

Field Guide for Collecting Samples for Analysis of Volatile Organic Compounds in Stream Water for the National Water-Quality Assessment Program

By Larry R. Shelton

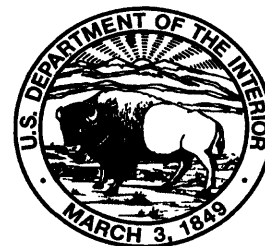
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Gordon P. Eaton, Director



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For additional information write to:

U.S. Geological Survey
Water Resources Division
Placer Hall
6000 J Street
Sacramento, California 95819-6129

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286
Federal Center
Denver, CO 80225

FOREWORD

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

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

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

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.

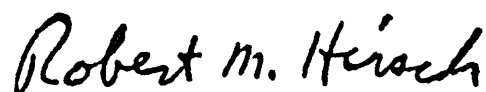
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

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

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

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

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



Robert M. Hirsch
Chief Hydrologist

CONTENTS

Glossary	vii
Abstract	1
Introduction	1
Overview	2
Preparation for Sample Collection	2
Site Selection	2
Sampling Equipment	5
Sampler.....	5
Support Equipment	6
Equipment Cleaning	6
Sample Collection Procedures	8
Preparation	8
Routine Sampling	8
Dip Sampling	8
Sample Processing Procedures	8
Field Measurements	9
Quality Assurance and Quality Control	9
Field Blanks	10
Trip Blanks	10
Field-Matrix Spikes	10
Replicate Samples	10
Documentation	11
Sample Identification	11
Shipping	13
References Cited	13
Appendix—Selected Technical Memorandums	14

FIGURES

1. Schematic of the volatile organic compound (VOC) sampler.....	5
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TABLES

1. List of volatile organic compound analytes for the National Water-Quality Assessment Program	3
2. List of equipment and supplies for collecting and processing stream-water volatile organic compound (VOC) samples	7

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
	quart (qt)	5.775	cubic inch

Temperature is given in degrees Celsius ($^{\circ}\text{C}$), which can be converted to degrees Fahrenheit ($^{\circ}\text{F}$) by the following equation: $^{\circ}\text{F}=1.8(^{\circ}\text{C})+32$

Abbreviations

L, liter

$\mu\text{g/L}$, microgram per liter

mL, milliliter

lb, pound

ASR, analytical services request

DIW, deionized water

FS, field spike

FSR, field-spike replicate

HCL, hydrochloric acid

ID, identification

QA, quality assurance

QC, quality control

VBW, pesticide/volatile blank water

VG, VOC grade blank

VOC, volatile organic compound

Acronyms

NAWQA, National Water-Quality Assessment

NWQL, National Water Quality Laboratory

USGS, U.S. Geological Survey

WRD, Water Resources Division

GLOSSARY

- Environmental Setting**—Land areas characterized by a unique, homogeneous combination of natural and human-related factors, such as row-crop cultivation on glacial-till soils.
- Gaging station**—A fixed site on a stream or river where hydrologic and environmental data are collected.
- 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 km²).
- Integrator Site**—Stream sampling sites located downstream from drainage basins that are large and complex and commonly contain multiple Environmental Settings. Most Integrator Sites are on major streams with drainage basins that include a substantial portion of the Study Unit area (typically, 10 to 100 percent).
- Point sample**—A sample collected at a single point in the stream cross section and at a single point in the stream vertical.
- 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 km² of land area. The NAWQA design is based on assessment of these 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.

Field Guide for Collecting Samples for Analysis of Volatile Organic Compounds in Stream Water for the National Water-Quality Assessment Program

By Larry R. Shelton

Abstract

For many years, stream samples for analysis of volatile organic compounds have been collected without specific guidelines or a sampler designed to avoid analyte loss. In 1996, the U.S. Geological Survey's National Water-Quality Assessment Program began aggressively monitoring urban stream-water for volatile organic compounds. To assure representative samples and consistency in collection procedures, a specific sampler was designed to collect samples for analysis of volatile organic compounds in stream water. This sampler, and the collection procedures, were tested in the laboratory and in the field for compound loss, contamination, sample reproducibility, and functional capabilities. This report describes that sampler and its use, and outlines field procedures specifically designed to provide contaminant-free, reproducible volatile organic compound data from stream-water samples.

These guidelines and the equipment described represent a significant change in U.S. Geological Survey instructions for collecting and processing stream-water samples for analysis of volatile organic compounds. They are intended to produce data that are both defensible and interpretable, particularly for concentrations below the microgram-per-liter level. The guidelines also contain detailed recommendations for quality-control samples.

