

5 NON-TIDAL WATER QUALITY MONITORING

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SECTION A PROJECT DESCRIPTION

1. Management Objectives

Chesapeake Bay Program partners are implementing management actions through the Chesapeake Bay TMDL process to reduce nutrient and sediment pollution entering the Chesapeake Bay watershed. The Chesapeake Bay Nontidal Water Quality Network (NTN) was developed in 2004, to estimate nutrient and sediment loadings discharged and trends in loads from each of the 36 tributary strategy basins. In 2009, the objectives were modified to measuring the effectiveness of best management practices at multiple scales.

The NTN includes the nine Chesapeake Bay River Input Monitoring (RIM) stations which require additional parameters for the Chesapeake Bay Estuarine Model. Further information about the RIM monitoring program may be found at the website <http://cbrim.er.usgs.gov/loadhighlights.html>.

Loadings and trend data, along with data sets on nutrient and sediment sources, Best Management Practices (BMPs), land-use changes and watershed characteristics may be used to assess the factors which affect local stream and river nutrient and sediment concentrations, flow and the resultant loads to downstream waters. The observed concentration trends and calculated loadings data will help the tributary strategy teams to:

- 1.1. Assess progress toward meeting nutrient and sediment cap load allocations;
- 1.2. Evaluate the effectiveness of state tributary strategy implementation to improve water-quality of local streams; and
- 1.3. Determine if tributary strategy implementation in the watersheds will result in achievement of water-quality standards in the Bay.

2. Monitoring and Data Quality Objectives

2.1. The monitoring objectives of the Chesapeake Bay Nontidal Watershed Water-Quality Network are to:

- 2.1.1. Compute annual loadings of total nitrogen, phosphorus and suspended sediment from tributary strategy basins;
- 2.1.2. Assess the status and trends of nutrient and sediment concentrations and loads at each station;
- 2.1.3. Compare concentration data and loadings estimates among rivers; and

- 2.1.4. Improve calibration and verification of partners' watershed models.
- 2.2. The data quality objectives for loadings computations are to: a) accurately sample stream conditions under the range of flow conditions during a given year and b) obtain a sample that is representative of the stream.
- 2.2.1. A minimum of 3 years of data are required to calculate loadings. The sampling design is a combination of fixed-interval and storm event samples to cover the range of concentration and flow conditions.
Section 4 below provides additional detail on the sampling design.
- 2.2.2. *Isokinetic, depth- integrated* samples are collected at equal-width increments across a stream channel to best represent the total nitrogen, phosphorus and sediment concentrations in the discharge. Sampling procedures for the NTN are based on methods in the *USGS National Field Manual for the Collection of Water-Quality Data*. For greater detail, see http://water.usgs.gov/owq/FieldManual/chapter4/pdf/Chap4_v2.pdf.
- 2.3. Data quality objectives for the purposes of calculating status and trends of stream concentrations are less stringent than for loadings. The main objective is to collect fixed-interval (monthly) stream samples for at least 5 years using consistent field and lab methods. Section 4 below specifies the field methods for obtaining a representative sample.
3. Participating State and Federal Agencies

Sampling is conducted by six State agencies and four USGS Water Science Centers as indicated below. Samples are analyzed by State and USGS Laboratories.

<u>State</u>	<u>Sampling Agencies</u>
Delaware	Delaware Department of Natural Resources and Environmental Control
Maryland	Maryland Department of Natural Resources • USGS Maryland-DC-Delaware WSC
New York	New York State Environmental Protection • Susquehanna River Basin Commission
Pennsylvania	Pennsylvania Department of Environmental Protection • USGS Pennsylvania WSC • Susquehanna River Basin Commission
Virginia	Virginia Department of Environmental Quality • USGS Virginia Water Science Center
West Virginia	West Virginia Department of Environmental Protection • USGS West Virginia WSC

4. Sampling Design

4.1. *Parameters:*

TABLE 5.1 Parameters for Chesapeake Bay Nontidal Water Quality Network

Required NTN Parameters	Additional RIM Parameters (Recommended for NTN)
Total Nitrogen, as N (TDN + PN) or (TKN + NO₂3) or (TN)	Total Dissolved Nitrogen (TDN)
Ammonium, as N (dissolved*) (NH₃F)	Particulate Nitrogen (PN)
Nitrate + Nitrite, as N (dissolved*) (NO₂3F)	Total Dissolved Phosphorus (TDP)
Total Phosphorus, as P (TP) or (TDP + PP)	Particulate Phosphorus (PP)
Phosphate, as P (dissolved*) (PO₄F)	Particulate Carbon (PC), or TOC
Total Suspended Solids (TSS)	Dissolved Organic Carbon (DOC)
Suspended Sediment Concentration (SSC) (High discharge days only)	Volatile Suspended Solids (VSS)
SSC-Sand & SSC-Fines (1 storm/quarter)	Chlorophyll-<i>a</i> (corrected) (CHLA)
* Dissolved fraction is preferred but whole water is acceptable	
Field Parameters: Dissolved Oxygen, Temperature, pH, Specific Conductance	

4.2. *Site Specifications:* There are two types of NTN sites – Primary and Supplemental. As of Water Year 2014, there are 113 Primary NTN stations and 11 Supplemental NTN sites.

