0	1	1	Trip

Appendix 5. Equipment required for bed-sediment and pore-water sampling in association with the National Water-Quality Assessment (NAWQA) Program reconnaissance and detailed mercury studies—Continued.

[cm, centimeter; *M*, molar; HCl, hydrochloric acid; mm, millimeter; mL, milliliter; WMRL, Wisconsin Mercury Research Laboratory; ®, registered trademark; THg, total mercury; MeHg, methylmercury; $Hg(II)_R$, reactive mercury; USEPA, U.S. Environmental Protection Agency; AVS, acid-volatile sulfide; LOI, loss on ignition; n/a, not applicable; SW, stream water; PW, pore water; QFF, quartz fiber filter; µm, micrometer; N, normal; L, liter; DOC, dissolved organic carbon; HDPE, high-density polyethylene; ORP, oxidation-reduction potential; SAOB, sulfide antioxidant buffer; cm^3, cubic centimeter; MPP, methylmercury production potential; MDP, methylmercury degradation potential; V, volt; m, meter; PVC, polyvinyl chloride; DI, deionized; %, percent; GPS, Global Positioning System; WAAS, wide area augmentation system; sample (to which quantities are related to) refers to all sediment and pore water (where applicable) collected from the same sampling area within a stream; study area (to which quantities are related to) refers to the NAWQA study area (for example, the Willamette Basin)]

Equipment	Cleaning procedure	Quantity per study				Quantity relates to each…
		Reconnaissance	Detailed			
			Reach characterization[1]	Spatial	Temporal	
Meter stick/ruler (for minipiezometer-head measurements)	n/a	0	0	1	1	Trip
Multiparameter instrument (for example, Hydrolab® Quanta®)	n/a	1	1	1	1	Trip
Barometer	n/a	1	1	1	1	Trip
Set of pH calibration standards	n/a	1	1	1	1	Trip
Specific-conductance calibration standards	n/a	1	1	1	1	Trip
Squirt bottle (for rinsing electrodes)	n/a	1	1	1	1	Trip
1-L bottle of dilute Liquinox® (for cleaning in the field)	New	1	1	1	1	Trip
Tap-water carboy (for cleaning in the field and for multiparameter-probestorage)	New	1	1	1	1	Trip
DI-water carboy (for cleaning equipment in the field and for rinsing the electrodes during calibrations)	New	1	1	1	1	Trip
Carboy of 5% HCl (for cleaning in the field)	New	1	1	1	1	Trip
Carboy for waste acid	New	1	1	1	1	Trip
Plastic shoulder-length veterinary gloves (boxes)	New	1	2	1	1	Trip
Non-powder nitrile gloves (boxes)	New	1	6	3	1	Trip
Ziploc® bags (boxes) (for storing samples)	New	1	3	1	1	Trip
Large clear/white garbage bags (boxes)	New	1	1	1	1	Trip
Kimwipes (boxes)	n/a	1	3	2	1	Trip
Chairs (for calibrations and processing)	n/a	1	2	2	2	Trip
Tarp (for covering equipment if it rains)	n/a	1	2	2	2	Trip
Table (for calibrations and processing)	n/a	1	1	1	1	Trip
GPS unit with WAAS, time-averaging capabilities, andan external antenna	n/a	0	1–2	1	1	Trip
Digital camera	n/a	1	1	1	1	Trip

Appendix 5. Equipment required for bed-sediment and pore-water sampling in association with the National Water-Quality Assessment (NAWQA) Program reconnaissance and detailed mercury studies—Continued.

