National Water-Quality Program

Quality-Control Design for Surface-Water Sampling in the National Water-Quality Network

Open-File Report 2018–1018

U.S. Department of the Interior
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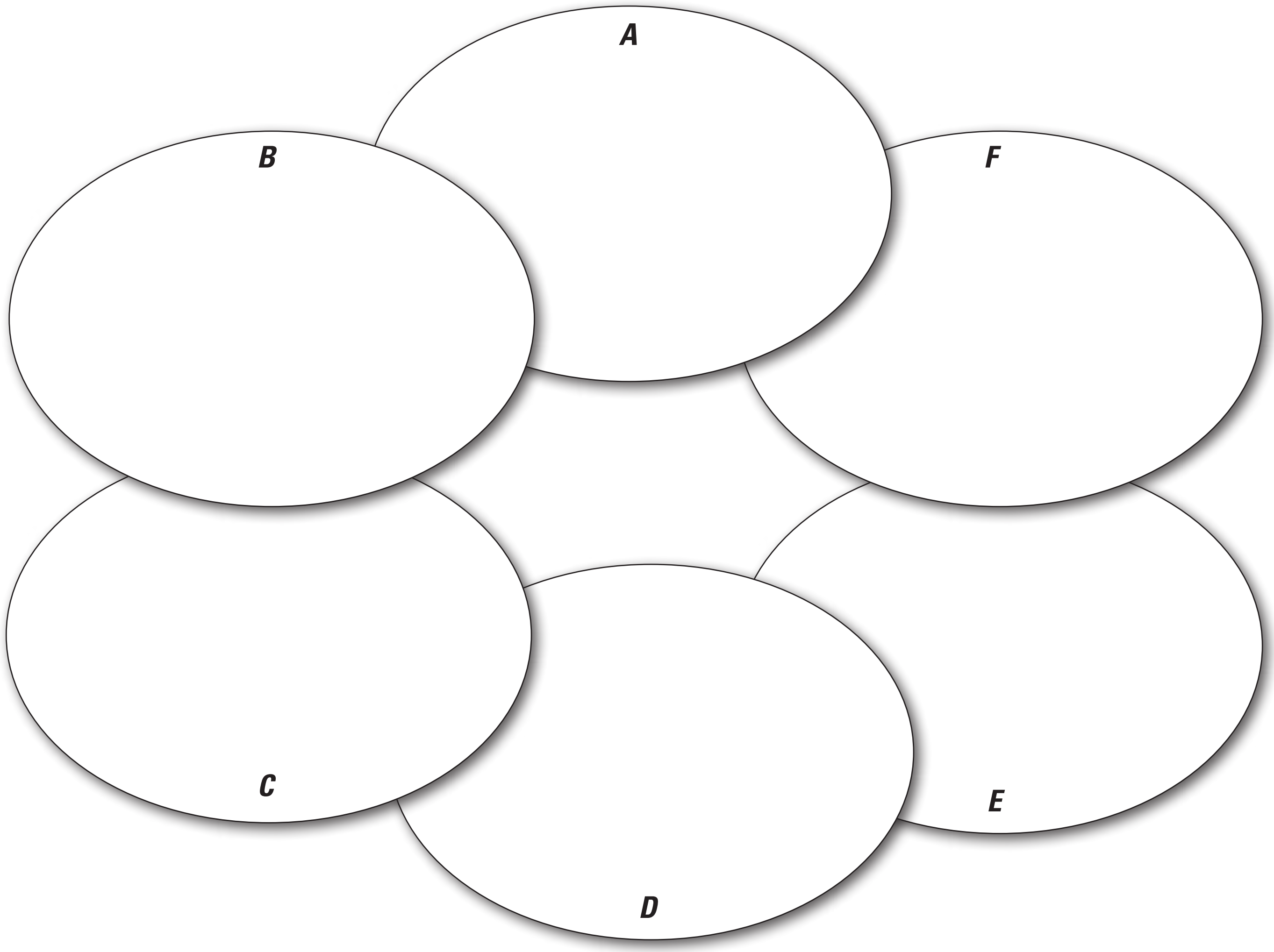

Cover. *A*, Neversink River near Claryville, New York 01435000 (Photograph by Pam Reilly, U.S. Geological Survey); *B*, DH-95 Sampler (Photograph by Michael DeLuca, U.S. Geological Survey); *C*, Neversink River Gage, New York (Photograph by Pam Reilly); *D*, Dunnfield Creek at Dunnfield, New Jersey 01442760 (Photograph by Kaitlin Zoida, U.S. Geological Survey); *E*, Esopus Creek at Allaben, New York 01362200 (Photograph by Pam Reilly); *F*, Wabash River at New Harmony, Indiana (Photograph by Molly Lott, U.S. Geological Survey).

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By Melissa L. Riskin, David C. Reutter, Jeffrey D. Martin, and David K. Mueller

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Foreword

Sustaining the quality of the Nation's water resources and the health of our diverse ecosystems depends on the availability of sound water-resources data and information to develop effective, science-based policies. Effective management of water resources also brings more certainty and efficiency to important economic sectors. Taken together, these actions lead to immediate and long-term economic, social, and environmental benefits that make a difference to the lives of the almost 400 million people projected to live in the United States by 2050.

In 1991, Congress established the National Water-Quality Assessment (NAWQA) to address where, when, why, and how the Nation's water quality has changed, or is likely to change in the future, in response to human activities and natural factors. Since then, NAWQA has been a leading source of scientific data and knowledge used by national, regional, state, and local agencies to develop science-based policies and management strategies to improve and protect water resources used for drinking water, recreation, irrigation, energy development, and ecosystem needs (https://water.usgs.gov/nawqa/applications/). Plans for the third decade of NAWQA (2013–23) address priority water-quality issues and science needs identified by NAWQA stakeholders, such as the Advisory Committee on Water Information and the National Research Council, and are designed to meet challenges related to population growth, increasing needs for clean water, and changing land-use and weather patterns.