4.2.1. Primary sites are characterized as having:

- 4.2.1.1. A close proximity to a continuous stream flow gage so that the water-quality and discharge information are comparable;
- 4.2.1.2. Twenty water chemistry samples collected per year over a range of flow conditions (12 routine + 8 storm flow);
- 4.2.1.3. Total nitrogen, total phosphorous, ammonium, nitrate, phosphate and total suspended solids analyses;
- 4.2.1.4. Storm samples must also include analyses of suspended sediment concentrations, and each quarter, a sand/fine particle size analysis; and

4.2.1.5. Equal-width increment (EWI), isokinetic, depth-integrated sampling techniques to obtain representative samples.

4.2.2. Supplemental stations do not have storm sampling, but follow primary station criteria such as:

4.2.2.1. Sites are associated with a stream-flow gage to allow computation of loadings trends;

4.2.2.2. Samples must be collected at least monthly;

4.2.2.3. Parameters shall include total nitrogen, total phosphorous and total suspended solids; and

4.2.2.4. Use of isokinetic, depth-integrated sampling techniques to obtain representative samples.

4.3. *Routine Sampling Frequency*

4.3.1. Primary and supplemental stations are sampled once per month on a predetermined schedule. These fixed-interval samples provide samples from a random, unbiased selection of flow conditions.

4.3.2. If high discharge occurs during routine monthly sampling, collect the samples on the scheduled date using procedures for storm event sampling, and including a SSC sample (primary stations only). These samples are to be counted as routine, monthly samples and designated as sample type "Routine, Storm-impacted". A routine, storm-impacted event has a rising discharge (cfs) of at least twice that of the pre-storm, average daily discharge.

4.4. *Storm Sampling Frequency*

4.4.1. Eight storm-event samples are required per year, preferably with at least one storm event per quarter to capture seasonal effects. Sampling of larger storm events is preferred, but in dry years smaller discharges of at least twice that of the pre-storm discharge may be sampled.

4.4.2. Samples may be collected at any point in the hydrograph, i.e., rising or falling limb, or at peak discharge.

4.4.3. Two samplings are permitted during a single storm event. However, samples must be collected on different days so that two estimates of daily load can be calculated. This practice also applies to taking a storm sample after the collection of a routine, storm-impacted sample.

4.4.4. SSC samples are collected each storm sampling day, with a sand/fine particle size analysis each quarter.

4.4.5. Monitor the hydrological conditions leading up to, and predicted for the storm, including:

4.4.5.1. *Rainfall*, e.g., total rainfall over last 24-48 hours, rainfall intensity, current radar and forecast for the next few days;

4.4.5.2. *Current Hydrology*, e.g., stage, rising or falling limb, shape of the storm hydrograph and upstream river conditions; and

4.4.5.3. *Previous Hydrology*, i.e., the size of the storm relative to discharge over the last 6 months.

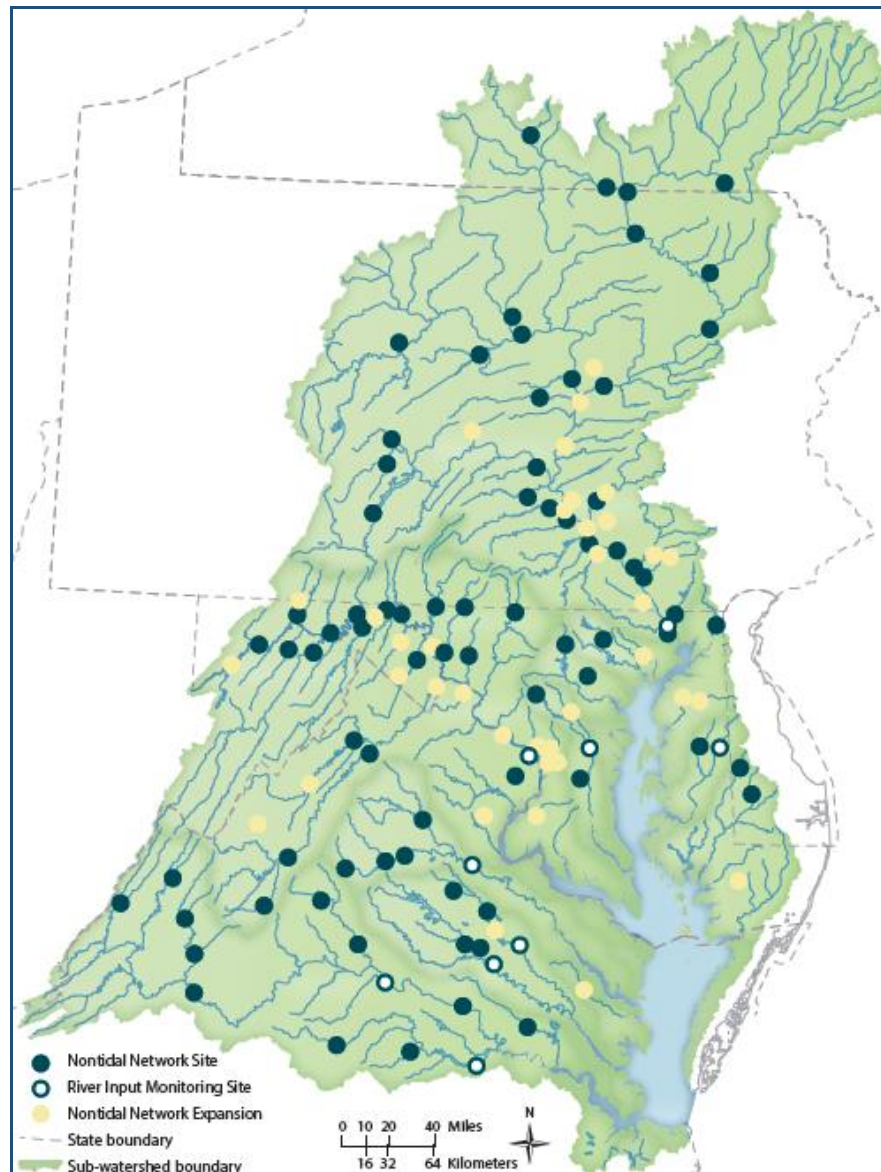
4.5. *Composite Samples*

The number of depth- integrated, equal-width interval (EWI) samples varies per station and waterway width. Table V.5 describes the minimum number of verticals to be composited at primary stations, for both routine and storm event sampling. To ensure the collection of representative samples, assess the cross-sectional variability of specific conductance, water temperature, dissolved oxygen and pH to determine that the sampling points across each river adequately represented the vertical and horizontal water-quality conditions within the cross-section. Ideally, this would include an analysis of the variability of suspended sediment concentration in the equal-width increments.

