July 2004

Environmental Technology Verification Report

YSI INCORPORATED 6600 EDS MULTI-PARAMETER WATER QUALITY PROBE/SONDE

Prepared by
Battelle

Battelle
The Business of Innovation

In cooperation with the
National Oceanic and Atmospheric Administration

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

July 2004

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

YSI Incorporated 6600 EDS Multi-Parameter Water Quality Probe/Sonde

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of seven environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. We would like to thank the National Oceanic and Atmospheric Administration's (NOAA) National Ocean Service, National Centers for Coastal Ocean Science staff at the Center for Coastal Environmental Health and Biomolecular Research. In addition, NOAA's Coastal Service Center is acknowledged for providing access to dock facilities on a tributary of Charleston Harbor for the saltwater testing, as well as the South Carolina Department of Natural Resources for the use of its land and pier. We also acknowledge the assistance of the ETV Advanced Monitoring Systems Center stakeholders Christine Kolbe of the Texas Commission on Environmental Quality, Vito Minei and Robert Waters of the Suffolk County New York Department of Health Services, and Paul Pennington and Geoff Scott of NOAA, as well as James O'Dell and Linda Sheldon of the U.S. Environmental Protection Agency.

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List of Abbreviations

AMS	Advanced Monitoring Systems
CCEHBR	Center for Coastal Environmental Health and Biomolecular Research
cm	centimeter
DAS	data acquisition system
DO	dissolved oxygen
EDS	Extended Deployment System
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
L	liter
µg	microgram
mg	milligram
mS	millisiemen
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NTU	nephelometric turbidity unit
PE	performance evaluation
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
RSD	relative standard deviation
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the YSI Incorporated 6600 Extended Deployment System (EDS).

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the 6600 EDS water probe by YSI Incorporated. Following is a description of the 6600 EDS, based on information provided by the vendor. The information provided below was not verified in this test.

Figure 2-1. YSI 6600 EDS

The 6600 EDS (Figure 2-1) is a multi-parameter water probe/sonde capable of measuring dissolved oxygen (DO), specific conductivity, temperature, pH, turbidity, and chlorophyll (total *in vivo*).

The 6600 EDS is maintained free of fouling by the Clean Sweep™ universal wiper assembly, as well as by individual optical wipers. 6600 EDS sensors are field-replaceable and integrate with data collection platforms. Flash memory prevents data loss, and C-cell battery power allows long-term deployment. The tested 6600 EDS was coated with YSI's optional anti-fouling paint.

The outer diameter of the 6600 EDS is 8.9 centimeters (cm) (3.5 inches). It is 52 cm (20.4 inches) long and weighs 2.7 kilograms (six pounds). The 6600 EDS sells for approximately $10,000. The range, resolution, and accuracy of the 6600 EDS, as indicated by the vendor, are listed in Table 2-1 for the parameters tested.

Table 2-1. 6600 EDS Range, Resolution, and Accuracy as Provided by the Vendor

Parameter	Range	Resolution	Accuracy
DO % Saturation	0 to 500%	0.1%	0 to 200% ±2%; 200 to 500% ±6% of reading
DO	0 to 50 milligrams/liter (mg/L)	0.01 mg/L	0 to 20 mg/L ±0.2 mg/L 20 to 50 mg/L ±0.6 mg/L
Specific conductivity	0 to 100 millisiemen (mS)/cm	0.001 to 0.1 mS/cm	±0.5% of reading +0.001 mS/cm
Temperature	-5 to +45˚C	0.01˚C	±0.15˚C
pH	0 to 14	0.01	±0.2
Turbidity	0 to 1,000 nephelometric turbidity unit (NTU)	0.1 NTU	±5% of reading or 2 NTU, whichever is greater
Chlorophyll	0 to 400 microgram (µg)/L 0 to 100% fluorescence	0.1 µg/L chlorophyll 0.1% fluorescence	NA

NA = not applicable (measures total fluorescence)

Chapter 3
Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Long-Term Deployment of Multi-Parameter Water Quality Probes/Sondes*.(1) The purpose of the verification test was to evaluate the performance of the 6600 EDS under realistic operating conditions. The 6600 EDS was evaluated by determining calibration check accuracy and by comparing 6600 EDS measurements with standard reference measurements and measurements from handheld calibrated probes. Two 6600 EDSs were deployed in saltwater, freshwater, and laboratory environments near Charleston, South Carolina, during a 3 ½-month verification test. Water quality parameters were measured both by the 6600 EDSs and by reference methods consisting of collocated field-portable instrumentation and analyses of collected water samples. During each phase, performance was assessed in terms of calibration check accuracy, relative bias, precision, linearity, and inter-unit reproducibility for each 6600 EDS.

The performance of the 6600 EDS was verified in terms of the following parameters:

- DO
- Specific conductivity
- Temperature
- pH
- Turbidity
- Chlorophyll (total *in vivo*).

3.2 Test Site Characteristics

The three test sites used for this verification were selected in an attempt to expose the 6600 EDS to the widest possible range of conditions while conducting an efficient test. The three sites included one saltwater, one freshwater, and one controlled location. Approximate ranges for the target parameters at each of the test sites as determined by reference measurements are given in Table 3-1.

Table 3-1. Water Characteristics at the Test Sites

Parameter	Saltwater		Freshwater		Mesocosm	
	Low	High	Low	High	Low	High
DO	3 mg/L	6 mg/L	6.8 mg/L	11.2 mg/L	9.3 mg/L	12.1 mg/L
Specific conductivity	31 mS/cm	41 mS/cm	0.27 mS/cm	29.3 mS/cm	0.5 mS/cm	28 mS/cm
Temperature	20°C	28°C	11°C	27°C	9°C	16°C
pH	7.2	7.8	6.9	7.5	7.1	8.5
Turbidity	8 NTU	37 NTU	1.7 NTU	3.6 NTU	0.4 NTU	15 NTU
Chlorophyll (total fluorescence)	2 µg/L	5 µg/L	0.0 µg/L	16 µg/L	0.2 µg/L	1.4 µg/L

3.3 Test Design

The verification test was designed to assess the performance of multi-parameter water probes and was closely coordinated with the National Oceanic and Atmospheric Administration (NOAA) through the Center for Coastal Environmental Health and Biomolecular Research (CCEHBR). The test was conducted in three phases at a saltwater site in a tributary of Charleston Harbor; a freshwater site at the Hollings wetland on the CCEHBR campus; and a controlled site at the CCEHBR mesocosm facility in Charleston, South Carolina. At each test site, two 6600 EDSs were deployed as close to each other as possible to assess inter-unit reproducibility. The first phase of the test was conducted at the saltwater site (Figure 3-1). The CCEHBR campus has access to the tributary of Charleston Harbor site, which is a predominantly tidal body of water that receives some riverine input; its salinities range from 20 to 35 parts per thousand. The second phase of the test was conducted at the freshwater site (Figure 3-2). The freshwater site was a wetlands area near the Hollings Marine Research Laboratory, located on the CCHEBR campus. The third phase was conducted at the CCEHBR's mesocosm facility (Figure 3-3). This facility contains modular mesocosms that can be classified as "tidal" or "estuarine." The mesocosm phase included both saltwater and freshwater conditions.

The precision measurements were performed before the 6600 EDS was deployed into the saltwater environment. The 6600 EDS was placed in a tank of saline water inside the NOAA laboratory. While in this stable environment, the 6600 EDS sampled at a rate of once per minute for approximately 30 minutes to collect data used in the percent relative standard deviation (RSD).

The schedule for the various testing activities is given in Table 3-2.

Figure 3-1. Saltwater Site

Figure 3-2. Freshwater Site

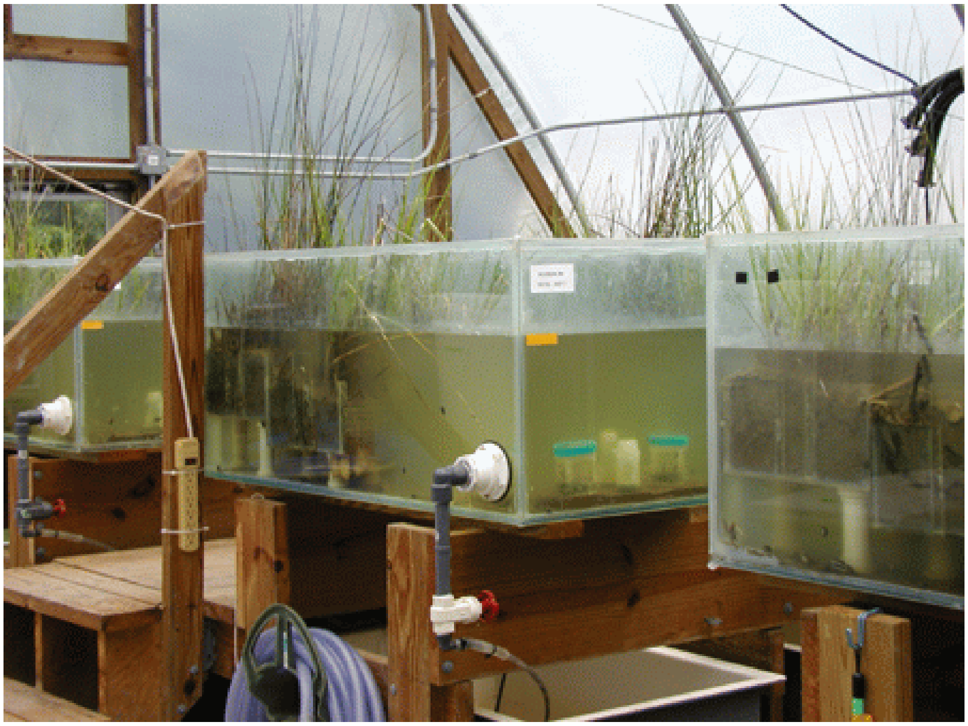


Figure 3-3. Mesocosm Tank

Table 3-2. Verification Test Schedule

Activity	Date
Vendor setup for saltwater phase	October 1, 2003
Begin saltwater phase	October 2, 2003
End saltwater phase	October 29, 2003
Set up freshwater phase	October 31, 2003
Begin freshwater phase	November 4, 2003
End freshwater phase	December 8, 2003
Vendor setup for mesocosm	December 9, 2003
Begin mesocosm phase	December 10, 2003
End mesocosm phase	January 5, 2004
Return all equipment	January 8, 2004

3.3.1 Saltwater Testing

The saltwater phase lasted for 28 days, during which time the 6600 EDS monitored the naturally occurring range of the target parameters 24 hours per day at 15-minute measurement intervals. Dockside reference measurements were made for DO, specific conductivity, temperature, and pH, while reference samples for turbidity and chlorophyll were collected and returned to the laboratory for analysis. Figure 3-4 shows the 6600 EDSs at the pier. The 6600 EDSs were mounted on iron posts that were driven into the river bed. The 6600 EDSs were approximately 0.5 meters apart in the shallows of the tidal river. Reference samples were collected throughout the day during the test. For the duration of this phase, the 6600 EDSs were deployed at depths between approximately one and 10 feet, varying according to the tide. Table 3-3 shows the times and numbers of samples taken throughout the saltwater phase.

Figure 3-4. Saltwater Deployment

Table 3-3. Schedule for Saltwater Sample Collection—Tributary of Charleston Harbor

Test Day	Date	# Reference Samples	Activities
1	10/2/2003		Deploy 6600 EDSs
7	10/8/2003	2	
8	10/9/2003	4	
14	10/15/2003	4	
15	10/16/2003	4	
22	10/23/2003	6	
26	10/27/2003	9	
27	10/28/2003	6	
28	10/29/2003	6	
29	10/30/2003		Retrieve 6600 EDSs

3.3.2 Freshwater Testing

Freshwater testing was conducted at the wetlands on the CCEHBR campus and lasted 35 days. As in the saltwater phase of the verification test, the 6600 EDSs monitored the naturally occurring target parameters 24 hours per day, while reference measurements were made and turbidity and chlorophyll reference samples collected, again rotating among collection times. Table 3-4 shows the sampling times and number of samples collected throughout the freshwater phase. The 6600 EDSs were hung from a large post suspended several feet from the bottom of the pond.

During this portion of the deployment, the salinity and stratification of the freshwater pond increased. Natural weather and extreme tidal events caused the freshwater pond to become brackish and highly stratified. Reference measurements taken at varying depths along the water column during the first week of December showed significant stratification between the top and bottom of the freshwater pond. As a result, the freshwater phase at the Hollings wetlands was discontinued on December 8. The mesocosm deployment (Section 3.3.3) was extended to collect data using a freshwater deployment.

Table 3-4. Schedule for Freshwater Sample Collection—Hollings Wetlands

Test Day	Date	# Reference Samples	Activities
1	11/4/2003		Deploy 6600 EDSs
2	11/5/2003	6	
3	11/6/2003	9	
4	11/7/2003	6	
17	11/20/2003	9	
30	12/03/2003	9	
35	12/08/2003	16	Retrieve 6600 EDSs

3.3.3 Mesocosm Testing

Mesocosm testing was performed over 27 days according to the schedule shown in Table 3-5. Reference measurements were made and water samples were collected during each test day throughout the normal operating hours of the facility (nominally 6 a.m. to 6 p.m.). During this phase, the mesocosm was manipulated to introduce variations in the measured parameters. The turbidity of the system was varied by operating a pump near the sediment trays to suspend additional solids in the water. Specific conductivity was varied by adding freshwater to the saltwater during the last three weeks of testing. These activities are detailed in Table 3-5.

Table 3-5. Schedule for Mesocosm Sample Collection

Test Day	Date	# Reference Samples	Activities
1	12/10/2003	4	Deploy 6600 EDSs in saltwater
3	12/12/2003	6	10:00 - Transition to freshwater (to change specific conductivity)
4	12/13/2003		Begin freshwater portion of deployment
6	12/15/2003	4	11:05 - Turn off air bubblers and turn off circulation pump
7	12/16/2003	4	10:40 - Turn on circulation pump 10:50 - Add mud slurry (to change turbidity) 13:00 - Add additional mud slurry 15:11 - Turn off circulation pump
8	12/17/2003	5	
9	12/18/2003	2	
24	1/2/2004	3	10:20 - Turn on air bubblers (to change DO)
27	1/5/2004	3	Retrieve 6600 EDSs

Variations in DO, temperature, pH, and chlorophyll were driven by natural forces and the changes in the other test parameters. Parameters over the ranges specified in Table 3-1 were monitored by the 6600 EDS. Samples were collected and analyzed using a reference method for comparison.

3.4 Reference Measurements

The reference measurements made in this verification test and the equipment used for the measurements were as follows:

- DO—National Institute of Standards and Technology (NIST)-traceable, commercially available probe (Orion 830A)

- Specific conductivity—NIST-traceable, handheld specific conductivity meter (Myron 4P)

- Temperature—NIST-traceable, handheld thermocouple and readout (Orion 830A)
- pH—NIST-traceable, handheld pH meter (Orion 230)
- Turbidity—Hach Ratio XR turbidity meter (Hach 43900)
- Chlorophyll—Turner 10-AU fluorometer (total *in vivo* fluorescence).

Reagents were distilled deionized water (for field blanks) and a Hach Ratio XR turbidity standard from Advanced Polymer Systems. Sampling equipment consisted of 0.5- to 1.0-L glass bottles, a Niskin sampling device, and provisions for sample storage. The maximum sample holding times are given in Table 3-6. All sample holding time requirements were met.

Table 3-6. Maximum Sample Holding Times

Parameter	Holding Time
DO	none[(a)]
Specific conductivity	none
Temperature	none
pH	none
Turbidity	24 hours
Chlorophyll	1 week

[(a)] "None" indicates that the sample analyses must be performed immediately after sample collection or in the water column at the site.

Chapter 4
Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[2] and the test/QA plan for this verification test.[1]

4.1 Instrument Calibration

Both the portable and laboratory reference instruments were calibrated by CCEHBR according to the procedures and schedules in place at the test facility, and documentation was provided to Battelle.

4.2 Field Quality Control

Replicate samples were taken during field sampling for assessment of the reference methods. The replicate samples were collected once each week during a regular sampling period by splitting field samples into two separate samples (containers) and analyzing both by the same laboratory reference methods. The results from the replicate analysis and the field blanks met the criteria listed in Tables 4-1 and 4-2, respectively. A container of deionized water (field blank) was taken to the field, brought back to the laboratory, and analyzed in the same manner as the collected samples.

4.3 Sample Custody

Samples collected at the saltwater, freshwater, and mesocosm sites were transported by the scientist performing the sampling at CCEHBR to the laboratory in an ice-filled cooler and analyzed immediately; therefore, no chain-of-custody forms were required.

Table 4-1. Replicate Analysis QC Criteria

Parameter	Observed Agreement
DO	±5%
Specific conductivity	±5%
Temperature	±1°C
pH	±0.1
Turbidity	±5 NTU
Chlorophyll	±5%

Table 4-2. Expected Values for Field Blanks

Parameter	Observed Maximum Difference
Turbidity	1 NTU
Chlorophyll	3 x average of three blank filters

4.4 Audits

4.4.1 Performance Evaluation Audit

A performance evaluation (PE) audit was conducted by the Battelle Test Coordinator once during the verification test to assess the quality of the reference measurements. For the PE audit, independent standards were used. Table 4-3 shows the procedures used for the PE audit and associated results.

Table 4-3. Summary of Performance Evaluation Audits

Audited Parameter	Audit Procedure	Acceptable Tolerance	Actual Difference	Passed Audit
DO	Oakton 100 monitor	±5%	1.1%	Yes
Specific conductivity	Myron 4P meter	±5%	0.9%	Yes
Temperature	Orion 230 thermometer	±1°C	0.0°C	Yes
pH	Oakton 300 pH meter	±0.1	0.05	Yes
Turbidity	Advanced Polymer Systems turbidity standard	±10%	0.72%	Yes
Chlorophyll	Independent chlorophyll standard	±5%	0.4%	Yes

The DO measurement made by the Orion 830A was compared with that from a handheld DO Oakton 100 monitor. Agreement within 1.1% was achieved. A handheld Oakton 300 specific conductivity meter was used to perform the specific conductivity audit. Agreement within 0.9% between the results of the Myron 4P meter and those of the Oakton reference meter was seen. A NIST-traceable Orion 230 thermometer was used for the temperature performance audit. The comparison was made with a sample of collected water, and agreement was within 0.0°C. The Oakton 100 handheld pH reference meter was compared with the Oakton 300 handheld pH meter. A pH tolerance of 0.05 was recorded. The Hach turbidity meter measurements were compared with an independent turbidity standard. Agreement within 0.4% was observed. The *in vivo* chlorophyll measurements agreed within 0.1%.

4.4.2 Technical Systems Audit

The Battelle Quality Manager conducted a technical systems audit (TSA) on October 28, 2003, to ensure that the verification test was performed in accordance with the test/QA plan[(1)] and the AMS Center QMP.[(2)] As part of the audit, the Battelle Quality Manager reviewed the reference methods used, compared actual test procedures to those specified in the test/QA plan, and reviewed data acquisition and handling procedures. Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

During the verification test, two deviations from the test/QA plan were necessary. The first occurred when natural weather events caused the freshwater pond to become brackish and highly stratified, resulting in reference measurements that were not representative of the water the 6600 EDS measured. An extended freshwater period, beginning on December 13, 2003, was added to the end of mesocosm deployment to provide data from a freshwater deployment. Therefore, relative bias and linearity data were not collected at the freshwater site. The data were collected from the mesocosm extension instead. The second deviation occurred when a problem with the Niskin sampler developed. The sampler broke after several uses at the beginning of the saltwater period and was replaced as soon as possible. However, this malfunction resulted in fewer reference samples. The deviations had no impact on the results of the test.

4.4.3 Audit of Data Quality

At least 10% of the data acquired during the verification test was audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.5 QA/QC Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[(2)] Once the assessment report was prepared, the Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.6 Data Review

Records generated in the verification test were reviewed within two weeks of generation before these records were used to calculate, evaluate, or report verification results. Table 4-4 summarizes the types of data recorded. The review was performed by a Battelle and a CCEHBR technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-4. Summary of Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data[a]
Dates, times of test events	CCEHBR	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 incorporated data into spreadsheets - stored in test binder
Test parameters	Battelle/ CCEHBR	Laboratory record books/data sheets	Each sample collection	Used to organize/check test results; manually incorporated data into spreadsheets - stored in test binder
6600 EDS data - digital display - electronic output	 CCEHBR CCEHBR	 Data sheets Probe data acquisition system (DAS); data stored on probe downloaded to personal computer	 Continuous 15-minute sampling; data downloaded to personal computer	Used to organize/check test results; incorporated data into electronic spreadsheets - stored in test binder
Reference monitor readings/reference analytical results	CCEHBR	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 incorporated data into spreadsheets - stored in test binder
Reference calibration data	CCEHBR	Laboratory record books/data sheets/DAS	Whenever zero and calibration checks are done	Documented correct performance of reference methods - stored in test binder
PE audit results	Battelle	Laboratory record books/data sheets/DAS	At times of PE audits	Test reference methods with independent standards/measurements - stored in test binder

(a) All activities subsequent to data recording were carried out by Battelle.

