

October 2005

# Environmental Technology Verification Report

ANALYTICAL TECHNOLOGY, INC.  
Q45WQ CONTINUOUS  
MULTI-PARAMETER WATER QUALITY  
MONITOR

Prepared by  
Battelle

**Battelle**  
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Under a cooperative agreement with

 **EPA** U.S. Environmental Protection Agency

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October 2005

# Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

## ANALYTICAL TECHNOLOGY, INC. Q45WQ CONTINUOUS MULTI- PARAMETER WATER QUALITY MONITOR

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION  
PROGRAM



## ETV Joint Verification Statement

**TECHNOLOGY TYPE:** MULTI-PARAMETER WATER MONITORS FOR DISTRIBUTION SYSTEMS

**APPLICATION:** MONITORING DRINKING WATER QUALITY

**TECHNOLOGY NAME:** Q45WQ Series

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The U.S. Environmental Protection Agency (EPA) supports 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 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. Information and ETV documents are available at [www.epa.gov/etv](http://www.epa.gov/etv).

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permittees), and with 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 six technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center evaluated the performance of the Analytical Technology, Inc., (ATI) Q45WQ Series water quality monitor in continuously measuring free chlorine, turbidity, temperature, conductivity, pH, and oxidation-reduction potential (ORP) in drinking water. This verification statement provides a summary of the test results.

### VERIFICATION TEST DESCRIPTION

The performance of the Q45WQ was assessed in terms of its accuracy, response to injected contaminants, inter-unit reproducibility, ease of use, and data acquisition. The verification test was conducted between August 9 and October 28, 2004, and consisted of three stages, each designed to evaluate a particular performance characteristic

of the Q45WQ. All three stages of the test were conducted using a recirculating pipe loop at the U.S. EPA's Test and Evaluation Facility in Cincinnati, Ohio.

In the first stage of this verification test, the accuracy of the measurements made by the Q45WQ units was evaluated during eight, 4-hour periods of stable water quality conditions by comparing each Q45WQ unit measurement to a grab sample result generated each hour using a standard laboratory reference method and then calculating the percent difference (%D). The second stage of the verification test involved evaluating the response of the Q45WQ units to changes in water quality parameters by injecting contaminants (nicotine, arsenic trioxide, and aldicarb) into the pipe loop. Two injections of three contaminants were made into the recirculating pipe loop containing finished Cincinnati drinking water. The response of each water quality parameter, whether it was an increase, decrease, or no change, was documented and is reported here. In the first phase of Stage 3 of the verification test, the performance of the Q45WQ units was evaluated during 52 days of continuous operation, throughout which reference samples were collected once daily. The final phase of Stage 3 (which immediately followed the first phase of Stage 3 and lasted approximately one week) consisted of a two-step evaluation of the Q45WQ performance to determine whether this length of operation would negatively impact the results from the Q45WQ. First, as during Stage 1, a reference grab sample was collected every hour during a 4-hour analysis period and analyzed using the standard reference methods. Again, this was done to define a formal time period of stable water quality conditions over which the accuracy of the Q45WQ could be evaluated. Second, to evaluate the response of the Q45WQ to contaminant injection after the extended deployment, the duplicate injection of aldicarb, which was also included in the Stage 2 testing, was repeated. In addition, a pure *E. coli* culture, including the *E. coli* and the growth medium, was included as a second injected contaminant during Stage 3. Inter-unit reproducibility was assessed by comparing the results of two identical units operating simultaneously. Ease of use was documented by technicians who operated and maintained the units, as well as the Battelle Verification Test Coordinator.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data.

This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at [www.epa.gov/etv/centers/center1.html](http://www.epa.gov/etv/centers/center1.html).

## **TECHNOLOGY DESCRIPTION**

The following description of the Q45WQ unit was provided by the vendor and does not represent verified information.

The Q45WQ unit can be customized based on users' needs to include various monitoring devices. The unit verified during this test included sensors for pH, conductivity, free chlorine, ORP, temperature, and turbidity. The purpose of the unit is to provide an integrated package of monitors that can be deployed throughout water distribution systems to collect general water quality data and transmit it to remote locations, giving water companies access to real-time data from throughout their systems.

In this verification test, pH was measured using a differential pH sensor containing two glass pH electrodes, one for sensing and another in buffer to serve as a reference electrode. ATI informed Battelle that, during the same time period as this verification test, several users of its pH sensors reported a drift in the pH measurement similar to that observed during testing. ATI stated that it determined that a problem with the salt bridge assembly was causing the downward drift, which impacted not only the accuracy of the pH measurement, but also of the chlorine measurement. According to ATI, the problem was subsequently corrected. Conductivity was measured with a four-electrode conductivity sensor that measures the current-carrying capacity of the water. ORP was measured in millivolts with a differential ORP sensor containing a platinum sensing electrode and separate glass electrode in buffer to serve as a reference electrode. A membrane-covered amperometric (polarographic) sensor provided direct chlorine response without the need for chemical reagents. The conductivity sensor provided the output for both the conductivity and temperature measurements. Turbidity was measured with a 90-degree scatter nephelometer, using an infrared light source for stability and a sealed flow chamber to reduce bubble formation.

The Q45WQ unit that was tested was 24 inches wide by 47 inches high. The units normally provide 4-20 mA outputs for each parameter and can be connected to virtually any type of user-specified data acquisition system. During this verification test, ATI provided HOB0® data loggers from Onset Computer Corp. (Bourne, Massachusetts) to collect the data. Data points were collected every 30 seconds. The data logger generated a file with a .dtf suffix that required conversion to a delimited text file using software from Onset. This file was then imported into Microsoft Excel prior to further data analysis. These data loggers were downloaded daily using a serial port on a personal computer and Onset's Boxcar® software. The cost of the unit as configured for the verification test is \$11,500. In addition, ATI estimates that the total cost of replacement parts is approximately \$150 per year. This includes replacement membranes, electrolytes, O-rings on the chlorine sensor, and the salt bridge on the pH and ORP electrodes. Total labor required for preventive maintenance is approximately one hour per month.

## VERIFICATION OF PERFORMANCE

Evaluation Parameter		Free Chlorine	Turbidity	Temperature	Conductivity	pH	ORP	
<b>Stage 1— Accuracy</b>	Units 1 and 2, range of %D (median)	-41.5 to 54.3 (-15.7)	-47.2 to -16.9 (-24.9)	-5.5 to 1.3 (-1.4)	-19.7 to -2.6 (-12.7)	-11.8 to -0.9 (-5.0)	(a)	
<b>Stage 2— Response to Injected Contaminants</b>	Nicotine	Reference	-	(b)	NC	NC	NC	-
		Q45WQ	-	+	NC	NC	NC	-
	Arsenic trioxide	Reference	-	(b)	NC	+	+	-
		Q45WQ	-	+	NC	+	+	-
Aldi-carb	Reference	-	(b)	NC	NC	NC	-	
	Q45WQ	-	+	NC	NC	NC	-	
<b>Stage 3— Accuracy During Extended Deployment</b>	Units 1 and 2, range of %D (median)	-33.7 to 29.7 (-7.3)	-88.0 to 18.2 (-42.3)	-4.9 to 1.5 (-1.4)	-19.4 to -5.3 (-13.6)	-8.3 to 1.5 (-3.5)	(a)	
<b>Stage 3— Accuracy After Extended Deployment</b>	Unit 1, %D	1.1	-5.9	0.0	-14.0	0.1	(a)	
	Unit 2, %D	-1.1	11.8	-0.9	-7.9	-2.2	(a)	
<b>Stage 3— Response to Injected Contaminants</b>	<i>E. coli</i>	Reference	-	+	NC	+(c)	-	-
		Q45WQ	-	+	NC	NC	-	-
	Aldi-carb	Reference	-	+	NC	NC	-	-
		Q45WQ	-	+	NC	NC	(c)	-
<b>Injection Summary</b>	For a reason that is not clear, aldcarb altered the pH, as measured by the reference method, during the Stage 3 injections, but not during the Stage 2 injections.							
<b>Inter-unit Reproducibility (Unit 2 vs. Unit 1)</b>	Slope (intercept)	0.88 (0.10)	0.97 (0.028)	0.97 (0.31)	1.09 (-1.1)	0.71 (2.4)	0.89 (40)	
	r <sup>2</sup>	0.77	0.99	1.00	0.97	0.85	0.96	
	p-value	0.59	0.76	0.41	0.00020	0.48	0.0093	
	The ORP and conductivity sensor generated results that were significantly different from one another. Each unit's results were highly correlated with one another; but, because of the small degree of variability in each sensor's results, they were significantly different.							
<b>Ease of Use and Data Acquisition</b>	Based on the performance of the free chlorine and pH sensors, the pH sensor may have to be adjusted periodically to maintain the accuracy of both measurements. No other maintenance was necessary during the test.							

(a) ORP was not included in the accuracy evaluation because of the lack of an appropriate reference method.

(b) Relatively large uncertainty in the reference measurements made it difficult to determine a significant change.

(c) Results from duplicate injections did not agree.

+/- = Parameter measurement was increased/decreased upon injection.

NC = No obvious change was noted through a visual inspection of the data.



## **Notice**

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

## 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 permittees, buyers, and users of the technology, thus 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 six verification 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 Roy Haight and John Hall of the U.S. Environmental Protection Agency's (EPA's) Test and Evaluation (T&E) Facility (operated by Shaw Environmental, Inc. [Shaw]) in Cincinnati, Ohio, for hosting the verification test. The U.S. EPA primary contract to Shaw provided significant support in interfacing the continuous monitors with the pipe loop, as well as facilitating the experimental plan. The T&E Facility's contribution included providing the reference analyses and operating the pipe loop, as well as reviewing the test/quality assurance (QA) plan and the reports. In addition, we would like to thank Steve Allgeier of EPA's Office of Water, Gary Norris and Alan Vette of the EPA National Exposure Research Laboratory, Lisa Olsen of the U.S. Geological Survey, Matthew Steele of the City of Columbus Water Quality Assurance Laboratory, and Ron Hunsinger of East Bay Municipal Utility District, who also reviewed the test/QA plan and/or the reports.

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## List of Abbreviations

AMS	Advanced Monitoring Systems
ATI	Analytical Technology, Inc.
cm	centimeter
°C	degree centigrade
DI	deionized
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
L	liter
µS/cm	microSiemens per centimeter
mg/L	milligram per liter
NIST	National Institute of Standards and Technology
ntu	nephelometric turbidity unit
ORP	oxidation reduction potential
%D	percent difference
PE	performance evaluation
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QMP	quality management plan
SD	standard deviation
T&E	Test and Evaluation
TSA	technical systems audit

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## **Chapter 1**

### **Background**

The U.S. Environmental Protection Agency (EPA) supports 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 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 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 EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center evaluated the performance of the Analytical Technology, Inc. (ATI) Q45WQ Series water quality monitor in continuously measuring free chlorine, turbidity, temperature, conductivity, pH, and oxidation-reduction potential (ORP), in drinking water. Continuous multi-parameter water monitors for distribution systems were identified as a priority technology verification category through the AMS Center stakeholder process.

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## 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 Q45WQ water quality monitor. Following is a description of the Q45WQ, based on information provided by the vendor. The information provided below was not verified in this test.

The Q45WQ unit (Figure 2-1) can be customized based on users' needs to include various monitoring devices. The unit verified during this test included sensors for pH, conductivity, free chlorine, ORP, temperature, and turbidity. The purpose of the unit is to provide an integrated



**Figure 2-1. Analytical Technology, Inc., Q45WQ**

package of monitors that can be deployed throughout water distribution systems to collect general water quality data and transmit it to remote locations, giving water companies access to real-time data from throughout their systems.

In this verification test, pH was measured using a differential pH sensor containing two glass pH electrodes, one for sensing and another in buffer to serve as a reference electrode. Conductivity was measured with a four-electrode conductivity sensor that measures the current-carrying capacity of the water. ORP was measured in millivolts with a differential ORP sensor containing a platinum sensing electrode and separate glass electrode in buffer to serve as a reference electrode. A membrane-covered amperometric (polarographic) sensor provided direct chlorine response without the need for chemical reagents. The conductivity monitor provided the output for both the conductivity and temperature measurements. Turbidity was measured with a 90-degree scatter nephelometer, using an infrared light source for stability and a sealed flow chamber to reduce bubble formation.

The Q45WQ unit that was tested was 24 inches wide by 47 inches high. The units normally provide 4-20 mA outputs for each parameter and can be connected to virtually any type of

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user-specified data acquisition system. During this verification test, ATI provided HOBO® data loggers from Onset Computer Corp. (Bourne, Massachusetts) to collect the data. Data points were collected every 30 seconds. The data logger generated a file with a .dtf suffix that required conversion to a delimited text file using software from Onset. This file was then imported into Microsoft Excel prior to further data analysis. These data loggers were downloaded daily using a serial port on a personal computer and Onset's Boxcar® software. The cost of the unit as configured for the verification test is \$11,500. In addition, ATI estimates that the total cost of replacement parts is approximately \$150 per year. This includes replacement membranes, electrolytes, O-rings on the chlorine sensor, and the salt bridge on the pH and ORP electrodes. Total labor required for preventive maintenance is approximately one hour per month.



