In Reply Refer To:
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Office of Water Quality Technical Memorandum 2008.03

Subject: National Monitoring Network Water-Quality Sampling, Fiscal Year (FY) 2008

This memorandum contains a summary of the activities related to water-quality sampling as part of the National Monitoring Network (NMN) for FY 2008, including the stations being operated, constituents measured, and funding allocations. This is a new effort begun in FY2008 with funds appropriated to support the National Monitoring Network component of the Ocean Action Plan. Information about the Ocean Action Plan can be found at http://ocean.ceq.gov/; information about the NMN can be found at http://acwi.gov/monitoring/network/. Stations will be operated in a manner identical to those being sampled for NASQAN with sampling beginning in April 2008 (i.e. same constituents and sampling strategy; sampling protocols are attached).

This effort is being managed by the National Stream Quality Accounting Network (NASQAN) Coordinator. Questions on NMN operations can be addressed to Charlie Crawford (NASQAN Coordinator) or Dave Reutter (NASQAN support). Contact information is contained at the end of this memorandum.

NMN stations

The highest priority rivers not included in the recently redesigned NASQAN network due to funding limitations will be sampled as part of the NMN. Five stations will be operated in FY2008 as part of the USGS NMN. These include:

Mississippi River near Vicksburg, MS (new site above the Yazoo River confluence)
Hudson River below Poughkeepsie, NY (01372058)
Delaware River at Trenton, NJ (01463500)
Brazos River near Rosharon, TX (08116650)
Apalachicola River near Sumatra, FL (02359170)

Sampling frequency and Constituents Measured

All NMN stations will be sampled semi-monthly with a part of the year containing additional seasonally-weighted samples determined by the NASQAN coordinator. The seasonally-weighted samples are targeted at the period of the year when the greatest constituent transport typically occurs. The number of samples to be collected by month for each station is shown in the attached NMN SWPLAN spreadsheet. Samples for months indicated as having two samples should be collected two weeks apart. NMN sampling will not be collecting samples based on hydrologic conditions ("event samples"). If you have questions or concerns about the information contained in the NMN SWPLAN, please contact the NASQAN Coordinator.

Constituents measured at NMN stations will be consistent across the country, although the lab schedules used will vary somewhat depending on local conditions. The constituents measured will include major ions, nutrients and carbon, pesticides, suspended sediment, isotopes, and field parameters (including alkalinity). Analytical services (National Water Quality Laboratory and sediment laboratory) for this sampling will be charged to account 4565-9U2LA.

Please ensure that all field personnel sampling at NMN stations have a copy of the attachments, which provide specific information on sample collection and processing in FY 2008. If you have questions about how to implement the protocols contained in the attachments, or NMN sampling procedures, please contact the NASQAN Sampling Coordinator. If you have concerns about the information contained in the attachments or the protocols specified, please contact the NASQAN Coordinator.

NMN Contact Information

For questions on the NMN Program, contact any of the following individuals:

NASQAN Coordinator: Charlie Crawford, Indiana WSC, cgcrawfo@usgs.gov, 317-290-3333 ext 176
NASQAN Support: Dave Reutter, Ohio WSC, dreutter@usgs.gov, 614-430-7732
NASQAN Sampling Coordinator: Richard Coupe, Mississippi WSC, rhcoupe@usgs.gov, 601-933-2982

Timothy L. Miller
Chief, Office of Water Quality

This memorandum does not supersede any other Office of Water Quality Technical Memorandum.

Distribution: A, B, DC, AO, WSC and Regional Water-Quality Specialists

Attachments

List of Attachments

Attachment 1. FY 2008 NMN Stations [See NMN SWPLAN spreadsheet for details on number of samples by constituent , number of QC samples, and number of samples to be collected per month.]

Station ID	Name	WSC	Fixed Samples[1]
new	Mississippi River above Vicksburg, MS	MS	6
01372058	Hudson River below Poughkeepsie, NY	NY	5
01463500	Delaware River at Trenton, NJ[2]	NJ	5
08116650	Brazos River near Rosharon, TX	TX	8
02359170	Apalachicola River near Sumatra, FL	FL	8

[1]12 samples will be routinely collected in a full water year. Samples shown are the seasonally-weighted samples prorated for 6 months (April-September).

[2] Site is also NAWQA station sampled every four years (NAWQA rotate4 site). NMN constituents not already collected by NAWQA program will be collected during regularly scheduled NAWQA field trips (NWQL major ion schedules 998 or 1201, nutrient/carbon schedules 997, 1010, or 1069, suspended-sediment sand/fine break, and isotopes). Sampling costs are borne by NAWQA for regularly scheduled samples at these stations except for $100/sample allocated by NMN for extra supplies/shipping expenses.

Attachment 2. NMN FY 2008 Funding Allocations by WSC and Account Number

WSC	Account	Amount
	Sample collection	
MS	2507-9LY12	$22,800
NY	2457-9U2MR	$22,250
NJ	2454-9U2MR	$4,600
TX	8653-9U204	$32,000
FL	2072-9U2MR	$28,800
	Stream gaging	
MS	2507-9LY12	$3000

Attachment 3. FY 2008 NMN Operations

Guidelines for NMN sampling procedures in FY 2008 are attached (attachments 4, 5, and 6 which describe NASQAN protocols also used by the NMN). WSC personnel are responsible for data review, rerun requests, and timely responses to contamination problems and other data issues. Secondary review of NMN data will be integrated into the NAWQA Data Warehouse.