Chapter 5
Statistical Methods

The statistical methods presented in this chapter were used to verify the performance parameters listed in Section 3.1.

5.1 Calibration Check Accuracy

The 6600 EDS was calibrated for each measured parameter at the beginning and end of each deployment period according to the vendor's instruction manual. The results from the calibration checks were summarized, and accuracy was determined each time the calibration check was conducted. Calibration check accuracy (*A*) is reported as a percentage, calculated using the following equation:

$$A=1-(C_s-C_p)/C_s \text{ x } 100 \quad (1)$$

where C_s is the value of the reference standard, and C_p is the value measured by the 6600 EDS. The closer *A* is to 100, the more consistent the calibration check accuracy.

5.2 Relative Bias

Water samples were analyzed by both the reference method and the 6600 EDS, and the results were compared. The results for each sample were recorded, and the accuracy was expressed in terms of the average relative bias (*B*), as calculated from the following equation:

$$B = \frac{C_R - C_P}{C_R} \text{ x } 100 \quad (2)$$

where C_P is a measurement taken from the 6600 EDS being verified at the same time as the reference measurement was taken, and C_R is the reference measurement. This calculation was performed for each reference sample analysis for each of the six target water parameters. In addition, relative bias was assessed independently for each 6600 EDS so the results may be used to determine inter-unit reproducibility.

5.3 Precision

The standard deviation (*S*) of the measurements made during a period of stable operation at the mesocosm was calculated and used as a measure of probe precision:

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

where n is the number of replicate measurements, C_k is the concentration reported for the kth measurement, and $\overline{C}$ is the average concentration of the replicate measurements.

Precision was calculated for each of the six target water parameters. Probe precision was reported in terms of the percent RSD of the series of measurements.

$$\%RSD = \frac{S}{\overline{C}} \text{ x } 100 \qquad (4)$$

5.4 Linearity

For target water parameters, linearity was 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 was assessed separately for each 6600 EDS.

5.5 Inter-Unit Reproducibility

The results obtained from the two 6600 EDSs were compiled independently and compared to assess inter-unit reproducibility. Inter-unit reproducibility was determined by calculating the average absolute difference between the two 6600 EDSs. In addition, the two 6600 EDSs were compared by evaluating the relative bias of each.

Chapter 6
Test Results

The results of the verification of the two 6600 EDSs (identified as YSI AA and YSI AB in this report) are presented in this section. The 6600 EDS data were recorded at 15-minute intervals throughout the verification test. First, a visual record of the condition of the 6600 EDSs pre- and post-deployment is discussed, then the statistical comparisons are made. Finally, a record of the activities involved in servicing and maintenance of the 6600 EDSs is presented.

Prior to the initial saltwater deployment, the 6600 EDSs were in "like-new" condition. That is, they arrived from the vendor crated and ready for installation. Figure 6-1 shows one of the two

Figure 6-1. 6600 EDS Prior to Deployment. Starting in the upper right and proceeding clockwise: (1) clean 6600 EDS, (2) close-up of clean probes, (3) close-up of wiping brushes, (4) protective shroud and mesh, (5) aluminum tube guarding against crushing damage.

6600 EDSs in its pre-deployment condition. As deployed, the end where the individual probes connect is protected by the PVC shroud shown in Figure 6-1. Over this shroud is a nylon mesh that was used to keep small animals away from the optical sensors of the 6600 EDS. Finally, this entire apparatus was placed inside an aluminum tube that guarded against crushing damage.

Following the saltwater deployment, the 6600 EDSs were retrieved from the water and immediately returned to the laboratory to record the post-deployment condition. Figure 6-2 shows the post-deployment condition of the 6600 EDSs. The 6600 EDSs were covered with a combination of green algae, silt, and some shell growth. The protective screens appeared to have helped keep some of this material off of the sensor heads.

Figure 6-2. 6600 EDS After Saltwater Deployment. 6600 EDSs on the pier (top), close-up of wiping brushes (bottom)

Prior to redeployment at the freshwater location, the 6600 EDSs were cleaned and serviced as necessary. Then the 6600 EDSs were placed overnight in a tank of oxygen-saturated water before deployment. Figure 6-3 shows the cleaned and reconditioned 6600 EDSs in this tank.

Figure 6-3. Cleaned and Reconditioned 6600 EDSs in Storage Tank Used Between Deployments

Finally, the condition of the 6600 EDSs after the freshwater deployment was recorded and is shown in Figure 6-4.

Figure 6-4. 6600 EDS After Freshwater Deployment

6.1 Calibration Check Accuracy

The 6600 EDSs were calibrated at the beginning of each deployment period, and the calibrations were checked at the end of each deployment. In the case of pH and turbidity, a two-point calibration was performed as instructed by the vendor. No check was performed for temperature. The calibration check levels were selected based on the manufacturer's instructions. Table 6-1 shows the results from these calibration checks for the saltwater, freshwater, and mesocosm tests. The "Calibration Standard" column refers to the listed concentration of the standards used in the calibrations, the "YSI AA and YSI AB Readings" columns give the 6600 EDSs results during the calibration checks, and the "YSI AA and YSI AB Accuracy" columns show the calibration check accuracy using the calculations given in Section 5.1. In the cases where the zero point was checked, only the absolute difference is listed. During the deployments, the accuracy for DO ranged from 87.0 to 105%; for specific conductivity, from 96.8 to 102%; for pH, from 98.3 to 102%; and for turbidity, from 98 to 101%. The zero point check for turbidity resulted in a difference of -0.2 to 0.3 NTU; and, for chlorophyll, the zero point check resulted in a difference of -0.5 to 0.9 total (*in vivo*) chlorophyll.

The two extreme points were found during the DO calibration checks on December 9, 2003, of 87% (YSI AA) and 105% (YSI AB) after the freshwater deployment. It was observed that the 6600 EDS had several bubbles under the membrane. These bubbles could have been formed during transit and may have decreased calibration check accuracy. These bubbles were not present during other calibration checks.

6.2 Relative Bias

Relative bias (the percent difference between the 6600 EDS measurements and the reference measurements) was assessed by comparing the reference measurements with the YSI AA and YSI AB readings. The 6600 EDS reading that was closest in time to the reference sample was used. Plots of the YSI AA and YSI AB data, along with the corresponding reference measurements that were used for the relative bias calculations, are shown in Figures 6-5a through l.

The relative bias results are summarized in Table 6-2. As mentioned in Section 3.3.2, due to the stratification of the freshwater pond, no relative bias calculations were conducted on measurements between November 11 and December 8, 2003. In general, the relative bias was less for temperature, specific conductivity, DO, and pH; while the optically measured parameters of chlorophyll and turbidity were much greater. This may be due to the fact that the 6600 EDS measurements for turbidity and chlorophyll are instantaneous, while the reference measurements are integrated over several seconds.

Specifically, the results from the temperature measurements yielded the smallest relative bias, being less than 1% over the test. Dissolved oxygen and pH were less than 1.7% during the mesocosm deployment and less than 8.1% during the saltwater deployment. Specific conductivity was less than 12.8% during the mesocosm deployment and less than 8.7% during the saltwater deployment. During the saltwater deployment, the 6600 EDS specific conductivity measurements

Table 6-1. Calibration Check Accuracy

		Calibration Standard					YSI AA Readings				
Deployment Location	**Date**	**DO (%)**	**Specific conductivity (mS/cm)**	**pH**	**Turbidity (NTU)**	**Chlorophyll (Total)**	**DO (%)**	**Specific conductivity (mS/cm)**	**pH**	**Turbidity (NTU)**	**Chlorophyll (Total)**
Saltwater	10/29/2003	100	50.0	7.00	0.0	0.0	99.6	50.1	7.02	0.3	-0.5
	10/29/2003			10.0	120				10.1	120	
Freshwater	12/9/2003	100	1.0	7.00	0.0	0.0	87.0	1.01	6.88	-0.2	0.9
	12/9/2003			10.0	120				10.1	120	
Mesocosm	1/13/2004	100	1.0	7.00	0.0	0.0	97.0	0.968	7.12	0.20	0.8
	1/13/2004			10.0	120				10.1	120	

Table 6-1. Calibration Check Accuracy (continued)

Deployment Location	Date	Calibraton Standard					YSI AB Readings				
		DO (%)	Specific conductivity (mS/cm)	pH	Turbidity (NTU)	Chlorophyll (Total)	DO (%)	Specific conductivity (mS/cm)	pH	Turbidity (NTU)	Chlorophyll (Total)
Saltwater	10/29/2003	100	50.0	7.00	0.0	0.0	101	49.7	7.12	0.2	-0.3
	10/29/2003			10.0	120				10.1	120	
Freshwater	12/9/2003	100	1.00	7.00	0.0	0.0	105	1.02	7.01	-0.2	-0.1
	12/9/2003			10.0	120				10.1	123	
Mesocosm	1/13/2004	100	1.00	7.00	0.0	0.0	99.1	0.98	7.06	0.2	-0.1
	1/13/2004			10.0	120				10.02	124	

Table 6-1. Calibration Check Accuracy (continued)

		YSI AA Calibration Check Accuracy (%)					YSI AB Calibration Check Accuracy (%)				
Deployment Location	Date	DO	Specific conductivity	pH	Turbidity	Chlorophyll	DO	Specific conductivity	pH	Turbidity	Chlorophyll
Saltwater	10/29/2003	99.6	100	100	0.3[a]	-0.5[b]	101	99.5	102	0.2[a]	-0.3[b]
	10/29/2003			101	100				101	98	
Freshwater	12/9/2003	87.0	101	98.3	-0.2[a]	0.9[b]	105	102	100	-0.2[a]	-0.1[b]
	12/9/2003			101	99				101	100	
Mesocosm	1/13/2004	97.0	96.8	102	0.2[a]	0.8[b]	99.1	98.1	101	0.2[a]	-0.1[b]
	1/13/2004			101	99				100	101	

[a] Because zero point was checked, only absolute difference in NTU is listed.
[b] Because zero point was checked, only absolute difference in total (*in vivo*) chlorophyll is listed.

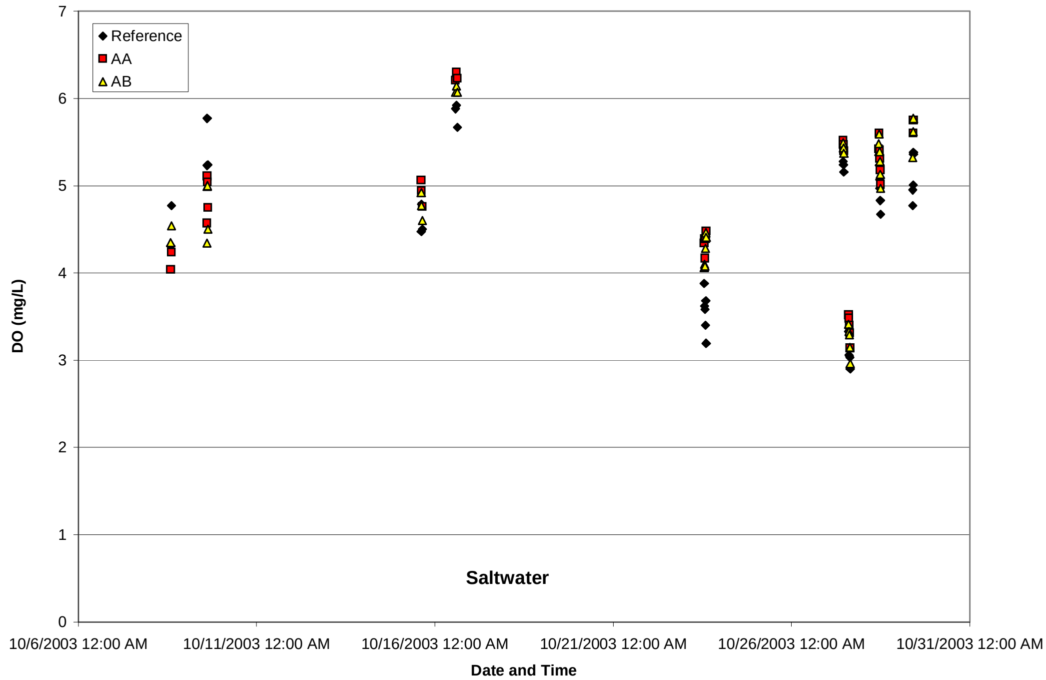


Figure 6-5a. Relative Bias Data for DO (Saltwater)

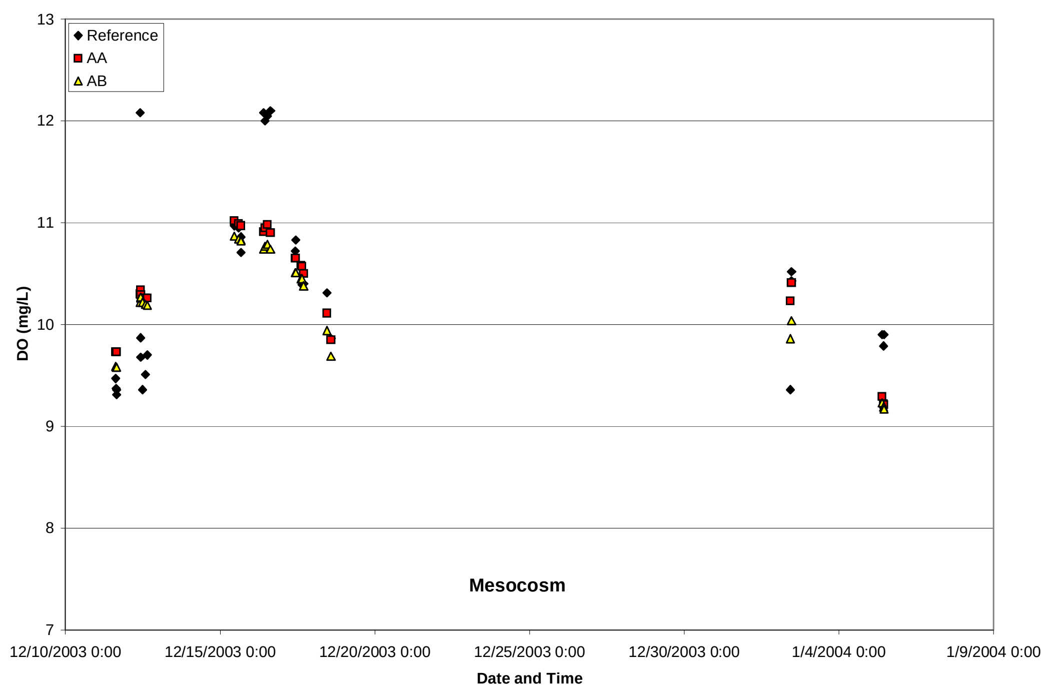


Figure 6-5b. Relative Bias Data for DO (Mesocosm)

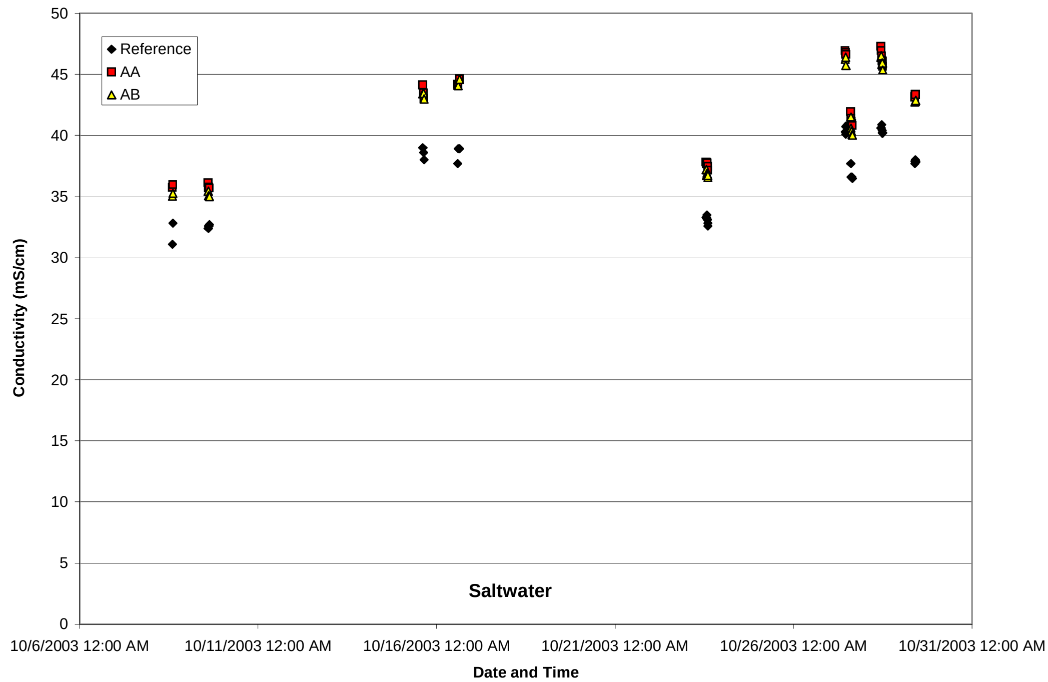


Figure 6-5c. Relative Bias Data for Specific Conductivity (Saltwater)

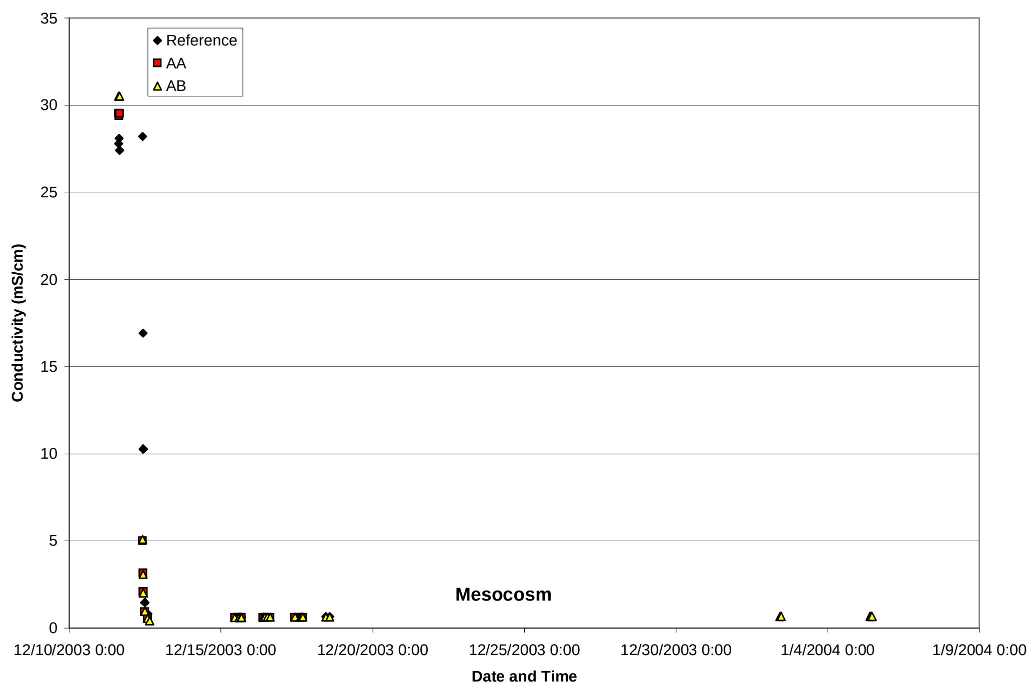


Figure 6-5d. Relative Bias Data for Specific Conductivity (Mesocosm)

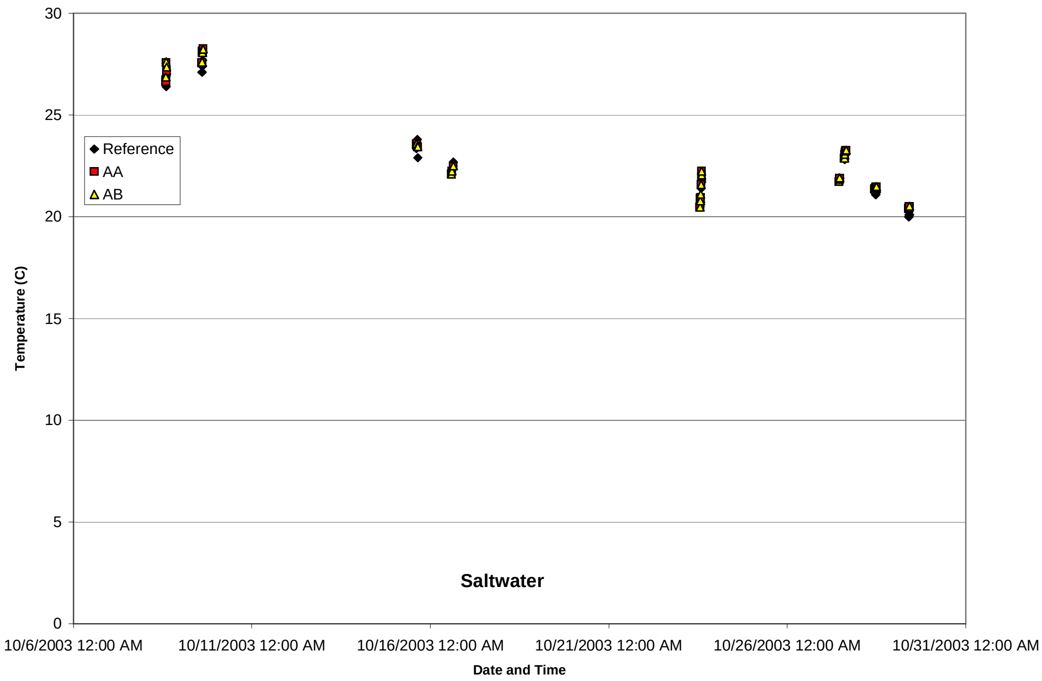


Figure 6-5e. Relative Bias Data for Temperature (Saltwater)

