

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE: MULTI-PARAMETER WATER QUALITY PROBE

APPLICATION: MEASURING WATER QUALITY

TECHNOLOGY NAME: 6600 Extended Deployment System

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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved 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 standards and testing organizations; with stakeholder groups, consisting of buyers, vendor organizations, and permittees; 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 Advanced Monitoring Systems (AMS) Center, one of seven technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of multi-parameter water quality probes. This verification statement provides a summary of the test results for the YSI Incorporated 6600 Extended Deployment System (EDS).

VERIFICATION TEST DESCRIPTION

The 6600 EDS was evaluated by comparing pre- and post-calibration results and their measurements with standard reference measurements and handheld calibrated probes. The 6600 EDS was deployed in saltwater, freshwater, and laboratory environments near Charleston, South Carolina, during a 2 ½-month verification test. Water quality parameters were measured both by the two 6600 EDS probes and by reference measurements consisting of field-portable instrumentation and water analyses of collected samples. During each phase, performance was assessed in terms of pre- and post-calibration results, relative bias, precision, linearity, and inter-unit reproducibility. The saltwater site was at the National Oceanic and Atmospheric Administration (NOAA) Pier Romeo on the Cooper River, the freshwater site was at Lake Edmunds, approximately one mile from the NOAA Center for Coastal Environmental Health and Biomolecular Research (CCEHBR), and the controlled site was the CCEHBR mesocosm facility in Charleston, South Carolina. Test parameters included dissolved oxygen (DO), conductivity, temperature, pH, turbidity, and chlorophyll.

Saltwater testing was conducted at two locations. The original location was in a small tidal creek tributary of the Charleston Harbor. However, due to structural problems at that site, the probes were redeployed in the NOAA Pier Romeo on the Cooper River. Pre- and post-calibration data obtained at the first location are presented in the verification report; however, no reference data from that location are presented. The saltwater test lasted for 31 days, during which time the 6600 EDSs monitored the naturally occurring range of the target parameters, collecting data every 15 minutes, 24 hours a day, except on days when the probes were in the laboratory for pre- and post-calibration checks. Reference sample collection times were rotated among the morning, afternoon, and evening hours throughout the test. More intense sampling occurred at the beginning (Days 1 and 2) and the end (Days 29 and 30) of the sampling period when samples were taken at 15-minute intervals for eight hours, except on Day 29, when only four hours of sampling occurred because of weather conditions. For the duration of the test, the 6600 EDSs were deployed at depths between approximately three and 10 feet, varying according to the tide. Freshwater testing was conducted at Lake Edmunds. Because this site is shallower than the Cooper River, only one depth (approximately 3 feet) was used. As in the saltwater portion of the verification test, the 6600 EDSs monitored the naturally occurring target parameters, while simultaneous reference measurements were made, again rotating among collection times. More intense sampling occurred at the beginning (Day 3) and the end (Day 23) of the sampling period when samples were taken at 15- to 30-minute intervals for periods ranging between six and eight hours, as weather permitted. The third and final stage of testing occurred at the CCEHBR mesocosm facility. The mesocosm tanks were filled with saltwater/freshwater and drained daily, simulating a tide. 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 period, 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. Conductivity was varied by adding freshwater to the saltwater during one of the fill-and-drain cycles. Variations in temperature, pH, DO, and chlorophyll were driven by natural forces and the changes in the other test parameters. Over all three sampling periods, approximately 6,000 data points were collected by the 6600 EDS, and 132 sets of reference measurements were obtained.

QA oversight of verification testing was provided by Battelle. Battelle QA staff conducted a technical systems audit. The ETV Test Coordinator performed the performance evaluation audit and a data quality audit of 10% of the test data.

TECHNOLOGY DESCRIPTION

The following description of the 6600 EDS was provided by the vendor and does not represent verified information. The 6600 EDS is a multi-parameter water probe/sonde capable of measuring pH, turbidity, DO, chlorophyll, conductivity, and temperature. Building upon the YSI Rapid Pulse™ DO system, 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 battery power options allow long-term deployment. The range, resolution, and accuracy of the 6600 EDS, as provided by YSI, are listed below for the parameters tested. The outer diameter of the 6600 EDS is 8.9 cm (3.5 inches). It is 52 cm (20.4 inches) long and weighs 2.7 kilograms (six pounds).

VERIFICATION OF PERFORMANCE

Pre-and post-calibration results: Pre-and post-calibration tests were performed for pH, DO, and conductivity since only those parameters are adjusted during calibration. The results showed that pH measurement values were accurate within a range of 99 to 102% of the true values, DO measurement values were accurate within a range of 100 to 109% of the true values (except for the very first result of 73%), and conductivity measurement values were accurate within a range of 98 to 104% of the true values.

Relative bias: A summary of the average relative bias for each deployment setting is provided in the table below. The relative bias for the temperature, conductivity, pH, and DO parameters was less than -28% in saltwater, freshwater, and the mesocosm. The bias for temperature was less than 0.1% and for conductivity less than 12%. The DO bias was less than 13.23% at the saltwater site and in the mesocosm, but averaged 22% at the freshwater site. Variability in DO concentration was much greater at the freshwater site, and DO measurements were consistently higher than reported by the reference unit. The higher DO bias could be at least partially because the reference unit (unlike the 6600 EDS) required a large flow dependence, making it necessary to move the sensor rapidly up and down in the water column. Inadequate agitation resulting in erroneously low DO values could explain some of the bias in the relative DO readings. The bias for pH was calculated at an average of -28%, when using units of mol/L of H⁺ concentration. The bias for turbidity ranged between -9.54% and -126%, but many of the values were close to or below the reported detection limit of the 6600 EDS. The bias for chlorophyll ranged between 43.0% and 229%; however, many of the values were taken at points where chlorophyll readings were very low; and, in addition, there was a sharp spike of phytoplankton during the mesocosm study.