INTRODUCTION

One of the goals of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) (Hirsch and others, 1988) is to establish a network of comprehensive and integrated urban water-quality studies to develop an understanding of the occurrence, significance, sources, movement, and fate of environmental chemicals in urbanized hydrologic systems (Lopes and Price, 1997; Squillace and Price, 1996). The occurrence of many contaminants, including volatile compounds, are being assessed in urban areas. For the information to be comparable among studies in different parts of the Nation, consistent procedures and equipment specifically designed to produce contaminant-free, reproducible volatile organic compound (VOC) data from stream-water samples are critical.

The assessment of VOCs in stream water is part of the Water-Column Studies (Gilliom and others, 1995), which focus on assessing the occurrence, concentrations and seasonal distribution of VOCs (Lopes and Price, 1997). The purpose of this report is to describe the equipment used to sample VOCs in streams and the procedures for using the VOC sampler. Companion reports by Koterba and others (1996) outline the procedures used for collecting VOC samples in ground-water, and Majewski and Capel (1995) discuss sampling of pesticides in the atmosphere.

The glossary at the front of this report includes brief definitions of some terms used in this report. Key terms used to describe the NAWQA Program are capitalized. Trade names used in connection with equipment or supplies do not constitute an endorsement of the product.

OVERVIEW

The sampling designs for stream-water 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 the large basins 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 with relatively homogeneous land use and, usually, are associated with smaller basins in specific Environmental Settings. Most, but not all VOC samples will be collected at urban Indicator Sites located in residential and commercial areas. Site selection and sampling strategies for urban Indicator Sites are described in Lopes and Price (1997).

Two primary sampling strategies are used at the selected Integrator and Indicator Sites: (1) fixed interval sampling (usually monthly) characterizes the spatial and temporal distribution of contaminants in relation to hydrologic conditions and contaminant sources, and (2) intensive sampling characterizes seasonal and short-term temporal variability of contaminant transport during high flows and at more frequent fixed intervals.

Most VOCs are man-made compounds that are components of gasoline, by-products of chlorinating drinking water, or solvents. Laboratory analysis is done by the purge-and-trap technique to separate the VOCs from the water matrix, and the quantitation is done by capillary-column gas chromatography/mass spectrometry. Results are reported in micrograms per liter. The USGS National Water Quality Laboratory (NWQL) VOC analysis schedule 2020 will be used. The analytes are summarized in table 1.

PREPARATION FOR SAMPLE COLLECTION

Site Selection

All VOC sampling sites should be at or near streamflow gaging stations because stream discharges associated with contaminant concentrations are needed to evaluate relations between streamflow and water-quality characteristics (Gilliom and others, 1995; Lopes and Price, 1997). The sample collection site should not be more than a few hundred feet from the station.

Collection sites should be located in relatively straight channel reaches where the flow is uniform. Collecting samples directly in a ripple, or from ponded or sluggish water, should be avoided. Sites directly upstream or downstream of confluences or direct sources of contamination also should be avoided to minimize problems caused by backwater effects or poorly mixed flows. In addition, samples collected downstream from a bridge can be contaminated by runoff from the road surface. Proper field judgement is crucial to achieve a sample representative of the typical environmental conditions.

Samples should be collected at the centroid of the stream in the same cross section throughout the project. This will eliminate many of the potential problems that might arise during the interpretation of the data. This does not mean that the same section used during the low-water wading stage must be used during higher stages that require the use of a bridge or cableway. However, the flow characteristics at different cross sections can result in incomparable data if the cross sections are not located near each other or in the same flow regime. Rapidly changing stage, discharge, and constituent concentrations dictate that sampling schemes and techniques be planned carefully in advance to ensure that representative samples are obtained.

Table 1. List of volatile organic compound analytes for the National Water-Quality Assessment Program

[CAS, Chemical Abstract Service number; PCODE, U.S. Geological Survey's Parameter Code; MRL, Method Reporting Limit. µg/L, microgram per liter. —, no data]