Quality-Control Samples

The specific types of QC samples to be collected at each NMN station are described in the NMN SWPLAN provided by the NASQAN Coordinator. Guidelines for collection, processing, and coding of QC samples are provided in attachment 6. Please carefully follow the coding instructions for all QC samples. Consistency across the network is necessary for efficient analysis of the QC data.

Laboratory Information

Basin Accounts

Account **4565-9U2LA** has been established for analysis of NMN chemistry and suspended-sediment samples. Please use this account number on your Analytical Service Request (ASR) and sediment analysis request for all NMN samples.

Laboratory Schedules

Laboratory schedules for analysis of NMN samples at the National Water Quality Laboratory (NWQL) are listed below. There are several choices for routine analyses of both nutrient and major ions, depending upon expected concentrations. **Please select the appropriate schedule for your stations to avoid nondetects.** If you have questions about this issue please contact the NASQAN Sampling Coordinator.

Schedules

997 Nutrients, particulate carbon, nitrogen, organic carbon
1010 Nutrients (low-level ortho-P), particulate carbon, nitrogen, organic carbon
1069 Nutrients (low-level P and N), particulate carbon, nitrogen, organic carbon
998 Major ions and miscellaneous trace elements (conductance < 2000)
1201 Major ions and miscellaneous trace elements (conductance > 2000)
2033 Pesticides in filtered water, extracted by NWQL (also used for pesticide blanks and spikes)
452 Nutrient blank
1675 Organic carbon blank
1674 Routine major ion blank

Updated information from the NWQL on sample requirements for these schedules can be obtained from the NWQL web page (http://nwql.cr.usgs.gov/usgs/catalog/index.cfm).

Sediment Laboratories

Suspended-sediment samples should be submitted to the Iowa WSC sediment laboratory. However, NAWQA stations also included in the NMN network may continue to use the sediment laboratory they have been using. A single sample will be submitted for each station. Samples may be composited in the field before being sent to the sediment lab. Samples should be analyzed for concentration and sand-fine break.

Isotope samples

Field crews at all NMN stations should collect aliquots from the composite water sample for analysis of stable isotopes of water. The 60-mL glass bottles for this sample are available from Ty Coplen. Email him at tbcoplen@usgs.gov to obtain the bottles. No filtering is required but a filtered aliquot may be sent. Fill the 60-mL bottle 2/3 full of water and put on the Polyseal cap. No preservation is needed. Label the sample bottle with station id and the date and time of sample collection. Samples should be packaged securely and sent directly to Ty for analysis. Samples can be stored for 4 to 12 months before shipping so that multiple samples may be mailed together to reduce shipping and handling costs. Samples should be shipped to:

U.S. Geological Survey
Isotope Laboratory
431 National Center
12201 Sunrise Valley Dr
Reston, VA 20192

More information on collection of stable isotope samples is available at http://isotopes.usgs.gov/ and http://isotopes.usgs.gov/Instructions.htm#489.

Attachment 4. NMN Water-Quality Sampling Protocols

Introduction

This document provides an overview of standard methods for collecting and processing water-column samples for use in large rivers as part of the NMN program. The methods are intended to provide water-quality data oriented to meet the specific goals of NMN, and conform to established methods of the U.S. Geological Survey as described in detail in the National Field Manual for the Collection of Water-Quality Data (NFM) [http://water.usgs.gov/owq/FieldManual/index.html]. Additional information on the rationale for and complete description of these sampling and processing procedures are also contained in Edwards and Glysson (1999) and Horowitz and others (1994), as well as selected Technical Memoranda issued by the Office of Water Quality.

Constituents routinely measured by the NMN program include field parameters, suspended sediment, major ions, nutrients, dissolved/particulate carbon, and pesticides. Additional special samples for stable isotopes of water (for Ty Coplen) are also collected. Specific information regarding the analytical method for particulate carbon/nitrogen is available as follows: OWQ Tech Memo 2000.05 and OWQ Tech Memo 2000.08.

Sampling equipment

To the greatest extent possible, isokinetic sampling techniques that provide samples representative of stream conditions are required by the NMN program. Until recently, the range of available samplers for use in large rivers was limited and the ideal sampling scenario was not always possible. Large-river sites traditionally used the US D-77 bag and frame-type bag samplers, which require field calibration each time they are used. Some sites where excessive depth is not an issue have used the US D-77 rigid-bottle sampler, although it is known to be difficult to use correctly because of the very small range in which it samples isokinetically and because it becomes unstable at relatively low velocities. The DH-81 sampler has been used at wadeable sites.

