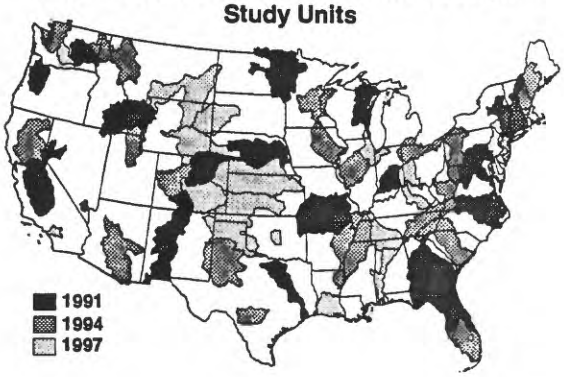
GUIDELINES FOR COLLECTING AND PROCESSING SAMPLES OF STREAM BED SEDIMENT FOR ANALYSIS OF TRACE ELEMENTS AND ORGANIC CONTAMINANTS FOR THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

U.S. GEOLOGICAL SURVEY
Open-File Report 94-458



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

By Larry R. Shelton *and* Paul D. Capel

U.S. GEOLOGICAL SURVEY
Open-File Report 94-458

8056-14

Sacramento, California
1994

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

For sale by the
U.S. Geological Survey
Earth Science Information Center
Open-File Reports Section
Box 25286, MS 517
Denver Federal Center
Denver, CO 80225

For additional information write to:
Chief, Pesticides National Synthesis Project, NAWQA
U.S. Geological Survey
Federal Building, Room W-2233
2800 Cottage Way
Sacramento, CA 95825

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

Conversion Factors

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
inch (in.)	25.4	millimeter
square inch (in^2)	645.2	square millimeter

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F=1.8(°C+32)$$

Abbreviations

cm, centimeter
g, gram
km^2, square kilometer
L, liter
m, meter
μm, micrometer
mL, milliliter
mm, millimeter

Acronyms

NAWQA, National Water Quality Assessment
NWQL, National Water Quality Laboratory
TOC, total organic carbon
USGS, U.S. Geological Survey

GLOSSARY

Basic Fixed Sites—Sites on streams at which streamflow is measured and samples are collected for temperature, salinity, suspended sediment, major ions and metals, nutrients, and organic carbon to assess the broad-scale spatial and temporal character and transport of inorganic constituents of stream water in relation to hydrologic conditions and environmental settings.

Bed-Sediment and Tissue Studies—Assessment of concentrations and distributions of trace elements and hydrophobic organic contaminants in stream bed sediment and tissues of aquatic organisms to identify potential sources and assess spatial distribution.

Ecological Studies—Studies of biological communities habitat characteristics to evaluate the effects of physical and chemical characteristics of water and hydrologic conditions on aquatic biota and to determine how biological and habitat characteristics differ among environmental settings in Study Units.

Indicator Sites—Stream sampling sites located at outlets of drainage basins with relatively homogeneous land use and physiographic conditions. Basins are as large and representative as possible, but still encompassing primarily one environmental setting (typically, 50 to 500 km^2).

Integrator Site—Stream sampling sites located downstream of drainage basins that are large and complex and often contain multiple environmental settings. Most Integrator Sites are on major streams with drainage basins that include a substantial portion of the Study Unit (typically, 10 to 100 percent).

Intensive Fixed Sites—Basic Fixed Sites with increased sampling frequency during selected seasonal periods and analysis of dissolved pesticides for 1 year. One or two integrator Intensive Fixed Sites and one to four indicator Intensive Fixed Sites are present in most Study Units.

Occurrence and Distribution Assessment—Assessment of the broad-scale geographic and seasonal distributions of water-quality conditions for surface and ground water of a Study Unit in relation to major contaminant sources and background conditions.

Occurrence Survey—The first phase of study of trace elements and hydrophobic organic contaminants in stream bed sediment and tissues of aquatic organisms. The primary objective is to determine which target constituents are common and important to water-quality conditions in each Study Unit.

Spatial Distribution Survey—Extension of the Occurrence Survey for bed sediments and tissues to improve geographic coverage, with particular emphasis on assessment of priority constituents identified in the Occurrence Survey.

Study Unit—A major hydrologic system of the United States in which NAWQA studies are focused. NAWQA Study Units are geographically defined by a combination of ground- and surface-water features and usually encompass more than 10,000 km^2 of land area. The NAWQA design is based on assessment of 60 Study Units, which collectively cover a large part of the Nation, encompass the majority of population and water use, and include diverse hydrologic systems that differ widely in natural and human factors that affect water quality.

Water-Column Studies—Assessment of physical and chemical characteristics of stream water, including suspended sediment, dissolved solids, major ions and metals, nutrients, organic carbon, and dissolved pesticides, in relation to hydrologic conditions, sources, and transport.

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

by Larry R. Shelton *and* Paul D. Capel

Abstract

A major component of the U.S. Geological Survey's National Water-Quality Assessment program is to characterize the geographic and seasonal distributions of water-quality conditions in relation to major contaminant sources. For streams, the assessment of trace elements and organic contaminants is accomplished through a two-phase assessment of stream bed sediments and tissues of aquatic organisms. The first phase of the strategy is to identify important constituents based on data collected from bed-sediment depositional zones. Fine-grained particles deposited in these zones are natural accumulators of trace elements and hydrophobic organic compounds. For the information to be comparable among studies in many different parts of the Nation, strategies for selecting stream sites and depositional zones are critical. Fine-grained surficial sediments are obtained from several depositional zones within a stream reach and composited to yield a sample representing average conditions. Sample collection and processing must be done consistently and by procedures specifically designed to separate the fine material into fractions that yield uncontaminated samples for trace-level analytes in the laboratory. Special coring samplers and other instruments made of Teflon are used for collection. Samples are processed through a 2.0-millimeter stainless-steel mesh sieve for organic contaminate analysis and a 63-micrometer nylon-cloth sieve for trace-element analysis. Quality assurance is maintained by strict collection and processing procedures, duplicate sampling, and a rigid cleaning procedure.

INTRODUCTION

The National Water Quality Assessment (NAWQA) program of the U.S. Geological Survey (USGS) is designed to assess the status of and trends in the quality of the Nation's ground- and surface-water resources (Gilliom and others, 1994) and to develop an understanding of the major factors that affect water-quality conditions (Hirsch and others, 1988; Leahy and others, 1990). The design is based on balancing the unique assessment requirements of individual hydrologic systems with a nationally consistent design structure that incorporates a multiscale, interdisciplinary approach. Investigations of water quality in 60 major hydrologic basins and aquifer systems, referred to as NAWQA Study Units, form the building blocks of the program.

The Occurrence and Distribution Assessment, described in Gilliom and others (1994), is the largest and most important component of the first intensive study phase in each Study Unit. The goal of the Occurrence and Distribution Assessment is to characterize, in a nationally consistent manner, the broad-scale geographic and seasonal distribution of water-quality conditions in relation to major contaminant sources and background conditions. The national study design for streams has three interrelated components. Water-Column Studies assess the occurrence and distribution of major ions, nutrients, and dissolved

pesticides and their relation to hydrologic conditions, sources, and transport. Bed-Sediment and Tissue Studies assess the occurrence and spatial distribution of trace elements and hydrophobic organic contaminants. Ecological Studies evaluate the physical, chemical, and biological characteristics of streams relative to environmental settings. Sampling designs for these components coordinate sampling of varying intensity and scope throughout the study.