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## Chapter 3 Test Design

### 3.1 Introduction

The multi-parameter water monitors tested consisted of instrument packages that connect to or are inserted in distribution system pipes for continuous monitoring. Also included in this technology category were technologies that can be programmed to automatically sample and analyze distribution system water at regular intervals. The minimum requirement for participation in this verification test was that the water monitors were able to measure residual chlorine, as well as at least one other water quality parameter. Residual chlorine is a particularly important water quality parameter because changes in its concentration can indicate the presence of contamination within a distribution system, and chlorination is a very common form of water treatment used by water utilities in the United States.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Multi-Parameter Water Monitors for Distribution Systems*<sup>(1)</sup> and assessed the performance of the Q45WQ units in continuously monitoring pH, conductivity, free chlorine, ORP, temperature, and turbidity in terms of the following:

- Accuracy
- Response to injected contaminants
- Inter-unit reproducibility
- Ease of use and data acquisition.

Accuracy was quantitatively evaluated by comparing the results generated by two Q45WQ units to grab sample results generated by a standard laboratory reference method. Response to injected contaminants was evaluated qualitatively by observing whether the measured water quality parameters were affected by the injection of several contaminants. Inter-unit reproducibility was assessed by comparing the results of two identical Q45WQ units operating simultaneously. Ease of use was documented by technicians who operated and maintained the units, as well as the Battelle Verification Test Coordinator.

### 3.2 Test Stages

This verification test was conducted between August 9 and October 28, 2004, and consisted of three stages, each designed to evaluate a particular performance characteristic of the Q45WQ units. All three stages of the test were conducted using a recirculating pipe loop at the U.S. EPA's Test and Evaluation (T&E) Facility in Cincinnati, Ohio. The recirculating pipe loop consisted of ductile iron pipe, 6 inches in diameter and 100 feet long, which contained approximately 240 gallons of Cincinnati drinking water with a flow rate of approximately

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1 foot/second. The water within the pipe loop had a residence time of approximately 24 hours. Water from the pipe loop was plumbed to two Q45WQ units by a 2-inch section of polyvinyl chloride (PVC) pipe in series with a shut-off valve with a ribbed nozzle that was connected to the Q45WQ units with a 1/2-inch PVC hose and a hose clamp. Reference samples of approximately 1 liter (L) (enough volume to perform all the required analyses) to be analyzed by each standard laboratory reference method were collected from the reference sample collection valve located approximately 23 feet from the Q45WQ units on the PVC pipe.

### ***3.2.1 Stage 1, Accuracy***

During the first stage of this verification test, the accuracy of the measurements made by both Q45WQ units was evaluated by comparing the results from each unit to the result generated by a standard laboratory reference method. Stage 1 testing simulated the characteristics of a variety of water quality conditions by changing two variables: pH and temperature. Using eight sets of pH and temperature conditions, this evaluation consisted of separate four-hour testing periods of continuous analysis, with reference method sampling and analysis every hour. Four sets of conditions involved varying only the pH by injecting the pipe loop with a steady stream of sodium bisulfate. Those sets consisted of pHs of approximately 7, 8, and 9 pH units (ambient pH at the T&E Facility was between 8 and 9) and a temperature between 21 and 23 degrees centigrade (°C) (T&E Facility ambient during the time of testing). Two other sets included changing the water temperature to between 12 and 14°C and testing at pHs of approximately 7 and 8; and two sets at approximately these pHs, but at a temperature of approximately 27°C. The pipe loop ambient conditions were analyzed at the start and end of this stage. Prior to each testing period with unique conditions, the water in the pipe loop was allowed to equilibrate until the pH and temperature were at the desired level, as determined by the standard reference methods. This equilibration step took approximately 12 hours from the time the sodium bisulfate was added (to decrease pH) or the temperature was adjusted.

### ***3.2.2 Stage 2, Response to Injected Contaminants***

The second stage of the verification test involved testing the response of the Q45WQ units to changes in water quality parameters by injecting contaminants into the pipe loop, i.e., testing whether the water quality parameter continuous monitors changed in a positive or negative direction upon the injection of a contaminant. Two injections of three contaminants were made into the recirculating pipe loop containing finished Cincinnati drinking water. Each injection was made over a period of approximately 15 seconds by connecting the injection tank to the pipe loop's recirculating pump. The three contaminants were nicotine, arsenic trioxide (adjusted to pH 12 to get it into solution), and aldicarb. With the exception of the first nicotine injection, each of these contaminants was dissolved in approximately 5 gallons of pipe loop water that had been dechlorinated using granular carbon filtration to prevent degradation of the contaminant prior to injection. Upon injection, concentrations of these contaminants within the pipe loop were approximately 10 milligrams per liter (mg/L). For the first nicotine injection, however, not enough nicotine to attain this concentration was available so the available nicotine was dissolved into 2 gallons of the dechlorinated pipe loop water and injected. The resulting nicotine concentration in the pipe loop was approximately 6 mg/L. Because the qualitative change in water quality parameters was similar for both nicotine injections despite the concentration difference, it was not necessary to repeat the 10 mg/L injection of nicotine. For all three sets of injections, a reference sample was collected prior to the injection and again at 3, 15, and

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60 minutes after the injection. The difference between reference method results occurring before and then again after each injection indicated the directional change in water quality caused by the injected contaminant. For each injected contaminant, the results from the Q45WQ units were evaluated based on how well their directional change matched the reference measurement result. After each injection, the pipe loop was allowed to re-equilibrate for approximately 12 hours so that each Q45WQ unit returned to a steady baseline. Injected contaminants were obtained from Sigma-Aldrich (St. Louis, Missouri) or ChemService (West Chester, Pennsylvania) and were accompanied by a certificate of analysis provided by the supplier. Battelle QA staff audited the gravimetric preparation of these solutions.

### **3.2.3 Stage 3, Extended Deployment**

In the first phase of Stage 3 of the verification test, the performance of the Q45WQ units was evaluated during 52 days of continuous operation. The Q45WQ units required no regularly scheduled maintenance during this deployment. To track the performance of the Q45WQ units with respect to the reference results, reference samples were collected and analyzed for the selected parameters at least once per day (excluding weekends and holidays) for the duration of Stage 3. All continuously measured data were graphed, along with the results from the reference measurements, to provide a qualitative evaluation of the data. Throughout the duration of the deployment, the average percent difference (%D), as defined in Section 5.1, between the results from the Q45WQ units and those from the reference methods was evaluated.

The final phase of Stage 3 (which immediately followed the first phase of Stage 3 and lasted approximately one week) consisted of a two-step evaluation of the Q45WQ unit performance after the 52-day extended deployment to determine whether this length of operation would negatively impact the results from the Q45WQ. First, while the Q45WQ units were continuously operating, a reference sample was collected every hour during a 4-hour analysis period and analyzed using the standard reference methods. This was done to define a formal time period of stable water quality conditions for the accuracy of the Q45WQ to be evaluated. Second, to evaluate the response of the Q45WQ units to contaminant injection after the extended deployment, the duplicate injection of aldicarb, which was also included in the Stage 2 testing, was repeated. In addition, a pure *E. coli* culture, including the *E. coli* and the growth medium, was included as a second injected contaminant during Stage 3. *E. coli* was intended as an injected contaminant during Stage 2, but was not available until later in the test. During this contaminant injection component of Stage 3, reference samples were collected as they were during Stage 2.

## **3.3 Laboratory Reference and Quality Control Samples**

The Q45WQ units were evaluated by comparing their results with laboratory reference measurements. The following sections provide an overview of the applicable procedures, analyses, and methods.

### 3.3.1 Reference Methods

To eliminate the possibility of using stagnant water residing in the reference sample collection valve (dead volume) as the reference samples, the first step in the reference sample collection procedure included collecting and discarding approximately 1 L of water, which was estimated to be approximately 10 times the dead volume of the reference sample collection value. Then, from the same valve, approximately 1 L of water was collected in a glass beaker and carried directly to a technician, who immediately began the reference analyses. All the analyses were performed within minutes of sample collection. The standard laboratory methods used for the reference analyses are shown in Table 3-1. Also included in the table are method detection limits and quality control (QC) measurement differences. Battelle technical staff collected the reference samples, and technical staff at the T&E Facility performed the analyses. The T&E Facility provided calibrated instrumentation, performed all method QA/QC, and provided calibration records for all instrumentation. The T&E Facility provided reference sample results upon the analysis of the reference samples (within one day). Because previous work at the T&E facility<sup>(2)</sup> showed that the laboratory reference method for ORP using a grab sample is not directly comparable to a continuous measurement in a flowing pipe, accuracy results were not included for ORP. ORP reference and continuous measurement results were, however, included for the purpose of a qualitative data evaluation in figures showing the continuous data and reference method results. Although the ORP reference value may not be equivalent to the continuous measurement, changes in the continuous measurements were evaluated with the reference results to determine whether the sensor was identifying increases and decreases correctly.

**Table 3-1. Reference Methods**

Parameter	Method	Reference Instruments	Method Detection Limit	Acceptable Differences for QC Measurements
pH	EPA 150.1 <sup>(3)</sup>	Corning 320 pH meter	NA	±0.3 pH units
Conductivity	SM 2510 <sup>(4)</sup>	YSI 556 multi-parameter water monitor	2 microSiemens/centimeter (µS/cm)	±25%D
Free chlorine	SM 4500-G <sup>(5)</sup>	Hach 2400 portable spectrophotometer	0.01 mg/L as Cl <sub>2</sub>	±25%D
ORP <sup>(a)</sup>	SM 2580-B <sup>(6)</sup>	YSI 556 multi-parameter water monitor	NA	±25%D
Temperature	EPA 170.1 <sup>(7)</sup>	YSI 556 multi-parameter water monitor	NA	±1°C
Turbidity	EPA 180.1 <sup>(8)</sup>	Hach 2100P turbidimeter	0.067 nephelometric turbidity unit (ntu)	±25%D

<sup>(a)</sup> The reference method for measuring ORP is not directly comparable because of the difference in potential in a flowing pipe compared to that measured in a grab sample.

NA = not applicable.

### 3.3.2 Reference Method Quality Control Samples

As shown in Table 3-2, duplicate reference samples were collected and analyzed once daily during Stages 1 and 2 and weekly during Stage 3. Also, laboratory blanks consisting of American Society for Testing and Materials Type II deionized (DI) water were analyzed with the same frequency. Reference analyses of these blank samples were most important for chlorine and turbidity because they were the only parameters that needed confirmation of the lack of contamination. For the other parameters, the performance evaluation (PE) audit confirmed the accuracy of the method and the absence of contamination. Duplicate measurements had to be within the acceptable differences provided in Table 3-1.

**Table 3-2. Reference Analyses and Quality Control Samples**

Stage	Sampling Periods (length)	Reference Sample Frequency	Reference Samples per Period	QC Samples per Period	Total QC Samples
1: Accuracy	8 (4 hours)	One at start, one every hour thereafter	5	One duplicate and one DI water blank daily	16
2: Response to injected contaminants	6 (one injection)	One pre-injection; one at 3, 15, and 60 minutes post-injection	4	One duplicate and one DI water blank daily	12
3: Extended deployment	1 (52 days)	Once each weekday	37	One duplicate and one DI water blank each week	16
3: Post-extended deployment accuracy	1 (4 hours)	Same as Stage 1	5	Same as Stage 1	2
3: Response to injected contaminants	4 (one injection)	Same as Stage 2	4	Same as Stage 2	8

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## Chapter 4

### Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center<sup>(9)</sup> and the test/QA plan<sup>(1)</sup> for this verification test.

#### 4.1 Audits

##### *4.1.1 Performance Evaluation Audit*

A PE audit was conducted to assess the quality of the reference measurements made in this verification test. With the exception of temperature, each type of reference measurement was compared with a National Institute of Standards and Technology (NIST)-traceable standard reference water sample. The standard reference water samples had certified values of each water quality parameter that were unknown to the analyst. These samples were analyzed in the same manner as the rest of the reference analyses to independently confirm the accuracy of the reference measurements. The temperature PE audit was performed by comparing two independent thermometer results. As Table 4-1 shows, all PE audit results were within the acceptable differences provided in Table 3-2. The percent difference (%D) was calculated using the following equation:

$$\%D = \frac{C_R - C_N}{C_N} \times 100\%$$

where  $C_R$  was the reference method result and  $C_N$  the NIST value (or, for temperature, data from the second thermometer) for each respective water quality parameter. Other QC data collected during this verification test were reference method duplicate analysis results, which are also shown in Table 4-1. With the exception of one duplicate measure of turbidity, all parameters were always within the differences defined in Table 3-2. Because pH units are measured on a logarithmic, rather than linear, scale, and the measurement of temperature is extremely precise; the quality control metrics for those two parameters were the absolute units rather than percent difference. No corrective action was taken for the one turbidity measurement (55.2%) that was outside the acceptable difference. If this outlier is removed, the upper range of percent differences was 18.2% and the average absolute value of differences was 5.4%.