Parameter	Units	Saltwater		Freshwater		Mesocosm	
		% Rel. Bias YSI Probe #1	% Rel. Bias YSI Probe #2	% Rel. Bias YSI Probe #1	% Rel. Bias YSI Probe #2	% Rel. Bias YSI Probe #1	% Rel. Bias YSI Probe #2
Temperature	K	-0.052	-0.034	0.00	0.02	-0.04	-0.01
Conductivity	mS/cm	11.08	11.4	7.70	8.77	3.91	3.00
DO	mg/L	13.23	-7.35	22.6	21.7	6.97	8.05
H ⁺	mol/L	-2.79	-2.79	4.80	-28.0	-15.9	-13.2
Turbidity	NTU	-10.9	-9.54	-34.1	-111	-36.7	-126
Chlorophyll	total	74	43	66.5	229	75.5	46.0

Precision: Precision was determined during the mesocosm deployments and is reported as percent relative standard deviation (RSD). Percent RSD was lowest for the pH and temperature, ranging between 0.00%RSD and 0.08%RSD. Precision for conductivity was 1.06%RSD and 1.07%RSD for the two 6600 EDSs. For DO it was 12.5%RSD and 12.6%RSD, and for chlorophyll 41.6%RSD and 38.5%RSD. Precision data for turbidity was not determined because an inadequate amount of data were available from a period of stable operation.

Linearity: Linearity was assessed by comparing probe readings against the reference values for each of the parameters at each deployment location. The table below provides the results of this comparison by showing the slope, intercept, and coefficient of determination (r^2) at each site for the 6600 EDS. The linear response for the 6600 EDS, expressed in terms of slope, intercept, and coefficient of determination (r^2) at each condition, was highest for conductivity and temperature, with slopes near 1 and r^2 values above 0.85. All the parameters during mesocosm deployment had strong correlations, with r^2 values above 0.80.

YSI Probe #	Parameter	Saltwater			Freshwater			Mesocosm		
		Slope	Intercept	r^2	Slope	Intercept	r^2	Slope	Intercept	r^2
1	DO	0.48	3.15	0.38	1.16	0.37	0.96	1.01	0.40	0.82
2	DO	0.42	2.45	0.16	1.13	0.46	0.97	1.01	0.45	0.81
1	Conductivity	NA	NA	NA	1.30	-0.09	0.95	1.05	-0.07	0.99
2	Conductivity	1.12	-0.14	0.97	1.3	-0.0817	0.85	1.05	-0.09	0.99
1	Temperature	1.00	-2.54	0.94	0.99	0.698	0.99	0.95	13.78	0.99
2	Temperature	0.97	9.00	0.94	1.03	-8.78	0.99	0.95	15.17	0.99
1	pH	0.87	0.00	0.58	0.56	0.00	0.83	0.78	0.00	0.91
2	pH	0.87	0.00	0.58	0.49	0.00	0.93	0.76	0.00	0.92
1	Turbidity	0.55	1.56	0.44	0.65	0.54	0.39	1.44	-3.14	0.99
2	Turbidity	0.31	2.73	0.01	0.52	-0.42	0.78	0.97	-4.17	0.98
1	Chlorophyll	1.38	0.65	0.76	1.21	42	0.01	3.22	-4.42	0.99
2	Chlorophyll	1.52	0.15	0.82	1.21	42	0.01	2.91	-4.30	0.98

Inter-unit reproducibility: Analysis of inter-unit reproducibility, presented in the table below, showed that the average difference in DO measurements between the two 6600 EDSs tested was 0.25 mg/L, while the readings for DO concentration varied from 3 to 15 mg/L. The difference in conductivity averaged 0.10 mS/cm over a range of 0.3 to 44 mS/cm. The average difference in temperature readings was 0.09°C, with actual temperature readings ranging between 24 and 35°C. The average difference in pH readings was 0.03 over a range of 6.8 to 8.7. The average difference in turbidity readings was 4.68 NTU, while actual turbidity readings ranged from 0 to 197 NTU. Finally, chlorophyll readings had an average difference of 0.92, while the actual chlorophyll readings varied from 0 to 154.

Location	Average Difference Between YSI Probe #1 and YSI Probe #1					
	DO (mg/L)	Conductivity (mS/cm)	Temperature (C)	pH	Turbidity (NTU)	Chlorophyll (total)
Saltwater	0.21	0.07	0.07	0.02	1.92	1.01
Freshwater	0.45	0.01	0.11	0.07	8.33	NA
Mesocosm	0.08	0.22	0.10	0.02	3.78	0.84
Average	0.25	0.10	0.09	0.03	4.68	0.92

The magnitude of the inter-unit reproducibility results was affected by spatial and temporal changes in the sampling environment. For example, the 6600 EDSs were sampling in an environment that was changing 8°C over a 24-hour period. Because they were not sampling in exactly the same location, differences in temperature, caused by the 24-hour fluctuations, resulted in some differences in measurement by the 6600 EDSs. Similar behavior occurs in any location that experiences similar dynamic changes in the environment. The comparison of relative bias (as described above) is also a measure of inter-unit reproducibility.

Other factors: The probes were set up to collect data with minimal difficulty, and data were downloaded without incident using the provided data cable and a Windows-based PC. The 6600 EDS, as verified in this test, cost \$10,740 per unit. All portions of the verification test were completed. However, there were periods of operation where known issues (such as erroneous readings from improperly installed sensors and a puncture in a

sensor possibly by a small marine animal) probably affected the performance of one of the 6600 EDSs. Approximately 28% of the data were affected in this manner and excluded from the data analysis.

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