This report describes methods for collecting and processing bed-sediment samples from streams for analysis of trace elements and hydrophobic organic contaminants as part of the Occurrence and Distribution Assessment component of the NAWQA program. Complimentary methods and procedures for collecting and processing biological tissues are described in Crawford and Luoma (1993). Although the methods and techniques described in this report are intended to meet the goals of the NAWQA program, they can be adapted for use in other programs of the USGS Water Resources Division, as well as by other Federal and State agencies. These methods will evolve as additional experience is gained and as measurement and analysis techniques improve. The glossary in this report includes brief definitions of study components, indicated throughout the report with capital first letters, and related key terms.

OVERVIEW OF BED-SEDIMENT STUDY DESIGN

Determination of constituent concentrations in bed sediments is a widely used approach to monitor and assess contaminant distributions in streams (Feltz, 1980; De Groot and others, 1982; Ackermann and others, 1983; Smith and others, 1988; Horowitz, 1990). There are several reasons for analyzing bed sediment for trace elements and hydrophobic organic contaminants. First, fine-grained particles and organic matter are natural accumulators of trace elements and hydrophobic organic contaminants in streams, the majority of which are highly sorptive and associated with particulate matter in almost all natural surface-water regimes. A large fraction of the total mass of these chemical constituents is usually associated with fine-grained sediments, including clay and silt particles and particulate organic carbon. Consequently, even though the water may contain only small quantities of these constituents, suspended sediment and bed sediment may contain relatively large concentrations. Second, nonpoint-source contributions of many of these contaminants may be intermittent or storm related; as a result, the contaminants may not be detected in single or periodic water samples. Bed sediments in depositional environments of streams provide a time-integrated sample of particulate matter transported by a stream. Third, when combined with biological tissue analysis, bed-sediment concentrations provide a useful measure of the potential bioaccumulation of trace elements and hydrophobic organic contaminants at a particular site.

The concentration of trace elements on stream bed materials is strongly affected by the particle-size distribution of the sample (Rickert and others, 1977; Wilber and Hunter, 1979). Generally, the concentration of trace elements on stream bed materials increases as particle size decreases. However, the concentration of organic contaminants attached to bed sediments is not significantly affected by particle-size distribution and is probably more a function of the concentration of organic matter in the sample (Goerlitz and Law, 1974). To increase the probability of detecting trace elements and to enhance the comparability of data among sites, bed-sediment samples should be sieved and the fine-grained fraction analyzed for the contaminants of interest. For trace elements, the silt-clay fraction smaller than 63 μm should be saved for analysis. For pesticides and other organic contaminants, sand and silt-clay fraction smaller than 2.0 mm should be saved for analysis.

The appropriate season and hydrologic conditions for sampling stream bed sediment are determined by current and antecedent discharge conditions. Access to the sampling site can be limited during seasonal high-flow conditions. Unusually high flows can wash out, redistribute, or bury substantial parts of semi-meant deposits; therefore, sampling should be delayed following major discharge to allow fresh sediment to deposit. The amount of time to reestablish sediment deposits depends on the amount of sediment in transport and on the streamflow. Independent judgement is needed in making these decisions. When sampling for bed sediment and tissues during summer or autumn, low-flow conditions are recommended to provide maximum direct access to the stream bed and to minimize seasonal streamflow variability.

Bed-Sediment and Tissue Studies are done in two phases to assess trace elements and hydrophobic organic contaminants, as described by Gilliom and others (1994). The Occurrence Survey is designed to provide an initial identification of important constituents in the Study Unit based on data from relatively few sites. The analytical constituents for bed sediments in the Occurrence Survey is summarized in table 1. The Occurrence Survey is the first phase of distribution assessment and its results guide the design of the more extensive Spatial Distribution Survey. Data from both phases are combined for assessing contaminant distribution.

The primary objective of the Occurrence Survey is to determine the target constituents and their importance to water-quality conditions in the Study Unit. Relative importance is determined by the magnitude of constituent levels and the extent of their occurrence. Highest importance is assigned to constituents at elevated levels over a wide geographic area or within many small areas over a substantial part of the Study Unit. Site selection and sampling strategy are designed to maximize the probability of detecting important constituents in the Study Unit.

The site-selection strategy for the 15 to 20 sites sampled for the Occurrence Survey builds on the selection of fixed sites for water-column and ecological sampling. Sampling designs for Bed-Sediment and Tissue Studies, Water-Column Studies, and Ecological Studies rely on coordinated sampling of varying intensity and scope at two general types of sites, Integrator Sites and Indicator Sites. Integrator Sites are chosen to represent water-quality conditions of streams and rivers in large basins that are often affected by complex combinations of land-use settings, point sources, and natural influences. Indicator Sites, in contrast, are chosen to represent water-quality conditions of streams in relatively homogeneous and usually smaller basins associated with specific individual environmental settings (for example, a particular combination of land-use and geologic setting). Most NAWQA Study Units have three to five Integrator Sites and four to eight Indicator Sites. The choice of additional Indicator Sites for the Occurrence Survey is a balance between locating sites where contamination is known to be probable and dispersing sites so that streams draining each major environmental setting in the Study Unit are sampled. Additional Integrator Sites for the Occurrence Survey are chosen on large streams to provide a coarse downstream network of sites where large-scale problems not detected in smaller basins have a reasonable chance of being detected. Usually one or two Indicator Sites are selected to represent the broadest possible range of background trace-element levels expected in the Study Unit. These reference Indicator Sites also serve to assess background occurrence of synthetic organic chemicals.

The Spatial Distribution Survey adds improved geographic coverage, with particular emphasis on assessment of priority constituents identified in the Occurrence Survey. Occurrence Survey results affect the analytical strategy and the geographic distribution of sampling sites. The combined data from the two phases of sampling provide a basic description of spatial distribution for the Study Unit, with emphasis on priority constituents, and support initial evaluation of sources and biological availability for priority constituents.

Twenty to 30 sites are typically sampled for the Spatial Distribution Survey, including a resampling of selected sites sampled during the Occurrence Survey. The general goals in site selection for the Spatial Distribution Survey are to attain (1) improved representation of the most important environmental settings in the Study Unit by increasing the number of Indicator Sites and (2) adequate spatial resolution in priority mainstem channels and major tributaries by increasing the number of Integrator Sites. Large areas with low contaminant levels and low variance require relatively few sites. However, parts of a Study Unit may require a significant increase in site density compared to the Occurrence Survey to assess priority constituents. The sampling strategy for bed sediment in the Spatial Distribution Survey is similar to the Occurrence Survey except that the scope is reduced, as appropriate, based on results of the Occurrence Survey.

Table 1. Analytical constituents for bed-sediment Occurrence Survey

[Bed sediments are analyzed for all constituents and tissues for those indicated by *]

Trace elements and major metals

Aluminum*	Cerium	Lead*	Potassium	Titanium
Antimony	Chromium*	Lithium	Scendium	Total carbon
(Stibium)	Cobalt	Magnesium	Selenium*	Uranium
Arsenic*	Copper*	Manganese*	Silver*	Vanadium*
Barium*	Europium	Mercury*	Sodium	Yttrium
Beryllium*	Gallium	Molybdenum	Strontium	Ytterbium
Bismuth	Gold	Neodymium	Sulfur	Zinc
Boron	Iron*	Nickel*	Tantalum	
Cadmium*	Holmium	Niobium	Thorium	
Calcium	Lanthanum	Phosphorus	Tin	

Organic contaminants

Organochlorine insecticides and polychlorinated biphenyls

Aldrin*	*o,p'*-DDT*	gamma-HCH	Polychlorinated
cis-chlordane*	*p,p'*-DDT*	(Lindane)*	biphenyls
trans-chlordane*	Dieldrin*	Isodrin	(PCBs-total)*
Chloroneb	Endosulfan I	Methoxychlor, *o,p'**	*cis*-Permethrin
Dacthal*	Endrin*	Methoxychlor, *p,p'**	*trans*-Permethrin
o,p'-DDD*	Heptachlor*	Mirex*	Pentachloroanisole*
p,p'-DDD*	Heptachlor epoxide*	*cis*-Nonachlor*	Toxaphene*
o,p'-DDE*	alpha-HCH*	*trans*-Nonachlor*	
p,p'-DDE*	beta-HCH*	Oxychlordane*	