Laboratory analyses: Schedule Number 2020		
CAS number	PCODE	Compound
Halogenated Alkanes		
630-20-6	77562	1,1,1,2-Tetrachloroethane
71-55-6	34506	1,1,1-Trichloroethane
79-34-5	34516	1,1,2,2-Tetrachloroethane
76-13-1	77652	1,1,2-Trichloro-1,2,2-trifluoroethane
79-00-5	34511	1,1,2-Trichloroethane
75-34-3	34496	1,1-Dichloroethane
96-18-4	77443	1,2,3-Trichloropropane
96-12-8	82625	1,2-Dibromo-3-chloropropane
106-93-4	77651	1,2-Dibromoethane
107-06-2	32103	1,2-Dichloroethane
78-87-5	34541	1,2-Dichloropropane
142-28-9	77173	1,3-Dichloropropane
594-20-7	77170	2,2-Dichloropropane
74-97-5	77297	Bromochloromethane
75-27-4	32101	Bromodichloromethane
74-83-9	34413	Bromomethane
124-48-1	32105	Chlorodibromomethane
75-00-3	34311	Chloroethane
74-87-3	34418	Chloromethane
74-95-3	30217	Dibromomethane
75-71-8	34668	Dichlorodifluoromethane
75-09-2	34423	Dichloromethane
67-72-1	34396	Hexachloroethane
74-88-4	77424	Iodomethane
56-23-5	32102	Tetrachloromethane
75-25-2	32104	Tribromomethane
75-69-4	34488	Trichlorofluoromethane
67-66-3	32106	Trichloromethane
Halogenated Alkenes		
75-35-4	34501	1,1-Dichloroethene
563-58-6	77168	1,1-Dichloropropene
107-05-1	78109	3-Chloro-1-propene
593-60-2	50002	Bromoethene
75-01-4	39175	Chloroethene
87-68-3	39702	Hexachlorobutadiene
127-18-4	34475	Tetrachloroethene
79-01-6	39180	Trichloroethene
156-59-2	77093	<i>cis</i> -1,2-Dichloroethene
10061-01-5	34704	<i>cis</i> -1,3-Dichloropropene
156-60-5	34546	<i>trans</i> -1,2-Dichloroethene
10061-02-6	34699	<i>trans</i> -1,3-Dichloropropene
110-57-6	73547	<i>trans</i> -1,4-Dichloro-2-butene
Aromatic Hydrocarbons		
71-43-2	34030	Benzene
91-20-3	34696	Naphthalene
100-42-5	77128	Styrene

Table 1. List of volatile organic compound analytes for the National Water-Quality Assessment Program—Continued

Laboratory analyses: Schedule Number 2020		
CAS number	PCODE	Compound
Alkyl Benzenes		
488-23-3	49999	1,2,3,4-Tetramethylbenzene
527-53-7	50000	1,2,3,5-Tetramethylbenzene
526-73-8	77221	1,2,3-Trimethylbenzene
95-63-6	77222	1,2,4-Trimethylbenzene
95-47-6	77135	1,2-Dimethylbenzene
108-67-8	77226	1,3,5-Trimethylbenzene
108-38-3	85795	1,3-Dimethylbenzene
106-42-3	—	1,4-Dimethylbenzene
611-14-3	77220	2-Ethyltoluene
100-41-4	34371	Ethylbenzene
98-82-8	77223	Isopropylbenzene
108-88-3	34010	Methylbenzene
104-51-8	77342	<i>n</i> -Butylbenzene
103-65-1	77224	<i>n</i> -Propylbenzene
99-87-6	77356	<i>p</i> -Isopropyltoluene
135-98-8	77350	<i>sec</i> -Butylbenzene
98-06-6	77353	<i>tert</i> -Butylbenzene
Halogenated Aromatics		
87-61-6	77613	1,2,3-Trichlorobenzene
120-82-1	34551	1,2,4-Trichlorobenzene
95-50-1	34536	1,2-Dichlorobenzene
541-73-1	34566	1,3-Dichlorobenzene
106-46-7	34571	1,4-Dichlorobenzene
95-49-8	77275	2-Chlorotoluene
106-43-4	77277	4-Chlorotoluene
108-86-1	81555	Bromobenzene
108-90-7	34301	Chlorobenzene
Ethers and other Oxygenated Compounds		
78-93-3	81595	2-Butanone
591-78-6	77103	2-Hexanone
108-10-1	78133	4-Methyl-2-pentanone
67-64-1	81552	Acetone
60-29-7	81576	Diethyl ether
108-20-3	81577	Diisopropyl ether
637-92-3	50004	Ethyl <i>tert</i> -butyl ether
1634-04-4	78032	Methyl <i>tert</i> -butyl ether
109-99-9	81607	Tetrahydrofuran
994-05-8	50005	<i>tert</i> -Amyl methyl ether
Others		
107-02-8	34210	2-Propenal
107-13-1	34215	2-Propenenitrile
75-15-0	77041	Carbon disulfide
97-63-2	73570	Ethyl methacrylate
96-33-3	49991	Methyl acrylate
126-98-7	81593	Methyl acrylonitrile
80-62-6	81597	Methyl methacrylate

Sampling Equipment

Sampler

Obtaining representative VOC samples in flowing streams is a difficult task. Of critical importance is the design and operation of the equipment and the sampling procedure (Brown and others, 1970). Samplers must be designed to collect an unbiased sample of environmental conditions. One important process is to flush atmospheric gases from the sampler before collecting a stream sample (Kilpatrick and others, 1989).