[cm, centimeter; *M*, molar; HCl, hydrochloric acid; mm, millimeter; mL, milliliter; WMRL, Wisconsin Mercury Research Laboratory; ®, registered trademark; THg, total mercury; MeHg, methylmercury; $Hg(II)_R$, reactive mercury; USEPA, U.S. Environmental Protection Agency; AVS, acid-volatile sulfide; LOI, loss on ignition; n/a, not applicable; SW, stream water; PW, pore water; QFF, quartz fiber filter; µm, micrometer; N, normal; L, liter; DOC, dissolved organic carbon; HDPE, high-density polyethylene; ORP, oxidation-reduction potential; SAOB, sulfide antioxidant buffer; cm^3, cubic centimeter; MPP, methylmercury production potential; MDP, methylmercury degradation potential; V, volt; m, meter; PVC, polyvinyl chloride; DI, deionized; %, percent; GPS, Global Positioning System; WAAS, wide area augmentation system; sample (to which quantities are related to) refers to all sediment and pore water (where applicable) collected from the same sampling area within a stream; study area (to which quantities are related to) refers to the NAWQA study area (for example, the Willamette Basin)]

Equipment	Cleaning procedure	Quantity per study				Quantity relates to each…
		Reconnaissance	Detailed			
			Reach characterization[1]	Spatial	Temporal	
Tap-water carboy with spigot (for hand washing)	New	1	1	1	1	Trip
Bottle of antimicrobial hand soap (for hand washing)	n/a	1	1	1	1	Trip
Paper towels (boxes)	n/a	1	3	3	1	Trip
Two-way radios	n/a	0	2–3	2–3	0	Trip
Sharp knife and toolbox	n/a	1	1	1	1	Trip
Clipboard	n/a	1	2	2	1	Trip
First-aid kit	n/a	1	1	1	1	Trip
Copies of old sediment field forms (for locating previously sampled areas)	n/a	0	1	0	1	Trip
Copies of orthophotos and topographic maps of stream	n/a	0	1	1	1	Stream
Blank field form – Reach-establishment sheet	n/a	0	1	0	0	Stream
Blank field form – Transect sheet	n/a	0	20	0	0	Stream
Blank field form – Reach-diagram sheet	n/a	0	1	0	0	Stream
Blank field form – General sediment form	n/a	1	1	1	1	Stream
Blank field form – MPP- and MDP-rates field form	n/a	0	0	1	1	Sample
Blank field form – Pore-water-sulfide datasheet	n/a	0	0	1	1	Stream
Blank field form – USGS Stream-water field form	n/a	1	1	1	1	Stream
Waterproof labels – Avery© label number 5520 (1 by 2 5/8 inches)	n/a	3	2	8	8	Sample
Pens	n/a	4	10	10	4	Trip
Sharpies	n/a	4	10	10	4	Trip

[1] Assume 100 grab samples for each reach characterization.

[2] Equipment is washed in a bath of 4-*M* HCl.

[3] Equipment is washed with dilute Liquinox®. It is then rinsed three times with tap water, three times with Milli-Q® water, and allowed to air dry.

[4] Tube is filled with 50% nitric acid, the ends of the tube are sealed, and it is soaked in a room temperature 10% HCl bath for a minimum of 7 days.

[5] Equipment is ashed in a muffle furnace at 550º C for a minimum of 2 hours.

[6] Bottles and caps are rinsed three times with tap water, and three times with DI water. Bottles are then baked at 450º C for 4 hours. Caps are dried at room temperature, and then secured onto clean, cooled bottles.

Appendix 6. Laboratory Contact Information for U.S. Geological Survey Laboratories Performing Analyses for the National Water-Quality Assessment (NAWQA) Program Reconnaissance and Detailed Mercury Studies.

[USGS, U.S. Geological Survey; MS, mail stop; CA, California; CO, Colorado; IA, Iowa; VA, Virginia; WI, Wisconsin]

USGS laboratory	Shipping address	Contact
Methylmercury production- and degradation-potential-rates laboratory	USGS Branch of Regional Research attn: Jennifer Agee 345 Middlefield Road Building 15, McKelvey Building MS 480 Menlo Park, CA 94025-3561	Mark Marvin-DiPasquale
Wisconsin Mercury Research Laboratory (WMRL)	USGS Wisconsin Water Science Center attn: John DeWild 8505 Research Way Middleton, WI 53562-3586	David Krabbenhoft
Carbon geochemistry laboratory	USGS Branch of Regional Research attn: Kenna Butler 3215 Marine Street Suite E-127 Boulder, CO 80303-1290	George Aiken
Sulfur geochemistry laboratory	USGS Branch of Regional Research attn: Margo Corum 12201 Sunrise Valley Drive MS 956 Reston, VA 20192-0002	William Orem
Sediment laboratory	USGS Iowa City Sediment Laboratory attn: Julie Nason 400 South Clinton Street Room #269 Iowa City, IA 52240-4105	Julie Nason

Appendix 7. Shipping Forms for Reconnaissance and Detailed Studies.