Other semivolatile organic contaminants

Acenaphthene*	Dibenzo(a,h)anthracene	2-Methylanthracene
Acenaphthylene*	Dibenzothiophene	2-Methyl-4,6-Dinitrophenol
Acridine	1,2-Dichlorobenzene	4,5-Methylenephenanthrene
C8-Alkylphenols	1,3-Dichlorobenzene	1-Methyl-9H-Fluorene
Anthracene*	1,4-Dichlorobenzene	1-Methylphenanthrene
Anthraquinone	2,4-Dichlorophenol	1-Methylpyrene
Azobenzene	Diethyl Phthalate	Naphthalene*
Benzo(a)anthracene*	3,5-Dimethylphenol	Nitrobenzene
Benzo(b)fluoranthene*	1,2-Dimethylnaphthalene	2-Nitrophenol
Benzo(k)fluoranthene*	1,6-Dimethylnaphthalene	4-Nitrophenol
Benzo(g,h,i)perylene*	2,6-Dimethylnaphthalene	N-Nitroso-Diphenylamine
Benzo(a)pyrene*	Dimethyl Phthalate	N-Nitroso-Di-n-Propyl Amine
Benzo(c)quinoline	Di-n-butyl Phthalate	Phenanthrene*
2,2'-Biquinoline	2,4-Dinitrophenol	Pyrene*
4-Bromophenylphenylether	2,4-Dinitrotoluene	Pentachloronitrobenzene
Butylbenzyl Phthalate	2,6-Dinitrotoluene	Pentachlorophenol
9H-Carbazole	Di-n-octyl Phthalate	Phenanthridine
bis(2-Chloroethoxy) methane	*bis*(2-Ethylhexyl) Phthalate	Phenol
bis(2-Chloroethyl) ether	2-Ethylnaphthalene	Quinoline
bis(2-Chloroisopropyl) ether	Fluoranthene	2,3,5,6-Tetramethylphenol
4-Chloro-3-methylphenol	9H-Fluorene	1,2,4-Trichlorobenzene*
2-Chlorophenol	Hexachlorobenzene*	2,4,6-Trichlorophenol
2-Chloronaphthalene	Hexachloroethane	2,4,6-Trimethylphenol
4-Chlorophenylphenylether	Indeno(1,2,3-cd) pyrene*	2,3,6-Trimethylnaphthalene
p-Cresol	Isophorone	
Chrysene*	Isoquinoline	

Carbon

Carbonate	Total organic carbon

PLANNING FOR SAMPLE COLLECTION

The sample-collection strategy for bed sediment focuses on obtaining samples of fine-grained surficial sediments from natural depositional zones during low-flow conditions and on compositing samples from several depositional zones within a stream reach. This strategy is designed to yield a representative sample of fine-grained surficial bed sediments. The procedures are suitable for sampling most stream sites, and every effort is made to follow this approach to ensure national consistency among Study Units. The exact approach described may not be attainable for some stream systems or sites, and local conditions may require some adaptation. However, the basic philosophy and conceptual approach outlined in these guidelines should be maintained.

SITE LOCATION AND SELECTION OF DEPOSITIONAL ZONES

The term "site" generally refers to a reach of the stream approximately 100 m in length upstream from a water-column sampling or streamflow measurement site. However, this definition is flexible and varies somewhat with local conditions. Actual reach length is defined at each site by a combination of factors, including stream geomorphology and meander wavelength (Meador and others, 1993). Locations in streams where the energy regime is low and fine-grained particles accumulate in the stream bed are termed "depositional zones." Depositional zones can cover large areas at some sites and small pockets at other sites. The stream velocities at these zones have decreased and the fine-grained particles have deposited in the stream bed. Depositional zones include areas on the inside bend of a stream or areas downstream from obstacles such as boulders, islands, sand bars, or simply shallow waters near the shore. Wadeable depositional zones are preferred because they are easy to identify and to sample.

The ideal site-planning procedure is to identify 5 to 10 wadeable depositional zones containing fine-grained particulate matter at each site and to estimate the areal extent of each zone. The goal is to select depositional zones that represent upstream influences and various flow regimes; that is, left bank, right bank, center channel, and different depths of water. This will ensure that the sediment sample represents depositional patterns from various flow regimes and sources within the reach. Each depositional zone at a sampling site will be subsampled several times, and the subsamples will be composited with samples from other depositional zones sampled at the same site (fig. 1). The number of samples from each zone will be based on the areal size of each zone (that is, the larger the areal size of the zone, the greater the number of subsamples collected). Compositing will smooth the local scale variability and represent the average contaminant levels present at the site.

ADAPTING TO LOCAL CONDITIONS

Moving variable distances upstream or downstream from the water-column sampling or streamflow measurement site to find suitable depositional zones may be necessary because of the diverse nature of different streams and site locations, some of which are selected primarily for purposes other than bed-sediment sampling. The ideal sampling reach can be expanded when needed to encompass suitable depositional zones (Klusman, 1980). The preferred approach is to extend the reach by selecting inundated depositional zones in the stream channel, but continuing to include only basin conditions representative for the chosen site. However, side channels and bodies of water disconnected seasonally can contain viable depositional zones if they are part of the active stream for most of the year.

The comparability of sediments exposed directly to the atmosphere to those continually covered with water is unknown, especially for organic contaminants. Therefore, all sampled zones should be underwater from the time of deposit until collection. If all the depositional zones within a reasonable distance of a site have dried, a bed-sediment sample should be collected from a partially wetted zone. This partially wetted zone would include low-wetland areas near, but not attached to, the actual stream channel. Partially wetted zones should only be sampled when no other sites are available, and sampling conditions should be documented in the field notes and data records as a potential outlier. An advisable alternative would be to revisit the site when additional depositional zones are available.