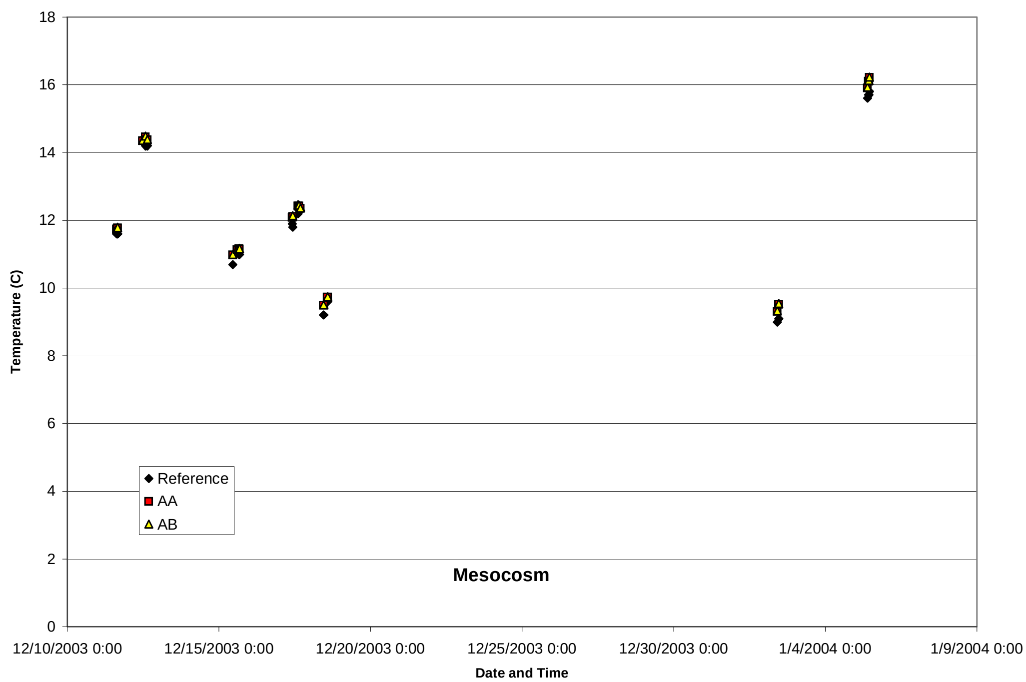


Figure 6-5f. Relative Bias Data for Temperature (Mesocosm)

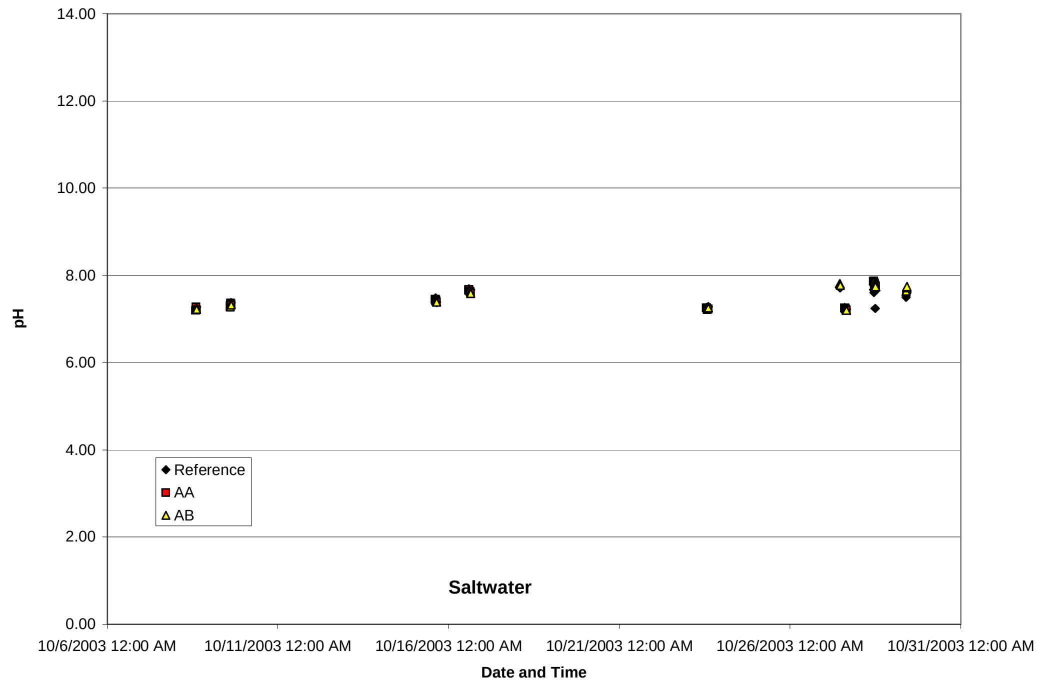


Figure 6-5g. Relative Bias Data for pH (Saltwater)

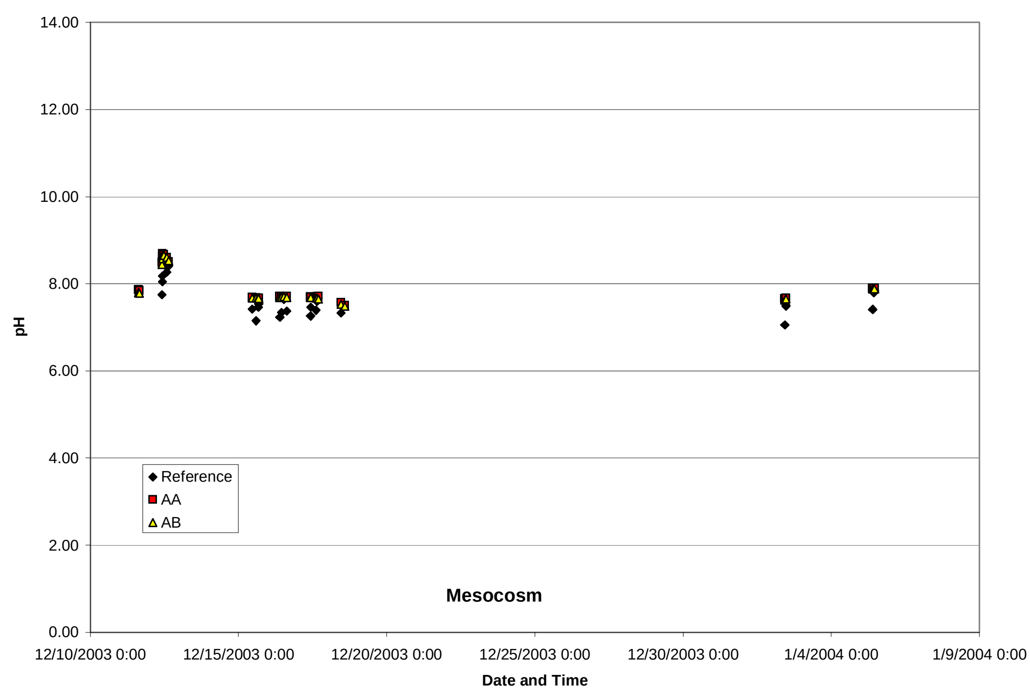


Figure 6-5h. Relative Bias Data for pH (Mesocosm)

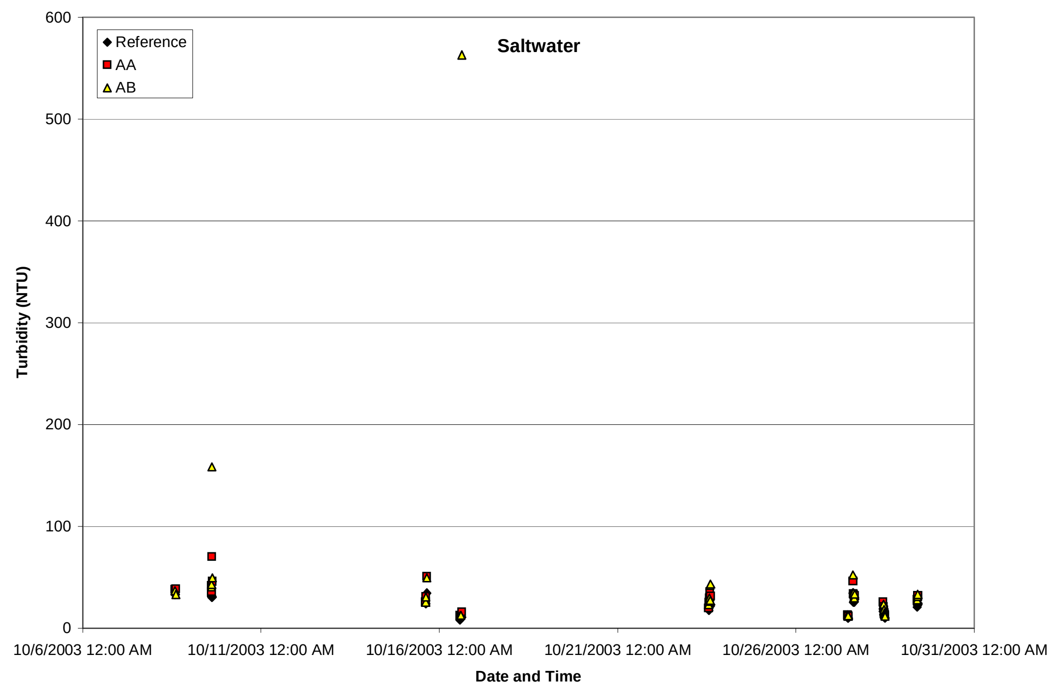


Figure 6-5i. Relative Bias Data for Turbidity (Saltwater)

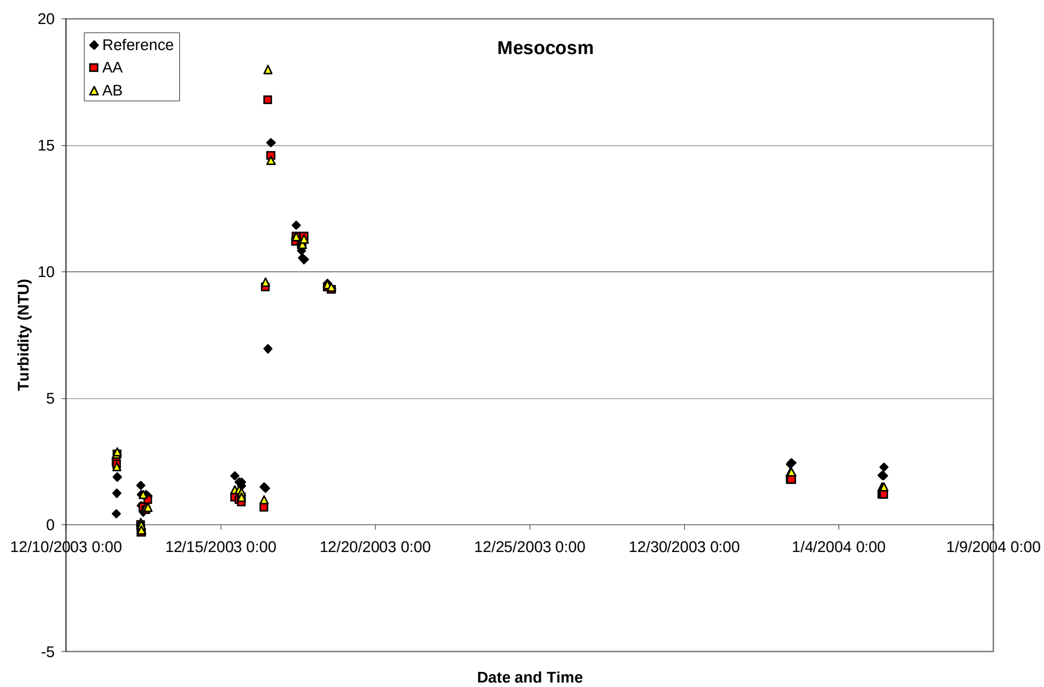


Figure 6-5j. Relative Bias Data for Turbidity (Mesocosm)

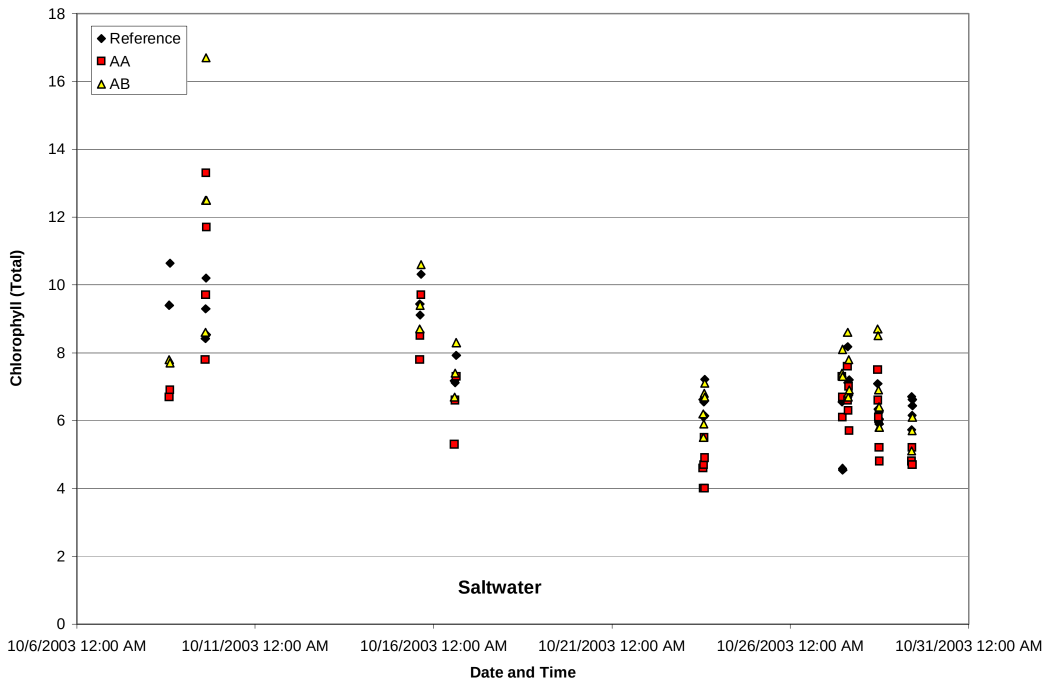


Figure 6-5k. Relative Bias Data for Chlorophyll (Saltwater)

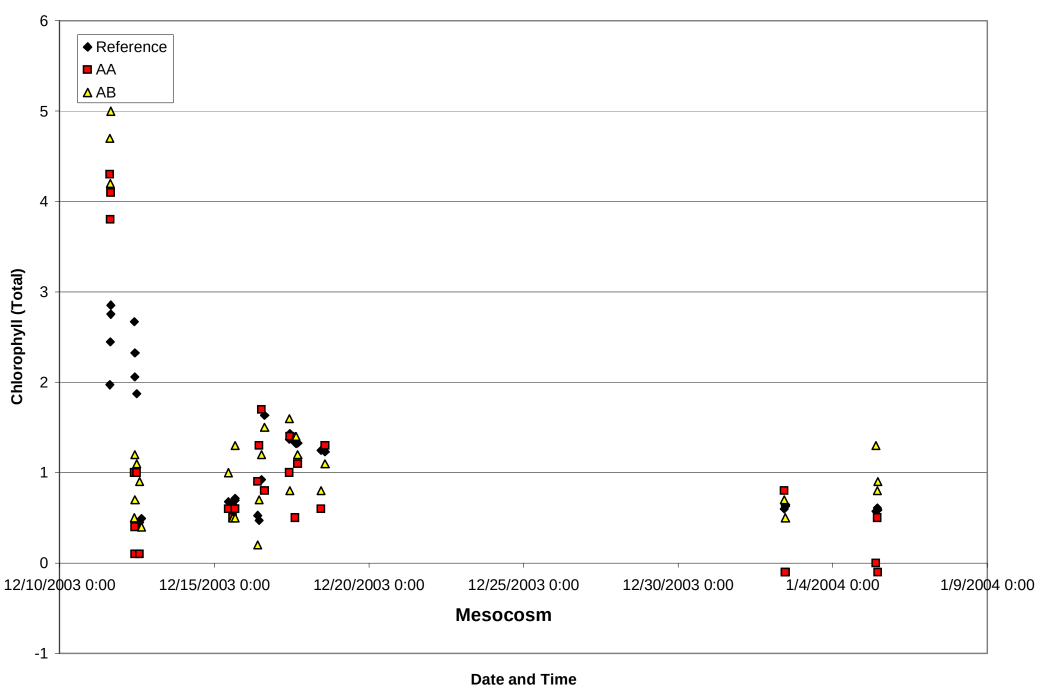


Figure 6-5l. Relative Bias Data for Chlorophyll (Mesocosm)

Table 6-2. Average Relative Bias Results for YSI AA and YSI AB

	Saltwater		Mesocosm	
Parameter	**% Rel. Bias AA**	**% Rel. Bias AB**	**% Rel. Bias AA**	**% Rel. Bias AB**
DO	-7.4	-5.7	0.3	1.7
Specific conductivity	-8.7	-7.6	12.8	10.2
Temperature	-0.1	-0.1	-0.2	-0.2
pH	7.5	8.1	0.39	0.35
Turbidity	-33.6	-184	-17.4	-30.1
Chlorophyll	-98.0	-133	-72.1	-131

displayed a positive 3 to 4 mS/cm relative to reference measurements. This shift was not present during the mesocosm deployment. Chlorophyll and turbidity ranged between -17.4% and -184%. Another representation of the 6600 EDS performance may be obtained by referring to the comparison of reference and 6600 EDS measurements for pre-and post-calibration results (Section 6.1), where the 6600 EDS displayed closer agreement to the reference standards.

6.3 Precision

Table 6-3 shows the results of calculations taken from measurements performed before the saltwater deployment. The precision, reported as %RSD, was less than 1% for DO, specific conductivity, temperature, and pH. Data from turbidity and chlorophyll resulted in higher %RSDs (19.4 and 29.6 for turbidity and 19.8 and 24.6 for chlorophyll). In the test procedures employed to determine precision, turbidity and chlorophyll were subject to possible spikes when a particle passed the field of view of the sensor head.

Table 6-3. Measurements and Percent Relative Standard Deviations for YSI AA and YSI AB During Stable Mesocosm Operation

	YSI AA						YSI AB					
	DO (mg/L)	Specific Conductivity (mS/cm)	Temperature (°C)	pH	Turbidity (NTU)	Chlorophyll (Total)	DO (mg/L)	Specific Conductivity (mS/cm)	Temperature (°C)	pH	Turbidity (NTU)	Chlorophyll (Total)
Maximum	7.38	44.0	20.7	7.35	2.00	2.20	7.79	43.8	20.7	7.46	2.10	2.70
Minimum	7.26	43.8	20.2	7.22	0.5	1.0	7.65	42.9	20.2	7.24	1.0	0.60
Standard Deviation	0.03	0.06	0.15	0.05	0.38	0.30	0.04	0.23	0.15	0.06	0.30	0.38
Average	7.32	43.9	20.4	7.27	1.29	1.49	7.72	43.3	20.5	7.33	1.52	1.55
%RSD	0.44	0.14	0.74	0.62	29.6	19.8	0.46	0.53	0.75	0.76	19.4	24.6

6.4 Linearity

Linearity was assessed by comparing probe readings against the reference values for each of the parameters at each deployment location. Figures 6-6a-l give the results of this comparison by showing the slope, intercept, and coefficient of determination (r^2) for each parameter. In general, linearity and regression coefficients indicated better agreement between the 6600 EDS readings and reference values for the parameters that do not use optical measurements, such as DO, specific conductivity, temperature, and pH. This may be because the test site water was dynamic and the measurements taken were instantaneous. In such cases, the reference method and the 6600 EDS were not measuring exactly the same water sample. The manifestation of this effect would be largest whenever the parameters being measured were rapidly changing, such as in the case of chlorophyll, turbidity, and the induced dynamic environment found in the mesocosm.

