Water-Quality Principles
QW1022–TEL

Lesson 12—Concepts in Quality Assurance and Quality Control

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Chapter A4, Collection of Water Samples, p. 11–24, 133–151, Appendix A4–C

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

COLLECTION OF WATER SAMPLES A4.

This chapter of the *National Field Manual* (NFM) describes standard USGS methods (sampling strategies, techniques, requirements, and recommendations) for the routine collection of representative water samples. Sample collection forms a continuum with sample processing; therefore, the information in this chapter overlaps with some of the information in NFM 5, *Processing of Water Samples*.

SAMPLING:
The act of collecting a portion of material for analytical purposes that accurately represents the material being sampled with respect to stated objectives.

Modified from Standard Methods, 1060A
(APHA and others, 2001)

Before sample collection begins, field personnel must take steps to ensure that the samples collected will be representative of the aqueous system being investigated. A representative sample is one that typifies ("represents") in time and space that part of the aqueous system to be studied, and is delineated by the objectives and scope of the study.

Obtaining representative samples is of primary importance for a relevant description of the environment. In order to collect a representative sample that will yield the information required, (1) study objectives, including data-quality requirements,[1] must be understood in the context of the water system to be sampled, and (2) artifacts of the sampling process must be minimized.[2] Field personnel must be alert to conditions that could compromise the quality of a sample.

- **Collect a representative sample.** Use appropriate methods and quality-assurance measures to ensure that the field sites selected and the samples collected accurately represent the environment intended for study and can fulfill data-quality objectives.

- **Think contamination!** To ensure the integrity of the sample, be aware of possible sources of contamination. Contamination introduced during each phase of sample collection (and processing) is additive and usually is substantially greater than contamination introduced elsewhere in the sample-handling and -analysis process. **Therefore, collect a sufficient number of quality-control samples, appropriately distributed in time and space, to ensure that data-quality objectives and requirements are met (section 4.3).**

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[1] As used in this report, data-quality requirements refer to that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the variability allowable to fulfill the scientific objectives of the study.

[2] The degree to which a sample can be considered representative of a water body depends on many interrelated factors including, for example, temporal and spatial homogeneity of the water body, sample size, and the method and manner of sample collection.

4.0 RESPONSIBILITIES, FIELD PREPARATIONS, AND PREVENTING SAMPLE CONTAMINATION

This section of the NFM presents guidelines, requirements, and recommendations for USGS field personnel as they prepare for sample collection at field sites. Collecting comparable data over the duration of the sampling effort and among sampling sites is necessary for a valid analysis and interpretation of the data. This usually requires consistent use of the methods and equipment selected and collection of sufficient quality-control data to verify the quality and comparability of the data collected.

USGS data-collection efforts often take a whole-system approach, meaning that the data-collection methods used are designed so that the entire stream reach or aquifer volume is represented. A modified approach is needed for studies in which samples are representative of a specific portion or aspect of an aqueous system; for example, a study of aquatic ecology may establish nearshore boundaries on the system of study, and an oil-spill study may target only the surface of a water-table aquifer.

- **What do your data represent?** Data collectors need to know what questions the data being collected are meant to address, and understand the level of accuracy and precision that are needed in the data to answer those questions. The data are no better than the confidence that can be placed in how well the sample represents the aqueous system (Horowitz and others, 1994). Therefore, understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- **Are your data of appropriate quality?** Quality-control samples yield information by which confidence brackets can be applied to the environmental data. Field quality control is vital for data interpretation and assessment and yields different information than laboratory-performed quality-control checks.

Data quality begins before the first sample is collected, by taking care to use proper equipment, being aware of data-quality requirements, and being alert to potential sources of sample contamination.

4.0.1 RESPONSIBILITIES AND FIELD PREPARATIONS

Field personnel are responsible for their safety and for the quality of the work performed.

- **Never compromise the safety of field personnel.** Be familiar with the safety requirements and recommendations described in NFM 9. Get the appropriate training and certification needed if you will be working at sites designated as hazardous.
- **Collect data of known quality.** Fundamental to water-quality sampling is the fact that the quality of the analytical results can be no better than the quality of the sample on which the analyses were performed. The sample collector has primary responsibility for the quality and integrity of the sample up to the time that the sample is delivered to the analyzing laboratory or office. Data quality is determined from analysis of quality-control data.
- **Know what you need to do.** Before departing for field work, review the workplan, and plan for the types of measurements and samples specified.
  - Be thoroughly familiar with your study objectives and requirements. Sampling plans, including quality-assurance and equipment requirements, need to be prepared and reviewed in advance. Some programs require a prescribed format for sampling, quality-assurance, and safety plans. Some projects require chain-of-custody documentation.
  - Review and understand the USGS protocols for collecting and processing your samples before field work begins. Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

All details of a field trip need to be planned well in advance (fig. 4-1). Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations; a common mistake is to put off these activities until the last minute (table 4-1).

- **Make reconnaissance trips** before selecting repeat sampling sites, if possible.
  - Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing or low-flow wells, or site-access peculiarities).
  - Evaluate potential sources of contamination at the site, based on the analytes[3] to be targeted in the sample analysis.
- **Review site files and field folders** (see sections 4.1.1 and 4.2.1). Check the site location, description, and access. Review any previously collected physical, chemical, and biological data.
- **When selecting field equipment**, understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

[3]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

- **Prepare a workplan and checklists**.
  - The workplan delineates study activities and establishes the timeframe in which the activities are to be completed (table 4-1).
  - Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 4-1). Generic checklist items apply to most studies, and the checklist customized for specific study requirements (for example, special equipment or supplies, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment).
- **Data management.** Field personnel also are responsible for providing the necessary information to establish USGS National Water Information System (NWIS) site files for each sampling site and for checking to see that the site file is functional, that the information it contains is correct, and that updates are made promptly. NWIS is the hydrologic data base for the USGS, and includes the following subsystems in which study site files are to be maintained:
  - **Quality-of-Water Data (QWDATA)** – contains field and laboratory data.
  - **Automatic Data Processing System (ADAPS)** – contains time-series information.
  - **Ground-Water Site Inventory (GWSI)** – contains aquifer and ground-water site information.

PLAN AHEAD! Take adequate time to prepare.

Table 4-1. Example of work-schedule elements

Work-schedule elements	Examples of items or activities in checklists	Completed by
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.	
Presampling activities	Prepare checklists (see figs. 4-1 and 4-7). Prepare NWIS site files.	
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.	
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.	
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.	
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of-custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with respect to: analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, chemical treatment and preservation procedures; sample shipment; quality-control samples.	
Field-folder contents	Prepare a list of logistical information needed for each site, such as permission to access site, keys, maps.	
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.	