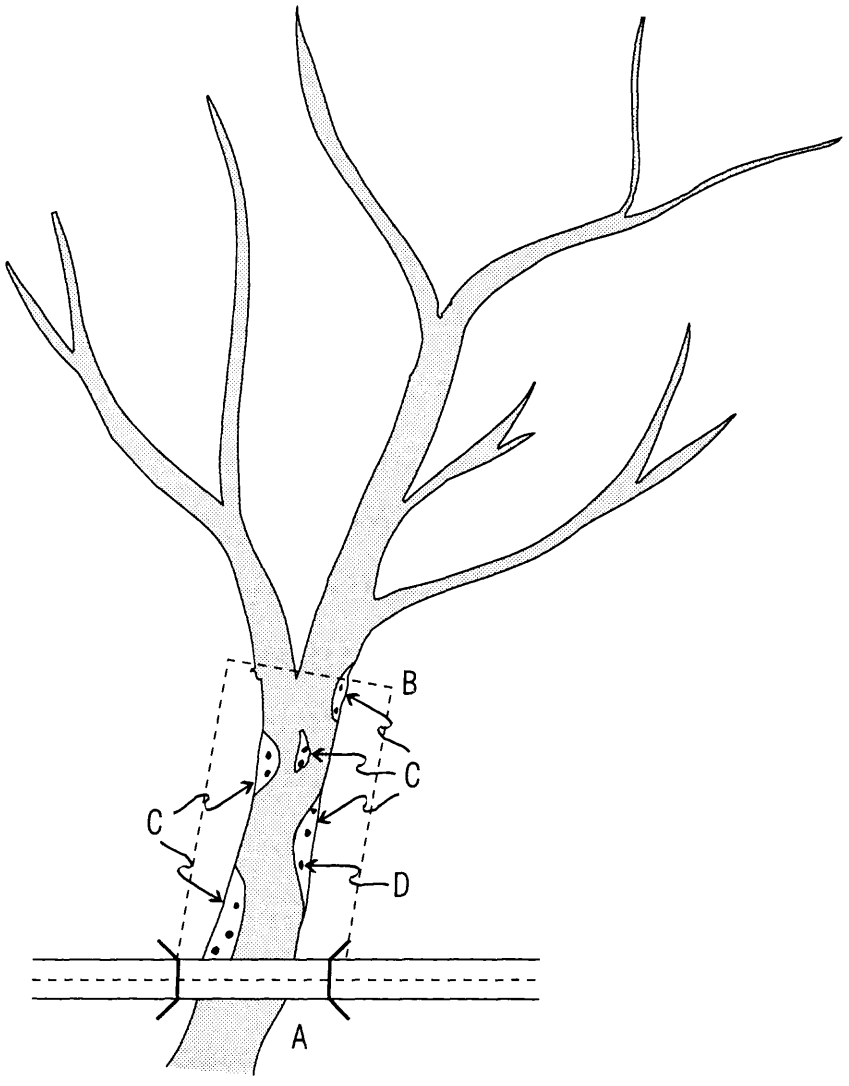


Figure 1. A typical depositional zone site. A. Water-column sampling site. B. One-hundred-meter stream reach. C. Depositional zones. D. Bed-sediment sampling locations.

EQUIPMENT

Equipment and supplies for collecting and processing stream bed-sediment samples for analyses of trace elements and organic contaminants are listed in table 2. The use of each is explained in the following discussions of samplers and sieving equipment, preparation for sampling, sampling procedures, and sample processing.

Table 2. Equipment and supplies for collecting and processing stream bed-sediment samples

[L, liter; mm, millimeter; mL, milliliter; in., inch; μm, micrometer; in^2, square inch; gal, gallon]

Guillotine coring sampler, Teflon
Ekman dredge, stainless steel (nonwadeable sites only)
Bowl, glass, flat bottom, 5 L, 12 inch diameter
Sieve, stainless steel, 2.0 mm, 3-inch diameter
Sieve frame, plastic, 8 in.
Sieve cloth, nylon mesh, 63 μm, 12-in^2 (one per site)
Funnel, plastic, 8-inch-diameter top, 3/4-inch-diameter stem
Spatula, Teflon
Scoop, Teflon
Spoon (large), Teflon
Policeman, Teflon
Syringe, plastic, 60 mL, 8- by 1/8-inch Tygon tube
Bottles, 500 mL (one per site)
Wash bottles, plastic, 500 mL (two per site)
Wash bottle, Teflon, 250 mL
Foil, aluminum, heavy duty
Containers (large), plastic, sealable
Trash bags, 5 gal
Tarpaulin, plastic
Thermister (electronic thermometer)
Containers, plastic
Protective sleeves (bubble wrap) (one per site)
Gloves, latex, powder free
Water, deionized
Detergent, liquid, phosphate-free
Nitric acid, high purity
Methanol, residue grade
Field forms
Sample containers (one each per site)
500-mL plastic bottle
1,000-mL glass jar, wide mouth
1,000-mL plastic jar, wide mouth

SAMPLERS

Given the multiple objectives of the Occurrence and Distribution Assessment phase of the NAWQA program and the simultaneous sampling for trace elements and organic contaminants, the choice of stream bed-sediment sampler(s) is particularly important. The attributes of the sampler must include (1) the ability to sample surficial sediments without loss of the fine material in the sediment/water interface and (2) the ability to sample sediment without contaminating the trace elements or organic compounds. These attributes exclude most of the traditional bed-sediment samplers and sampling techniques.

Three types of samplers meet the above attributes. One is a suspended-coring sampler (box core, dredge, or gravity core) for use in nonwadeable, low-velocity areas of the streams. The second is a hand-coring sampler like the Guillotine, a Teflon sampler specifically designed to sample shallow depositional zones. The third is simply a scoop or Teflon spoon that can remove the fine surficial material deposited between rocks and debris in wadeable areas. These three types of samplers should be suitable for most environments encountered in the Occurrence and Distribution Assessment phase of the NAWQA program. The use of these samplers is described in the section "Sample Collection."

The suspended-coring samplers should be made of stainless steel. These samplers are best suited for sampling soft sediments during low-flow conditions. One possible suspended-coring sampler is the Ekman dredge, with spring-loaded jaws that close on the bottom and flaps that close on the top to completely enclose a 9-in^2 parcel of sediment and overlying water. The dredge or box core can be inserted into the bed with a long handle or lowered from a boat on a cable through the water. A gravity-core sampler is a weighted tube that is dropped from a boat into the stream bed, and the resulting core is held in place by vacuum inside the tube when top flaps are closed. With care these samplers can collect a core without disturbing the fine surficial materials.

The Guillotine sampler (fig. 2) is a hand-held core sampler designed to sample fine-grained materials in the depositional zones without disturbing or contaminating the sediments. The parts of the Guillotine in contact with the final core (the fraction for analyses) are made exclusively of Teflon. The Guillotine is inserted by hand into the depositional zone in the stream bed. A bottom plug and a top blade confine the core and overlying water, which allows a 1.5-inch-diameter core to be removed from the stream without disturbing the sediment, fine surficial particles, or trapped native water. The overlying native water is removed, and the sediment core is positioned to separate the upper layer of fine-sediment fraction for sieving (fig. 3). The clear Teflon tube allows inspection of the upper fraction of the core for the selection that best fits the study criteria for sampling only fine-grained depositional layers.

At many sampling sites, application of the suspended-coring or Guillotine samplers do not produce enough useable sample of the fine-bed material. A Teflon spoon, scoop, or spatula also can produce the desired sample. The spatula can remove thin layers of surficial sediments, and the scoop or spoon can remove the bed material from between rocks and debris. Care must be taken to prevent the fine sediments from being washed away by the stream when bringing the sample to the surface.

Some sampling situations can require alternative equipment and methods. Alternatives should be utilized only when the recommended approach is not possible. Quality-assurance requirements for trace-level analyses should be followed, and undisturbed, near-surface bed sediments should be sampled in a manner that yields samples comparable to the recommended methods. Alternative equipment and methods need to be fully documented.

SIEVES

Two different sieves are required to process a sample for trace elements and organic contaminants. A 63-μm mesh nylon-sieve cloth held in a plastic frame is used for sieving sediment samples for trace-element analyses, and a 2.0-mm stainless-steel sieve is used for processing samples for organic-contaminants analyses. Procedures for sieving these samples are described later in the section "Sample Processing."

