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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Generic Verification Protocol for Long-Term Deployment of Multi-Parameter Water Quality Probes/Sondes

GENERIC VERIFICATION PROTOCOL

FOR

LONG-TERM DEPLOYMENT OF MULTI-PARAMETER WATER QUALITY PROBES/SONDES

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Prepared by

Battelle
505 King Avenue
Columbus, OH 43201-2693

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ACRONYMS

AMS	Advanced Monitoring Systems
CCEHBR	Center for Coastal Environmental Health and Biomolecular Research
DO	dissolved oxygen
EPA	United States Environmental Protection Agency
ETV	Environmental Technology Verification
l	liter
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NTU	nephelometric turbidity unit
QA	quality assurance
QMP	Quality Management Plan
SOP	standard operating procedure
TSA	technical systems audit

1 INTRODUCTION

1.1 Environmental Technology Verification Background

This generic verification protocol provides detailed procedures for implementing a verification test of multi-parameter water quality probes/sondes that continuously measure water quality parameters. Verification tests are conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through its Environmental Technology Verification (ETV) program. The purpose of the ETV program is to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed purchase and application decisions about these technologies. ETV does not imply approval, certification, or designation by EPA, but rather provides a quantitative assessment of the performance of a technology under specified test conditions.

The verification tests are coordinated by Battelle, of Columbus, Ohio, which is EPA's partner in the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing verification tests, Battelle follows the procedures specified in this test protocol and complies with the requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Center" (QMP).[1]

1.2 Test Objective

The purpose of verification tests of multi-parameter water quality probes/sondes is to evaluate their performance under realistic operating conditions. Specifically, these probes are deployed in a location or locations similar to those that would be used by members of the water monitoring community, and the probes are evaluated by comparing their measurements with reference measurements. For example, a verification might require deploying probes in laboratory, freshwater, and saltwater environments for a 2½-month field test in which the probes are operated continuously for periods up to 30 days. During such time, water quality parameters

such as turbidity, chlorophyll A, nitrate, conductivity, temperature, dissolved oxygen (DO), and pH are measured both by the probes (when applicable) and by reference methods. In the laboratory environment, these parameters are controlled, while in the freshwater and saltwater phases of the verification, these parameters are not controlled. During each phase, assessments of performance are based upon comparisons to the reference results and include determinations of accuracy, precision, linearity, and inter-unit reproducibility. Different locations, target analytes, and test periods may be accommodated, if appropriate for the water probes being tested, by specifying those features of the verification in the test/quality assurance (QA) plan for the test.

1.3 Test Applicability

This generic protocol is applicable to verification testing of probes that operate unattended in lakes, rivers, coastal areas, estuaries, bays, and other fresh, salt, or brackish bodies of water and that continuously measure one or more water quality parameters, such as turbidity, chlorophyll A, nitrate, conductivity, temperature, DO, or pH. In accordance with the intent of the ETV program, the probes tested are commercially available and not developmental products or prototypes. No enhancements of a commercially available product can be used. This includes using any special anti-fouling coating or paints that are not part of the standard product.

2 TECHNOLOGY DESCRIPTION

The probes to be tested under this protocol typically consist of a sensor or sensors in a rugged housing at the end of a tethered line. The probes are portable and usually must be tethered to a buoy, dock, piling, or similar structure. While some may be capable of wireless transmission of data, many probes require that stored data be physically downloaded by the user.

The multi-parameter water probes verified under this protocol must be able to undergo the testing explained in Chapter 4. In general, probes must be able to measure two or more of the parameters listed in Section 1.3 in both salt and freshwater. The probe must be deployable, in the sense that the probe must be able to make the water quality measurements without the assistance or intervention of an operator. A probe must be able to store the measured water quality values

for a minimum of two weeks at an hourly sampling rate and must be able to sample at depths between 1 and 15 feet.

3 VERIFICATION APPROACH

3.1 Scope of Testing

The objective of the verification test derived from this generic protocol is to establish the performance capabilities of multi-parameter water probes under operating conditions that are realistic in terms of type of water body, depth, duration of unattended operation, etc., as well as in a laboratory or controlled setting. To achieve this goal, the verification test involves three phases. In the first phase, the probes are tested in a saltwater location. The second phase takes place at a freshwater location. In each of these two phases, the probes monitor the naturally occurring levels of each parameter. These phases of 30 sampling days each are used to determine how well the probes compare with the reference methods while being continuously deployed in a field setting. The third phase takes place in a laboratory or controlled environment. During this week-long phase, the probes are tested over target parameter ranges that are partially controlled. The turbidity and conductivity are adjusted while recording the response of the probes. In all tests, two units of each probe are operated side by side to make inter-unit comparisons.

3.2 Experimental Design

The verification test is designed to assess the performance of multi-parameter water probes relative to reference methods that may consist of using either a grab sample and laboratory analysis or another real-time probe. Collaboration with a partner organization is highly recommended. For example, a test conducted under this protocol was coordinated with the National Oceanic and Atmospheric Administration (NOAA) through the Center for Coastal Environmental Health and Biomolecular Research (CCEHBR). The test described in this protocol follows the design of that performed at or near CCEHBR facilities in Charleston, South

Carolina. The approach to the verification test is summarized below, and the statistical methodology for establishing performance parameters is described in Section 7.3.

The first phase of the test shall occur at a saltwater site such as CCEHBR and last approximately one month. CCEHBR, for example, has direct access to Charleston Harbor, which is a tidally dominated body of water that receives some riverine input, with salinities ranging from 20 to 35 parts per thousand. The South Carolina Department of Natural Resources has several piers and docks that can be used to deploy the instruments. Also, other areas in close proximity can be used if the instruments need to be deployed away from dock and boat activity. Many types of land use (including residential, industrial, urban, and dredge spoil) in the area surrounding Charleston Harbor can affect overall water quality.