In 2002, the Office of Water Quality, in concurrence with the Office of Surface Water, recommended that the US D-77 rigid-bottle and bag samplers and the frame-type bag sampler be phased out for collection of water-quality and sediment samples. According to OWQ Technical Memo 2002.09, the US DH-2, US DH-95, US D-95, and US D-96 isokinetic samplers have been approved by the Interagency Technical Committee of the Subcommittee on Sedimentation, and provide the field with a well-tested and documented set of samplers that work in most sampling conditions. Accordingly, the D-77 rigid-bottle and bag samplers should have been replaced with the newer samplers. Please contact the NASQAN Coordinator (Charlie Crawford) if you are still using one of the phased-out samplers.

The decision on which sampler to use is based upon the hydrologic conditions in the stream, the limits of the samplers, and informed judgement in the field which is essential to collect a representative sample. Further information is available on the D-96 sampler (http://fisp.wes.army.mil/Instructions%20US%20D-96%20Instructions%20020709.pdf), the DH-2 sampler (http://fisp.wes.army.mil/Instructions%20050720%20US%20DH-2.pdf), and the DH-81 sampler (http://fisp.wes.army.mil/Instructions%20US_DH-81_010612.pdf). For information

on USGS guidelines for equipment selection, consult Chapter 2 in the National Field Manual and USGS Open-File Report 2005-1087 – A Guide to the Proper Selection and Use of Federally-Approved Sediment and Water-Quality Samplers.

A brief overview of the guidelines for the use of each sampler type is provided below.

1. D-96
    - must be coated with Plasti-Dip to prevent trace-element contamination---if plastic coating becomes scratched, reapply Plasti-Dip (spray plastic paint, available locally or online- www.usplastic.com is a source)
    - collects a maximum of nearly 3 L sample per vertical
    - approved for flow velocities between 2 to 15 ft/s
    - nozzle sizes are 3/16, 1/4, and 5/16 inch and give the sampler the capability to sample to depths of 110, 60, and 39 feet respectively
    - Teflon® is required for all components that are in contact with the water sample—nozzle holder, nozzles, and bags
2. DH-2
    - must be coated with Plasti-Dip to prevent trace-element contamination---if plastic coating becomes scratched, reapply Plasti-Dip (spray plastic paint, available locally or online- www.usplastic.com is a source)
    - collects a maximum of 1 L sample per vertical
    - approved for flow velocities between 2 to 6 ft/s
    - nozzle sizes are 3/16, 1/4, and 5/16 inch and give the sampler the capability to sample to depths of 37, 20, and 13 feet, respectively
    - Teflon® is required for all components that are in contact with the water sample—nozzle holder, nozzles, and bags
3. DH-81
    - suspended from a rod--used for wadeable streams
    - uses standard D-77 cap and accessories, 1-L bottle
    - collects a maximum of 800 mL sample per vertical
    - approved for flow velocities between 2 and 7 ft/s
    - nozzle sizes are 3/16, 1/4, and 5/16 inch and give the sampler the capability to sample to depths up to 12 ft
    - Teflon® is required for all components that are in contact with the water sample—bottle, cap, and nozzles

4. Support equipment
    - when using metal support equipment, such as cranes and reels, or sampling from bridges or cable cars, always use the clean hands/dirty hands technique--GREAT CARE IS NEEDED TO AVOID CONTAMINATING THE SAMPLE DURING COLLECTION
    - to prevent contamination during sample processing, especially of low-level trace element samples, field vehicles will ideally be dedicated to water-quality work
    - when a dedicated WQ vehicle is not available, the processing area in the vehicle must be free of contaminants including metallic objects, dirt, and oil residue
    - separate storage areas for the sampling equipment must be available

- prepare areas separately for processing inorganic and organic samples --if necessary, cover metal cabinets and shelves with plastic sheeting before processing the inorganic samples; cover the counter space with aluminum foil before processing organic compounds
- processing and preservation chambers must be used for processing inorganic constituents; use portable chambers for multi-use vehicles
- field equipment blanks must be collected regularly to document contaminant-free samples

Processing equipment

The inorganic protocol requires the use of protected environments for processing and preservation of water-quality samples in order to reduce the possibility of contamination. They can be easily constructed with several plastic bags and a plastic milk crate, or a frame built with PVC tubing.

- two types of compositing vessels will be used in general, depending upon the constituent-
    1. churn splitter for major ions and alkalinity, nutrients, carbon, and isotopes
        - to reduce the potential for contamination from atmospheric inputs, the churn splitter must be modified with a cappable plastic (polyethylene or polypropylene) funnel in the lid
        - this funnel is usually made by cutting off the bottom section of a 1-liter sample bottle and inserting the top into a 1-inch hole drilled into the lid of the churn splitter; the bottom is used for the funnel cap
        - as a further precaution against contamination, the churn splitter should be placed inside two large, clear plastic bags which are kept closed except when adding sample to the churn
        - the churn, inside the plastic bags, is then placed inside a large, covered plastic container (i.e. garbage can) which serves as the churn carrier
    2. glass carboy for pesticides (note: 8-L or 14-L Teflon® churn splitter may alternatively be used for pesticides)
        - wrap the cork with aluminum foil
- **since the churn splitter has been approved for processing whole-water samples only when concentrations of suspended sediment do not greatly exceed 1,000 mg/L, the cone splitter is recommended for use at a small number of stations where these sediment concentrations are observed**.
    - if logistical concerns preclude the use of the cone splitter at a particular site, however, the rationale for the decision must be documented and the churn may be used
    - for those stations where the cone splitter is used, it will probably be necessary for the entire sample to be collected first and later poured into the cone for splitting; the individual vertical samples must be saved in containers composed of Teflon®, either Teflon® bags or 3-liter Teflon® bags
    - due to the large volume of water which is collected, 2- or 3-liter bottles may be required under the ports of the cone splitter during the first split

