November 2005

Environmental Technology Verification Report

HACH COMPANY WATER DISTRIBUTION MONITORING PANEL AND THE EVENT MONITOR™ TRIGGER SYSTEM

Prepared by
Battelle

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The Business of Innovation

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

HACH COMPANY WATER DISTRIBUTION MONITORING PANEL AND THE EVENT MONITOR™ TRIGGER SYSTEM

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

Battelle
The Business of Innovation

ETV Joint Verification Statement

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

APPLICATION: **MONITORING DRINKING WATER QUALITY**

TECHNOLOGY NAME: **Water Distribution Monitoring Panel and Event Monitor™ Trigger System**

COMPANY: **Hach Company**

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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.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), 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 Hach Company Water Distribution Monitoring Panel (WDMP), as well as the Hach Event Monitor™ Trigger System (EMTS), in continuously measuring total chlorine, turbidity, temperature, conductivity, pH, and total organic carbon (TOC) in drinking water. This verification statement provides a summary of the test results.

VERIFICATION TEST DESCRIPTION

The performance of the WDMP and EMTS units was assessed in terms of their accuracy, response to injected contaminants, inter-unit reproducibility, ease of use, and data acquisition. The verification test was conducted between August 9 and November 12, 2004, and consisted of four stages, each designed to evaluate a particular performance characteristic of the WDMP and EMTS units. The first 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. Stage 4 used a single-pass pipe at the same facility.

In the first stage of this verification test, the accuracy of the measurements made by the WDMP units was evaluated during eight, 4-hour periods of stable water quality conditions by comparing each WDMP 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 WDMP units to changes in water quality parameters caused 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. Grab samples were collected prior to the contaminant injections and at 3, 15, and 60 minutes after injection to confirm the response of each water quality parameter, whether it was an increase, decrease, or no change. In the first phase of Stage 3 of the verification test, the performance of the WDMP 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 WDMP to determine whether this length of operation would negatively affect results. 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 WDMP could be evaluated. Second, to evaluate the response of the WDMP 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. The fourth and final stage of the verification test involved testing whether the EMTS detected the injection of 13 contaminants (aldicarb, arsenic trioxide, colchicine, dichlorvos, dicamba, *E. coli* bacteria, glyphosate, lead nitrate, mercuric chloride, methanol, nicotine, potassium ferricyanide, and sodium fluoroacetate), as well as whether it correctly identified the contaminants. Because the Stage 4 results were qualitative, grab samples were not collected. Throughout the test, 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.

TECHNOLOGY DESCRIPTION

This verification report provides results for the verification testing of the Hach WDMP, as well as the EMTS, which functions in concert with the WDMP. For the purposes of this report, the astroTOC online ultraviolet (UV) TOC analyzer was considered a part of the WDMP, even though the TOC analyzer is actually a stand-alone continuous monitor. Following is a description of the combined system, based on information provided by the vendor. The information provided below was not verified in this test.

The WDMP contains online monitors for free or total chlorine, pH, turbidity, electrolytic conductivity, temperature, sample pressure, and TOC. Chlorine residual is measured by a Hach CL17 chlorine analyzer. The CL17 collects a water sample every 2.5 minutes and uses the EPA-approved colorimetric diethyl-p-phenylene diamine method. The CL17 uses minimal reagents and a mixing system that operates with no moving parts, including a self-cleaning stir bar in the sample chamber. A differential pH electrode, which uses a pH buffer as a reference point, measures pH. Turbidity is measured using a Hach 1720D process turbidimeter. The sample flows continuously through a patented bubble removal system that vents entrained air from the sample, eliminating interference in low-level turbidity measurement. Incandescent light is directed from the sensor head assembly down into the turbidimeter body and is scattered by suspended particles in the sample. A sensor detects light scattered at 90 degrees from the incident beam, which is a measure of the turbidity in the water. Electrolytic conductivity is continuously measured by a two-electrode cell. Temperature is measured by the temperature-sensing element in the conductivity cell.

The astroTOC UV analyzer combines a chemical and UV oxidation technique in a low-temperature reactor to measure the TOC. A 4-20 mA analog signal carries the TOC information to the EMTS. The WDMP is fed by a single, 1/2-inch sample line. Free-flowing waste drains through a single outlet. A sample line runs from the WDMP to the astroTOC, which has a drain line from a single outlet.

The EMTS integrates the multiple sensor outputs from the WDMP and astroTOC. Once each minute, software applies an algorithm (patent pending) to the sensor measurements, calculating the site’s water quality baseline. The EMTS alarms when the trigger signal exceeds a trigger threshold, indicating an “event.” The EMTS may be equipped with an agent library containing profiles of various contaminants. The EMTS also contains a plant event library that has no entries when the system is first installed. If an event occurs and its signature cannot be matched to any signature in the agent library, the plant event library is searched for a match. If a match is found, the event is reported. If no match is found, the signature for the event is stored in case the event recurs. In addition to a trigger signal alarm, the EMTS can also alarm on high/low parameter excursions. It logs all input data, trigger signal values, and diagnostic data in a database that can be extracted to a memory stick. Operators can view and recall logged data for each parameter and the trigger signal using a touch-screen. The EMTS can also act as “slave” on an RS485 Modbus network to provide data whenever polled by a Modbus “master.”

The combined system of the WDMP and the EMTS, designed for wall or rack mounting, is approximately 3.3 feet tall by 6.6 feet wide. The WDMP costs $12,800, the EMTS costs $8,450, and the online TOC analyzer costs $14,076 in the recommended configuration for a total cost of approximately $35,000 for the units tested. The monthly cost for consumables is approximately $260.

VERIFICATION OF PERFORMANCE

Evaluation Parameter			Total Chlorine	Turbidity	Temperature	Conductivity	pH	TOC
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		-47.4 to 4.5 (-3.9)	-53.9 to -1.3 (-34.1)	-3.0 to 44.3 (-0.2)	-15.5 to 8.1 (2.2)	-6.6 to 3.1 (0.9)	-64.7 to 147.5 (-14.8)
Stage 2—Response to Injected Contaminants	Nicotine	Reference	–	[a]	NC	NC	NC	+
		WDMP	–	+	NC	NC	NC	+
	Arsenic trioxide	Reference	–	[a]	NC	+	+	NC
		WDMP	–	+	NC	+	+	NC
	Aldicarb	Reference	–	[a]	NC	NC	NC	+
		WDMP	–	+	NC	NC	NC	+
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-15.9 to 6.9 (-3.2)	-81.1 to 245.5 (-21.3)	-7.4 to 8.5 (-0.1)	-1.8 to 9.6 (4.8)	-2.7 to 0.5 (-0.9)	-47.3 to 103.0 (-6.9)
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		-4.9	-5.9	-0.2	6.7	-2.2	-20.5
	Unit 2, %D		-4.9	-11.8	4.6	0.3	0.2	3.4
Stage 3—Response to Injected Contaminants	*E. coli*	Reference	–	+[b]	NC	+	–	+
		WDMP	–	+	NC	+	–	+
	Aldicarb	Reference	–	+[b]	NC	NC	–	+
		WDMP	–	+	NC	NC	–	+
Injection Summary	Total chlorine and TOC were dramatically affected by injections of nicotine, *E. coli,* and aldicarb; and turbidity, pH, and conductivity were affected by some or all of the injections, but not as consistently as total chlorine and TOC. Aldicarb altered the pH during Stage 3, but not Stage 2.							
Inter-unit Reproducibility (Unit 2 vs. Unit 1)	Slope (intercept)		0.98 (0.03)	0.97 (0.005)[c]	0.72 (7.68)	0.92 (4.19)	1.06 (-0.40)	0.97 (0.31)
	r^2		0.994	0.881[c]	0.758	0.961	0.919	0.991
	p-value		0.779	0.884[c]	5.5×10^{-6}	0.006	0.517	0.374
	With the exception of temperature and conductivity, both units generated similar results.							
Stage 4—Contaminant Identification	Each time a contaminant was injected, the EMTS detected a deviation in baseline conditions, causing a "trigger event." Eleven of 13 contaminants were correctly identified at some point during the injection time. Ferricyanide and lead nitrate were identified correctly 100% of the time. The rest of the injected contaminants were identified as a contaminant other than themselves at some point throughout the duration of the injection. Only nicotine and arsenic trioxide were never correctly identified.							
Ease of Use and Data Acquisition	Neither the WDMPs nor the EMTSs required daily operator attention. Hach Company staff adjusted the flows on the turbidity and total chlorine meters as needed to keep them at the required levels and rebooted the EMTS when it was not displaying data properly. The chlorine sensors and turbidimeters needed periodic cleaning, and the TOC analyzer was calibrated three times.							

[a] Relatively large uncertainty in the reference measurements made it difficult to detect a significant change.

[b] Magnitude of change different between duplicate injections.

[c] Outlier excluded.

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

NC = No change in response to the contaminant injection.

Original signed by Gregory A. Mack 11/23/05	Original signed by Andrew P. Avel 1/17/06
Gregory A. Mack Date	Andrew P. Avel Date
Assistant Division Manager	Acting Director
Energy, Transportation, and Environment Division	National Homeland Security Research Center
Battelle	U.S. Environmental Protection Agency

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 permitters, 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 Haught and John Hall of the U.S. Environmental Protection Agency's (EPA's) Testing and Evaluation (T&E) Facility (operated by Shaw Environmental, Inc.) in Cincinnati, Ohio, for hosting the verification test. 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, Ron Hunsinger of East Bay Municipal Utility District, and Matthew Steele of the City of Columbus Water Quality Assurance Laboratory, who also reviewed the test/QA plan and/or the reports.

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List of Abbreviations

AMS	Advanced Monitoring Systems
°C	degree centigrade
DI	deionized
EMTS	Event Monitor™ Trigger System
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
L	liter
µSiemens/cm	microSiemens per centimeter
mg/L	milligram per liter
mV	millivolt
NIST	National Institute of Standards and Technology
ntu	nephelometric turbidity unit
%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
TOC	total organic carbon
TSA	technical systems audit
UV	ultraviolet
WDMP	Water Distribution Monitoring Panel

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

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center evaluated the performance of the Hach Company Water Distribution Monitoring Panel (WDMP) in continuously measuring total chlorine, turbidity, temperature, conductivity, pH, and total organic carbon (TOC) in drinking water, as well as the Event Monitor™ Trigger System's (EMTS) ability to identify contaminants as they are injected into a pipe of flowing drinking water. Continuous multi-parameter water monitors for distribution systems were identified as a priority technology verification category through the AMS Center stakeholder process.

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 WDMP as well as the EMTS, which functions in concert with the WDMP. For the purposes of this report, the astroTOC online ultraviolet (UV) TOC analyzer was considered a part of the WDMP, even though the TOC analyzer is actually a stand-alone continuous monitor. Following is a description of the combined system, based on information provided by the vendor. The information provided below was not verified in this test.

Figure 2-1. Hach Company WDMP

The WDMP (Figure 2-1) contains online monitors for free or total chlorine, pH, turbidity, conductivity, temperature, sample pressure, and TOC. Chlorine residual is measured by a Hach CL17 chlorine analyzer. The CL17 collects a water sample every 2.5 minutes and uses the EPA-approved colorimetric diethyl-p-phenylene diamine method. The CL17 uses minimal reagents and a mixing system that operates with no moving parts, including a self-cleaning stir bar in the sample chamber. A differential pH electrode, which uses a pH buffer as a reference point, measures pH. Turbidity is measured using a Hach 1720D process turbidimeter. The sample flows continuously through a patented bubble removal system that vents entrained air from the sample, eliminating interference in low-level turbidity measurement. Incandescent light is directed from the sensor head assembly down into the turbidimeter body and is scattered by suspended particles in the sample. A sensor detects light scattered at 90 degrees from the incident beam, which is a measure of the turbidity in the water. Conductivity is continuously measured by a two-electrode cell. Temperature is measured by the temperature-sensing element in the conductivity cell.

The astroTOC UV analyzer combines a chemical and UV oxidation technique in a low-temperature reactor to measure the TOC. A 4-20 mA analog signal carries the TOC information to the EMTS. The WDMP is fed by a single, 1/2-inch sample line. Free-flowing waste drains through a single outlet. A sample line runs from the WDMP to the astroTOC, which has a drain line from a single outlet.