The second phase of the test shall occur at a freshwater site and last approximately one month. A five-acre freshwater pond named Lake Edmunds, located approximately one mile from the CCEHBR, exemplifies an appropriate site.

The third phase shall take place over a one-week period at a facility such as CCEHBR's Mesocosm Facility. The test facility should contain modular estuarine mesocosms, consisting of a 300-liter tank containing elevated sediment trays and stream channels. Each sediment tray should be arranged so that an elevated salt marsh surface is formed. The sediment trays contain sediment, salt marsh vegetation, and benthic communities. Stream channels contain phytoplankton, zooplankton, and endemic macrofaunal species. Another component of the mesocosm is a reservoir or sump that provides tidal water to the system through a pump system controlled by a timer. Twice daily, seawater is pumped up into the mesocosm tank from the sump to simulate a flood tide. After six hours of flooding tide, the seawater is allowed to drain back into the sump, simulating an ebb tide for another six hours. Mesocosms used for this test can be classified as "tidal" or "estuarine." Figure 1 shows a single mesocosm tank.

A suggested schedule for the various testing activities is given in Table 1. In each phase, individual vendor's probes are positioned as close to each other as possible so that inter-unit comparisons can be made. In addition, the probes from all vendors are placed near each other so that parameters such as photosynthesis and mixing are as similar as possible.

3.3 Reference Methods

Figure 1. Mesocosm Tank

During a verification test, various analytical methods are used to monitor turbidity, chlorophyll A, nitrate, conductivity, temperature, DO, and pH. Temperature, pH, DO, and conductivity are monitored in real time with devices that are collocated with the probes being verified. Turbidity, chlorophyll A, and nitrate concentrations are measured using laboratory analysis of collected samples. Turbidity is measured using a benchtop ratio turbidity meter, chlorophyll A is measured by fluorometry, and nitrate is measured colorimetrically.

Table 1. Schedule for the Multi-parameter Water Probe Test

Activity	Day Number
Vendor setup for saltwater site	1
Begin saltwater test	8
End saltwater test	39
Vendor setup for freshwater test	40
Begin freshwater test	50
End freshwater test	82
Vendor setup for mesocosm test	86
Begin mesocosm test	91
End mesocosm test	95
Vendor removal of equipment	98

3.4 Test Facility

CCEHBR exemplifies the requirements of a test facility for this verification. Specifically, a test facility must be capable of providing a secure and realistic location for deploying the multi-parameter water probes, must have standard operating procedures (SOPs) or written methods in place for the reference measurements, have trained personnel capable of performing

these activities according to those SOPs, and have documented QA procedures in place. Documentation of the staff training, SOPs, and other pertinent materials are provided to Battelle prior to test initiation.

3.5 Roles and Responsibilities

The verification test is coordinated and supervised by Battelle personnel. Staff from the test facility participate in this test by operating the reference equipment, collecting the water samples, downloading the data from the multi-parameter water probes, and informing Battelle staff of any problems encountered. Vendor representatives install, maintain, and operate their respective technologies throughout the test unless they give written consent to Battelle or the test facility to carry out these activities. QA oversight is provided by the Battelle Quality Manager and the EPA ETV Quality Manager at his/her discretion. The chart in Figure 2 shows the organization of responsibilities for Battelle, the vendor companies, EPA, and the test facility. Specific responsibilities are detailed below.

3.5.1 Battelle

The Battelle Verification Test Coordinator has the overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. The Verification Test Coordinator shall

- Prepare the draft test/QA plan, verification reports, and verification statements
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments
- Coordinate distribution of the final test/QA plan, verification reports, and verification statements
- Coordinate testing, measurement parameters, and schedules at the testing site

