Appendix D
INTERIM GUIDANCE FOR NONTIDAL NETWORK
WY 2013 FIELD BLANK AND DUPLICATE SAMPLE COLLECTION
March 12, 2013

Introduction

The Nontidal Data Upload and Evaluation Tool (DUET) will include pre-programmed subroutines to generate statistical measures of the completeness, precision and bias of nontidal network (NTN) monitoring data. These statistics will enhance the ability of end users to comprehend, use and defend the data.

Programming for the required or "expected" number and types of water quality (WQ) and quality control (QC) samples, as originally determined by the Nontidal Workgroup, has been difficult due to: 1) insufficient detail in the guidance and 2) implementation differences among agencies, such as the collection of additional WQ samples and different types of QC samples.

The following interim guidance is meant to address these problems for collecting and reporting WY2013 nontidal data. Specifically, this guidance provides:

- Standard names, definitions and preparation procedures for NTN field blank and field duplicate samples to improve comparability among agencies, and

- A QC-sampling design for WY 2013 that will improve the representativeness of QC concentration data across time and space by sampling a variety of locations, flow conditions and months. The frequency of QC sample collection is proportional to the number of stations sampled by each collection group.

Field Blank Sample Collection for WY 2013

The current guidance for collecting NTN field blank samples appears in Chapter V – Nontidal Water Quality Monitoring, Section B - Sampling Procedures as follows:

> 6.1 **Field blanks**: A field blank is an aliquot of DI water that mimics the sampling procedures. Prepare at least one field-filtered blank per month for both dissolved and particulate parameters. Pour the DI water into the sampler bottle, churn splitter, graduated cylinder and through the filters, exactly the same as the samples. If the concentration of an analyte in the field blank exceeds the laboratory MDL, equipment contamination should be suspected and investigated to identify the source of contamination.

In addition to the above procedures, the following guidance is desired for WY 2013.

A. Definition and Purpose of NTN Field Blanks

- 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.

- USGS: "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." Quality-Control Design for Surface Water Sampling in the National Water-Quality Assessment Program

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

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.

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.

C. WQ Parameters

Blanks are required for laboratory parameters only. They must cover the lab-analyzed nitrogen, phosphorus, TSS and sediment parameters routinely collected by each Data Collector. Field blank results for additional parameters may be submitted, but may not be evaluated by DUET.

D. Preparing a Field Blank Sample

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 WQ samples.

E. Reporting Field Blank Results

It's important that the laboratory 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. Assign all FB detects ≥ MDL with one of the Problem Codes cited in Section F. below to avoid erroneous conclusions using FB information. See report by the USGS NAWQA monitoring program[1].

[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

F. Identify Source(s) of Contamination and Implications: *Problem Codes For Field Blanks >MDL*

Consistent with existing 2008 NTN Guidance, investigate potential sources of contamination in FBs > MDL. When reporting FB concentration data, use one of the following Problem Codes to indicate source of contamination:

- **UB** – Isolated or initial occurrence of contamination, source of contamination unknown, with no apparent effect on associated WQ parameter concentrations.
- **BB** – Spurious or persistent contamination which appears to affect 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.

G. Tentative Definition of Biased WQ Data

DUET has initially adopted a decision criterion that if a FB concentration is ≥ 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. Once sufficient FB data are collected (e.g., 1 or 2 years) the NT Workgroup may decide to adjust the ≥ 10% criterion.

Field Duplicate Sample Collection for WY2013

The current guidance for collecting NTN field duplicate samples appears in Chapter V – Nontidal Water Quality Monitoring, Section B - Sampling Procedures as follows:

> 6.2 **Field duplicates:** Two representative portions are taken from one homogeneous churn sample and processed identically. Field duplicate data provide an indicator of sample preparation and analytical reproducibility (precision). The minimum frequency for collecting a field duplicate sample is one per month or once for every 20 samples.

In addition to the above procedures, the following guidance is desired for WY 2013.

A. Definition and Purpose of Field Duplicate Samples

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.

B. Acceptable Types of Duplicate Samples

Field duplicate (split) samples are usually taken in the field from a single container (e.g., churn) which contains a composite stream sample. These fields split samples are labeled FS1 & FS2.