The data-quality objectives for surface-water sampling at long-term NAWQA sites include estimating the extent to which contamination, matrix effects, and measurement variability affect interpretation of environmental conditions. Quality-control samples help meet these objectives by providing insight into how well the samples collected at surface-water sites represent the true environmental conditions. Quality-control samples used in NAWQA include field blanks, replicates, and field matrix spikes. This report describes the quality-control design for collection of these quality-control samples.

We hope this publication will provide you with insights and information to meet your water-resource needs and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

Dr. Donald W. Cline
Associate Director for Water
U.S. Geological Survey

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Conversion Factors

International System to U.S. customary units

Multiply	By	To obtain
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
Milliliter (mL)	0.03382	ounce, fluid (fl. oz)
Microliter (µL)	0.00003382	ounce, fluid (fl. oz)

Additional Units

Micrograms per liter (µg/L)

Micrograms per milliliter (µg/mL)

Milligrams per liter (mg/L)

Abbreviations

ASR	analytical services request
DAI	direct aqueous injection
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
DQI	data quality indicator
HBN	Hydrologic Benchmark Network
IBW	inorganic blank water
LC-MS/MS	liquid chromatography-tandem mass spectrometry
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment
NFM	National Field Manual
NWIS	National Water Information System
NWIS-RA	National Water Information System Data Portal and Reports Application
NWQL	National Water Quality Laboratory
NWQN	National Water-Quality Network

NWQP	National Water-Quality Program
OBW	organic blank water
PIC	particulate inorganic carbon
QC	quality-control
TPCN	total particulate carbon and nitrogen
UAS	ultraviolet absorbing substance
USGS	United States Geological Survey
WSC	water science center

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Abstract

The data-quality objectives for samples collected at surface-water sites in the National Water-Quality Network include estimating the extent to which contamination, matrix effects, and measurement variability affect interpretation of environmental conditions. Quality-control samples provide insight into how well the samples collected at surface-water sites represent the true environmental conditions. Quality-control samples used in this program include field blanks, replicates, and field matrix spikes. This report describes the design for collection of these quality-control samples and the data management needed to properly identify these samples in the U.S. Geological Survey's national database.

Introduction

Restructuring of the United States Geological Survey (USGS) Water Mission Area has led to the formation of the National Water-Quality Program (NWQP), and within it, a single, integrated National Water-Quality Network for Rivers and Streams (NWQN – Rivers and Streams). The NWQN–Rivers and Streams is a combination of several previously separate USGS monitoring networks, including the National Water-Quality Assessment (NAWQA) surface-water status and trends monitoring sites, National Stream Quality Accounting Network (NASQAN) sites, and sites in the National Monitoring Network for U.S. Coastal Waters and Tributaries. As part of further network integration, the Hydrologic Benchmark Network (HBN) has also merged with reference sites already in the NWQN – Rivers and Streams to form a reference site subnetwork, referred to as NWQN – Reference Streams (Committee Report for Merging Hydrologic Benchmark-NAWQA References Sites, Robert Gilliom-Committee Chair, written commun., 2016).

A primary goal of the NWQN is to describe the occurrence, distribution, and trends of selected chemical constituents in the Nation's surface and ground water. Water-quality studies must make sure that samples are handled and analyzed in a manner that does not compromise how well the results represent the environment and meet the study objectives (Mueller and others, 2015). Water-quality sampling procedures include a number of factors which can contribute to differences between the analytical result and the true value in the sampled environment. Such factors include the environmental conditions, personnel, equipment, supplies, collection and processing techniques as well as sample storage in the field and laboratory shipment.

To interpret water-quality data properly, additional information is needed to estimate the bias and variability. Bias is the systematic error in a method or measurement system and may be either positive or negative. Variability is the degree of random error in repeated measurements of the same quantity. Sampling bias and variability in surface-water chemical analyses are evaluated to determine the extent to which

1. Environmental conditions, sampling methods, and analytical methods introduce contaminants (positive bias) into water samples.
2. Analytical method performance, sample-matrix interference, and analyte degradation affect the recovery (positive or negative bias) of organic compounds.
3. Environmental conditions, sampling methods, and analytical methods introduce random error (variability) to measured constituent concentrations.

Data obtained from routine quality-control (QC) samples are used by the NWQN to meet these objectives and to evaluate potential effects on the interpretation of environmental data.

Purpose and Scope

This report is an update of the original quality-control design report for surface water sampling, which was written in 1997 at the onset of the NAWQA (Mueller and others, 1997). It describes

1. Procedures used to collect QC samples at surface-water sites in the NWQN–Rivers and Streams.

2. QC sampling design, including frequency, timing, and location of sample collection.
3. QC data management, including coding used to submit samples for laboratory analysis and to store results in electronic databases.
4. QC data review practices and procedures.

The scope of this report is applicable to the ongoing NWQN-Rivers and Streams effort that began in water year 2013 (October 2012).

Types of Quality-Control Samples

Three types of QC samples are routinely collected for the National Water-Quality Network: field blanks, field replicates, and field matrix spikes. Blanks and spikes are used to estimate bias, and replicates are used to estimate variability. QC samples collected and prepared in the field can help to identify, quantify, and document bias and variability resulting from sample collection, processing, shipping, and handling of samples by the field and laboratory personnel. These and other types of QC samples are described in more detail by Mueller and others (2015). The following is summarized from that report.