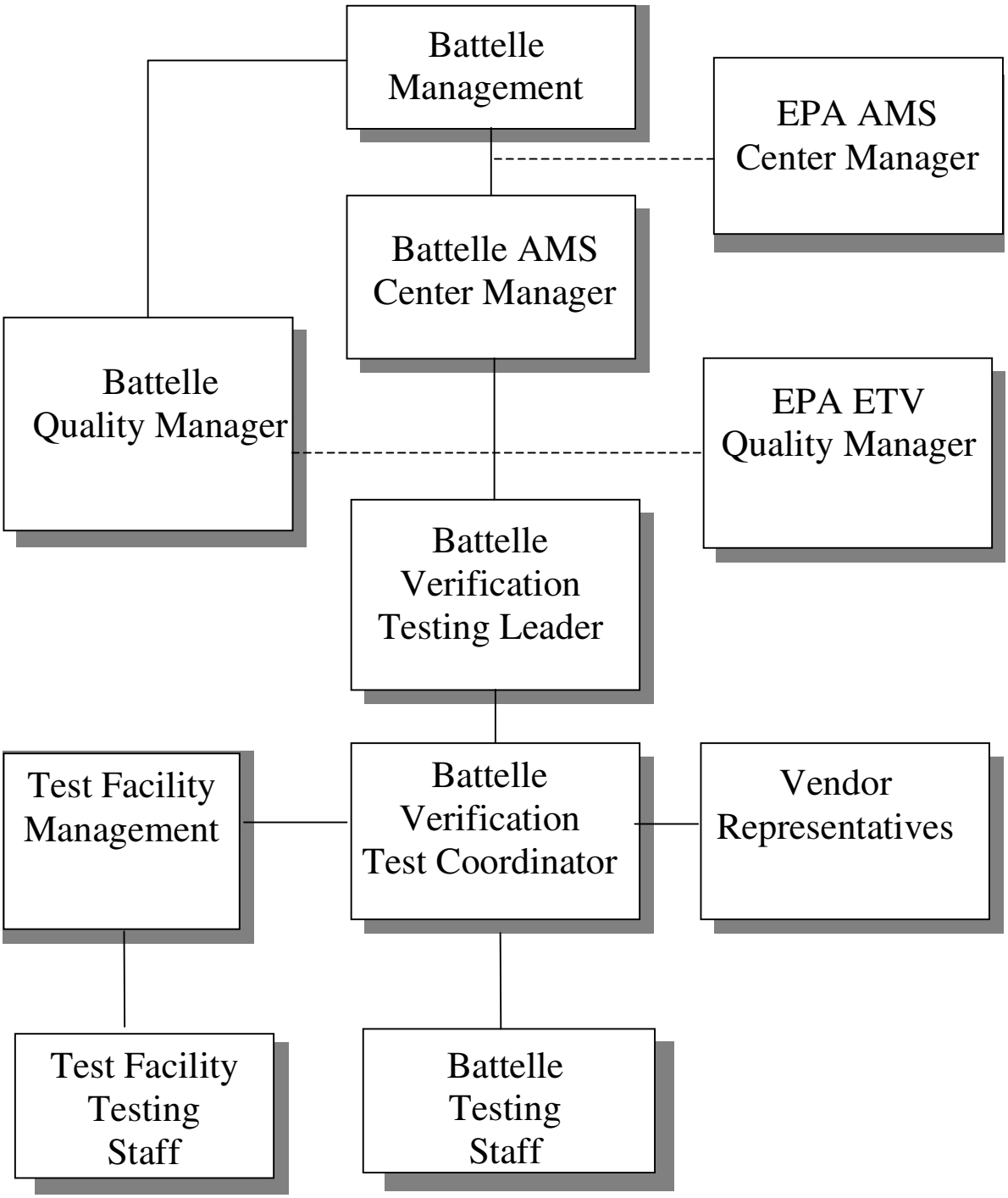

Figure 2. Organization Chart for Multi-Parameter Water Probe Verification

- Ensure that all quality procedures specified in the test/QA plan and in the QMP are followed
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary
- Serve as the primary point of contact for vendor and test facility representatives
- Establish a budget for the verification test and monitor staff effort to ensure that the budget is not exceeded
- Ensure that confidentiality of proprietary vendor technology and information is maintained
- Coordinate with sample analysis laboratory to ensure timely reporting of results.

The Verification Testing Leader for the AMS Center provides technical guidance and oversees various stages of the verification test and shall

- Support the Verification Test Coordinator in preparing the test/QA plan and organizing the testing and budgeting for the verification activities
- Review the draft test/QA plan
- Review the draft verification reports and statements
- Ensure that confidentiality of proprietary vendor technology and information is maintained.

Battelle's AMS Center Manager shall

- Review the draft test/QA plan
- Review the draft verification reports and statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's AMS Center and ETV Quality Managers

- Ensure that confidentiality of proprietary vendor technology and information is maintained.

Battelle's Quality Manager for the verification test shall

- Review the draft test/QA plan
- Conduct a technical systems audit (TSA) once during the verification test
- Audit at least 10% of the verification data
- Prepare and distribute an assessment report for each audit
- Verify implementation of any necessary corrective action
- Issue a stop work order if self-audits indicate that data quality is being compromised or if proper safety practices are not followed; notify the Battelle AMS Center Manager if a stop work order is issued
- Provide a summary of the audit activities and results for the verification reports
- Review the draft verification reports and statements
- Have overall responsibility for ensuring that the test/QA plan and ETV QMP are followed
- Ensure that Battelle management is informed if persistent quality problems are not corrected
- Interface with EPA's ETV Quality Manager
- Ensure that confidentiality of proprietary vendor technology and information is maintained.

3.5.2 Vendors

Vendors shall

- Review the draft test/QA plan and provide comments and recommendations
- Approve the revised test/QA plan

- Work with Battelle to commit to a specific schedule for the verification test
- Provide duplicate commercial-ready probes for testing
- Provide an on-site operator(s) throughout the verification test period to install the probes and maintain them during testing, unless written consent is given for Battelle or the test facility staff to perform those responsibilities
- Remove probes and other related equipment from the test facility upon completing the verification test
- Review and comment upon their respective draft verification reports and statements.

3.5.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)"[2] or the most current update of this document. The roles of the specific EPA staff are as follows:

EPA's ETV Quality Manager shall

- Review the draft test/QA plan
- Perform, at his/her option, one external TSA during the verification test
- Notify the Battelle AMS Center Manager to facilitate a stop work order if an external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing the results of an external audit, if performed
- Review draft verification reports and statements
- Ensure that confidentiality of proprietary vendor technology and information is maintained.

EPA's AMS Center Manager shall

- Review the draft test/QA plan
- Approve the final test/QA plan
- Approve the final verification reports
- Review the draft verification statements
- Ensure that confidentiality of proprietary vendor technology and information is maintained.

3.5.4 Test Facility

Test facility staff shall

- Assist in developing the test/QA plan for the verification test
- Allow facility access to the vendor, Battelle, and EPA representatives during the field test periods
- Provide safety instructions to Battelle, EPA, and vendor personnel for operations at the test facility
- Select a secure location for each of the three testing phases
- Assist vendors in installing the probes at each location
- Perform sample collections and analyses as detailed in the test procedures section of the test/QA plan
- Perform reference measurements
- Provide all test data to Battelle electronically, in mutually agreed upon format
- Provide EPA and Battelle staff access to and /or copies of appropriate QA documentation of test equipment and procedures (e.g., SOPs, calibration data)
- Provide information regarding education and experience of each researcher involved in the verification
- Assist in Battelle's reporting of the test facility's QA/quality control results

- Review portions of the draft verification reports to assure accurate descriptions of the test facility operations and to provide technical insight on verification results.