Alternatively, the collector may choose to collect concurrent duplicates, which consist of concurrently collected interval samples that are transferred into to two separate containers (e.g., churns) and then processed as individual samples. These duplicate samples are labeled S1 & S2. Note: Sequentially collected and processed duplicates are unacceptable.

C. Site Selection and Frequency (Representativeness of precision estimate):

Each sample collection group is to routinely prepare field duplicate samples throughout the year which are representative of the WQ samples being collected, through randomized site selection, with stratification across flow conditions. The minimum number of field duplicates is 2 pairs of duplicate samples per station per year, which is 10% of the samples.

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.

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.

D. WQ Parameters

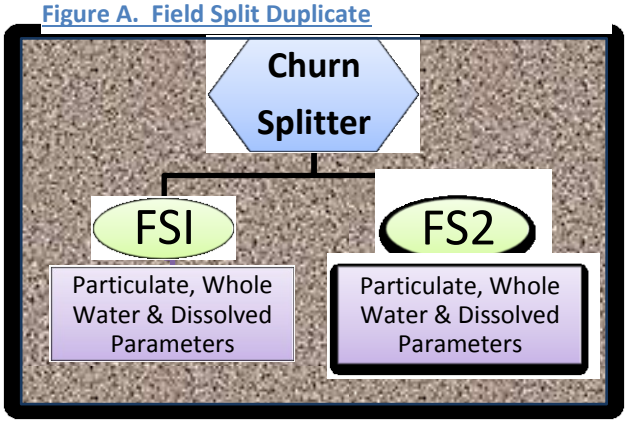
Field duplicates are required for laboratory parameters only, not the *in-situ* measurements. However, provide field measurements for one of the duplicates so that it may serve as a complete environmental sample.

Data Collectors often have duplicate results for parameters other than those required by the NTN (chloride, alkalinity, BOD, etc.) These results may be submitted through DUET; however DUET will evaluate only the precision of the nitrogen, phosphorus and sediment species.

E. Preparing Duplicate Samples

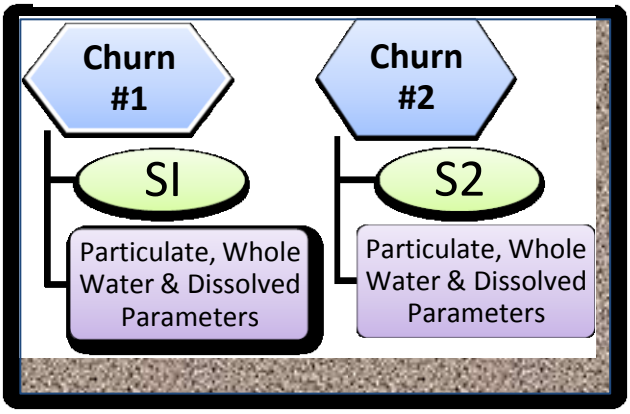
A split duplicate is prepared by dividing a single volume of water into two sets of samples. Field split duplicate samples provide a measure of the variability introduced during sample processing and laboratory analysis. Mix and dispense the particulate and whole water FS1 and FS2 duplicates first, then dissolved parameter FS1/FS2 sets last. (See Fig. A)

Figure A. Field Split Duplicate



A concurrent field duplicate pair is prepared by collecting a second aliquot of sample immediately after the first at each equal-width interval. These duplicates measure the added the variability from filling the sampler with water. Place each aliquot 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)

Figure B. Concurrent Duplicate



F. Reporting Field Duplicate Results

It's important that laboratories report analytical results for field duplicates to at least 3 significant figures to obtain the most accurate estimates of precision[2]. 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.

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.

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.

[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

G. Acceptance Level or High Imprecision Level

DUET will calculate the Relative Percent Difference (RPD) using field duplicates to assess field and laboratory precision. If RPD values exceed 30% for particulate parameters (i.e., TN, TP, TSS, SSC), or 20% for dissolved and total N, P, or C parameters, *and* the reported values are above the reporting limit, the Precision Problem Code "HI" will be added to the CIMS database. Once there are sufficient data (~1-2 yrs.) the NT Workgroup can choose a different statistic or keep the above limits. The intent at this time is to obtain duplicate data from which to establish realistic precision objectives.