A newly developed VOC sampler designed by the USGS and built by Wildco (fig. 1) will be used to collect stream-water samples for VOC analysis. This sampler has been tested for analyte loss, reproducibility, and carryover contamination in the laboratory and in field settings. The sampler, which is made of noncontaminating materials (stainless steel and refrigeration-grade copper) that will not sorb the analytes of interest, can collect a sample representative of environment conditions in most streams. An important function of the sampler design is to evacuate air and other gases from the sampler before collecting a sample. The VOC sampler weighs 11 lb and can be suspended, by hand, from a short rope or chain while wading a stream. However, when sampling during periods of high flow, 10-lb weights can be added to keep the sampler vertical when it is suspended from a bridge or cableway.

The sampler is designed to collect a sample at a single point in the stream. The stainless-steel sampler holds four 40-mL vials. Copper tubes extend to the bottom of each vial from the inlet ports on top of the sampler. The vials fill and overflow into the sampler body, displacing the air in the vials and in the sampler through the exhaust

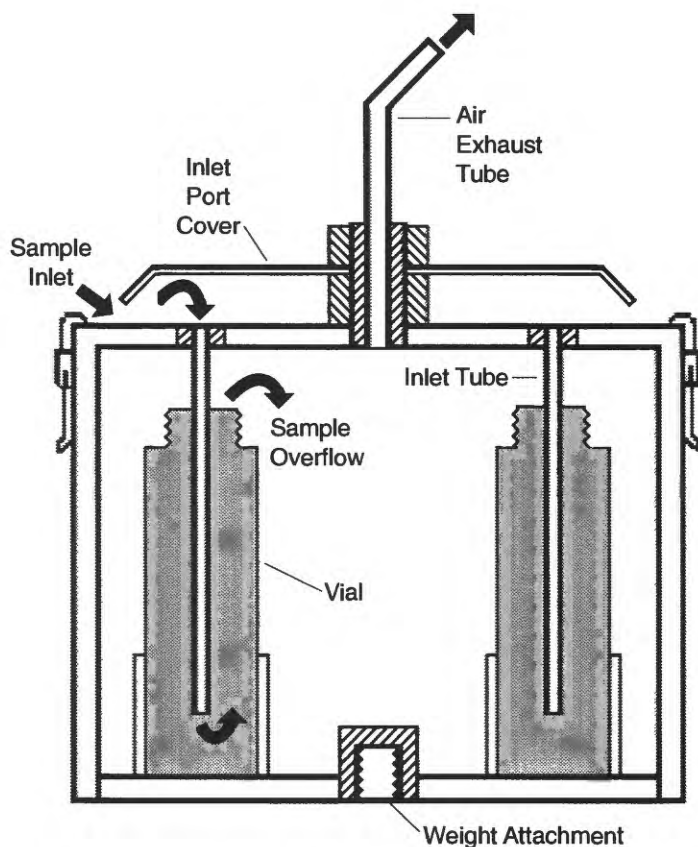


Figure 1. Schematic of volatile organic compound (VOC) sampler. The sampler body is made of stainless steel, weighs 11 pounds, and is 6 inches in diameter and 6 inches high. It has an air exhaust tube extending above the sampler, and four copper inlet tubes that extend into four 40-milliliter sample vials.

tube. The total volume of the sampler is eight times larger than the vials; therefore, the vials are flushed seven times (removing the air) before the final volume is retained in the vial. The small (1/16-in. inside diameter) copper inlet ports results in a slow (3 to 4 minutes) filling time. This important design feature helps to produce a representative sample and allows sufficient time to place the sampler at the desired depth. The sampler begins to fill as soon as it enters the stream; however, the final sample is retained in the vial during the last 15 to 20 seconds of the filling process. A cover over the inlet ports prevents contamination from surface oil and debris when the sampler is removed from the stream.

Support Equipment

Field vehicles are commonly used for more than one purpose (such as streamflow measurements, gaging station maintenance, construction, stream sampling, and sample processing). Sample contamination is more likely to occur when these multiuse vehicles are used to collect and process water samples. Glues and adhesives used in vehicles, and the cabinet construction, can contaminate samples for VOCs. Therefore, it is important that the processing area be free of contaminants, plastics, dirt, fumes, and oil residue. Samples should be removed from the sampler, processed, and capped streamside to avoid possible contaminants in the vehicles. Each vehicle should have a separate storage area for the VOC sampling equipment and supplies. A complete equipment list is given in table 2.