A blank is a sample that is prepared with water intended to be free of measurable concentrations of the analytes of interest. Blank samples are analyzed to estimate positive bias that could result from extraneous contamination of environmental samples. Blank samples are defined, in part, by the location where the blank sample is collected or in regard to the equipment that is used during sample collection. A source solution blank is sometimes collected to understand potential contamination from the water used for the field blank, transport of the blank water to the field, and collection environment. Field blanks are prepared in a manner that exposes the blank water to all of the potential sources of contamination that might affect environmental water samples during collection and processing. In addition, field blanks, like any other laboratory-analyzed sample, include potential contamination introduced during laboratory handling and analysis. Field blanks are used to evaluate the adequacy of field and laboratory protocols. Specifically, they can indicate whether (1) equipment has been adequately cleaned to remove contamination introduced by samples obtained at previous sites, (2) sample collection and processing have not resulted in contamination, (3) sample handling and transport have not introduced contamination, and (4) laboratory analysis has not introduced contamination.

An equipment blank is used to demonstrate that the sample-collection and sample-processing equipment is not introducing contamination. Equipment blanks can be prepared using individual pieces of the collection and processing equipment. For example, a sample prepared by exposing the blank solution just to the filter apparatus would be a filter blank. In the NWQN, equipment blanks are not routinely collected. When new equipment is purchased or old equipment that has been in storage for an extended period of time is put into use, an equipment blank may be required.

Replicates are two or more samples collected, prepared, and analyzed such that the samples are considered to be essentially identical in composition. Replicate environmental samples are used to estimate the variability (random measurement error) in analytical results. Replicates can be collected in several ways. Split replicates are produced by splitting a single, large volume of water collected from the stream into two samples, each of which is submitted to one or more laboratories for the identical analysis. Concurrent replicates are multiple samples collected as closely as possible to the same location and time in two separate sampling vessels. Different types of replicates assess different sources of variability. Split replicates allow assessment of potential sources of variability (sample processing, handling, preservation, and analysis) that can be introduced by field and laboratory procedures. Concurrent replicates account for the same sources of potential variability plus the additional variability that could be introduced by sample collection. Depending on sample collection procedures and conditions, concurrent replicates might also include an unknown amount of short-term environmental variability owing to samples collected at slightly different times, locations, or using different sampler types. Split replicates are chosen for most analytes to exclude variability caused by short-term environmental fluctuations during sample collection, which could be captured from a concurrent replicate.

A spike is an environmental sample that has been fortified (spiked) with known concentrations of analytes. Spiked samples are used to estimate bias resulting from method performance, matrix effects, or analyte degradation during sample shipment and storage. Matrix effects are the chemical, physical, and biological characteristics of environmental water that might interfere with or compromise chemical analysis of the sample. Types of spiked samples are defined by the location where the spike solution is added to the sample, either in the field or in the laboratory, and by the type of water that is spiked, either environmental (matrix) water or blank (reagent) water. A field matrix spike is an environmental water sample that is spiked in the field prior to shipping. Bias is estimated by calculating the percentage of the spiked analyte that is measured (recovered) in the sample. Recovery can be either greater than or less than 100 percent, so the bias can be either positive or negative.

Collection and Processing of Quality-Control Samples

Quality-Control Samples

Field quality-control samples are to be collected on site during routinely scheduled sampling trips with the same equipment used to collect the environmental samples. When new equipment is purchased or old equipment that has been in storage for an extended period of time is put into use, additional quality-control samples may be required. Contact the NWQN coordinators to determine the extent to which additional QC samples are needed in such circumstances.

Documentation of the sampling event is important and must be as complete as possible. Include details that describe how, when, where, and why the QC samples were collected, and observations about the site or sampling conditions. Chemical preservatives from the same lot numbers are to be used for a given set of environmental and associated QC samples. Record the preservative lot number on field forms and field notes. All QC data, including all associated metadata, must be stored in an electronic database devoted to QC data; this should be a QC-designated database within the National Water Information System (NWIS). Refer to chapter 4.3 of the Quality Control section of the National Field Manual (NFM) for the Collection of Water-Quality Data for addition information (U.S. Geological Survey, variously dated).

Field Blanks

Field blanks are prepared immediately **before** collecting and processing an environmental sample at a selected site. Approximately two to three gallons of blank water (either inorganic- or organic free, depending on the type of analyses requested) with the same lot numbers are required for adequate rinsing and processing of the samples. Field blanks are collected and processed at the field site in the same manner, with the same equipment, as the environmental sample(s). All equipment must be cleaned according to USGS protocols, either in the field or in the laboratory following use at the previous site. Chapter 3 in the NFM fully describes the cleaning procedures. To avoid the necessity of rinsing equipment with both inorganic blank water (IBW) and organic blank water (OBW), field blanks for inorganic constituents should not be prepared during the same site visit as field blanks for pesticides and other organic compounds. Field blanks are required for all constituents except suspended sediment. Suspended sediment blanks are excluded because concentrations rarely have been detected in past field blanks; therefore, the collection of these blanks is no longer required.

Prior to the collection of a field blank, a source solution blank is sometimes collected to understand potential contamination from the water used for the field blank, transport of the blank water to the field, and collection environment. Source solution blanks are collected by rinsing with, and then pouring, blank water directly from the blank solution container into the appropriate sample bottles. Source solution blanks are collected at the field site prior to the collection of the field blank, and must be collected within a clean field environment, such as a sampling chamber. As part of the NWQN, source solution blanks are not routinely collected at each site, although several source solution blanks are collected annually by field teams within the program. The collection of carbon and nutrient source solution blanks is coordinated throughout the year by the NWQN advisors as needed in cases where there are concerns about specific batches of blank water, constituent analyses, or collection procedures. Source solution blanks for pesticides are only collected when directed by the network coordinator.

Water for field blank samples must be produced and certified by a laboratory to assure analyte concentrations do not exceed a specified method detection limit. The water used for blanks must be IBW for blanks that will be analyzed for inorganic constituents or OBW for blanks that will be analyzed for pesticides and other organic compounds. Organic blank water from the National Water Quality Laboratory (NWQL) is available for use in two forms: (1) Nitrogen-purged OBW, for use when collecting VOC blanks; and (2) Pesticide-grade OBW, for use when collection blanks are analyzed for pesticides and other organic compounds. Blanks must be prepared with water from a sealed bottle, as opened bottles might no longer be free of organic carbon species. To avoid contamination, water bottles must be stored in a clean environment (for example, an office area as opposed to a garage where solvents might be present).