Appendix 7a. Generic shipping form for the methylmercury production- and degradation-potential-rates laboratory, the Wisconsin Mercury Research Laboratory (for transect samples only), the carbon geochemistry laboratory, and the sulfur geochemistry laboratory.

This form is available for download at http://pubs.usgs.gov/ofr/2008/1279/

Generic shipping form

Filename:	HgStudy_SUID_YYYYMMDD.xls	**Shipper instructions:**
Study area contact:		(1) Enter sample login data into this spreadsheet
Fax number:		(2) Sign, date, and ship hard copy of this form with samples.
Shipped by:		(3) Email electronic copy to laboratory to facilitate lab log-in.
Shipping date:		**Lab Instructions:**
Received by:		(4) Sign, date, and note comments upon receipt of samples.
Received date:		(5) Save form. Fax or mail copy to study area contact.
Lab notes / condition of samples:		

Sample data									
Station-identification number (STAID)	Date (DATES)	Time (TIMES)	Medium code (MEDIM)	Station name (SNAME)	Analyses requested	Number of containers	General description		
15	9	4	1	50					

Appendix 7. Shipping forms for reconnaissance and detailed studies—Continued.

Appendix 7b-1. Analytical services request form for the Wisconsin Mercury Research Laboratory (WMRL).

These forms are available for download at http://pubs.usgs.gov/ofr/2008/1279/

Analytical services request form, page 1

WISCONSIN MERCURY RESEARCH LABORATORY REQUEST FOR ANALYSIS

SITE NAME:_____ SITE NUMBER:_____

PROJECT NAME:_____ PROJECT NUMBER:_____

DATE:_____ TIME:_____ DEPTH (M):_____ REPLICATE:_____

container identification	sample medium	analysis type	filter type	volume filtered	<----------preservative----------> type	identification	volume

COMMENTS: _____

SPECIAL REQUESTS

LABORATORY FILTERING			LABORATORY SPLITTING	
container identification	analysis types	filter type	container identification	analysis types

LABORATORY USE ONLY

LOGIN DATE: _____ ANALYST: _____

COMMENTS: _____

PAGE 1 OF ____

WMRL FORM F03 REVISION 4 , 7/25/07

Appendix 7. Shipping forms for reconnaissance and detailed studies—Continued.

Appendix 7b-1. Analytical services request form for the Wisconsin Mercury Research Laboratory (WMRL).

These forms are available for download at http://pubs.usgs.gov/ofr/2008/1279/

Analytical services request form, page 2

SAMPLE MEDIUM -- REGULAR	
1	suspended sediment
6	ground water
7	wet deposition
9	surface water
C	animal tissue
D	plant tissue
F	interstitial (pore) water
G	soil
H	bottom material (sediment)

SAMPLE MEDIUM -- QUALITY ASSURANCE	
Q	artificial
R	surface water
S	ground water
T	wet deposition
V	suspended sediment
W	bottom material (sediment)
X	animal tissue
Y	plant tissue
Z	interstitial (pore) water

ANALYSIS TYPE	
UTHG	unfiltered total mercury
UMHG	unfiltered methyl mercury
FTHG	filtered total mercury
FMHG	filtered methyl mercury
PTHG	suspended sediment (particulate) total mercury
PMHG	suspended sediment (particulate) methyl mercury
STHG	bottom sediment total mercury
SMHG	bottom sediment methyl mercury
BTHG	biological total mercury
BMHG	biological methyl mercury
UTHGI	unfiltered total mercury isotopes
UMHGI	unfiltered methyl mercury isotopes
FTHGI	filtered total mercury isotopes
FMHGI	filtered methyl mercury isotopes
PTHGI	suspended sediment (particulate) total mercury isotopes
PMHGI	suspended sediment (particulate) methyl mercury isotopes
STHGI	bottom sediment total mercury isotopes
SMHGI	bottom sediment methyl mercury isotopes
BTHGI	biological total mercury isotopes
BMHGI	biological methyl mercury isotopes
URHG	unfiltered reactive mercury
FRHG	filtered reactive mercury
HG^0	gaseous mercury
SPM	suspended particulate matter
AVS	acid volatile sulfide
UV ABS	uv absorbance
DOC	dissolved organic carbon
TOC	total organic carbon
LOI	loss on ignition

