In Reply Refer To:
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Office of Water Quality Technical Memorandum 2008.01

Subject: National Stream Quality Accounting Network, Fiscal Year (FY) 2008

This memorandum contains a summary of the activities of the National Stream Quality Accounting Network (NASQAN) for FY 2008, including the stations being operated, constituents measured, and initial funding allocations. Further details on NASQAN operations can be obtained from Charlie Crawford (NASQAN Coordinator) or Dave Reutter (NASQAN support). Contact information is contained at the end of this memorandum.

Concerns about the NASQAN II design, given available funding, led to the creation of the NASQAN ad hoc Technical Committee (NTC) in February 2007. The principal objectives of the NTC were to transition NASQAN into a Federal Surface Water Quality Fixed Station Network. The NTC Report detailing the redesign of the NASQAN program can be found at http://in.water.usgs.gov/nawqa/ntc/ntc.html. FY 2008 is the first year to implement the changes recommended by the NTC.

NASQAN stations

Most notable to operations is the reorganization of NASQAN into a network design-- a Coastal Network and a Mississippi Basin Network. This network design has resulted in the discontinuation of some stations previously sampled for NASQAN, but the addition of new stations that will be sampled for NASQAN beginning in FY 2008. The number of stations operated in each network is shown in Table 1. Attachment 1 provides a listing of the stations that will be sampled for NASQAN in FY 2008. The initial fund transfers, by Water Science Center (WSC) and by account number, are contained in Attachment 2 (if there are updates/corrections to the account numbers, please contact the NASQAN Coordinator). **Please note that the NASQAN budget allocations are not final because the USGS is operating on a continuing resolution and the NASQAN funding level has not been finalized. Consequently, initial sample collection allocations shown in attachment 2 are only 90 percent of planned.** If NASQAN funding is less than anticipated, the number of samples collected in FY 2008 will have to be reduced.

Table 1. Number of NASQAN stations by Network.

Network	*Number of Stations*
Mississippi	18
Coastal	13
Total	31

Sampling Frequency and Constituents Measured

All NASQAN stations will be sampled semi-monthly with a part of the year containing additional seasonally-weighted samples determined by the NASQAN coordinator. The number of samples to be collected by month for each station is shown in the attached NASQAN SWPLAN spreadsheet. Samples for months indicated as having two samples should be collected two weeks apart. NASQAN has discontinued collecting samples based on hydrologic conditions ("event samples"). If you have questions or concerns about the information contained in the NASQAN SWPLAN, please contact the NASQAN Coordinator.

With only limited exceptions, constituents measured at NASQAN 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). Note that sampling for trace elements [both dissolved (schedule 1050) and suspended (large-volume samples for Art Horowitz], continuous turbidity (Columbia River), and chlorophyll-*a* and phaeophytin have been discontinued. Note also that pesticide schedule 2001 has been replaced by schedule 2033.

Please ensure that all field personnel sampling at NASQAN stations have a copy of the attachments that 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 NASQAN 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.

NASQAN Networks

Mississippi Basin Network

NASQAN will continue to address questions specific to the Mississippi River Basin related to hypoxia in the Gulf of Mexico. The general scheme used to select stations for this network was to have one station mid-basin and one station near the mouth of the Missouri and Ohio Rivers, one station in the upper and mid-basin region of the Mississippi River, several stations in the Lower Mississippi River Basin, and the most important tributaries to these rivers in terms of nitrogen and phosphorus inputs. As a result, the NTC selected 18 stations for the Mississippi Basin Network (Attachment 1) (note: Mississippi River at Belle Chasse and Atchafalaya River at Melville are included in the Coastal Network). NASQAN

will continue to sample the four Lower Mississippi stations that were added to NASQAN in 2005 [Mississippi at Baton Rouge (station 0737400), Mississippi River at Belle Chasse (station 07374525), Atchafalaya River at Morgan City (station 07381600), and Wax Lake Outlet (station 07381590)]. The intent is to collect concurrent data at the six Lower Mississippi stations for several years and then, based on an analysis of the data, select stations that best meet the needs for monitoring nutrient delivery to the Gulf of Mexico. NASQAN will continue sampling at these additional stations until 5 years of data are available for analysis (end of FY09). Samples will be collected at the Mississippi Basin stations twelve times a year; however, an additional 4 spring samples will be collected at the Mississippi River at Baton Rouge, LA, and the Atchafalaya River at Morgan City, LA, to allow for better prediction of the size of the hypoxia zone in the Gulf of Mexico.