EQUIPMENT CLEANING

All equipment that will come in contact with the sample should be soaked in a dilute phosphate-free detergent solution; rinsed with tap water, VOC grade blank (VG) water, and methanol; and then air dried prior to each field trip and between sites (Shelton, 1994). Detergents and methanol should be used with care to avoid the possibility of the residue contaminating the sample. A thorough native-water rinse is required at each field site before sampling to remove any remaining cleaning agents and to equilibrate the equipment to the sampling conditions. A list of the supplies needed for equipment cleaning is given in table 2, and detailed procedures for cleaning the VOC sampler are outlined below.

1. Open sampler.
2. Submerge top and base in a 0.2-percent solution of phosphate-free detergent. Scrub the sampler thoroughly with a nylon brush. Use a small squeeze bottle, filled with the detergent, to flush the copper tubing.
3. Rinse the sampler thoroughly with warm tap water or deionized water (DIW) to remove all soap residue.
4. Using a Teflon squeeze bottle, rinse with a minimum amount of methanol. Place the used methanol in a waste container for proper disposal (see Water Resources Division [WRD] memorandum 94.07, Appendix).
5. Allow to air dry (cover loosely with aluminum foil to avoid airborne contamination). If complete air drying is not possible, rinse three times with VG water.
6. Wearing vinyl gloves, reassemble the sampler.
7. Wrap areas that will come in contact with the sample with aluminum foil, and place in a sealable plastic bag. Use a large sealed container to protect the sampler in storage and during transport.
8. Rinse the sampler (without the vials) with 2 to 3 L of native water prior to sampling.

Table 2. List of equipment and supplies for collecting and processing stream-water volatile organic compound (VOC) samples

[Sources for some items are listed to maintain quality standards. OCALA, U.S. Geological Survey Water-Quality Service Unit at Ocala, Florida; NWQL, National Water Quality Laboratory; VG, VOC grade blank; VBW, pesticide/volatile blank water]

Sampling equipment and supplies

- Volatile organic compound (VOC) sampler (Wildco 990-J98)
- Vial, glass, amber septum, 40 milliliter (NWQL and OCALA 333FLD)
- Rope, nylon, 1/4-inch diameter (OCALA 84FLD)

Cleaning and storing equipment and supplies

- Gloves, vinyl, powderless (OCALA 155HWS)
- Detergent, phosphate free, 0.2 percent by volume (OCALA 62FLD)
- Methanol, pesticide grade
- Deionized water
- VOC grade blank water (VG or VBW) (NWQL)
- Bottles, wash, plastic, for detergent (OCALA 357FLD)
- Bottles, wash, Teflon, for VG water (OCALA 377FLD)
- Bottles, wash, Teflon, for methanol (OCALA 377FLD)
- Basins, wash, plastic (2)
- Brush, scrub, soft metallic
- Bag, plastic, sealable, medium (OCALA 23FLD)
- Storage container, sealable, 8 inches x 8 inches x 12 inches
- Foil, aluminum, heavy duty
- Container, waste, solvent, 5 gallons

Processing equipment and supplies

- Cannister, stainless steel, 8 quarts with cover (for field blanks)
- Flask tongs
- Gloves, vinyl, powderless (OCALA 155HWS)
- Hydrochloric acid 1:1 acid, in Teflon vials (NWQL)
- Kit, matrix spike (NWQL)
- pH paper (alkacid test ribbon)
- Bottle labels (OCALA 84FLD)
- Sleeves, foam (OCALA 358FLD)
- Coolers, shipping, 1 gallon
- Coolers, shipping, 5 gallons
- Bags, plastic, 5 gallons
- Ice

Miscellaneous equipment and supplies

- Boots, hip
 - Waders, chest
 - Tools
 - First aid kit
 - Highway emergency kit
 - Forms, field documentation (OCALA)
 - Forms, analytical request (NWQL)
 - Tissues, laboratory
 - Pens, marking, permanent, (OCALA 77FLD)
 - Field meters, conductance, pH, dissolved oxygen
 - Supplies for field measurements
-

SAMPLE COLLECTION PROCEDURES

Preparation

The timing of the VOC sampling should be planned to avoid possible contamination by other collection and processing activities (such as procedures and equipment that use methanol). Before beginning any other activity collect and process the VOC samples at the site. The entire sampling and processing procedure (removing it from the storage container, loading the sampler, sampling, and acidifying the sample) should be done at streamside, well away from other processing activities.