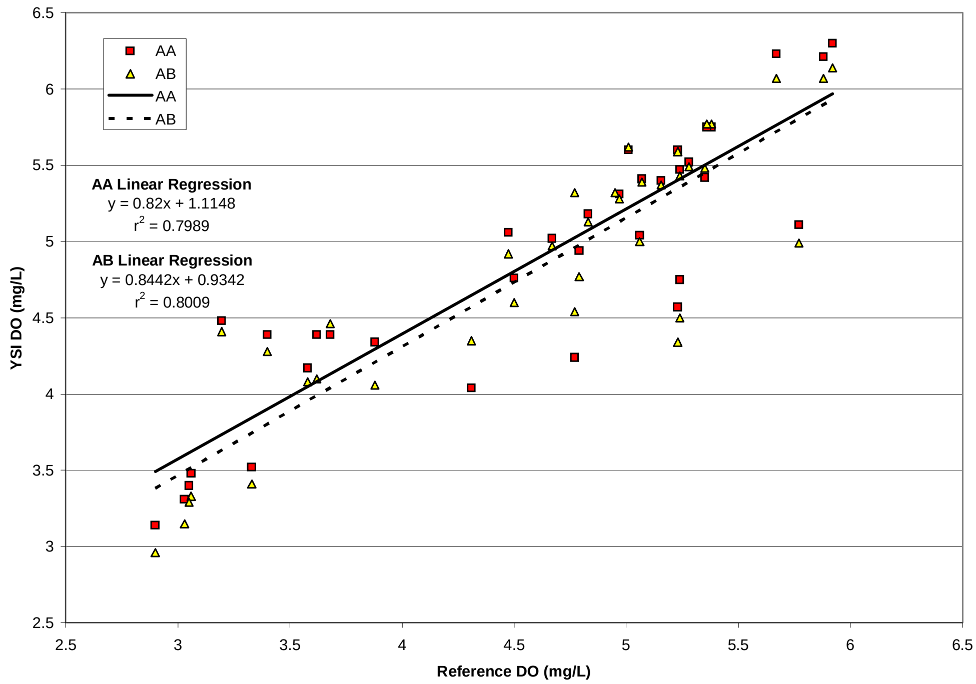


Figure 6-6a. Linearity Data for DO (Saltwater)

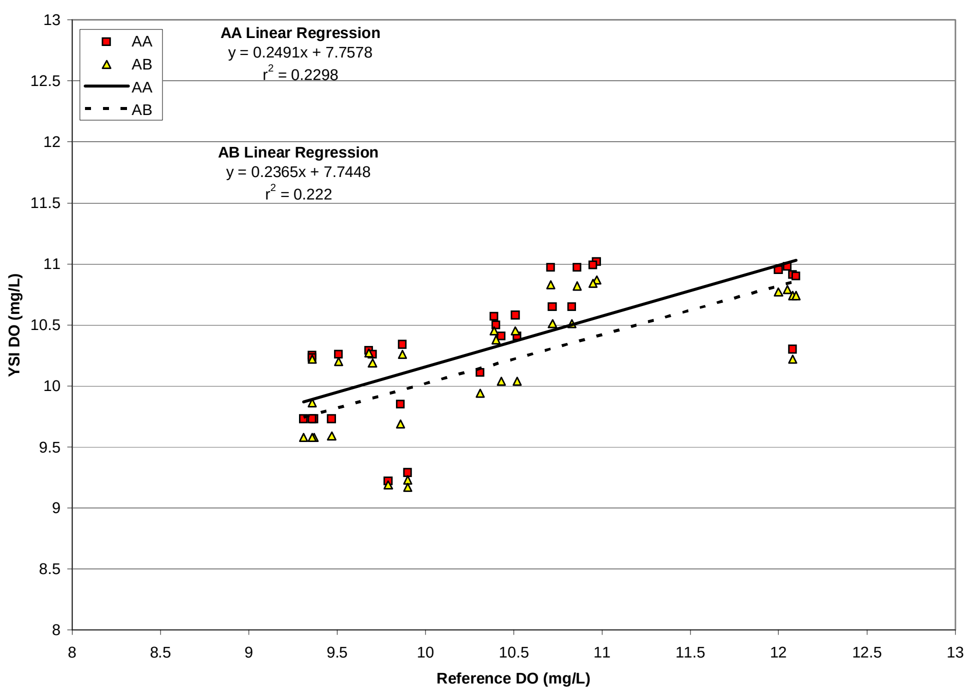


Figure 6-6b. Linearity Data for DO (Mesocosm)

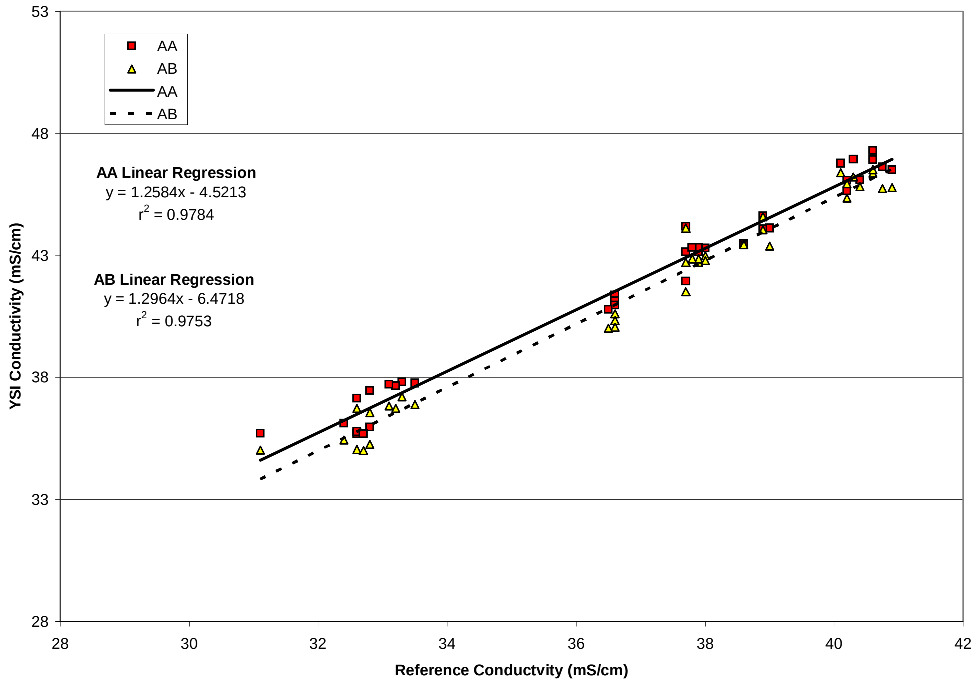


Figure 6-6c. Linearity Data for Specific Conductivity (Saltwater)

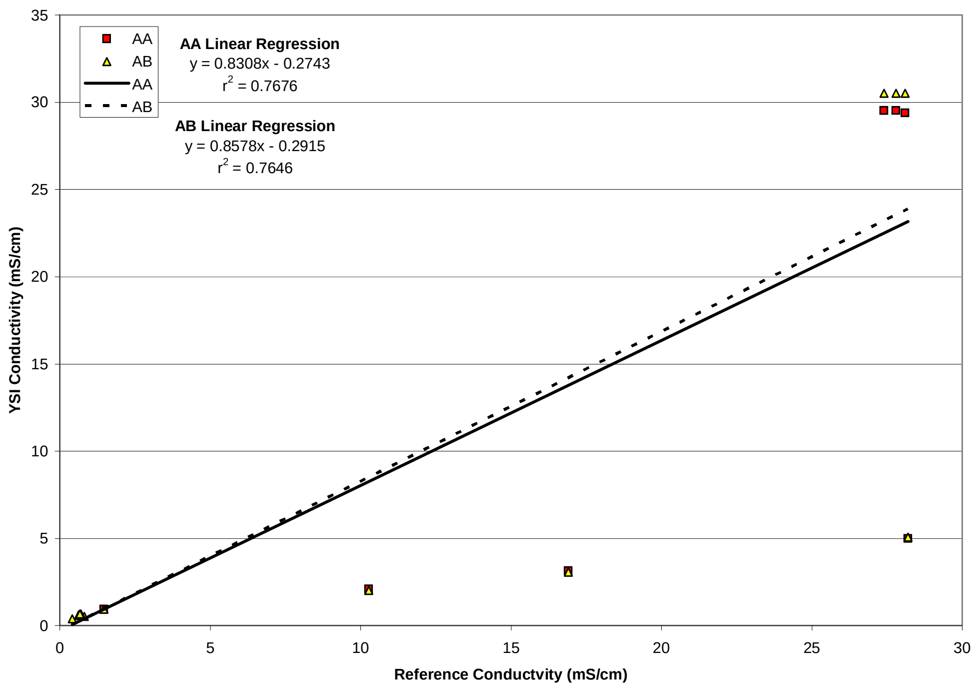


Figure 6-6d. Linearity Data for Specific Conductivity (Mesocosm)

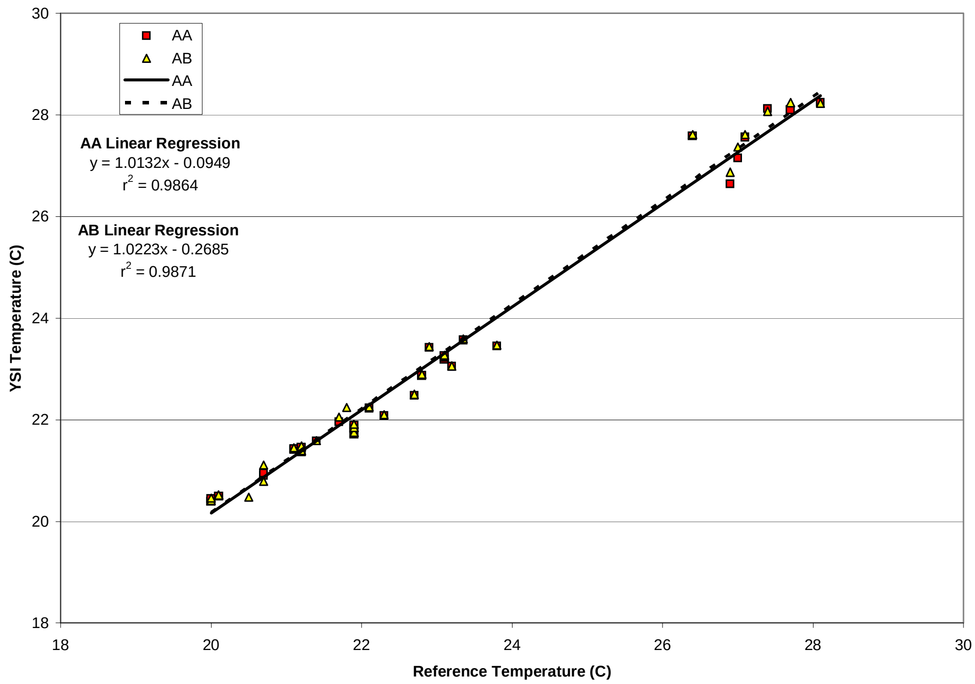


Figure 6-6e. Linearity Data for Temperature (Saltwater)

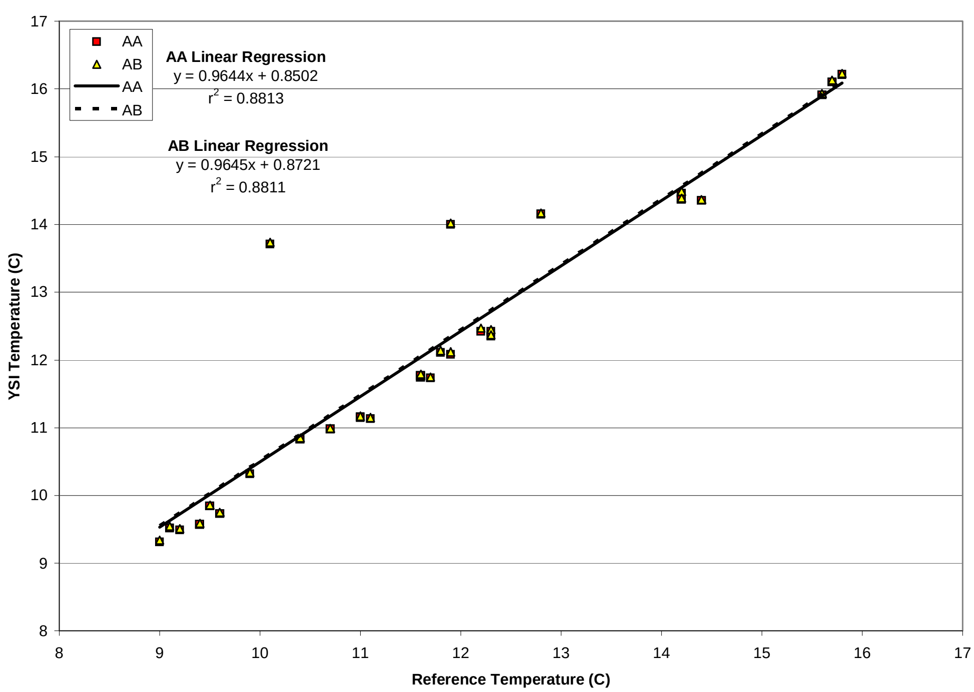


Figure 6-6f. Linearity Data for Temperature (Mesocosm)

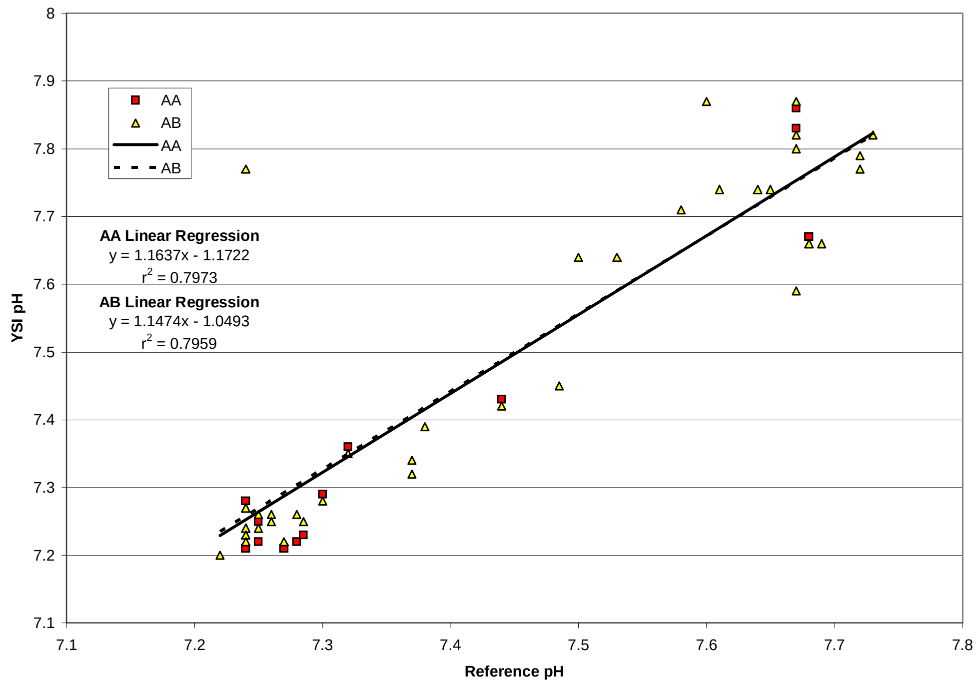


Figure 6-6g. Linearity Data for pH (Saltwater)

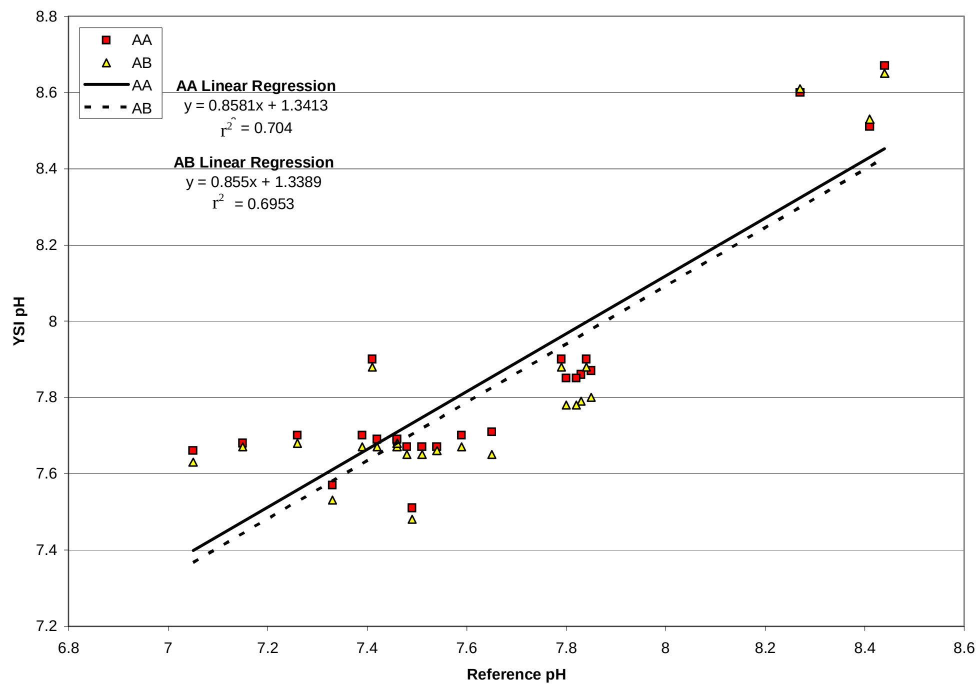


Figure 6-6h. Linearity Data for pH (Mesocosm)

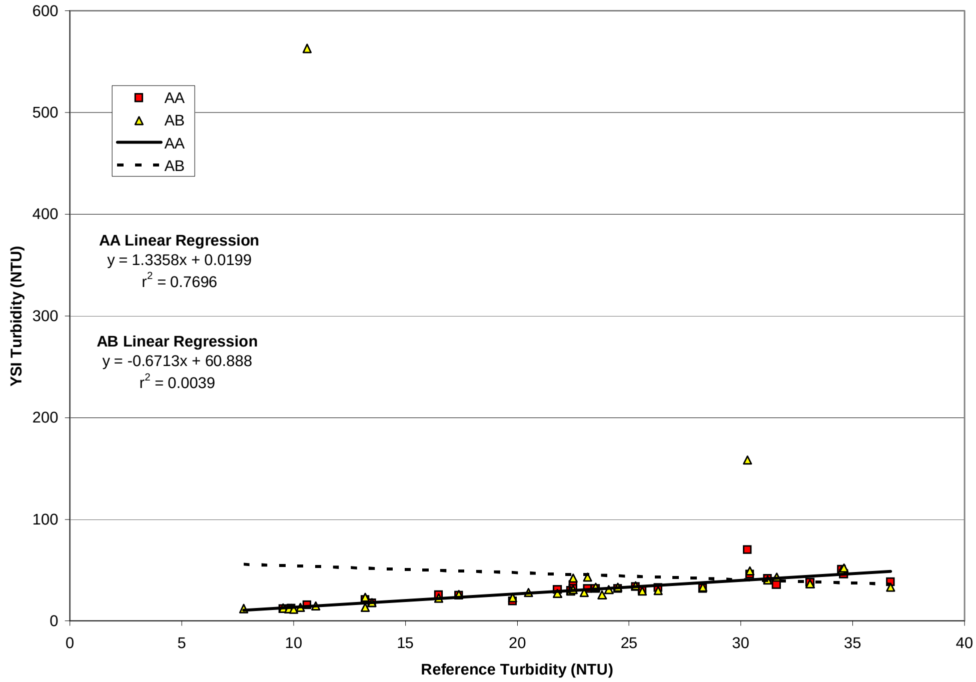


Figure 6-6i. Linearity Data for Turbidity (Saltwater)

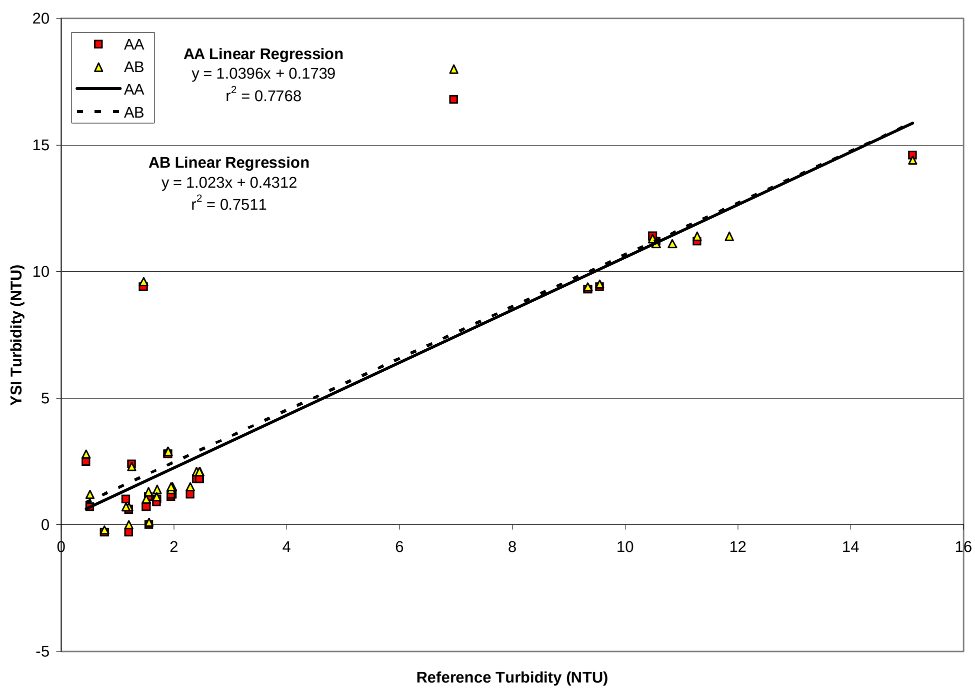


Figure 6-6j. Linearity Data for Turbidity (Mesocosm)