FIELD-TRIP PREPARATIONS

PROJECT: _____

SITES: _____DATE:_____

✓	Prefield activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ , Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (Water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare field forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check field vehicle for safety equipment and supplies, such as material safety data sheets, flares, and remote communications system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update field folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with field-trip and call-in (check-in) schedule	Provided on _____ to _____
	Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
	Other	

Figure 4-1. Example of a presampling activities checklist.

PREVENTING SAMPLE CONTAMINATION 4.0.2

The USGS prescribes specific protocols for avoiding contamination of water samples. In addition, collection of quality-control samples (section 4.3) – scaled as appropriate to the objectives of the study and site conditions – is mandated to check for, address, and measure sample contamination and any resulting bias to the data. The most common causes of sample contamination during sample collection include poor sample-handling techniques, input from atmospheric sources, inadequately cleaned equipment, and use of equipment constructed of materials inappropriate for the analytes targeted for study. To prevent or minimize sample contamination from these sources:

- **Implement good field practices**, summarized on table 4-2.

- **Use Clean Hands/Dirty Hands sampling techniques,** summarized on table 4-3.

USGS clean-sampling procedures (sometimes called the parts-per-billion or ppb protocol) involve (1) using equipment that is constructed of noncontaminating materials (NFM 2) and that has been cleaned rigorously before field work and between field sites (NFM 3); (2) handling equipment in a manner that minimizes the chance of altering ambient sample composition; (3) handling samples in a manner that prevents contamination; and (4) routinely collecting quality-control (QC) samples. **Good Field Practices and Clean Hands/Dirty Hands (*CH/DH*) are an integral part of routine USGS water-quality field work.**

The nine major elements that comprise Good Field Practices are listed on table 4-2. Four of the principles are further clarified below.

Field rinse equipment. Field rinsing of equipment used to collect or process samples should not be confused with the procedures used for equipment cleaning or decontamination; directions for field rinsing specific types of surface-water and ground-water equipment are described in sections 4.1.3 and 4.2.2.C, respectively. Collection of equipment blanks and field blanks is necessary to help identify potential sources of sample contamination (section 4.3). The same equipment that is used for collecting and processing environmental samples is used for collecting and processing blanks and other types of quality-control samples; however, equipment-cleaning and -rinsing procedures differ somewhat.

Follow a prescribed sampling order. One dictate of Good Field Practices is to follow a prescribed order for collecting samples. An aspect of this is that cross-contamination between sites can be avoided by planning the order in which field sites will be sampled. Sites should be sampled in the order of least to greatest potential for equipment fouling or contamination, if possible. The cleanest sites are often – although not always – those that are in pristine environments, in areas where concentrations of dissolved solids are low, or upstream or upgradient from known or suspected sources of contamination.

RULE OF THUMB: Collect samples first at sites having the least contamination or lowest chemical concentrations.

Table 4-2. Good field practices for collection of water-quality samples

[Modified from "Rules for Trace-Metal Sampling" by Howard Taylor, U.S. Geological Survey, written communication, 1992; NFM, *National Field Manual for the Collection of Water-Quality Data*]

- Be aware of and record potential sources of contamination at each field site.
- Wear appropriate disposable, powderless gloves:
  - Change gloves before each new step during sample collection (and processing).
  - Avoid hand contact with contaminating surfaces (such as equipment, coins, food).
  - Gloved as well as ungloved hands must not contact the water sample.
- Use equipment constructed of materials that are relatively inert with respect to the analytes of interest (NFM 2).
- Use only equipment that has been cleaned according to prescribed procedures (NFM 3).
- Field rinse equipment, but only as directed. Some equipment for organic-compound and other analysis should not be field rinsed.
- Use correct sample-handling procedures:
  - Minimize the number of sample-handling steps.
  - Use Clean Hands/Dirty Hands techniques (table 4-3) as required for parts-per-billion trace-element sampling. Adapt Clean Hands/Dirty Hands techniques for other sample types, as appropriate. Obtain training for and practice field techniques under supervision before collecting water samples.
- Collect (and process) samples in enclosed chambers so as to minimize contamination from atmospheric sources.
- Collect a sufficient number of blanks and other types of quality-control samples.
- Follow a prescribed order for collecting samples.

Table 4-3. Clean Hands/Dirty Hands techniques for water-quality sampling

- Clean Hands/Dirty Hands techniques require two or more people working together.

- At the field site, one person is designated as Clean Hands (*CH*) and a second person as Dirty Hands (*DH*). Although specific tasks are assigned at the start to *CH* or *DH*, some tasks overlap and can be handled by either, as long as the prescribed care is taken to prevent contaminating the sample.

- *CH* and *DH* wear appropriate disposable, powderless gloves during the entire sampling operation and change gloves frequently, usually with each change in task. (Wearing multiple layers of gloves allows rapid glove changes.) **Gloves must be appropriate to withstand any acid, solvent, or other chemical substance that will be used or contacted.**

- *CH* takes care of all operations involving equipment that contacts the sample; for example, *CH*
  - Handles the surface-water sampler bottle
  - Handles the discharge end of the surface-water or ground-water sample tubing
  - Handles the inner protective bag on the churn splitter
  - Transfers sample to churn or cone splitter
  - Prepares a clean work space (inside vehicle)
  - Sets up processing and preservation chambers
  - Places equipment inside chambers (for example, sample bottles, filtration and preservation equipment)
  - Works exclusively inside chambers during collection/processing and preservation
  - Changes chamber covers, as needed
  - Sets up field-cleaning equipment and cleans equipment

- *DH* takes care of all operations involving contact with potential sources of contamination; for example, *DH*
  - Works exclusively exterior to processing and preservation chambers
  - Prepares and operates sampling equipment, including pumps and discrete samplers, peristaltic pump switch, pump controller, manifold system
  - Operates cranes, tripods, drill rigs, vehicles, or other support equipment
  - Handles the compressor or other power supply for samplers
  - Handles tools such as hammers, wrenches, keys, locks, and sample-flow manifolds
  - Handles single or multiparameter instruments for field measurements
  - Handles the churn carrier, including outer protective bags
  - Handles stream-gaging or water-level equipment
  - Sets up and calibrates field-measurement instruments
  - Measures and records water levels and field measurements

Use Clean Hands/Dirty Hands (*CH/DH*) sampling procedures. *CH/DH* procedures were developed for collecting (and processing) samples vulnerable to contamination. *CH/DH* procedures separate field-duty chores and dedicate one individual (designated as Clean Hands or *CH*) to tasks related to direct contact with sample-wetted equipment and sample containers (table 4-3). Implementation of this protocol requires hands-on training and field-team coordination.[4]

- **Requirement:** *CH/DH* procedures are required when collecting samples for analysis of metals and other inorganic trace elements (hereafter referred to collectively as trace elements), as follows:
  - For trace elements with ambient concentrations at or near 1 µg/L.
  - For iron, aluminum, or manganese with ambient concentrations to about 200 µg/L.