**Table 4-1. Performance Evaluation Audit and Reference Method Duplicate Analysis Results**

Parameter	PE Audit			Duplicate Analysis	
	NIST Standard Value	Reference Method Result	Difference	Average of Absolute Values of Difference	Range of Difference
pH	9.26	9.18	-0.08 pH units	0.04 pH units	0.0 to 0.13 pH units
Conductivity (µS/cm)	1,920	1,706	-11.1%	0.25%	-1.9 to 0.7%
Free chlorine (mg/L)	4.19	3.62	-13.6%	2.62%	-7.3 to 2.1%
Temperature (°C)	23.80 <sup>(a)</sup>	23.80	0.00°C	0.02°C	-0.18 to 0.29°C
Turbidity (ntu)	20	22.3	11.5%	7.49%	-8.7 to 55.2%

ORP was not included in the accuracy evaluation because of the lack of an appropriate reference method.

<sup>(a)</sup> Since a standard for temperature does not exist, the PE audit for temperature was performed by comparing the results with those from a second thermometer.

#### 4.1.2 Technical Systems Audit

The Battelle Quality Manager performed a technical systems audit (TSA) to ensure that the verification test was performed in accordance with the AMS Center QMP,<sup>(9)</sup> the test/QA plan,<sup>(1)</sup> published reference methods, and any standard operating procedures used by the T&E Facility. The TSA noted no adverse findings. A TSA report was prepared, and a copy was distributed to the EPA AMS Center Quality Manager.

#### 4.1.3 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 also were checked.

### 4.2 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 of the QMP for the ETV AMS Center.<sup>(9)</sup> Once the assessment report was prepared, the Battelle 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.

### 4.3 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-2 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record.

**Table 4-2. Summary of Data Recording Process**

<b>Data to Be Recorded</b>	<b>Where Recorded</b>	<b>How Often Recorded</b>	<b>By Whom</b>	<b>Disposition of Data</b>
Dates, times, and details of test events	ETV data sheets and testing notebook	Start/end of test and at each change of a test parameter	Battelle and T&E Facility	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
Calibration information (Q45WQ units and reference methods)	ETV data sheets and testing notebook	Upon each calibration	Battelle and T&E Facility	Manually incorporated in data spreadsheets as necessary
Q45WQ unit results	Recorded electronically by each unit and then downloaded to computer daily	Recorded continuously	Battelle	Comma delimited text files.
Reference method procedures	ETV laboratory record books or data recording forms	Throughout sample analysis process	T&E Facility	Transferred to spreadsheets or laboratory record book



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## Chapter 5

### Statistical Methods

The statistical methods presented in this chapter were used to verify the Q45WQ units' accuracy, response to injected contaminants, and inter-unit reproducibility.

#### 5.1 Accuracy

Throughout this verification test, results from the Q45WQ units were compared to the results obtained from analysis of a grab sample by the reference methods. During Stage 1, the percent difference between these two results was calculated using the following equation:

$$\%D = \frac{C_m - C_R}{C_R} \times 100\%$$

where  $C_R$  is the result determined by the reference method and  $C_m$  is the result from a Q45WQ unit; the Q45WQ unit results were recorded every 30 seconds, whereas collecting the reference samples took only a few seconds. Therefore,  $C_m$  was the measurement recorded closest to the time the reference sample was collected. Water quality stability, as well as the stability of each sensor, was evaluated during the four-hour time period when reference samples were analyzed every hour for each of the parameters. Ideally, if the result from a Q45WQ unit and a reference method measurement were the same, there would be a percent difference of zero. It should be noted that the formula for percent difference is sensitive to reference results that are small in magnitude. For example, if the reference turbidity is 0.1 ntu, and the online instrument reads 0.2, the percent difference is 100%. Alternatively, if the reference turbidity is 1.0 ntu, and the online instrument reads 1.1, the percent difference is only 10%. During Stages 2 and 3, the continuous data, graphed with the reference method results, were visually examined to evaluate the response of the Q45WQ unit to the injection of contaminants and their stability over an extended deployment. During the accuracy and contaminant injection components of Stage 3, the data were evaluated as they were for Stages 1 and 2, respectively.

#### 5.2 Response to Injected Contaminants

To evaluate the response (i.e., the increase or decrease of water quality parameter measured by the Q45WQ units) to contaminant injections, the pre- and post-injection reference samples were graphed as individual data points, along with the continuous measurements. The reference results showed the effect of each injection on the chemistry of the water in the pipe loop, and the continuous results from the Q45WQ units highlighted their response to such changes.

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### 5.3 Inter-unit Reproducibility

The results obtained from two identical Q45WQ units were compared to assess inter-unit reproducibility. Each time a reference sample was collected and analyzed (approximately 127 times throughout this verification test), the results from each Q45WQ unit were compared to evaluate whether the two units were generating similar results. This was done in two ways. First, the results from one unit were graphed against the results of the other unit. In this evaluation, a slope of unity and a coefficient of determination of 1.0 would indicate ideal inter-unit reproducibility. Slopes above 1.0 may indicate a high bias from Unit 2 (graphed on the y-axis) or a low bias for Unit 1 with respect to each other. Similarly, slopes below 1.0 may indicate a low bias for Unit 2 or a high bias for Unit 1, again with respect to each other. Second, the data from each unit were included in a paired t-test, with the assumption that the data from each unit had equal variances. The t-test calculated the probability of obtaining the subject results from the two units if there was no significant difference between their results. Therefore, probability values (p-values) of less than 0.05 (i.e., less than a 5% probability that this data set would be generated if there actually was no difference between the two units) indicated a significant difference between the two units. In addition, the results from both units were graphed together for the Stages 2 and 3 results, allowing a visual comparison.

## Chapter 6 Test Results

As mentioned previously, this verification test was conducted in three stages that focused on three different aspects of multi-parameter water monitors for distribution systems. The three stages are summarized in Table 6-1. The first stage consisted of an evaluation (with varied pHs and temperatures) of the accuracy of each Q45WQ sensor: free chlorine, turbidity, temperature, conductivity, and pH. ORP was also measured; but, because a laboratory reference measurement equivalent to the on-line continuous measurement was not available, ORP was not included in the accuracy evaluation. The second stage of the verification test consisted of an evaluation of the response of the Q45WQ units to the injection of several contaminants into the pipe loop. The third stage consisted of deploying the Q45WQ units for 52 consecutive days with minimal intervention for maintenance. In addition, contaminant injections were performed at the close of Stage 3 to confirm that the Q45WQ units were still responsive to contaminant injection after the extended deployment. Two Q45WQ units were tested to evaluate inter-unit reproducibility. In addition, required maintenance and operational characteristics were documented throughout the verification test. This chapter provides the results of the three testing stages, the inter-unit reproducibility data, and ease of use information.

**Table 6-1. Summary of Test Stages and Type of Data Presentation**

Stage	Summary	Data Presentation
1	Accuracy when pH and temperature were varied	Table of percent differences between Q45WQ units and reference measurements
2	Response to contaminant injection	Graphs of Q45WQ unit measurements and reference measurements, table showing the effect of injections on both reference and Q45WQ measurements
3	Extended deployment with minimal maintenance along with post-extended deployment accuracy and response to contaminant injections	Graphs of Q45WQ unit measurements with reference measurements, table showing average percent differences throughout extended deployment, table showing the effect of injections on both reference and Q45WQ measurements

## 6.1 Accuracy

Tables 6-2a–e list the data from the accuracy evaluation performed during the first stage of the verification test. During four-hour periods, the water quality conditions were held stable, and reference samples were collected and analyzed five times, once at the start of the designated test period and four times at one-hour increments thereafter. Because reference sample collection took just a few seconds, and the results from the Q45WQ units were recorded every 30 seconds, the water quality parameter measurement at the time closest to reference sample collection was compared to the reference sample. For each unit, this approach resulted in five paired Q45WQ and reference results for each of the eight sets of water conditions used to simulate pH and temperature variations at a water utility. The average and standard deviations of these five results are shown in the tables below, as well as the percent difference between the average results from both Q45WQ units and the average of the reference results.

**Table 6-2a. Accuracy Evaluation Under Various Conditions—Free Chlorine**

Set	Conditions	Reference Average (SD) [mg/L]	Unit 1		Unit 2	
			Average (SD) [mg/L]	% D	Average (SD) [mg/L]	% D
1	ambient pH, ambient temperature	0.94 (0.04)	1.17 (0.01)	24.5	1.45 (0.01)	54.3
2	decreased pH, ambient temperature	0.65 (0.01)	0.38 (0.04)	-41.5	0.57 (0.00)	-12.3
3	decreased pH, ambient temperature	0.29 (0.02)	0.18 (0.01)	-37.9	0.19 (0.01)	-34.5
4	ambient pH, decreased temperature	0.41 (0.08)	0.41 (0.01)	0.0	0.54 (0.01)	31.7
5	decreased pH, decreased temperature	1.47 (0.06)	1.00 (0.04)	-32.0	1.19 (0.04)	-19.0
6	ambient pH, increased temperature	0.60 (0.04)	0.48 (0.01)	-20.0	0.67 (0.01)	11.7
7	decreased pH, increased temperature	0.54 (0.05)	0.40 (0.03)	-25.9	0.49 (0.05)	-9.3
8	ambient pH, ambient temperature	0.91 (0.03)	0.73 (0.02)	-19.8	1.10 (0.05)	20.9

**Table 6-2b. Accuracy Evaluation Under Various Conditions—Turbidity**

Set	Conditions	Reference Average (SD) [ntu]	Unit 1		Unit 2	
			Average (SD) [ntu]	% D	Average (SD) [ntu]	% D
1	ambient pH, ambient temperature	0.88 (0.07)	0.64 (0.02)	-27.3	0.66 (0.03)	-25.0
2	decreased pH, ambient temperature	0.97 (0.33)	0.64 (0.04)	-34.0	0.73 (0.05)	-24.7
3	decreased pH, ambient temperature	1.54 (0.20)	1.28 (0.06)	-16.9	1.24 (0.06)	-19.5
4	ambient pH, decreased temperature	0.89 (0.41)	0.53 (0.21)	-40.4	0.47 (0.07)	-47.2
5	decreased pH, decreased temperature	0.99 (0.21)	0.79 (0.03)	-20.2	0.81 (0.04)	-18.2
6	ambient pH, increased temperature	0.92 (0.16)	0.70 (0.02)	-23.9	0.69 (0.02)	-25.0
7	decreased pH, increased temperature	1.00 (0.35)	0.77 (0.01)	-23.0	0.76 (0.01)	-24.0
8	ambient pH, ambient temperature	0.46 (0.11)	0.29 (0.03)	-37.0	0.31 (0.03)	-32.6

**Table 6-2c. Accuracy Evaluation Under Various Conditions—Temperature**

Set	Conditions	Reference Average (SD) [°C]	Unit 1		Unit 2	
			Average (SD) [°C]	% D	Average (SD) [°C]	% D
1	ambient pH, ambient temperature	22.60 (0.33)	22.58 (0.31)	-0.1	22.12 (0.36)	-2.1
2	decreased pH, ambient temperature	21.66 (0.08)	21.72 (0.11)	0.3	21.14 (0.09)	-2.4
3	decreased pH, ambient temperature	21.93 (0.15)	21.76 (0.17)	-0.8	21.62 (0.47)	-1.4
4	ambient pH, decreased temperature	13.82 (0.44)	13.60 (0.26)	-1.6	13.66 (0.88)	-1.2
5	decreased pH, decreased temperature	12.63 (0.26)	12.16 (0.23)	-3.7	11.94 (0.22)	-5.5
6	ambient pH, increased temperature	26.60 (0.27)	26.94 (0.25)	1.3	26.44 (0.25)	-0.6
7	decreased pH, increased temperature	26.69 (0.23)	26.78 (0.11)	0.3	26.30 (0.22)	-1.5
8	ambient pH, ambient temperature	22.79 (0.21)	22.24 (0.37)	-2.4	21.98 (0.41)	-3.6

**Table 6-2d. Accuracy Evaluation Under Various Conditions—Conductivity**

Set	Conditions	Reference Average (SD) [ $\mu\text{S}/\text{cm}$ ]	Unit 1		Unit 2	
			Average (SD) [ $\mu\text{S}/\text{cm}$ ]	% D	Average (SD) [ $\mu\text{S}/\text{cm}$ ]	% D
1	ambient pH, ambient temperature	451 (1)	362 (4)	-19.7	390 (9)	-13.5
2	decreased pH, ambient temperature	503 (6)	421 (13)	-16.3	443 (14)	-11.9
3	decreased pH, ambient temperature	694 (12)	587 (27)	-15.4	649 (24)	-6.5
4	ambient pH, decreased temperature	412 (1)	335 (0)	-18.7	362 (8)	-12.1
5	decreased pH, decreased temperature	501 (10)	417 (9)	-16.8	456 (9)	-9.0
6	ambient pH, increased temperature	447 (1)	388 (5)	-13.2	431 (4)	-3.6
7	decreased pH, increased temperature	529 (2)	464 (4)	-12.3	515 (5)	-2.6
8	ambient pH, ambient temperature	442 (1)	384 (0)	-13.1	419 (5)	-5.2