5. Sampling Sites and Locations

5.1. Figure V-1 is a map showing the Chesapeake Bay Nontidal Monitoring Stations

FIGURE 5.1, CHESAPEAKE BAY NON-TIDAL NETWORK MONITORING STATIONS



SECTION B

SAMPLING PROCEDURES

1. Equipment

1.1. Samplers*

- 1.1.1. **DH-81:** A hand-held, depth-integrating suspended sediment and water quality sampler. The DH-81 samplers consist of a 1-L sample bottle, a D-77 sample cap that holds the nozzle, and a DH-81A adapter that snaps over the cap and to which a wading rod is attached. Under most flow conditions a 5/16" nozzle is preferred for sampling, but a ¼ or ¾-inch nozzle may be utilized under very low or higher than normal flows. Make sure to collect an isokinetic sample if the discharge velocity is 1.5 ft/s or more.
- 1.1.2. **DH-95:** A hand-line suspended sediment and water-quality sampler, for sampling depths ≤ 15 ft. The DH-95 weighs 29 lbs and is designed to be used with a 1-L bottle. Use a ¼ or 5/16-inch nozzle and be sure to collect a depth integrated, isokinetic sample if the discharge velocity is 1.5 ft/s or more.
- 1.1.3. **WBH-96:** A weighted bottle sampler used to collect samples where discharge velocities are less than 1.5 ft/s.
- 1.1.4. **D-95 or D-77:** These heavy samplers must be suspended from a bridge using a cable, reel and bridge board. The D-95 and D-77 bottle samplers may be used to a maximum depth of 15 ft. deep. To collect an isokinetic sample, use a 5/16-inch nozzle and make sure the discharge velocity is 1.5 ft/s or more. Use a D-77 bag sampler if the discharge velocity exceeds 3 ft/s and the depth is > 15 feet, using a ¼ or 5/16-inch nozzle.

* For additional information on samplers see: USGS TWRI, Book 3, Chapter C2
(<http://pubs.usgs.gov/twri/twri3-c2/>)

- 1.2. Churn Splitter: A 4-liter or 8-liter churn splitter is recommended.
- 1.3. 1-liter Sampler Bottles: A narrow-mouth 1-liter bottle is used with the WBH-96; a wide-mouth 1-liter bottle is used with the DH-81 and DH-95 samplers.
- 1.4. Sample/lab bottles: Pre-cleaned polyethylene bottles, as specified by the laboratory. Ensure that sample bottles are in a clean state or have been thoroughly cleaned before reuse. Where ever possible, do not use sample bottles from high concentration samples for low level events.

- 1.5. Preservatives as required by the laboratory, e.g., nitric acid (HNO_3), sulfuric acid (H_2SO_4), magnesium carbonate (MgCO_3), etc.
- 1.6. Filtration apparatus
 - 1.6.1. Filters with a pore size of 0.45 μm are recommended, however, 0.7 μm GFF filters are acceptable.
 - 1.6.2. Filter supports may be capsule, syringe, or a tower unit with a glass fritted base.
- 1.7. Vacuum pump and lean Masterflex tubing;
- 1.8. Water-quality meters for DO, temperature, pH, conductivity;
- 1.9. Field forms and permanent ink pens;
- 1.10. Field folders containing the following:
 - Site-specific sampling procedures
 - Directions to both the sampling location and gaging station
 - Table of velocities vs. stage height
 - Job Hazard Analysis
 - Traffic Safety Plans;
- 1.11. Cleaning supplies (tap water, DIW, non-phosphate detergent mix, 5 % HCl acid rinse, baking soda to neutralize the used acid-rinsed water);
- 1.12. Disposable, powderless gloves; and
- 1.13. Safety equipment: Orange safety vest, flotation device (pfd, float coat), hip-boots, chest waders, traffic safety cones.

2. Sample Collection – Primary Stations

The procedures that follow are used for the collection of routine, storm event and routine, storm-impacted sample types.

- 2.1. Determine the number of equal width increments (EWI) in the cross-section, based on the width of the stream channel. The minimum number of verticals required is listed in Table V-5. An odd number of vertical samples is specified to facilitate the reporting of median values for the *in-situ* parameters (pH, temperature, specific conductance, and dissolved oxygen).