Table D1. NTN Sample Collection Groups for Field Blank and Duplicate Sample Frequency Determinations (New 2013 Stations and Frequencies to be Added)

AGENCY	SOURCE	STATION_TYPE	EVENT_TYPE	STATIONS	FREQUENCY
DEDNREC	DEDNREC	Primary	R, RSI, S, ONS or OS	304191, 302031	
USGSWV	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, 1ASOQ006.73, 8-PCT000.76	
VADEQ	VADEQ/SCRO or USGSVA	Primary	R, RSI, S, ONS, or OS	2-JMS279.41, 2-APP110.93	
VADEQ	VADEQ/NRO or USGSVA	Primary	R, RSI, S, ONS, or OS	1AACO014.57(MD/USGSVA), 3-RPP147.49, 8-MPN094.94	
VADEQ	VADEQ/VRO or USGSVA	Primary	R, RSI, S, ONS, or OS	2-RVN015.97, 1BSSF100.10	
VADEQ	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	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)

Addendum:

An Annual Randomized and Stratified Procedure to Obtain Field Quality Control Samples Representative of Varying Environmental, Weather, and Flow Conditions among Nontidal Network Monitoring Sites during Water Quality Sampling

The objective of QC sampling is to provide FB and DS data that represent the WQ sampling being conducted by each NTN Data Collector for all the NTN stations where similar WQ data are being collected at those Stations (Appendix D, Table D1). If the WQ sampling is to cover all Stations and flow conditions that occur at those Stations throughout a WY, and do this WY after WY, then our QC design should strive to do the same at least over time. However, although our QC sampling can occur at every Station every WY, the frequency of QC sampling is but a fraction of the frequency of WQ sampling at a Station—roughly 5 % for FBs and 10% for DS. So we cannot cover all flow conditions at a Station every WY. So how do we ensure our QC sampling covers those major seasonal variations in environmental conditions at a Station (including weather and streamflow conditions) associated with the WQ sampling? This question is addressed through a fully randomized QC sampling design process that is repeated for each new WY.

Background and Perspective on QC Sampling Design and Process

The QC sampling design and process described below provides a completely randomized design that over time (several WYs) will provide representative QC samples that cover all Data Collector's Stations every WY, at the frequency required for Field Blanks (FBs) and Duplicate Samples (DSs) every WY, and for both nonstorm and storm or storm impacted flows during different seasons of a WY (just not at the same Station). However, if this design process is repeated for every new WY, it also will provide QC data for every Station that accounts for Seasonal x WY variations in the environmental conditions at each Station.

The QC sampling design and process for each WY must be done twice—once for FB collection and again for DS collection. We do not want to make the collection of FBs and DSs totally dependent upon one another for pragmatic reasons. It also is much easier to design their collection independently. That said, both types of QC samples could be collected during the same sample visit to a Station when the independent designs indicate both types of QC samples are to be collected for similar flow conditions during a similar time period and field crews aren't heavily pressed to also sample many other Stations as well.

The QC sampling design and process described below is meant to provide a common starting point for all NTN Data Collectors to determine QC sampling for a given WY. However, as two examples also provided below which utilize this QC design and process will illustrate, a final pragmatic step at the end of the design could be required to actually obtain a meaningful and/or operationally performable QC sampling design.

In addition, as the WY actually unfolds, logic and common sense and safety issues will influence whether or not one can collect the targeted QC sampling of flow conditions at a given Station during the specified time period that this design initially provides. For example, if the design indicates DSs are to be collected at three specific NTN Stations sometime during the months of October through December, and Hurricane Charley hits, does the field crew give up sampling at ten of their NTN Stations in order to collect WQ samples at only 7 of these stations and the DSs as dictated by the design at 3 of those 7 stations? Common sense would say no. But the field crew might take DSs at one of these Stations because the water quality at that Station under such storm conditions is extremely important (for example, that particular Station among all others is a huge contributor to nutrients and suspended sediment at high flows). As another example, what happens if for the same design results above, the region is locked into a severe drought during this time period? Does the field crew not take

any DSs at these three stations because there aren't any storms or storm impacted flows? Again, common sense would dictate that one obtain the QC data for non-storm impacted flows because that in the end was the extended flow condition at each of these Stations during the period QC samples were to be taken at these Stations. However, one also might spread out the DS sample collection at these three Stations during this three-month period on the off chance that a storm could occur in the latter part of the period, rather than take all three DS at these three Stations in the last month of the period.