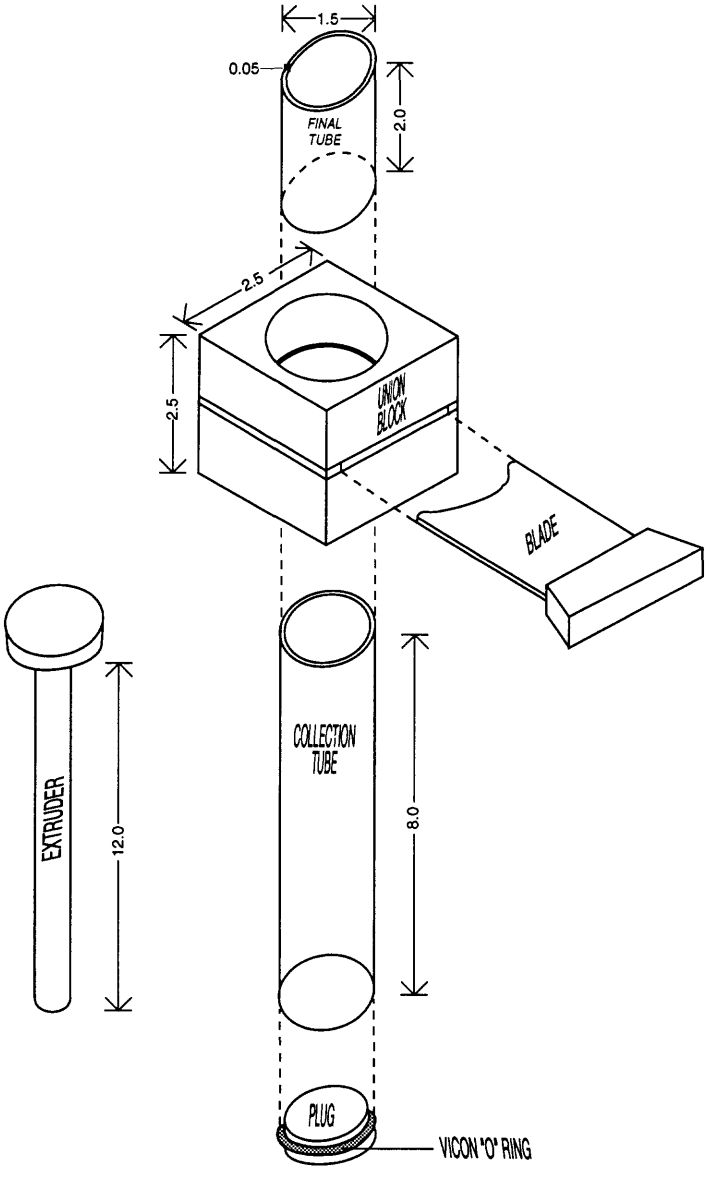


Figure 2. Guillotine, a hand-held core sampler. Collection and final tubes are fluorinatedethylene polyvinyl chloride Teflon, union block and blade are polytetrafluorethylene Teflon, and extruder and plug are polyvinyl chloride. All dimensions are in inches.

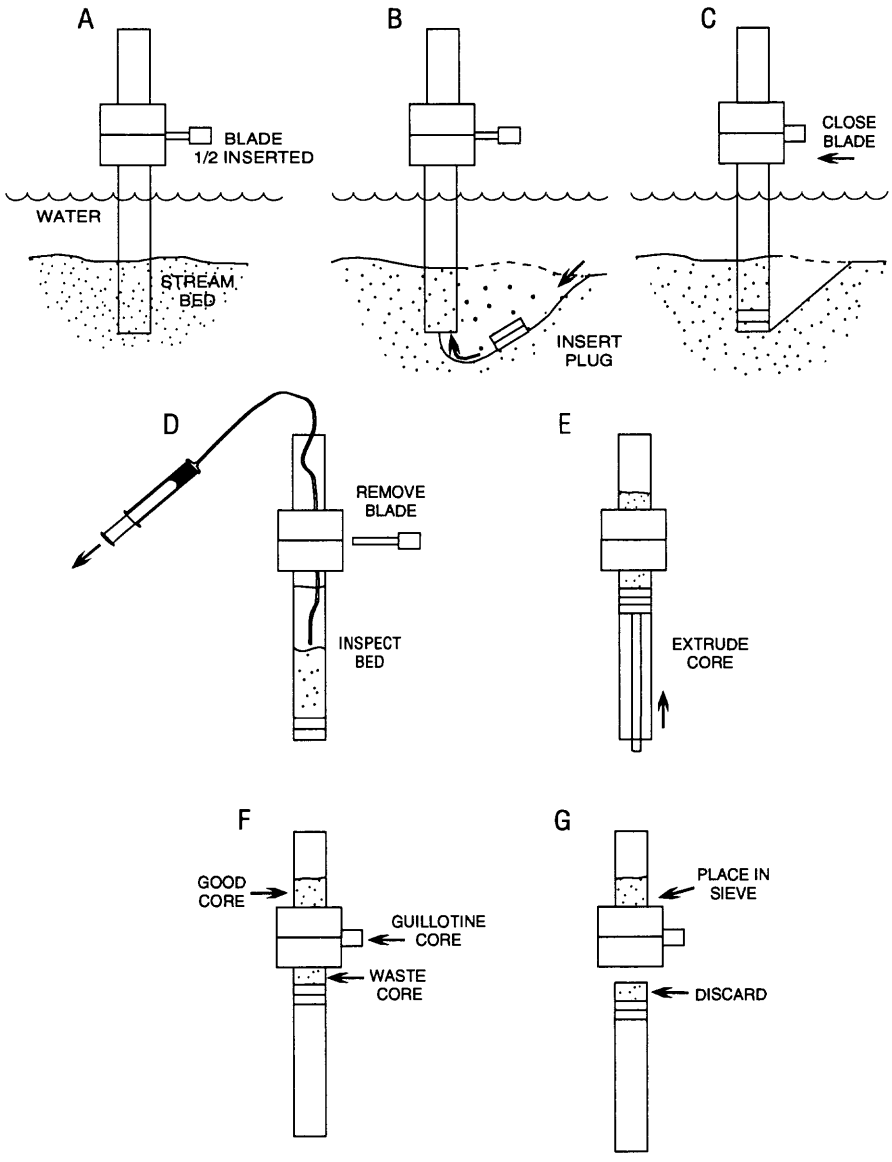


Figure 3. Schematic of the Guillotine sampler in operation. A. Insert into depositional zone. B. Clear bed material. C. Insert plug and close blade. D. Move from stream, remove blade, and decant water. E. Extrude core. F. Close blade-guillotining core. G. Discard lower core and save upper core.

EQUIPMENT CLEANING

All equipment should be cleaned prior to field activities and between sites. Cleaning procedures are designed to control contamination by removing paper, glue, plasticizers, oils, and metals from the sampling and processing equipment. The equipment should be stored in a plastic food-storage container after cleaning. An overview of the proper cleaning procedures is given in table 3.

Prepare a large tub or sink with a 0.2-percent phosphate-free detergent. Wash and soak for 30 minutes all equipment–the Guillotine, spatula, spoon, scoop, Ekman dredge, glass bowl, policeman, stainless-steel sieve, plastic sieve frame, nylon-mesh sieve material, plastic funnel, and the Teflon and plastic wash bottles. Rinse with copious amounts of tap water and then with deionized water as the final rinse. Three sequential 1-L rinses are more efficient then one 3-L rinse.

Fill the Teflon wash bottle with methanol for further cleaning of the equipment used for processing the samples for organic contaminant analyses. Fill the 500-mL plastic wash bottle with deionized water and add 25 mL of nitric acid. This 5.0 percent solution will clean the equipment used for preparing the samples for trace-element analyses.

Trace-Element Equipment–Rinse equipment used in collecting and processing samples for trace-element analyses (plastic-sieve frame, mesh nylon-sieve material, plastic funnel, Teflon policeman, and plastic wash bottles) with a 5-percent, high-purity, nitric-acid solution. Follow the acid rinse with multiple rinses of deionized water. Store in sealable plastic containers.

Organic-Contaminants Equipment–Rinse equipment used in collecting and processing samples for organic-contaminant analysis (stainless-steel sieve and a separate Teflon policeman) with residue-grade methanol. Air dry equipment and wrap in aluminum foil and place in sealable plastic containers.