    - careful precautions against atmospheric contamination must also be taken when using the cone splitter, preferably involving the use of the splitter only within an enclosed lab vehicle
    - space limitations may dictate that the splitter be used outdoors; if this is the case, a splitting container is recommended to shield the bottles from atmospheric inputs
    - consult NFM Ch. 5.1.1.B for further details on the use of the cone splitter
- glass or plastic bottles will be used to collect the sample for suspended sediment

Overview of filtration systems:

- for inorganics and pesticides--a variable-speed pump fitted with a peristaltic pump head that forces the sample through either C-Flex or Teflon® tubing into a filter assembly
    - for inorganic constituents and dissolved organic carbon--a capsule filter system (effective pore size=0.45 μm)
    - for pesticide samples--a 142-mm-diameter plate filter with a glass fiber filter (pore size of 0.7 μm) which has been baked to remove any organic residue
- for particulate carbon and nitrogen samples--a Teflon® pressure-filtration assembly (One-Stop Shopping Item No. Q444FLD) that holds a 25-mm glass fiber filter (nominal pore size of 0.7 μm) (One-Stop Shopping Item No. Q441FLD)

Equipment cleaning

Cleaning procedures are described in detail in Chapter 3 in the National Field Manual. Briefly, they include the following--

- use of gloves, which are changed between each step
- 30-minute soak in Liquinox (0.1% solution), or other phosphate-free detergent, followed by scrubbing with a nonmetallic, noncolored brush **(except for the organic carbon filtration unit, unless deemed necessary because of exposure to high concentrations of organic carbon)**
- thorough rinsing with hot tap water
- final rinses:
    1. sampling equipment (and cone splitter, if used)
        - 30-minute soak in a solution of 5% hydrochloric acid (trace-element free)
        - three rinses with DIW
        - rinse with a small amount of methanol (pesticide grade)
        - final rinse with organic-free water
    2. churn splitter and associated tubing
        - 30-minute soak in a solution of 5% hydrochloric acid (trace-element free)
        - three rinses with DIW
    3. glass carboy (or Teflon® churn splitter) and Teflon® tubing for pesticide filtration
        - rinse with a small amount of methanol (pesticide grade)
- for the organic carbon filtration unit and sampling equipment--thorough rinse with organic-free water
- allow everything to air dry completely

- protect areas of the sampling equipment and Teflon® tubing that will contact the sample with a Teflon® bag and place in another sealable double plastic bag or other container for storage and transport
- wrap filtration units for pesticides and organic carbon with aluminum foil or place in a Teflon® bag and store in a sealable container
- rinse all inorganic sample bottles three times with DIW, then half-fill with DIW for transport to the field

Field analyses

Complete descriptions of standard protocols for field measurements are provided in Chapter 6 of the National Field Manual.

Specific guidelines for the NMN program include the following:

- Obtain a cross-section stream profile of field measurements at least once/year
    - record observations from at least three depths in the cross section
    - repeat during the year under different flow regimes.
    - code these measurements as follows--
        - medim=9 (surface water)
        - stype=B (other QA)
- Routine measurements
    - water temperature and dissolved oxygen should be measured directly in the stream (see NFM Ch. 6.1 and 6.2)
    - specific conductance and pH can be measured in the stream or from an unfiltered sample from the churn splitter (see NFM Ch. 6.3)
    - alkalinity, bicarbonate, and carbonate concentrations are measured using a filtered sample as soon as possible after sample collection is complete, using the incremental method of alkalinity determination with the digital titrator (see NFM Ch. 6.6)

Collection methods

A complete description of sample collection guidelines is provided in Chapter 4 of the National Field Manual.

- Overview of multivertical, depth-integrated sampling for water-quality constituents:
    - EDI method is suitable for rivers with well-defined and relatively stable discharge patterns and streambeds
    - EWI method is preferable for wadeable streams or large rivers with unstable streambeds
    - rinse all sampling and processing equipment thoroughly with river water prior to collecting the first sample
        - **IMPORTANT NOTE!!** copious field rinsing of sample equipment prior to collecting the sample is necessary to remove the methanol residue which may remain from the cleaning procedures and contaminate the DOC/PC sample

    - **THREE vigorous field rinses with at least 3-4 liters each time is REQUIRED**
  - if possible, collect samples at the same cross section throughout the period of record (may not be possible if station is wadeable during part of the year, and sampled from a bridge or cableway during the rest of the year)
  - the number of verticals should be based primarily on the requirement to collect a representative sample of the cross section, and secondarily to obtain the required sample volume
  - the vertical transit rate and operational depth for the DH-81 is a function of the stream velocity, sample-container volume, and nozzle size--

Sampler	Nozzle diameter (inches)	Ratio	Depth (feet)
DH-81	3/16	0.1	wadeable
	1/4	0.2	wadeable
	5/16	0.4	wadeable

Stream velocity x ratio = maximum vertical transit rate.