The QC sampling design and process described below also uses some very simple tools and processes to randomize the QC sampling design. Other truly randomizing tools and techniques no doubt exist and can be used. However, the four-step sequence used makes it simple to carry out the design. However, using the described process, it took only 20 minutes to complete the FB and DS designs for each of two NTN Data Collectors featured as examples of this process. Albeit it did take almost as much time again to obtain and write Station ID's on the markers used for both NTN Data Collectors but these can be saved and added to or removed in Stations change from WY to WY.

The two examples chosen to illustrate the QC sampling design and process are for WY2013 and assume both NTN Data Collectors are sampling the same Stations they were sampling in WY2012, which may or may not be the case. So when the design is repeated each WY it has to be based on the actual Stations as grouped in Appendix D, Table D1 being monitored by an NTN Data Collector for that WY.

The examples chosen also reflect extremes in terms of the number of NTN Stations being sampled for WY2013 year by a NTN Data Collector—2 in one case, 21 in the other. Therefore, the last step in the QC sampling design for each NTN Data Collector modifies the strict result of the design to adjust QC sampling but for different pragmatic reasons for each NTN Data Collector.

Finally, if this QC sampling and design process is used for WY2013, Appendix D, Table D1 reflects WY2012. If Stations have been added or dropped from your Agency x Source (Provider x Collector) group(s), that should be reflected in the design. In addition, the design would be carried out for the entire WY, but would be implemented on whatever is the current period for QC sampling (as of today's date February 20 2013) that would put most NTN Data Collector's in the 2nd quarterly or triennial period of their QC sampling for WY2013.

Randomized Design and Design Process for NTN Quality-Control Sampling

The process described below is for Field Blank (FB) collection for one WY. It is simply repeated for Duplicate Sample (DS) collection for that WY taking into account that twice as many DSs than FBs are to be collected at a NTN Station each WY. The process for FBs and that for DSs would be repeated each WY before sample collection began for that WY. Repeating these processes for FBs and DSs each Calendar Year for the upcoming new WY is essential to ensuring sampling is representative of varying environmental, weather, and flow conditions that can occur at each station within a WY from WY to WY.

For each Agency x Source Group for which your agency is the Source (see Appendix D, Main Text, Table D1, p. 7):

Determine the Number of FBs to collect: Equals the number of NTN Stations being monitored that WY by the NTN Data Collector (Source); given one FB is to be collected per Station per WY. (Assume Source monitors N stations in that Agency x Source Group from Appendix D, Table D1 (WY2012) – annually updated to reflect actual stations in that group for the upcoming new WY).

- **Determine Order of FB Collection at those Stations**: Place an identical type, but station ID labeled, marker for each of the N Stations in a bag; shake and select one marker from the bag without replacement; repeat process until all N markers have been withdrawn. List each marker station ID in the order in which it was withdrawn. The order of Stations selection is the order in which FBs are collected at those Stations during the WY.

- **Determine EVENT_TYPEs for which FBs will be Collected:** For **1st** Station in ordered list, flip a fair coin to determine whether the FB will be collected during a nonstorm impacted (NSI) Event_Type, or a storm-impacted (SI) or storm (S) Event_Type; assign all other "odd" numbered Stations in the ordered list the same Event_Type as that determined for the 1st Station; assign all remaining and "even" numbered Stations on the ordered list the other Event_Type.

- **Determine who collects FBs at Stations where more than one Source Agency is collecting data:** At shared monitoring stations, FB collection is logically distributed among the Source Agencies on the FB Event Types (e.g., USGSVAWSC collects SI/S FBs, VADEQ Regional Offices collect NSI event types at their shared stations) and or their intra-annual periods of monitoring (e.g., NYSDEC collects FBs for only NSI events for half the WY they conduct monitoring; SRBC collects FBs for NSI Event_Types during the other half of the WY they conduct monitoring; in addition, SRBC collects FBs for all S/SI Event_Types throughout the WY).