The EMTS (Figure 2-2) integrates the multiple sensor outputs from the WDMP and astroTOC. Once each minute, software applies an algorithm (patent pending) to the sensor measurements, calculating the site's water quality baseline. The EMTS alarms when the trigger signal exceeds a trigger threshold, indicating an "event." The EMTS may be equipped with an agent library containing profiles of various contaminants. The EMTS also contains a plant event library that has no entries when the system is first installed. If an event occurs and its signature cannot be matched to any signature in the agent library, the plant event library is searched for a match. If a match is found, the event is reported. If no match is found, the signature for the event is stored for future reference in case the event recurs. Thus, the plant event library records the signatures for events that occur at that location, over time. Operators can label plant event profiles by name and severity level, allowing recognition of events that have previously been found, thus decreasing the frequency of unknown alarms over time. The ability of the EMTS to learn over time in no way compromises its ability to trigger on events as soon as deployment occurs. Also, once a baseline measurement has been established (taking a few minutes), any deviation from baseline (excursion) matching the water quality parameter pattern of an agent found in the supplied agent library will be classified as such. Unlike traditional monitoring/classification systems, the EMTS is able to trigger on excursions that are not as yet found in either the agent library or plant library and alert the operator to an unknown excursion that represents a significant change in water quality. Operator input is required to investigate and name the unknown event.

Figure 2-2. Hach Company EMTS

In addition to a trigger signal alarm, the EMTS can also alarm on predetermined high/low parameter settings. It logs all input data, trigger signal values, and diagnostic data in a database that can be extracted to a memory stick. Operators can view and recall logged data for each parameter and the trigger signal using a touch-screen. The EMTS can also act as "slave"on an RS485 Modbus network to provide data whenever polled by a Modbus "master."

The combined system of the WDMP and the EMTS, designed for wall or rack mounting, is approximately 3.3 feet tall by 6.6 feet wide. The WDMP costs $12,800, the EMTS costs $8,450, and the online TOC analyzer costs $14,076 in the recommended configuration for a total cost of approximately $35,000 for the units tested. The monthly cost for consumables is approximately $260.

Chapter 3
Test Design

3.1 Introduction

The multi-parameter water monitors tested consisted of instrument packages that connect to 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*(1) and assessed the performance of the WDMP units in continuously monitoring pH, conductivity, total chlorine, TOC, temperature, and turbidity in terms of the following:

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

In addition, the ability of the EMTS units to identify when a contaminant injection had occurred and what contaminant had been injected was verified.

Accuracy was quantitatively evaluated by comparing the results generated by two WDMP 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 units operating simultaneously. Ease of use was documented by technicians who operated and maintained the units, as well as the Battelle Verification Test Coordinator. Contaminant identification was verified by reporting whether the EMTS recognized an injection and correctly identified the presence of the contaminant during the injection.

3.2 Test Stages

This verification test was conducted between August 9 and November 12, 2004, and consisted of four stages, each designed to evaluate a particular performance characteristic of the WDMP and EMTS units. The first 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 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 the two WDMP units by a section of 2-inch polyvinyl chloride (PVC) pipe in series with a shut-off valve with a ribbed nozzle that was connected to the WDMP and EMTS units with an 18-foot, 1/2-inch outside diameter hose. Reference samples of approximately 1 liter (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 on the PVC pipe.

The fourth stage of the verification test was conducted using a single-pass pipe at the same facility. The single-pass pipe consisted of fiberglass-lined ductile iron pipe that was 3 inches in diameter. The flow rate of the single-pass pipe was approximately 20 L/minute. The distance between the injection portal and the WDMP and EMTS was approximately 82 feet. The WDMP and EMTS were plumbed to a sampling valve in a manner similar to that described previously. This stage of testing was conducted to accommodate the Hach EMTS. No other technologies participated.

3.2.1 Stage 1, Accuracy

During the first stage of this verification test, the accuracy of the measurements made by the WDMP 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 nine 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 ambient 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, finally, two sets at approximately these pHs, but at a temperature of approximately 27°C. One set (Set 2) was repeated as Set 3. 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 equilibrated 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 WDMP units to changes in water quality parameters caused by injecting contaminants into the pipe loop. 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 calculated to be approximately 6 mg/L. Because the qualitative change (increase or decrease) 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. The concentration of injected contaminants was not confirmed after injection; therefore, the concentration in the pipe loop is based on the gravimetric measurements during solution prep and subsequent dilution in the pipe loop. For all three sets of injections, a grab sample was collected prior to the injection and again at 3, 15, and 60 minutes after the injection. The difference between reference method results before and after injection indicated the approximate change in water quality caused by the injected contaminant. For each injected contaminant, the results from the WDMP units were evaluated based on how well their directional change matched that of the reference method result. After each injection, the pipe loop was allowed to re-equilibrate for at least 12 hours so that each WDMP 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 WDMP units was evaluated during 52 days of continuous operation. To track the performance of the WDMP 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 WDMP units and those from the reference methods throughout the duration of the deployment was evaluated to determine how well the WDMP unit results compared to the reference method was evaluated.

The second 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 WDMP unit performance after the 52-day extended deployment to determine whether this length of operation would negatively affect the results from the WDMP. First, while the WDMP 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 WDMP units to be evaluated. Second, to evaluate the response of the WDMP units to contaminant injection after the extended deployment, two injections of aldicarb, which were also included in the Stage 2 testing, were 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.

3.2.4 Stage 4, Contaminant Identification

The purpose of the fourth and final stage of the verification test was to determine whether the EMTS detected the injection of selected contaminants, as well as whether it correctly identified each contaminant. Two separate injections of 13 contaminants (see Table 3-1) were made into the single-pass pipe described previously. The contaminants were selected from 22 compounds whose agent signatures were included in the Hach library at the time of testing. To protect the integrity of this portion of the test, the Hach Company was not informed of the identity of the contaminant injected until the contaminant identification data from each injection was in Battelle's possession. Also, duplicate injections were never performed subsequent to one another. All the contaminants were injected randomly once over approximately two days and, thereafter, each contaminant was injected a second time, again in random order. To test the capability of the EMTS appropriately, Hach suggested that the concentration of each contaminant be at least 10 mg/L once injected into the pipe and that the injection duration be 10 to 20 minutes. To attain an in-pipe concentration well above that, a 10-L injection solution of each contaminant was prepared at approximately 600 mg/L. This solution was injected for 20 minutes at a flow rate of 0.5 L/minute, while the pipe flow rate was approximately 20 L/minute. Because of the higher flow rate in the pipe, a dilution factor had to be applied to calculate the resulting concentration within the pipe, which was approximately 15 mg/L. Of course, concentrations at the leading and trailing edges of the sample slug were expected to be less than 15 mg/L because of dilution with unspiked water in front of and behind the injected slug of contaminant. Note that the concentrations of each contaminant were not confirmed using analytical methodology. Table 3-1 lists the contaminants that were injected during this stage of the verification test.

Table 3-1. Stage 4 Injected Contaminants

Injected Contaminants	Approximate Concentration
Aldicarb, arsenic trioxide, colchicine, dichlorvos, dicamba, *E. coli* bacteria, glyphosate, lead nitrate, mercuric chloride, methanol, nicotine, potassium ferricyanide, and sodium fluoroacetate.	15 mg/L

3.3 Laboratory Reference and Quality Control Samples

The WDMP 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. With the exception of TOC, all the analyses were performed within minutes of sample collection. TOC analyses were performed within the method's required 14-day holding time period. The standard laboratory methods used for the reference analyses are shown in Table 3-2. Also included in the table are method detection limits and 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).

3.3.2 Reference Method Quality Control Samples

As shown in Table 3-3, 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 analysis of these blank samples were most important for total chlorine, turbidity, and TOC 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 percent differences provided in Table 3-2. Because the objective of Stage 4 was to verify the EMTS's ability to trigger when an injection was made and to identify injected contaminants, no reference measurements were performed during this stage.

Table 3-2. Reference Methods

Parameter	Method	Reference Instruments	Method Detection Limit	Acceptable Differences for QC Measurements
pH	EPA 150.1(2)	Corning 320 pH meter	NA	±0.3 pH units
Conductivity	SM 2510(3)	YSI 556 multi-parameter water monitor	2 microSiemens per centimeter (µS/cm)	±25 %D
Total chlorine	SM 4500-Cl-G(4)	Hach 2400 portable spectrophotometer	0.01 milligram per liter (mg/L) as Cl_2	±25 %D
TOC	EPA 415.1(5)	Phoenix 8000 TOC analyzer	0.01 mg/L	±25 %D
Temperature	EPA 170.1(6)	YSI 556 multi-parameter water monitor	NA	±1°C
Turbidity	EPA 180.1(7)	Hach 2100P turbidimeter	0.067 nephelometric turbidity unit (ntu)	±25 %D

NA = Not applicable.

Table 3-3. 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	9 (4 hours)	One at start, one every hour thereafter	5	One duplicate and one DI water blank daily	18
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
4: Contaminant identification	No reference measurements collected				

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center(8) and the test/QA plan (1) 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 for each respective water quality parameter (or, for temperature, data from the second thermometer). 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 six 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 tolerance criteria. If this outlier is removed, the upper range of percent difference 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

	PE Audit			Duplicate Analysis	
Parameter	NIST Standard Value	Reference Method Result	Difference	Average of Absolute Values of Difference	Range of Difference
pH (pH unit)	9.26	9.18	-0.08 pH unit	0.04 pH unit	0.0 to 0.13 pH unit
Conductivity (µS/cm)	1,920	1,706	-11.1%	0.25%	-1.9 to 0.7%
Total chlorine (mg/L)	4.19	3.62	-13.6%	2.62%	-7.3 to 2.1%
Temperature (°C)	23.80(a)	23.80	0.00°C	0.02°C	-0.18 to 0.29°C
TOC (mg/L)	11.8	11.7	-0.8%	1.5%	-5.6 to 11.6%
Turbidity (ntu)	20.0	22.3	11.5%	7.49%	-8.7 to 55.2%

(a) 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,(8) the test/QA plan,(1) 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 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.(8) 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

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
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 (WDMP, EMTS, and reference methods)	ETV data sheets and testing notebook	Upon each calibration	Battelle and T&E Facility	Manually incorporated in data spreadsheets as necessary
WDMP and EMTS 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

Chapter 5
Statistical Methods

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

5.1 Accuracy

Throughout this verification test, results from the WDMP units were compared to the results obtained from analysis of a grab sample by the reference methods. During Stage 1, the percent difference (%D) 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 the WDMP unit. The WDMP unit results were recorded every 30 seconds, while 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 WDMP 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 WDMP 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 WDMP 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 WDMP units highlighted its response to such changes.

5.3 Inter-unit Reproducibility

The results obtained from two identical WDMP units were compared to assess inter-unit reproducibility. Each time a reference sample was collected and analyzed (approximately 138 times throughout this verification test), the results from each WDMP 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 (r^2) 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 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.

5.4 Contaminant Identification

During Stage 4 of the test, the ability of the EMTS to detect a contaminant injection was verified by confirming that a trigger event (caused by the trigger signal's exceedence of a user-specified threshold) occurred during the period of time that each WDMP unit was exposed to the contaminant (approximately 20 minutes), as well as evaluating whether the injected contaminant was identified correctly. The EMTS searches the agent signature library once per minute during trigger events. During that search, if a match is found between the experimental data and the agent library data, an agent alarm occurs. Because the experimental injection data may match the EMTS data from several contaminants, more than one agent alarm can result from a single search of the agent library, although some may have strong and some may have weak match angles. That is, in an exposure time of approximately 20 minutes, more than 20 agent alarms can result. Similarly, if there are no matches, the event is recorded as an "unknown" event. If an agent alarm is the result of a library search, the EMTS reports the identified agent, as well as a match angle, which is a unitless measure of the quality of the match between the experimental data and the library data. Lower match angles correspond to better match quality and higher match angles correspond to poorer match quality. While the detailed approach to obtaining the match angle is proprietary, and the practice of determining the quality of a match is somewhat subjective; in general, Hach suggests that match angles greater than 7 should be considered questionable or weak matches; angles between 4 and 7 moderately good matches; and angles less than 4 good matches. Overall, Hach suggests that the best way to interpret EMTS identification data in a controlled experimental situation such as this ETV test is to evaluate

- Whether the injection or contamination event triggered an agent alarm
- How many times the correct contaminant was identified by the EMTS

- What the quality of the match was, as determined from the match angle criteria described above
- How many and how frequently other contaminants were found during the injection
- What the quality of the match was for those contaminants, again using the match angle criteria.

In Chapter 6, the contaminant identification data are presented in a format that allows the interpretation of the ETV data in this way. Each agent alarm is accounted for (whether correct or not) in a column specifying the quality of the match.