4 TEST PROCEDURES

4.1 Site Selection

Below are the general procedures followed at each of the test sites. Three test sites are used for this verification in an attempt to expose the probes to as wide a range of conditions as possible while conducting an efficient test. The site selection process requires that several important criteria be met. First, the three sites must include one controlled, one saltwater (or brackish), and one freshwater location. The sites must allow for collocation of numerous probes because each vendor will provide duplicate probes for the test. The sites must be accessible daily so that timely water collections can be made; and the sites must, to the extent possible, be free from interference from the public. A secure facility is not required, but is preferred. For this protocol, the three locations described are the Mesocosm Facility at the CCEHBR in Charleston, the Charleston Harbor, and Lake Edmunds. Figure 3 shows a map of South Carolina and a close-up map showing the testing sites. If another facility is used, it must meet the requirements described above.

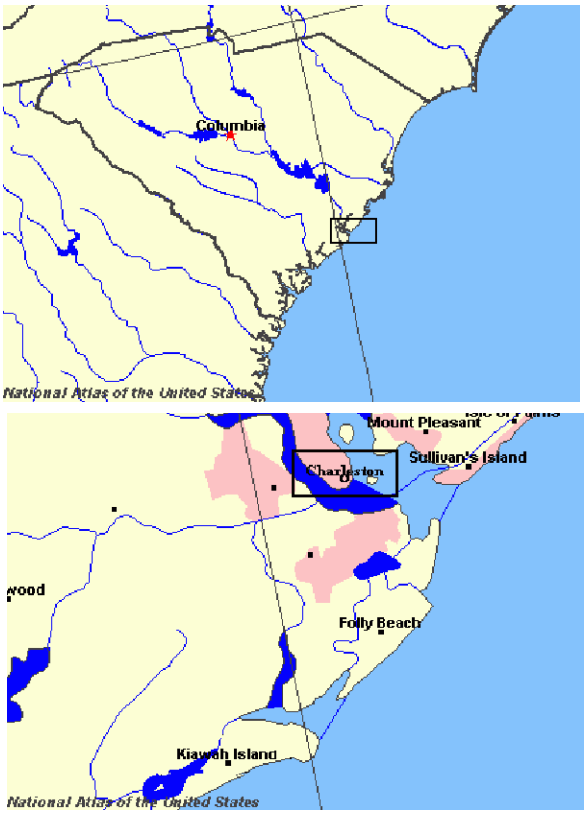

Figure 3. Major Bodies of Water Leading into the Test Area

The sites at or near the CCEHBR are appropriate for several reasons. First it was beneficial to involve a major user (NOAA) of multi-parameter water probes to allow a broader verification test than would be possible using only Battelle facilities. Second, CCEHBR has secure, nearby sites available for all three phases

of the test (mesocosm, freshwater, and saltwater), which allows resources to be devoted to testing rather than to building infrastructure for the test. Finally, these sites offer a useful variation of water conditions for testing. Typical ranges for the target parameters to be monitored are given in Table 2. The remainder of this protocol uses the CCEHBR as a specific test facility example. A similar range of water conditions should be characteristic of alternate test facilities.

Table 2. Expected Ranges of Water Characteristics at the Example Test Sites

Parameter	Mesocosm		Bay		Lake Edmunds	
	Low	High	Low	High	Low	High
pH	7.5	8.3	7.5	8.3	7.0	8.0
Turbidity	0.1 NTU[a]	10 NTU	-[b]	-	-	-
DO	2.0 mg/L	10.00 mg/L	2.5 mg/L	8.0 mg/L	-	-
Conductivity	0.0	36mS/cm^2	-	-	-	-
Temperature	15C	35C	-	-	-	-
Nitrate	0.1 mg/L	1 mg/L	0.1 mg/L	1 mg/L	0.1 mg/L	1 mg/L
Chlorophyll A	5 µg/L	60 µg/L	5 µg/L	60 µg/L	5 µg/L	60 µg/L
Salinity	0 ppt	20 ppt	20 ppt	30 ppt	0 ppt	<1 ppt

[a] NTU = nephelometric turbidity unit.
[b] "-" = no information.

4.2 Multi-Parameter Water Probe Deployment

The saltwater test shall take place at a site similar to a portion of the Charleston Harbor located on the CCEHBR campus. The probes are set up for a 30-day test. Each of the probes are located within the same area, moored to the piling of the pier and accessible to CCEHBR staff for daily observation, reference measurements, and water sample collection. The freshwater phase of the verification test shall occur at a lake such as Lake Edmunds on James Island, located approximately one mile from the CCEHBR. Probes shall then be set up in a controlled environment, such as the 300-liter mesocosm tank at the Mesocosm Facility, and prepared for a one-week test. Because of space considerations, more than one mesocosm tank may be used; but, in all cases, each probe is provided with water from the same source, and each individual vendor's probe is collocated within the same tank so that inter-unit reproducibility can be evaluated.

Vendors are responsible for setting up their probes at each test location unless written permission is given to the test facility or Battelle to set up the probe. Vendors may set up at the first site while training the appropriate Battelle or test facility staff so that, during the next two deployments, the probes may be redeployed without vendor staff members present.