Equipment may not need to be cleaned nor filters changed between processing the field blank and the environmental sample. However, certain pieces of equipment must be cleaned if they have obviously been contaminated or if there is a significant potential for contamination, such as a sample splitter sitting exposed to the environment for a long period of time.

Inorganic Constituents

1. Rinse the sample collection bottle and assembly with IBW. Rinsing of the sampling assembly is to simulate as closely as possible the field rinsing that occurs prior to collection of the environmental sample (for more information on the collection of water samples see chapter 4 of the NFM, substituting blank water for sample water). Shake and swirl the water through the assembly to simulate water contact with all components as done during sample collection.

2. After the initial rinsing of the sample collection bottle and assembly with blank water, fill the sample collection bottle with blank water and dispense through the nozzle into the churn until it contains 2–3 liters (L) of blank water.

3. Rinse the churn splitter by swirling and shaking the water inside, and empty the churn completely through the valve spigot.

4. Decant the remainder of the blank water into the churn splitter by refilling the sample-collection bottle and pouring the water into the churn until the churn contains

sufficient volume to prepare all the necessary subsamples (approximately 5 L of water).

5. Process the samples according to routine procedures for a surface-water site by using blank water instead of sample water (for more information on processing water samples see chapter 5 of the NFM).

6. Record the lot number of the blank water in field notes and on the comments line of the analytical services request (ASR) form. Also, record the last site and date at which the sampling equipment was used so this possible source of contamination can be identified. This information also needs to be entered into the QC database upon sample login.

Carbon

In order to obtain a blank sample for the analysis of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total particulate carbon and nitrogen (TPCN), particulate inorganic carbon (PIC), and ultraviolet absorbing substances (UAS), the samples are collected using the same sampler and collection method as the inorganic water-quality samples and composited into a splitter that has **not** been rinsed with methanol. The specific processing method to be used depends on the filter type and filtration equipment. Although IBW and OBW are certified for DOC concentrations, the NWQL prefers that IBW be used for DOC blanks (Donna Damrau, U.S. Geological Survey, written commun., 2014). IBW should be used for DIC blanks and OBW should be used for UAS blanks.

1. Using a splitter that has **not** been rinsed with methanol, rinse the sample collection bottle and assembly with the appropriate type of blank water. Rinsing of the sampling assembly should simulate as closely as possible the field rinsing that occurs prior to collection of the environmental sample. Do not rinse the baked amber glass sample bottles.

2. After the initial rinsing of the sample collection bottle and assembly with blank water, fill the sample collection bottle with blank water and dispense though the nozzle into the churn splitter until it contains 2–3 L of blank water.

3. Rinse the churn splitter by swirling and shaking the water inside, and empty the water from the splitter completely through the valve spigot.

4. Decant the remainder of the blank water into the churn splitter by refilling the sample-collection bottle and pouring the water into the churn until the churn contains sufficient volume to prepare all the necessary subsamples (approximately 4 L of water).

5. Process the carbon samples according to procedures documented in chapter 5.2.2.C of the NFM. Samples for DOC, DIC, and UAS can be processed with either a capsule filter or the polytetrafluoroethylene (hereafter referred to by its commercial name of Teflon®) pressure-filtration assembly with a 25-millimeter (mm) glass-fiber filter, whereas the TPCN sample must be processed with a 25-mm glass-fiber filter. A standardized volume of 125 milliliters (mL) of IBW per filter for the TPCN field blank is requested by the analytical laboratory.

6. Record the lot number of the blank water in field notes and on the comments line of the ASR form. Also, record the last site and date at which the sampling equipment was used so this possible source of contamination can be identified. This information also must be entered into the QC database upon sample login.

Pesticides

Samples collected in the NWQN are analyzed for pesticides by two methods: (1) a broad spectrum direct aqueous-injection (DAI) liquid chromatography tandem mass spectrometry (LC–MS/MS) method, such as USGS NWQL Schedule 2437 (DAI-LC-MS/MS, pesticides in filtered water; Sandstrom and others [2015]); and (2) determination of glyphosate, its degradation product aminomethylphosphonic acid, and glufosinate in water by isotope dilution and online solid-phase extraction and liquid chromatography/tandem mass spectrometry, (Meyer and others, 2009). The collection and processing protocols, as well as equipment used to process pesticide samples, are the same for both. Pesticide blanks are processed following guidance in the NFM chapter 5.2.2.B. Collection of the field blanks must mirror those guidelines substituting OBW for sample water. Pesticide samples can be composited using a Teflon® churn splitter (8-L or 14-L), Teflon® bottle, or glass carboy.

1. Rinse the sample collection bottle and assembly with OBW. Rinsing of the sampling assembly should simulate as closely as possible the field rinsing that occurs prior to the collection of the environmental sample.

2. After the initial rinsing with blank water, fill the sample collection bottle with blank water and dispense through the nozzle into the compositing container.

3. Rinse the compositing container by swirling and shaking the water inside, and empty the water completely through the valve spigot, if applicable.

4. Decant the remainder of the blank water into the compositing container by refilling the sample-collection bottle and pouring the water into the container until it contains sufficient volume to prepare all the necessary subsamples.

5. Rinse the pesticide bore needle, syringe, and filter with blank water, but do not rinse the 20 mL baked amber glass sample bottle.
6. Process the pesticide samples according to procedures for the Syringe-Filter Procedure for Processing Samples for Analysis of Organic Compounds by DAI-LC-MS/MS by using blank water instead of sample water (NFM chapter 5.2.2.B).
7. Record the lot number of the blank water in field notes and on the comments line of the ASR form. Also, record the last site and date at which the sampling equipment was used so this possible source of contamination can be identified. This information also must be entered into the QC database upon sample login.