Another approach to evaluating the identification data that may be easier to interpret, but that is less rigorous because the match angles are not accounted for, is also presented in Chapter 6. Using this approach, the fraction of agent alarms attributable to the injected contaminant (correct identifications) was called the classification rate (*CR*) and was calculated using the following equation:

$$CR = \frac{N_C}{N_T} \, x \, 100\%$$

where N_C is the number of correct identifications of the injected contaminant during each injection period, and N_T is the total number of contaminant identifications (no matter which contaminant was identified) that occurred during an injection event. For example, if, upon injection of aldicarb, the EMTS identified 20 contaminants, and 19 of them were correct, the classification rate for aldicarb would be 95%. Alternatively, a correct identification for 1 out of 20 identifications would correspond to a classification rate of 5%.

To present the data in a more concise way, classification rates of greater than 70% for the injected contaminant were assigned a Level 5; classification rates between 31% and 70%, a Level 4; classification rates between 1% and 30%, a 3; classification rates of 0% with other contaminants identified, a 2; and no detection of injection a 1.

Chapter 6
Test Results

As mentioned previously, this verification test was conducted in four stages that focused on four different aspects of multi-parameter water monitors for distribution systems. The four stages are summarized in Table 6-1. The first stage consisted of an evaluation (with varied pHs and temperatures) of the accuracy of each WDMP sensor: total chlorine, turbidity, temperature, conductivity, pH, and TOC. The second stage of the verification test consisted of an evaluation of the response of the WDMP units to the injection of several contaminants into the pipe loop. The third stage consisted of deploying the WDMP 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 WDMP units were still responsive to contaminant injection after the extended deployment. The fourth stage evaluated the ability of the EMTS to detect the injection of a contaminant, as well as to identify the contaminant. Throughout all stages of the test, two WDMP 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 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 WDMP units and reference measurements
2	Response to contaminant injection	Graphs of WDMP unit measurements and reference measurements, table showing the effect of injections on both reference and WDMP measurements
3	Extended deployment with minimal maintenance along with post-extended deployment accuracy and response to contaminant injections	Graphs of WDMP unit measurements with reference measurements, table showing average percent differences throughout extended deployment, table showing the effect of injections on both reference and WDMP measurements
4	Injection detection and contaminant identification	Table of EMTS contaminant identifications that, for each injection, gives the number of agent alarms and associated match quality attributable to each possible contaminant; table of classification rate levels

6.1 Accuracy

Tables 6-2a–f 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. In evaluating accuracy in each four-hour period, measurements from each reference sample were compared with the WDMP unit measurement taken closest to the time of the reference sample collection and analysis. For each unit, this approach resulted in five paired WDMP and reference results for each of the nine 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 WDMP units and the average of the reference results.

Table 6-2a. Accuracy Evaluation Under Various Conditions—Total 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	0.97 (0.07)	0.96 (0.01)	-1.0	0.99 (0.00)	2.1
2	decreased pH, ambient temperature	0.86 (0.02)	0.82 (0.01)	-4.7	0.84 (0.02)	-2.3
3	decreased pH, ambient temperature	0.73 (0.01)	0.49 (0.09)	-32.9	0.49 (0.09)	-32.9
4	decreased pH, ambient temperature	0.38 (0.03)	0.20 (0.06)	-47.4	0.32 (0.01)	-15.8
5	ambient pH, decreased temperature	0.51 (0.08)	0.50 (0.01)	-2.0	0.50 (0.01)	-2.0
6	decreased pH, decreased temperature	1.57 (0.06)	1.63 (0.07)	3.8	1.64 (0.07)	4.5
7	ambient pH, increased temperature	0.69 (0.01)	0.64 (0.01)	-7.2	0.65 (0.01)	-5.8
8	decreased pH, increased temperature	0.65 (0.07)	0.60 (0.05)	-7.7	0.60 (0.05)	-7.7
9	ambient pH, ambient temperature	0.98 (0.02)	0.95 (0.03)	-3.1	0.96 (0.03)	-2.0

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

Set	Conditions	Reference Average (SD) [ntu]	Unit 1 Average (SD) [ntu]	Unit 1 % D	Unit 2 Average (SD) [ntu]	Unit 2 % D
1	ambient pH, ambient temperature	1.27 (0.95)	0.59 (0.04)	-53.5	0.63 (0.04)	-50.4
2	decreased pH, ambient temperature	1.14 (0.40)	0.98 (0.48)	-14.0	0.79 (0.07)	-30.7
3	decreased pH, ambient temperature	0.97 (0.33)	0.69 (0.11)	-28.9	0.68 (0.09)	-29.9
4	decreased pH, ambient temperature	1.54 (0.20)	1.37 (0.11)	-11.0	1.52 (0.52)	-1.3
5	ambient pH, decreased temperature	0.89 (0.41)	0.45 (0.02)	-49.4	0.41 (0.03)	-53.9
6	decreased pH, decreased temperature	0.99 (0.21)	0.48 (0.09)	-51.5	0.68 (0.01)	-31.3
7	ambient pH, increased temperature	0.92 (0.16)	0.44 (0.03)	-52.2	0.58 (0.01)	-37.0
8	decreased pH, increased temperature	1.00 (0.35)	0.69 (0.00)	-31.0	0.74 (0.00)	-26.0
9	ambient pH, ambient temperature	0.46 (0.11)	0.27 (0.02)	-41.3	0.29 (0.02)	-37.0

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	22.66 (0.33)	22.74 (0.38)	0.4	24.89 (1.11)	9.8
2	decreased pH, ambient temperature	22.73 (0.23)	22.55 (0.16)	-0.8	24.42 (0.80)	7.4
3	decreased pH, ambient temperature	21.66 (0.08)	21.46 (0.18)	-0.9	21.44 (0.17)	-1.0
4	decreased pH, ambient temperature	21.93 (0.15)	21.28 (0.13)	-3.0	21.39 (0.30)	-2.5
5	ambient pH, decreased temperature	13.82 (0.44)	14.33 (0.20)	3.7	19.53 (0.36)	41.3
6	decreased pH, decreased temperature	12.63 (0.26)	13.91 (0.68)	10.1	18.22 (0.99)	44.3
7	ambient pH, increased temperature	26.60 (0.27)	26.35 (0.38)	-0.9	26.58 (0.78)	-0.1
8	decreased pH, increased temperature	26.69 (0.23)	26.58 (0.38)	-0.4	26.58 (0.087)	-0.4
9	ambient pH, ambient temperature	22.79 (0.21)	22.72 (0.38)	-0.3	23.97 (0.58)	5.2

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

		Reference	Unit 1		Unit 2	
Set	**Conditions**	**Average (SD) (µS/cm)**	**Average (SD) [µS/cm]**	**% D**	**Average (SD) (µS/cm)**	**% D**
1	ambient pH, ambient temperature	451 (1)	474 (3)	5.1	439 (5)	-2.7
2	decreased pH, ambient temperature	484 (10)	511 (12)	5.6	409 (26)	-15.5
3	decreased pH, ambient temperature	503 (6)	540 (8)	7.4	540 (8)	7.4
4	decreased pH, ambient temperature	694 (12)	742 (13)	6.9	693 (11)	-0.1
5	ambient pH, decreased temperature	412 (1)	421 (2)	2.2	383 (3)	-7.0
6	decreased pH, decreased temperature	501 (10)	512 (10)	2.2	461 (9)	-8.0
7	ambient pH, increased temperature	447 (1)	483 (3)	8.1	454 (5)	1.6
8	decreased pH, increased temperature	529 (2)	571 (6)	7.9	538 (8)	1.7
9	ambient pH, ambient temperature	442 (1)	469 (1)	6.1	438 (3)	-0.9

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

Set	Conditions	Reference Average (SD) [pH unit]	Unit 1 Average (SD) [pH unit]	Unit 1 % D	Unit 2 Average (SD) [pH unit]	Unit 2 % D
1	ambient pH, ambient temperature	8.76 (0.02)	8.85 (0.01)	1.0	9.03 (0.03)	3.1
2	decreased pH, ambient temperature	7.89 (0.09)	7.87 (0.16)	-0.3	7.37 (0.70)	-6.6
3	decreased pH, ambient temperature	7.52 (0.04)	7.33 (0.04)	-2.5	7.34 (0.05)	-2.4
4	decreased pH, ambient temperature	6.73 (0.12)	6.37 (0.06)	-5.3	6.42 (0.07)	-4.6
5	ambient pH, decreased temperature	8.48 (0.02)	8.55 (0.02)	0.8	8.57 (0.01)	1.1
6	decreased pH, decreased temperature	7.31 (0.08)	7.15 (0.08)	-2.2	7.18 (0.08)	-1.8
7	ambient pH, increased temperature	8.37 (0.05)	8.25 (0.02)	-1.4	8.32 (0.02)	-0.6
8	decreased pH, increased temperature	7.60 (0.06)	7.25 (0.03)	-4.6	7.29 (0.02)	-4.1
9	ambient pH, ambient temperature	8.74 (0.01)	8.60 (0.01)	-1.6	8.63 (0.01)	-1.3

Table 6-2f. Accuracy Evaluation Under Various Conditions—Total Organic Carbon

Set	Conditions	Reference Average (SD) [mg/L]	Unit 1 Average (SD) [mg/L]	Unit 1 % D	Unit 2 Average (SD) [mg/L]	Unit 2 % D
1	ambient pH, ambient temperature	0.59 (0.03)	0.87 (0.29)	47.5	1.46 (0.05)	147.5
2	decreased pH, ambient temperature	0.56 (0.05)	0.36 (0.04)	-35.7	0.34 (0.06)	-39.3
3	decreased pH, ambient temperature	0.43 (0.25)	0.22 (0.03)	-48.8	0.51 (0.04)	18.6
4	decreased pH, ambient temperature	0.51 (0.02)	0.18 (0.11)	-64.7	0.44 (0.04)	-13.7
5	ambient pH, decreased temperature	1.20 (0.40)	1.24 (0.09)	3.3	1.20 (0.44)	0.0
6	decreased pH, decreased temperature	0.48 (0.02)	0.18 (0.08)	-62.5	0.70 (0.41)	45.8
7	ambient pH, increased temperature	0.57 (0.02)	0.23 (0.08)	-59.6	0.48 (0.06)	-15.8
8	decreased pH, increased temperature	0.54 (0.01)	0.25 (0.09)	-53.7	0.51 (0.06)	-5.6
9	ambient pH, ambient temperature	0.55 (0.12)	(a)	(a)	0.53 (0.01)	-3.6

(a) Ongoing instrument maintenance resulted in a zero reading.

As can be seen in Tables 6-2a-f, for total chlorine, the percent differences (with the median shown in parentheses) ranged from -47.4 to 4.5 (-3.9); for turbidity, -53.9 to -1.3 (-34.1); for temperature, -3.0 to 44.3 (-0.2); for conductivity, -15.5 to 8.1 (2.2); for pH, -6.6 to 3.1 (0.9); and for TOC, -64.7 to 147.5 (-14.8).[1] Across all of the water quality parameters that were measured, the pH measurements had the smallest range of percent differences. Total chlorine, temperature, and conductivity also had relatively small ranges, with the exception of one or two sets of conditions. For total chlorine, with the exception of Sets 3 and 4, the range of percent differences was -7.7 to 5.1. For temperature, if Unit 2's Sets 5 and 6 (the decreased temperature sets) were not considered, the range of percent differences was -3.0 to 10.1; and, for conductivity, the only percent difference greater than 10 was for Unit 2 during Set 2 (at -15.5%). For temperature, an experimental design factor seemed to affect the accuracy of the measurements. Because of the space requirement, the WDMP units were plumbed to the pipe loop from one floor below, with a PVC tube (1/2-inch outside diameter) that was approximately 18 feet long. During the sets with decreased temperature, by the time the water reached the WDMP units, the temperature had begun equilibrating with the ambient air temperature, increasing or contributing to the positive

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[1] 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.

percent differences. The temperature percent differences from the other sets of test conditions were not as greatly affected because the ambient and increased water temperatures did not differ as much as the ambient and decreased water temperatures did.

The turbidity measurements were consistently low with respect to the reference measurement. As shown in Table 4-1, the comparison of the reference method to the NIST standard indicated that the reference method was biased high. When combined with the Stage 1 results shown in Table 6-2b, this may suggest that the turbidity reference result was typically higher than the actual turbidity in the water. Note that, because of the relatively low turbidity in the Cincinnati water, small absolute differences between the reference samples and the WDMP unit's measurements increased the value of the percent differences between the two numbers. For TOC, the results were somewhat inconsistent between the two units throughout this stage of the verification test. The Unit 1 TOC analyzer was below the reference result by at least 35% in eight out of the nine sets. However, the Unit 2 TOC results matched the reference results more consistently, with six out of the nine results falling within 20% of the reference result.