Routine Sampling

VOC samples should be collected where the stream velocity represents the average flow, which is typically near mid-channel in the cross section. The following procedure is designed to produce a single-vertical point sample. When collecting samples for VOC analyses, special care must be taken to avoid contamination from any oily film and debris floating on the stream surface. The samples should be collected directly into the prebaked 40-mL amber-glass vials as follows:

1. Reclean the sampler, if necessary (see 'Equipment Cleaning' section).
2. Transport the sampler to the collection site and rinse three times with native water or submerge it in the stream for several minutes.
3. In a protected area, away from any direct source of contamination and wearing vinyl gloves, uncap four 40-mL unlabeled vials and place them in the sampler. Secure and lock the sampler top in position. Store the vial caps in a protected area.
4. Lower the sampler into the stream near mid-channel to about one half of the total depth at that vertical. Add weights if the stream velocity is great enough to pull the sampler downstream.
5. Collect a sample by holding the sampler in one position until the sampler is full. Air bubbles will rise to the surface while the sampler is being filled, but may be difficult to see. This takes about 3 to 4 minutes. The sample will be retained in the vial during the last 15 to 20 seconds of sampling.
6. Remove the sampler when bubbles are no longer present or after about 5 minutes, and return to a protected area at the side of the stream for processing.

Dip Sampling

In very shallow streams where the VOC sampler cannot be submerged, a representative sample usually can be obtained manually by immersing an open vial (dip sample) near the centroid of flow. Wearing vinyl gloves, lower a 40-mL vial to about one half of the stream depth. Point the vial into the stream current, remove the cap, allow the vial to fill, then slowly bring it to the surface. Add hydrochloric acid (HCL), carefully cap the vial, and check for air bubbles that may be trapped in the vial. A dip sample should never be taken when it is possible to use the sampler. Consistent procedures will avoid the possibility of a sampling bias.

SAMPLE PROCESSING PROCEDURES

Biodegradation and chemical reactions, such as oxidation and volatilization, can change many of the compounds present in natural waters before analyses in a laboratory. Therefore, samples must be preserved as soon as possible after collection. The method of preserving VOCs includes the addition of 1:1 HCL and refrigeration to 4°C to arrest microbiological activity and to minimize volatilization. Great care must be exercised in the field to prevent compound loss or sample contamination. Because exhaust fumes and adhesives in field vehicles may be a

source of contamination, processing samples streamside can best prevent contamination. Evaluate trip and field blanks to confirm that the processing area is appropriate.

To preserve the samples, add 1:1 HCL to lower the pH to 2 or less, and immediately place the vials on ice. To determine the volume of acid to add, collect a hand dipped test sample in a used 40-mL vial. Add HCL to the test sample to lower the sample pH to less than 2.0. Two drops of HCL should be adequate for most conditions; however, some environmental samples may require additional HCL. At no time should you use more than six drops of HCL. Alkacid test ribbons can be used to estimate the pH.

By following this sequence for sample preservation, the risk of contaminating a sample is reduced. Acid should be stored and transported properly (see WRD memorandum 94.06, Appendix). These procedures are summarized below.

1. Wearing vinyl gloves, open the sampler carefully at streamside.
2. Using metal tongs, slowly lift each vial from the sampler reservoir. Do this carefully to avoid losing the convex meniscus.
3. Add drops (usually two, but no more than six) of 1:1 HCL to lower the pH to less than 2, and cap the vial.
4. Agitate the vial and check for air bubbles. Discard if bubbles are present.
5. Three vials from the same sampler set are required for one complete sample. Resample completely, if necessary.
6. Label the samples, wrap each with a foam sleeve, and place them on ice.
7. Clean the sampler and store it properly (see 'Equipment Cleaning' section).

The minimum information required on each vial is the site identification (ID) number, date and time sampled, preservation, and schedule number, as shown on the example below:

09498500
04-24-1997 @ 1200
HCL to <2.0 pH
SCH – 2020

FIELD MEASUREMENTS

Water temperature, specific conductance, pH, dissolved oxygen, and alkalinity could change dramatically within minutes or hours after sample collection. Immediate analysis in the field is required if the results are to be representative of in-stream conditions.

Water temperature and dissolved oxygen should be measured directly from the stream, and several readings are required in the cross section to obtain a stream average. A composite stream sample should be collected for specific conductance, pH, and alkalinity. A single field meter that measures specific conductance, water temperature, pH, and dissolved oxygen directly in the stream may be used. Detailed information on the procedures, equipment, and supplies necessary for the field analyses is presented in reports by Shelton (1994) and Wilde and Radtke (in press).

QUALITY ASSURANCE AND QUALITY CONTROL

The sources of variability and bias introduced by sample collection and processing affect the interpretation of water-quality data. Quality-assurance (QA) plans ensure that the data collected are compatible and of sufficient quality to meet program objectives. These guidelines and the Study Unit design guidelines for NAWQA should be used when preparing QA plans. Specific details for QA plans are described by Shampine and others (1992).

Investigators in each Study Unit must document the quality of their data by collecting quality-control (QC) samples. A series of QC samples (blanks, replicates, and spikes) must be obtained during VOC investigations because the quality of the data collected, and the validity of any interpretation, cannot be evaluated without QC data. Detailed procedures for preparing QC samples for VOCs, and the recommended frequencies, are described in Mueller and others (1997).