Replicates

Replicates can be collected in several ways. Split replicates for the analysis of inorganic constituents and pesticides are produced by splitting a single, large volume of water collected from the stream into two samples (one environmental and one replicate), each of which is submitted to one or more laboratories for the identical analysis. Sampling teams must procure an additional amount of water and process sufficient volumes of water for split replicate samples. The split replicates (environmental and replicate samples) are processed sequentially by analyte group (trace elements, nutrients, major ions, or pesticides).

Concurrent replicate samples are collected simultaneously in two separate sampling vessels. Replicates for the analysis of suspended sediment concentration are collected as concurrent replicates because these samples are not composited in a churn splitter but rather filled at multiple verticals along a cross section. Inorganic sediments coarser than 62 micrometers cannot be split with an accuracy of less than about ±10–15 percent, therefore the churn splitter is not recommended for the collection of this constituent (U.S. Geological Survey, 1980). This difference in collection methods requires suspended sediment replicates to be collected during a trip separate from when the other replicates are collected. If these sample replicates are collected during the same sampling trip, the replicate type (split or concurrent) cannot be properly documented. For more information about the collection of suspended sediment samples, refer to Nolan and others (2005).

Inorganic Constituents (Split Replicate)

1. With a single compositing container, collect a volume of stream water large enough for all samples that are required for the environmental and replicate samples. Often this volume is double the amount normally collected.
2. Field-rinse the environmental and replicate unfiltered sample-collection bottles with unfiltered sample water.
3. Split the whole-water, unfiltered sample into environmental and replicates. Split the environmental sample first, followed by the replicate sample.
4. Set up the filtration apparatus with a capsule filter and field-rinse the environmental sample-collection bottles with filtered water.
5. Filter the samples in the order used for the different analyte groups (trace elements, nutrients, or major ions). Filter the environmental sample for all analyte groups that normally use the same filter before proceeding to the replicate sample.
6. With a new capsule filter, so that all potential sources of variability are included in the analysis, process the replicate samples in the same manner as the environmental samples.
7. Collect and process a separate alkalinity measurement for the replicate sample.

Suspended Sediment (Concurrent Replicate)

Suspended-sediment samples (and associated replicates) should be collected separately from the water-chemistry samples. The suspended sediment sample should not come from the churn but rather individual bottles collected at multiple verticals during sampling. The replicate bottle must be collected immediately after the primary bottle at each vertical. This difference in collection methods requires suspended sediment to be collected as a concurrent replicate rather than a split replicate and during a trip separate from when the other constituent replicates are collected. If these sample replicates are collected during the same sampling trip, the replicate type (split or concurrent) cannot be properly documented.

Carbon (Split Replicate)

In order to obtain a replicate sample for the analysis of DOC, DIC, TPCN, and UAS, these samples are collected using the same sampling assembly and collection methods as the inorganic water-quality samples and composited into a splitter **not** rinsed with methanol. Do not rinse any laboratory-cleaned and baked glass bottles used for these samples.

1. Process the environmental carbon samples according to procedures documented in chapter 5.2.2.C of the NFM. Samples for DOC, DIC, and UAS can be processed with either a capsule filter or the Teflon-pressure filtration assembly with a 25-mm glass-fiber filter. The TPCN sample must be processed with a 25-mm glass-fiber filter.

2. The amount of water needed to obtain a sufficient quantity of material for TPCN analysis depends on the concentration of suspended material in the sample. Guidelines for selecting the volume needed for filtration of samples are available in table 5-6d in chapter 5.2.2.C of the NFM. It is critical for the calculation of the TPCN concentrations that the filtrate volume passed through each filter be recorded.

3. With a new filter, process the replicate sample after the environmental sample in the same manner. Similar sample volumes are filtered for the environmental and replicate samples.

Pesticides (Split Replicate)

The collection equipment (bore needle, syringe, and filter) and protocols used for processing the USGS NWQL Schedule 2437 (DAI-LC-MS/MS, pesticides in filtered water) samples are the same used to process glyphosate pesticide samples.

1. Collect samples by following sample collection guidelines found in chapter 4 of the NFM, obtaining enough water for the extra replicate samples.

2. Pesticide samples can be composited using a Teflon® churn splitter (8-L or 14-L), Teflon® bottle, or glass carboy that have been rinsed with methanol.

3. Process the environmental samples for the analysis of pesticides, including the glyphosate sample, by following the Syringe-Filter Procedure for Processing Samples for Analysis of Organic Compounds by DAI-LC-MS/MS in chapter 5.2.2.B of the NFM.

4. With a new filter, process the pesticide and glyphosate replicate samples after the environmental sample in the same manner.

Field Matrix Spikes

Field matrix spikes are required for USGS NWQL Schedule 2437 (DAI-LC-MS/MS, pesticides in filtered water) samples; a field matrix spike solution is currently not available for glyphosate samples.

Field matrix spikes are used to determine potential bias from analytical method performance, sample matrix interference, and analyte degradation after collection. Spikes require at least one environmental sample (unspiked) along with the spiked sample(s) to determine the background levels of any organic analytes in the samples. Spike recovery is the proportion of a target analyte that is quantified by an analytical method, and is a primary indicator of the analytical bias of a measurement. Recovery is calculated from the measured concentration of an analyte in the spiked sample in comparison to the measured concentration in the background environmental sample (see equations in Mueller and others [2015]).