- 2.2. Measure the increments according to the procedure in *USGS National Field Manual(NFM) for the Collection of Water-Quality Data, Chapter A4, Collection of Water Samples* (p.45-53)
http://water.usgs.gov/owq/FieldManual/chapter4/pdf/Chap4_v2.pdf
 - 2.3. On each sampling day, record the stream discharge or stage height from the gaging station or from real-time reports on the USGS website.
 - 2.4. Select the appropriate sampling device based on flow conditions, safety, and the type of sampling being collected. If the discharge exceeds 1.5 ft/s, depth-integrated, isokinetic samples must be collected at the mid-point of each EWI across the stream channel. This applies to both routine and storm event samples. See Table V.4 for details.
 - 2.5. Isokinetic, depth-integrating samplers such as the DH-81 and DH-95 are to be used when the velocity of the stream is 1.5 ft/s or greater. Each sampler/nozzle combination has an optimum transit rate for surface to bottom collection. Refer to the NFM (2006), *Appendix A4 -Transit Rate and Volume Guidelines and Filling Times for Isokinetic Samplers*.
 - 2.6. If the velocity of the stream is < 1.5 ft/s it may not be feasible to collect an isokinetic sample. In this case it is acceptable to obtain one or more depth-integrated grab samples. If the stream is at least 2-3 ft. deep, depth integration with a DH-59 sampler is feasible.
 - 2.7. Pre-determine the vertical transit rate by starting at the increment with the largest discharge (depth x velocity) to find the maximum transit rate. Lower and raise the sampler at the same rate – if the sampler overflows, discard the sample and repeat the collection at a faster rate. If under-filled, discard and repeat at a slower rate until the appropriate volume is obtained.
 - 2.8. Beginning at the first increment, lower the sampler at the pre-determined rate until a few inches from the bottom, then immediately raise it to the surface using the same rate. The designated “clean-hands” person removes the sample bottle and empties the contents into the churn splitter. The reel operator should not touch the sample bottles.
 - 2.9. Sample the remaining intervals using the same transit rate as in the first increment, compositing them in the churn splitter. (See Section 4. below.) The volume of sample may be less in the remaining verticals.
3. Sample Collection – Supplemental Stations
 - 3.1. It is recommended that supplemental stations be sampled according to primary station procedures.
 - 3.2. If it is not possible to collect the number of verticals in Table V.5, at least one depth-integrated sample is to be collected at the centroid of flow. This is the point where half of the flow is to the left, and half is to the right.
 - 3.3. Isokinetic samplers are recommended for discharges ≥ 1.5 ft/s to produce more representative suspended sediment and total phosphorus data.

Station Type	Discharge	Sample Type	Sampler	Number of Samples
Primary	≥ 1.5 ft/s	EWI, Isokinetic Depth-integrated	Hand Held: DH-81 or DH-95 Cable & Reel: D-95 or D-77	See Table V.5
	< 1.5 ft/s	EWI, Depth-integrated	Weighted Bottle: DH-59	See Table V.5
Supplemental	≥ 1.5 ft/s	Isokinetic, Depth-integrated	DH-81, DH-95	1 centroid, or Table V.5
	< 1.5 ft/s	Depth-integrated	Weighted Bottle: DH-59	1 centroid, or Table V.5

Table 5.2 Minimum Requirements for Nontidal Network Sample Types

Width of Waterway (ft.)	Minimum # of verticals*
0-25	1
25-100	3
100-250	5
250-500	7
>500	9

*Routine and storm event sampling

Table 5.3 Minimum Number of EWI Vertical Samples at Primary Stations

4. Compositing

- 4.1. Empty the EWI subsamples into a pre-cleaned churn splitter. Collect sufficient subsample volumes for at least 3.35 liters of composited sample in a 4-liter churn; or at least 5.25 liters in an 8-liter churn. If the volume of sample in the churn is insufficient, collect a second, identical set of EWI subsamples across the channel.
- 4.2. Follow the procedures below to fill sample bottles. (Adapted from the USGS National Field Manual, Chapter 5. <http://water.usgs.gov/owq/FieldManual/chapter5/pdf/chap5.pdf>)
- 4.3. Take precautions to avoid sample contamination. Prepare a clean work area at the site or in the van for processing samples. Designate a “clean hands” person to churn and handle the sample bottles. The use of disposable, powderless gloves is highly recommended while dispensing and filtering the samples.
- 4.4. Churn the composite sample at a uniform rate by raising and lowering the disk inside the churn splitter with smooth, even strokes.
- 4.5. When churning, the disk should touch the bottom on every stroke, and the stroke length should be as long as possible without breaking water surface. Do not break the surface of the water.
- 4.6. The churning rate should be about 9 inches per second (in/s). Inadequate churning can result in withdrawal of misrepresentative whole-water or suspended-material samples.
- 4.7. Pre-mix the composite sample by churning for about 10 strokes to uniformly disperse suspended material before subsampling.
- 4.8. Continue churning while subsampling. Dispense whole water samples first, in the following order:
 - 4.8.1. Suspended Sediment and TSS
 - 4.8.2. Particulate Nitrogen and Carbon
 - 4.8.3. Chlorophyll
 - 4.8.4. Whole water samples
 - 4.8.5. Dissolved parameters to be filtered on site
- 4.9. Do not interrupt the churning/subsampling process, if possible. If an interruption occurs, reestablish the churning rate and remix the sample by churning ten strokes before resuming subsampling.
- 4.10. As the volume of composite sample in the churn decreases, adjust the stroke length to maintain a churning rate of about 9 in/s and avoid breaking the surface of the water being sampled.

5. Sample Processing and Preservation

5.1. Whole water samples:

- 5.1.1. SSC samples from the churn splitter may be held at room temperature for 120 days. Ship the samples prior to September 1st so that the results are available for water-year based data analyses.
- 5.1.2. If the laboratory is to filter the samples, place whole-water nutrient and TSS samples in a cooler on ice ($4 \pm 2^{\circ}\text{C}$).

5.2. Field Filtered Samples

Samples are filtered in the field using a vacuum or peristaltic pump and a cleaned length of Masterflex tubing. Most sampling groups use Gelman® 0.45 µm capsule filters, although 0.7 µm GF/F filters are also acceptable. Hand pumps and syringe filters are also acceptable.