The D-96 is not subject to the same transit rate limitations of rigid bottle samples. The minimum transit rate is one at which the sample volume does not exceed 3 L. The sampling time for the three diameter nozzles at varying stream velocities is given in USGS OFR 2005-1087 (Davis and FISP, 2005) that describes the D-96 sampler. The minimum transit rate can be calculated using the sample time from the table and the total distance to be transited.

Complete depth- and width-integrated samples are collected for suspended sediment and percent fines as part of the routine NMN sample trip. Samples may be composited in the field. (NAWQA stations also in the NMN network may use existing protocols for collecting suspended-sediment samples although percent fines should be requested as part of the analysis.)

Composite samples are collected for splitting into sub-samples for all other constituents, as described below:

- Compositing with the churn splitter
  - in order to obtain a sample for DOC/PC which is representative and comparable to other constituents, **assuming ongoing acceptable results are obtained from laboratory blank samples for DOC,** this sample will be collected using the same sampler and collection method as the other water-quality samples and composited into the churn splitter
  - A total of three to four passes are necessary at each vertical in the cross section, collected into different sets of containers. The order of sample collection for specific analytes should be consistent; the constituent groups most affected are DOC/PC and suspended sediment/chemistry (when both are collected). **It is necessary to flush the sampling equipment with the maximum volume of**

ambient water prior to collection of the DOC/PC sample to avoid potential contamination with methanol. Additionally, to minimize temporal variability between the suspended sediment concentration and chemistry samples, it is necessary that they be collected as close in time as possible. For these reasons, the order of sample collection should be as follows:

1. bottles for suspended-sediment concentration
2. glass carboy (or Teflon® churn splitter) for pesticides
3. churn splitter (inorganics and DOC/PC)

- Compositing with the cone splitter
  - two to three passes are necessary at each vertical in the cross section, collected into different sets of containers as follows--
    1. bottles for suspended sediment concentration
    2. Teflon® containers for pesticides, inorganics and DOC/PC
  - **copious field rinsing of the Teflon® containers and the cone splitter is necessary to remove any residue of methanol that may remain from cleaning and contaminate the DOC/PC sample; THREE vigorous rinses with native water, at least 3-4 liters each time, is required**

Sample processing

A description of bottle types required for NMN schedules can be found at the NWQL web page (http://nwql.cr.usgs.gov/usgs/catalog/index.cfm).

Complete descriptions of sample processing details are provided in Chapter 5 of the National Field Manual.

- Overview of filtration guidelines:
  - **Withdraw samples for whole-water constituents first,** including nutrients, and particulate carbon
  - Specifics on procedures for particulates--
    - **Particulate carbon and nitrogen**
      - a total of three filters are required be sent to the NWQL for analysis of particulate carbon and nitrogen
      - the pressure must be regulated to less than **15** lb/in^2
      - each filter is carefully removed, folded in half with the sediments inside, and placed on a 6-inch square of aluminum foil; after the volume of sample that passed through the filter is recorded on the foil, it is folded and placed in two plastic Whirl-Pak bags
      - samples for the NWQL should be shipped as soon as possible
  - Inorganic constituents and dissolved organic carbon
    - in addition to dissolved nutrients, major ions, and alkalinity, **capsule filters are used for filtration of all NMN samples for dissolved organic carbon**
    - the filter is preconditioned with 1 liter DIW, using the pump to drain the water remaining in the filter as much as possible
    - samples should be filtered according to the following order:

        - no more than 100 mL should be filtered for use in rinsing before filling bottles for major ions, dissolved nutrient analysis, and alkalinity
        - **without rinsing the sample bottle, filter 100 mL for DOC analysis last**

Because the DOC sample requires acidification (see below), a separate bottle must be filtered for UV absorption (see NWQL Policy Memo 2000.04)

        - 40 mL is sufficient volume, filtered into a baked-glass amber DOC bottle
        - label bottle "for UV-254 and UV-280"
    - Pesticides
        - prerinse the filter with at least 100 mL of native water
        - collect approximately 1 L of filtered sample, without prerinsing, leaving about a 2-cm headspace in the bottle

- Preservation
    - the FA bottle for schedule 998/1201/1674 is preserved with 2 mL of 7.5-7.7 Normal Ultrex-grade nitric acid, provided in polypropylene vials (see NFM Ch. 5.4 for more information). The pH of the preserved sample must be <2.
    - samples for whole-water nutrients and dissolved organic carbon are preserved with 1 mL of 4.5 normal sulfuric acid (see and NWQL Policy Memo 2000.04 for more information
    - all nutrient and organic samples are stored at 4°C
- Shipping
    - A detailed description of shipping requirements is provided in NWQL Technical Memorandum 02.04
    - All sample bottles must be clearly labeled with pre-printed labels or a waterproof marker with the following minimum information--site identification number, date, time, and sample designation code
    - Include a NWQL Analytical Services Request (ASR) Form for each sample sent to the laboratory, retaining a copy; place the ASR form inside a sealable plastic bag and tape the bag to the inside of the cooler lid

References

- Davis, Broderick and the Federal Interagency Sedimentation Project, 2005, A guide to the selection and proper use of federally approved sediment and water-quality samplers: U.S. Geological Survey Open-File Report 2005-1087, 20 pp. [http://water.usgs.gov/osw/pubs/OFR_2005_1087/index.html]
- Edwards, T.K. and Glysson G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water Resources Investigations Book 3, Ch. C2, 89 pp. [http://pubs.usgs.gov/twri/twri3-c2/]
- Horowitz, A.J.; Demas, C.R.; Fitzgerald, K.K.; Miller, T.L.; and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S.