Coastal Network

The Coastal Network will address questions about the annual transport of selected constituents from selected large rivers to coastal waters of the United States. The NTC selected 13 stations for the Coastal Network. This will include 12 stations in the conterminous United States and the re-establishment of the Yukon River station in Alaska. Together, the 12 stations on rivers in the conterminous United States measure approximately 80 percent of the total discharge of streamflow, nitrogen, phosphorus, and suspended sediment to coastal waters. Samples will be collected at most coastal stations twelve times a year. Samples will be collected at the Yukon River station seven times a year; however, pesticide samples will be collected only 3 times per year at the Yukon River.

NASQAN Contact Information

For any questions on the NASQAN 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

Attachments

This memorandum supersedes OWQ Technical Memorandum 2007.02.

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

List of Attachments

Attachment 1. FY 2008 NASQAN Stations [See NASQAN 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
	Mississippi Basin Network		
03303280	Ohio R at Cannelton, IN	KY	12
03374100	White River at Hazleton, IN[1]	IN	12
03378500	Wabash R at New Harmony, IN	KY	12
03609750	Tennessee R near Paducah, KY	KY	12
03612500	Ohio R near Grand Chain, IL	KY	12
05420500	Mississippi R at Clinton, IA	IA	12
05586100	Illinois R. at Valley City, IL	IL	12
05587455	Mississippi R blw Grafton, IL	MO	12
06610000	Missouri R at Omaha, NE	IA	12
06805500	Platte R. at Louisville, NE[1]	NE	12
06934500	Missouri R at Hermann, MO	MO	12
07022000	Mississippi R at Thebes, IL	MO	12
07263620	Arkansas R at Terry Lock & Dam, AR	AR	12
07288955	Yazoo R. near Long Lake, MS[1]	MS	12
07373420	Mississippi R at St. Francisville, LA	LA	12
07374000	Mississippi R at Baton Rouge, LA	LA	**16**
07381590	Wax Lake Outlet at Calumet, LA	LA	12
07381600	Atchafalaya River at Morgan City, LA	LA	**16**
	Coastal Network		
01578310	Susquehanna R. at Conowingo, MD	MD	12
01646580	Potomac R at Washington, DC[1]	MD	12
04264331	St. Lawrence R. at Cornwall, ON	NY	12
02226160	Altamaha R. at Everett City, GA	GA	12
02470500	Mobile R. at Mt. Vernon, AL	AL	12
07374525	Mississippi R at Belle Chasse, LA	LA	12
07381495	Atchafalaya R. Melville, LA	LA	12
08475000	Rio Grande nr Brownsville. TX	TX	12
09522000	Colorado R. at NIB, AZ	AZ	12
11303500	San Joaquin R. near Vernalis, CA[1]	CA	12
11447650	Sacramento R. at Freeport, CA	CA	12
14246900	Columbia R. near Beaver Army Term., OR	OR	12
15565447	Yukon R. at Pilot Station, AK	AK	**7**

[1] Site is NAWQA station sampled every year (NAWQA core site). NASQAN constituents not already collected by NAWQA program will be collected during subset of 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 at these stations except for $100/sample allocated by NASQAN for extra supplies/shipping expenses.

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

[NA, not applicable; TBD, to be determined]

WSC	Account	Amount
	Sample collection	
AK	9054 - 00300	$63,000
AL[1]	TBD	TBD
AR	8578-9M4	$49,650
AZ	9671-9ES	$38,750
CA	9677-CRM54	$47,740
CA	9677-CRM86	$1,080
GA	2503-00300	$70,430
IA	4859-19MU	$47,170
IA	48591-9MU	$46,950
IL	2407-9CE07	$61,780
IN	2412-CRM64	$1,080
KY	2419-APB	$174,140
LA	8601-AEE	$293,160
MD	2427-B4800	$9,720
MD	2427-CRM26	$1,080
MO	8611-9CS	$122,760
MS	2507-CRM03	$1,080
NE	8626-CRM84	$1,080
NY	2457-CRM23	$39,310
OR	9711-9H2	$46,870
TX	8653-AGS	$64,370
	Stream gaging	
AL[1]	TBD	TBD
AR	8578-9M4	$5,242
GA	2503-00100	$24,250
KY	2419-APB	$26,000
	Other (Coordination/Data management, analysis, etc./transition costs)	
AL[1]	TBD	TBD
GA	2503-00100	$30,000
GA	2503-AB270	$117,000
MS	2507-9LY11	$30,000
OR	9711-9H400	$76,600
WI	2491-9CE06	$25,000

[1] Arrangements for the new NASQAN station on the Mobile River are not yet finalized

Attachment 3. FY 2008 NASQAN Operations

Guidelines for NASQAN sampling procedures in FY 2008 are attached (attachments 4, 5, and 6). WSC personnel are responsible for data review, rerun requests, and timely responses to contamination problems and other data issues. Previously, NASQAN maintained a secondary level of data review and management that was provided by the Oregon WSC. Given the limited resources of the NASQAN program, maintaining duplicate data systems operated by both the NASQAN and NAWQA programs was deemed too inefficient to continue. Therefore, secondary review of NASQAN data will be integrated into the NAWQA Data Warehouse in FY 2008. However, the Oregon WSC will continue to process NASQAN data collected in FY 2007, prepare this data for transition into the new system, and check data collected in FY 2008 until integration of NASQAN secondary data checks into the NAWQA data warehouse is complete.