- **Recommendation:** *CH/DH* procedures are recommended when collecting samples for analysis of most trace elements with concentrations to about 100 µg/L.

- **Recommendation:** *CH/DH* procedures are recommended when collecting samples for analysis of trace-organic compounds and major inorganic elements, particularly when the target analyte could be subject to contamination from field or laboratory procedures at a level that could exceed data-quality requirements.

[4]A detailed description of Clean Hands/ Dirty Hands techniques for surface-water sampling can be found in Horowitz and others (1994). Clean Hands/Dirty Hands techniques have been incorporated in the procedures for ground-water sampling (refer to section 4.2), equipment cleaning (NFM 3), and sample processing (NFM 5).

Minimize atmospheric contamination. Water bodies that are isolated from the atmosphere or that have dissolved-oxygen concentrations that are substantially less than that of air can be found in surface-water systems (deeper sections of stratified lakes and reservoirs, for example), but are more common in ground-water systems. For such sites, exposure of the sample to the atmosphere can increase dissolved-oxygen concentrations, causing reduced metal ions to oxidize and precipitate as a hydroxide.

Collection of environmental samples from water bodies for which concentrations of dissolved gases differ substantially from atmospheric concentrations might require special field equipment or procedures. Equipment and procedures should be selected that minimize contact with the atmosphere or minimize the effect of pressure changes from the source of the sample to the point of field measurement or sample processing. Sampling methods and equipment for preventing contact of anoxic and suboxic water samples with atmospheric gases are described in section 4.2.2.C.

TECHNICAL NOTE: Exposure of anoxic or suboxic samples to atmospheric oxygen can cause reduced metal ions to oxidize and precipitate as a hydroxide (for example, oxidation of iron species from ferrous (Fe^{+2}) to ferric (Fe^{+3}) iron). Precipitation of an iron (or other metal) hydroxide can occur either before or during sample filtration, thereby lowering concentrations of soluble iron and co-precipitating metals in the sample. Examples of nonmetal analytes for which atmospheric exposure can compromise sample integrity include volatile organic compounds (VOCs), pH, alkalinity, sulfide, chlorofluorocarbons (CFCs), and some bacteria species.

QUALITY CONTROL 4.3

Collection and analysis of quality-control (QC) samples are mandated components of USGS water-quality field studies. The goal of QC sampling is to identify, quantify, and document bias and variability in data that result from the collection, processing, shipping, and handling of samples. **The bias and variability associated with environmental data must be known for the data to be interpreted properly and be scientifically defensible** (Horowitz and others, 1994; Koterba and others, 1995; Mueller and others, 1997). This section addresses quality control for aqueous samples to be analyzed for inorganic and organic analytes (see NFM 7 for quality control of microbiological sampling and analysis). Quality-assurance terminology in general, and quality-control terminology in particular, can differ within and among organizations; see "*Conversion Factors, Selected Terms, and Abbreviations*" for a glossary of definitions as used in this report.

Bias: systematic, directional error measured by the use of blank, spike, or reference-material samples.

Variability: random error measured by the use of environmental or QC sample replicates.

The types of QC samples to be collected and their temporal and spatial frequency and distribution depend on study objectives, data-quality requirements, site conditions, and management or regulatory policy. QC sampling is part of an overall strategy for quality assurance of the data collected and generally is described in the Quality Assurance Plan (QAP) or Sampling and Analysis Plan (SAP). QC samples of various types can be used to measure environmental data quality (for example, assign error bars to measurement sets), identify data-quality problems, and locate the sources or causes of data-quality problems. **Field personnel need to understand the purpose for each QC sample type (Appendix A4-C) and how the resulting QC data will be used so they can account for and accommodate QC needs that arise from unforeseen site conditions.**

- **Basic QC samples** are collected routinely to document the quality of the environmental data and to identify whether data-quality problems exist. They are designed to measure most sources of error that affect environmental samples. Basic QC samples include field blanks, field matrix spikes, and field replicates.
- **Topical QC samples** address specific QC needs or topics and commonly are designed to (1) help determine when sampling should commence; (2) locate the cause and source of data-quality problems; and (3) assess comparability among field methods. Topical QC samples include all the QC sample types not specifically designated "basic" QC samples.

Good science requires consideration of measurement errors – such as bias and variability – in data analysis.

The field team or person collecting samples should be involved in assessing the analytical results of the QC samples collected, because only they have all of the information about the site conditions and procedures that were followed. This knowledge could be crucial in understanding QC sample results. For any water-quality sampling event, USGS field personnel must:

- Be knowledgeable about and alert to potential sources of contamination (table 4-11). When in doubt, it usually is wisest to collect additional QC samples and decide later whether to have them analyzed.
- Collect field QC samples at approximately the same time as environmental samples are collected, using the same equipment.
- Document in the field log as complete a description of the sampling event as possible. Include how, when, where, and why the QC sample was collected, and observations about site or sampling conditions.
- Implement the prescribed procedures for equipment cleaning and QC sample collection and processing.

- Use chemical preservatives from the samelot number for a given set of environmental and associated QC samples. Record the preservative lot number on field forms and in field notes.
- Store QC data in an electronic database devoted to QC data. For USGS studies, this should be a QC-designated data base within NWIS.

Use Good Field Practices (table 4-2) and Clean Hands/Dirty Hands techniques (table 4-3) when collecting and processing QC samples.

Table 4-11. Common sources of contamination related to field activities

[SPMDs, semi-permeable membrane devices; DIW, deionized/distilled water of ASTM grade one or better; DEET, N,N-diethyl-meta-toluamide (the active ingredient commonly used in insect repellents)]

Contaminant source type	Examples
Sampling environment	Airborne particulates; precipitation; dust, soil, solid particles; fumes from engine exhaust, chemical preservatives, upwind industrial emissions.
Sample-collection equipment	Pumps, isokinetic samplers, bailers, sample tubing, SPMDs.
Sample-processing equipment	Filtration devices, churn splitter, cone splitter, bottles, water (DIW, tap, blank).
Sample-cleaning processes	Cleaning equipment (basins, brushes); carryover from cleaning solutions or tainted water; methanol carryover; insufficient decontamination or rinsing.
Transport and shipping	Field vehicles; coolers or other shipping containers; improperly closed or protected sample bottles.
Storage	Warehouse; refrigerator; field vehicle; office laboratory; office storage space.
Personnel	Dirty hands; sweat; sunscreen; DEET; nicotine, caffeine, and alcohol (breath); dirty gloves; gloved or ungloved contact with the sample to be analyzed; shedding clothing; hair and dandruff.