4.3 Saltwater Testing

The saltwater test shall occur at a site similar to the Charleston Harbor site. This portion of the verification test lasts for 30 days, during which time the probes monitor the naturally occurring range of the target parameters, while samples for simultaneous reference measurements are collected during each sampling event. Sample collection times are rotated among the morning, afternoon, and evening throughout the test. In addition, two periods of intense sampling occur at the beginning (Days 1 and 2) and the end (Days 29 and 30) of the sampling period, during which time samples are collected for reference analysis at 30-minute intervals for eight hours. For the first 15 days, the probes are deployed to a depth of one to two feet. For the last 15 days, the probes are deployed to a depth of 15 feet. At the saltwater site, samples for laboratory reference measurements are taken using a Niskin sampling device, which allows a sample to be taken at depth. Three replicate samples are collected per sampling event, and each replicate sample is analyzed by the laboratory reference methods. Temperature measurements are taken at depth using a thermocouple on the end of a five-meter pole. For the parameters shown in Table 3, the average value of the three replicates will be used as the reference value. Table 4 shows the recommended sampling times and number of sampling events throughout the test period.

The probes are deployed by tethering them to the side of a bulkhead already located in the harbor. The probes from an individual vendor are attached to the bulkhead so that they are as close to each other as possible and near the probes from the additional vendors participating in the test. If possible, the probes from each of the vendors shall be hung at the corners of a one-meter square frame.

Table 3. Sample Analysis Location

Parameter	Analysis Location
pH	on site
Turbidity	laboratory
DO	on site
Chlorophyll A	laboratory
Conductivity	on site
Temperature	on site
Nitrate	laboratory

4.4 Freshwater Testing

Freshwater testing shall be done at a site similar to Lake Edmunds. Because this site is more shallow than Charleston Harbor, only one depth is used; however, the same sample collection schedule is followed. This portion of the verification test lasts for 30 days, during which time the probes monitor the naturally occurring target parameters, while simultaneous reference measurements are made and replicate samples are collected during each sampling event, again rotating among collection times. Two periods of intense sampling also occur at the beginning (Days 1 and 2) and the end (Days 29 and 30) of the sampling period, during which time samples are collected for reference analysis at 30-minute intervals for eight hours. Three replicate samples are collected per sampling event and each replicate sample is analyzed for the parameters shown in Table 3. The average value of the three replicates is used as the reference value. Table 5 shows the recommended sampling times and number of sampling events throughout the test period.

Probes can be deployed in a shallow pond by driving large posts into the bottom of the pond and tethering the instruments onto the posts with cable ties. While wearing appropriate gear, the testers can wade into the pond and force the posts into the bottom with a sledgehammer. Samples shall be collected at the freshwater site without entering the water to limit errors induced by disturbing the water.

Table 4. Schedule of Reference Method Sample Events on Each Day of Testing at the Saltwater Site

Sampling Day	Morning	Afternoon	Evening	Total Sampling Events
Shallow Deployment				
1	6	6	4	16
2	6	6	4	16
3	1[a]	1[b]	1	3
4				0
5				0
6				0
7		1	1[c]	2
8				0
9				0
10				0
11	1[c]	1[a]	1[b]	3
12				0
13				0
14				0
15	1	1[a]	1[b]	3
Deep Deployment				
16	1	1[a]		2
17				0
18				0
19	1[b]	1	1	3
20				0
21				0
22		1[a]	1[b]	2
23		1[a]		1
24				0
25	1[a]			1
26	1[a]			1
27				0
28		1[c]	1[b]	2
29	6	6	4	16
30	6	6	4	16

[a] Sample to be split into a laboratory replicate.

[b] Field blank taken simultaneously.

[c] Field spike taken simultaneously.

Table 5. Schedule of Reference Method Sample Events on Each Day of Testing at the Freshwater Site

Sampling Day	Morning	Afternoon	Evening	Total Sampling Events
Shallow Deployment				
1	6	6	4	16
2	6	6	4	16
3	1[a]	1[b]	1	3
4				0
5				0
6				0
7		1	1[c]	2
8				0
9				0
10				0
11	1	1[a]	1[b]	3
12				0
13				0
14				0
15	1[c]	1[a]	1[b]	3
16	1	1[a]		2
17				0
18				0
19	1[b]	1	1	3
20				0
21				0
22		1	1[b]	2
23		1[a]		1
24				0
25	1[a]	1	1[c]	3
26				0
27				0
28		1	1[b]	2
29	6	6	4	16
30	6	6	4	16

[a] Sample to be split into a laboratory replicate.

[b] Field blank taken simultaneously.

[c] Field spike taken simultaneously.

4.5 Mesocosm Testing

Mesocosm testing shall be performed according to the schedule shown in Table 6. The mesocosms should fill and drain with water daily, simulating a tide. Water samples are collected at four intervals during each test day, spaced evenly throughout the normal operating hours of the facility (nominally 6 a.m. to 6 p.m.). During this period, the mesocosms are manipulated to introduce variations in the measured parameters. The turbidity of the systems is varied by operating a pump near the sediment trays to suspend additional solids in the water. Conductivity is varied by adding fresh water to the salt water during one of the fill-and-drain cycles. Nitrate is varied by spiking the mesocosms with an appropriate amount of chemical during the fill cycle. Temperature, pH, and DO are allowed to vary naturally, with any variations driven by natural forces and the changes in the other test parameters (for example, nutrient spiking is likely to vary the corresponding chlorophyll A concentrations). The parameters are varied over the ranges specified in Table 2 and monitored by the multi-parameter probes undergoing testing. During this period, each of the collected samples is analyzed using a reference method for comparison. Three replicate samples are collected from each tank per sampling event, and each replicate sample is analyzed for the parameters shown in Table 3. The average value of the three replicates is reported as the reference value, along with the standard deviation.