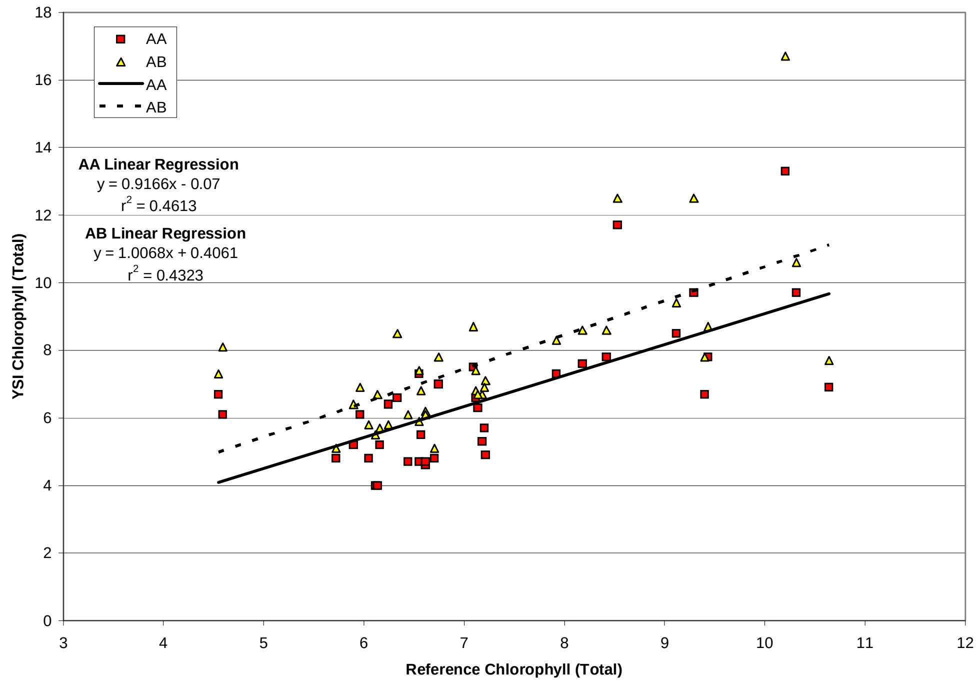


Figure 6-6k. Linearity Data for Chlorophyll (Saltwater)

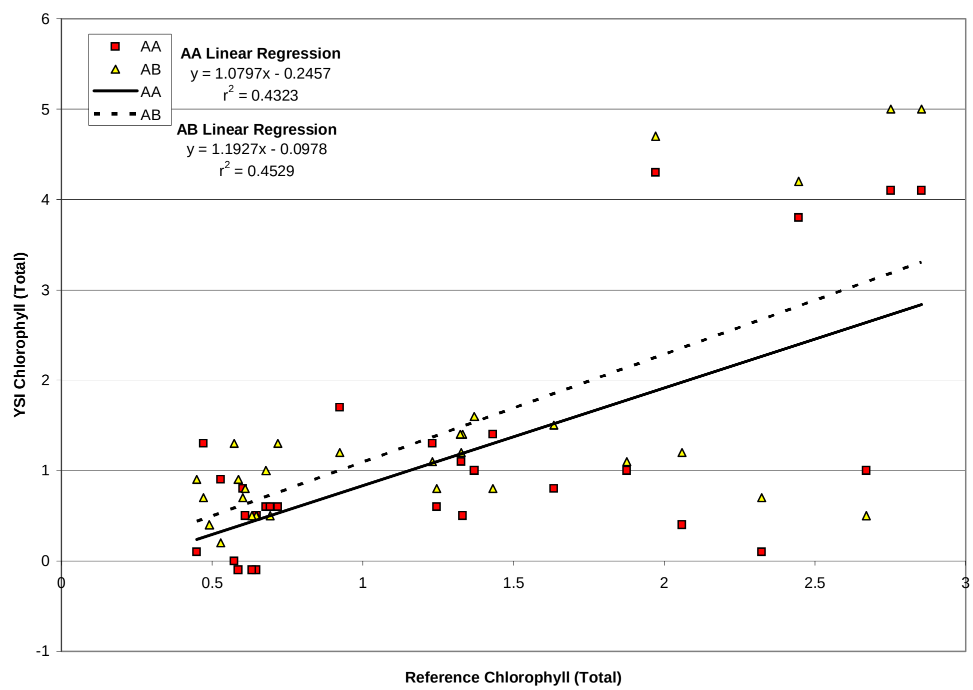


Figure 6-6l. Linearity Data for Chlorophyll (Mesocosm)

6.5 Inter-Unit Reproducibility

Inter-unit reproducibility was assessed both by comparing the relative bias of the two 6600 EDSs (Section 6.2) and by comparing the average differences between the two 6600 EDS readings for each parameter at each deployment location. Freshwater results are included because the two 6600 EDSs were deployed to the same depth. The assessment using the relative bias data is done by looking at the relative bias results in Table 6-2 and comparing the percent relative bias for AA and AB. That comparison, in general, does not show a difference in the relative bias between YSI AA and AB.

This section presents all the 6600 EDS data collected during the deployments for both AA and AB. A comparison of the average absolute differences between the two 6600 EDS readings for each parameter at each deployment location is used to indicate inter-unit reproducibility. Figures 6-7 through 6-12 show the data used for these calculations. Note that Figure 6-11a is on a log scale, since the range of turbidity results was unusually broad. The results of average difference comparisons are shown in Table 6-4, where “n” is the number of measurements.

In most cases, the absolute difference between YSI AA and AB was less in the mesocosm phase than in the saltwater or freshwater phase. The DO difference between the two 6600 EDSs tested averaged 0.28 mg/L (Figures 6-7a-c) across all three test phases. The difference in specific conductivity 0.28 mS/cm (Figures 6-8a-c). The average difference in temperature readings was 0.02°C (Figures 6-9a-c). The average difference in pH readings was 0.04 (Figures 6-10a-c). The average difference in turbidity readings was 3.67 NTU, (Figures 6-11a-c). Finally, chlorophyll readings had an average difference of 1.07 (Figures 6-12a-c).

See Table 2-1 for vendor’s specifications and Table 4-1 for quality control criteria and tolerances associated with the reference monitors.

Table 6-4. Average Absolute Difference Between YSI AA and YSI AB Readings for Each Parameter at Each Deployment Location

		Average Absolute Difference Between YSI AA and YSI AB					
Location	**(n)**	**DO (mg/L)**	**Specific Conductivity (mS/cm)**	**Temperature (°C)**	**pH**	**Turbidity (NTU)**	**Chlorophyll (total)**
Saltwater	2,802	0.14	0.42	0.03	0.01	10.5	0.78
Freshwater	2,800	0.48	0.38	0.02	0.08	0.29	1.95
Mesocosm	2,588	0.19	0.05	0.02	0.03	0.27	0.48
Average		0.28	0.28	0.02	0.04	3.67	1.07

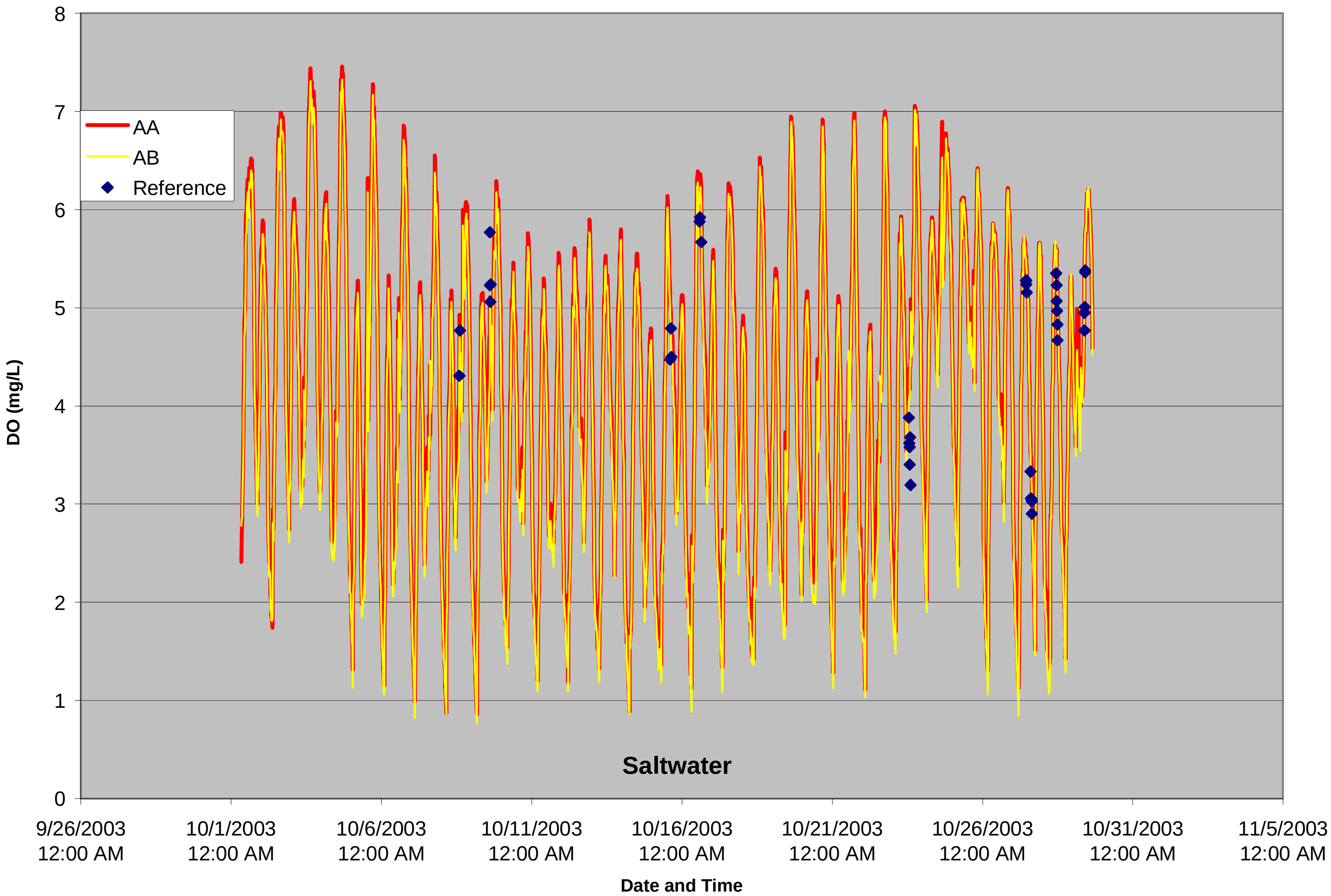


Figure 6-7a. Inter-Unit Reproducibility Data for DO During Saltwater Tests

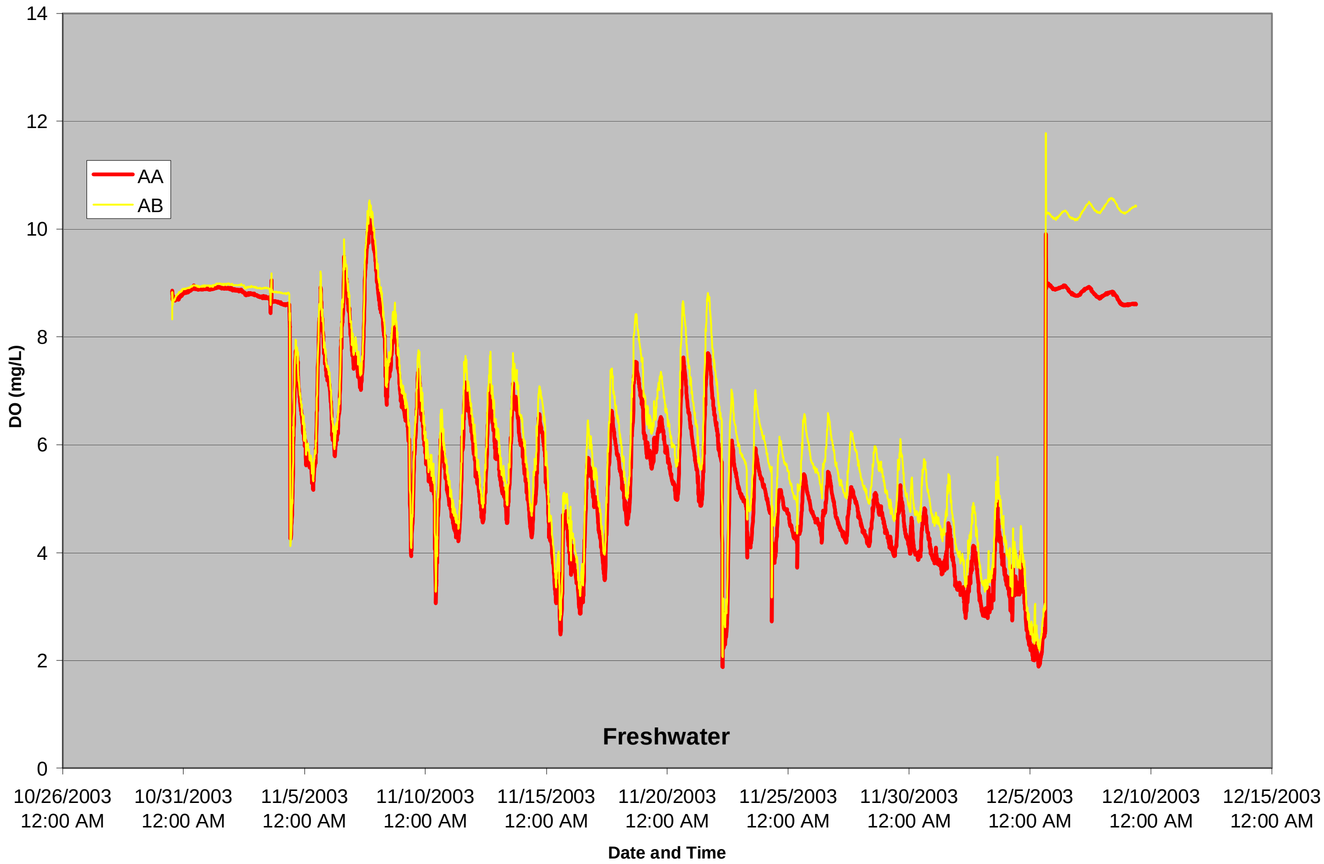


Figure 6-7b. Inter-Unit Reproducibility Data for DO During Freshwater Tests

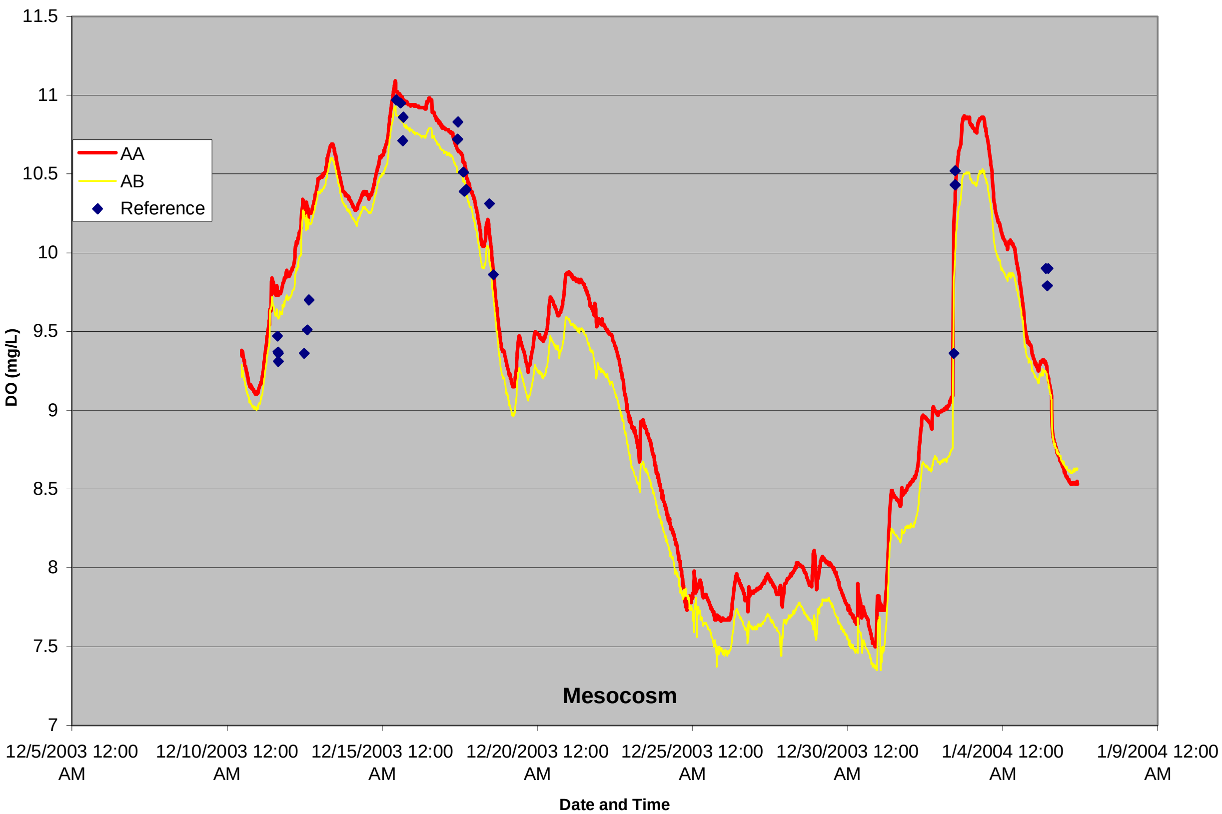


Figure 6-7c. Inter-Unit Reproducibility Data for DO During Mesocosm Tests

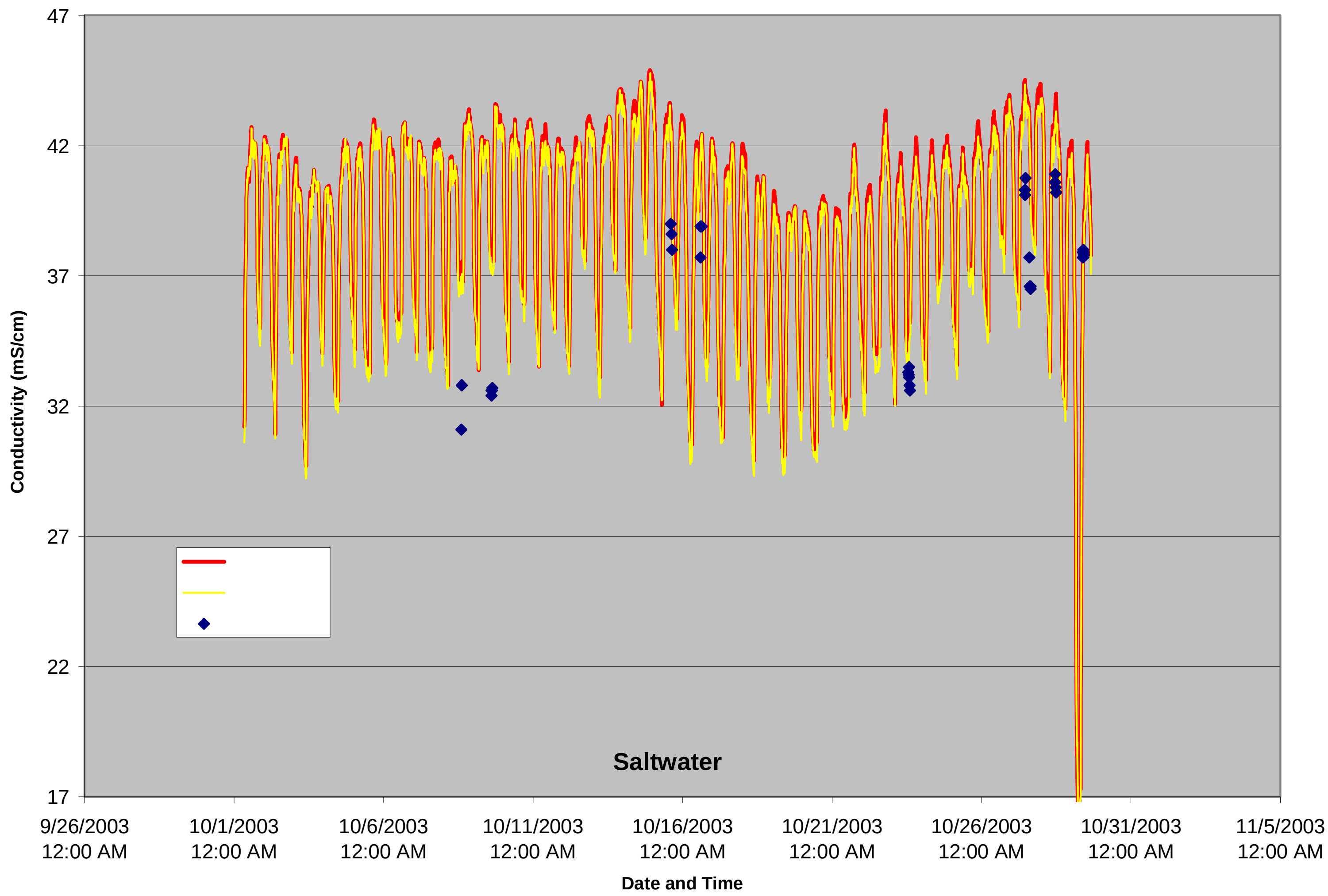


Figure 6-8a. Inter-Unit Reproducibility Data for Specific Conductivity During Saltwater Tests