**Table 6-2e. Accuracy Evaluation Under Various Conditions—pH**

Set	Conditions	Reference Average (SD) [pH units]	Unit 1		Unit 2	
			Average (SD) [pH units]	% D	Average (SD) [pH units]	% D
1	ambient pH, ambient temperature	8.76 (0.02)	8.60 (0.00)	-1.8	8.60 (0.00)	-1.8
2	decreased pH, ambient temperature	7.52 (0.04)	7.08 (0.04)	-5.9	7.30 (0.00)	-2.9
3	decreased pH, ambient temperature	6.73 (0.12)	6.04 (0.05)	-10.3	6.30 (0.10)	-6.4
4	ambient pH, decreased temperature	8.48 (0.02)	8.20 (0.00)	-3.3	8.40 (0.00)	-0.9
5	decreased pH, decreased temperature	7.31 (0.08)	6.62 (0.08)	-9.4	7.00 (0.07)	-4.2
6	ambient pH, increased temperature	8.37 (0.05)	7.68 (0.04)	-8.2	8.16 (0.05)	-2.5
7	decreased pH, increased temperature	7.60 (0.06)	6.70 (0.00)	-11.8	7.10 (0.00)	-6.6
8	ambient pH, ambient temperature	8.74 (0.01)	8.00 (0.00)	-8.5	8.40 (0.00)	-3.9

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Of the parameters that were evaluated for accuracy, the free chlorine percent differences (with the median shown in parentheses) ranged from -41.5 to 54.3 (-15.7); for turbidity, -47.2 to -16.9 (-24.9), for temperature, -5.5 to 1.3 (-1.4), for conductivity, -19.7 to -2.6 (-12.7), and for pH, -11.8 to -0.9 (-5.0).<sup>1</sup> These ranges show that the free chlorine sensor generated results with the largest spread of percent differences compared to the reference method. The results may be because of the chlorine sensor's dependence on pH correction. As will be discussed in Section 6.3, regular calibration of the pH sensor was required to maintain accurate free chlorine measurements. Periodically, the accuracy of the pH sensor drifted, affecting the free chlorine results. The standard deviations of the reference and continuous measurements collected during each test period were, with few exceptions, very small with respect to the average result. In only a few instances was the standard deviation greater than 5% of the average result. This shows both that the water conditions during these test periods were very stable and that there was very little variability in the sensors themselves. The results were not remarkably different among the various sets of water quality conditions; therefore, the Q45WQ unit performance was apparently not dependent on the water conditions.

## 6.2 Response to Injected Contaminants

Six injections of contaminants were performed during the second stage of this verification test; i.e., duplicate injections of nicotine, arsenic trioxide, and aldicarb. Table 6-3 shows the directional change of each reference and Q45WQ measurement in response to the contaminant injections. In general, free chlorine and ORP were the only parameters clearly affected (for both the reference and continuous measurements) by all six injections. Figures 6-1 through 6-5 show the responses of free chlorine, ORP, turbidity, pH, and conductivity. The blue and yellow lines on the graphs represent the measurements made by each Q45WQ unit, and the magenta data points represent the results from the laboratory reference method. Because accuracy was the focus of the first stage of verification testing, percent differences between the Q45WQ units and the reference method results are not presented here; however, the reference method results are included in these figures to confirm that the fluctuations in the continuous results are due to changes in water chemistry as the result of the injected contaminants. The figures are divided with vertical lines that define the approximate time period for each injection. Each injection time period defined on the figures is approximately 24 hours, but the times vary somewhat depending on when chlorine was added to restore the system to pre-injection conditions. The contaminant that was injected and whether it was the first or second replicate are shown at the top of each section of the figures. For each injection, at least four reference sample results were collected, and are included in these figures. The first occurred within approximately one hour prior to contaminant injection during a period of stable water quality conditions. The next three reference data points were from samples collected 3, 15, and 60 minutes after contaminant injection. For some of the injections, another reference sample was collected the following day to show that the pipe loop system had recovered or was in the process of recovering after the injection. This

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<sup>1</sup> Throughout this report, median values are provided when a range of values is presented. The median of a set of positive and negative numbers provides a good indicator of the overall direction of the percent differences in the data set (i.e., whether most values were positive or negative). The disadvantage is that, unless the signs of all the data are the same, information about the magnitude of change is not available from the median. In summary, the medians in this report provide the direction, not magnitude, of difference information.



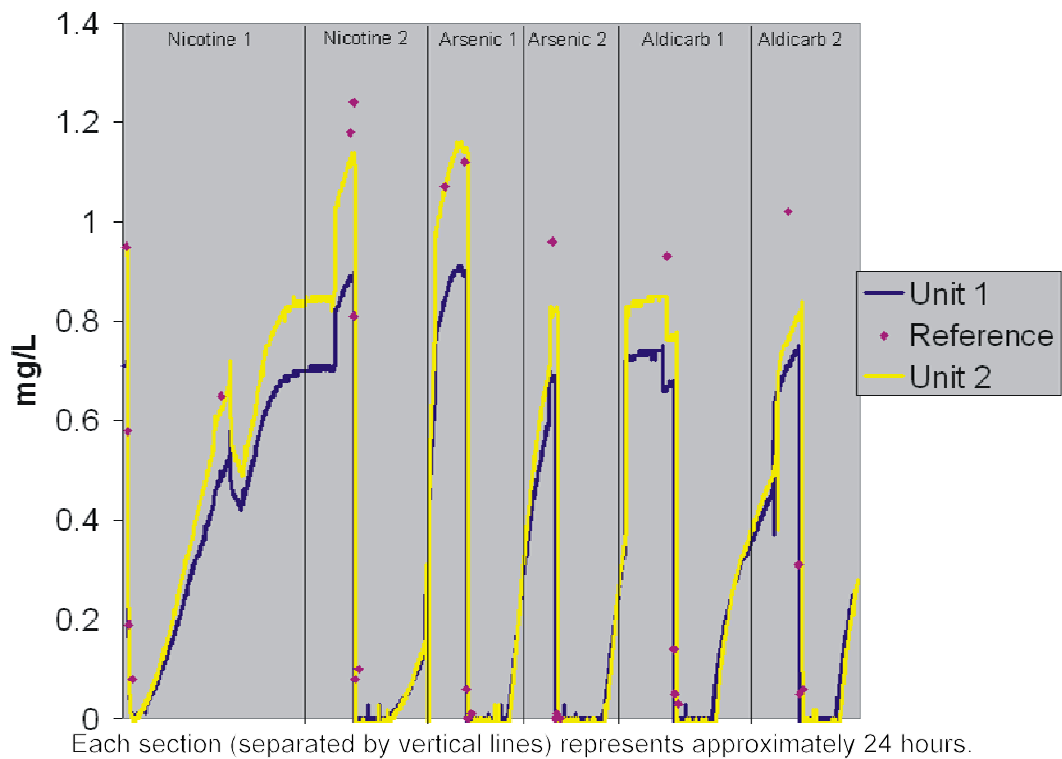
**Table 6-3. Effect of Contaminant Injections Prior to Extended Deployment**

Parameter	Nicotine		Arsenic Trioxide		Aldicarb	
	Reference	Q45WQ	Reference	Q45WQ	Reference	W45WQ
Free chlorine	– (a)	–	– (a)	–	– (a)	–
Turbidity		+		+		+
Temperature	NC	NC	NC	NC	NC	NC
Conductivity	NC	NC	+	+	NC	NC
pH	NC	NC	+	+	NC	NC
ORP	–	–	–	–	–	–

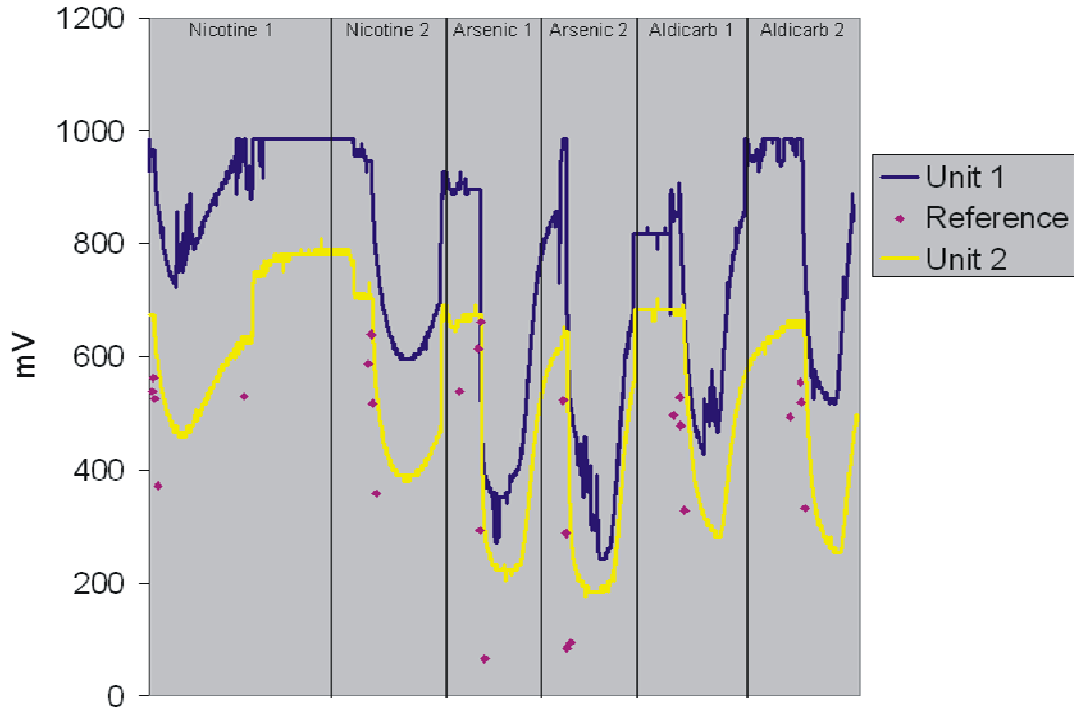
(a) Relatively large uncertainty in the reference measurements made it difficult to detect a significant change.  
 +/- = Parameter measurement increased/decreased upon injection.  
 NC = No change in response to the contaminant injection.

final reference data point also served as the first reference sample collected for some of the injections, representing the stable baseline just prior to injection.

Figure 6-1 shows how the measurement of free chlorine was affected by the contaminant injections. Prior to the injections, the free chlorine level was maintained at approximately 1 mg/L, as is evidenced by the magenta data points near the start of each section of the figure. In