- **Determine when FBs actually are collected during the WY:** Using the table provided (Appendix D, Addendum, Table D2 below), and given the total number of FBs to be collected (N) in the WY, determine the type and number of FB collection periods, over which the N FBs will be distributed in accordance with the order in which they were listed. This timing schedule effectively provides for the uniform distribution of FB collection throughout the WY across environmental conditions (possible weather x flow (EVENT_TYPES) x Station setting).

- **Final Adjustments to FB collection:** Using of a fixed protocol requiring one FB be collected at each NTN station every WY doesn't provide representative FB data throughout the WY if N is very small (2 stations). It also could adversely affect WQ sampling at many Stations during Storm or Storm-Impacted conditions because of the required high frequency of FB collection each WY when N is very large (12 or more stations). Two examples below illustrate not only how the design process described above is implemented, but also the need to possibly adjust the in FB collection design to clearly avoid obvious limitations in the QC design, better meet the overall QC sampling objective, and (or) avoid having the QC sampling objective override the WQ sampling objective. its intent, and (or) reduce the WQ sampling when it is most needed at many Stations reduce these types of problems.

Appendix D Addendum Table D2. Timing schedule for distributing Nontidal Network (NTN) field blank (FB) or duplicate sample (DS) collection through a Water Year [1]

Total number of Field Blanks, or pairs of Duplicate Samples, to collect per Water Year	Within Water Year timing schedule for Field Blank (FB) or Duplicate Sample (DS) collection
1	Not applicable at present
2	Semiannual: Collect one FB (DS) in each of two sequential 6-month periods of WY
3	Triennially: Collect one FB (DS) in each three sequential 4-month periods of WY
4	Quarterly: Collect one FB (DS) in each of four sequential 3-month periods in the WY
5	Quarterly: Collect one FB (DS) in each of four sequential 3-month periods in the WY, randomly select one 3-month period in which 5th FB (DS) is collected
6	Triennially: Collect two FBs (DSs) in each of three sequential 4-month periods in WY
7	Triennially: Collect two FBs (DSs) in each of three sequential 4-month periods, randomly selected one 3-month period in which the 7th FB is collected
8	Quarterly: Collect two FBs (DSs) in each of four sequential 3-month periods of WY
9	Triennially: Collect three FBs (DSs) in each of three sequential 4-month periods of WY
10	Triennially: Collect three FBs (DSs) in each of three 4 month-periods, randomly selected one three-month period when 10 FB (DS) is collected
11	Quarterly: Collect three FBs (DSs) in three 3-month periods, randomly selecting one 3-month period in WY when only two FBs (DSs) are collected
12	Quarterly: Collect three FBs (DSs) in each of four sequential 3-month periods month in WY
If NTN Workgroup limits FB collection to 12 per Water Year, timing schedules below apply only to DS collection in excess of 12 pairs of duplicate samples per Water Year	
13	Quarterly: Collect three FBs (DSs) in each of four 3-month periods month in WY, randomly select one 3-month period when 13th FB (DS) is collected
14	Triennially: Collect five FBs (DSs) in each of two 4-month periods in WY, randomly select one 4-month period when 14th FB is collected
15	Triennially: Collect five FBs (DSs) in each of three sequential 4-month periods in WY
16	Quarterly: Collect four FBs (DSs) in each of four sequential 3-month periods of the WY
17	Quarterly: Collecting four FBs (DSs) in each of four sequential 3-month periods, randomly selected one 3-month period in which 17th FB is collected
18	Triennially: Collect six FBs (DSs) in each of three 4-month periods of WY
19	Quarterly: Collect five FBs (DSs) in each of three 3-month periods, randomly selected one 3-month period in which 4 FBs (DSs) are collected
20	Quarterly: Collect five FBs (DSs) in each sequential 3-month period of WY
21	Triennially: Collect seven FBs (DSs) in each sequential 4-month period of WY
22	Triennially: Collect seven FBs (DSs) in each sequential 4-month period of WY, randomly selected one 4-month period in which 22nd FB (DS) is collected
23	Quarterly: Collect six FBs (DSs) in each of four 3-month periods, randomly select one 3-month period in which five FBs (DSs) are collected
24	Quarterly: Collect six FBs (DSs) in each of four sequential 3-month periods of WY