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 10% of the average result. The only exceptions to this were for turbidity and TOC, which were not controlled as part of the verification test, but were dependent on events occurring in the Cincinnati water utility. Also, small changes in reference and continuous measurements corresponded to rather large relative changes because of the low turbidity and low concentration of TOC in the Cincinnati water. Overall, the low standard deviations show that the water conditions during the test periods were very stable and that there was little variability in the measurements.

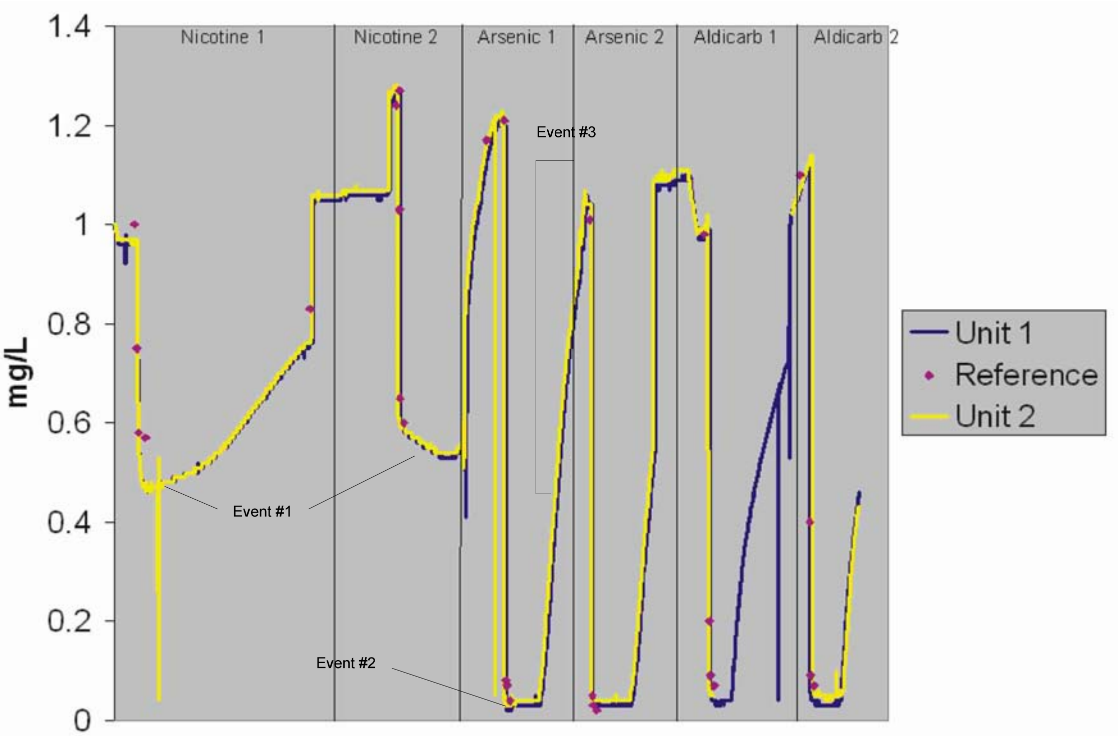
6.2 Response to Injected Contaminants

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 WDMP measurement in response to the contaminant injections. In general, total chlorine was the only parameter clearly affected (for both the reference and continuous measurements) by all six injections. Figures 6-1 through 6-5 show the water quality parameters for which there was a response. The blue and yellow lines on the graphs represent the measurements made by each WDMP 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 WDMP 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 interval that the sensor measurement was affected by the injection. Normally, the sensors were allowed to return to baseline overnight after the injections. Therefore, each injection time period defined on the figures is approximately 24 hours. The times vary somewhat, however, depending on when chlorine was added to restore the system to pre-injection conditions. The contaminant that was injected and whether it

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

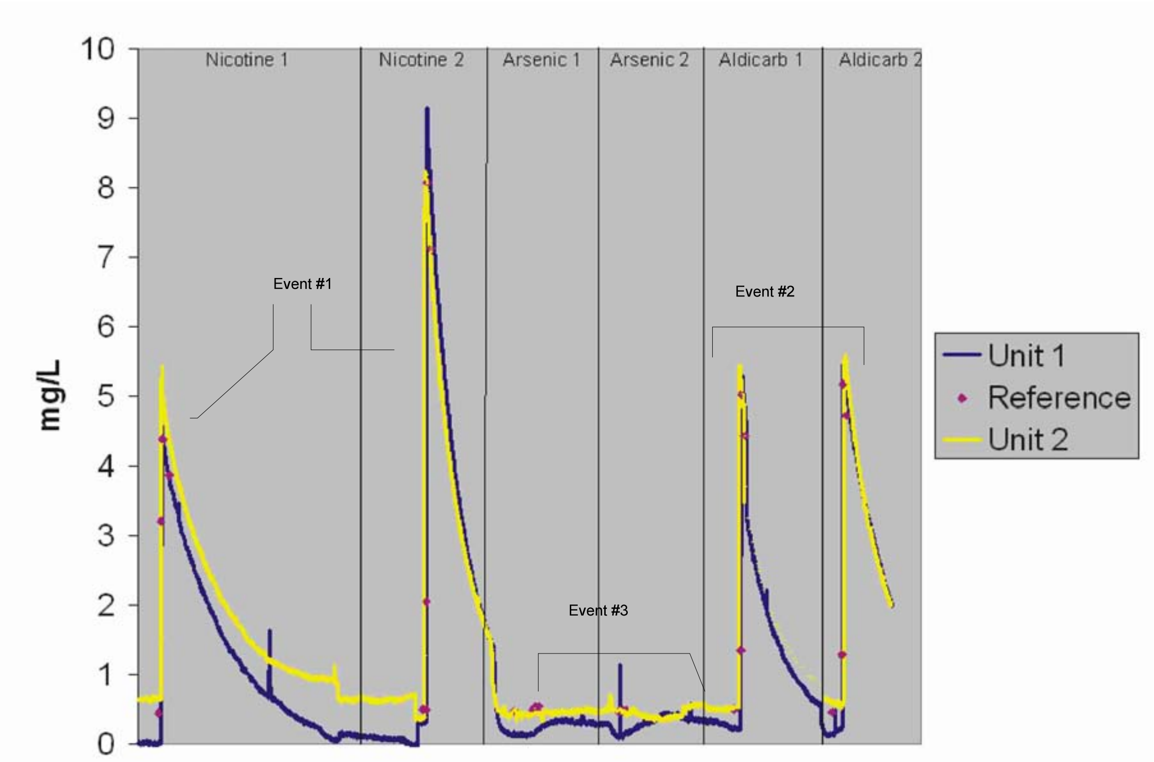
	Nicotine		Arsenic Trioxide		Aldicarb	
Parameter	**Reference**	**WDMP**	**Reference**	**WDMP**	**Reference**	**WDMP**
Total chlorine	–	–	–	–	–	–
Turbidity	(a)	+	(a)	+	(a)	+
Temperature	NC	NC	NC	NC	NC	NC
Conductivity	NC	NC	+	+	NC	NC
pH	NC	NC	+	+	NC	NC
TOC	+	+	NC	NC	+	+

(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.



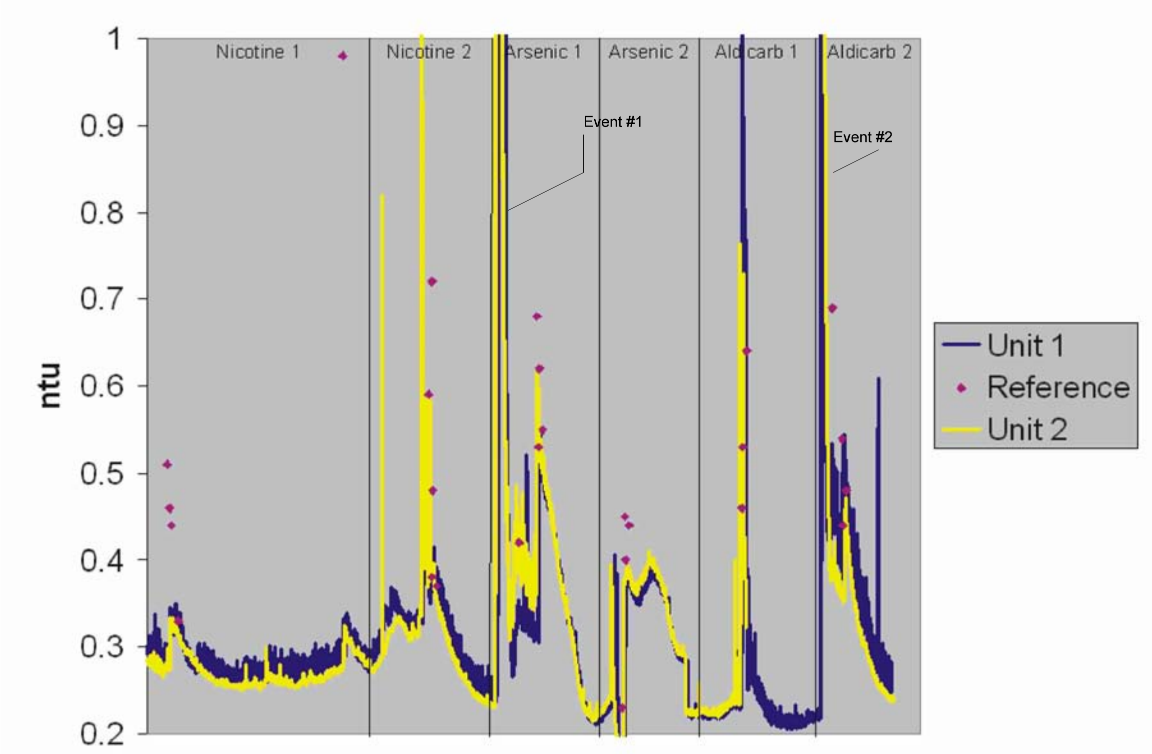
Each section (separated by vertical lines) represents approximately 24 hours.