Quality-Control Samples

The specific types of QC samples to be collected at each NASQAN station are described in the NASQAN 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 **4565-9CE00** has been established for analysis of NASQAN chemistry and suspended sediment samples. Please use this account number on your Analytical Service Request (ASR) and sediment analysis request for all NASQAN samples.

Laboratory Schedules

Laboratory schedules for analysis of NASQAN 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 one of two central sediment laboratories, described below. However, NAWQA stations also included in the NASQAN 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.

Iowa WSC Sediment Laboratory:
Mississippi Basin
Rio Grande Basin
Other stations east of Mississippi River Basin

Cascade Volcanic Observatory:
Stations west of Mississippi River Basin

Trace element sampling
Sampling for trace elements at NASQAN stations has been discontinued.

Isotope samples
Field crews at all NASQAN stations should continue to 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.

Additionally, crews should collect two filters for analysis of stable isotopes in particulate organic matter (POM): the glass fiber filter from filtration of pesticide samples, and a separate glass fiber filter from the filtration of particulate carbon/nitrogen. These filters should be clearly labeled and stored in the freezer. ***For stations in the Mississippi Basin only***: an additional filtered sample will be collected and sent to Carol Kendall with the POM filters described above. The sample is filtered through the 0.45 µm capsule filter into two 20 mL scintillation vials, which will be provided by the NASQAN Sampling Coordinator

(Richard Coupe). After filtering, the sample should be clearly labeled and frozen as soon as possible. Approximately quarterly, these filters should be sent to Carol Kendall at:

U.S. Geological Survey
Stable Isotope and Tritium Laboratory
345 Middlefield Road
MS 434
Menlo Park CA 94025

Attachment 4. NASQAN 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 NASQAN program. The methods are intended to provide water-quality data oriented to meet the specific goals of NASQAN, 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. Additional information on the rationale for and complete description of these sampling and processing procedures are also contained in Edwards and Glysson (1988), as well as selected Technical Memoranda and Water-Quality Information Notes issued by the Office of Water Quality.

Constituents routinely measured by the NASQAN program include field parameters, suspended sediment, major ions, nutrients, dissolved/particulate carbon, and pesticides. Additional special samples are collected, as described below:

1. All stations
    - Stable isotopes of water (Ty Coplen)
    - Stable isotopes of particulate organic matter (Carol Kendall)
        - Two separate filters are required: one from pesticide processing, and one from the processing of particulate carbon
2. Mississippi Basin only
    - Stable isotopes of water (Carol Kendall)

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 NASQAN 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-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 judgment 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) 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.

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

1. D-96
    - must be coated with teflon or plastic paint to prevent trace-element contamination---if plastic coating becomes scratched, reapply with white Plasti-Dip (spray plastic paint, may be available locally or can be ordered from various vendors)
    - collects a maximum of nearly 3 L sample per vertical
    - approved for flow velocities between 2 to 15 ft/s
    - nozzle sizes range from 3/16, 1/4, and 5/16 inch to 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--caps and nozzles, and bags
2. DH-81
    - suspended from a rod--used for wadeable streams
    - uses standard D-77 cap and accessories, 1-L bottle
3. 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: Teflon churn splitter may alternatively be used for pesticides as well as the other constituents)
        - 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 Shelton (1994) for further details on the use of the cone splitter
- 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 that holds a 25-mm glass fiber filter (nominal pore size of 0.7 µm) (available from the National Field Supply Service through One-Stop Shopping as item 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 within 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 NASQAN 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
    - specific conductance and pH can be measured in the stream or from an unfiltered sample from the churn splitter
    - 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

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 (feet)	Depth
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 as rigid bottle samplers. 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 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 NASQAN sample trip. Samples may be composited in the field. (NAWQA stations also in the NASQAN 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 NASQAN schedules can be found in the NWQL catalog loacated at 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 four filters are required:
        - three to be sent to the NWQL for analysis of particulate carbon and nitrogen
        - a separate filter to be sent to Carol Kendall for stable isotope analysis of particulate organic material (POM)
      - the pressure must be regulated to less than 40 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 which passed through the filter is recorded on the foil, it is folded and placed in a plastic Whirl-bag
      - samples for the NWQL should be shipped as soon as possible

POM samples for Carol Kendall should be stored in the freezer and shipped approximately quarterly to her lab (further information can be found in NWQL Policy Memo 2000.05).