[1] All scheduling generally is done on short time period and require such conditions for FBs or DSs. See Addendum text for further discussion. A quarterly or triennial period provides ample time for flow conditions to occur within the specified time intervals at the specific Stations that were randomly selected to be used for FB or DS collection during that portion of the WY. Forcing schedules to monthly or bimonthly periods will increase the likelihood that flow conditions such as storm or storm impacted flows will not occur at the selected Stations that are assigned to such short time periods.

Examples of Quality Control Sampling Designs for Two NTN Data Collectors

First example: Agency x Source Group with few NTN monitoring stations (N=2)

From Appendix D, Main Text Table D1 (p. 7): DEDNREC x DEDNREC x Primary x [304191, 302031]

DEDNREC is Source Agency, and having 2 stations will collect 2 FBs each WY;

1. **Assume order of random selection of stations from bag was:** 302031 then 304191;
2. **Assume random selection of FB Event_Type on basis of coin flip for the 1st station (304191) selected from bag was:** A NSI Event type; implying the 2nd Station (302031) is assigned an S/SI Event_Type.
3. **Using Timing Schedule Addendum Table D2, with N=2, the scheduled timing for FB collection by DEDNREC for their two stations in the order listed would be:** Semiannual, with the first FB, which is to be collected at Station 304191, collected during a monthly fixed time interval WQ sampling event under NSI flow conditions within the October to March period of the WY. The second FB would be collected at Station 302031 during a WQ sampling event under S or SI conditions, or a monthly fixed time interval WQ sampling event under SI flow conditions.
4. **Additional Considerations:** Two FBs per WY for DEDNREC will not provide sufficient QC data to accurately assess the extent of contamination bias if just one of these two FBs is contaminated and that contamination appears to also affect the associated WQ data. With just two FB samples possibly collected many months apart, the paucity of FB data will create considerable uncertainty in the establishment of the actual period of time during which WQ samples were being contaminated. Perhaps DEDNREC also independently obtains other FB data from other non-NTN Stations for all the same possibly biased WQ parameters over the WY with the same sampling and sample processing methods, equipment, supplies, etc., as used at these two NTN sites, and analyzes those FB samples with the same laboratories and laboratory methods used for WQ samples from these two NTN sites, it is recommended that they increase their FB collection to at least quarterly. However, even if they did, how would CBP document that in a way any end user of the NTN data they provide clearly understand that when they saw the WQ parameter and FB data? To avoid the complications the above entails, DEDNREC could at least go to a quarterly FB design (see Table below). To create this design, the two NTN stations markers were randomly chosen to determine their sequential order. The two station markers then were returned to the bag and randomly selected again and added to the ordered station list in the order they were reselected. A coin flip for the 1st Station in the list determined the Event_Types for all four FBs, and with N=4 and Addendum Table D2, the sequential station list was mapped to quarterly sampling. DEDNREC is likely to encounter the appropriate flow conditions sometime during each quarter that are needed at each Station to collect the required FB.

5. The described design process for FB collection for DENREC is repeated for DS. (Only the summary table is provided below.) Because twice as many DS are collected as FBs, we end up with quarterly DS sample collection. Within any given quarterly period where both types of QC samples for a particular Station call for the same flow condition, DEDNREC has the option when those flow conditions occur to collect both types of QC samples on the same sampling visit, For example, this option could be used in third and fourth quarters, but not first or second quarters within the WY.