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



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

Figure 6-2. Stage 2 Contaminant Injection Results for TOC



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

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

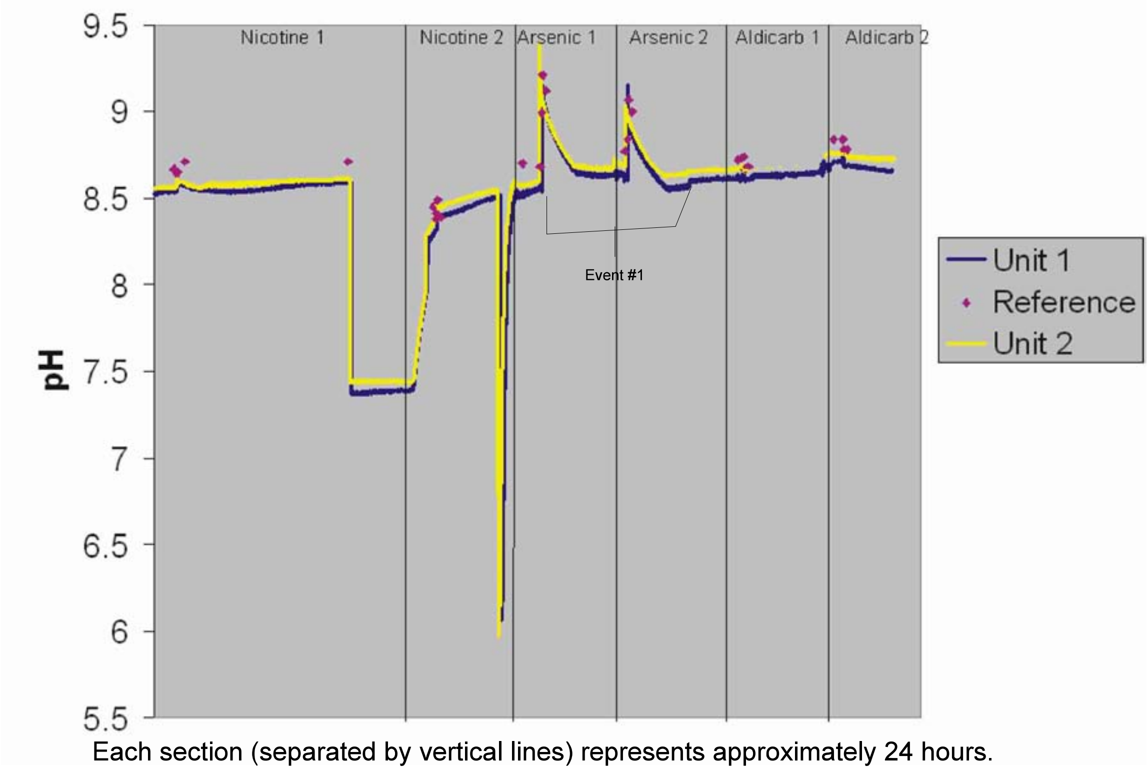


Figure 6-4. Stage 2 Contaminant Injection Results for pH

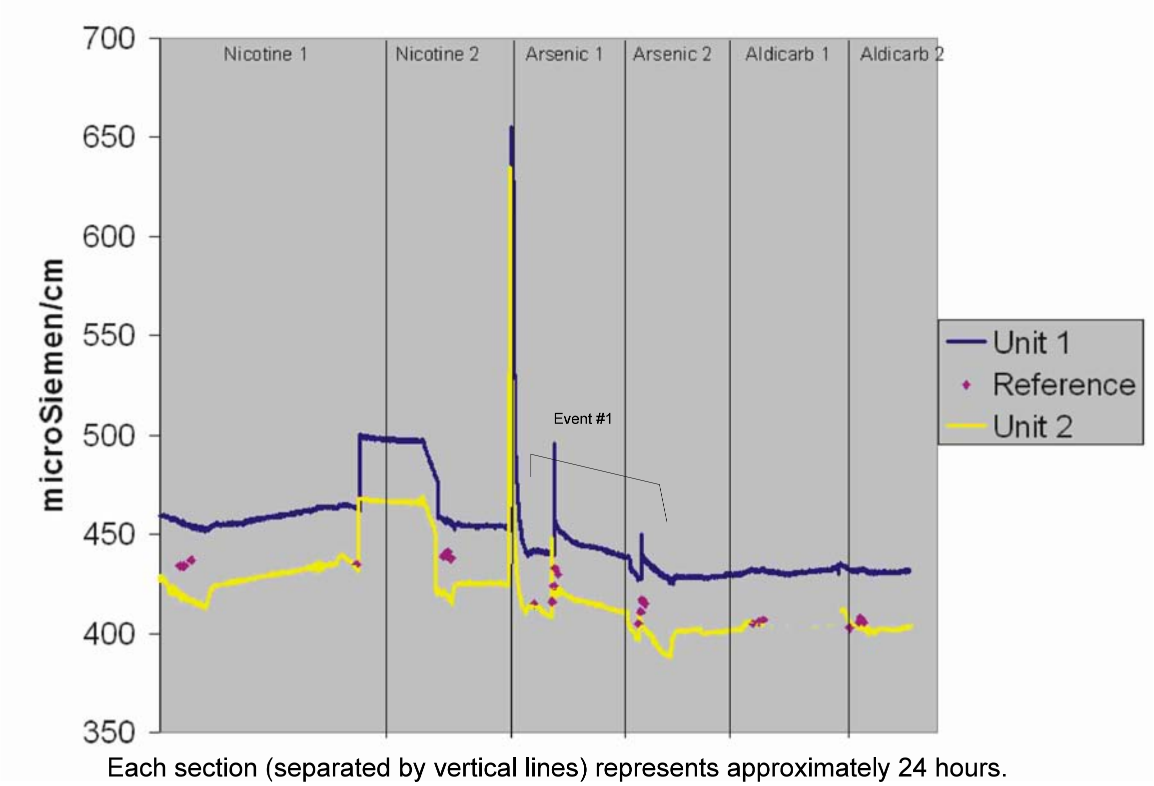


Figure 6-5. Stage 2 Contaminant Injection Results for Conductivity

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 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. Following the first aldicarb injection, it appears as if Unit 2's data may be missing. At this time, Unit 2 reverted unexpectedly to recording data every hour rather than every 30 seconds, as was done for the rest of the injections. There was no explanation for why this happened, but it was the only occurrence throughout the verification test. The hourly measurements are visible on some figures, but are overwritten by the Unit 1 measurements on some others.

Figure 6-1 shows how the measurement of total chlorine was affected by the contaminant injections. Prior to the injections, the total chlorine level was maintained between approximately 1 and 1.2 mg/L, as is evidenced by the magenta data points near the start of each section of the figure. In each case, within one hour of contaminant injection, the total chlorine level, as measured by the laboratory reference method, dropped to approximately 0.5 mg/L for nicotine (total chlorine Event #1 in Figure 6-1) and near zero for the other two contaminants (for an example, see total chlorine Event #2). Upon injection, the vertical drop in the line representing the total chlorine concentration made it clear that the chlorine sensor on the WDMP units were responsive to the drop in total chlorine levels. For each injection, the drop in total 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 total chlorine concentration after the sensor reaches a low point in total chlorine concentration (for an example, see total chlorine Event #3).

As shown in Figure 6-2, the TOC measurement responded significantly to nicotine (TOC Event #1 in Figure 6-2) and aldicarb (TOC Event #2), the two organic contaminants. Arsenic trioxide is an inorganic compound and, as expected, did not increase the TOC concentration in the pipe loop water (TOC Event #3). The WDMP TOC measurements tracked the reference results very well for each of the nicotine and aldicarb injections.

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 WDMP 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 WDMP measurements was very small, while the changes during the arsenic and aldicarb injections were 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 just prior to the arsenic injection (turbidity Event #1 in Figure 6-3) and just prior to the final aldicarb injection (turbidity Event #2), 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 (see pH and conductivity Events #1 in Figures 6-4 and 6-5, respectively). 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 WDMP 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 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, and the y-axis gives the results of each water quality measurement. Data points were recorded every 30 seconds during the verification test; but, 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 the figures.

The objective of this stage of the verification test was to evaluate the performance of the WDMP 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 indicated 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 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 WDMP 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 deviations of the reference results. Because of this, total 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