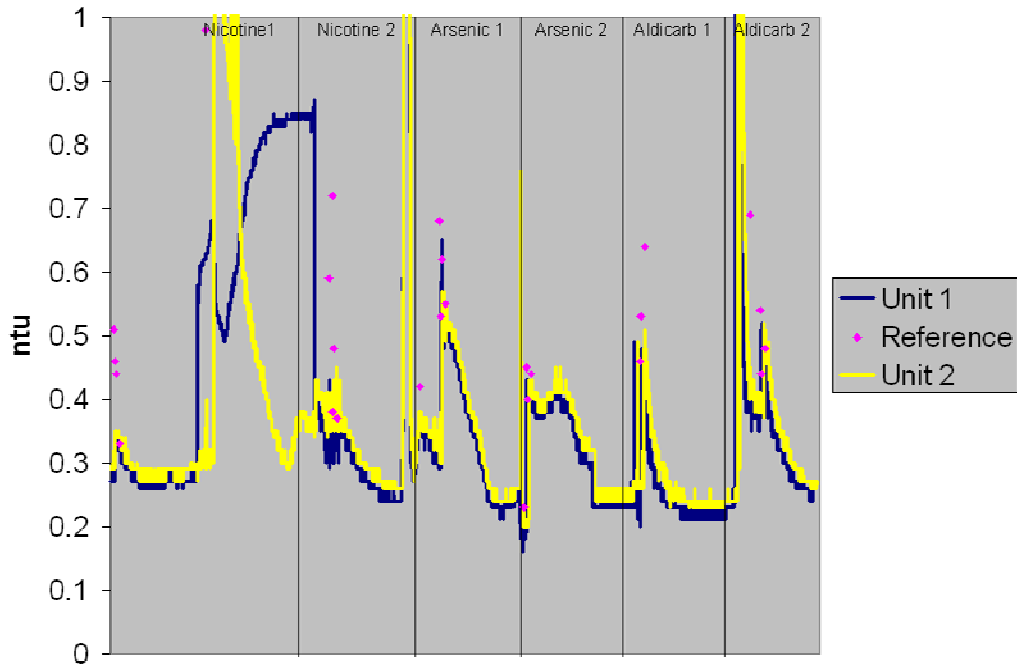


**Figure 6-1. Stage 2 Contaminant Injection Results for Free Chlorine**



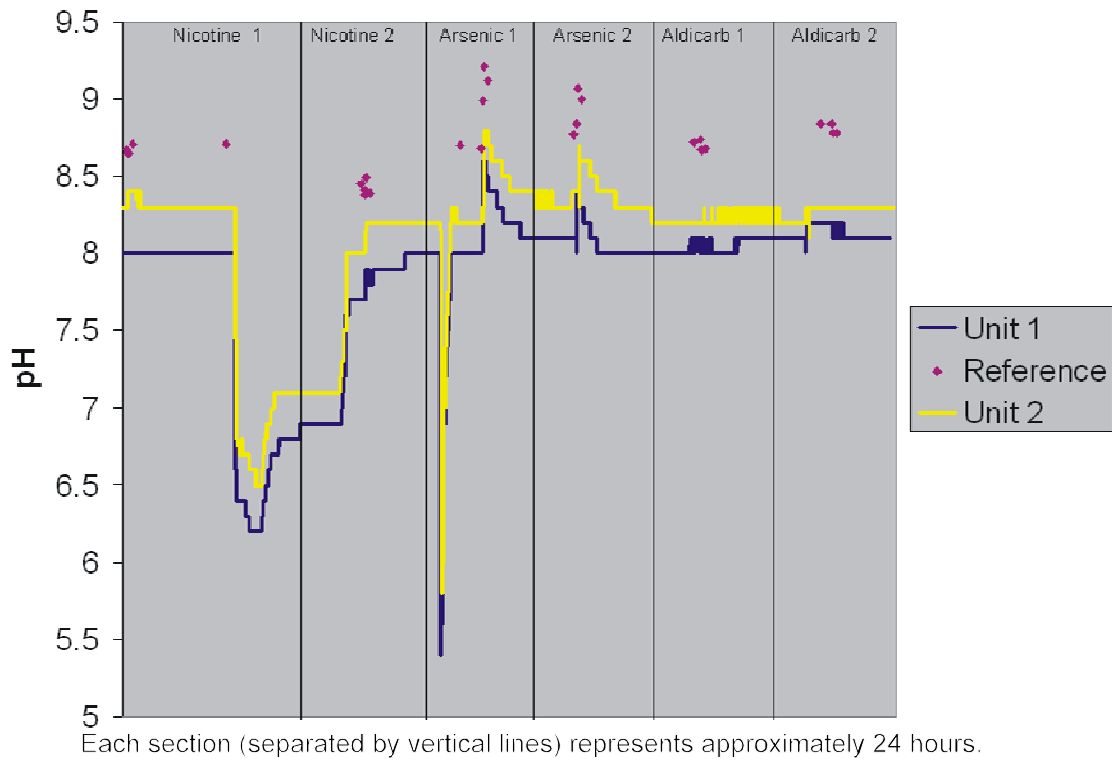
Each section (separated by vertical lines) represents approximately 24 hours.

**Figure 6-2. Stage 2 Contaminant Injection Results for ORP**

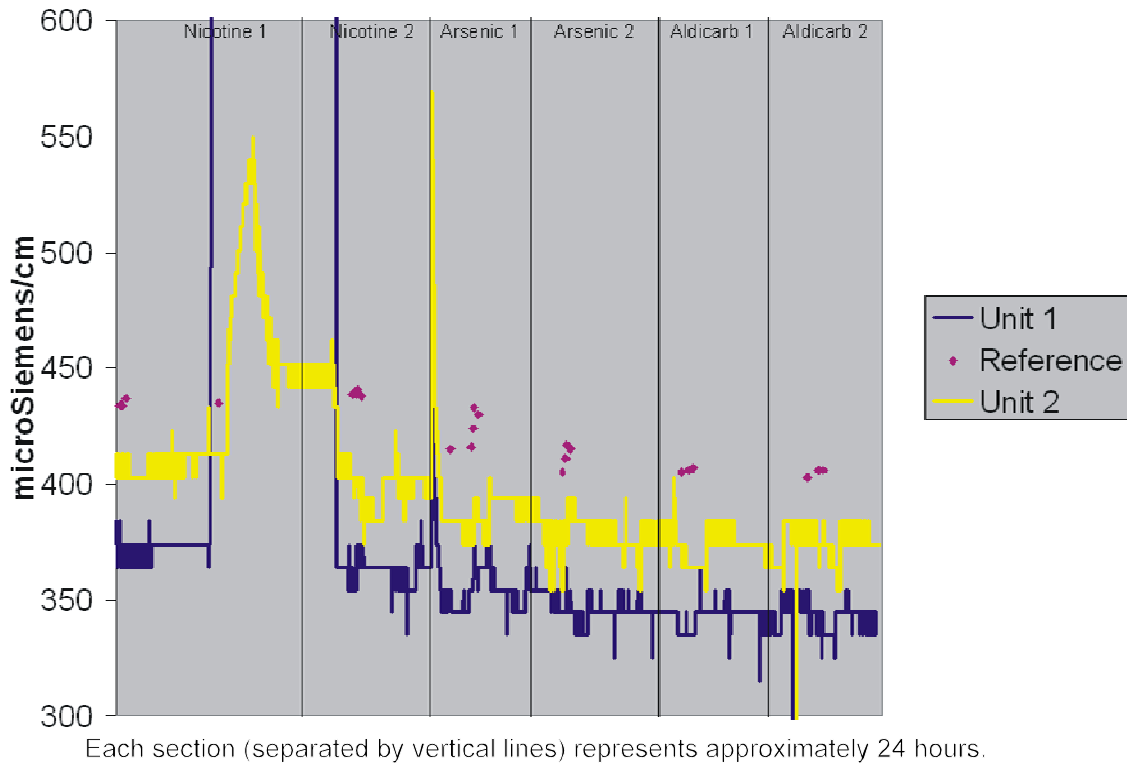


Each section (separated by vertical lines) represents approximately 24 hours.

**Figure 6-3. Stage 2 Contaminant Injection Results for Turbidity**



**Figure 6-4. Stage 2 Contaminant Injection Results for pH**



**Figure 6-5. Stage 2 Contaminant Injection Results for Conductivity**

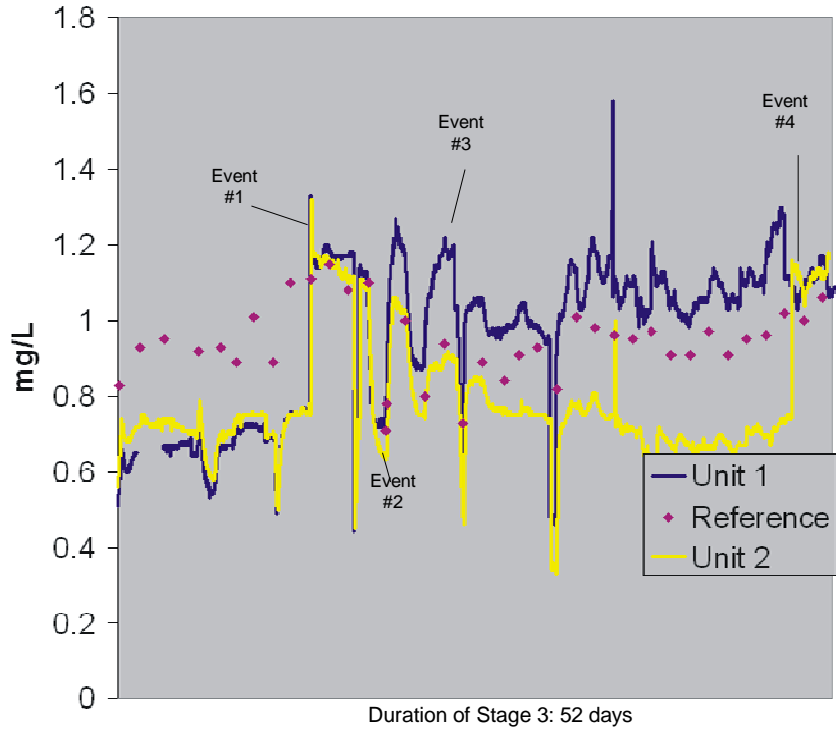
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each case, within one hour of contaminant injection, the free chlorine level, as measured by the laboratory reference method, dropped to near zero. As shown by the vertical drop in the line representing the free chlorine concentration, it was clear that the chlorine sensor on the Q45WQ units responded to the drop in free chlorine levels as a result of the presence of the contaminant. For each injection, the drop to nearly zero free chlorine levels was followed by the restoration of the pipe loop system to approximately pre-injection conditions through the addition of sodium hypochlorite. This is shown in Figure 6-1 by the rapidly increasing free chlorine concentration after the sensor reached a low point in free chlorine concentration following each injection. The ORP in water is highly dependent on the occurrence of oxidation-reduction chemical reactions within the water. Therefore, when free chlorine is reacting with injected contaminants, it can be expected that the ORP would be affected. Figure 6-2 shows that this parameter tracked the concentration of free chlorine upon injection of the contaminants. However, it is not conclusive whether the change in ORP is due to the change in chlorine or to the presence of the contaminants. Additional controls would be needed to make that determination. Note that the offset between Unit 1 and Unit 2 was due to a loose wire to Unit 1's data logger. That problem was corrected by ATI during Stage 3 of the verification test.

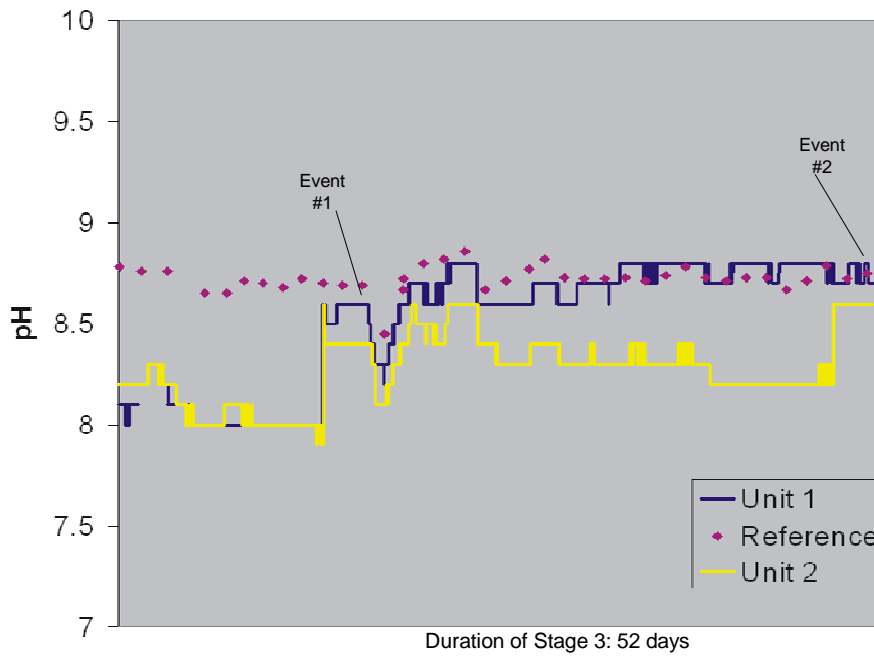
Figure 6-3 shows the turbidity measurements during the contaminant injections. As for the other water parameters, the reference samples were collected prior to the contaminant injection and at 3, 15, and 60 minutes following the contaminant injection. Therefore, each cluster of magenta symbols on the figure indicate when a contaminant injection had occurred. However, for all the injections except the second arsenic injection, the level of turbidity measured by the reference method decreased from the time the pre-injection reference sample was collected until the subsequent reference samples were collected and analyzed. This suggests that 1) the contaminant injections did not increase the turbidity in the flowing water or, 2) that the uncertainty in the reference measurements was too large to determine whether turbidity was significantly affected. Because the continuous turbidity measurement of the Q45WQ seemed to increase at least slightly (through a visual inspection of the data) with each injection, it seems that the latter scenario is more likely to be the case. For the nicotine injections, the change in turbidity according to the Q45WQ measurements was very small, while the changes during the arsenic and aldicarb injections were slightly more pronounced. Because each of these contaminants was dissolved in water prior to injection, these observed increases could have been due to changes in the optical properties of the water resulting from the dissolution of the contaminant or the co-injection of small amounts of air, introducing a few bubbles into the pipe, thus causing an increase in turbidity. Note that during the latter half of the first and second nicotine injections and just prior to the final aldicarb injection, there were turbidity spikes that were not due to the injection of any contaminants. Apparently, some outside perturbations in the water system caused these brief events. For both pH and conductivity, there was a small increase measured by both the reference and continuous measurements during the injection of arsenic trioxide only. For both water quality parameters, the increase may have been due to the pH adjustment required to get this contaminant into solution.