FILTER TYPE	
Q	quartz fiber filter
C22	0.22um capsule
C45	0.45um capsule
M45	0.45um meissner
N22	0.22um nitrocellulose
N45	0.45um nitrocellulose
PC40	0.45um polycarbonate
OTHER	please describe

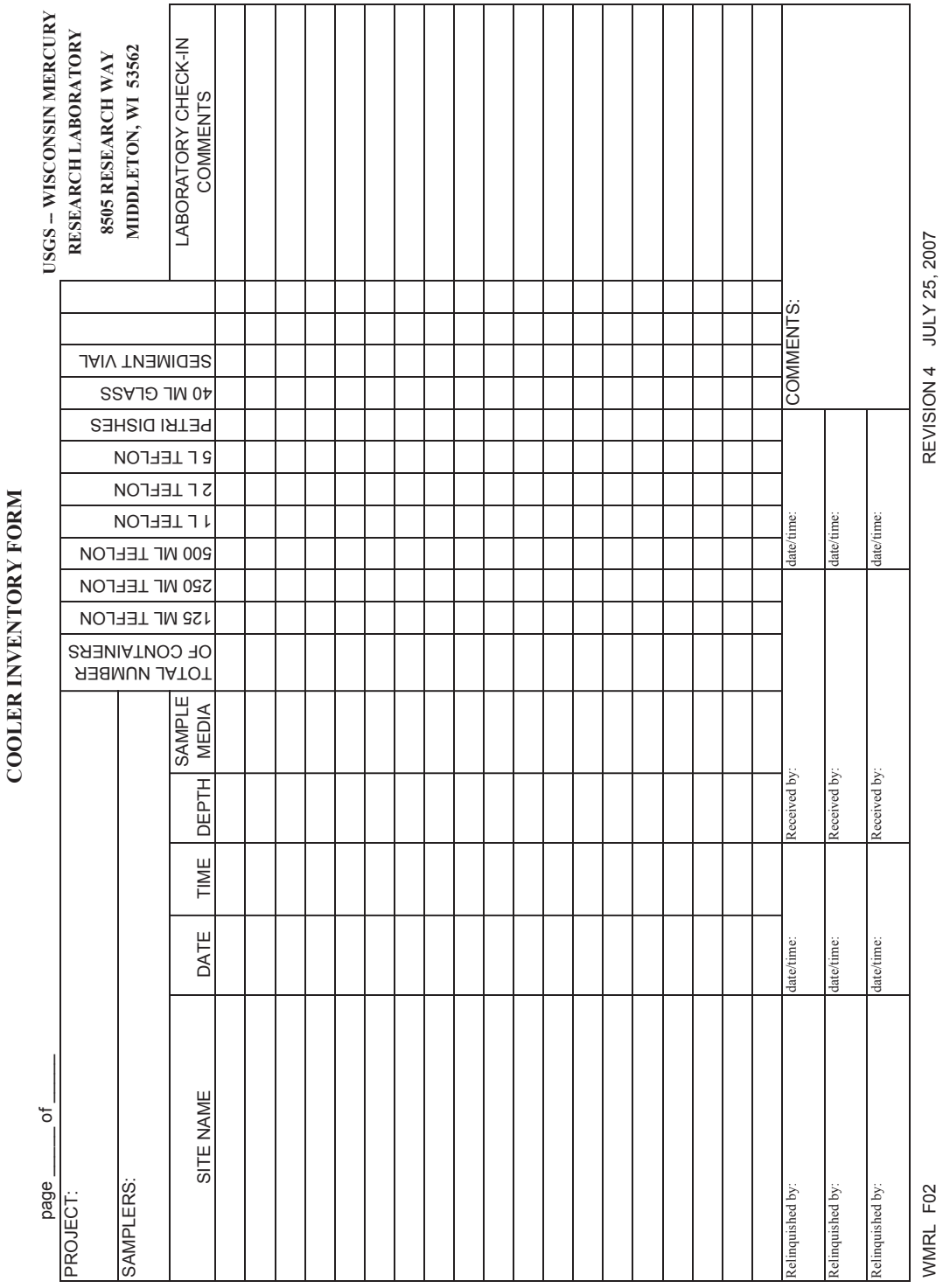
PRESERVATION TYPE	
A	acidification
F	freezing
N	none