4.6 Multi-Parameter Water Probe Calibration

The multi-parameter water probes are calibrated for each measured parameter according to that vendor's instructions. This calibration uses National Institute of Standards and Technology (NIST)-traceable standards when applicable. Vendors may choose to supply the necessary calibration solutions and devices specific to the probe being verified.

Table 6. Schedule for Mesocosm Sample Collection

Task	Day 1				Day 2				Day 3				Day 4				Day 5			
	Sampling Time																			
	8 am	10 am	1 pm	5 pm	8 am	10 am	1 pm	5 pm	8 am	10 am	1 pm	5 pm	8 am	10 am	1 pm	5 pm	8 am	10 am	1 pm	5 pm
Turbidity							B											E		
Conductivity													C							
Nitrate					A												D			
Temperature																				
pH																				
Chlorophyll																				
DO																				

A - Nitrate spike
B – Stir sediment
C – Add freshwater
D – Nitrate spike
E – Stir sediment

4.7 Reference Methods

pH, turbidity, dissolved oxygen, nitrate, chlorophyll A, conductivity, and temperature shall be measured during the verification test, using a variety of methods.

4.7.1 pH

A NIST-traceable handheld pH meter, operated according to the manufacturer's instructions, is used to measure pH.

4.7.2 Turbidity

A benchtop ratio turbidity meter, operated according to the manufacturer's instructions, is used to measure turbidity according to EPA Method 180.1.[3]

4.7.3 Dissolved Oxygen

DO is measured using a NIST-traceable commercially available probe, operated according to the manufacturer's instructions.

4.7.4 Nitrate

Nitrate concentrations are determined colorimetrically using a Lachat Instruments QuikChem autoanalyzer, operated according to the manufacturer's instructions.[4]

4.7.5 Chlorophyll A

Chlorophyll A or total chlorophyll concentrations are determined using a fluorescence technique conducted according to the manufacturer's instructions. Both methods for this determination are based on EPA Method 445.0.[5]

4.7.6 Conductivity

A NIST-traceable handheld conductivity meter, operated according to the manufacturer's instructions, is used to measure conductivity.

4.7.7 Temperature

A NIST-traceable handheld thermocouple and readout, operated according to the manufacturer's instructions, is used to monitor the water temperature (°C).

5 Materials and Equipment

5.1 Reagents

Reagents used include distilled deionized water (for field blanks), appropriate turbidity standards from Hach or Advanced Polymer Systems, chlorophyll standards from Sigma (C6144), a nitrate standard, and preservation reagents, as specified in the test methods.[3-5]

5.2 Sampling Equipment and Handling

Sampling equipment consists of 0.5- or 1-liter (l) sample containers (glass bottles) and the Niskin sampling device, along with all sample storage equipment. The recommended maximum sample holding time is given in Table 7.

Table 7. Maximum Holding Time

Parameter	Holding Time
pH	none[a]
Turbidity	24 hours
DO	none
Chlorophyll A	1 week
Conductivity	none
Temperature	none
Nitrate	2 weeks

[a]Sample analysis performed immediately after sample collection.

5.3 Reference Equipment

Reference equipment includes a handheld pH meter, benchtop turbidity meter (Hach Ratio XR or similar meter), autoanalyzer (Lachat Instruments QuikChem 8000), fluorometer (Turner 10-AU or similar fluorometer), handheld conductivity meter, handheld thermocouple, and a DO meter.

6 QUALITY ASSURANCE/QUALITY CONTROL

6.1 Calibration

Both the on-line and laboratory reference instrumentation used in the verification test shall be calibrated by the test facility according to the SOPs and schedules in place at the test facility. Documentation of these calibration results is provided to Battelle. The conductivity, DO, and pH meters are calibrated before each sampling event. The autoanalyzer, turbidity meter, and fluorometer used to measure nitrate, turbidity, and chlorophyll A, respectively, are calibrated at each sample analysis period. The thermocouple is calibrated in the six months prior to the test completion date.

6.2 Field Quality Control

To ensure that the sample collection and analysis procedures are properly controlled, a field blank and a laboratory replicate sample shall be taken at the times shown in Tables 4 and 5. The field blank is a container of deionized water taken to the field and then brought back to the laboratory. It is analyzed in the same manner as the collected samples. The laboratory replicate sample is collected once each week during a regular sampling period. These replicate samples are the field samples split into two and analyzed by the same methods. The results from the replicate analysis should be within the accuracy reported in Table 8. The expected maximum values for the field blanks are given in Table 9. In addition, sample spikes are taken in distilled water on the schedule shown in Tables 4 and 5. Sample spikes are taken for only nitrate. The nitrate spike is at 0.5 mg/l.

Table 8. Replicate Analysis Results

Parameter	Accuracy (±)
pH	0.1
Turbidity	5 NTU
DO	5%
Chlorophyll A	5%
Conductivity	5%
Temperature	1°C
Nitrate	10%

Table 9. Expected Values for Field Blanks

Parameter	Expected Maximum
Turbidity	1 NTU
Chlorophyll A	3 x average of three blank filters
Nitrate	5 µg at N/l[a]

[a] at N/l = atoms of nitrogen per liter.

6.3 Sample Custody

Collected samples are transported to the laboratory in an ice-filled cooler. All samples are accompanied by a sample collection sheet and chain-of-custody form prepared for the test.

6.4 Audits

Independent of test facility and EPA QA activities, Battelle is responsible for ensuring that the following audits are conducted as part of this verification test.