How, when, where, and why a QC sample was collected must be known to understand the sources of error measured.

4.3.1 BLANK SAMPLES

The primary purpose of a blank sample ("blank") is to measure the magnitude of contaminant concentration (for analyte(s) of specific interest) that might have been introduced into the sample as a result of sampling-related activities (table 4-11 and Appendix A4-C). Various types of blanks can be used or customized to identify the source of sample contamination (table 4-12 and Appendix A4-C). Appendix A4-D provides examples for estimating the volume of blank solution needed.

It is necessary to obtain blank water of the quality and type appropriate for the chemical analysis to be performed on the sample. Blank water is strictly defined within the USGS as specially prepared distilled/deionized water (DIW) that is laboratory produced, quality-controlled, and that carries a certificate of analyte concentrations for each grade and lot of water produced. USGS water-quality projects obtain quality-assured blank water through the One-Stop Shopping system of the National Water-Quality Laboratory (NWQL).

- **Inorganic-grade blank water (IBW)** is required for blanks that will be analyzed for inorganic constituents (major and minor ions including nutrients, trace elements) and suspended sediments.
- **Pesticide-grade (PBW)** is required for blanks that will be analyzed for pesticide compounds and organic carbon.
- **VOC/Pesticide-grade (VPBW)** has been purged with nitrogen gas (N_2) and is required for blanks that will be analyzed for volatile organic compounds. VPBW is appropriate as a blank sample for analysis of pesticides, organic carbon, and suspended sediments.

Before collecting blank samples, the laboratory certification of concentration for each analyte in the blank water should be compared with the expected concentration in the environmental samples and with the detection limit of the laboratory method to be used for sample analysis. **The laboratory certificate of analysis for each lot of blank water should be kept on file with project records, and the lot number(s) used for each sample should be recorded on field forms.**

Wear clean, powderless, disposable gloves and conform meticulously to other Clean-Hands practices when working with blank solutions.

Table 4-12. Common types of blank samples and the questions they address
[QC, quality control; IBW, inorganic-grade blank water; PBW, pesticide-grade blank water; VPBW, volatile-organic-compound and pesticide-grade blank water]

Type	Targeted Source(s) of Bias[1]
Field blank	Sample-collection, -processing, -transport process ***Basic QC sample****: Was my sample contaminated as a result of field activities and exposure?*
Equipment blank	Sample-collection and processing equipment system ***Topical QC sample****: Does an initial equipment assessment[2] confirm the suitability of the equipment to provide samples within my data-quality requirements?* ***Topical QC sample****: Is my equipment-cleaning protocol adequate?*
Sampler blank	Sampling device (for example, the D-95 sampler, Fultz pump, or peristaltic-pump tubing) ***Topical QC sample****: Is my sampling device the source of contamination?*
Filter blank	Filtration device (for example, the capsule filter, in-line filter holder, aluminum plate filter) ***Topical QC sample****: Is my filtration device the source of contamination?*
Ambient blank	Exposure to atmospheric outfall or other conditions ***Topical QC sample****: Was sample exposure to the atmosphere a contaminant source?*
Source-solution blank	The blank water used (for example, IBW, PBW, or VPBW) ***Topical QC sample****: Was my blank water tainted with respect to my analyte(s) of interest?*

[1]The bias and variability measured includes that from laboratory handling, processing, and analysis of the sample in addition to the targeted source listed.
[2]An equipment blank is required for U.S. Geological Survey investigations to determine the equipment suitability to provide the analyte data needed to meet study objectives.

To prepare for processing blank samples:

1. Label the capped, precleaned sample bottle with the site identification number, laboratory sample designation code (NFM 5), date and time, or affix the proper bar-code label to the sample container, as appropriate. Record this information on field forms.
2. Put on gloves. Place each stock container of the blank solution to be used (IBW, PBW, and VPBW) into a clean plastic bag. If pumping blank water from a standpipe, change gloves and then rinse the precleaned standpipe three times using a small volume of blank solution of the type selected. Keep standpipe covered until use.
3. Change gloves. Place precleaned, labeled sample bottle(s) and the stock of blank solutions to be used into processing chamber (or standpipe).
   - IBW blanks—Discard the deionized water that half fills the precleaned polyethylene sample bottle. Rinse the sample bottle with a small quantity of blank solution and discard rinsate before filling with IBW.
   - PBW or VPBW blanks—Do not prerinse the sample bottle. Use glass bottles or vials as received precleaned from the laboratory.

Do not substitute DIW for IBW.

Pre-Field Blanks 4.3.1.A

The source-solution and initial equipment blanks are common types of blank samples that are collected by the study field team in preparation for environmental sampling. **Collection of an equipment blank is mandated by USGS policy before the sampling phase of the study begins**, to determine if the sample-wetted components of the equipment proposed for use could be a source of contamination by introducing the study's target analytes to a blank or environmental sample. Collection of pre-field equipment blanks is recommended annually, or as appropriate for the sampling schedule of the study.

- **Source-solution blank**. Collect in a designated clean, draft-free area of the office laboratory, such as under a laminar-flow hood or laminar-flow bench. Do not collect the source-solution blank in a fume hood. Submit the sample for analysis along with or after the equipment blank and field-collected samples, depending on study objectives and the data resulting from other blank samples.
- **Equipment blank (pre-field)**. Collect in a designated clean area of the office laboratory at least 4 weeks before using the equipment in the field to allow enough time for sample analysis and review of the resulting data.

A variety of other types of blank samples that are collected in the controlled office-laboratory environment can be designed to test some aspect of sample handling not related to the field environment. Examples of these types of blanks include the refrigerator blank, the shelf blank, and the preservation blank (Appendix A4-C).

4.3.1.B Field Blanks

Field blanks are collected and processed at the field site in the same manner and using the same equipment as the environmental sample(s). Equipment must be cleaned meticulously before field blanks are collected (NFM 3).