Pesticide spikes are split replicates from an environmental sample. **For all routine spiked samples, the spiking solution should be added to the split replicate in the field, even if extraction is done at the NWQL.** Spike solutions are prepared and distributed by the NWQL and should be used before the expiration date. Matrix-spike ampoules should be chilled at less than 6 degrees Celsius (°C) at all times after they arrive from the lab. Many of the compounds included in the spike solutions are unstable and can degrade rapidly at room temperature. Once opened, the spike solutions should be used as soon as possible to prevent changes in concentration caused by evaporation of the solvent. Matrix spike solutions and glass capillaries are used only once and unused solution must be discarded into a waste container that is labeled for disposal.

Perform spiking in a well-ventilated, yet contained, area to avoid inhaling vapors from the spike solution, and wear gloves and other protective gear to avoid contact with skin and eyes. Organic-analyte spike solutions contain toxic substances that are either known to cause, or are suspected of causing, cancer and other diseases.

1. Collect samples by following sample-collection guidelines found in chapter 4 of the NFM. Obtain enough water for the extra pesticide samples.

2. Pesticide samples can be composited by using a Teflon® churn splitter (8-L or 14-L), Teflon® bottle, or glass carboy that has been rinsed with methanol.

3. Process two pesticide samples by following procedures for Syringe-Filter Procedure for Processing Samples for Analysis of Organic Compounds by DAI LC-MS/MS in section 5.2.2.B of the NFM. One of these samples is prepared as the environmental sample, the other (replicate) is used to prepare the field matrix spike. For steps 4–6 below, follow instructions documented in chapter 5.3.2 of the NFM for the field use of spike solutions for organic-analyte samples.

4. Allow the spike solution to warm to room temperature before spiking. The chilled spike solution must be warmed because some methods have compounds that are less soluble in methanol at low temperatures; warming to room temperature ensures all analytes are in solution before the spike (Mark Sandstrom, U.S. Geological Survey, written commun., 2017).

5. Add 0.1 mL (100 microliters [µL]) of the appropriate spike solution to the replicate using a micropipette, following documentation in the NFM.

6. Record the lot number of the spike solution and the volume, in milliliters of spike solution (generally 0.1 mL) used in the field notes and on the comments line of the ASR form. This information is essential for computing spike recovery, and therefore must be entered into the QC database upon sample login.

Frequency, Timing, and Location of Quality-Control Sample Collection

The QC requirements for the NWQP are specified by the project's leadership team. For more information on the guidance for the design of a field quality-control program see Mueller and others (2015). For the NWQN, the minimum number of each type of QC sample required to meet the stated QC objectives is listed in table 1. The criteria used in determining this sampling distribution is based on characteristics of the constituents, expected constituent concentrations at the site, and results of previous QC analyses. If necessary, the minimum numbers can be increased to meet individual study objectives with coordination and subsequent approval from the NWQN.

The first field blank is to be collected as soon as a sampling routine has been established. Subsequent field blanks are collected throughout the sampling period in proportion to the number of environmental samples. Field blanks can be prepared at any surface-water site; however, certain sites should be targeted to test the greatest potential risk of contamination (for example, sites sampled following use of the equipment in water with high analyte concentrations). Field blanks do not need to be prepared at every surface-water site. If surface water samples are collected by more than one sampling team, each team should prepare a number of blanks throughout the year in proportion to the number of surface-water samples the team collects. The goal is to evaluate each sampling team and equipment set often enough to ensure that cleaning and sampling procedures are adequate and if not, then corrective actions may need to be taken. As previously mentioned, equipment blanks are not routinely collected. However, when new equipment is purchased or old equipment that has been in storage for an extended period of time is put into use, they may be required and should be coordinated through the NWQN advisors.

Replicates are to be targeted at sites and times where concentrations of at least some target analytes are expected to exceed detection limits. If concentrations of most target analytes are expected to be less than detection, collection of replicates should be deferred until conditions are more favorable. Attempt to collect replicates over the range of detectable concentrations expected at the site, but give greater emphasis to collecting replicates at high concentrations. Replicate samples need not be collected uniformly throughout the sampling period or at all surface-water sites; however, they should be scheduled to cover a broad range of hydrologic conditions. If surface-water samples are collected by more than one sampling team, each team should collect at least one replicate during the sampling period.

Field matrix spikes are performed when environmental concentrations of the spiked analyte are expected to be low (no more than 10 percent of the expected concentration in the spiked sample), which, for pesticide field-matrix spikes, is generally in the winter (outside of the regular growing season). Ideally, other chemical characteristics, particularly the concentration of organic carbon, should be similar to characteristics present when environmental concentrations of the spiked analyte are high.

Table 1. Collection frequencies for routine quality-control samples.

[–, no samples required]

Constituent or group	Number of sampling trips at site per water year	Number of quality-control samples per site		
		Field blanks	Replicates	Spikes
Major ions	Less than 10	1 every alternate year	1 every alternate year	–
	10 or greater	1 per year	1 per year	–
Nutrients/carbon	Less than 10	1 every alternate year	1 every alternate year	–
	10–20	1 per year	1 per year	–
	Greater than 20	2 per year	2 per year	–
Suspended sediment	Less than 10	–	1 per year	–
	10–20	–	1 per year	–
	Greater than 20	–	2 per year	–
Pesticides	Less than 5	1 every third year	1 every third year	1 every third year
	5 or greater	1 per year	1 per year	1 per year

Sample Coding for Data Management

Consistent coding of routine QC samples among sites and water science centers (WSC) is essential. For this reason, data management protocols have been developed for the NWQP. Coding requirements for QC samples and associated environmental samples collected as part of the NWQN are listed in the appendix. For a complete list of coding options, refer to the water-quality sample-coding outline at https://my.usgs.gov/confluence/display/nawqadatasynth/complete+descriptive+version.

The most critical codes for proper sample identification are the station identification number, sample medium, sample type, and the quality-control parameter codes. All routine QC samples should be associated with an environmental sample. Do not use fictitious station identification numbers for routine QC samples. Time coding of the sample is specified to distinguish among multiple samples at the same site visit. Each type of sample (environmental, field blank, replicate, and field matrix spike) that is coded for a particular site and date must have a unique time.