Table 3. Reference guide for collecting and processing stream bed-sediment samples

[min, minute; cm, centimeter; L, liter; μm, micrometer; mL, milliliter; g, gram]

EQUIPMENT CLEANING (prior to sampling)

Wash and soak equipment in phosphate-free detergent for 30 min.
Rinse with copious amounts of tap water.
Rinse with deionized water.

Trace-element processing equipment

Rinse with nitric acid solution.
Rinse multiple times with deionized water.
Allow to air dry.
Store in plastic bags.

Organic-contaminant processing equipment

Rinse with methanol.
Allow to air dry.
Wrap in aluminum foil.

COLLECTING PROCEDURE

Prepare an area near the depositional zone for processing.
Place equipment on aluminum foil.
Rinse all equipment with native water prior to use.

Wadeable zone (Guillotine sampler)

Assemble the Guillotine sampler.
Wade to the depositional zone, approach from downstream.
Insert Guillotine into the bed at least 2 cm.
Clear the bed material from the exterior of the core.
Slide the plug under the Guillotine and into the collection tube.

Insert the blade into the union block.
Move to the processing area.
Inspect for adequate fine material; if not appropriate, discard.
Remove the blade.
Decant the liquid from the top of the core using a syringe.

Discard the native water.
Extrude the core into the final tube to the desired depth.
Guillotine the core by reinserting the blade.
Remove and discard the core in the collection tube.
Remove blade.

Place the remaining core from the final tube into the compositing bowl.
Rinse the Guillotine in the stream before reusing.
Repeat the process for 5 to 10 cores within each depositional zone.
Use a total of 5 to 10 zones per sampling site.
Collect a sample volume of approximately 1.5 L of wet sediment prior to sieving.

Table 3. Reference guide for collecting and processing stream bed-sediment samples--*Continued*

COLLECTING PROCEDURE--*Continued*

Wadeable zone (spoon, scoop, or spatula sampler)

Wade to the depositional zone, approach from downstream.
Remove the top layer of fine sediment carefully (approximately 1.0 cm).
Avoid loosing the fines when bringing the sample to the surface.
Inspect for adequate fine material; if not appropriate, discard.
Composite appropriate material in bowl.

Repeat the process at 5 to 10 locations within each depositional zone.
Use a total of 5 to 10 zones per sampling site.
Collect a total volume of approximately 1.5 L of wet sediment.

Nonwadeable zone (Ekman dredge)

Open and lock the dredge jaws.
Lower the dredge into the depositional zone at least 10 cm.
Deploy the messenger to close the jaws.
Bring the dredge (and bed sample) to the surface.

Open the doors on the top of the dredge.
Remove 4 to 12 subcores using one of the above procedures.
Repeat process for a total volume of approximately 1.5 L of wet sediment.

SAMPLE PROCESSING

Homogenize the composite sample in a glass bowl using the Teflon spatula.

Trace elements

Sieve-frame method

Cover sieve frame with the 63-μm mesh nylon-sieve cloth, attach retaining ring.
Place sieve on the plastic funnel over a 500-mL plastic bottle.
Add a small amount of composite sample onto the sieve.

Wet-sieve the sample using native water (450 mL maximum).
Collect the wash water in the receiving bottle.
Shake the sieve aggressively.
Work small amounts of bed material through the sieve.

Discard the material remaining on the sieve.
Decant the native water back into the wash bottle for more wash water.
Sieve until the sediment is approximately 1 cm deep in the receiving bottle.
Pack on ice and return to local lab.

Bag method

Add 2 to 3 tablespoons of sample to 63-μm mesh nylon-sieve cloth (without frame).
Draw up corners to form a bag.
Fill beaker with 450 mL of native water.
Dip, shake, and squeeze into beaker aggressively.

Sieve until the sediment is approximately 1 cm deep in the beaker.
Transfer the sample to a 500-mL plastic bottle.
Pack on ice and return to local lab.

Table 3. Reference guide for collecting and processing stream bed-sediment samples--*Continued*

SAMPLE PROCESSING--*Continued*

Office or local lab processing

Allow the sediment to settle 2 to 3 days.
Decant the liquid to approximately 1 cm of the sediment.
Discard liquid.
Pack without ice and ship to lab for distribution or analyses.

Organic contaminants

Place the 2.0-mm stainless-steel sieve over a 1,000-mL glass jar.
Work an aliquot of sample gently through the sieve using the policeman.
Do not use water.
Fill the jar about 3/4 full, 750 mL (50 g dry weight).
Place in a protective sleeve, pack in ice.
Ship to the lab within 3 days of collection for analysis.

Particle size

Place the 2.0-mm stainless-steel sieve over a 1,000-mL plastic jar.
Work an aliquot of sample gently through the sieve using the policeman.
Do not use water.
Fill the jar about 3/4 full, 750 mL (50 g dry weight).
Ship to the local sediment lab for a percent sand/silt analyses.

FIELD DOCUMENTATION

Use the standard surface-water-quality field notes.
Draw an areal sketch of the stream reach.
Identify the depositional zones.

FINAL CLEANING

Inspect, remove sediments, wash equipment with deionized water after each use.
Discard equipment that cannot be cleaned.
Store the equipment properly in appropriate containers.

SAMPLE COLLECTION

The surficial 2 to 3 cm of bed sediment within each depositional zone at a sampling site is subsampled several times, and the subsamples are composited with samples from other depositional zones sampled at the same site (fig. 1). The number of samples from each zone should be proportional to the relative size of each zone (for example, the larger the areal size of the depositional zone, the larger the number of subsamples collected). Compositing subsamples from different depositional zones will smooth the local scale variability and provide samples that are more representative of the average or mean contaminant concentrations. Confidence in the estimate of the mean concentration of contaminants in a composite sample increases as the number of subsamples in the composite increases.

In situations where the guidelines for sample collection are feasible with reasonable modifications, but the Study Unit team members determine that an alternative type of sample is required to assess site conditions adequately, both types of samples should be collected for analysis. In situations where the guidelines for sample collection cannot be met, independent judgement of the Study Unit team members is important. For example, at stream sites where the amount of available fine-grained material is insufficient for trace-element analysis, an alternative particle-size fraction is necessary. Similarly, in situations where large amounts of organic matter in bed sediments make field sieving impossible, an alternative procedure may be necessary. Whenever sample collection or processing methods deviate significantly from these guidelines, the specific procedures used need to be documented.

Prior to sampling depositional zones at each site, prepare an area on shore near the zones to accumulate the sample and for later processing. On a clean plastic tarpaulin, using latex gloves, unwrap the precleaned equipment and rinse with native water. For an overview of sampling procedures, see table 3.

Consider other activities simultaneously occurring at the site when planning the sample collection. Plan carefully the location of each activity in the stream reach and the sequence of events to avoid the possibility of contaminating the results. For example, the sampling of organisms for tissue analysis may be done during the same site visit as stream bed-sediment sampling, but the depositional zones for stream bed-sediment sampling should not be disturbed during biological sampling. Therefore, bed-sediment sampling should be prior to or upstream from biological sampling and other activities.

Avoid collecting a stream bed-sediment sample near or downstream of a bridge, bridge pier, or debris. The potential for sediment contamination is high in these areas.

WADEABLE ZONE

Approach the identified depositional zone by moving upstream to avoid disturbing the area to be sampled. Place an electronic thermistor into the stream bed and record the temperature.

GUILLOTINE SAMPLER

Assemble the Guillotine sampler: collection tube, union block, and final tube (fig. 3). Mark graduations (in centimeters) on the inside top portion of the union block to assist in determining the extruded core depth.

Insert the Guillotine into the stream bed at least 2 cm. Avoid inserting any deeper than necessary and, if possible, stay within the layers of fine-grained material. The extraction process is easier if the coarse-grained sediments are avoided.