- A single field blank is a "basic" QC sample that represents the entire sampling system. The feld blank is collected routinely for basic quality control of the sampling process, rather than identifying the specific source of the contamination. The field blank consists of an aliquot of blank water processed sequentially through each component of the sampling system (fig. 4-14 and Appendix A4-C). The field blank provides a measure of the total contamination (bias) present in the sample.
- To address topical quality-control questions, blanks can be collected onsite that represent components of the sampling system; for example, the sampler blank (surface water), splitter blank, filter blank, or pump or bailer blank (ground water). Such topical field blanks can be used to trace the specific source of contamination.
- When collecting field blanks for inorganic and organic analyses after sampling at a site, use the following sequence and the protocols described in NFM 3 and shown in NFM 3, fig. 3-1 for equipment cleaning.
    1. Clean equipment for inorganic-constituent sampling: detergent → tapwater/DIW → acid, if needed → DIW.
    2. Rinse equipment with IBW at least three times.
    3. Collect the IBW blank sample for analysis of inorganic constituents.
    4. Resume equipment cleaning for organic-compound sampling: methanol, if needed → air-dry exposed surfaces →IBW or PBW, as appropriate. Remove methanol from pumps, tubing, and other equipment, as described in NFM 3.
    5. Rinse equipment at least three times with the appropriate organic-grade blank water (VPBW or PBW).
    6. Collect the VPBW (or PBW) blank sample for analysis of organic compounds.

The process of producing a field blank can be designed to collect simultaneously blanks for each component of the sampling system (fig. 4-14). If laboratory analysis of the analytes being quality controlled is not time dependent, the sequential blank samples representing components of the sampling system, as well as any associated source-solution and ambient blanks, normally can be stored for up to 6 months.

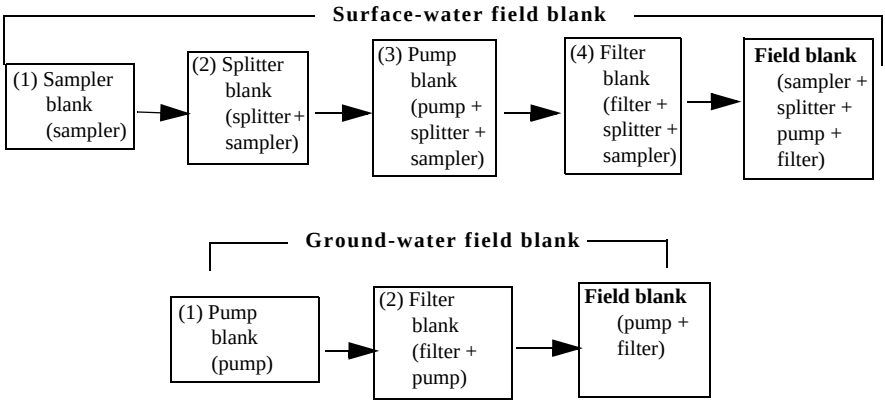
- If the field-blank data indicate constituent concentrations at acceptable levels, then the associated set of sequential blanks can be discarded. (Be sure to use appropriate means for disposing of chemically treated solutions.)
- If laboratory data indicate greater than acceptable concentrations:
  - Submit the source-solution blank, ambient blank(s), and equipment-component blank(s) (the sampler blank, splitter blank, pump blank, and so forth) to the laboratory for analysis.
  - Use the data from equipment-component blank samples to identify the source(s) of contamination detected in the field blank.
- Once the source of contamination has been identified, take the measures needed to mitigate or eliminate the contamination for future sampling efforts.

Prevent contamination of the source-solution and blank sample by capping the respective bottles immediately after decanting the volume of blank solution needed.

EXAMPLE OF FIELD-BLANK SAMPLE COLLECTION

A set of blanks can be generated that is associated with the field blank to help determine which equipment component in the system could be a source of contamination. The **field blank** is the final sample that represents all equipment components of the sampling system. After each blank sample is collected, preserve and store sample as required.

- → **Surface-water field blank: follow steps 1 through 4.** In this example, the equipment used includes a US D-95 sampler, 8-liter (L) churn splitter, peristaltic pump, and filter assembly.
- → **Ground-water field blank: follow steps 1 and 2.** In this example, the equipment used includes a submersible pump and a filter assembly.



Sampler Blank. Using the blank water selected, rinse and then fill the sampler; attach sampler cap and nozzle; pour the required volume through nozzle into sample bottle.

Splitter Blank.[1] Rinse churn splitter with blank water. Pour the blank water remaining in the sampler through the sampler nozzle and into the 8-L churn splitter. Refill sampler, repeat until churn contains 3 to 5 L of blank water. Process the required blank-sample volume through the churn spigot into the splitter-blank bottle. (If a cone splitter is used instead of a churn splitter, the blank sample is processed through the exit port tubes.)

Pump Blank.[1]

- **Surface-water example:** Using the peristaltic pump, thread the intake end of clean tubing into churn splitter through the funnel, and cap the funnel loosely. Insert the discharge end of the pump tubing into a processing chamber and pump blank water through the tubing for an initial rinse, discharging rinse water to waste. After the rinse, pump the required volume of blank water from the churn splitter into the pump-blank bottle.
- **Ground-water example:** Rinse a precleaned, noncontaminating standpipe with blank water and discard rinse water. Place submersible pump into the standpipe and pour in blank water—keep water level above the pump intake. Insert discharge end of pump tubing into a processing chamber. Circulate blank water through pump and tubing to rinse, discharging rinse water to waste. Pump the required volume of blank water from the standpipe into the pump-blank bottle.

Field Blank. The **field blank** in this example is identical to the **filter blank**[1] because the filter assembly is the final component of the equipment system through which the blank is processed. Working in the processing chamber, precondition the filter with blank water (NFM 5).

- **Surface-water example:** Pump the required volume of blank water from the churn splitter through the prerinsed filter assembly into the field-blank bottle.
- **Ground-water example:** Pump the required volume of blank water from the standpipe through the prerinsed filter assembly into the field-blank bottle.

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[1]These are special cases of a splitter blank, pump blank, and filter blank, respectively, because the equipment component named is the final component but not the only component contacting the blank sample.

Figure 4-14. Example procedure for collecting a field-blank quality-control sample.

REPLICATE SAMPLES 4.3.2

The primary purpose of replicate samples is to identify and (or) quantify the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or greater multiples—are considered identical or nearly identical in composition and are analyzed for the same chemical properties. Common types of replicates are described below and summarized in Appendix A4-C. Field personnel should be careful to keep detailed notes on exactly how the replicate samples were collected and processed, to help distinguish the sources of variability that affected the samples.

Replicate samples are collected simultaneously or close in time with the associated environmental sample, using identical procedures.