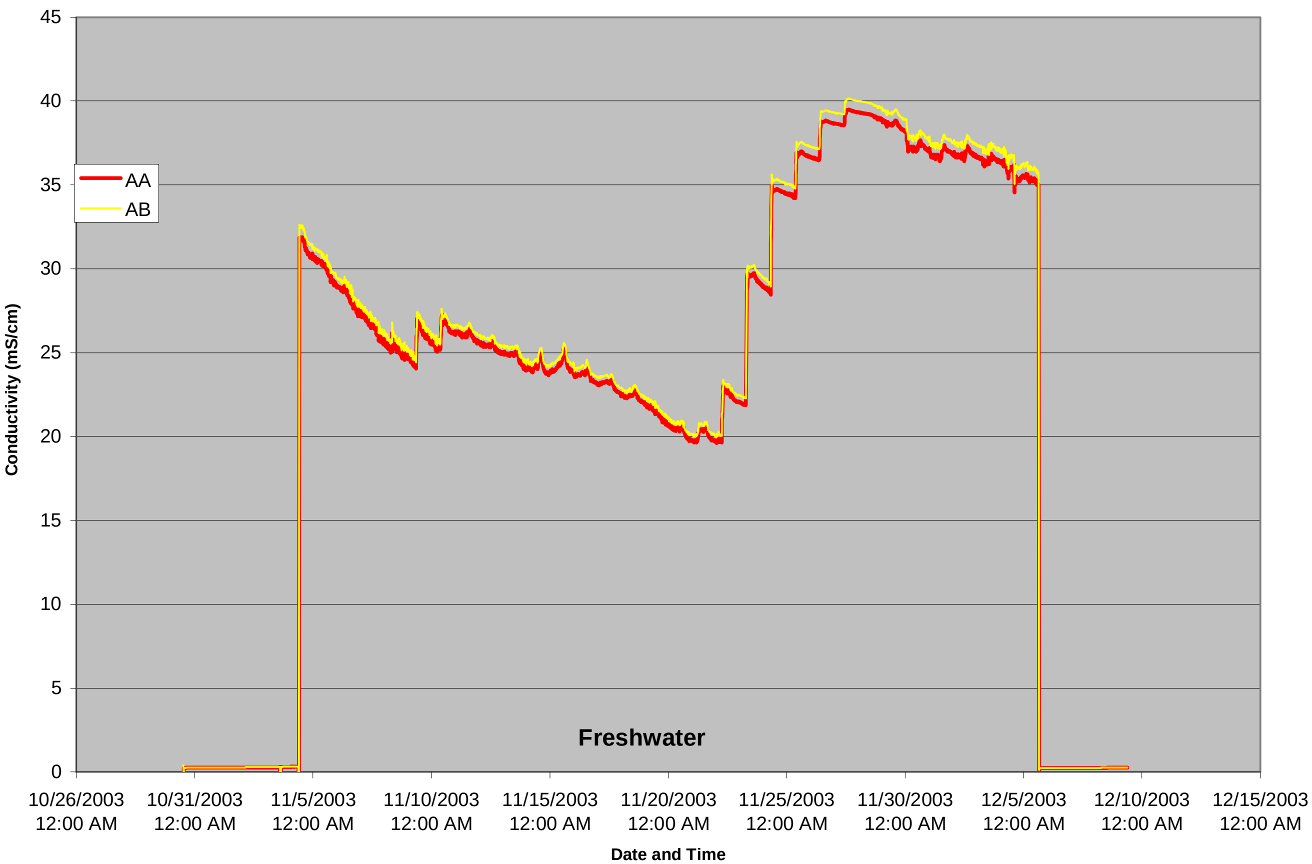


Figure 6-8b. Inter-Unit Reproducibility Data for Specific Conductivity During Freshwater Tests

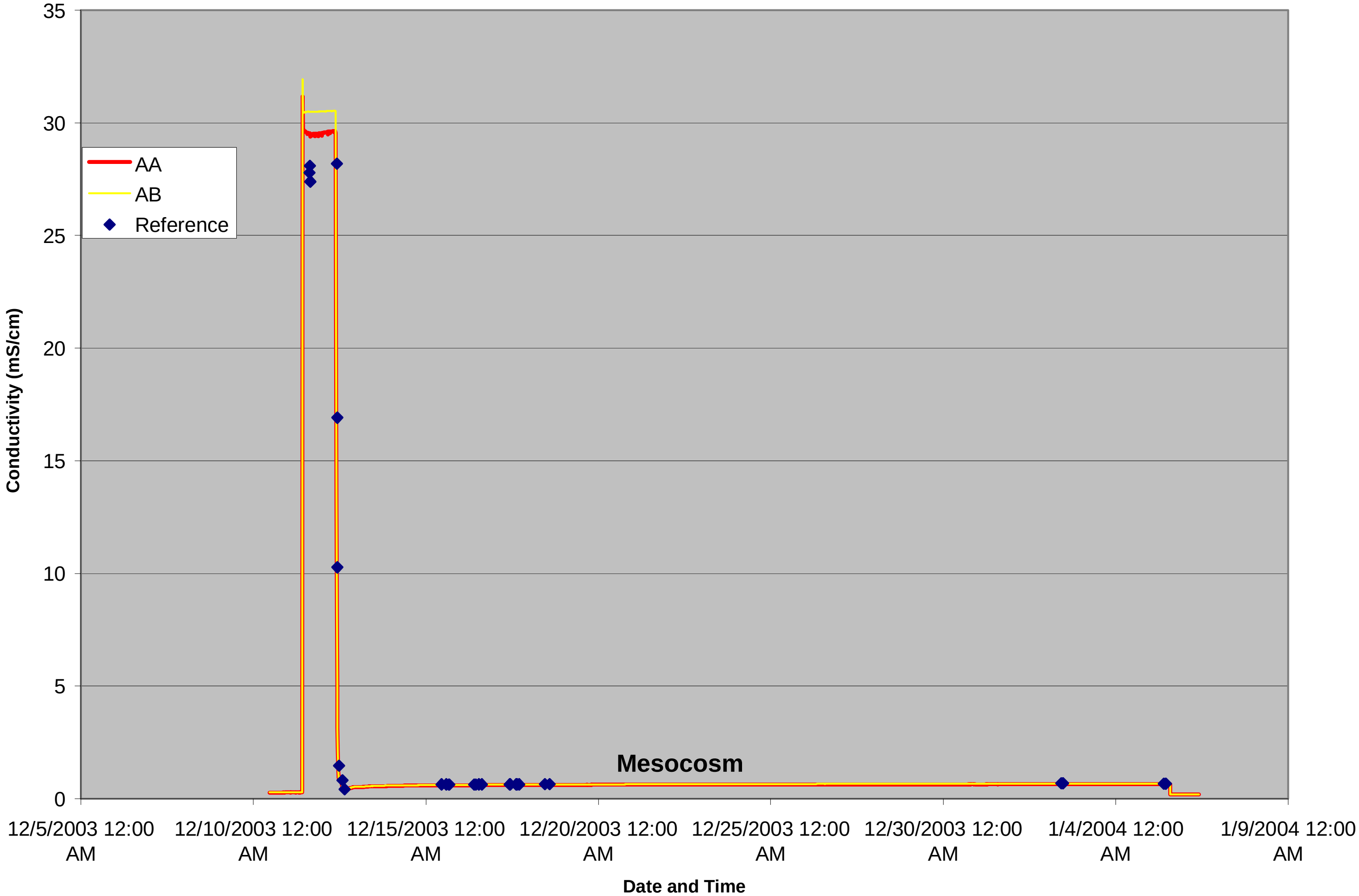


Figure 6-8c. Inter-Unit Reproducibility Data for Specific Conductivity During Mesocosm Tests

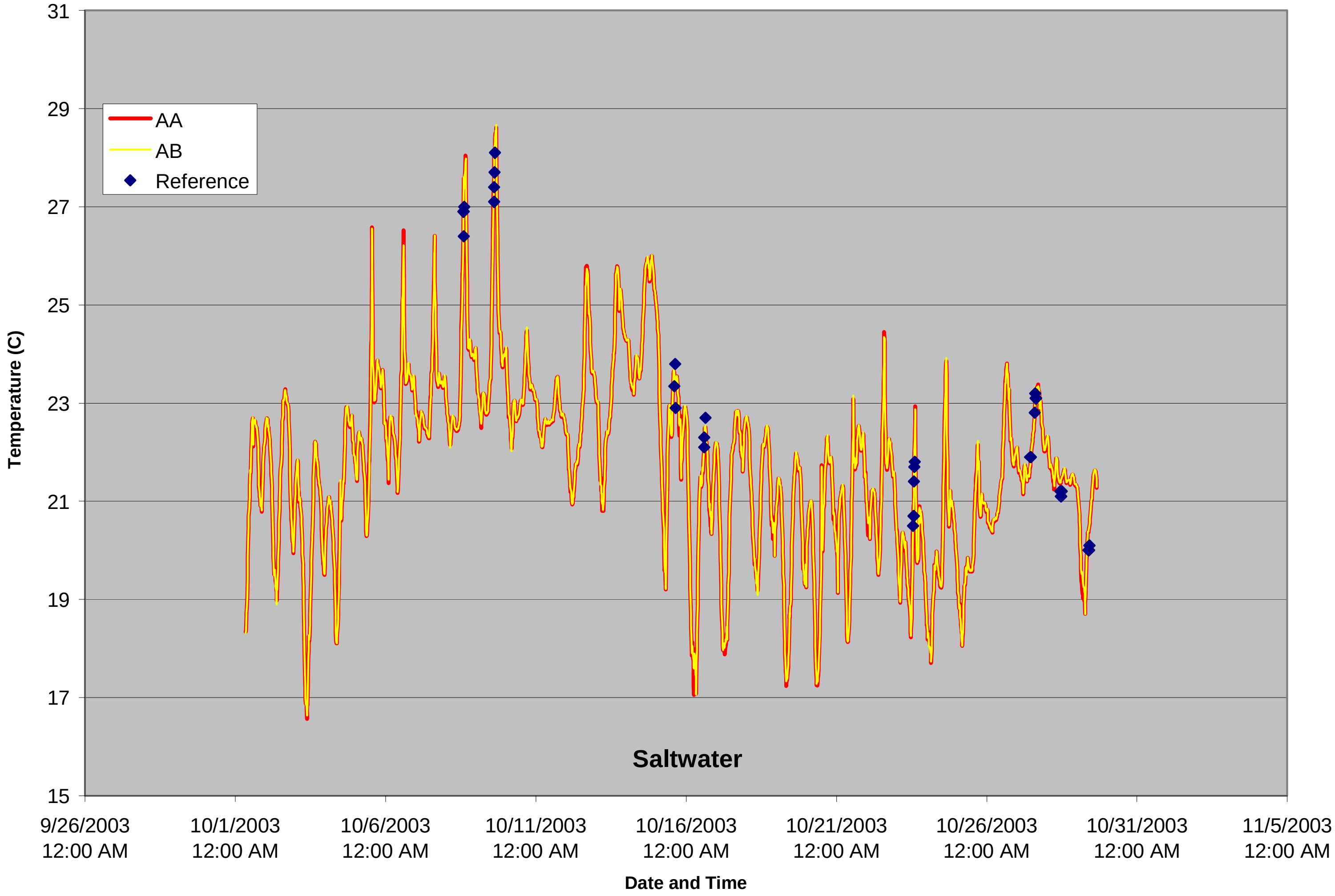


Figure 6-9a. Inter-Unit Reproducibility Data for Temperature During Saltwater Tests

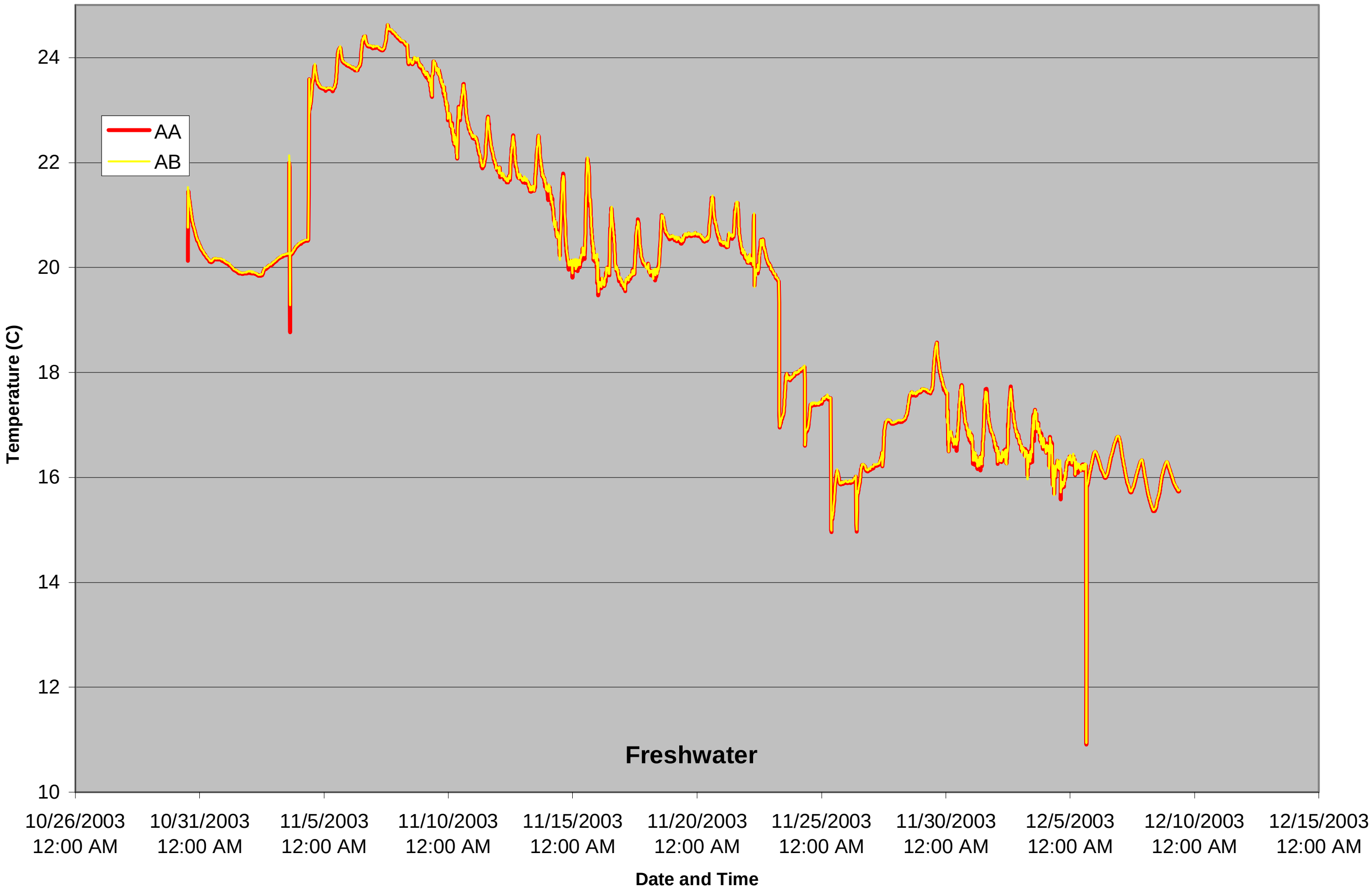


Figure 6-9b. Inter-Unit Reproducibility Data for Temperature During Freshwater Tests

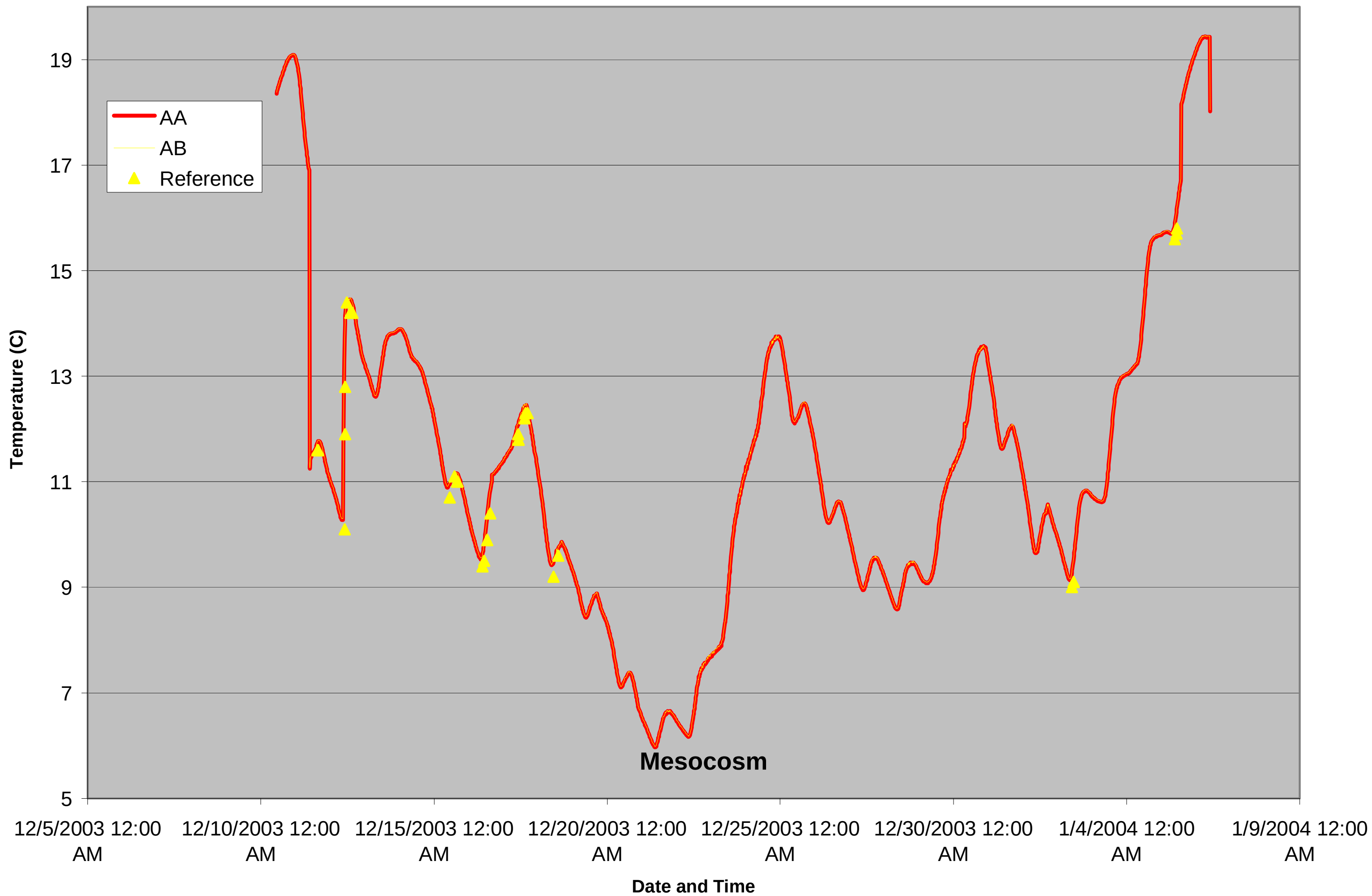


Figure 6-9c. Inter-Unit Reproducibility Data for Temperature During Mesocosm Tests