- 5.2.1. *Dissolved ammonium, nitrite, nitrate + nitrite, orthophosphate, nitrogen, phosphorus, and organic carbon*: Samples for dissolved constituents should be filtered in the field, or before the end of the sampling day. Using a new filter for each sample, rinse the filter and receiving vessel with dissolved sample water.
- 5.2.2. Collect sufficient sample filtrate to rinse and fill necessary bottles. If required by the laboratory, add acid preservative to the samples for ammonium, nitrate + nitrite and DOC analyses. Place the samples on ice ($4^{\circ}\pm 2^{\circ}\text{C}$).
- 5.2.3. *Total suspended solids (TSS)*: Shake the sample and pour quickly into a graduated cylinder a known volume (50-1000 mL) and filter the aliquot through a pre-rinsed, tared, 47mm GF/F filter. Rinse the filter and residue three times with DI water, allowing the suction to dry the residue after the final rinse. If the filtrate is to be used for dissolved parameters, dispense the filtrate into sample bottles prior to rinsing. Place the TSS filter in a plastic case or foil pouch and immediately put in a cooler on ice ($4 \pm 2^{\circ}\text{C}$).
- 5.2.4. *Particulate carbon and particulate nitrogen*: Shake the sample and pour quickly into a graduated cylinder a known volume (25-500 mL) of sample and filter through a 13 mm GF/F filter. Keep the vacuum at or below 10in. Hg (5 psi) while filtering. Do not rinse the filter. Place the filter into a plastic case or foil pouch and immediately put in a cooler on ice ($4 \pm 2^{\circ}\text{C}$).
- 5.2.5. *Chlorophyll*:
 - 5.2.5.1. Immediately after collecting the sample, shake and pour quickly into a graduated cylinder to a known volume and filter the sample aliquot through a glass fiber filter to concentrate the algae. Use sufficient sample (100-1500 mL) to produce a green color on the filter pad. To avoid cell damage and loss of contents during filtration, do not exceed a vacuum of 12 in. Hg (≤ 6 psi or ≤ 40 kPa), or a filtration duration greater than 10 minutes. Do not suck the filter dry with the vacuum; instead slowly release the vacuum as the final

volume approaches the level of the filter and completely release the vacuum as the last bit of water is pulled through the filter. Add 1mL of saturated MgCO_3 solution during the last few seconds of filtering.

5.2.5.2. Remove the filter from the fritted base with tweezers, fold once with the particulate matter inside, lightly blot the filter with a tissue to remove excess moisture and place it in a Petri dish or other suitable container. Wrap the container in aluminum foil to protect the phytoplankton from light and store the filter at -20°C . Processed filters may be stored for up to 12 hours (DISCUSS?) on ice before storing at -20°C . The residue on the filter may be stored in the dark at $-20 \pm 2^\circ\text{C}$ for 28 days before extracting the pigments.

5.2.5.3. Chlorophyll samples that cannot be filtered immediately after collection may be held at $4 \pm 2^\circ\text{C}$ in the dark for 4 hours before the plankton are concentrated, however any delay is strongly discouraged due to the possible growth or lysis of phytoplankton cells.

5.3. Labeling

5.3.1. Follow the sampling agency's protocol for labeling sample bottles.

5.3.2. Sediment bottles for the USGS Sediment Laboratory in Kentucky must be labeled with the following:

5.3.2.1. Collection site numbers

5.3.2.2. Date and Time

5.3.2.3. Discrete or composite sample (if composite, by transect or time)

5.3.2.4. Constituents: SSC and/or particle size. (Both analyses can be done from the same bottle.)

5.4. Sample Handling and Transportation

Deliver the nutrient and TSS samples to the laboratory as soon as possible, preferably at the end of the day, or ship them on ice for next morning delivery. If the water samples must be held overnight, refrigerate them at $4 \pm 2^\circ\text{C}$. Filters for chlorophyll-*a* and particulate parameters must be frozen overnight at $-20 \pm 2^\circ\text{C}$.

6. Field Blanks

6.1. *Definition and Purpose*

6.1.1. A NTN field blank (FB) is an aliquot of deionized water, free of the analytes of interest, which is placed in a sample container in the field and treated as a sample in all respects, including exposure to sampling site conditions, processing, preservation, storage and all analytical procedures. Field blank results are used to evaluate the extent or lack of positive bias in the

associated WQ data. Because a field blank is treated exactly like an environmental sample at the laboratory it includes any contamination introduced during laboratory handling and analysis.

6.1.2. A field blank is prepared in the field and used to demonstrate that: (1) equipment has been adequately cleaned to remove contamination introduced by samples obtained at previous sites; (2) sample collection and processing have not resulted in contamination; and (3) sample handling and transport have not introduced contamination. (USGS 1997.) [Quality-Control Design for Surface Water Sampling in the National Water-Quality Assessment Program](#)

6.1.3. Blanks are required for laboratory samples only and include all nitrogen, phosphorus, carbon, TSS and sediment species routinely requested by each Data Collector. Field blank data for state-required parameters such as alkalinity, chloride, sulfate, etc., may be submitted and made available through the CEDR.

6.2. Site Selection and Frequency (Representativeness of bias estimates)

6.2.1. Each sample collection group (see Table D1, below) is to collect FBs throughout the year, in proportion to the number of NTN stations that are routinely sampled. A minimum frequency of 1 blank per station per year is required. If a sampling group has fewer than 4 stations, the collection of quarterly blanks is recommended.

6.2.2. Collect the field blanks during storm and routinely-scheduled events throughout the year to ensure that a variety of flow conditions and seasonal variability of concentrations are well represented. **The Addendum at the end of this document provides an example of an unbiased randomized procedure to obtain FBs representative of the variations in these conditions throughout the year and from year to year.**

6.3. Preparation of Field Blanks

FBs are to be prepared at the sampling site **prior to** collecting the water-quality samples. They are created by pouring blank water into the sample collection bottle and transferring it to the churn splitter. This process is repeated the same number of times routinely required to obtain the associated WQ sample at that NTN Monitoring site. The composite sample is then sub-sampled, processed, preserved and handled exactly the same as done for the WQ samples.