Appendix 7. Shipping forms for reconnaissance and detailed studies—Continued.

Appendix 7b-2. Cooler inventory form for the Wisconsin Mercury Research Laboratory (WMRL).

These forms are available for download at http://pubs.usgs.gov/ofr/2008/1279/

Cooler inventory form



Appendix 7. Shipping forms for reconnaissance and detailed studies—Continued.

Appendix 7c. Shipping form for the Iowa City Sediment Laboratory (ISCL).

This form is available for download at http://pubs.usgs.gov/ofr/2008/1279/

ISCL shipping form, page 1

U. S. GEOLOGICAL SURVEY SEDIMENT LAB ANALYSIS REQUEST
SW / SEDIMENT SAMPLE INFORMATION AT A SITE (SLAR v. 1.04)

This is___ of ___ sites [cases] in this case [shipment]. ___total bottles in this case.

Lab_____ Date Shipped_____ Date Rec'd _____by____
Possibly Hazardous? Yes No Explain_____

Station No._____ Station Name_____ Time Datum _____ [ie., PDT]
Shipped by_____@usgs.gov Phone No _____ Billing Account No._____ Project Chief_____@usgs.gov
Parameter Family: ☐Suspended ☐Bed-Material ☐ Bedload ☐ Total Hydrologic Condition:_____ Hydrologic Event:_____ District Code____

Enter in table below: **Sampling Method** (82398) **Bedload:** Single Equal Width Increment (**1000**) Multiple Equal Width Increment (**1010**) Unequal Width Increment (**1020**)
Suspended: EWI(**10**) EDI(**20**) Single-Vertical(**30**) Multiple-vertical (**40**) Fixed Single Vertical-BOX (**920**) Pumping (**900**) Single-stage (**910**) Partial-Depth (**930**) Partial-Width (**940**) Point (**50**) Grab (**70**)
Lab Analysis Codes Requested: (**C**) Concentration (**SF**) Sand-Fine (**SA**) Sand (**Z**) Full-Size (**BD**) Bulk-Density (**LOI**) Loss-on-Ignition (**DS**) Dissolved-Solids (**T**) Turbidity
(**CC**) Composite-Concentration (**CSF**) Composite Sand-Fine (**CSA**) Composite Sand-Analysis (**CZ**) Composite Full-Size (**SC**) Specific Conductance

INDIVIDUAL BOTTLE INFORMATION -- 1 line for each bottle (arrow/ditto down to duplicate) Grey columns required

Pos. No. in Case	Sample Start Date (mm-dd-yy)	Start or Mean Time (24hr)	Sample End Date (mm-dd-yy) OPTIONAL	End Time (24hr) OPT.	Medium	Sample Type	Set ID	Bottle No. in Set	Gage Height	Water Temperature (° C)	Sampling Method (see codes above)	Lab Analysis Code(s) Requested (above)	Collector Initials	Remarks	(for Lab use only) Bottle Condition codes	(for Lab use only) Lab Sample ID
1																
2																
3																
4																
5																
6																
7																
8																
9																
10																
11																
12																
13																
14																
15																
16																
17																
18																
19																
20																

Appendix 7. Shipping forms for reconnaissance and detailed studies—Continued.

Appendix 7c. Shipping form for the Iowa City Sediment Laboratory (ISCL).