### **6.3 Extended Deployment**

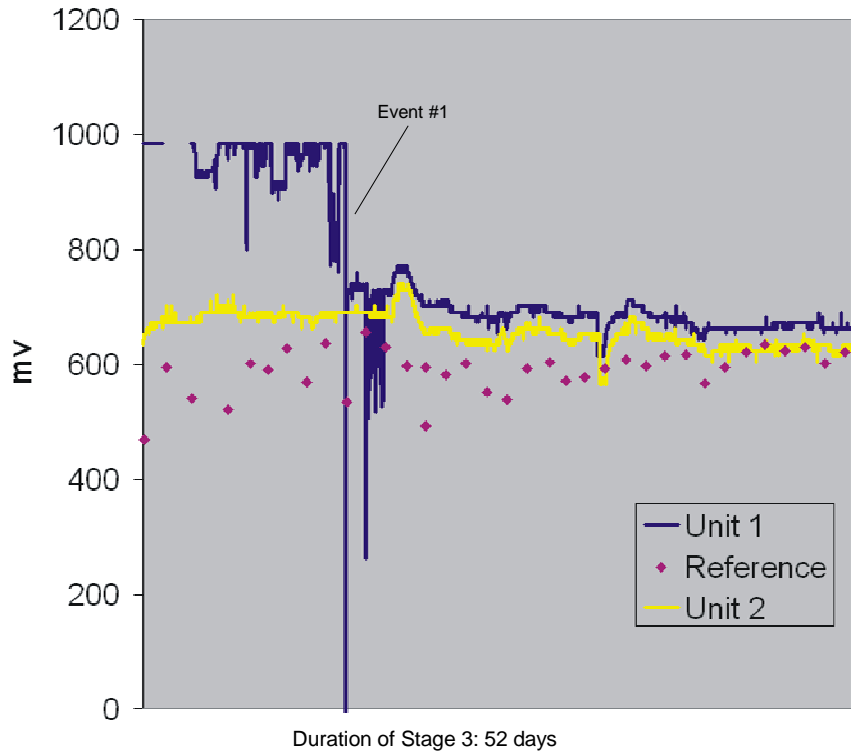
Figures 6-6 through 6-11 show the continuous measurements from both Q45WQ units during the 52-day extended deployment stage of the verification test. Those measurements are represented by the blue and yellow lines, while the results of the reference samples, collected once daily



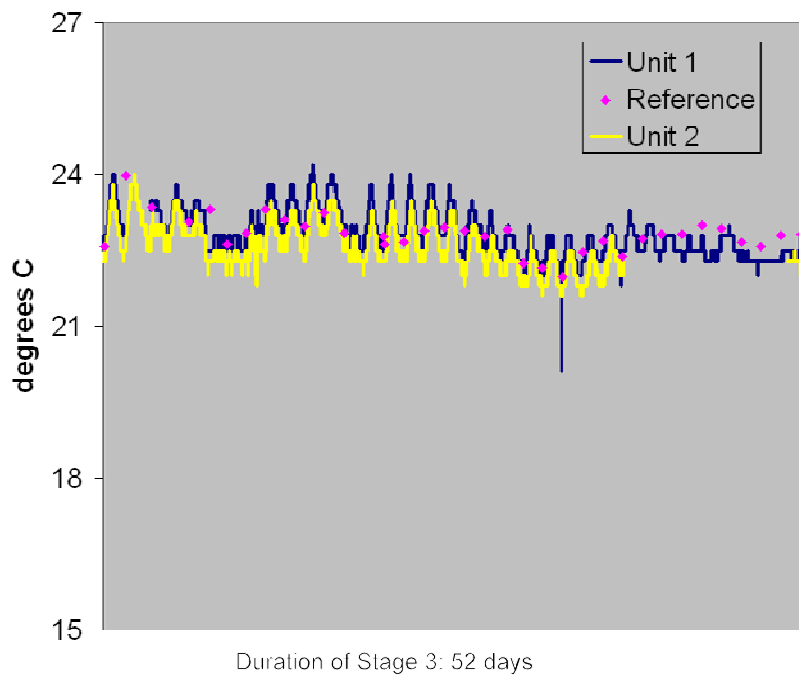
**Figure 6-6. Extended Deployment Results for Free Chlorine**



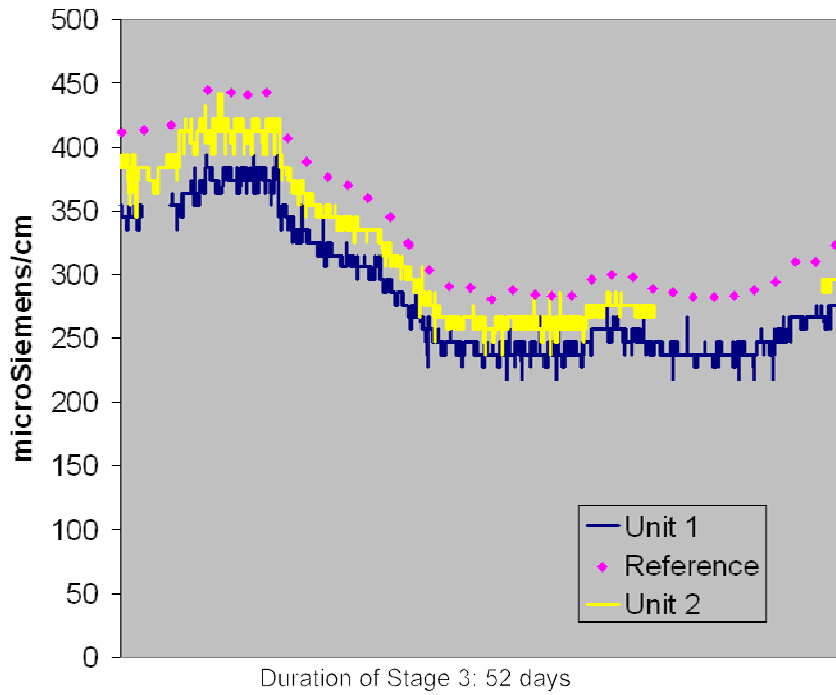
**Figure 6-7. Extended Deployment Results for pH**



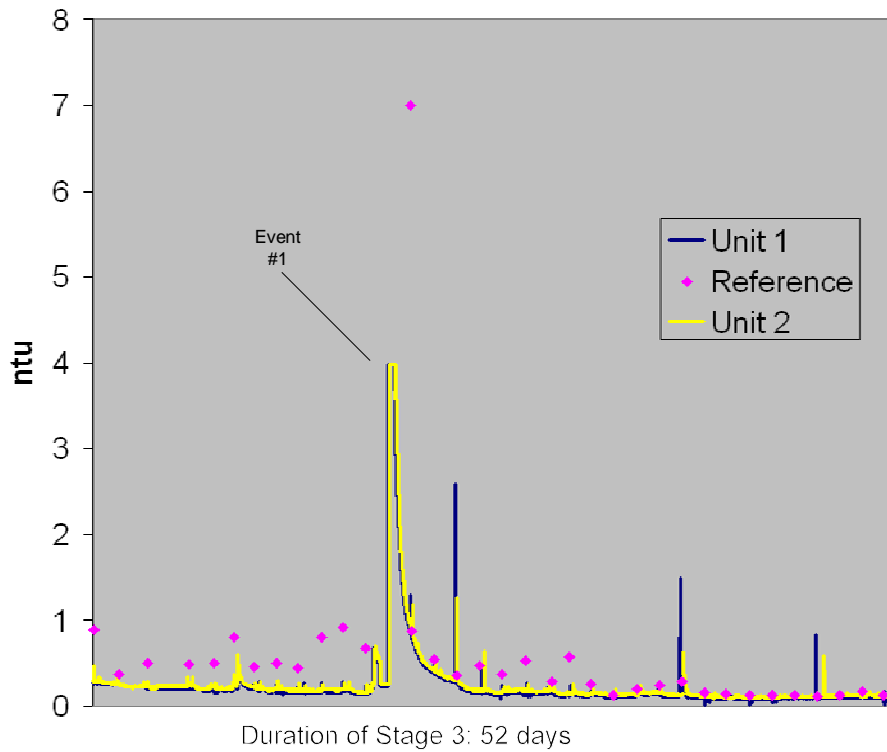
**Figure 6-8. Extended Deployment Results for ORP**



**Figure 6-9. Extended Deployment Results for Temperature**



**Figure 6-10. Extended Deployment Results for Conductivity**



**Figure 6-11. Extended Deployment Results for Turbidity**

throughout this deployment, are represented by the magenta symbols. The x-axis on each figure represents the period of time between September 1, 2004, and October 22, 2004, while the y-axis gives the results of each water quality measurement. Data points were recorded every 30 seconds during the verification test; and, for the extended deployment figures, only data points collected approximately every 2 minutes were depicted. This was done so that a standard spreadsheet could be used to generate these figures. This approach was inconsequential to interpreting figures.

The objective of this stage of the verification test was to evaluate the performance of the Q45WQ units over an extended period of time with minimal intervention to simulate a situation in which the units may be deployed at a remote location. The continuous trace was evaluated visually to see whether any aspects of the data were noteworthy. A second, more quantitative, evaluation was then performed to get an indication of the accuracy of the extended deployment measurements. This evaluation, much like the accuracy evaluation conducted during the first stage of testing, included calculating the percent differences between the average continuous measurements and average reference sample results throughout the extended deployment, as well as the standard deviation of each of those measurements. The standard deviation of the results provided a means to evaluate the stability of the water conditions during Stage 3, as well as how the standard deviations of the continuous measurements differed from the standard deviations of the reference measurements. Similar relative standard deviations between the continuous and reference measurements indicate that the variability was mostly dependent on the water conditions and not due to systematic variability in the Q45WQ unit results. (Note that reference results were only generated during business hours, so any fluctuations occurring during off hours are not reflected in the standard deviation of the reference results. Because of this, free chlorine, a parameter that varied at times during weekends when the supply of chlorine ran low, might have been expected to have a larger variability than other more stable parameters.) Table 6-4 lists the percent differences, along with the average and standard deviations of the reference and continuous results during the extended deployment. The range and median (see the footnote in Section 6.1 for direction on interpreting the median) percent difference for each water quality parameter, as measured for each reference sample analyzed during the extended deployment, are also given.

**Table 6-4. Accuracy During Extended Deployment**

Parameter	Reference	Unit 1		Unit 2		Both Units %D Range (median)
	Average (SD) <sup>(a)</sup>	Average (SD) <sup>(a)</sup>	%D	Average (SD) <sup>(a)</sup>	%D	
Free chlorine	0.95 (0.10)	0.99 (0.21)	4.2	0.79 (0.17)	-16.8	-33.7 to 29.7 (-7.3)
Turbidity	0.73 (1.55)	0.29 (0.64)	-60.8	0.32 (0.64)	-56.2	-88.0 to 18.2 (-42.3)
Temperature	22.83 (0.36)	22.65 (0.30)	-0.8	22.35 (0.32)	-2.1	-4.9 to 1.5 (-1.4)
Conductivity	335 (57)	285 (51)	-14.9	319 (54)	-4.8	-19.4 to -5.3 (-13.6)
pH	8.72 (0.07)	8.54 (0.30)	-2.1	8.28 (0.17)	-5.0	-8.3 to 1.5 (-3.5)

<sup>(a)</sup> Free chlorine, mg/L; turbidity, ntu; temperature, °C; conductivity, µS/cm; pH, pH units.

For free chlorine, visual inspection of the data in Figure 6-6 revealed that, for the first approximately one-third of the extended deployment, the free chlorine measurements were approximately 0.7 mg/L (with some variation) for both units, while the reference method measurements ranged from approximately 0.8 mg/L to 1.1 mg/L. At that point, the ATI representative visited the testing facility and adjusted the pH sensor (that works in concert with



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the free chlorine sensor) to correct the free chlorine measurement to match the reference method result (free chlorine Event #1 in Figure 6-6). When this was done, both Q45WQ units tracked the free chlorine reference measurements rather well until the supply of sodium hypochlorite (used to maintain the chlorine concentrations in the pipe loop) ran low after a weekend (free chlorine Event #2). When this occurred, the chlorine level dropped significantly from background levels. After this variation, the chlorine sensor on Q45WQ Unit 1 recovered to a measurement somewhat higher than the reference results, and the Q45WQ Unit 2 recovered to a measurement somewhat lower than the reference result (free chlorine Event #3). Unit 1 continued to have a higher measurement until near the end of the extended deployment when the results from the two units abruptly converged to a measurement slightly higher than the reference measurement. This marked the time that ATI again adjusted the pH sensor to match the reference method result (free chlorine Event #4). During the extended deployment, the percent differences for both units ranged from -33.7 to 29.7, with a median of -7.3. The average free chlorine concentration, as measured by the reference method, was  $0.95 \text{ mg/L} \pm 0.10 \text{ mg/L}$ . Prior to the first pH adjustment, the percent difference ranged from -33.7 to -16.9, with a median of -24.7; and, after the pH sensor adjustment, the average percent difference ranged from -29.9 to 29.7, with a median of 4.6. The accuracy of the free chlorine sensor on the Q45WQ units was heavily dependent on the accuracy of the pH sensor that is used to correct the chlorine measurement.