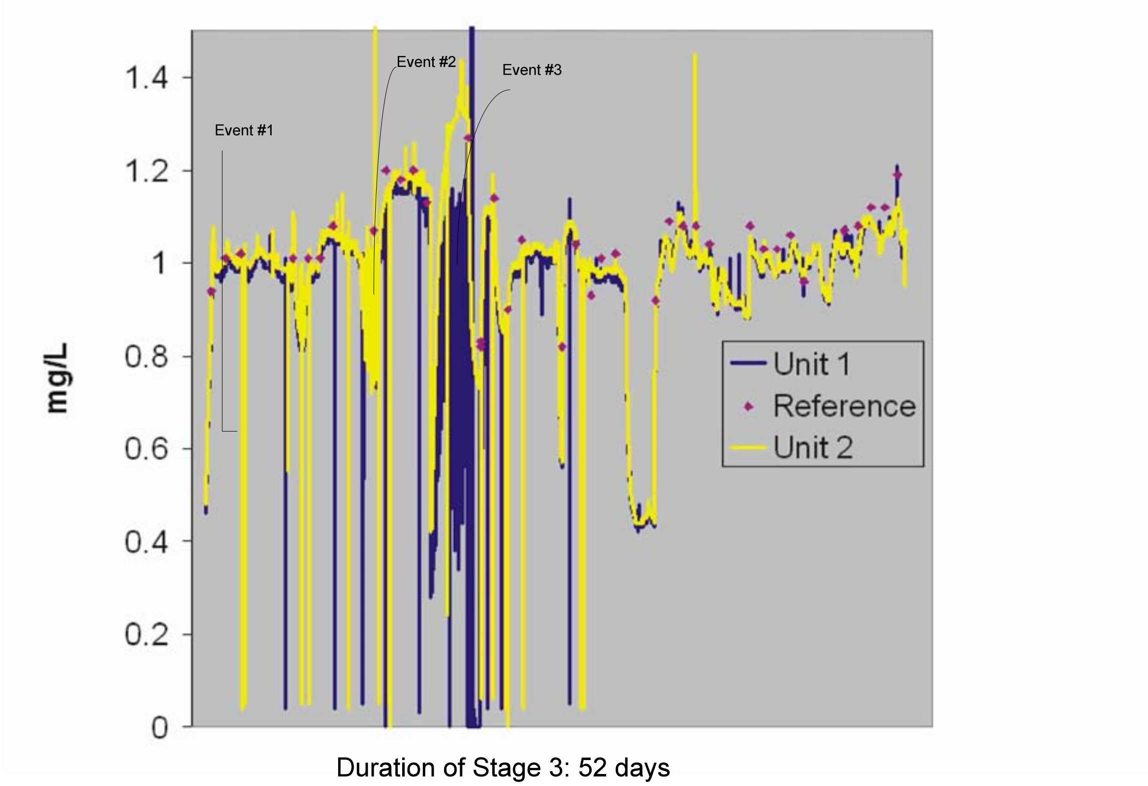


Figure 6-6. Extended Deployment Results for Total Chlorine

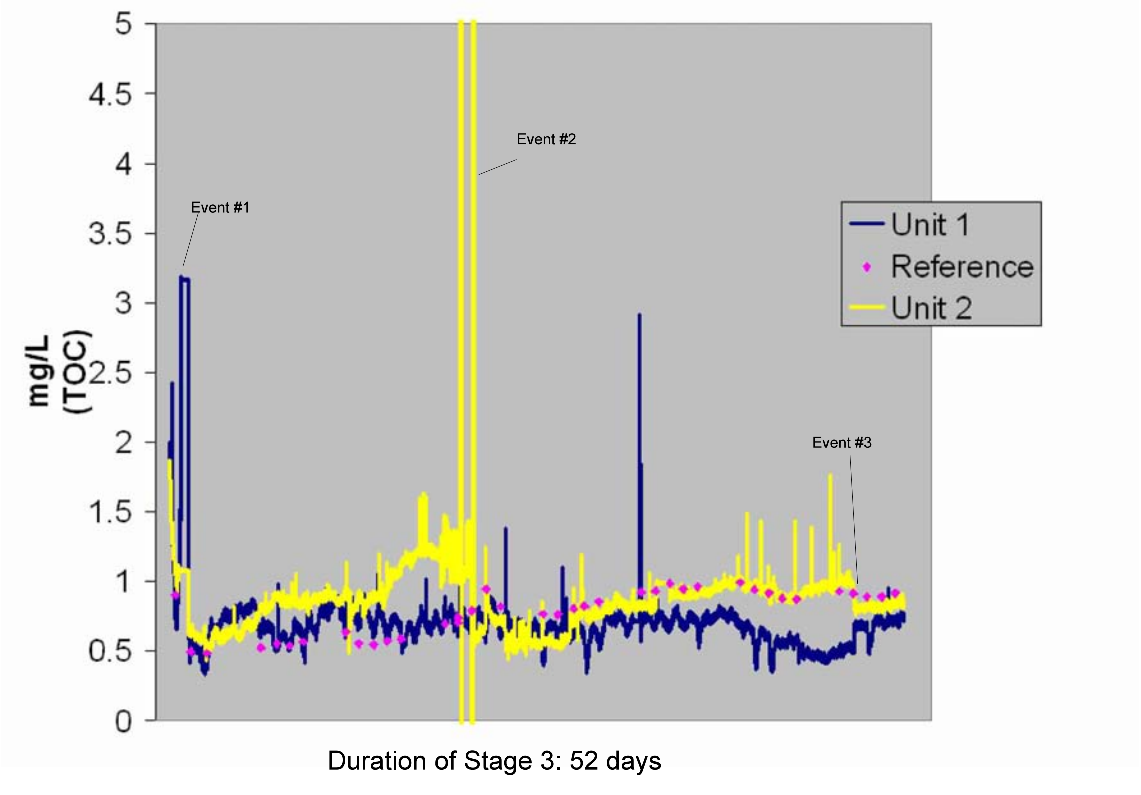


Figure 6-7. Extended Deployment Results for TOC

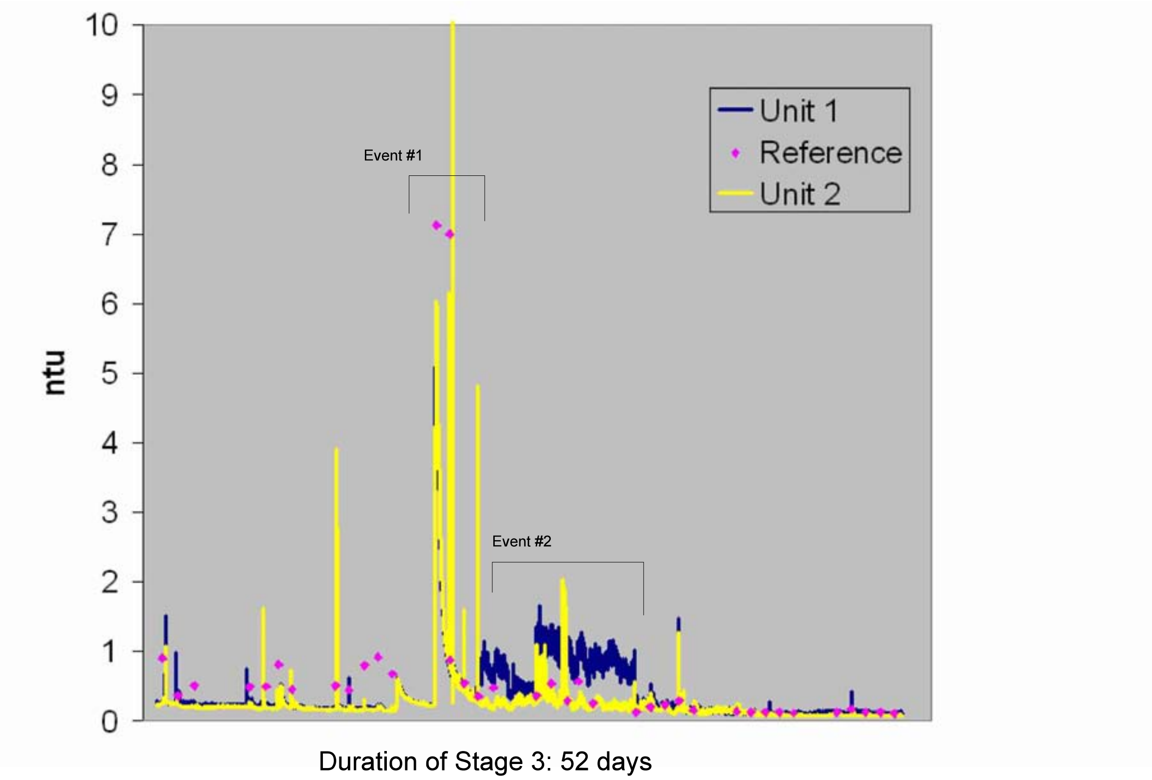


Figure 6-8. Extended Deployment Results for Turbidity

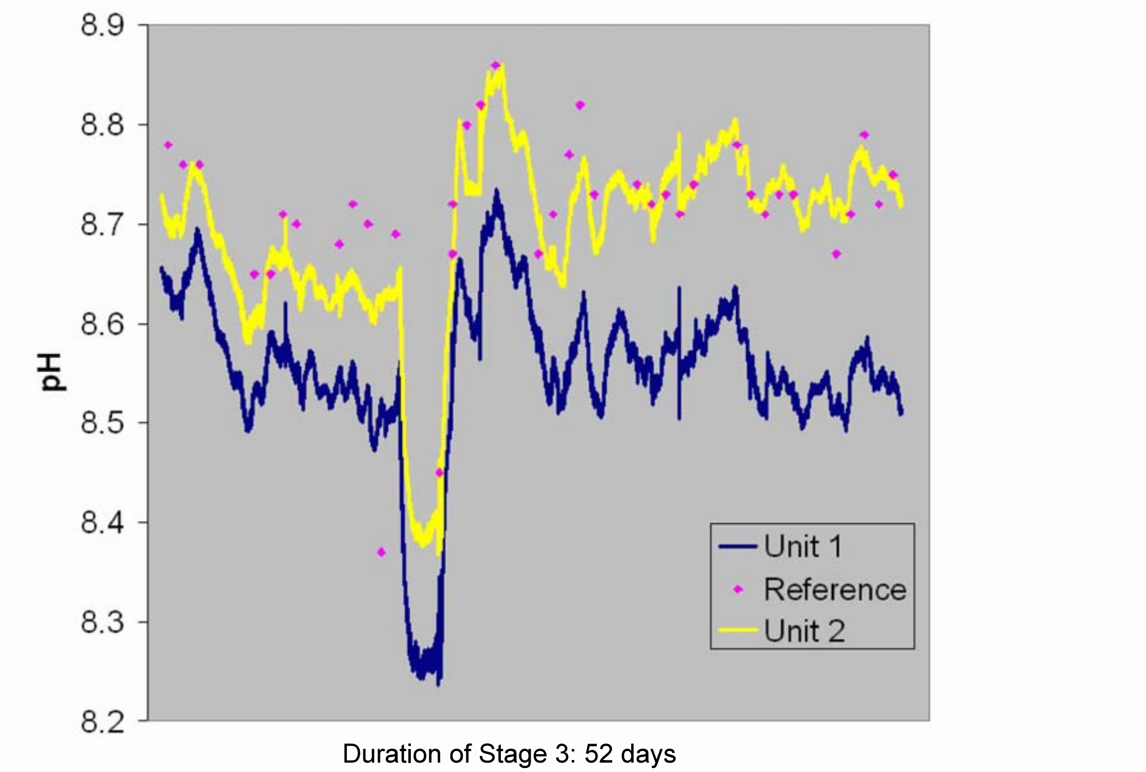


Figure 6-9. Extended Deployment Results for pH

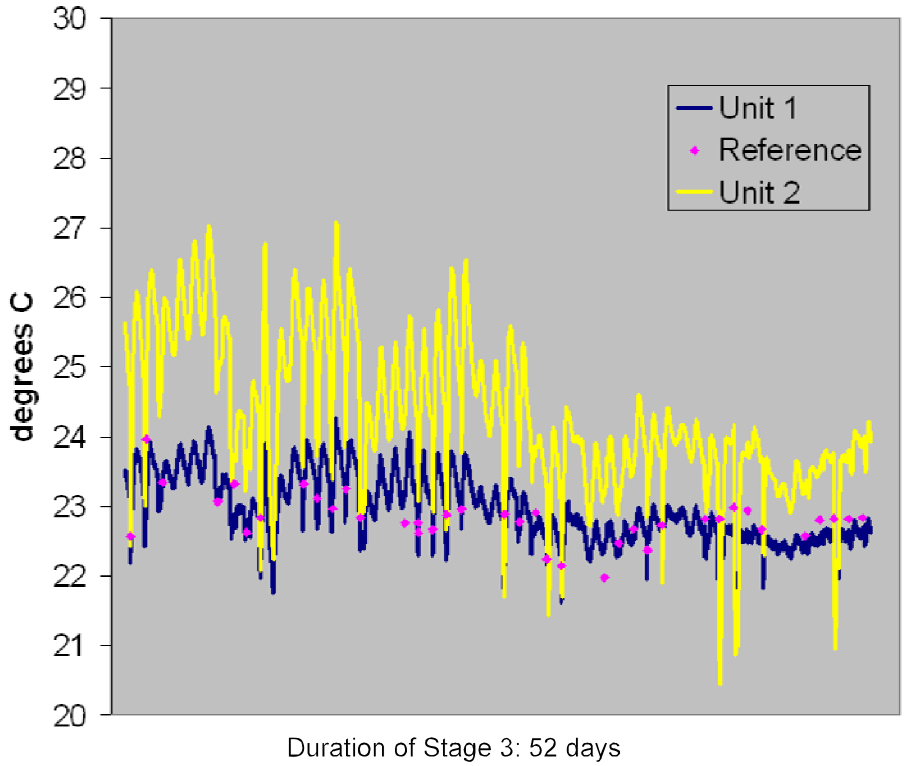


Figure 6-10. Extended Deployment Results for Temperature

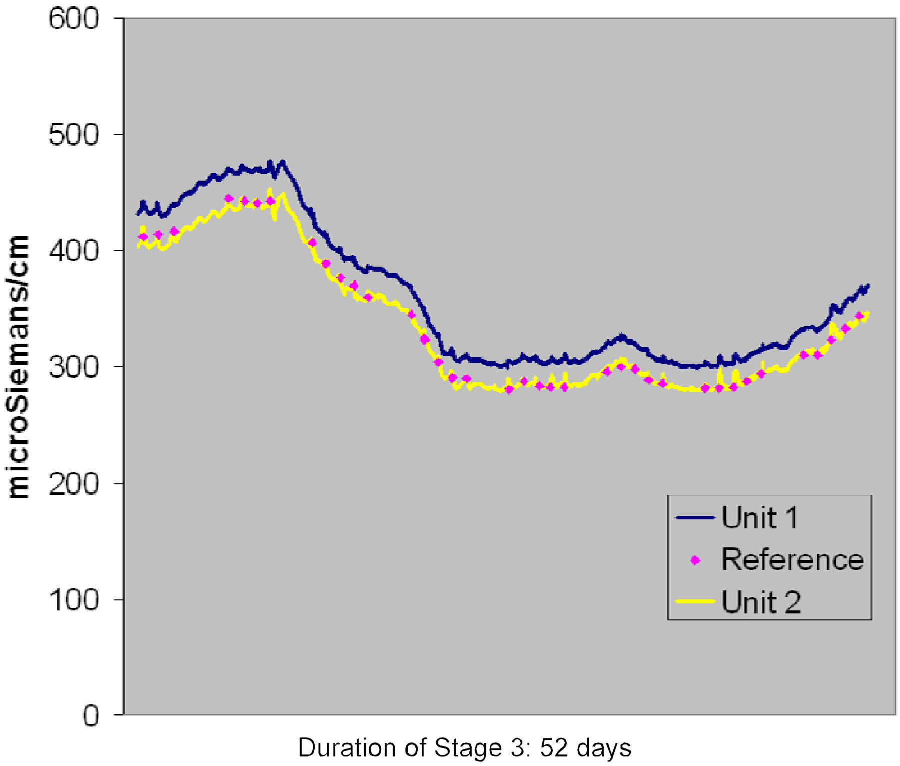


Figure 6-11. Extended Deployment Results for Conductivity

Table 6-4. Accuracy During Extended Deployment

Parameter	Reference Average (SD)(a)	Unit 1		Unit 2		Both Units %D Range (median)
		Average (SD)(a)	%D	Average (SD)(a)	%D	
Total chlorine	1.05 (0.10)	1.02 (0.09)	-2.9	1.03 (0.10)	-1.9	-15.9 to 6.9 (-3.2)
Turbidity(b)	0.38 (0.26)	0.35 (0.31)	-7.9	0.24 (0.17)	-36.8	-81.1 to 245.5 (-21.3)
Temperature	22.83 (0.34)	22.57 (0.38)	-1.1	23.50 (0.82)	2.9	-7.4 to 8.5 (-0.1)
Conductivity	334 (55)	357 (57)	6.9	335 (54)	0.3	-1.8 to 9.6 (4.8)
pH	8.72 (0.07)	8.56 (0.07)	-1.8	8.70 (0.07)	-0.2	-2.7 to 0.5 (-0.9)
TOC	0.79 (0.17)	0.62 (0.09)	-21.5	0.89 (0.19)	12.7	-47.3 to 103.0 (-6.9)

(a) Total chlorine, mg/L; turbidity, ntu; temperature, °C; conductivity, µS/cm; pH, pH units; TOC, mg/L.

(b) The turbidity data from one very high turbidity day were removed from the calculation of average and standard deviation.

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.

For total chlorine, visual inspection of the data in Figure 6-6 revealed that, for most of the extended deployment, the total chlorine measurements were approximately 1 mg/L (with some variation) for both WDMP units as well as the reference method. There were two notable aspects of the total chlorine data. First, throughout the first half of the extended deployment, both units measured periodic drops in the total chlorine concentration to near zero. This is shown in Figure 6-6 by the frequent spikes in the downward direction (for an example, see total chlorine Event #1 in Figure 6-6). These downward spikes are mostly the result of single measurements of nearly zero that did not correspond to any maintenance activities or pipe loop events. In most cases, the next reported measurement was very similar to the background concentration of total chlorine. During the latter half of the extended deployment, the downward spikes were not observed. Hach said that the negative spikes were due to a production problem in which a hole in the sample cell was being drilled improperly. They said that the normal cell-cleaning procedure would often correct the flaw in the drilling, which was apparently true in this case, considering the rather drastic improvement during the latter half of this stage (after the two cell cleanings mentioned below). Hach also informed us that the manufacturing problem has since been corrected. Second, twice during the extended deployment, the WDMP unit measurements varied more than had been observed previously. The first instance of this variation was in the Unit 2 results (yellow line), about one-third of the way through this stage (total chlorine Event #2), and the other instance was in the Unit 1 results (blue line) about one-half of the way through this stage (total chlorine Event #3). In both cases, the remedy was to clean the sample cell within the WDMP total chlorine sensor. This cleaning step only was performed after the two instances of increased variability. Otherwise, the sensors operated uninterrupted. During the extended deployment, the percent differences for both WDMP units ranged from -15.9 to 6.9, with a median of -3.2. The average total chlorine concentration, as measured by the reference method, was 1.05 mg/L ± 0.10 mg/L.