DEDNREC Field Blank Collection Summary Table

Selection Seq. No.	Station ID	Time period of collection	Event_ Type	Timing schedule
1	302031	1st Quarter	NSI	Either the Oct, Nov, or Dec monthly fixed time interval, whichever has a non-storm impacted (NSI) flow condition.
2	304191	2nd Quarter	S or SI	Storm (S) event in Jan through Mar time period or monthly fixed time interval with a storm impacted (SI) flow condition.
3	304191	3rd Quarter	NSI	Either the Apr, May or Jun monthly fixed time interval, whichever has a non-storm impacted (NSI) flow condition.
4	302031	4th Quarter	SI	Storm event in Jul through Sep time period or monthly fixed time interval with Storm impacted (SI) flow conditions

DEDNREC Pairs of Duplicate Sample Pairs Collection Summary Table

Selection Seq. No.	Station ID	Time period of collection	Event_ Type	Timing schedule
1	30491	1st Quarter	NSI	Either the Oct, Nov, or Dec monthly fixed time interval, whichever has a non-storm impacted (NSI) flow condition.
2	302031	2nd Quarter	S or SI	Storm (S) event in Jan through Mar time period or monthly fixed time interval with a storm impacted (SI) flow condition.
3	304191	3rd Quarter	NSI	Either the Apr, May or Jun monthly fixed time interval, whichever has a non-storm impacted (NSI) flow condition.
4	302031	4th Quarter	SI	Storm event in Jul through Sep time period or monthly fixed time interval with Storm impacted (SI) flow conditions

Second example: Agency x Source Group with many NTN monitoring stations (N=21)

From Appendix D, Main Text, Table D1 (p. 7): PADEP x SRBC x Primary x [21 Stations]
SRBC needs 21 FBs, one per Station, for the WY
Random process: Randomly selected 21 markers individually, sequentially, with shaking, and without replacement from bag; on basis of sequential order withdrawn, coin flip for 1st station, yielded an S/SI Event_Type and assigned all odd-numbered Stations in list that Event_Type, and assigned all remaining even-numbered Stations in the list a NSI Event_Type. Using N=21 and Appendix D Addendum Table D2, the distribution of FB sample collections will be quarterly, with at least 5 FBs taken during three quarters and 6 FBs taken in one randomly selected quarter (for this example, the fourth quarter) during the WY. The summary table below illustrates the FB collection design for 21 FB samples for SRBC (Pennsylvania sites).

SRBC (PA) Field Blank Collection Summary Table

Selection Seq. No.	Station ID	Time period of collection	Event _ Type	Timing schedule
1	WQN0305*	1st Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Dec period
2	WQN0201*	1st Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Oct through Dec period
3	WQN0401*	1st Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Dec period
4	WQN0229	1st Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Oct through Dec period
5	WQN0223	1st Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Dec period
6	WQN0272	1st Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jan through Mar period
7	WQN0273*	2nd Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jan through Mar period
8	WQN0282	2nd Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jan through March period
9	WQN0204	2nd Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jan through Mar period
10	WQN0404	2nd Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jan through March period
11	WQN0271	3nd Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jan through Mar period
12	WQN0210	3rd Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jan through March period

(Table continues on next page)

SRBC Field Blank Collection Summary Table for Pennsylvania, continued

Selection Seq. No.	Station ID	Time period of collection	Event _ Type	Timing schedule
13	WQN0214*	3rd Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Dec period
14	WQN0243	3rd Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Oct through Dec period
15	WQN0263	3rd Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Dec period
16	WQN0263	4th Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Oct through Dec period
17	WQN0226	4th Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Dec period
18	WQN0302	4th Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jan through Mar period
19	WQN0448	4th Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jan through Mar period
20	WQN0445	4th Quarter	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jan through March period
21	WQN0301*	4th Quarter	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jan through Mar period

* SRBC conducts additional baseflow sampling

A similar DS collection table would be created using a process similar to that used to create the FB data collection Table above. However, on the basis of the QC guidance this would entail the collection of twice as many pairs of duplicate samples (42) as FBs (21). The implications of this are that the SRBC DS Table would show twice as many pairs of DS samples as FBs would have to be collected per quarter (10-11 pairs of DS per quarter), and generally half of those pairs of DS per quarter (5-6 pairs) would have to be collected under storm or storm impacted flow conditions. Unless it is a very wet WY this implies collecting DSs and FBs at at least several selected stations per quarter under storm conditions.. In meeting this challenge, particularly for QC samples that must be collected under storm or storm impacted conditions, it is conceivable that the QC sampling requirements outweigh the WQ sampling requirements—for example, when there are not many storm or storm-impacted events in a given season. Does the SRBC focus on QC sampling at the Stations targeted for storm or storm impacted Event Types during that period or on getting WQ storm samples at more than just these Stations?