Geological Survey Open-File Report 94-539, 57 pp. [http://pubs.er.usgs.gov/usgspubs/ofr/ofr94539]

- Office of Surface Water Technical Memorandum 94.05, 1994, Maximum sampling depths and transit rates for suspended sediment and water-quality samplers [http://water.usgs.gov/admin/memo/SW/sw94.05.html].
- Office of Water Quality Technical Memorandum 92.06, 1992, Report of committee on sample shipping integrity and cost [http://water.usgs.gov/admin/memo/QW/qw92.06.html].
- Office of Water Quality Technical Memorandum 97.06, 1997, Comparison of the suspended-sediment splitting capabilities of the churn and cone splitters [http://water.usgs.gov/admin/memo/QW/qw97.06.html].
- 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-A9, available online at http://pubs.water.usgs.gov/twri9A.

Attachment 5. Sample coding guidance

Blanks

(1) Analytical Services Request Forms

	Environmental	Field blank
Time	Time of collection rounded to nearest 10-minute interval	8 minutes after environmental sample time
Sample medium	9 (surface water)	Q (QA, artificial)
Sample type	9 (regular)	2 (blank)

Login comment: Laboratory blank OR field blank prepared before sampling station ID on date/time; blank water lot number ____

(2) QWDATA

Parameter	Environmental sample
99111 (QA data associated w/sample)	10 (blank)
71999 (sample purpose)	25 (NMN)
	Blank sample
99104 (numeric part of current lot number)	_____
71999 (sample purpose)	25 (NMN)
99100 (type or blank solution)	10 (distilled/deionized water)
99101 (source of blank solution)	
or	
99100 (type of blank solution)	40 (organic-free water)
99101 (source of blank solution)	10 (NWQL)
99102 (type of blank sample)	100 (field)
	150 (lab)
	1 (source)

Replicates

(1) Analytical Services Request Forms

	Primary	Secondary
Time	Time of collection rounded to nearest 10-minute interval	Ten minutes later than primary sample
Sample medium	9 (surface water)	R (QA, surface water)
Sample type	7 (replicate)	7 (replicate)

(2) QWDATA

Parameter	Primary sample
99111 (QA data associated w/sample)	30 (replicate)
99105 (replicate type)	10 (concurrent) 30 (split)
71999 (sample purpose)	25 (NMN)
	Secondary sample
99105 (replicate type)	10 (concurrent) 30 (split)
71999 (sample purpose)	25 (NMN)

Pesticide field spikes

(1) Analytical Services Request Forms

	Environmental	Spike
Time	Time of collection rounded to nearest 10-minute interval	Three minutes after environmental sample time
Sample medium	9 (surface water)	R (QA, surface water)
Sample type	9 (regular)	1 (spike)

(2) QWDATA

Parameter	Primary sample
99111 (QA data associated w/sample)	40 (spike)
99106 (spike type)	10 (field)
71999 (sample purpose)	25 (NMN)
	Secondary sample
99106 (spike type)	10 (field)
99104 (numeric part of current lot number)	_____
99107 (spike source)	10 (NWQL)
99108 (spike volume)	0.1 (mL)
71999 (sample purpose)	25 (NMN)

Login comment: Field spike for S2033 for station ID on date/time; spike lot number is _____.

Attachment 6. Guidelines for collection of NMN QC samples

The collection and evaluation of QC samples are essential elements of the NMN program, which contains a strong interpretive component. Without QC information, the quality of the environmental data can not be evaluated or qualified, limiting the interpretive value of the data.

Objectives of the QC sample analysis include the following--

- to determine the extent of contamination introduced from the equipment and methods used for sampling and processing
- to provide information about the variability and bias of measured concentrations
- to evaluate the effect of the natural-water matrix on the bias and recovery of measured concentrations for selected analytes

QC samples for NMN include field-equipment blanks, replicates, and field-matrix spikes. Consult the NMN SWPLAN for information on the QC samples required of the individual NMN sites in FY 2008.

Equipment blanks

A field-equipment blank is a blank solution that is generated under actual field conditions and is subjected to the same aspects of sample collection, field processing, preservation, transportation, and laboratory handling as the environmental samples.

Field equipment blanks should be prepared immediately before collecting and processing a native-water sample at a selected site.

- equipment should already be pre-cleaned in preparation for the routine environmental sampling
- it is not necessary to clean the equipment after sampling and processing of the field equipment blank before using it to collect and process the environmental sample
- field-equipment blanks will be required for all constituents except suspended sediment
- use the following schedules--

Schedule	Analysis	Source solution
452	Nutrients	IBW
1674	Major ions	IBW
1675	PC/PIC/POC/DOC	OBW
2033	Pesticides	OBW

The bottling requirements for these schedules can be found from the links in the NMN Schedule Description document.