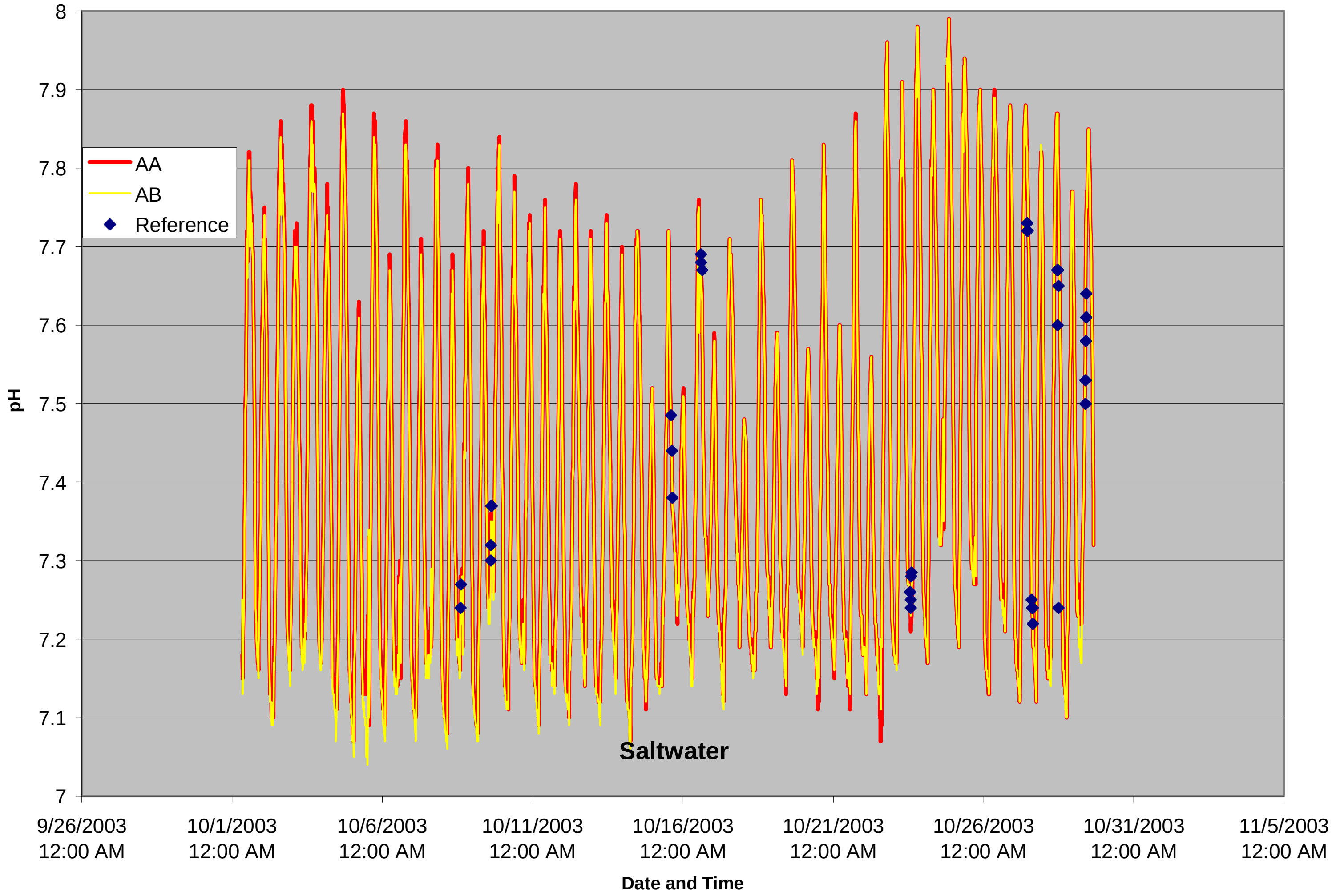


Figure 6-10a. Inter-Unit Reproducibility Data for pH During Saltwater Tests

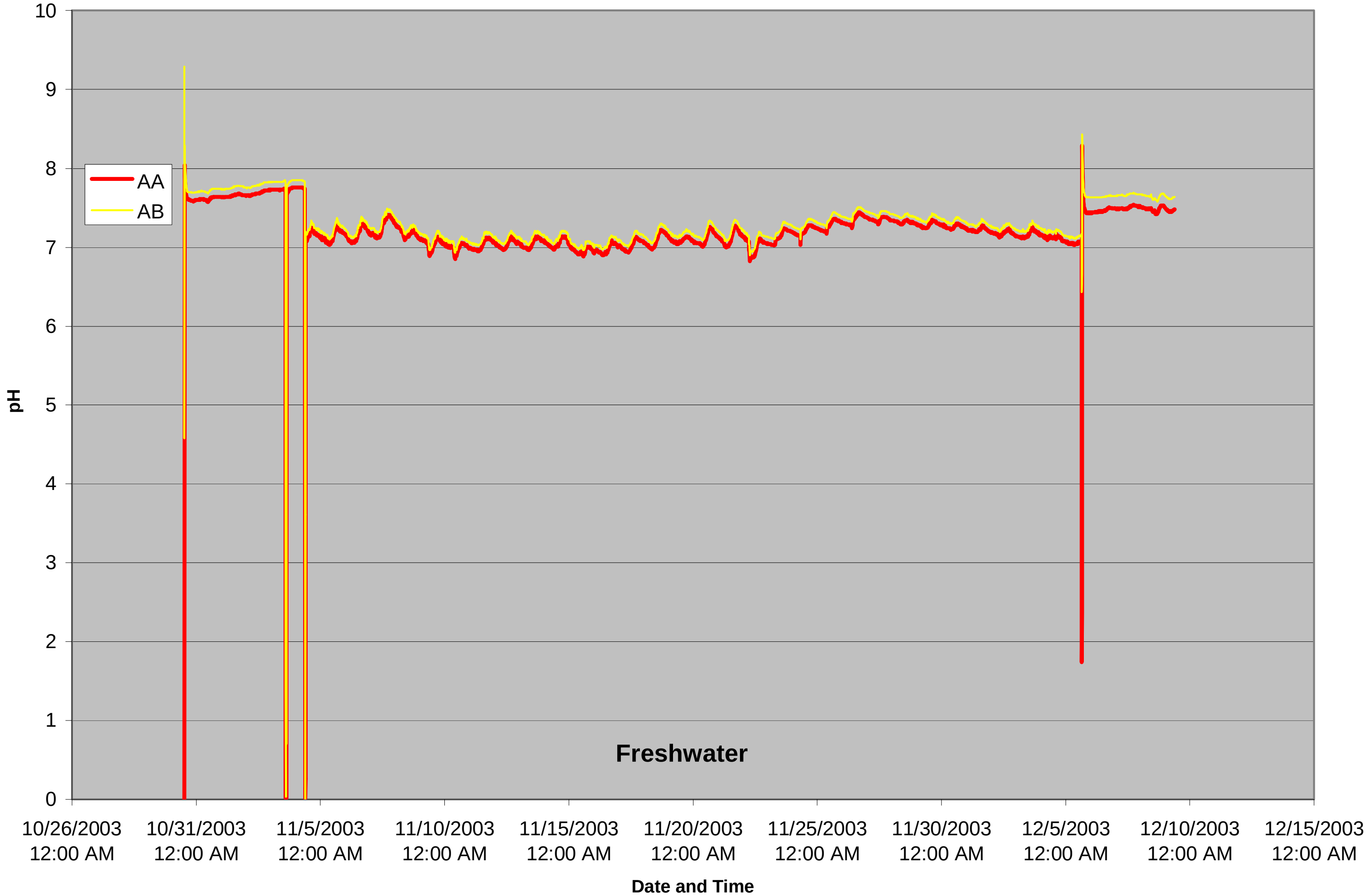


Figure 6-10b. Inter-Unit Reproducibility Data for pH During Freshwater Tests
(on 10/31 and 11/5 YSI AA and AB drop to a pH of zero when removed from water)

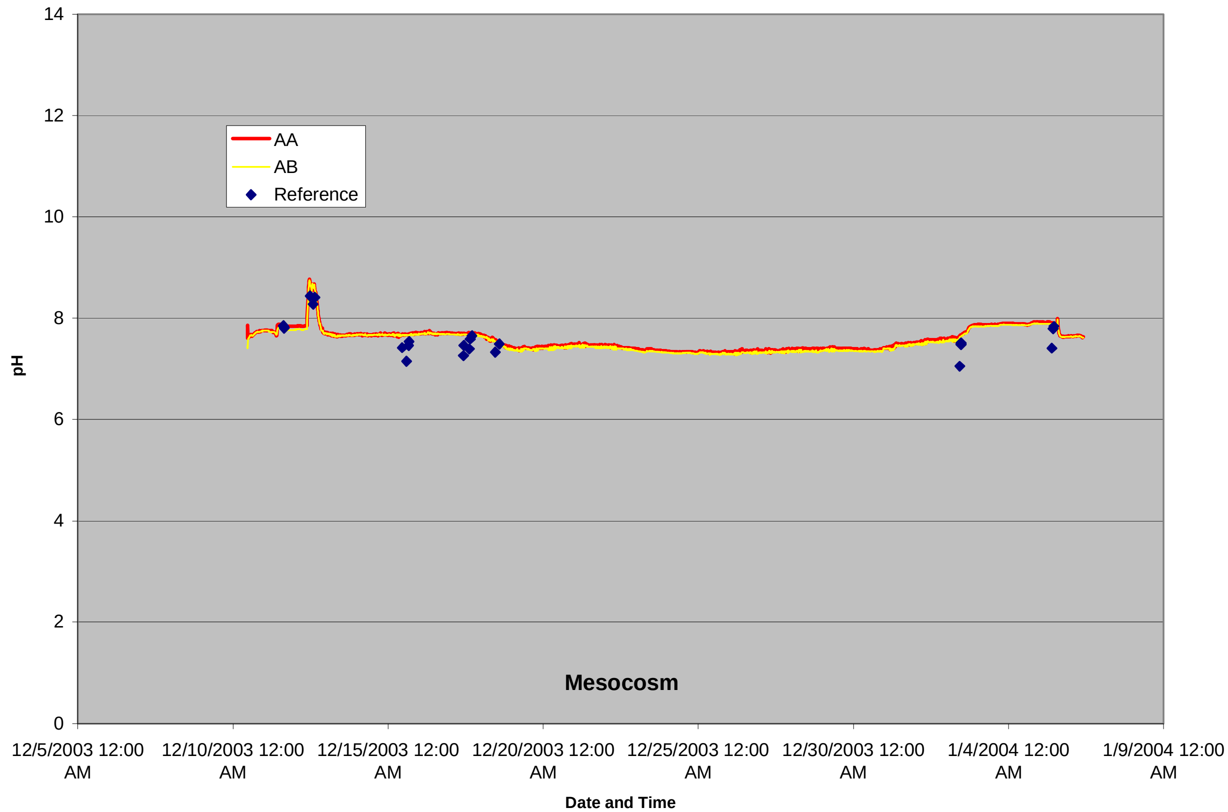


Figure 6-10c. Inter-Unit Reproducibility Data for pH During Mesocosm Tests

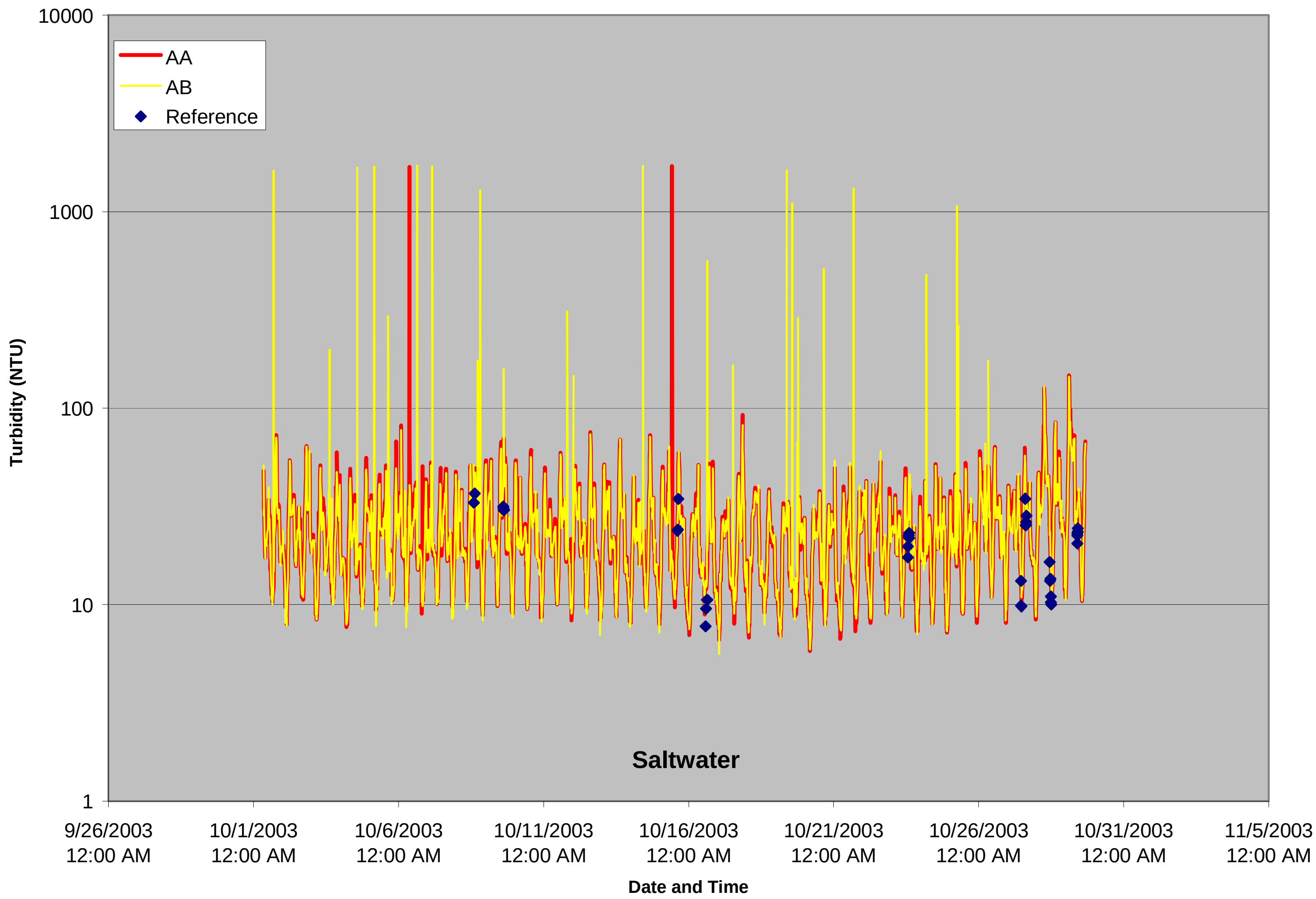


Figure 6-11a. Inter-Unit Reproducibility Data for Turbidity During Saltwater Tests (log scale)

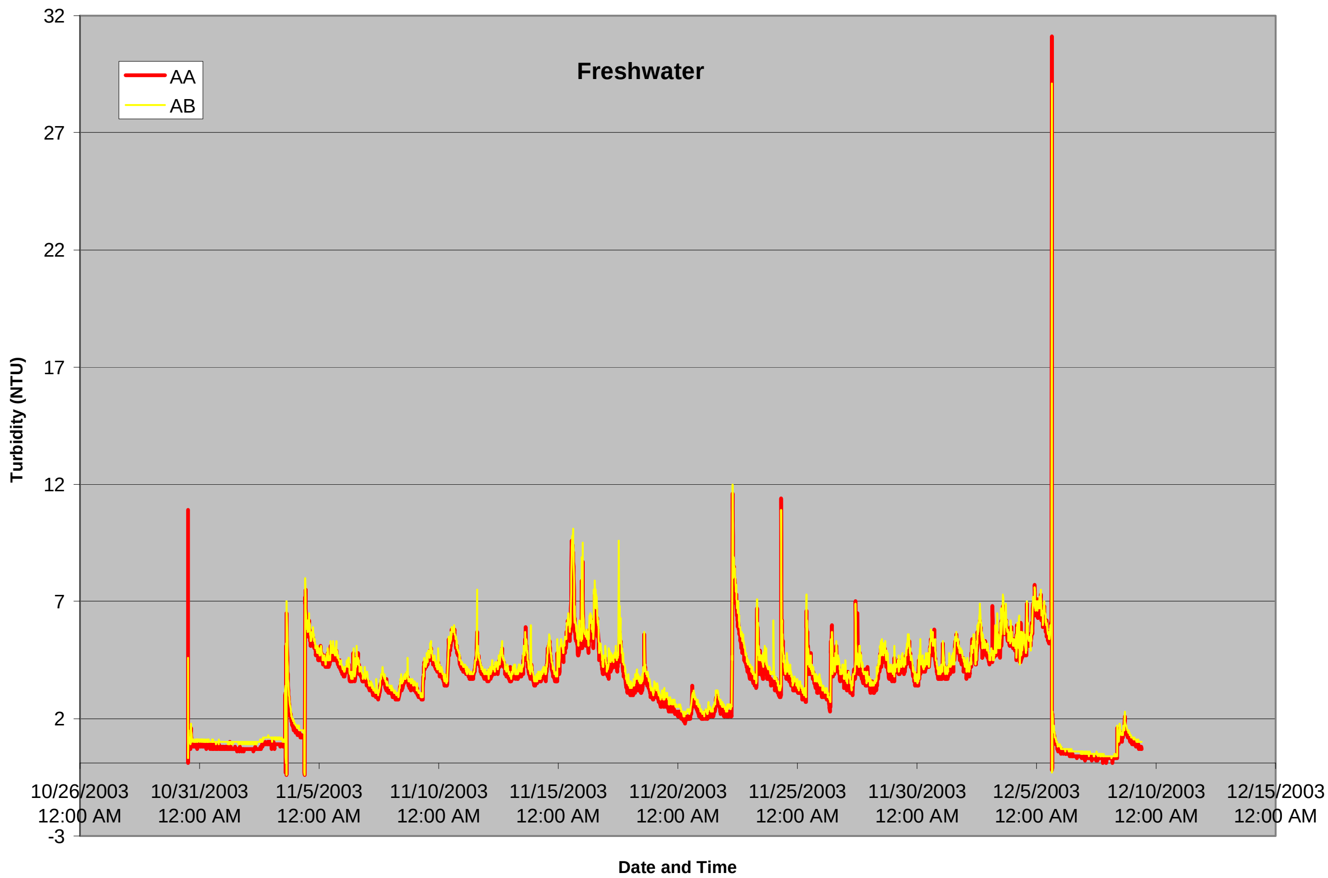


Figure 6-11b. Inter-Unit Reproducibility Data for Turbidity During Freshwater Tests

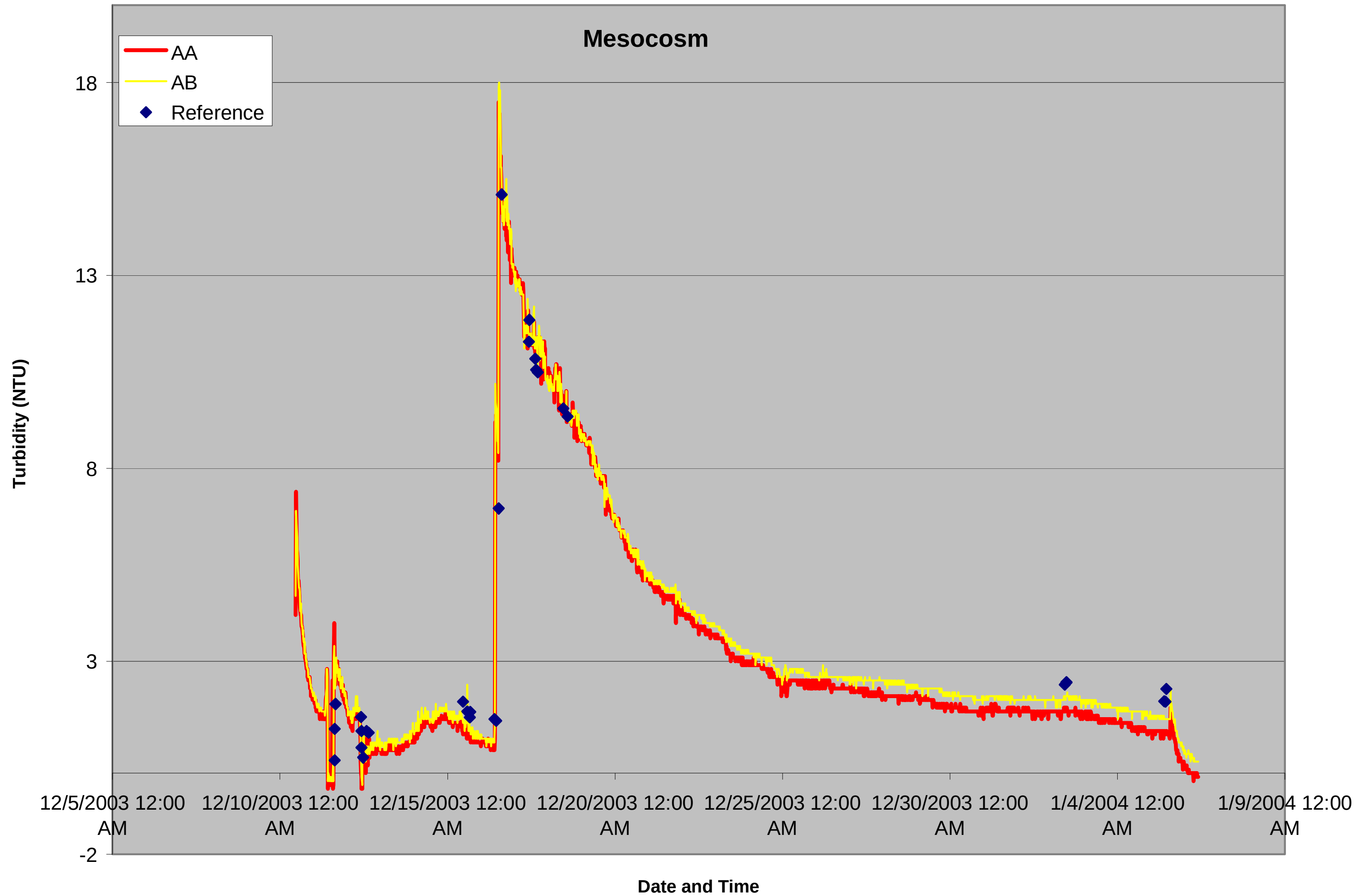


Figure 6-11c. Inter-Unit Reproducibility Data for Turbidity During Mesocosm Tests