  - Inorganic constituents and dissolved organic carbon
    - in addition to dissolved nutrients, major ions, and alkalinity, **capsule filters are used for filtration of all NASQAN 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 to 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"
    - Stable isotopes of water
        - **Mississippi Basin only**
        - samples are collected in 20 mL scintillation vials, which are provided by Richard Coupe
        - label the vial with station, date, and time
        - using filtrate from the 0.45 µm capsule filter, rinse the cap and bottle
        - fill the vial with filtrate from the 0.45 µm capsule filter, making sure to leave some head space, and cap the vial
        - freeze the sample as soon as possible
        - send to Carol Kendall with the POM filters, approximately every quarter
    - 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
        - **save the filter for stable isotope analysis**
            - carefully remove the filter, place on a small sheet of aluminum foil, and fold in quarters
            - wrap and label foil package with station name, ID, sample date, and time
            - place in a ziplock bag, and chill until the bag can be stored in the freezer
            - continue to accumulate filters until notified to send them to Carol Kendall
- 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 ampules (see for more information
    - 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^{o}C
    - filters for analysis of stable isotope are stored in the freezer

- Shipping
    - A detailed description of shipping requirements is provided in NWQL Technical Memorandum 02.04 [http://nwql.usgs.gov/Public/tech_memos/nwql.02-04.html]
    - All sample bottles must be clearly labeled with 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

- Edwards, T.K. and Glysson G.D., 1988, Field methods for measurement of fluvial sediment: USGS Open-File Report 86-531, 118 pp.
- Office of Surface Water Technical Memorandum 94.05, 1994, Maximum sampling depths and transit rates for suspended sediment and water-quality samplers
- Office of Water Quality Technical Memorandum 92.06, 1992, Report of committee on sample shipping integrity and cost
- Office of Water Quality Technical Memorandum 97.06, 1997, Comparison of the suspended-sediment splitting capabilities of the churn and cone splitters
- Sylvester, M.A., Kister, L.R., and Garrett, W.B., eds., 1990, Guidelines for the collection, treatment, and analyses of water samples--U.S. Geological Survey Western Region Field Manual: U. S. Geological Survey, Western Region, Internal Document, 144 pp.
- 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)	20 (NASQAN)

	Blank sample
99104 (numeric part of current lot number)	_____
71999 (sample purpose)	20 (NASQAN)
99100 (type or blank solution)	10 (distilled/deionized water)
99101 (source of blank solution)	80 (Ocala)
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) 40 (sampler) 50 (splitter/tubing)

Replicates (NWQL Only)

(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)
71999 (sample purpose)	20 (NASQAN)

Parameter	Secondary sample
99105 (replicate type)	10 (concurrent)
71999 (sample purpose)	20 (NASQAN)

Replicates (suspended sediment)

(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)	V (QA, suspended sediment)
Sample type	9 (regular)	7 (replicate)

(2) QWDATA

Parameter	Primary sample
99111 (QA data associated w/sample)	30 (replicate)
71999 (sample purpose)	20 (NASQAN)

	Secondary sample
99105 (replicate type)	10 (concurrent)
71999 (sample purpose)	20 (NASQAN)

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	7 (replicate)	1 (spike)

(2) QWDATA

Parameter	Primary sample
99111 (QA data associated w/sample)	40 (spike)
99106 (spike type)	10 (field)
71999 (sample purpose)	20 (NASQAN)

	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)	20 (NASQAN)

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

Attachment 6. Guidelines for collection of NASQAN QC samples

The collection and evaluation of QC samples are essential elements of the NASQAN 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 NASQAN include field-equipment blanks, replicates, and field-matrix spikes. Consult the NASQAN SWPLAN for information on the QC samples required of the individual NASQAN 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 bottle requirements for these schedules can be found from the links in the NASQAN 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 Chapter 4.3.1.B of the National Field Manual) 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

Concurrent replicate samples for suspended sediment will be collected at every sample visit as composite samples, and analyzed for sand/silt split and concentration.

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 which 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 NASQAN 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

Leahy, Patrick P., 1993a, QA/QC plan for Intensive Fixed Sites, unpublished memorandum, July 8, 1993

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

U.S. Geological Survey, September 2006, Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed November 2, 2007 at http://pubs.water.usgs.gov/twri9A4

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: USGS Open-File Report 95-181, 49 pp.

Attachment 7. NASQAN 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