The TOC measurements during the extended deployment are shown in Figure 6-7. Notable aspects of the data include a sharp increase in the Unit 1 concentration measurement near the start of this stage (TOC Event #1 in Figure 6-7), two spikes in the Unit 2 measurements nearly halfway through this stage (TOC Event #2), and a convergence of both TOC analyzer measurements near the end of the extended deployment (TOC Event #3). The increase in the Unit 1 measurement occurred when the liquid nitrogen supply ran out, thus causing the result to be measured as total carbon (which would be expected to be higher) rather than TOC. The first Unit 2 spike during Event #2, which actually overlays an identical spike in the Unit 1 results that is not visible in Figure 6-7, corresponds to stopping the flow to perform maintenance activities on both units. A day later, the second Unit 2 spike corresponds to the calibration of both units. However, there was not a signal spike in the Unit 1 results. Finally, the convergence of the results from both WDMP units near the end of this stage indicates another calibration of both units. Overall, the Unit 1 measurements tracked the reference measurements more accurately prior to the first calibration, and the Unit 2 results did so after the calibration. This is also observed in the statistical evaluation of the data. Prior to the first calibration, the average percent difference for Unit 1 was 6.6 ± 18.7 and for Unit 2, 55.9 ± 27.6. After the first calibration, the percent differences were -30.6 ± 8.0 and -6.2 ± 9.1 for Units 1 and 2, respectively.

The turbidity measurements are shown in Figure 6-8. Throughout the extended deployment, the baseline turbidity was less than 0.5 ntu most of the time except for several high turbidity events that were not anticipated. Some of the smaller turbidity events seemed to correspond with collection of the reference samples. The perturbation of water in the pipe may have caused brief increases in turbidity. The one rather large turbidity event shown by the large peak near the middle of the extended deployment (turbidity Event #1 in Figure 6-8) was not caused by reference sampling or any other known event. However, it was clearly measured by both the WDMPs and the reference method. Just after the large peak there is a spike in the signal of both units, which occurred when flow was stopped to perform maintenance on the turbidity meter. Because of the large difference between the data from the high turbidity event and the rest of the test, these data were removed from the calculation of average and standard deviation. During the second half of the extended deployment, Unit 1 generated results that were biased high with respect to the Unit 2 and reference results and that, at times, displayed a high degree of variability (turbidity Event #2). This persisted for approximately two weeks. The end of that period of variable results from Unit 1 did not seem to correlate with any maintenance or calibration performed on the WDMPs, but the signal stabilized for the remainder of the stage.

Overall, during the first half of the extended deployment, the WDMP turbidity measurements were biased low with respect to the reference measurements. However, the reference measurements during that time were higher than during the second half of the extended deployment when the reference measurements were more in alignment with the WDMP measurements. Because neither the water source nor the baseline results from the WDMP changed considerably between the first and second halves of the extended deployment, it seems possible that the reference method measurements were biased high during the first half. During the first half, the average differences for Units 1 and 2 were 55% ± 23% and 59% ±21%, respectively. During the second half, the difference for Unit 1 (excluding the high variability results) was -6% ± 12% and for Unit 2, -6% ± 9%.

The pH, temperature, and conductivity measurements are shown in Figures 6-9 through 6-11. Each of these sensors operated without intervention throughout this stage of the verification test.

Each sensor tracked the sensor from the other WDMP unit rather well. However, in each case, one unit's measurements more closely matched those generated by the reference method. For pH and conductivity, Unit 2 was more accurate with respect to the reference result, while, for temperature, Unit 1 was more accurate. The temperature measurements from both Units 1 and 2 showed 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 temperature for the day. However, it is not apparent why the Unit 2 measurements seem to have a wider range of daily temperature variation than Unit 1. With the exception of the Unit 2 temperature measurements, the standard deviations for each sensor across the entire extended deployment were either very similar or less than the standard deviations for the reference method. This indicates that the variability observed in most of the measurements was actually due to variability in the measured water quality parameters rather than any systematic error in the sensors.

6.4 Accuracy and Response to Injected Contaminants After Extended Deployment

After the 52-day deployment of the WDMP 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. The percent differences between the WDMP units and the reference measurements during this post-extended deployment accuracy evaluation for total chlorine, temperature, conductivity, and pH were, for the most part, similar in magnitude to measurements during the Stage 1 accuracy evaluation. For turbidity and TOC, however, the percent differences were considerably smaller than in Stage 1. The WDMP turbidity measurements during Stage 1 were generally between 30% and 80% below the reference method measurements while, during this stage, the percent differences were approximately -6% and -12% for Units 1 and 2, respectively. Similarly, the TOC measurements during Stage 1 varied widely between sets of conditions. The Unit 1 percent differences ranged from -65% to 47% and Unit 2 from -39% to 148%. These results, and the extended deployment results, both with average percent differences of less than 21% and relatively small standard deviations, indicate that the TOC measurements were more accurate at the close of the verification test than at the start. Apparently, calibration of the TOC analyzers during the extended deployment stage was the reason for these improved results. It was not apparent what caused the improved agreement between the reference and continuous measurements.

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 gives the directional change of each reference and WDMP measurement in response to the contaminant injections. In general, total chlorine and TOC were the two parameters that were most obviously affected (through visible inspection of the data) by all four injections. This is shown in Figures 6-12 and 6-13 (see total chlorine and TOC Events #1 through 4). In addition, the duplicate injections generated very similar changes in each of the parameters. Turbidity, pH, and conductivity, shown in Figures 6-14 through 6-16, also were affected by some or all of these injections, but the magnitude and consistency of change was not as obvious as for total chlorine and TOC.

Table 6-5. Post-Extended Deployment Results

		Unit 1		Unit 2	
Parameter	Reference Average (SD)	Average (SD)	%D	Average (SD)	%D
Total chlorine	1.03 (0.03)	0.98 (0.02)	-4.9	0.98 (0.02)	-4.9
Turbidity	0.17 (0.02)	0.16 (0.03)	-5.9	0.15 (0.04)	-11.8
Temperature	22.66 (0.16)	22.61 (0.03)	-0.2	23.70 (0.06)	4.6
Conductivity	356 (1)	380 (1)	6.7	357 (1)	0.3
pH	8.59 (0.01)	8.40 (0.01)	-2.2	8.61 (0.00)	0.2
TOC	0.88 (0.01)	0.70 (0.01)	-20.5	0.91 (0.01)	3.4

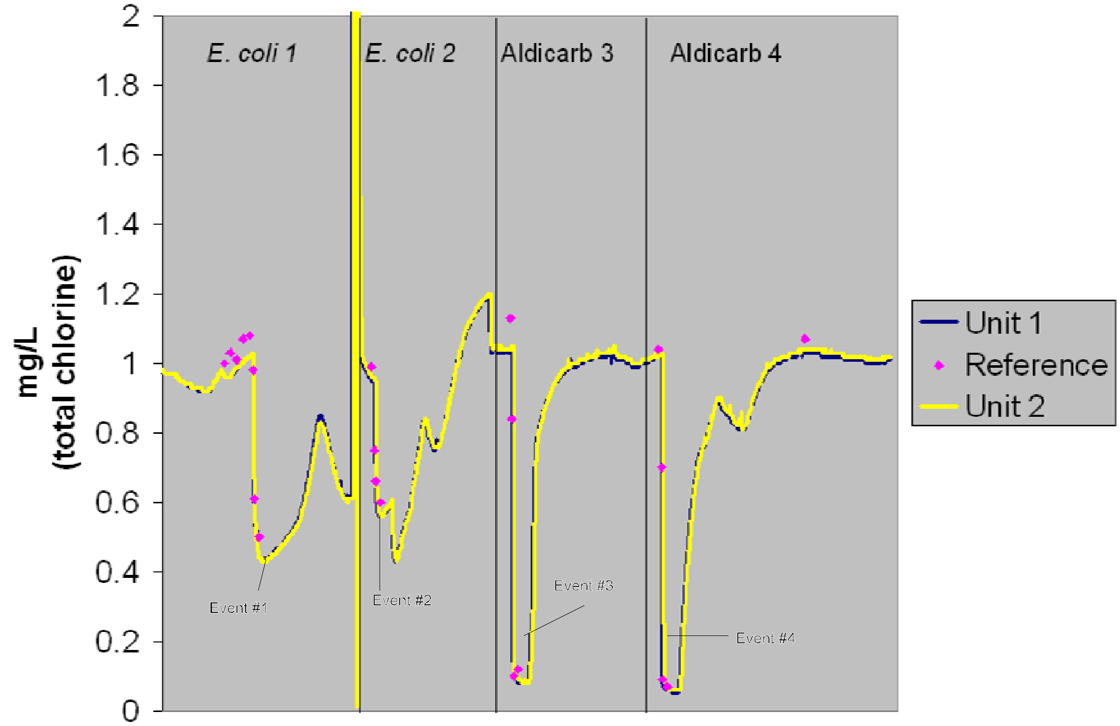
(a) Total chlorine, mg/L; turbidity, ntu; temperature, °C; conductivity, µS/cm; pH, pH units; TOC, mg/L.

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

	E. coli		Aldicarb	
Parameter	Reference	WDMP	Reference	WDMP
Total chlorine	–	–	–	–
Turbidity	+(a)	+	+(a)	+
Temperature	NC	NC	NC	NC
Conductivity	+	+	NC	NC
pH	–	–	–	–
TOC	+	+	+	+

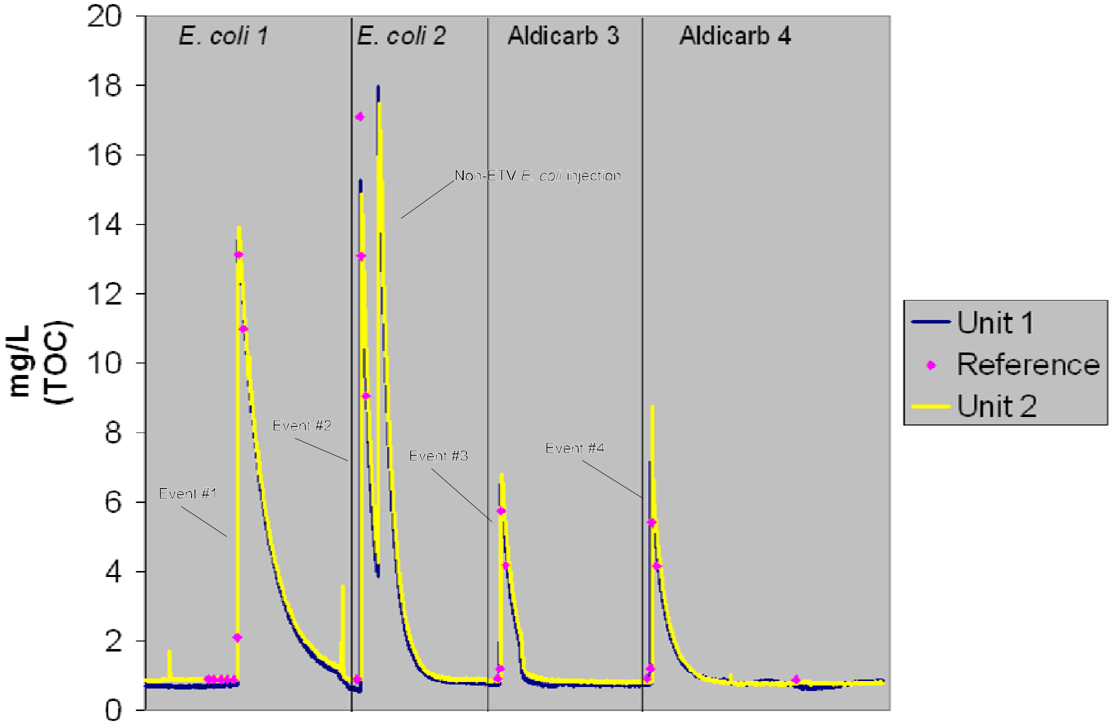
(a) Magnitude of change different between duplicate injections.
+/– = Parameter measurement increased/decreased upon injection.
NC = No change in response to the contaminant injection.