Clear the bed material from the exterior of the core (by hand) from the downstream side. Carefully slide the plug under the Guillotine and insert it into the bottom of the collection tube. Slide the blade into the union block (closing the Guillotine) to prevent disturbance of the water/bed interface. Sometimes the coring tube can be inserted into the depositional zone deep enough to seal the bottom in a tight clay lens. The plug will not be needed if this can be achieved.

Visually inspect the core for adequate fine material. An appropriate core will have layers of fine- to coarse-grained material with the finer material near the sediment/water interface. Discard the entire core if it does not contain the desired fine material or if the core is disturbed in any way. Keep the sampler upright and carefully move the assembly (with stream bed core) from the stream to the processing area. Avoid disturbing the sediment/water interface. Decide how much of the core to save. Select the top portion of the core that best represents the fine depositional material, but no deeper than approximately 2.0 cm.

Remove the blade and decant the liquid from the top of the core with a syringe and tubing. Do not disturb the particulate matter. Discard the liquid. With the extruder, push the core (and plug) through the collection tube and union block and into the final tube to the depth previously selected.

Slice the core by reinserting the blade through the union block. Remove the collection tube containing the lower portion of the core and discard the unwanted bed material. Invert the remaining assembly (union block, blade, and final tube) into the glass bowl for compositing. Remove the blade and assist the core removal by tapping the tube against the bowl. Rinse the Guillotine in the stream before reusing.

Repeat the sampling process by collecting core samples from 5 to 10 locations in each depositional zone. If possible, use a total of 5 to 10 different depositional zones at each sampling site to ensure representative sampling. Approximately 1.5 L of wet sediment (about 50 cores 1 cm deep or 25 cores 2 cm deep) will be needed in the composite sample. Obtain more than enough composite sample for the sieving and splitting steps as adding additional sample to the composite without bias once the processing begins is difficult.

SPOON, SCOOP, OR SPATULA SAMPLER

A Teflon spoon, scoop, or spatula can be used to remove thin layers of sediment from the bottom of stream beds when the water is shallow (less than a foot) and there is little or no flow. Carefully remove the top layer of surficial fine material from the stream bed (approximately 1 to 2 cm). Avoid removing more material than necessary. Sieving is easier if the sandy material is avoided. Use the Teflon scoop or spatula for removing large smooth deposits and the Teflon spoon for removing the fine material in tight areas between rocks and debris. Each scoop or spoon should represent approximately 2 in^2 of bottom area 1 to 2 cm deep.

Extra care is necessary to protect the fine sediments from being washed away by the stream. Bring the sample to the stream surface in such a way as to avoid losing the fine material. Inspect the sample for adequate fine material and then deposit the sample in the glass bowl for compositing.

The depositional zone should be subsampled 5 to 10 times. Vary the number of subsamples in each zone when the scoop or spoon yields different volumes. Sample a total of 5 to 10 different depositional zones per site to complete the areal coverage and produce the necessary volume of material, approximately 1.5 L of wet sediment (about 50 scoops 1 cm deep or 25 scoops 2 cm deep). Obtain more than enough composite sample for the sieving and splitting steps as adding additional sample to the composite without bias once the processing begins is difficult.

NONWADEABLE ZONE

If there are no wadeable depositional zones, a 9-in^2 stainless-steel Ekman dredge or similar coring device can be used as an alternate collection method. The dredge is either suspended from a cable on a reel or hand operated at the end of a long rigid handle. The dredge can remotely collect a bottom core of fine-grained material without seriously disturbing the sediment/water interface.

Open and lock the jaws of the dredge and then lower it into a known depositional zone. Allow the open box to settle into the sediment to a depth dependent on the porosity and composition of the sediment and the mass of weights attached to the sampler. The dredge should penetrate the depositional zone at least 6 cm to avoid disturbing the particulate matter when the jaws close. Additional weights on the dredge may be required for deeper streams. Deploy the messenger to close the jaws and then carefully bring the dredge (and stream bed-sediment sample) to the surface.

Open the doors on the top of the dredge. Remove 4 to 12 subcores from the dredge with the Guillotine sampler, spoon, or scoop. Avoid extracting the subcores near the metal edges of the dredge. It may be easier to decant the overlying water from the dredge before subcoring. Continue to process the subcores following the procedures described in the "Wadeable Zone" section. The final coring and compositing methods should be identical, no matter what initial procedure is used for sampling.

NOTE--Independent field judgements are important in this procedure. The intent of the guidelines is to provide a consistent national framework for making good and reasonable decisions that best achieve study goals. Specific numbers of zones and cores are included only to give a sense of the general level of intensity and detail required.

SAMPLE PROCESSING

Sediment samples for several types of analyses can be processed from the composite depositional sample. This guide describes the processing for three sample types. One sample will be sieved to less than 63 µm and analyzed for trace elements, major ions, and organic and inorganic carbon. A second sample will be sieved to less than 2.0 mm and analyzed for organic contaminants, total-organic carbon (TOC), total-inorganic carbon, and percent moisture. The third sample also will be sieved to less than 2.0 mm and analyzed for percent particle-size distribution less then 63 µm (sand/silt). An overview of the proper sampling procedures is given in table 2.

SIEVING

Wear latex gloves and thoroughly mix (homogenize) the composite sample in the glass bowl using the Teflon spatula.

TRACE ELEMENTS

Sieve-Frame Method

Stretch the 63-µm mesh nylon-sieve cloth over the plastic-sieve frame and attach retaining ring. Assemble in series the 63-µm mesh nylon cloth sieve and the plastic funnel over a 500-mL plastic receiving bottle.

Place a small amount of composite sample onto the 63-µm mesh nylon sieve with the spatula. Pressure sieve the sample using native water that has been collected directly from the stream into the 500-mL plastic-wash bottle. The fine sediments pass through the sieve with a stream of water (pressure sieved) delivered by a wash bottle.

Work small amounts of bed material through the sieve at a time, discarding the material remaining on the sieve. It is not necessary to sieve all the material that is less than 63 μm in each aliquot.

NOTE: Shaking the sieve aggressively will help separate the fines.

If additional wash water is needed, allow the sieved sediment/native water to settle several minutes and decant only the native water back into the wash bottle for reuse. Continue to reuse the native water until the necessary sample is obtained (a depth of approximately 1 cm in the receiving bottle). The analyses of inorganic constituents will require 10 g (dry weight) of sieved sediment.

Bag Method

This method can be used in place of the pressure-sieving procedure. The plastic sieve frame is not used for this method; instead, place an aliquot (2 to 3 tablespoons) of the composite sample directly on the mesh nylon-sieve cloth and draw up each corner of the cloth to form a bag with the sample inside. Aggressively dip the bag in a beaker filled with 450 mL of native water. Continual dipping and squeezing will help separate the fines. Care should be taken to ensure that the nylon mesh is not stretched or damaged. Use additional aliquots until the proper volume of fine material is sieved, and then transfer the sample to a 500-mL plastic bottle.

Decanting

Pack the sediment/native-water samples on ice (do not freeze) for transport to the local office/ laboratory for further processing as follows: store the sample in a refrigerator and allow the sediments to settle until water is clear. This process could take 2 to 3 days, but no longer than 1 week. Decant the liquid to approximately 1 cm of the sediment/water interface with a syringe. Discard the decanted liquid. Centrifuging the sample might be necessary if the fine sediment has not settled within a week. Follow the cleanup procedure for preparing the centrifuge tubes.

ORGANIC CONTAMINANTS

Place the 2.0-mm stainless-steel sieve over a 1,000-mL glass jar. Gently work an aliquot of the sample through the sieve with a Teflon policeman or spatula. Do not use water. Collect the sample in a 1,000-mL wide-mouth glass jar. The bottom of the sieve may require periodic removal of the material that adheres to it. Fill the jar approximately half full; 500 mL of wet sediment is needed for analyses of organic contaminants, TOC, and percent moisture.