The NWIS database cannot store lot numbers exactly as assigned from vendors for blank water or spike solutions. Because NWQL performs rigorous testing on the lots of blank water prepared by vendors, the blank water is assigned an internal lot number by NWQL. These lot numbers, established by NWQL, should be stored in NWIS. For consistency within the NWQP, parameter code 99200 is used for IBW, parameter code 99202 is used for OBW, and parameter code 99104 is used for the pesticide spike solution lot number. USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website.

Review of Quality-Control Analytical Data

Project personnel responsible for the management of sampling data must routinely review and approve their environmental and quality-control sample results throughout the year. The review of the data is to begin following receipt of all sample data or groups of sample data. Timely review of data is important as holding times and windows for requesting laboratory reruns can be short. To assist in this review process, a number of automated data checks have been written to identify sample records that have missing information, inconsistent NWIS coding, or unusual analytical results. The data-check program is available to USGS staff through the NWIS Data Portal and Reports Application (NWIS-RA; https://reporting.nwis.usgs.gov/login.jsp), where the specific data checks are explained and documented in the Discrete Data Checks Resources section. To facilitate the review of spike recovery, NWIS has developed a spike recovery calculator which is available to USGS staff at http://internal.cida.usgs.gov/spikecalculator/.

Data reviewers should be familiar with previously collected environmental and field quality-control data at the site (and perhaps nearby/similar sites) and should develop conceptual models of the chemical concentrations, co-occurrence of chemicals, and their relations to season and streamflow conditions. Reviewers must request an analysis to be rerun or verified to confirm that unusual chemical concentrations or numbers/co-occurrence of detections were not caused by sample containers inadvertently switched in the field or laboratory, or by other errors. If unusual quality-control analytical data are verified by NWQL, reviewers are to contact the NAWQA data review committee (GS-W NAWQA Data Review, gs-w_nawqa_data_review@usgs.gov) to discuss follow-up actions. These actions may include setting the NWIS Data Quality Indicator (DQI) code to “Rejected” per Office of Water Quality Technical Memorandum 2017.05 (U.S. Geological Survey, 2017). However, quality-control data that appear unusual in a local context may make sense in a national context, thus the requirement that reviewers contact the NAWQA data review email committee before rejecting results with the DQI code.

Reviewers are not to change or delete unusual quality-control data (or environmental data) in NWIS except in the rare circumstances described in Office of Water Quality Technical Memorandum 2017.05 (U.S. Geological Survey, 2017). Methods to analyze and interpret environmental data in light of bias or variability measured by field quality-control samples are presented in Mueller and others (2015).

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References Cited

Meyer, M.T., Loftin, K.A., Lee, E.A., Hinshaw, H.H., Dietze, J.E., and Scribner, E.A., 2009, Determination of glyphosate, its degradation product aminomethylphosphonic acid, and glufosinate, in water by isotope dilution and online solid-phase extraction and liquid chromatography/tandem mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. A10, 32 p., accessed January 19, 2018, at https://pubs.usgs.gov/tm/tm5a10/pdf/tm5a10.pdf.

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 1997–223, 17 p. [Also available at https://pubs.usgs.gov/of/1997/223/index.html.]

Mueller, D.K., Schertz, T.L., Martin, J.D., and Sandstrom, M.W., 2015, Design, analysis, and interpretation of field quality-control data for water-sampling projects: U.S. Geological Survey Techniques and Methods, book 4, chap. C4, 54 p., accessed January 18, 2018, at http://dx.doi.org/10.3133/tm4C4.

Nolan, M.K., Gray, J.R., and Glysson, G.D., 2005, Introduction to suspended-sediment sampling: U.S. Geological Survey Scientific Investigations Report 2005–5077, 1 CD. [Also available at http://pubs.usgs.gov/sir/2005/5077/]

Sandstrom, M.W., Kanagy, L.K., Anderson, C.A., and Kanagy, C.J., 2015, Determination of pesticides and pesticide degradates in filtered water by direct aqueous-injection liquid chromatography-tandem mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B11, 54 p., accessed January 18, 2018, at https://doi.org/10.3133/tm5B11.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A10. [Also available at https://water.usgs.gov/owq/FieldManual/index.html.]

U.S. Geological Survey, 1980, Equipment and supplies—New sample splitter for water-quality samples: U.S. Geological Survey Office of Water Quality Technical Memorandum 80.17, accessed January 18, 2018, at https://water.usgs.gov/admin/memo/QW/qw80.17.html.

U.S. Geological Survey, 2017, Policy and guidance on making changes to laboratory results in the QWDATA Subsystem (QWDATA) of the National Water Information System (NWIS): U.S. Geological Survey Office of Water Quality Technical Memorandum 2017.05, 5 p., accessed January 18, 2018, at https://water.usgs.gov/admin/memo/QW/qw2017.05.pdf.

Appendix. Analytical Services Request Forms and National Water Information System Database Coding Commonly Required for Quality-Control Samples and Associated Environmental Samples Collected as Part of the National Water-Quality Network

[ASR, analytical services request; NWQN, National Water-Quality Network; NAWQA, National Water-Quality Assessment; NWIS, National Water Information System; NWQL, National Water Quality Laboratory; USGS, United States Geological Survey; QC, quality-control]

Blanks

Environmental Sample Associated with the Blank

Parameter	Coding
Analytical services request forms	
Sample time	Time of sample collection rounded to the nearest 10-minute interval
Sample medium	WS (surface water)
Sample type	9 (regular)
Analysis status	U (unrestricted)
Program/Project on ASRs	NWQN
For entry into QWDATA (QC database)	
71999 (sample purpose)	15 (NAWQA)
50280 (purpose of site visit)	1001 (fixed frequency)
99111 (QA data associated with sample)	10 (blank)
84164 (sampler type code)	See link below for USGS fixed value codes
82398 (sampler method code)	See link below for USGS fixed value codes
84171 (splitter type code)	See link below for USGS fixed value codes
99206 (0.45 µm filter NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99156 (Sulfuric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99159 (Nitric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99207 (Pesticide syringe filter lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website