Concurrent Replicates 4.3.2.A

Concurrent replicates are two or more samples of environmental water that are collected simultaneously or at approximately the same time. Concurrent replicates provide basic QC data for surface-water sampling and incorporate, for example, the total variability introduced from collection, processing, and shipping of the sample; the variability inherent in the aqueous system across a short distance in space and time; and the variability inherent in laboratory handling and analysis of the samples.

Depending on study objectives, duplicate samples can be collected concurrently by using two sampling devices of the same type or by filling separate sample-compositing containers using the same sampling device.

The following procedure, adapted from Horowitz and others (1994), is used at surface-water sites to fill two or more sample-compositing containers (usually churn splitters):

1. Complete equipment field-rinsing procedures (surface water, section 4.1.3; ground water, section 4.2.2.C), using two clean churn splitters. Label the sample bottles appropriately. Change gloves.
2. At the first vertical of an EWI or EDI section, collect a sample and pour it into the churn splitter 1 (section 4.1).
3. Using identical technique, resample at the first vertical and pour the sample into churn splitter 2.
4. Move to the second vertical, collect the sample, and pour it into churn splitter 2.
5. Using the identical technique, resample at the second vertical and pour the sample into churn splitter 1.
6. Collect and pour samples into each churn splitter in this manner for each of the remaining verticals, alternating churn splitters as described in steps 2 to 5 above.
7. Using identical technique, process and preserve a sample from churn splitter 1 and then from churn splitter 2.

4.3.2.B Sequential Replicates

Sequential replicates are samples of environmental water – commonly ground water – that are collected consecutively (one after the other) from the same sampling site and that are subjected to identical laboratory analysis. The sequential replicate can be collected, for example, as a sample pumped from a well or stream. Sequential replicates are used to assess variability among samples that result from field activities (collection, processing, and shipping procedures). Because sequential replicates are not collected simultaneously, inhomogeneities in the water resource are incorporated into the variability measured. Also included is the variability inherent in laboratory handling and analysis of the samples.

When collecting sequential replicates for whole-water samples:

1. Use identical sampling procedures and supplies, collecting the sample for each analysis one after the other.

2. Preserve the replicate-sample set in the same order as the order in which the samples were collected.

When collecting sequential replicates for filtered samples, use the procedure that best fits study objectives:

1. Trace-element samples or sample set for inorganic and nutrient analyses that includes trace metals:[16]
   a. For each replicate prepare a capsule filter unit as described in NFM 3 and NFM 5.2. Two replicates, for example, require two precleaned capsule filters.
   b. Install "Filter A" and follow filtration procedures and analyte sequence described in NFM 5.2. Trace-element (FA) samples are filtered first, passing no more than 200 mL of sample water through the capsule filter.
   c. Remove and discard Filter A. Change gloves.
   d. Install "Filter B." Use identical procedures and sampling sequence as were used for the "Filter A" sample set.
   e. Continue with this procedure for each additional replicate. This procedure helps assess the variability in sample chemistry over the time period of sample collection that results from sampling and laboratory procedures, including a potential effect from using different capsule filters. Potential effects from using different filter units is considered insignificant compared to those from particulate loading of the filter (Horowitz and others, 1994; USGS Office of Water Quality Technical Memorandums 92.13 and 93.05).

2. Pesticides and other filtered organic-compound samples:
   - If there is minor or no visible loading of particulate matter on the filter, then replicate samples can be collected one after another without changing filters.
   - If filter loading is observed, using a different filter in the manner described above for trace-element samples is recommended. The decision, however, depends on the data-quality requirements of the study and professional judgment.

[16]This method fulfills the objective to maintain the operational pore-size definition of the filtered-sample for trace-element analysis; one filter unit is designated per trace-element sample set in order to maintain comparable particulate loading on the filter.

4.3.2.C Split Replicates

Split replicates are samples obtained by dividing one sample that is designated for a specific laboratory analysis into two or more subsamples (replicates), each of which is submitted to one or more laboratories for identical analysis. Split replicates can be collected for different purposes, depending on the procedures employed and whether the purpose is to determine variability from field plus laboratory processes (the field-replicate split sample) or from laboratory procedures (the lab-replicate split sample).

When collecting split replicates, sample bottles must be labeled carefully, and the sequence of procedures used must be recorded.

- **Lab-replicate split sample**. A sample collected in a single bottle that is split into two or more replicates **after** having been processed and preserved is used to answer the question: "What is the variability associated with laboratory handling and analysis of the sample?" This type of split replicate sample typically is prepared from filtered samples; it is not appropriate, generally, for whole-water samples containing noticeable concentrations of suspended material.

  To collect a lab-replicate split sample (adapted from Horowitz and others, 1994):

  1. Wearing disposable, powderless gloves and working inside a processing chamber, start with a full bottle of sample[17] to which the appropriate chemical treatment has been added. Shake the sample thoroughly to mix.
     - For inorganic samples only, use a bottle rinsed at least twice with IBW and then field rinse the bottle with a small volume of processed sample.
     - Do not prerinse bottles for organic samples.
  2. Transfer the entire contents of the first bottle to the second bottle. Cap and shake the second bottle.
  3. Uncap the second bottle and pour its entire contents back into the first bottle. Cap and shake.
  4. Uncap the bottles and pour one-half of the sample from the first bottle into the second bottle. Cap both bottles tightly.

[17]The volume of sample collected and that of the split replicates depends on the volume of sample required by the laboratory for the analysis desired.

▶ **Field-replicate split sample.** A sample split into subsamples by use of a churn splitter, cone splitter, or T-valve (such as that used on a ground-water manifold device, fig. 4-10), for example, can be used to answer the question, "What is the variability associated with the entire sampling (including any sample collection, processing, preservation, shipping, and laboratory handling and analysis) processes?" Bottles of the replicate samples must be labeled appropriately, and the sequence of procedures used must be recorded. To split concurrent replicate samples that were processed through separate compositing devices (such as churn splitters), follow the procedure shown in steps 1-4 above and label the samples as follows:

To collect a field-replicate split sample (adapted from Horowitz and others, 1994):

Churn splitter 1:	first bottle	"Site (X), Sample 1, Split A"
		"Site (X), Sample 1, Split B"
Churn splitter 2:	first bottle	"Site (X), Sample 2, Split A"
		"Site (X), Sample 2, Split B"

4.3.3 SPIKE SAMPLES

A "spike" sample is an environmental sample to which target compounds (the field-matrix spike mixture) are added after the sample has been processed. Field-spike samples are used to measure bias and answer the question "What loss or gain of target analytes occurred because of degradation and water-matrix characteristics?" Bias determined from spikes is termed "recovery" and reflects the amount of analyte(s) measured expressed as a percentage of the amount spiked.