PARTICLE SIZE

Using the same 2.0-mm sieve described above, continue to sieve until approximately 2 cm of wet sediment accumulates into a 1,000-mL plastic jar. For particle-size analyses, 50 g dry weight of material is needed.

PREPARATION FOR SHIPPING

Trace-Element Samples—Pack without ice and ship to the National Water Quality Laboratory (NWQL) for distribution to the appropriate laboratories for analyses.

Organic-Contaminant Samples—Place in a protective sleeve, pack in ice (do not freeze), and ship by overnight carrier to the NWQL within 3 days of collection.

Particle-Size Samples–Ship in plastic container to the local sediment laboratory for a percent sand/silt analyses.

FIELD DOCUMENTATION

Use the standard U.S. Geological Survey surface-water-quality field notes. Complete pages 1, 2, and 3, expanding on the section describing the "bottom." Include standard field measurements of water temperature, stream bed-sediment temperature, specific conductance, pH, dissolved oxygen, and alkalinity, as described in Shelton (1994). Record a rated or measured stream discharge. Draw an areal sketch of the stream reach identifying the depositional zones. Note and describe the nature and extent of zones selected for sampling and the approximate locations within each zone where cores were extracted. Note the time and location of other activities at the site such as fish shocking, discharge measurements, and dredging. Identify the following: map scale, compass direction, bridges, bridge piers, trees, and so forth. Document derivation from the sampling protocol that may introduce anomalies or bias to the results.

FINAL CLEANING

Inspect and thoroughly wash all equipment with deionized water after each use. All traces of sediment should be removed prior to storage or reuse. Equipment that cannot be cleaned (for example, the 63-μm mesh nylon-sieve cloth) should be discarded. Refer to "Equipment Cleaning" section for the proper procedure to use prior to sampling at the next site. Store the equipment used exclusively for trace-element processing in sealable plastic containers and plastic food-storage containers. Wrap the equipment used exclusively for organic-contaminant processing in aluminum foil and store in plastic food-storage containers. Equipment common to both processes should be protected from contamination and stored in a sealed container.

QUALITY ASSURANCE AND QUALITY CONTROL

Quality data are assured through a sampling and analytical approach designed to minimize or compensate for potential sources of contamination and variability. Quality assurance is verified through independent sampling and analyses.

CONTROL OF CONTAMINATION

The awareness and avoidance of chemical contamination are necessary in each step of sample collection and processing: sampling, subsampling, field processing, shipping, and laboratory processing. Because sediments are natural accumulators of the target analytes, there is less concern of gross-sample contamination than in the water column. Nevertheless, extreme care must be taken to avoid contamination. The simultaneous sampling and field processing of stream bed sediment for trace elements and organic contaminants make the avoidance of con-tamination a unique challenge. The optimum materials for contacting samples collected for organic-contaminant analyses include glass, stainless steel, and Teflon. The optimum materials for trace-element analyses include plastics, glass, and Teflon (avoid contact with the stainless-steel coring samplers). The materials common to both lists, glass and Teflon, are the materials of choice to contact the bed sediments when analyzing for both trace elements and organic contaminants.

The cleaning procedures are designed to control contamination by removing paper, glue, plasticizer, oils, and metals from the sampling and processing equipment. This removal of contaminants is accomplished by a thorough soap and water cleaning and rinsing followed by solvent rinses for the organic-contaminant processing equipment and acid rinses for the trace-element processing equipment.

CONTROL OF VARIABILITY

The primary potential sources of variability in stream bed-sediment composition at a site are temporal variability, areal variability among depositional zones, areal variability within depositional zones, and depth variability. Temporal variability is managed by collecting all samples during low-flow conditions when changes with time are expected to be minimal. Areal variability is minimized by compositing samples within and among zones to yield an average for the reach. Variability in depth is managed through a consistent sampling approach of surficial sediment, visual inspection, and sampling-depth management.

VERIFICATION

The quality-assurance steps designed into the sampling strategy and methods will be verified during the first phase of sampling by a comparative study of duplicate sample collection and analyses that aggregates all potential sources of variability. If the verification indicates quality-control problems, more specific tests will be designed as required. Specific types of quality-assurance samples should be outlined for specific projects within the division. A set of guidelines in the NAWQA program assist the Study Unit team members in the collection of quality-assurance samples (NAWQA/NWQL Quality Assurance Committee for Organics in Bed Sediment, U.S. Department of the Interior, written commun., Geological Survey Memorandum dated January 20, 1994, on guidance on use of quality-control data for schedule 2501–organochlorine compounds in bottom material). Laboratory precision is monitored and verified by routinely analyzing spit or blank samples with every set of 20 samples analyzed.

References Cited

Ackermann, F., Bergmann, H., and Schleichert, V., 1983, Monitoring of heavy metals in coastal and estuarine sediments--a question of grain size: 20 μm versus <60 μm: Environmental Technology Letters, v. 4, p. 317-328.

Crawford, J.K., and Luoma, S.N., 1993, Guidelines for studies of contaminants in biological tissues for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 92-494, 69 p.

De Groot, A., Zshuppe, K., and Salomans, W., 1982, Standardization of methods of analysis for heavy metals in sediments: Hydrobiologia, v. 92, p. 689-695.

Feltz, H.R., 1980, Significance of bottom material data in evaluating water quality, *in* Baker, R., ed., Contaminants and Sediments, v. 1: Ann Arbor Michigan, Ann Arbor Science Publishers, Inc., p. 271-287.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1994, Design of the National Water-Quality Assessment program: Occurrence and distribution assessment: U.S. Geological Survey Open-File Report 94-314, 50 p.

Goerlitz, D.F., and Law, L.M., 1974, Distribution of chlorinated hydrocarbons in stream-bottom material: U.S. Geological Survey, Journal of Research, v. 21, no. 5, p. 443-541.

Hirsch, R.M., Alley, W.M., and Wilber, W.G., 1988, Concepts for a National Water-Quality Assessment program: U.S. Geological Survey Circular 1021, 42 p.

Horowitz, A.J., 1990, The role of sediment-trace element chemistry in water-quality monitoring and the need for standard analytical methods, *in* Hall, J., and Glysson, D., eds., Monitoring water in the 1990's: Meeting new challenges: Philadelphia, American Society for Testing and Materials STP 1102.

Klusman, R.W., 1980, Sampling designs for biochemical baseline studies in the Colorado oil shale region: A manual for practical application: U.S. Department of Energy Report DOE/EV/10298-2, 180 p.

Leahy, P.P., Rosenshein, J.S., and Knopman, D.S., 1990, Implementation plan for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 90-174, 10 p.

Meador, M.R., Hupp, C.R., Cuffney, T.F., and Gurtz, M.E., 1993, Methods for characterizing stream habitat as part of the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 93-408, 48 p.

Rickert, D.A., Kennedy, V.C., McKenzie, S.W., and Hines, W.G., 1977, A synoptic survey of trace metals in bottom sediments of the Willamette River, Oregon: U.S. Geological Survey Circular 715-F, 27 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 94-455, 44 p.

Smith, J.A., Witkowski, P.J., and Fusillo, T.V., 1988, Manmade organic compounds in the surface waters of the United States: A review of current understanding: U.S. Geological Survey Circular 1007, p. 2.

Wilber, W.G., and Hunter, J.V., 1979, The impact of urbanization on the distribution of heavy metals in bottom sediments of the Saddle River: Water Resources Bulletin, v. 15, no. 3, p. 790-800.