6.4. Reporting Field Blank Results

- 6.4.1. Laboratories are to quantify and report all field blank results above the method detection limit (MDL) to ensure that low-level contamination is not a significant contributor to low-level WQ concentrations just above the reporting limit.
- 6.4.2. For FBs >MDL, data collectors and/or agency staff will investigate potential sources of contamination and assess the significance of the contamination. Corrective action is required for significant problems, especially for chronic detections above a reporting limit.
- 6.4.3. Agencies will assign all FB detections \geq MDL with one of the Problem Codes cited below.
- **UB** – Isolated **or initial** occurrence of contamination; the source of contamination unknown, with no apparent effect on associated WQ parameter concentrations.
 - **BB** – Spurious or persistent contamination which appears to affect the field blanks only. Contamination is related to the manner, equipment or supplies used to obtain the blank, such as contaminated source water.
 - **CB** – Spurious or persistent contamination, which appears to reflect the manner, equipment or supplies used to obtain blanks AND water quality samples.

The use of these problem codes informs end-users of FB data of the implications of the contaminated FB. It also permits aggregation (normalization) of FB results beyond the individual Data Collector level. For further information, see report by the USGS NAWQA monitoring program¹.

6.4.4. Definition of Biased WQ Data

DUET has initially adopted a decision criterion that if a FB concentration is \geq 10% of the associated WQ concentration, the latter is considered biased and electronically assigns the Problem Code “BM” to the water-quality data collected on that day.

¹ *Quality of Nutrient Data from Streams and Ground Water Sampled During Water Years 1992–2001*, by David K. Mueller and Cindy J. Titus. URL: <http://pubs.usgs.gov/sir/2005/5106/pdf/sir2005-5106.pdf>

7. Field duplicates

7.1. Definition and Purpose

7.1.1. A field duplicate sample set consists of two samples collected and processed so that the samples are considered to be essentially identical in composition. The purpose of collecting field duplicate samples is twofold: 1) to estimate the reproducibility of water-quality sample measurements and 2) to provide water-quality data from those samples.

7.1.2. Field duplicate (split) samples are usually taken in the field from a single container (e.g., churn) which contains a composite stream sample. Field duplicate samples (FS1 & FS2) provide a measure of the variability introduced during sample processing and laboratory analysis.

7.1.3. Alternatively, collectors may choose to prepare concurrent duplicates, which consist of concurrently collected EWI samples that are poured into two separate containers (e.g., churns) and then processed as individual samples. These duplicate samples (S1 & S2) include the added variability of filling the sampler bottle with water.

Note: Sequentially collected and processed duplicates are unacceptable.

7.2. Site Selection and Frequency (Representativeness of precision estimate)

7.2.1. Each sample collection group is to prepare field duplicate samples throughout the year that are representative of the WQ samples being collected, through randomized site selection, and with stratification across flow conditions.

7.2.2. The minimum number of field duplicates is 2 pairs of duplicate samples per station per year, which is 10% of the samples.

7.2.3. Sample collection groups (see Table D1) with more than 12 stations may limit the number of pairs of duplicate samples to 24 per year (i.e., 2 pairs per month), making sure that all stations have at least one duplicate pair per year.

7.2.4. The Addendum at the end of this document provides an example of an unbiased randomized procedure to obtain duplicate samples representative of the variations in these conditions throughout the year and from year to year.

7.3. Preparing Duplicate Samples

7.3.1. A split duplicate (FS1/FS2) sample pair is prepared by dividing a single volume of water into two sets of samples. Mix and dispense the particulate and whole water duplicates first, then the dissolved parameter FS1/FS2 sets last. (See Fig. A)

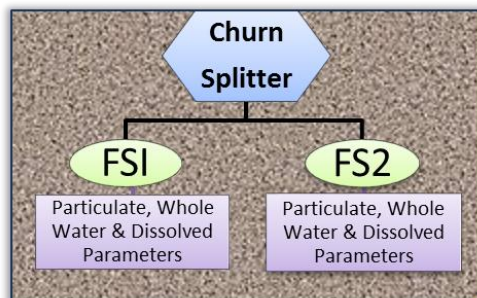


Figure A. Field Split Duplicates

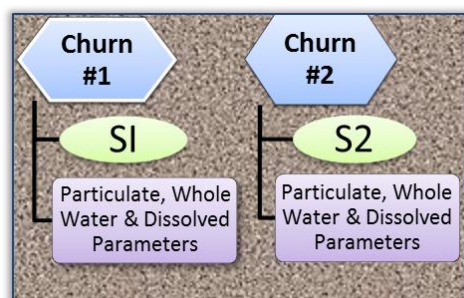


Figure B. Concurrent Field Duplicates

7.3.2. A concurrent field duplicate pair is prepared by collecting a second aliquot of sample immediately after the first at each equal-width increment (EWI). Place two or more aliquots from a single EWI into two separate churn splitters. Process the water from each churn to prepare a pair of concurrent duplicate samples. Label and report concurrent duplicates as sample types S1 and S2. (See Fig. B)

7.4. Reporting Field Duplicate Results

7.4.1. It's important for laboratories to report analytical results for field duplicates to at least 3 significant figures to obtain the most accurate estimates of precision². Low concentrations near the MDL are typically reported to one or two significant figures but in the case of field duplicate samples, request that the lab submit unrounded low- concentration data to at least 3 figures. For example, the value 0.005 has only one significant figure and the raw, unrounded version of this value is needed.

7.4.2. Another exception for field duplicate data involves those rare cases where one or both field duplicates fails a consistency check (e.g., TDP > TP). Data collection groups should evaluate both field duplicates for consistency and assign an appropriate problem codes for failures, however, unlike normal data, failed duplicate results must be reported along with the problem code "NQ". This practice is necessary to obtain representative QC data, even if the sample data would normally be censored.