This form is available for download at http://pubs.usgs.gov/ofr/2008/1279/

ISCL shipping form, page 2

U. S. GEOLOGICAL SURVEY SEDIMENT LAB ANALYSIS REQUEST

BACK OF FORM – EXPLANATION (SLAR v. 1.04)

Lab: Sediment lab you are shipping sample to.
Shipped by: email_id@usgs.gov or phone will be used for login questions.
Project Chief: email_id@usgs.gov will be used for data transmittal information or questions.
District Code: NWQL "Users code" for NWIS host computer for data return to NWIS. Usually the same as the "State Postal code" (although some districts have a modified postal code for multiple NWIS hosts in a District, e.g. CA1 or FL1). Enter NONE for non-USGS collectors
Parameter Family: Check the box for the appropriate type of sediment, each of which has its own group of NWIS Parameter codes for size fractions.

NWIS codes:

Medium: 9 = Surface Water, R = Surface Water QC, H = Bottom Material, W = Bottom Material QC, 1 = Suspended Sediment, V = Suspended Sediment QC, B = Solids, E = Core Material, G = Soil, J = Sludge, 3 = Dry Deposition, 8 = Bulk Deposition, U = Bulk Deposition QC, Q = Artificial QC (ie., equip. blank)
Sample Type: 9 = Regular, 7 = Replicate, B = Other QA, H = Composite (time), 1 = Spike, 2 = Blank, 3 = Reference, 4=Blind
Hydrologic Condition: A = Not determined, 4 = Stable, low stage, 5 = Falling stage, 6 = Stable, high stage, 7 = Peak stage, 8 = Rising stage, 9 = Stable, normal stage, X = Not applicable
Hydrologic Event: A = Spring breakup, B = Under ice cover, C = Glacial lake outbreak, D = Mudflow, E = Tidal action, F = Fire, H = Dam break, J = Storm, K = Backwater, 1 = Drought, 2 = Spill, 3 = Regulated flow, 4 = Snowmelt, 5 = Earthquake, 6 = Hurricane, 7 = Flood, 8 = Volcanic action, 9 = Routine sample, X = Not applicable
Sampling Method: Enter one numeric NWIS fixed-value sampling method (NWIS Pcode 82398) per sample.

NOTE THAT ONE LINE ON THE BOTTOM TABLE IS USED FOR EACH BOTTLE.
DUPLICATE INFORMATION MAY BE DITTOED DOWN OR SHOWN BY ARROWS.

Analysis Codes Requested – Enter code[s] for analyses requested in the column next to the remarks.
Remarks – add remarks pertaining to the sample set or bottle.

SHIPPING INSTRUCTIONS

- ✓ Follow placement guide for packing – Bottle #1 information on the form should match Bottle #1 in case.
- ✓ Collection date (mm-dd-yy) and time (military) on the information sheet matches the bottle(s)
- ✓ Please include both Shipper and Project Chief's email userids
- ✓ Please make sure the containers are properly labeled and sealed.
- ✓ Enclose paperwork in a Ziploc type bag. Ship samples and accompanying paperwork in a well-padded and securely-strapped case.

GUIDE "A"			
17	18	19	20
13	14	15	16
9	10	11	12
5	6	7	8
1	2	3	4

SHIPPING CASE BOTTLE PLACEMENT GUIDE

GUIDE "B"		
10	11	12
7	8	9
4	5	6
1	2	3

Guide "C"			Fill-in	

(Lab use only)

Bottle Condition Codes: use on front side, 2nd to last column

NWL = Water Line NOT Marked
WBL = Water level below water line
NTP = Tape NOT Properly Applied
BRK = Broken or Spilled
Sender will be notified by email when leakage or breakage is noted.

This page intentionally left blank.

Publishing support provided by:
Columbus and Tacoma Publishing Service Centers

For more information concerning this publication, contact:
Chief, USGS National Water Quality Assessment Program
MS 413 National Center
Reston, VA 20192
(703) 648–5716
Or visit the National Water Quality Assessment Program site at:
http://water.usgs.gov/nawqa/