6.4.1 Performance Evaluation Audits

A performance evaluation audit shall be conducted to assess the quality of the reference measurements made in the verification test. Each type of reference measurement is compared with an independent probe or a NIST-traceable standard that is independent of those used during the testing. This audit is performed once during the verification test. The acceptance criteria for the results of this audit are noted in Table 10, which is a summary of the audits to be performed.

Table 10. Summary of Performance Evaluation Audits

Audited Parameter	Audit Procedure	Acceptable Tolerance
pH	Independent monitor	±0.1 pH
Turbidity	Independent turbidity standard	±10%
DO	Independent monitor	±5%
Nitrate	Independent nitrate standard	±10%
Chlorophyll A	Independent chlorophyll standard	±10%
Conductivity	Independent monitor	±5%
Temperature	Independent monitor	±1°C

6.4.1.1 pH

The handheld pH meter shall be compared with another handheld pH meter made by a different manufacturer and operated according to the manufacturer's instructions. A tolerance of ±0.1 pH unit is expected.

6.4.1.2 Turbidity

The measurement of an independent turbidity standard shall be compared using the turbidity meter. An agreement of within 10% in NTUs is expected.

6.4.1.3. Dissolved Oxygen

The DO measurement shall be compared with a handheld DO monitor made by a different manufacturer. Agreement within 5% is expected.

6.4.1.4 Nitrate

A nitrate audit shall be performed, using an independent nitrate standard, by delivering a spiked sample to the autoanalyzer. Agreement between the results of this analysis and the spiked concentration is expected to be within 10%.

6.4.1.5 Chlorophyll A

A chlorophyll A audit shall be performed, using an independent chlorophyll A standard, by delivering a diluted standard to the fluorometer. Agreement between the results of this analysis and the spiked concentration is expected to be within 10%.

6.4.1.6 Conductivity

An independent handheld conductivity meter made by a different manufacturer shall be used to perform the conductivity audit. Agreement between the results of this meter and those of the test reference meter is expected to be within 5%.

6.4.1.7 Temperature

A NIST-traceable mercury-in-glass thermometer shall be used for the temperature performance audit. The comparison is done on a sample of collected water. An agreement within ±1°C is expected.

6.4.2 Technical Systems Audits

Battelle's Quality Manager shall perform a TSA at least once during this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP[(1)], this protocol, published reference methods, and any SOPs used by the test facility. In this audit, the Battelle Quality Manager may review the reference methods used, compare actual test procedures to those specified or referenced in this protocol, and review data acquisition and handling procedures. A TSA report shall be prepared, including a statement of findings and the actions taken to address any adverse findings. The EPA ETV Quality Manager shall receive a copy of Battelle's TSA report.

At EPA's discretion, EPA QA staff also may conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to testing staff at the time of the audit and documented in a TSA report.

6.4.3 Audit of Data Quality

Battelle's Quality Manager shall audit at least 10% of the verification data acquired in the verification test. The Battelle Quality Manager traces the data from initial acquisition,

through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing audit are checked.

6.4.4 Assessment Reports

Each assessment and audit shall be documented in accordance with Section 2.9.7 of the QMP for the AMS Center.[1] Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Possible recommendations for resolving problems
- Citation of any noteworthy practices that may be of use to others
- Confirmation that solutions have been implemented and are effective.

6.5 Corrective Action

The Battelle Quality Manager, during the course of any assessment or audit, shall identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator ensures that a response is provided for each adverse finding or potential problem and implements any necessary follow-up corrective action. The Battelle Quality Manager shall ensure that follow-up corrective action has been taken.

7 DATA HANDLING AND REPORTING

7.1 Documentation and Records

A variety of data shall be acquired and recorded electronically and manually by either Battelle or the test facility staff. Operational information, required maintenance, and results from the reference methods are documented in a laboratory record book and on data sheet/chain-of-custody forms. In general, the results from the multi-parameter water probes are recorded electronically. The electronic data stored on the probe are collected by the field staff during each sampling event. Once collected, these data reside at the test facility until the entire test is finished. All of the electronic raw data is then transferred to Battelle, where it will be permanently stored with the study binder, along with the rest of the test data. Table 11 summarizes the types of data to be recorded and the process for recording data. At the conclusion of the test, the test facility is provided with an electronic copy of the raw data generated during the verification.

7.2 Data Review

Data generated by the test facility and vendors in the verification test shall be provided to Battelle and reviewed by the Verification Test Coordinator before they are used to calculate, evaluate, or report verification results. All data are recorded directly in the laboratory record book as soon as they are available. Records are written legibly in ink, and any corrections are initialed by the person performing the correction. The data include electronic data, entries in laboratory record books, operating data from the test facility, and equipment calibration records. The person performing the review adds his/her initials and the date to a hard copy of the record being reviewed within two weeks of the measurement. This hard copy is placed in the files for the verification test by the Verification Test Coordinator. In addition, data calculations performed by Battelle are spot-checked by Battelle technical staff to ensure that calculations are performed correctly.