² Review of Trace Element Blank and Replicate Data Collected in Ground and Surface Water for the National Water-Quality Assessment Program, 1991–2002, by Lori E. Apodaca, David K. Mueller, and Michael T. Koterba. URL: http://pubs.usgs.gov/sir/2006/5093/sir_2006-5093.pdf

After the precision calculations are completed, DUET will censor the “NQ” coded data prior to uploading to CIMS. Similarly, the unrounded low concentration data will be rounded to the appropriate decimal place prior to the upload. All original duplicate sample data, including the unrounded and uncensored results, will be archived and made available through a request to the CBP NTN Project Data manager.

7.5. Precision Problem Codes

DUET will calculate the Relative Percent Difference (RPD) using field duplicates to assess a combined field and laboratory precision. If RPD values exceed 30% for particulate parameters (i.e., PN, PP, PC, TSS, SSC and Chlorophyll), or 20% for dissolved and total N, P, or C parameters, *and* the both reported values are above the reporting limit, the Precision Problem Code “HI” will be added to the CIMS database. These qualifiers are subject to change once sufficient duplicate data are generated from which to establish different precision objectives.

8. Documentation and Records

Field sheets, calibration records, log books and laboratory forms must be maintained to permit a complete historical reconstruction of the data back to the calibration standards, sample volumes and preservatives used. A unique sample number or ID must be assigned to each sample processed. See Chapter II.4 for additional document control protocols.

9. Decontamination

- 9.1. Cleaning procedures are detailed in the USGS NFM, *Chapter 3.2.1 – Cleaning of Equipment Used to Sample for Inorganic Constituents*. Two deviations from the National Field Manual are permitted: 1) the time for soaking the churn splitter in detergent solution may be less than 30 minutes, and 2) the use of 5% HCl for rinsing equipment is optional.
- 9.2. Start the cleaning procedures as early as possible after processing. Soak the churn splitter as close to 30 minutes as feasible given the time constraints of the day. Do preservation, paperwork, and packing of samples in the interim.
- 9.3. If cleaning the equipment in the field (e.g., sampler, churn splitter, filtration units), it is recommended that a 5-gallon polyethylene container for each solution below be transported in the vehicle.
 - 9.3.1. Detergent water (0.1 percent v/v ratio of Liquinox: tap water)
 - 9.3.2. Tap water
 - 9.3.3. 5% Hydrochloric Acid, ACS grade (this rinse is optional)
 - 9.3.4. Deionized Water

SECTION C

FIELD MEASUREMENTS

1. Field Measurement Procedures

1.1. *Parameters:* *In-situ* field measurements shall be collected for pH, dissolved oxygen, temperature, and specific conductance (at 25 °C).

1.2. *Equipment:* A multi-parameter instrument or a combination of meters that can provide these same measurements.

1.3. Calibration

1.3.1. All probes must be calibrated according to the manufacturers' recommended methods. Field staff must document calibration, maintenance and repair information for each instrument and sensor in logbooks using permanent ink.

1.3.2. *Specific Conductance sensor:* The conductivity sensor must be calibrated against a reference solution, according to manufacturer's specifications. As a minimum, conductivity should be verified before and after each sampling date using standards that bracket the expected range.

1.3.3. *pH sensor:* The pH sensor should be calibrated at the beginning of every sampling event using two standard solutions of pH 4, pH 7 or pH10 buffer solutions. The standards should bracket the expected pH of the streams. Follow the manufacturer's instruction for cleaning and storing the pH probe. If the post calibration drift is ± 0.2 pH units or more, censor all pH data back to the last calibration with the problem code "V".

1.3.4. *Dissolved oxygen (DO) sensor:* The DO sensor must be fully calibrated at the beginning and end of each multiple-day cruise according to manufacturer's specifications. Typically, DO sensors are calibrated against water-saturated air.

Check the DO calibration at the beginning of each sampling day. If daily checks drift by ± 0.3 mg DO/L or more, the sensor must be serviced and recalibrated before using again. If post-calibration drift is ≥ 0.5 mg/l, censor all DO data back to the last calibration with the problem code "V".

1.3.5. *Thermistor:* Check the agreement of the thermistor reading at least once a year against a NIST certified thermometer over a range of temperatures.

1.4. Procedure

- 1.4.1. Temperature, and DO measurements **must** be collected *in-situ* at the center of each width increment from which samples are collected. Do not take measurements on a discrete sample and avoid taking measurements near the stream banks, or in sections with turbulence or high velocities.
- 1.4.2. Lower the sensors below the surface and allow at least 1 minute to equilibrate. When stable, record the values on the field data sheet or data logger. Move to the next EWI in the cross-section and repeat the procedure.
 - 1.4.2.1. Record all readings and report the median temperature and median DO values within the cross-section.
- 1.4.3. Specific Conductance should be measured *in-situ* at the center of each EWI increment. (If this is not feasible, measure the conductivity of a composite sample dispensed from the churn splitter. Do not take conductivity and pH measurements on the same discrete sample because the pH electrode solution may contaminate the sample and affect the specific conductance.)
 - 1.4.3.1. The use of a temperature-compensating instrument is recommended so that manual temperature corrections are unnecessary.
 - 1.4.3.2. Lower the conductivity sensor below the surface and gently move it up and down to remove trapped air bubbles. Continue moving until the meter display stabilizes. Record the value on the field data sheet and then move to the next EWI in the cross section and repeat the procedure above.
 - 1.4.3.3. Record all readings and report the median specific conductance and pH values to three or more significant figures.