Approximately two to three gallons of blank water (either inorganic- and organic-free) are required for adequate rinsing and processing.

- because of the potential for contamination, an equipment blank should be prepared using either inorganic- or organic-free blank water, **but not both at the same site**

- equipment blanks (see Horowitz and others, 1994) for inorganic constituents (schedules 1674 and 452) should be prepared as follows--
    - collect two initial samples of the source solution one for each schedule if necessary
    - after the initial rinsing with blank water, fill the sampler bottle or bag and pour through the nozzle into a sample bottle for the sampler blank
    - pour the remainder of the blank water from the sampler into the churn splitter; refill the sampler and repeat until the churn contains about 5 liters of water; pump an aliquot of blank water from the churn splitter, using the routine pumping system, into a sample bottle for the pump blank
    - pump an aliquot of blank water from the churn splitter through the preconditioned filtration system into a sample bottle for the equipment blanks
    - preserve all samples as required; submit only the final field equipment blank samples (filtered nutrients) to the laboratory and store the remainder of the samples for later analysis, if necessary
- equipment blanks for organic constituents (schedules 1675 and 2033) should be prepared as follows--
    - collect two initial samples (1-L and 125-mL) of the source solution, one for each schedule if necessary
    - **rinsing of the sampler should simulate as closely as possible the field rinsing that occurs prior to collection of the environmental sample**
    - after the initial rinsing, fill the sampler bottle or bag with blank water and pour through the nozzle into the glass carboy or Teflon® churn splitter; refill the sampler and repeat until the carboy/churn contains at least 2 to 3 liters of water; pump an aliquot of blank water from the glass carboy/churn through the preconditioned pesticide filtration system for the pesticide equipment blank
    - refill the sampler and pour another 2 to 3 liters of blank water into the churn splitter; collect three aliquots through the churn spigot and pump through the preconditioned PC filtration system for PC analysis
    - after conditioning the capsule filter with 100 mL, filter an additional 100 mL from the churn splitter and submit the filtrate for the DOC equipment blank

If the data from the laboratory fall within the QC requirements (described below), the equipment blank is acceptable and the other samples may be discarded.

- If all or some of the data exceed the acceptable levels, further investigation will be required to determine the source of the contamination.

Quality-control requirements

Acceptable concentrations for the equipment blank for inorganic constituents and pesticides are either less than or no higher than the MDL (minimum detection limit) +/- 100 percent. If all or some of the concentrations exceed this criteria, the blank is still acceptable if the concentrations are less than or equal to half the appropriate reporting limit.

Blanks for organic carbon are considered acceptable if concentrations are either less than or no higher than twice the MRL (0.15 mg/L). Concentrations higher than this must be evaluated in context with environmental data, and may still be considered acceptable.

Consult the sample coding guidelines document for filling out ASR's and entering data into QWDATA.

Replicates and Splits

Concurrent replicates are two or more samples that are collected as closely as possible in time and space, but processed, handled, and analyzed separately; these samples provide information about the total variability inherent in the observed concentrations, including sampling, processing, and laboratory variability.

- collection of concurrent replicate samples requires two separate passes for the particular suite of constituents at each vertical in the cross section, composited in separate compositing vessels

Splits are two or more separate subsamples split from a single stream sample; these samples provide information about the variability inherent in the observed concentrations due to sample processing and laboratory analysis

- collection of split samples requires a single pass for the particular suite of constituents, composited in one compositing vessel; separate samples are dispensed from the compositing vessel, following the routine procedures

Consult the sample coding guidelines document for filling out ASR's and entering data into QWDATA.

Field-matrix spikes

Environmental sample fortified in the field with known concentrations of all, or a representative selection of, the analytes for a particular method; this sample must be submitted along with a split sample that is not spiked.

- Field matrix spikes (supplied by NWQL) will be collected only for pesticides (Schedule 2033).

Detailed instructions for using the pesticide spike mixture for S2033 are provided with the spike mixture (500 microliters in a 1 mL ampule), along with 100 microliter micropipets and a Teflon® squeeze bottle.

- the ampule should be kept in the freezer if long-term storage is required

Consult the sample coding guidelines document for filling out ASR's and entering data into QWDATA.

The contacts for NMN regarding questions about QA/QC sampling and review of QC data are Richard Coupe (rhcoupe, 601-933-2982) or Dave Reutter (dreutter, 614-430-7732).

References

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Leahy, Patrick P., 1993b, QA/QC objectives and procedures for NAWQA SW Basic Fixed Sites, unpublished memorandum, August 17, 1993

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-A9, available online at http://pubs.water.usgs.gov/twri9A.