Field Blanks

Field blanks are used to determine whether (1) equipment-cleaning protocols adequately remove residual contamination from previous use, (2) sampling and sample-processing procedures result in contamination, and (3) equipment handling and transport periods of sample collection do not introduce contamination. Field blanks for VOCs are collected immediately before processing a routine environmental sample. Load four 40-mL vials into the sampler. Pour VG water into a clean (see 'Equipment Cleaning' section) stainless-steel cannister, and then collect two 40-mL vials from the cannister for the cannister-blank sample. Submerge the sampler containing four 40-mL vials in the cannister and allow to fill. Remove the vials and process the field and cannister blanks in the same manner as the environmental sample. Process the samples using the NWQL analytical schedule for environmental samples. If analytical results indicate carryover of residues, perform additional field tests to determine the source of the contamination. A more rigorous cleaning procedure might be necessary. Field blanks produce the most valuable QC data to evaluate potential contamination.

Trip Blanks

Trip blanks are used to determine whether external VOCs from bottle handling and analytical processes, independent of the field sample processing scheme, are contaminating the samples. Trip blanks are provided upon request and are prepared and distributed to each Study Unit by the NWQL. These trip blanks bottles should be stored and transported with the other bottles used for collecting the environmental sample, and then submitted for analysis in the same manner. Trip blanks should never be opened in the field. If analytical results indicate that samples have been contaminated, additional blanks should be processed to identify the source. Trip blanks should only be prepared with field blanks.

Field-Matrix Spikes

Field-matrix spikes are designed to (1) assess recoveries from field matrices and (2) assist in evaluating the precision of results for the range of target analytes in different matrices. Biases and interferences can result from sample matrices and from other processes that occur from the time the sample vial is preserved in the field to the time the vial is analyzed in the laboratory. After collecting the environmental sample, immediately collect a second set of four vials for the field-matrix spikes and preserve each using HCL. Add a standard spike solution using a microliter gas-tight syringe. Matrix-spike kits (solution and syringe) with instructions are available from the NWQL. Label two vials 'FS' (field spike) and two vials 'FSR' (field-spike replicate). Record the lot number and volume of the spike solution on the field notes and on the NWQL analytical services request (ASR) form. Send each set of vials—two FS and two FSR—as separate sample sets, including the environmental sample, to the laboratory for analyses.

Replicate Samples

Sample replicates are designed to provide information needed to (1) estimate the precision of concentration values determined from the combined sample-processing and analytical method and (2) evaluate the consistency of identifying target analytes for VOCs. Each replicate sample is an aliquot of the environmental sample collected in

the same sampler, processed at the same time, and stored and shipped in the same way. Compare the analytical results to determine if accurate, consistent data can be reproduced.

DOCUMENTATION

All field activities and site information should be documented on standard surface-water-quality field notes (Shelton, 1994). A complete documentation will aid in future analyses of the collected information.

Field notes should include the following information:

- a. Station name and number.
- b. Date and time (1 minute earlier than environmental sample).
- c. Gage height, discharge, or both; stage conditions.
- d. Type of sample (single-vertical point sample).
- e. Sampler (VOC sampler).
- f. Sampling method (bridge, cableway, wading).
- g. Depth and width of stream at sampling location.
- h. Location within the cross section (midstream).
- i. Depth of sampling (mid depth).
- j. Field analyses and calibration (temperature, conductance, pH, alkalinity, oxygen).
- k. Detailed alkalinity titration.
- l. Type of samples collected (VOC, major ions, quality control, and others).
- m. Name of sample collector(s).
- n. Site information: color and odor of the stream, weather conditions, and others.

SAMPLE IDENTIFICATION

Consistent specific identification of samples is essential for national data aggregation. For this reason, a data-coding strategy has been developed for the NAWQA Program. Use the following instructions for coding information onto the water quality field notes and on the NWQL ASR forms. The most critical codes for proper sample identification are the station ID number, sample medium, and sample type. Different sample-time coding is specified to distinguish among multiple samples collected during the same site visit. VOC samples will have a time 1 minute earlier than all other environmental samples to segregate the VOC analytical results from other analyses. For QC samples, the time codes are used to establish a rationale for associating the necessary sample codes with each individual sample. Do not use fictitious station ID numbers for routine QC samples.