Spike samples can be customized to address the source of the bias (water matrix, degradation, laboratory method performance) in the data. To address bias from degradation, samples should be spiked in the field as soon as possible after collection. A combination of a laboratory spike, field spike, and field-spike replicate provides the most information, but may not be needed for a given study.

RULE OF THUMB:

Spike when target compounds are expected to be low; specifically, when target compounds are at least a factor of two less than the spiking level.

The numbers and types of spike samples to be selected depend on study objectives and data-quality requirements. However, **an unspiked environmental sample must accompany each spiked environmental sample to correct the data for background concentrations.** Training is required before personnel attempt to spike samples. USGS personnel obtain spike solutions, spike kits, and instructions through the NWQL One-Stop Shopping system.

Field-matrix spike mixtures are prepared in a laboratory and commonly are added to environmental samples designated for organic-compound analysis.

- Short-term use: keep matrix-spike ampoules chilled at all times. Spike compounds are unstable and degrade rapidly at room temperature.
- Long-term use: store spike mixtures in a freezer.
- Spike mixtures contain toxic compounds. Dispose of waste materials in accord with current local and State regulations and USGS Science Center guidelines.

When preparing field-spiked samples for pesticides or VOCs, follow the procedure listed below:

1. Samples should be processed, spiked, and chilled immediately after collection. If spiking is delayed, keep sample chilled until and after it is spiked. Check that the sample bottles are labeled appropriately:
   - FS = field-spiked sample
   - FSR = field-spiked replicate
   - LS = lab-spiked sample
2. Wearing disposable gloves and working in a preservation chamber, follow the laboratory instructions for spiking the sample. Be sure that the spike mixture is the one intended for the sample, in terms of analytes, volume, and concentration.
3. Chill field-spiked samples to 4°C or below without freezing, and handle in a manner identical to that of the unspiked environmental sample.
4. Record the following information related to the spike sample on field and NWQL Analytical Services Request forms: lot number of spike solution, volume of spike solution, and source of spike solution.

CAUTION: Spike mixtures can be toxic and might cause cancer or other diseases. Follow the laboratory-prescribed spiking instructions meticulously. Work in a well-ventilated area and avoid inhalation and skin and eye contact.

4.3.4 REFERENCE SAMPLES

Standard-reference-water samples (SRS) and reference-material samples that are submitted by field personnel for laboratory analysis can be used to answer questions, such as "What are the bias and variability associated with field-handling, shipping, and laboratory procedures"? Reference samples typically are submitted from the field as blind samples (section 4.3.5) and as split replicate samples (section 4.3.2.C) because the composition is known, thus eliminating guesswork regarding the accuracy of the analytical results.

Reference samples for inorganic analytes in a natural water matrix currently are available to USGS personnel from the USGS Branch of Quality Systems. The National Institute of Standards and Technology and some commercial laboratories also supply reference materials.

When preparing reference samples, follow the procedure listed below:

1. **Prepare this sample before leaving for the field site.**

    a. Relabel the reference-sample bottle with the site identification code and a field date and time. The sample should appear as if it is an environmental sample.

    b. Process SRS or reference-material samples in a clean environment in the office laboratory, under a laminar-flow hood or other protective chamber, to avoid atmospheric contamination. **Do not process these QC samples under a fume hood.**

    c. Rinse each sample bottle three times with a small volume of SRS or reference-material sample, fill the bottle with the reference solution, and cap securely.

2. Prepare an Analytical Services Request (ASR) form; record the SRS or reference-material sample identification code (from the original container) in field notes.

3. Pack the sample and the accompanying ASR form to take to the field site.

4. Ship SRS or reference-material samples in the same container with the environmental and other QC samples collected at the field site.

4.3.5 BLIND SAMPLES

For blind samples, the source and chemical composition of the samples are known to the submitter but typically not known to the analyst; therefore, blanks, SRS, or reference material often are used as blind samples. Blind samples can be designed to answer questions such as "What bias and variability are introduced by procedures used within a single laboratory or among laboratories?" Replicate or spike samples sometimes are used to answer a similar question, but with greater potential for more variability.

APPENDIX A4-C
Quality-control samples collected by field personnel for water-quality studies

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Reference, spike, and blind samples.....APP.C6

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

BLANK SAMPLES[2]		
Sample type	**General description[3]**	**Purpose[3]**
Field blank	Blank water that is passed through the entire sampling equipment system **onsite** and subjected to identical collection, processing, preservation, transportation, and storage procedures and laboratory handling as for environmental samples. • The field blank is processed onsite through clean equipment on the same day as, and along with, the environmental samples, either, (*a*) directly after the equipment has been field cleaned and before leaving for the next site (NFM 3), ***or***, (*b*) at the next site, just before environmental samples for that site are processed. • A set of blanks can be processed and associated with the field blank (fig. 4-14).	Determine the concentrations of target analyte(s) present in the environmental sample that could be attributed to field procedures for equipment cleaning and sample handling. Results include effects from laboratory handling. Examples related to (*a*) and (*b*) (see "General description"): (*a*) Check the adequacy of field-cleaning procedures (demonstrate that equipment was adequately decontaminated after previous use); (*b*) Identify contamination of sampling equipment while in transport from office to field site or between field sites, and ambient field conditions at the field site.
Equipment blank	Blank water that is passed sequentially through each component of the equipment system to be used for collecting and processing environmental samples and resulting in a single final blank sample. • Differs from a field blank in that the equipment blank is processed under controlled conditions in an office laboratory and before equipment will be used for field work. Standard USGS procedure is to collect an annual equipment blank if the equipment is not in active use. • Can result in collecting a series of blank samples sequentially, each sample of which represents a different component or components of the equipment system; for example, sampler-equipment blank, splitter-equipment blank, filter-equipment blank.	• Identify effects of the equipment system used to collect and process samples on analyte concentrations. • Verify adequacy of equipment-cleaning procedures (NFM 3). • Relating to components of the equipment system, assess potential of sample contamination and adequacy of equipment-cleaning procedures associated with each component of the equipment system to be used for field work. • Can be used to help identify or eliminate source(s) of contamination.