Zaugg, A.D., Sandstrom M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the USGS NWQL--determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography-mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 pp. [http://nwql.usgs.gov/Public/pubs/OFR95-181/OFR95-181.html]

Attachment 7. NMN parameter codes

Schedule	Analyte	Parameter Code
Field parameter	Temperature	00010
Field parameter	Specific conductance	00095
Field parameter	Dissolved oxygen	00300
Field parameter	pH	00400
Field parameter	Alkalinity, filtered, field	39086
998/1201	Calcium	00915
998/1201	Magnesium	00925
998/1201	Sodium	00930
998/1201	Potassium	00935
998/1201	Chloride	00940
998/1201	Sulfate	00945
998/1201	Fluoride	00950
998/1201	Silica	00955
998/1201	Arsenic	01000
998/1201	Boron	01020
998/1201	Iron	01046
998/1201	Strontium	01080
998/1201	Vanadium	01085
998/1201	Lithium	01130
998/1201	Selenium	01145
998/1201	Residue, 180 degrees Celsius (TDS)	70300
997/1010/1069	Nitrogen, ammonia, filtered	00608
997/1010/1069	Nitrogen, nitrite, filtered	00613
997/1010/1069	Nitrogen, ammonia + organic (Kjeldahl), filtered	00623
997/1010/1069	Nitrogen, ammonia + organic (Kjeldahl), unfiltered	00625
997/1010/1069	Nitrogen, nitrite + nitrate, filtered	00631
997/1010/1069	Phosphorus, unfiltered, total as phosphorus	00665
997/1010/1069	Phosphorus, filtered	00666
997/1010/1069	Phosphorus, phosphate, ortho, filtered	00671
997/1010/1069	Carbon, organic, filtered, recoverable (DOC)	00681
997/1010/1069	Carbon, inorganic, sediment, suspended (PIC)	00688
997/1010/1069	Carbon, organic, sediment, suspended, recoverable (POC)	00689
997/1010/1069	Carbon, inorganic + organic, sediment, suspended (PC)	00694
997/1010/1069	Total nitrogen	49570
997/1010/1069	Ultraviolet absorbing organic constituents - 254 nm	50624
997/1010/1069	Ultraviolet absorbing organic constituents - 280nm	61726
SusSed	Suspended sediment, percent finer than 62 microns	70331
SusSed	Suspended sediment	80154

Schedule	Analyte	Parameter Code
2033	Terbuthylazine	04022
2033	Hexazinone	04025
2033	Simazine	04035
2033	Prometryn	04036
2033	Prometon	04037
2033	2-Chloro-4-isopropylamino-6-amino-s-triazine {CIAT}	04040
2033	Cyanazine	04041
2033	Fonofos	04095
2033	alpha-Endosulfan	34362
2033	Dicrotophos	38454
2033	Dichlorvos	38775
2033	Chlorpyrifos	38933
2033	Dieldrin	39381
2033	Metolachlor	39415
2033	Malathion	39532
2033	Diazinon	39572
2033	Atrazine	39632
2033	Alachlor	46342
2033	Acetochlor	49260
2033	1-Naphthol	49295
2033	Cyfluthrin	61585
2033	Cypermethrin	61586
2033	Endosulfan sulfate	61590
2033	Fenamiphos	61591
2033	Iprodione	61593
2033	Isofenphos	61594
2033	lambda-Cyhalothrin	61595
2033	Metalaxyl	61596
2033	Methidathion	61598
2033	Myclobutanil	61599
2033	Oxyfluorfen	61600
2033	Phosmet	61601
2033	Tefluthrin	61606
2033	Tribufos	61610
2033	2-Chloro-2,6-diethylacetanilide	61618
2033	2-Ethyl-6-methylaniline	61620
2033	3,4-Dichloroaniline	61625
2033	3,5-Dichloroaniline	61627
2033	4-Chloro-2-methylphenol	61633
2033	Azinphos-methyl-oxon	61635
2033	Chlorpyrifos, oxygen analog	61636
2033	Diazinon, oxygen analog	61638
2033	Disulfoton sulfone	61640
2033	Ethion monoxon	61644
2033	Fenamiphos sulfone	61645
2033	Fenamiphos sulfoxide	61646
2033	Malaoxon	61652
2033	Paraoxon-methyl	61664
2033	Phorate oxygen analog	61666
2033	Phosmet oxon	61668

Schedule	Analyte	Parameter Code
2033	Terbufos oxygen analog sulfone	61674
2033	Fipronil	62166
2033	Fipronil sulfide	62167
2033	Fipronil sulfone	62168
2033	Desulfinylfipronil amide	62169
2033	Desulfinylfipronil	62170
2033	Tebuconazole	62852
2033	cis-Propiconazole	79846
2033	trans-Propiconazole	79847
2033	Ethion	82346
2033	Metribuzin	82630
2033	2,6-Diethylaniline	82660
2033	Trifluralin	82661
2033	Dimethoate	82662
2033	Phorate	82664
2033	Parathion-methyl	82667
2033	EPTC	82668
2033	Tebuthiuron	82670
2033	Molinate	82671
2033	Ethoprophos	82672
2033	Benfluralin	82673
2033	Carbofuran	82674
2033	Terbufos	82675
2033	Propyzamide	82676
2033	Disulfoton	82677
2033	Propanil	82679
2033	Carbaryl	82680
2033	Thiobencarb	82681
2033	Dacthal	82682
2033	Pendimethalin	82683
2033	Propargite	82685
2033	Azinphos-methyl	82686
2033	cis-Permethrin	82687