Table 11. Summary of Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Purpose of Data
Dates, times of test events	Test Facility	Laboratory record books/data sheets	Start/end of test; at each change of a test parameter; at sample collection.	Used to organize/check test results; manually incorporate data into spreadsheets - stored in study binder
Test parameters	Battelle/Test Facility	Laboratory record books/data sheets	Each sample collection	Used to organize/check test results; manually incorporate data into spreadsheets - stored in study binder
Probe data - digital display - electronic output	Test Facility Test Facility	Data sheets Probe data acquisition system (data logger, PC, laptop, etc.).	Each sample collection; data downloaded at least once per day	Used to organize/check test results; incorporate data into electronic spreadsheets - stored in study binder
Reference monitor readings/reference analytical results	Test Facility	Laboratory record book/data sheets or data management system, as appropriate	After each batch sample collection; data recorded after reference method performed	Used to organize/check test results; manually incorporate data into spreadsheets - stored in study binder
Reference calibration data	Test Facility	Laboratory record books/data sheets/ data aquisition system	Whenever zero and calibration checks are done	Document correct performance of reference methods
Performance evaluation audit results	Battelle	Laboratory record books/data sheets/ data acquisition system	At times of performance evaluation audits	Test reference methods with independent standards/ measurements

7.3 Statistical Procedures

7.3.1 Pre- and Postcalibration Results

A tabulation of the pre- and postcalibration results shall be presented, where applicable, for each of the measured parameters. The results are expressed as percent change for a given

time period (days). If not prohibited by the vendor's typical operating instructions, a weekly check of the calibration is performed as well.

The results from the calibration checks are summarized, and accuracy is determined each time the calibration check is conducted. This accuracy is reported as a percentage, calculated using the following equation:

$$A = 1 - (Cs-Cp)/Cs \quad (1)$$

where *Cs* is the value of the standard and *Cp* is the value measured by the vendor's probe.

7.3.2 Relative Bias

Results from the multi-parameter water probes being verified are compared to the results obtained from the reference analyses. Water samples are analyzed by both the reference method and the probes being verified. The results for each sample are recorded, and the accuracy is expressed in terms of the relative bias (*B*), as calculated from the following equation:

$$B = \frac{C_p - \overline{C}_R}{\overline{C}_R} \times 100 \quad (2)$$

where C_P is the reading from the probe being verified, and $\overline{C_R}$ is the average of the replicate reference measurements. This calculation is performed for each reference sample analysis for each of the eight target water parameters (Table 2). Readings of pH are converted to H^+ concentration, and temperature readings are converted to absolute units prior to making this calculation. Relative bias is assessed independently for each analyzer provided by a single vendor to determine inter-unit reproducibility.

7.3.3 Precision

The standard deviation (*S*) of the results for replicate measurements made during stable operation at the mesocosm is calculated and used as a measure of probe precision at each sampling period:

$$S = \left[\frac{1}{n-1} \sum_{k=1}^{n} \left(C_k - \overline{C} \right)^2 \right]^{1/2} \tag{3}$$

where n is the number of replicate samples, C_k is the concentration reported for the k^{th} measurement, and $\overline{C}$ is the average concentration of the replicate samples, i.e.,

$$\%\, RSD = \frac{S}{\overline{C}} 100 \tag{4}$$

Precision is calculated for each of the eight target water parameters. Probe precision is reported in terms of the percent relative standard deviation of the series of measurements.

7.3.4 Linearity

For target water parameters with a sufficiently wide range of variation, linearity is assessed by linear regression, with the analyte concentration measured by the reference method as an independent variable, and the reading from the analyzer verified as a dependent variable. Linearity is expressed in terms of the slope, intercept, and coefficient of determination (r^2). Linearity for pH is assessed by converting pH results to H^+ concentration before comparison. Linearity is assessed separately for each unit of each water probe being tested and for each of the mesocosm, saltwater, and freshwater test sites.

7.3.5 Inter-Unit Reproducibility

The results obtained from identical units of each probe are compiled independently for each analyzer and compared to assess inter-unit reproducibility. The results are interpreted using a *t*-test, or other appropriate comparison, to assess whether significant differences exist between the units tested.

7.4. Reporting

The statistical comparisons that result from each of the tests described above shall be conducted separately for each of the probes being tested, and information on the additional performance parameters are compiled and reported. Separate verification reports are prepared, each addressing a technology provided by one commercial vendor. Each report shows separate verification results from the duplicate probes undergoing testing, along with calculations of the inter-unit reproducibility of the technology. For each test, the verification report presents the test procedures and test data, as well as the results of the statistical evaluation of those data.

All interaction with the probes (such as during maintenance, cleaning, and calibration) is noted at the time of the test and reported. In addition, descriptions of the data-recording procedures, consumables used, and required reagents are presented in the report.

The verification report shall briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. These sections shall be common to each verification report resulting from this verification test. The results of the verification test shall then be stated quantitatively, without comparison to any other technology tested or comment on the acceptability of the technology's performance. The preparation of draft verification reports, review of reports by vendors and others, revision of the reports, final approval, and distribution of the reports shall be conducted as stated in the "Generic Verification Protocol for the Advanced Monitoring Systems Pilot."[6] Preparation, approval, and use of verification statements summarizing the results of this test also are subject to the requirements of that same protocol.

8 HEALTH AND SAFETY

The test facility shall provide appropriate safety instructions regarding potential hazards during the verification testing to Battelle, EPA, and vendor staff, both at the test facility site and upon arrival at the test sites.

9 REFERENCES

1. "Quality Management Plan for the ETV Advanced Monitoring Systems Center," U.S. EPA, Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2001.

2. "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)," U. S. Environmental Protection Agency, EPA-600/R-98/064, Cincinnati, Ohio, May 1998.

3. "Methods for the Determination of Inorganic Substances in Environmental Samples," U.S. Environmental Protection Agency, Method 180.1, EPA/600/R-93/100, 1993.

4. QuikChem® Method 31-107-04-1-D, "Determination of Nitrate and/or Nitrite in Brackish Waters by Flow Injection Analysis," November 20, 2000.

5. "In-vitro Determination of Chlorophyll A and Pheophytin A in Marine and Freshwater Phytoplankton by Fluorescence," U.S. Environmental Protection Agency, Method 445.0, September 1997.

6. "Generic Verification Protocol for the Advanced Monitoring Systems Pilot," Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, October 1998.