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

BLANK SAMPLES[2]		
Sample type	**General description[3]**	**Purpose[3]**
Ambient blank	Blank water that is exposed to the identical collection and processing areas and time period as environmental samples. The blank water is transferred from the stock-solution container to the same type of bottle used for an environmental sample. The specific mode of exposure to the atmosphere is determined by the QC objective. **Examples:** (*a*) The blank water is transferred to a sample bottle while in the sample-processing chamber used for environmental samples. (*b*) Container such as a sample bottle is prefilled with blank water, opened while in the processing chamber, and exposed to the chamber atmosphere throughout the processing of environmental samples.	Determine analyte concentrations present in the environmental sample that could be attributed to exposure of sample to the ambient atmosphere in which samples are collected, processed, and analyzed. Referring to the general description: • Example (*a*) is used to assess concentrations after processing the blank in a manner that mimics collection of the environmental sample. • Example (*b*) is used to indicate the maximum analyte concentration that would result from prolonged sample exposure to ambient conditions.
Source-solution blank	Stock solution of PBW, VPBW, or IBW that is transferred to a sample bottle in an area of the office laboratory within a controlled atmosphere that is relatively clean and protected with respect to target analytes.	Determine the source of water used for blanks and the degree to which the composition of blank solution could have changed (with respect to target analytes) from time of laboratory certification to time of use.
Sampler blank	Blank water processed through the same sampler used for environmental samples after the sampler has been cleaned. (Blanks processed through pump samplers usually are designated pump blanks).	• Identify effects of sampler components on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Splitter blank	Blank water processed through the same sample-splitting device used to collect or to process environmental samples (such as a churn splitter, cone splitter, or manifold system), after the splitter has been cleaned.	• Identify effects of splitter components on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC control samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

BLANK SAMPLES[2]		
Sample type	**General description[3]**	**Purpose[3]**
Pump blank	Blank water processed through the pump-and-tubing system used for environmental samples, after pump and tubing have been cleaned.	• Identify effects of pump components and tubing on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Filter blank	Blank water processed through the filter assembly used for environmental samples, after the filter unit or assembly has been cleaned.	• Identify effects of filtration assembly on analyte concentrations. • Verify adequacy of cleaning procedures, if a plate or cartridge assembly is used—see NFM 3. • If the filter blank is to represent the same filter media, the blank is processed prior to the environmental samples.
Preservation blank	Blank water that is transferred to a sample bottle and chemically treated with a preservative in an area protected from atmospheric contamination (usually under a clean hood environment in the office laboratory). The preservative used is from the same lot number used for the other QC and environmental samples.	Determine the potential for, and magnitude of, sample contamination from the chemical treatment to be used to preserve the environmental sample.
Shelf blank ("Hold" blank)	Blank water that is transferred into the same type of bottle used for an environmental sample (usually in a protected environment in the office laboratory) and stored adjacent to stored environmental samples for the same length of time.	Determine the potential for and magnitude of sample contamination from sample storage in a designated area for a designated length of time.
Refrigerator blank	Blank water that is transferred to a sample bottle (usually in a protected environment in the office laboratory) and stored adjacent to environmental samples in a refrigerated area for the same length of time.	Determine the potential for, and magnitude of, sample contamination from refrigeration of the sample for a designated length of time.

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

	REPLICATE SAMPLES	
Sample type	**General description[3]**	**Purpose[3]**
Replicates (duplicates, triplicates, etc. of sequential, split, concurrent, or other type of replicate sample)	A set of samples that is collected close in time and space and in a manner so that the samples are thought to represent virtually the same physical, chemical, and biological properties.	Depending upon its type, a replicate is used to determine variability in some part of the sample collection, processing, and analysis system.
Concurrent replicates	Samples obtained simultaneously using two or more samplers or by using one sampler and alternating collection of samples into two or more compositing containers (Horowitz and others, 1994).	Identify and (or) quantify the variability in the system being sampled.
Sequential replicates	Samples that are collected one after the other and considered virtually identical in composition.	• Identify and (or) quantify the variability introduced from collection, processing, shipping, and laboratory handling and analysis. • Can be designed to indicate temporal variability resulting from consecutive collection of samples.
Split replicates	Samples obtained by dividing one sample into two or more subsamples either before or after sample processing and preservation. **Each of the subsamples is to be analyzed for concentrations of the same constituents or compounds**. Examples: (*a*) A processed and treated sample in a sample bottle is split into two or more aliquots and subjected to identical handling and analysis. (*b*) Environmental water is passed through a splitting device (such as a cone splitter or T-valve) from which subsamples are collected simultaneously and subjected to identical handling and analysis. (*c*) Environmental water is collected into a compositing device from which subsamples are collected sequentially and subjected to identical handling and analysis.	• Assess variability for a given sample matrix. • Compare differences in analyses obtained from the same or separate laboratories.

APPENDIX A4-C—Quality-control samples collected by field personnel for water-quality studies.—*continued*

[Common types of quality-control (QC) samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for QC samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Koterba and others (1995), Mueller and others (1997), unpublished notes from the USGS course "Quality-Control Sample Design and Interpretation," and the following USGS Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations[1]: PBW, pesticide-grade (not nitrogen-gas purged) blank water; VPBW, volatile-organic-compound and pesticide-grade, nitrogen-gas-purged blank water; IBW, inorganic-grade blank water]

	REFERENCE, SPIKE, AND BLIND SAMPLES	
Sample type	**General description[3]**	**Purpose[3]**
Reference sample	A laboratory-prepared solution or material whose composition is certified for one or more properties so that it can be used to assess a measurement method or for assigning concentration values of specific analytes.	Tests for bias and variability of the laboratory measurement process.
Spike sample	Environmental ("field-matrix spikes") or reference-material sample to which a spike solution has been added in known concentrations and in a manner that does not substantially change the original sample matrix. **Spike solution** is a solution having laboratory-certified concentrations of selected analytes and that are added in known quantities to a sample.[4]	Assess the recovery of target analytes relative to the actual conditions to which samples have been exposed; quantify effects of sample-matrix interferences and analyte degradation on analyte recovery.
Blind sample	A sample (typically, reference material) submitted for laboratory analysis with composition known to the submitter but unknown (blind) to the analyst. Every blind sample analyzed should have an associated reference to the source and preparation procedure.	Test for bias and variability of the laboratory measurement process.

[1]Blank water is a solution that is free of analyte(s) of interest at a specified detection limit and that is used to develop specific types of QC samples.USGS personnel are required to use blank water that has been analyzed and certified to be of a specific grade.

[2]Blank samples (blanks) for trace-element analysis have a unique NWQL schedule of analysis, different from that of the environmental sample.

[3]The description of a QC sample depends to some extent on the purpose for which it is collected. The purpose for the QC sample can govern the mode of its collection, processing, and treatment, and the equipment to which it is exposed. Purposes for a specific type of QC sample are varied. Analysis of all QC samples includes the bias and variability introduced from shipping and laboratory handling and analysis of the sample.

[4]For USGS studies, obtain spike solutions in spike kits for pesticide and volatile organic compound analyses from the USGS National Field Supplies Service (NFSS) through One-Stop Shopping.