VOC Environmental Sample

STATION ID – Same as other environmental sample
DATE – Same as other environmental sample
TIME – One minute earlier than the other environmental samples
SAMPLE MEDIUM – ‘9’ (surface water)
SAMPLE TYPE – ‘9’ (regular)
Parameter 71999 (Sample purpose) – ‘15’ (NAWQA)
Parameter 99111 (QA data with sample) – ‘10’ (blank)

Field Blank

STATION ID – Same as environmental sample
DATE – Same as environmental sample
TIME – Exact time of preparation (different from other blanks)

SAMPLE MEDIUM – ‘Q’ (QA sample, artificial)
SAMPLE TYPE – ‘2’ (blank)
COMMENTS – ‘PREVIOUS SAMPLE AT:’ station ID, date/time
Parameter 71999 (Sample purpose) – ‘15’ (NAWQA)
Parameter 99102 (Type of blank sample) – ‘100’ (field)
Parameter 99104 (Blank lot number) – Enter first five digits
Parameter 99101 (Source of blank solution) – ‘10’ (NWQL)

Cannister Blank

STATION ID – Same as environmental sample
DATE – Same as environmental sample
TIME – One minute earlier than field blank (different from other blanks)
SAMPLE MEDIUM – ‘Q’ (QA sample, artificial)
SAMPLE TYPE – ‘B’ (other)
COMMENTS – ‘CANNISTER BLANK’
Parameter 71999 (Sample purpose) – ‘15’ (NAWQA)
Parameter 99102 (Type of blank sample) – ‘100’ (field)
Parameter 99104 (Blank lot number) – Enter first five digits
Parameter 99101 (Source of blank solution) – ‘10’ (NWQL)

Trip Blank

STATION ID – Same as environmental sample
DATE – Same as environmental sample
TIME – Exact time of preparation (end of trip)
SAMPLE MEDIUM – ‘Q’ (QA sample, artificial)
SAMPLE TYPE – ‘2’ (blank)
Parameter 71999 (Sample purpose) – ‘15’ (NAWQA)
Parameter 99102 (Type of blank sample) – ‘30’ (trip)
Parameter 99101 (Source of blank solution) – ‘10’ (NWQL)
Parameter 99109 (Start date YMMDD) – Date trip blanks received from NWQL
Parameter 99110 (End date YMMDD) – Date trip blanks shipped to NWQL

Field-Matrix Spike

STATION ID – Same as environmental sample
DATE – Same as environmental sample
TIME – ‘SPIKE (FS)’ 6 minutes later than environmental sample (HH:X6)
‘SPIKE REPLICATE (FSR)’ 7 minutes later than environmental sample (HH:X7)
SAMPLE MEDIUM – ‘R’ (QA surface water)
SAMPLE TYPE – ‘1’ (spike)
COMMENTS – ‘FS or FSR’, ‘SCH 9090 spike lot number _____’
Parameter 71999 (Sample purpose) – ‘15’ (NAWQA)
Parameter 99104 (Spike lot number) – Enter first five digits
Parameter 99105 (Replicate type) – ‘10’ (concurrent)
Parameter 99106 (Spike type) – ‘10’ (field)
Parameter 99107 (Spike source) – ‘10’ (NWQL)
Parameter 99108 (Spike volume) – volume used, in milliliters

Replicate Samples

STATION ID – Same as environmental sample
DATE – Same as environmental sample

TIME – Same as VOC environmental sample
SAMPLE MEDIUM – ‘9’ (surface water)
SAMPLE TYPE – ‘7’ (replicate)
Parameter 99111 (QA data with sample) – ‘30’ (replicate sample)
Parameter 99105 (Replicate type) – ‘10’ (concurrent)
Parameter 71999 (Sample purpose) – ‘15’ (NAWQA)

SHIPPING

Samples should be shipped by overnight express mail to the NWQL the same day of collection. A NWQL ASR form must be included with each sample. Place all glass vials in padded sleeves or pack in some other suitable manner to prevent breakage during shipment. Insulated water coolers (1 or 5 gal in volume) make good shipping containers. Chill with an adequate amount of ice to maintain the sample temperature between 0 and 4°C. The amount of ice needed depends on the length of time in transit from field to laboratory and on the season of the year. Ice should be placed inside a double plastic bag in the shipping container. Protect the NWQL ASR form and return labels from the ice by placing them in a sealable plastic bag and fastened it to the inside of the cooler lid with tape. Detailed guidelines on shipping samples are discussed in NWQL memorandum 95.04 (Appendix).

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APPENDIX—SELECTED TECHNICAL MEMORANDUMS

These Water Resources Division (WRD) and National Water Quality Laboratory (NWQL) memorandums are available in U.S. Geological Survey offices, nationwide:

WRD 94.06 SAFETY: Storage, transport, handling, and disposal of hydrochloric acid

WRD 94.07 SAFETY: Storage, transport, handling and disposal of methyl alcohol

NWQL 95.04 OPERATIONS: Shipping to the National Water Quality Laboratory