FINAL SRBC DESIGN CONSIDERATIONS: When the number of NTN monitoring stations is 12 or greater in number for a given Agency by Source group (Appendix D, Table D1), limit the number of unique NTN Stations at which a FBs to be collected to 12 per WY and pairs of DS to be collected to 24 per WY at least for the next few WYs. This will give NTN Data Collector's with large numbers of NTN Stations the chance to develop their QC sampling programs and abilities. For SRBC (PA) FB data collection this would be the first 12 Stations randomly selected from all Agency x Source Group NTN stations monitoring by that Source (Appendix D, Table D2). For the DS collection design the entire QC design process would be repeated starting with randomly selecting 12 Stations from all NTN monitoring stations.

For our revised FB data collection example with SRBC, assume we selected the same first 12 Stations in their order of selection as in the example above. Assuming a coin flip again assigned the Event Types for each FB as in our example above. We would then take N=12 and using Appendix D Addendum Table D2, we would assign a Triennial Sampling Interval, and re-summarize the FB Collection for SRBC as it appears in the table below. Under a triennial sampling interval only 4 FBs are collected per 4-month interval, which provides time for a given Station requiring a FB for either NSI or S/SI to experience the required flow conditions. (In addition, SRBC also does additional baseflow and storm sampling at selected NTN sites...see Table, during which the appropriate QC sample could be taken.)

SRBC (PA) Field Blank Collection Revised Summary Table

Selection Seq. No.	Station ID	Time period of collection	Event _ Type	Timing schedule
1	WQN0305*	1st Triennial period	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Jan period
2	WQN0201*	1st Triennial period	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Oct through Jan period
3	WQN0401*	1st Triennial period	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Oct through Jan period
4	WQN0229	1st Triennial period	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Oct through Jan period
5	WQN0223	2nd Triennial period	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Feb through May period
6	WQN0272	2nd Triennial period	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Feb through May period
7	WQN0273*	2nd Triennial period	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Feb through May period
8	WQN0282	2nd Triennial period	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Feb through May period
9	WQN0204	3rd Triennial period	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jun through Sep period
10	WQN0404	3rd Triennial period	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jun through Sep period
11	WQN0271	3rd Triennial period	S/SI	Storm (S) or storm impacted (SI) flow during monthly fixed interval sampling anytime during Jun through Sep period
12	WQN0210	3rd Triennial period	NSI	Nonstorm impacted (NSI) flow during monthly fixed interval sampling anytime during Jun through Sep period

- SRBC conducts additional baseflow sampling

The approach used to revise FB collection would be repeated in its entirety for DS sample collection for the WY. In so doing, the number of DS sample pairs minimally would be twice the number of FBs or 24 pairs of DS. (Compared to 42 pairs of DSs under the original design.) (Did not create Summary Table for DS). This independent design process for each QC sample type ensures FB and DS collections are entirely independent of one another.

In combination, the revised FB and DS collection designs still require a considerable amount of QC data collection. In total 12 QC samples (4 FBs and 8 pairs of DSs) are targeted for collection during each 4-month triennial period, at somewhere between 4-12 different NTN sites, and with generally half the FBs (2) and half the pairs of DSs (4) being targeted for storm or storm impacted flows.

Also, upon implementation of the QC sample collection design, if the targeted flow conditions for either FB or DS collection call for storm or storm impacted flows, and these conditions materialize, every reasonably sane effort is made to obtain the QC samples; if they don't materialize at designated Stations within the designated time period for that Station, then that FB or DS sample is still taken during that period, but for nonstorm impacted flow conditions. The opposite condition also is covered, if no nonstorm impacted flow conditions arise, then QC samples targeted for such conditions are taken for storm or storm impacted flow conditions.

As in the case of the previous example, the design process for FB collection is to be redone each WY. The design process for DS collection also is redone by repeating the entire design process each WY. Redoing the QC design each WY for FBs and then DS collection ensures the QC (FB and DS) data ultimately will be an unbiased representation of the variations in environmental conditions (weather, station location, flow types) throughout the WY as well as from WY to WY.