The pH results presented in Figure 6-7 reflect the adjustments made to the pH sensor during the verification test. For the first approximately one-third of the extended deployment, Units 1 and 2 were measuring the pH as approximately 8.0, while the reference method was measuring it as approximately 8.8. At that time, ATI made the adjustment to the pH sensor to bring both units' measurements in line with the reference measurement. This is shown by the abrupt convergence of both Unit 1 and 2 measurements with the reference measurement (pH Event #1 in Figure 6-7). After that point, the Unit 1 pH sensor was more accurate than Unit 2, which seemed to drift lower. Near the end of the extended deployment, ATI adjusted the pH results again in both units so both of their results were in line with the reference results (pH Event #2). Again, this is shown by the abrupt convergence of all three measurements. The average pH, as measured by the reference method, was  $8.72 \pm 0.07$ , and the average pH as measured by Q45WQ Units 1 and 2 was  $8.54 \pm 0.30$  and  $8.28 \pm 0.17$ , respectively. Overall, during the extended deployment, the percent difference for the pH sensors ranged from -8.3 to 1.5, with a median of -3.5. ATI informed Battelle that, during the same time period as this verification test, several users of its pH sensors reported a similar drift in the pH measurement. ATI determined that a problem with the salt bridge assembly was causing the downward drift, which affected not only the accuracy of the pH measurement, but also of the chlorine measurement. ATI subsequently corrected this problem.

The other four water quality parameters were not affected by the pH adjustment. The ORP, temperature, conductivity, and turbidity sensors were allowed to operate without intervention throughout the extended deployment. The measurements from these four sensors are shown in Figures 6-8 through 6-11. In Figure 6-8, the ORP results are shown along with a laboratory reference method result. The reference method is not an accurate representation of water in a flowing pipe, but it can be used to evaluate a trend in the decrease and increase in the ORP, as it was in the previous section for the contaminant injections. With the exception of Unit 1 for the first one-third of the extended deployment, the ORP results were steady with few abrupt increases or decreases. The large consistent positive bias in the Unit 1 results early in the extended deployment was caused by a loose wire extending from the ORP sensor to the data collection port, which was corrected by ATI (ORP Event #1 in Figure 6-8).

The temperature, conductivity, and turbidity results for both Units 1 and 2 mostly tracked the reference method results throughout the extended deployment. The temperature results from both Units 1 and 2 had regular variability because the test was conducted in a facility where the water temperature was heavily affected by the outdoor temperature; therefore, the water temperature changed as a function of the high and low for the day. No aspects of the conductivity or turbidity results were notable, except for a turbidity spike that lasted for approximately a day (turbidity Event #1 in Figure 6-11), which occurred about half-way through the stage and was measured by both the Q45WQ units and the reference method. It was not evident what caused this spike. In addition, in the early part of Stage 3, the continuous turbidity results were generally lower than the reference method result; however, this improved during the second half of the stage. Note that the missing Unit 2 conductivity and temperature data from the latter part of this stage (see Figures 6-9 and 6-10) were the result of a problem with the data logger used with the Q45WQ. The data logger was replaced just prior to the end of this stage of the test.

#### 6.4 Accuracy and Response to Injected Contaminants After Extended Deployment

After the 52-day deployment of the Q45WQ units with minimal intervention, their performance was evaluated during a 4-hour period of ambient pH and temperature during which reference samples were collected hourly. The results of this evaluation are given in Table 6-5. With the exception of free chlorine and turbidity, these results seemed comparable to those collected during Stage 1. During Stage 1, the free chlorine percent differences ranged from -41.5% to +54.3%. During this final stage, the percent differences were less than 2%. This improvement is because the pH sensors were adjusted to match the reference result just prior to Stage 3. For turbidity, the Stage 1 results ranged from -47.2 to -16.9; while, during this final stage, the percent differences were -5.9% and 11.8%. The reason for this improvement in turbidity measurements is not apparent.

**Table 6-5. Post-Extended Deployment Results**

Parameter	Reference	Unit 1		Unit 2	
	Average (SD) <sup>(a)</sup>	Average (SD) <sup>(a)</sup>	%D	Average (SD) <sup>(a)</sup>	%D
Free chlorine	0.92 (0.02)	0.93 (0.03)	1.1	0.91 (0.02)	-1.1
Turbidity	0.17 (0.02)	0.16 (0.03)	-5.9	0.19 (0.03)	11.8
Temperature	22.66 (0.16)	22.65 (0.17)	0.0	22.45 (0.10)	-0.9
Conductivity	356 (1)	306 (0)	-14.0	328 (5)	-7.9
pH	8.59 (0.01)	8.60 (0.00)	0.1	8.40 (0.00)	-2.2

<sup>(a)</sup> Free chlorine, mg/L; turbidity, ntu; temperature, °C; conductivity, µS/cm; pH, pH units.

A second evaluation of the response to injected contaminants after the extended deployment used four contaminants. Two were a repeat of the aldicarb injections performed during Stage 2 and two were injections of *E. coli*, which was not available for injection during the earlier stage of the test. Table 6-6 shows the directional change of each reference and Q45WQ measurement in response to the contaminant injections. Figures 6-12 through 6-16 show the effect of the injections on free chlorine, ORP, turbidity, pH, and conductivity. In general, free chlorine, ORP, and turbidity were the only parameters visibly affected (for both the reference and continuous measurements) by all four injections. The response and recovery of the continuous chlorine sensor was consistent for all

four injections and, as during Stage 2, the ORP sensor tracked the chlorine response for each injection. Turbidity seemed to be affected by all four injections as well, but the results were not as consistent. For example, the first aldicarb injection produced an increase in turbidity of only 0.12 ntu, while the first and second *E. coli* injections and the second aldicarb injection produced increases according to the reference method of 0.82, 0.43, and 1.03 ntu, respectively. Because of the inherent turbidity of an *E. coli* culture, it was expected that turbidity would be consistently responsive to that contaminant. Also, because aldicarb was completely dissolved, it was not expected to increase the turbidity of the water upon injection. However, the conditions surrounding the injection of both contaminants, such as the co-injection of air bubbles, may have affected the turbidity as much as or more than the contaminant itself. Regardless of what caused the variable turbidity, the continuous monitor tracked the relative magnitude of the change in turbidity rather well.

**Table 6-6. Effect of Contaminant Injections After Extended Deployment**

Parameter	<i>E. coli</i>		Aldicarb	
	Reference	Q45WQ	Reference	Q45WQ
Free chlorine	-	-	-	-
Turbidity	+	+	+	+
Temperature	NC	NC	NC	NC
Conductivity	+(a)	NC	NC	NC
pH	-	-	-	(a)
ORP	-	-	-	-

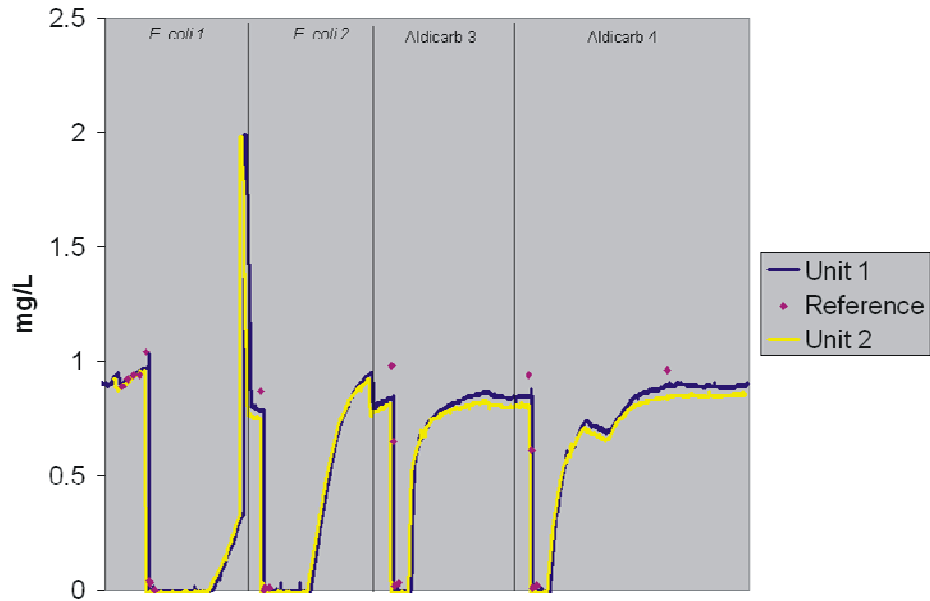
(a) Results from duplicate injections did not agree.

+/- = Parameter measurement increased/decreased upon injection.

NC = No change in response to the contaminant injection.

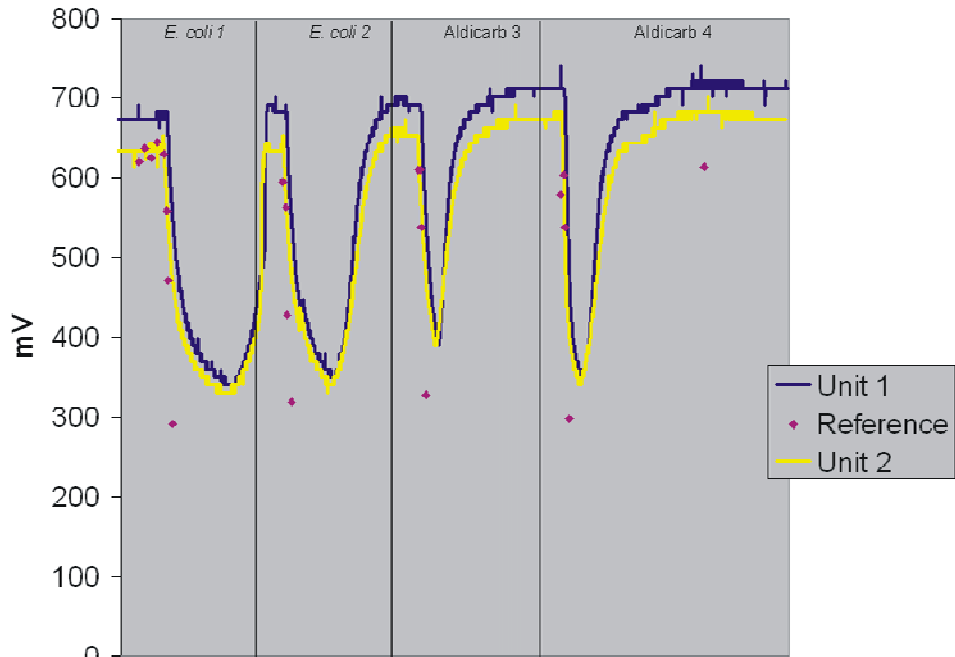
The pH was clearly affected by both *E. coli* injections (as shown by both the reference and continuous measurements) and, to a lesser extent, by the aldicarb injections. The reference method displayed a slight decrease for both aldicarb injections, while the continuous measurement only detected a change during the final aldicarb injection. In addition, during the *E. coli* injections, a very slight increase in conductivity was measured by the reference method; however, no such change was detected by the continuous measurement. Aldicarb had not altered the pH during the Stage 2 injections, so this result was unexpected. The continuous measurements were similar to these results for the *E. coli* injections and the second aldicarb injection.

The conductivity results increased according to the reference method for the first injection of *E. coli*. However, for the continuous measurements for all of the injections and the reference measurements for the rest of the injections, there was very little effect. Note that an unexplained occurrence of high variability in Unit 2 took place during the final aldicarb injection.



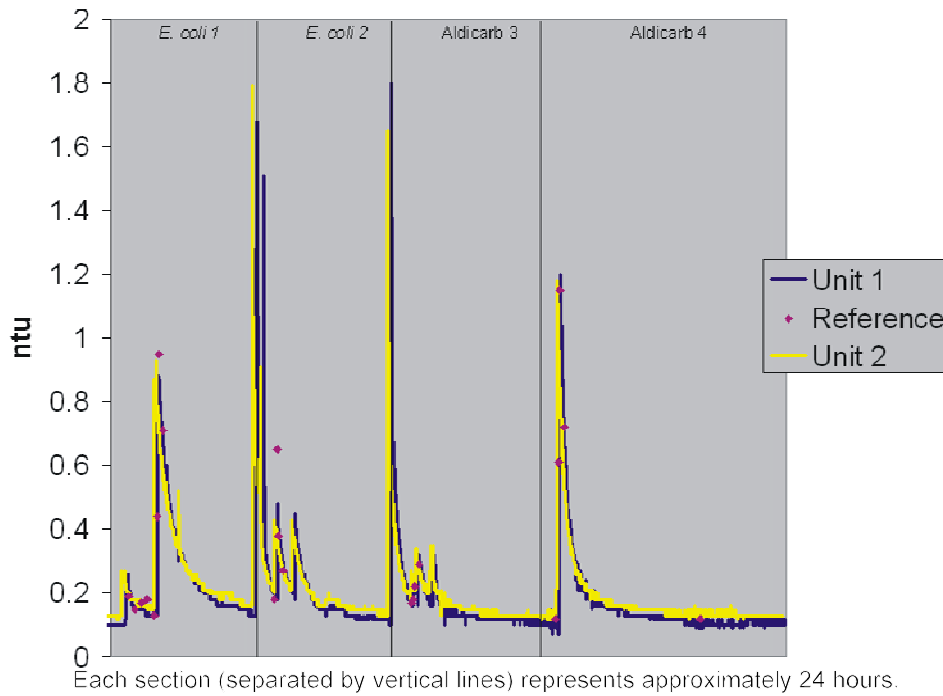
Each section (separated by vertical lines) represents approximately 24 hours.