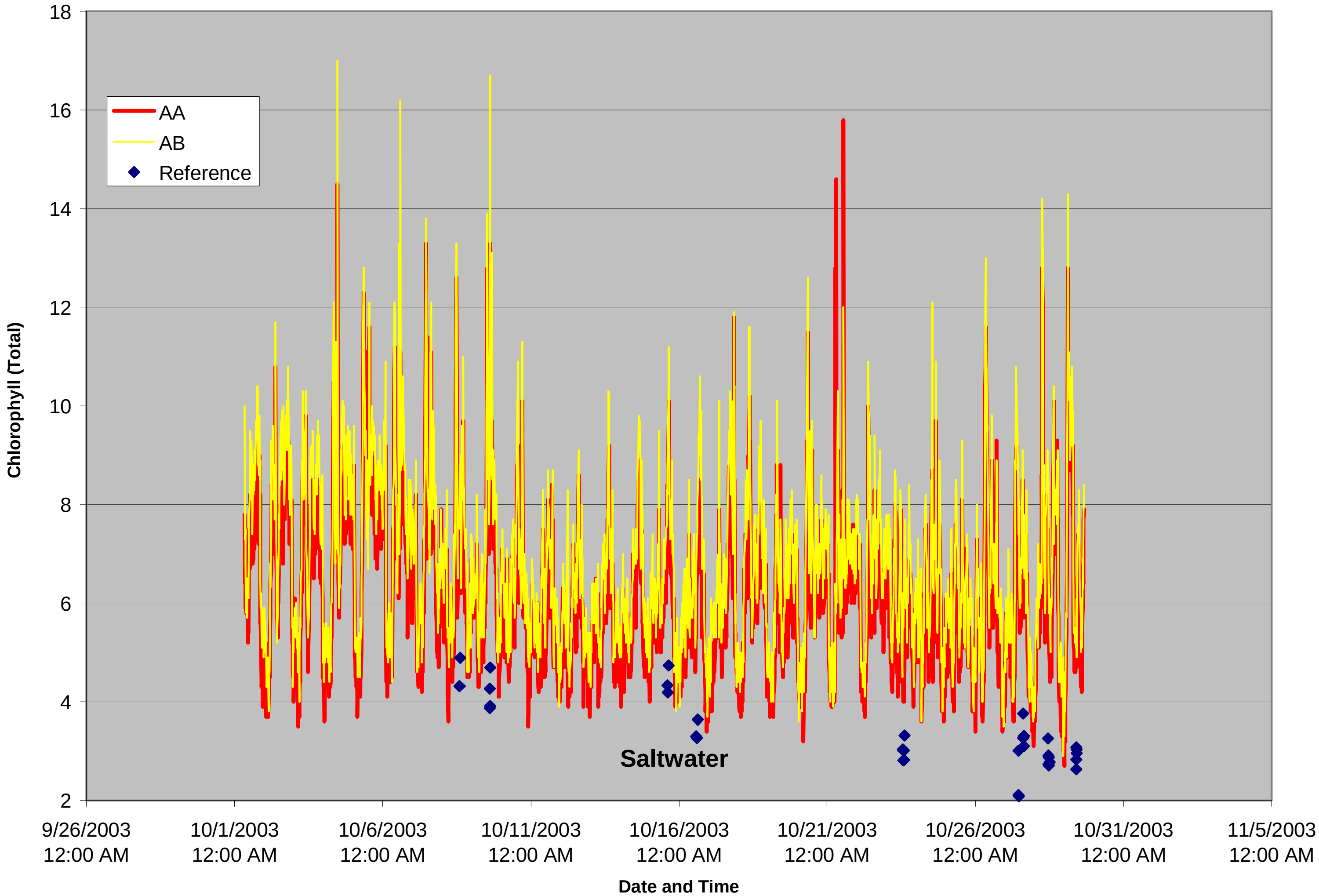


Figure 6-12a. Inter-Unit Reproducibility Data for Total Chlorophyll During Saltwater Tests

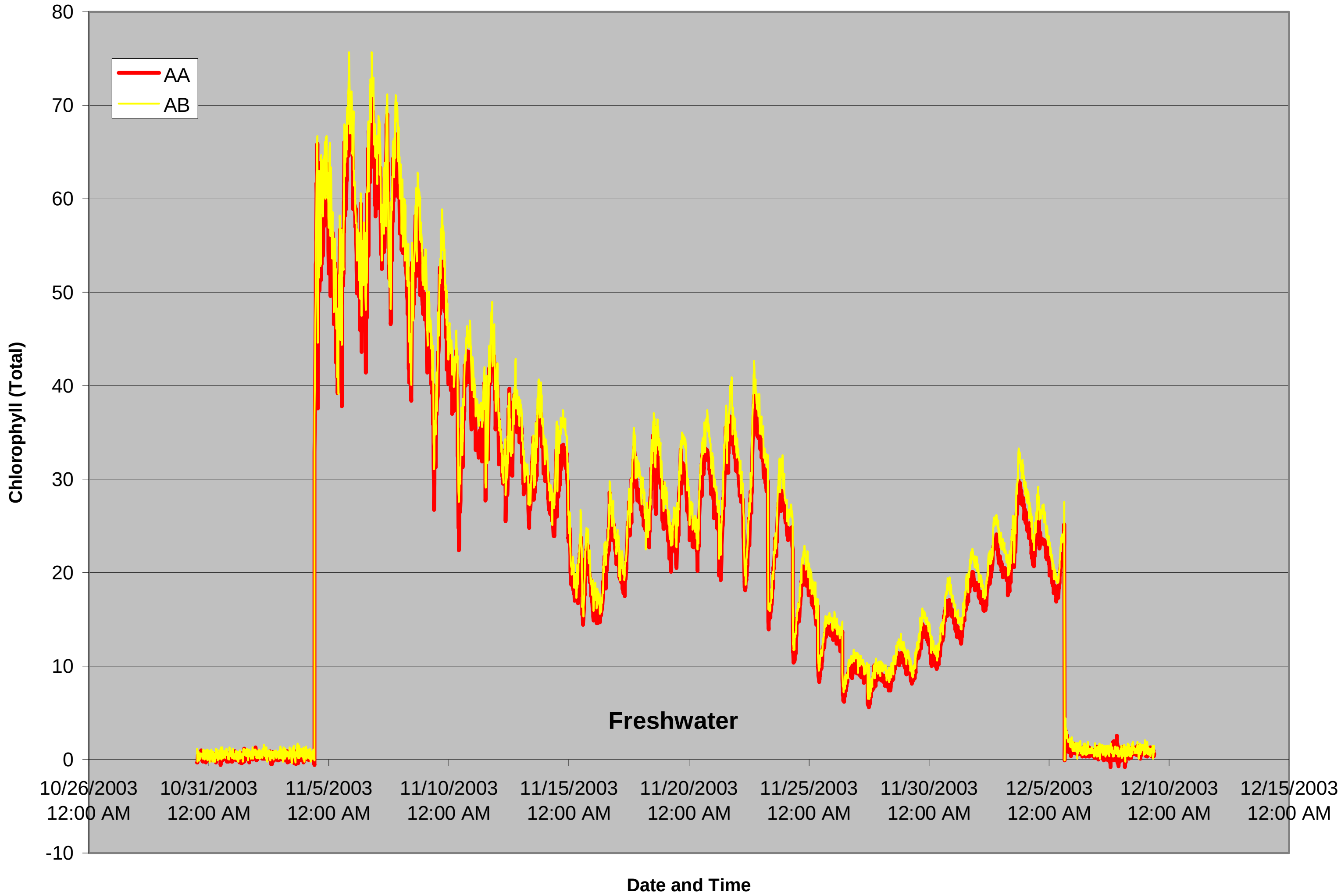


Figure 6-12b. Inter-Unit Reproducibility Data for Total Chlorophyll During Freshwater Tests

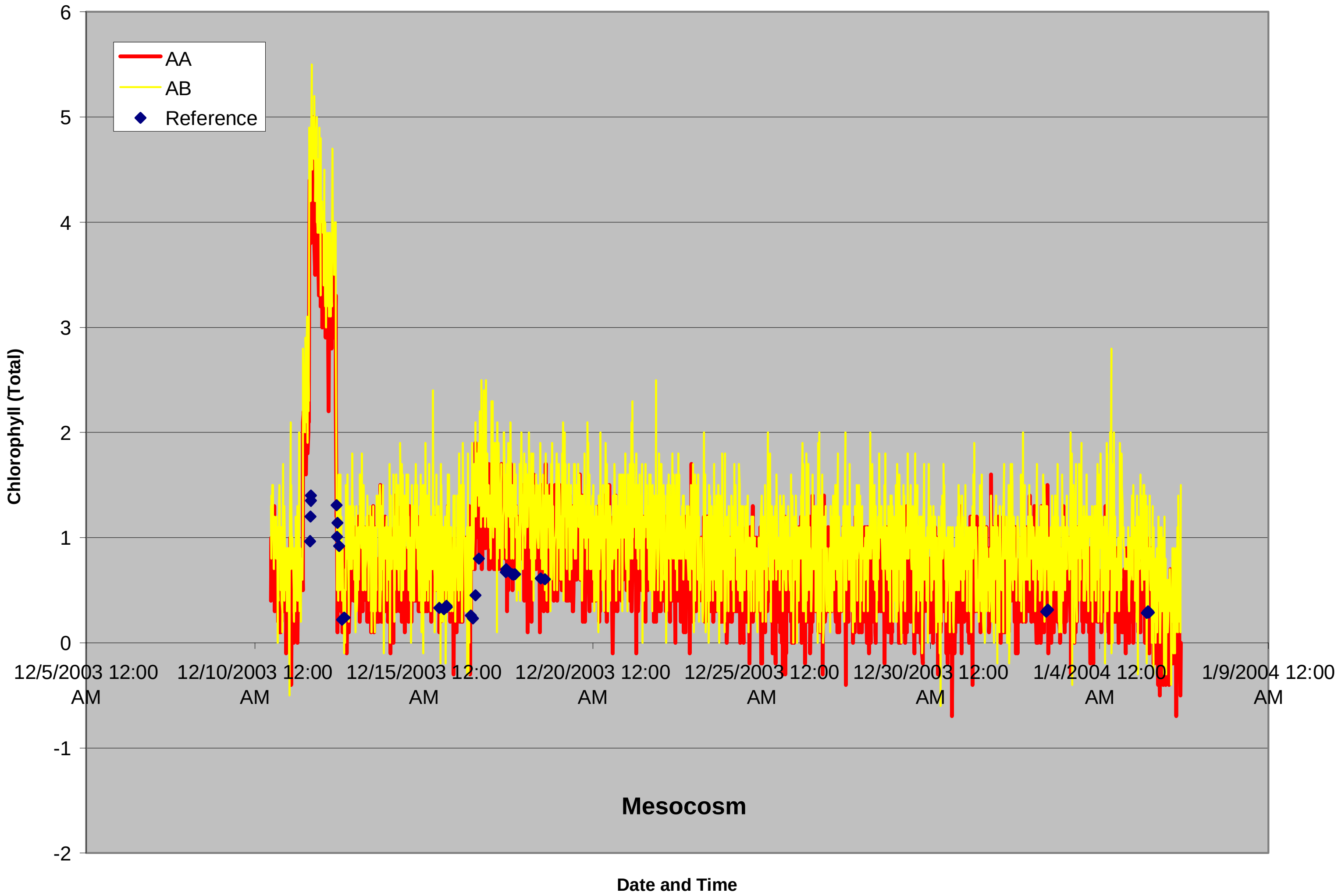


Figure 6-12c. Inter-Unit Reproducibility Data for Total Chlorophyll During Mesocosm Tests

6.6 Other Factors

6.6.1 Ease of Use

The 6600 EDSs were installed and deployed by CCEHBR staff with the oversight of YSI during installation and Battelle during deployment. The only maintenance required was periodically changing the DO membrane and recalibrating the measured parameters at the end of the deployment periods. Data were collected from the 6600 EDS to a personal computer using a vendor-supplied serial connection cable and YSI software, Ecowatch version 3.15.00. A sample printout of the data is shown in Appendix A. The software provided simple access to the data for downloading and viewing. The 6600 EDSs required minimal interaction by operators during the test. Those interactions that did occur are described in Table 6-5.

Table 6-5. Installation, Operation, and Maintenance Activities

Date	Service Time	Activity
10/1/2003	—	Vendor representatives arrived on site.
10/2/2003	—	6600 EDS deployed.
10/30/2003	—	6600 EDS collected.
10/31/2003	180 minutes	Data downloaded; oxygen membrane changed; 6600 EDS cleaned and calibrated.
11/4/2003	—	6600 EDS deployed.
12/8/2003	180 minutes	6600 EDS collected; data downloaded; oxygen membrane changed; 6600 EDS cleaned and calibrated.
12/10/2003	—	6600 EDS deployed.
1/5/2004	15 minutes	6600 EDS collected; data downloaded.
1/5/2004		End of test.
Total	375 minutes	

6.6.2 Data Completeness

All of the required data were recorded during this verification. The two 6600 EDSs submitted for this test collected data at 15-minute intervals from October 1, 2003, until January 5, 2004, without any interruption in data collection. One hundred percent of the required data was collected by the 6600 EDS.

Chapter 7
Performance Summary

Two 6600 EDSs were evaluated in saltwater, freshwater, and mesocosm environments between October 2, 2003, and January 5, 2004. These 6600 EDSs measured DO, specific conductivity, temperature, pH, turbidity, and chlorophyll in water at 15-minute intervals throughout these deployments. Table 7-1 summarizes the performance of the 6600 EDSs.

Table 7-1. Summary of Performance

Statistical Measure	Parameter	YSI AA Saltwater	YSI AA Freshwater	YSI AA Mesocosm	YSI AB Saltwater	YSI AB Freshwater	YSI AB Mesocosm
Calibration check accuracy [a]	DO (%)	99.6	87.0	97.0	101	105	99.1
	Specific conductivity (%)	100	101	96.8	99.5	102	98.1
	pH (%)	100-101	98.3-101	102-101	101-102	100-101	100-101
	Turbidity at 120 NTU (%)	100	99	99	98	100	101
	Turbidity at 0 NTU (NTU)	0.3	-0.2	0.2	0.2	-0.2	0.2
	Chlorophyll (total *in vivo*)	-0.5	0.9	0.8	-0.3	-0.1	-0.1
Average relative bias [b]	DO (%)	-7.4	—[c]	0.3	-5.7	—[c]	1.7
	Specific conductivity (%)	-8.7	—[c]	12.8	-7.6	—[c]	10.2
	Temperature (%)	-0.1	—[c]	-0.2	-0.1	—[c]	-0.2
	pH (%)	7.5	—[c]	0.39	8.1	—[c]	0.35
	Turbidity (%)	-33.6	—[c]	-17.4	-184	—[c]	-30.1
	Chlorophyll (%)	-98.0	—[c]	-72.1	-133	—[c]	-131
		YSI AA			**YSI AB**		
Average precision	DO (%RSD)	0.44			0.46		
	Specific conductivity (%RSD)	0.14			0.53		
	Temperature (%RSD)	0.74			0.75		
	pH (%RSD)	0.62			0.76		
	Turbidity (%RSD)	29.6			19.4		
	Chlorophyll (%RSD)	19.8			24.6		
Linearity		Linearity and regression coefficients indicated better agreement between the 6600 EDS readings and reference values for the parameters that do not use optical measurements, such as DO, specific conductivity, temperature, and pH.					
		Average Difference Between YSI AA and AB Readings					
		Saltwater	**Freshwater**	**Mesocosm**			
Inter-unit reproducibility	DO (mg/L)	0.14	0.48	0.19			
	Specific conductivity (mS/cm)	0.42	0.38	0.05			
	Temperature (°C)	0.03	0.02	0.02			
	pH	0.01	0.08	0.03			
	Turbidity (NTU)	10.5	0.29	0.27			
	Chlorophyll (total)	0.78	1.95	0.48			

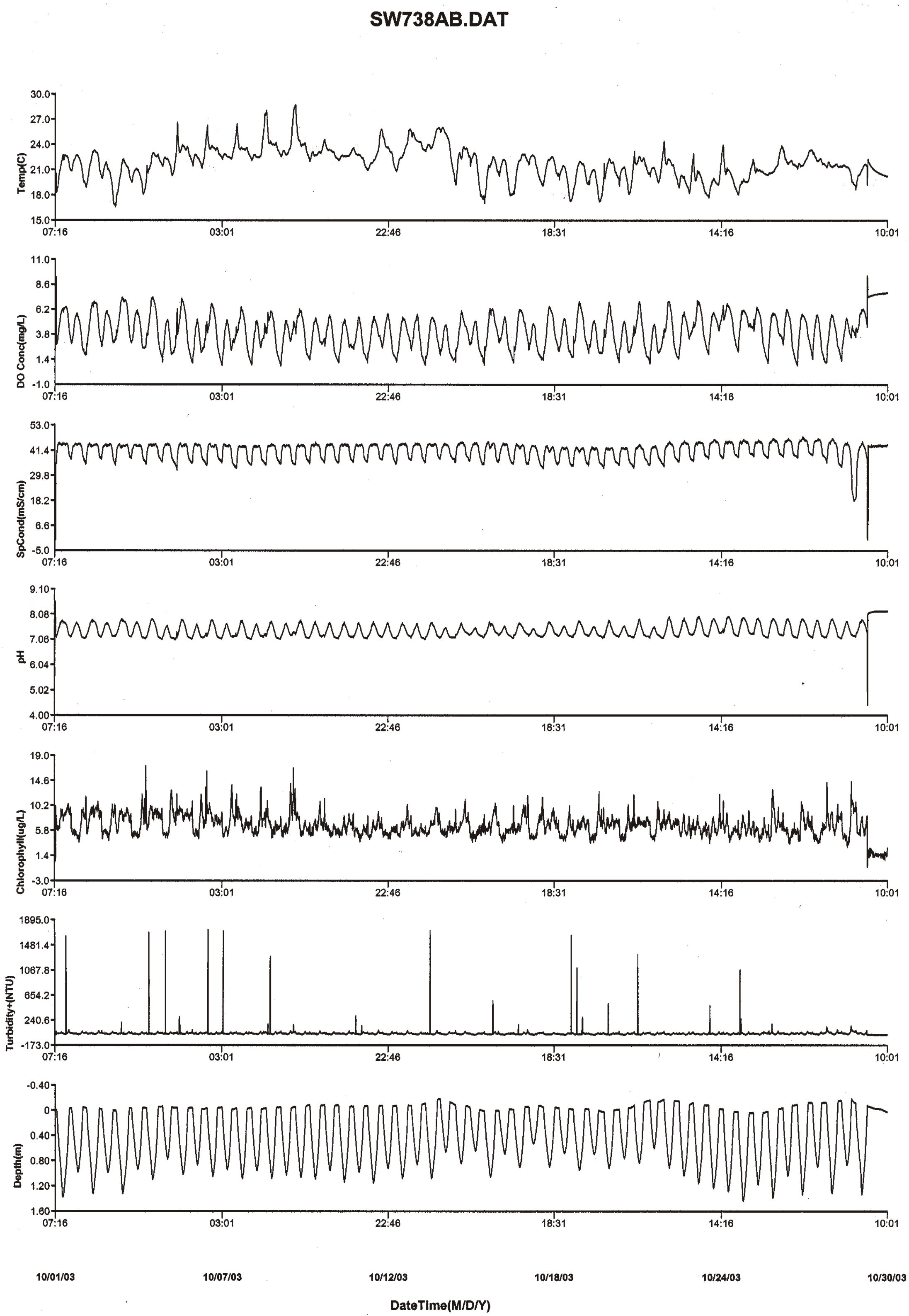
[a] The closer the percentage is to 100, the better.
[b] The closer the percentage is to zero, the better.
[c] Stratification; no data reported.

Chapter 8
References

1. *Test/QA Plan for Long-Term Deployment of Multi-Parameter Water Quality Probes/Sondes*, Battelle, Columbus, Ohio, Version 1.0, May 2002.

2. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 4.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2002.

Appendix A
Reference Sample and Probe Readings


SW738AB.DAT
Temp(C)
30.0
27.0
24.0
21.0
18.0
15.0
DO Conc(mg/L)
11.0
8.6
6.2
3.8
1.4
-1.0
SpCond(mS/cm)
53.0
41.4
29.8
18.2
6.6
-5.0
pH
9.10
8.08
7.06
6.04
5.02
4.00
Chlorophyll(ug/L)
19.0
14.6
10.2
5.8
1.4
-3.0
Turbidity+(NTU)
1895.0
1481.4
1067.8
654.2
240.6
-173.0
Depth(m)
-0.40
0
0.40
0.80
1.20
1.60
07:16
03:01
22:46
18:31
14:16
10:01
10/01/03
10/07/03
10/12/03
10/18/03
10/24/03
10/30/03
DateTime(M/D/Y)