SECTION D

LABORATORY METHODS

Table 5.5 Laboratory Methods for Chesapeake Bay Nontidal Water Quality Network

Parameter	Recommended Method
Total Nitrogen, as N (TN)	Standard Methods - 20 th ed. 4500-N C
Ammonium, as N (dissolved) (NH ₃ F)	EPA 350.1
Nitrate + Nitrite, as N (dissolved) (NO ₂ 3F)	EPA 353.2
Total Phosphorus, as P (TP)	EPA 365.1 or 365.4
Phosphate, as P (dissolved) (PO ₄ F)	EPA 365.1
Total Suspended Solids (TSS)	Standard Methods - 20 th ed. 2540 D, or USGS I-3765
Suspended Sediment Concentration (SSC)	ASTM 3977-97, Method B (filtration)
Suspended Sediment – Coarse (> 62 µm)	ASTM 3977-97, Method C (wet sieve)
Suspended Sediment – Fine (< 62 µm)	ASTM 3977-97, Method C
Total Dissolved Phosphorus (TDP)	Acid or alkaline persulfate digestion, then EPA 365.1
Total Dissolved Nitrogen (TDN)	Standard Methods - 20 th ed. Method 4500-N C (alkaline persulfate)
Particulate Nitrogen (PN)	EPA 440.1
Particulate Carbon (PC)	EPA 440.1
Total Organic Carbon (or Particulate C)	Standard Methods - 20 th ed. Method 5310 B
Dissolved Organic Carbon (DOC)	Standard Methods - 20 th ed. Method 5310 B
Chlorophyll- <i>a</i> (CHLA)	Standard Methods - 20 th ed. Method 10200H
Volatile Suspended Solids (VSS)	Standard Methods - 20 th ed. 2540 E, or

	USGS I-3765
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Table 5.6 NTN Sample Collection Groups for Field Blank and Duplicate Sample Frequency Determinations					
AGENCY	SOURCE	STATION_TYPE	EVENT_TYPE	STATIONS	FREQUENCY
DEDNREC	DEDNREC	Primary	R, RSI, S, ONS or OS	304191, 302031	
	USGSWV	Primary	R, RSI, S, ONS or OS	01604500, 01608500, 01616500, 01613030, 01616400, 01611500, 01618100	
USGSWV	USGSWV	Primary	R, RSI, S, ONS or OS	01595300, 01614000, 01636500	
SRBC	SRBC	Primary	R, RSI, S, ONS or OS	01502500, 01503000, 01529500, 01511500	
SRBC	SRBC or NYSDEC	Primary	R, RSI, S, ONS or OS	01515000, 01531000	
MDDNR	MDDNR	Primary	R, RSI, S, ONS or OS	TUK0181, BEL0053, DER0015, GUN0258, NPA0165, GWN0115, PXT0972, TF1.2, GEO0009, WIL0013, ANT0047, CAC0148, MON0546, LXT0200, MGN0062, NWA0016, WCK0001, MKB0016, CVA0046, WIL0065	
MDDNR	USGSMD	Primary_RIM	R, RSI, S, ONS or OS	01491000, 01578310, 01594440, 01646580	
PADEP	SRBC	Primary	R, RSI, S, ONS or OS	WQN0201, WQN0214, WQN0273, WQN0301, WQN0305, WQN0401, WQN0204, WQN0210, WQN0223, WQN0229, WQN0243, WQN0263, WQN0271, WQN0272, WQN0302, WQN0404, WQN0445, WQN0448, WQN0226, WQN0281, WQN0282	
PADEP	USGSPA	Primary	R, RSI, S, ONS or OS	WQN0317, WQN0410, WQN0224, WQN0217, WQN0212, WQN0269, WQN0278, WQN0280	
PADEP	PADEP	Primary	R, RSI, S, ONS or OS	WQN0501, WQN0509, WQN0510, WQN0511, WQN0512, WQN0513	
VADEQ	USGSVA	Primary_RIM	R, RSI, S, ONS or OS	TF5.0A, TF4.0P, TF5.0J, TF3.0, TF4.0M, 2-JMS113.20	
VADEQ	USGSVA	Primary	R, RSI, S, ONS or OS	1BNFS010.34, 1BSMT004.60, 1BSSF003.56, 2-CHK035.26, 2-JMS113.20, 3-RAP030.21, 8-NAR005.42, 1BMDD005.81, 1ADIF000.86, 7-DRN010.48,	

Table 5.6 NTN Sample Collection Groups for Field Blank and Duplicate Sample Frequency Determinations

AGENCY	SOURCE	STATION_TYPE	EVENT_TYPE	STATIONS	FREQUENCY
VADEQ				1ASOQ006.73, 8-PCT000.76	
	VADEQ/SCRO or USGSVA	Primary	R, RSI, S, ONS, or OS	2-JMS279.41, 2-APP110.93	
	VADEQ/NRO or USGSVA	Primary	R, RSI, S, ONS, or OS	1AACO014.57(MD/USGSVA), 3-RPP147.49, 8-MPN094.94	
	VADEQ/VRO or USGSVA	Primary	R, RSI, S, ONS, or OS	2-RVN015.97, 1BSSF100.10	
	VADEQ/NRO	Secondary	R (but w possibly RSI flows) or ONS	3-RAP066.54, 3-ROB001.90, 8-POR008.97, 1ACAX004.57→MDNR(1°)	4 blanks, 4duplicates (quarterly)
	VADEQ/VRO	Secondary	R (but w possibly RSI flows) or ONS	1BSTH027.85, 2-BCC004.71, 2-BLP000.79, 2-CFP004.67, 2-MCM005.12, 2-MRY014.78	
VADEQ	VADEQ/PRO	Secondary	R (but w possibly RSI flows) or ONS	8-LTL009.54, 2-DPC005.20	4 blanks, 4duplicates (quarterly)

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2. 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>.
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