**Figure 6-12. Stage 3 Contaminant Injection Results for Free Chlorine**

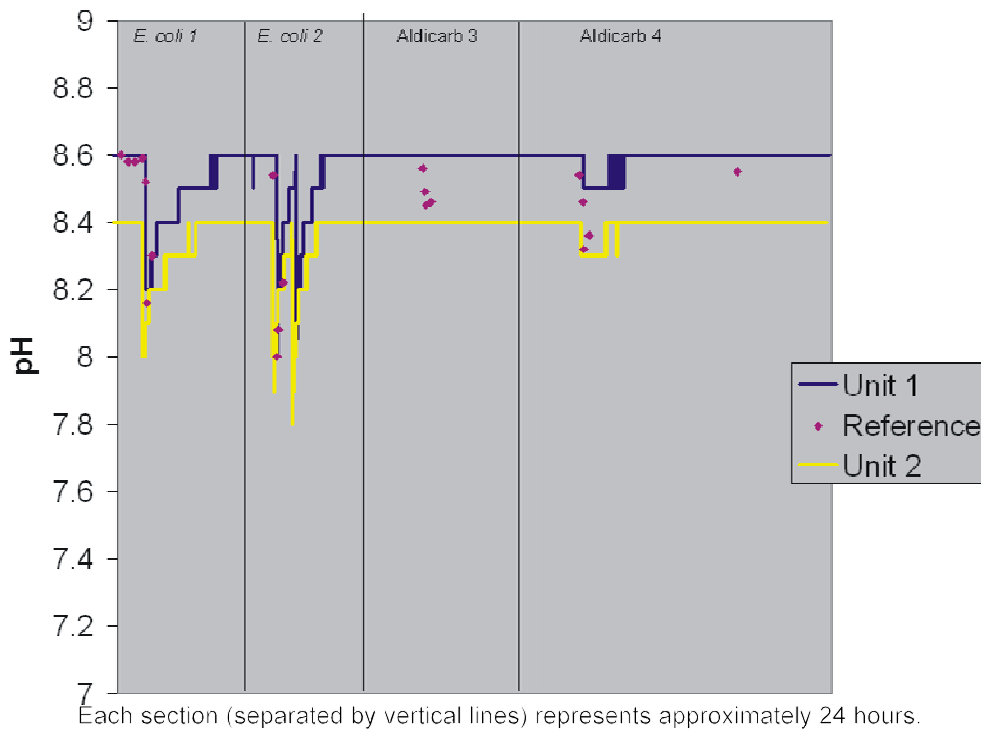


Each section (separated by vertical lines) represents approximately 24 hours.

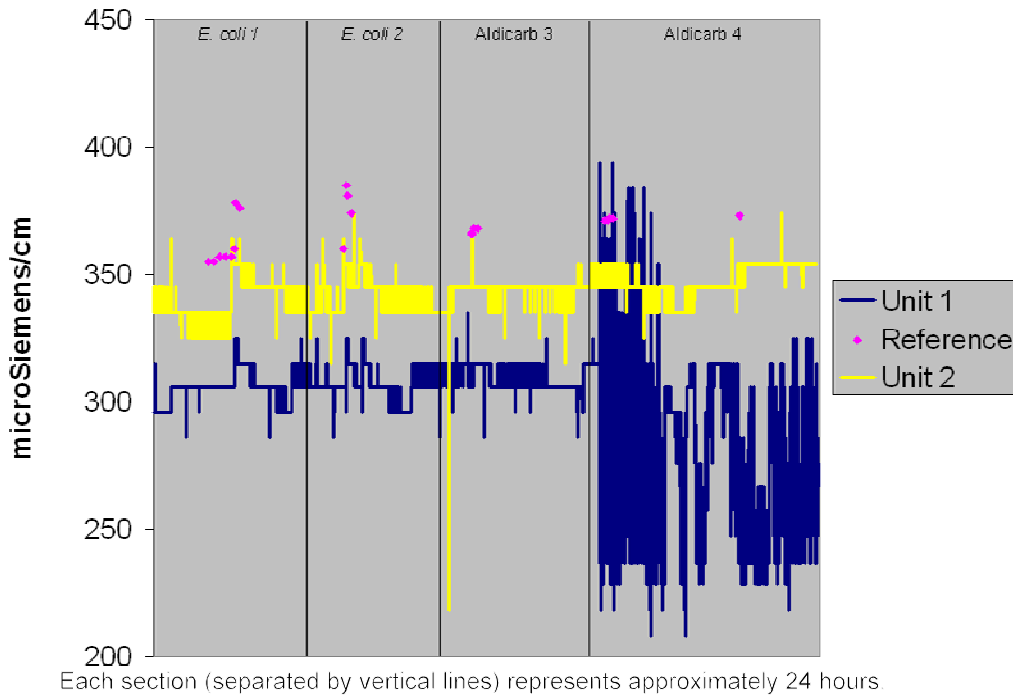
**Figure 6-13. Stage 3 Contaminant Injection Results for ORP**



**Figure 6-14. Stage 3 Contaminant Injection Results for Turbidity**



**Figure 6-15. Stage 3 Contaminant Injection Results for pH**



**Figure 6-16. Stage 3 Contaminant Injection Results for Conductivity**

### 6.5 Inter-unit Reproducibility

Two Q45WQ units were compared throughout the verification test to determine whether they generated results that were similar to one another. This was done using the Q45WQ data collected whenever a reference sample was collected throughout the verification test. Two evaluations were performed to make this comparison. First, the results from Unit 2 were graphed on the y-axis, those from Unit 1 were graphed on the x-axis, and a line was fitted to the data. Second, a t-test assuming equal variances was performed on those same data. For the linear regression analysis, if both units reported the identical result, the slope of such a regression would be unity (1), the intercept zero (0), and the coefficient of determination ( $r^2$ ) 1.0. The slope can indicate whether the results are biased in one direction or the other, while the coefficient of determination provides a measure of the variability of the results. The t-test shows whether the sensors generated statistically similar data. Small p-values ( $<0.05$  at a 5% confidence level) would suggest that the results from the two units are significantly different from one another. Table 6-7 gives the slope, intercept, and coefficient of determination for the regression inter-unit reproducibility evaluation and the p-value for the t-test performed for each sensor.

As can be seen from Table 6-7, the temperature and turbidity sensors had coefficients of determination greater than 0.99 and slopes of 0.97, indicating that their results were very similar and repeatable. Confirming that evaluation, the t-test p-values for temperature and turbidity were 0.41 and 0.76, respectively, indicating that each sensor generated statistically similar results. The ORP and conductivity sensors had coefficients of determination greater than 0.95, indicating that they were highly correlated with one another, but their slopes were approximately 11% and 9%

**Table 6-7. Inter-unit Reproducibility Evaluation**

Parameter	Slope	Intercept	r <sup>2</sup>	t-test p-value
Free chlorine	0.88	0.10	0.77	0.59
Turbidity	0.97	0.028	0.99	0.76
Temperature	0.97	0.31	1.00	0.41
Conductivity	1.09	-1.1	0.97	0.00020
pH	0.71	2.4	0.85	0.48
ORP	0.89	40	0.96	0.0093

Shading = significant difference between units as determined by a t-test.

from unity. For ORP, the slope was less than unity, indicating that the results for Unit 2 were consistently lower than those for Unit 1; and for conductivity, the slope was greater than unity, indicating that Unit 2 results were consistently higher. For both sensors, this evaluation was confirmed by the t-test since the p-values for these two sensors were much less than 0.05 (shaded), indicating a significant difference in their results. This difference is driven by the small amount of variability in the conductivity and ORP measurements; therefore, small differences in the means were statistically significant. In addition to the inter-unit statistical evaluation, the results for all four sensors were confirmed through a visual evaluation of the figures throughout Chapter 6. For temperature and turbidity, the results from the two units are graphed nearly on top of one another, while for ORP and conductivity, a small but consistent difference was evident. With respect to Unit 2, Unit 1 was biased high for ORP and low for conductivity.

The free chlorine and pH sensors had lower coefficients of determination and slopes that deviated from unity by at least 10%. This lower correlation was observed in the figures for the extended deployment when Unit 2 drifted to lower pHs (and therefore lower chlorine results), while Unit 1 remained steady or drifted upward slightly. In addition, adjusting the chlorine sensor twice during the verification test increased the variability in the pH and free chlorine results. Because of this, the t-test indicated that the results from each of the free chlorine and pH sensors were statistically the same, despite the observed differences.

## 6.6 Ease of Use and Data Acquisition

Throughout the duration of the verification test, the verification staff was not required to perform any routine maintenance. However, on two occasions, ATI representatives adjusted the pH sensor reading to match the reference sample measurement. The measurement of free chlorine is a function of the pH measured by the pH sensor; therefore, the accuracy of the free chlorine measurement was directly affected by this adjustment. Based on the performance of the free chlorine and pH sensors, the pH sensor may have to be adjusted periodically to maintain the accuracy of both measurements. This would require a means of measuring the pH of the water, as well as a site visit, to make the adjustment. No other maintenance was necessary during the test.

ATI provided HOBOb<sup>®</sup> data recorders for use during the verification test. Each sensor was plugged into a HOBOb<sup>®</sup> data recorder, and data were collected based upon preset recording frequency. With a 30-second data collection frequency, the storage capacity of the HOBOb<sup>®</sup> recorder was approximately 3 days. Generally, data were downloaded every working morning by attaching a

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serial connector to an output on the HOBO<sup>®</sup> recorder. After affirming that the data (named for the test period) had properly exported to a spreadsheet program, the data were deleted from the data logger and the loggers were reinitialized. During the test period, two of the HOBO<sup>®</sup> recorders experienced problems upon relaunch that necessitated their replacement. In those instances, several days of data were not recorded while waiting for a replacement data logger.



## Chapter 7 Performance Summary

Evaluation Parameter		Free Chlorine	Turbidity	Temperature	Conductivity	pH	ORP	
<b>Stage 1—Accuracy</b>	Units 1 and 2, range of %D (median)	-41.5 to 54.3 (-15.7)	-47.2 to -16.9 (-24.9)	-5.5 to 1.3 (-1.4)	-19.7 to -2.6 (-12.7)	-11.8 to -0.9 (-5.0)	(a)	
<b>Stage 2—Response to Injected Contaminants</b>	Nicotine	Reference	-	(b)	NC	NC	NC	-
		Q45WQ	-	+	NC	NC	NC	-
	Arsenic trioxide	Reference	-	(b)	NC	+	+	-
		Q45WQ	-	+	NC	+	+	-
Aldicarb	Reference	-	(b)	NC	NC	NC	NC	-
	Q45WQ	-	+	NC	NC	NC	NC	-
<b>Stage 3—Accuracy During Extended Deployment</b>	Units 1 and 2, range of %D (median)	-33.7 to 29.7 (-7.3)	-88.0 to 18.2 (-42.3)	-4.9 to 1.5 (-1.4)	-19.4 to -5.3 (-13.6)	-8.3 to 1.5 (-3.5)	(a)	
<b>Stage 3—Accuracy After Extended Deployment</b>	Unit 1, %D	1.1	-5.9	0.0	-14.0	0.1	(a)	
	Unit 2, %D	-1.1	11.8	-0.9	-7.9	-2.2	(a)	
<b>Stage 3—Response to Injected Contaminants</b>	<i>E. coli</i>	Reference	-	+	NC	+(c)	-	-
		Q45WQ	-	+	NC	NC	-	-
	Aldicarb	Reference	-	+	NC	NC	-	-
		Q45WQ	-	+	NC	NC	(c)	-
<b>Injection Summary</b>	For a reason that is not clear, aldicarb altered the pH, as measured by the reference method, during the Stage 3 injections, but not during the Stage 2 injections.							
<b>Inter-unit Reproducibility (Unit 2 vs. Unit 1)</b>	Slope (intercept)	0.88 (0.10)	0.97 (0.028)	0.97 (0.31)	1.09 (-1.1)	0.71 (2.4)	0.89 (40)	
	r <sup>2</sup>	0.77	0.99	1.00	0.97	0.85	0.96	
	p-value	0.59	0.76	0.41	0.00020	0.48	0.0093	
	The ORP and conductivity sensors on each unit generated results that were significantly different from one another. Each unit's results were highly correlated with one another; but, because of the small degree of variability in each sensor's results, they were determined to be significantly different.							
<b>Ease of Use and Data Acquisition</b>	Based on the performance of the free chlorine and pH sensors, the pH sensor may have to be adjusted periodically to maintain the accuracy of both measurements. No other maintenance was necessary during the test.							

(a) ORP was not included in the accuracy evaluation because of the lack of an appropriate reference method.

(b) Relatively large uncertainty in the reference measurements made it difficult to determine a significant change.

(c) Results from duplicate injections did not agree.

+/- = Parameter measurement increased/decreased upon injection.

NC = No obvious change was noted through a visual inspection of the data.

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## Chapter 8 References

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