Blank Sample

Parameter	Coding
Analytical services request forms	
Station ID and date	Same as environmental sample
Sample time	8 minutes after environmental sample time
Sample medium	OAQ (QA sample – artificial)
Sample type	2 (blank)
Analysis status	I (internal-use only)
Program/Project on ASRs	NWQN
Comments to NWQL	Field blank prepared before sampling; equipment last used at station ID on date; blank water lot number (see NWQL internal website for coding)
For entry into QWDATA (QC database)	
71999 (sample purpose)	15 (NAWQA)
50280 (purpose of site visit)	1098 (QC sample)
99100 (type of blank solution)	10 (IBW) or 40 (OBW)
99101 (source of blank solution)	10 (NWQL) or 200 (other)
99102 (type of blank sample)	100 (field) or 80 (equipment) or 1 (source solution)
99200 (inorganic blank water lot number)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99202 (organic blank water lot number)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99206 (0.45 µm filter NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99156 (Sulfuric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99159 (Nitric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99207 (Pesticide syringe filter lot number)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website

NOTE: Please avoid collecting the inorganic blank and the organic blank samples during the same sampling trip.

Coding for USGS parameter codes with fixed values are available at http://waterdata.usgs.gov/usa/nwis/qwdata?codes_table26_help.

Replicates

Environmental Sample Associated with the Replicate

Parameter	Coding
Analytical services request forms	
Sample time	Time of sample collection rounded to the nearest 10-minute interval
Sample medium	WS (surface water)
Sample type	7 (replicate)
Analysis status	U (unrestricted)
Program/Project on ASRs	NWQN
For entry into QWDATA (QC database)	
71999 (sample purpose)	15 (NAWQA)
50280 (purpose of site visit)	1001 (fixed frequency)
99111 (QA data associated with sample)	30 (replicate)
99105 (replicate type)	30 (split) or 10 (concurrent) (required for suspended sediment samples)
84164 (sampler type code)	See link below for USGS fixed value codes
82398 (sampler method code)	See link below for USGS fixed value codes
84171 (splitter type code)	See link below for USGS fixed value codes
99206 (0.45 µm filter NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99156 (Sulfuric Acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99159 (Nitric Acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99207 (Pesticide syringe filter lot number)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website

Replicate Sample

Parameter	Coding
Analytical services request forms	
Station ID and date	Same as environmental sample
Sample time	1 minute after environmental sample time
Sample medium	WSQ (QA sample - surface water)
Sample type	7 (replicate)
Analysis status	I (internal-use only)
Program/Project on ASRs	NWQN
For entry into QWDATA (QC database)	
71999 (sample purpose)	15 (NAWQA)
50280 (purpose of site visit)	1098 (QC sample)
99105 (replicate type)	30 (split) or 10 (concurrent) (concurrent required for suspended sediment samples)
84164 (sampler type code)	See link below for USGS fixed value codes
82398 (sampler method code)	See link below for USGS fixed value codes
84171 (splitter type code)	See link below for USGS fixed value codes
99206 (0.45 µm filter NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99156 (Sulfuric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99159 (Nitric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99207 (Pesticide syringe filter lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website

NOTE: Please avoid collecting the suspended sediment replicate on the same day as other replicates are collected. If the sample replicates are collected during the same sampling trip, the replicate type (split or concurrent) cannot be properly documented.

Coding for USGS parameter codes with fixed values are available at http://waterdata.usgs.gov/usa/nwis/qwdata?codes_table26_help.

Spikes

Environmental Sample Associated with the Spike

Parameter	Coding
Analytical services request forms	
Sample time	Time of sample collection rounded to the nearest 10-minute interval
Sample medium	WS (surface water)
Sample type	9 (surface water)
Analysis status	U (unrestricted)
Program/Project on ASRs	NWQN
For entry into QWDATA (QC database)	
71999 (sample purpose)	15 (NAWQA)
50280 (purpose of site visit)	1001 (fixed frequency)
99111 (QA data associated with sample)	40 (spike)
84164 (sampler type code)	See link below for USGS fixed value codes
82398 (sampler method code)	See link below for USGS fixed value codes
84171 (splitter type code)	See link below for USGS fixed value codes
99206 (0.45 µm filter NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99156 (Sulfuric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99159 (Nitric acid NWIS lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99207 (Pesticide syringe filter lot numbers)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website

Field Matrix Spike Sample

Parameter	Coding
Analytical services request forms	
Station ID and date	Same as environmental sample
Sample time	3 minutes after environmental sample time
Sample medium	WSQ (QA sample - surface water)
Sample type	1 (spike)
Analysis status	I (internal-use only)
Program/Project on ASRs	NWQN
Comments to NWQL	Pesticide field spike for Schedule 2437; NWQL spike lot number (parameter code 99104) is _______
For entry into QWDATA (QC database)	
71999 (sample purpose)	15 (NAWQA)
50280 (purpose of site visit)	1098 (QC sample)
99104 (spike lot number)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website
99106 (spike type)	10 (field)
99107 (spike solution source)	10 (NWQL)
99108 (spike volume in mL)	0.1 mL
84164 (sampler type code)	See link below for USGS fixed value codes
82398 (sampler method code)	See link below for USGS fixed value codes
84171 (splitter type code)	See link below for USGS fixed value codes
99207 (Pesticide syringe filter lot number)	USGS staff can access the current list of lot numbers and certificates from the quality section of the NWQL internal website

Coding for USGS parameter codes with fixed values are available at http://waterdata.usgs.gov/usa/nwis/qwdata?codes_table26_help.

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