Turbidity seemed to be affected by all four injections, but the results were not as clear. The reference response to both *E. coli* injections and the final aldicarb injection indicated an obvious increase in turbidity between the pre-injection reference sample and the subsequent reference samples. This is shown by the first aldicarb injection producing an increase in turbidity of only 0.12 ntu, while the first and second *E. coli* injections and the second aldicarb injection produced changes 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 with respect to the reference measurements rather well (turbidity Events #1 through #4 in Figure 6-14).



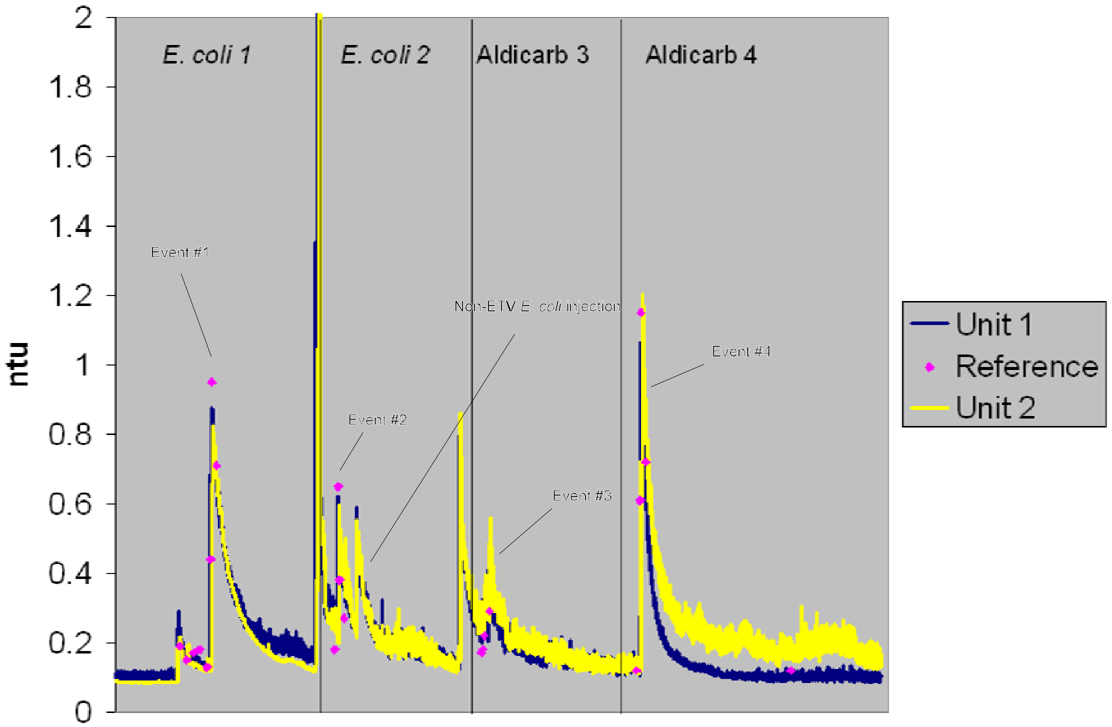
Each section (separated by vertical lines) represents approximately 24 hours.

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



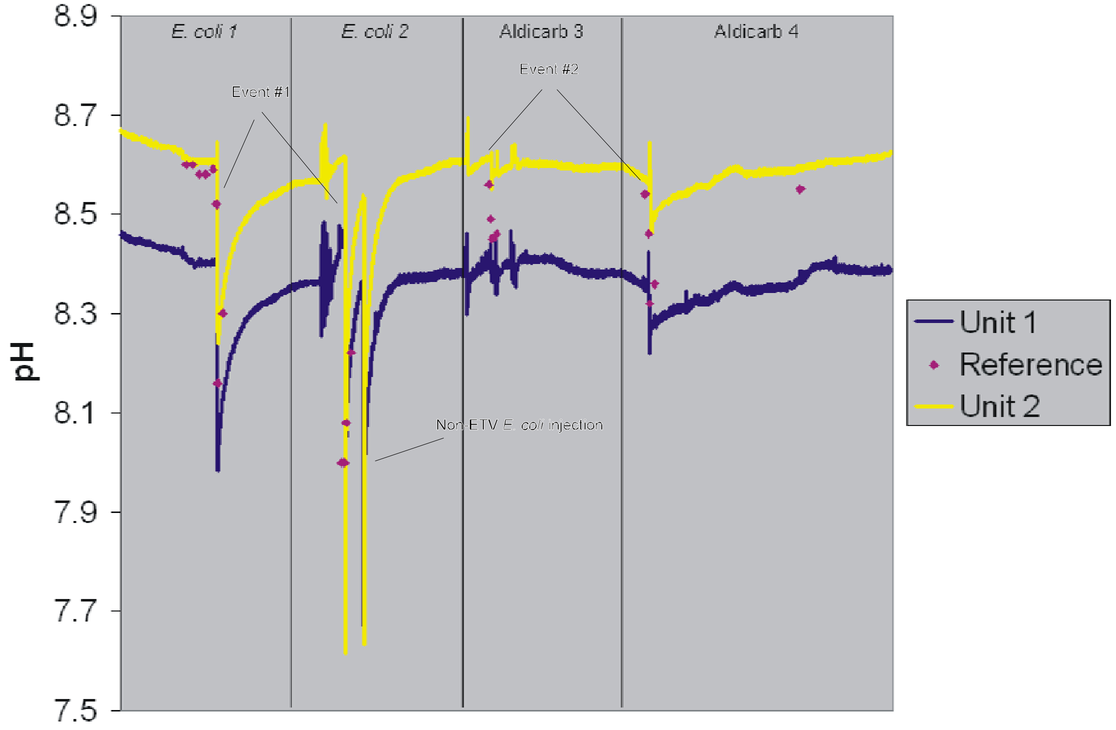
Each section (separated by vertical lines) represents approximately 24 hours.

Figure 6-13. Stage 3 Contaminant Injection Results for TOC



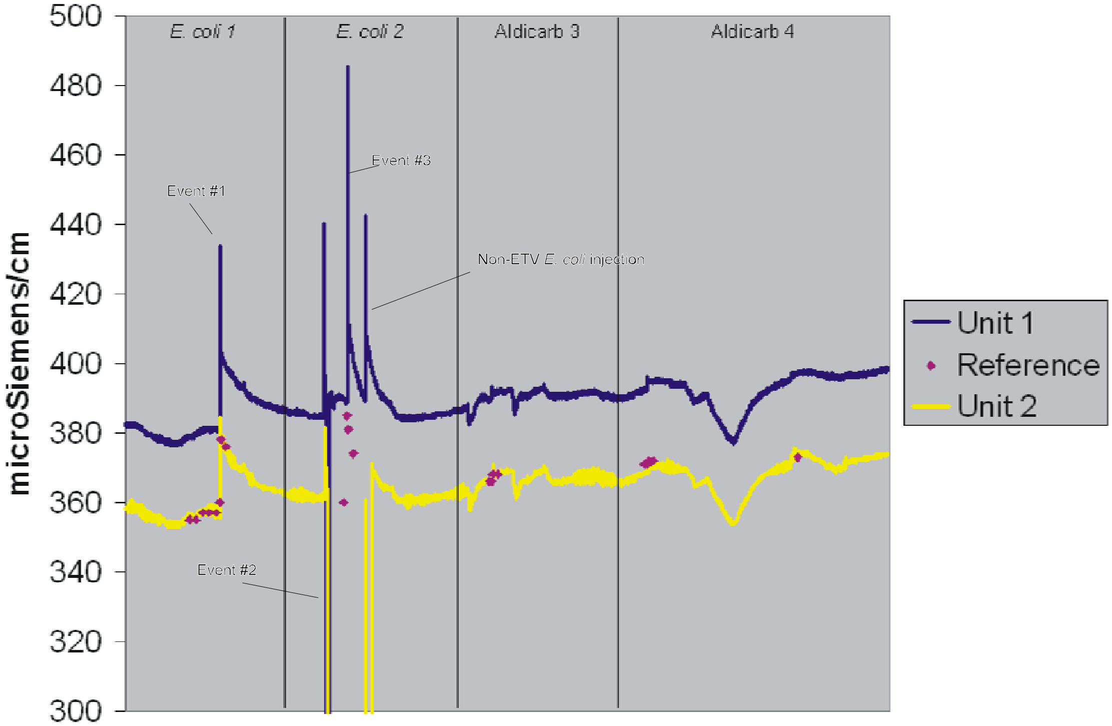
Each section (separated by vertical lines) represents approximately 24 hours.

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



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

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



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

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

The reference method indicated a decrease in pH corresponding to the injection of *E. coli* and aldicarb. No change in pH was observed during the Stage 2 injections of aldicarb so the Stage 3 response was unexpected. The WDMP units both detected the change in pH due to the *E. coli* injections (pH Event #1 in Figure 6-15), while the change during the aldicarb injections was detected only by a small inflection of the pH signal (pH Event #2) rather than an obvious peak in the negative direction, as was observed for the *E. coli* injections. Finally, conductivity increased slightly in response to the injection of *E. coli*. Both the reference method and the WDMP units detected this change during the first *E. coli* injection (conductivity Event #1 in Figure 6-16); but, during the second injection, WDMP Unit 2 generated a zero reading because some air bubbles had become trapped inside the conductivity sensor (conductivity Event #2). Unit 1 did detect the change (conductivity Event #3). Note that the second peak (just after the *E. coli* injection) in the TOC, turbidity, pH, and conductivity data (labeled non-ETV *E. coli* injection) reflects a second injection of *E. coli* performed that day by the T&E facility staff that was not part of the ETV test.

6.5 Inter-unit Reproducibility

Two WDMP units were compared throughout the verification test to determine whether they generated results that were similar to one another. This was done using the data collected whenever a reference sample was collected throughout the verification test. Two evaluations were performed to make this comparison. First, the results from each sensor from Unit 2 were graphed on the y-axis, those from Unit 1 were graphed on the x-axis, and a linear regression line was fitted to the data. For the linear regression analysis, if both units reported the identical result, the slope of such a regression would be unity, 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. Second, a t-test assuming equal variances was performed on those same data. 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 inter-unit reproducibility evaluation and the p-value for the t-test performed for each sensor.

Table 6-7. Inter-unit Reproducibility Evaluation

Parameter	Slope	Intercept	r^2	t-test p-value
Total chlorine	0.98	0.03	0.994	0.779
Turbidity	0.77	0.09	0.696	0.584
Turbidity (outlier removed)	0.97	0.005	0.881	0.884
Temperature	0.72	7.68	0.758	5.5×10^{-6}
Conductivity	0.92	4.19	0.961	0.006
pH	1.06	-0.40	0.919	0.517
TOC	0.97	0.31	0.991	0.374

Shading indicates a significant difference between the two units.

As shown in Table 6-7, the total chlorine, pH, and TOC sensors had coefficients of determination greater than 0.91 and slopes within 6% of unity, indicating that their results were very similar and repeatable. Confirming that evaluation, the t-test p-values for those same parameters were significantly greater than 0.05, indicating that each sensor was generating statistically similar results. The turbidity measurement, however, generated a slope of 0.77 and a coefficient of determination of 0.696, suggesting that the results from both units were not well correlated with one another. However, those results were affected by a single data point in which Unit 1 generated a result of 3.75 ntu and Unit 2 generated a result of 0.45 ntu. While the reason for this outlier was not apparent, if this data point were removed, the slope would change to 0.97, the intercept to 0.005, and the coefficient of determination to 0.881, indicating very similar results between the two units. In addition, with or without the outlying data point, the t-test results indicated that the two units were generating statistically similar turbidity data. Figures 6-8 and 6-14 confirm the statistical evaluation of inter-unit reproducibility for turbidity. With the exception of Unit 1 about halfway through the extended deployment when it drifted high and displayed a relatively high degree of variability, the results from both units tracked one another well.

The conductivity meters had a coefficient of determination of 0.961 and a slope of 0.92, indicating that the data were highly correlated with one another. The t-test generated p-values significantly less than 0.05, which indicated that the results from the two conductivity sensors were significantly different. This difference was driven by the small amount of variability in the conductivity measurements; therefore, the small difference between the means of the two units was statistically significant. The temperature measurements had a slope of 0.72 and a coefficient of determination of 0.758, suggesting that the two units were generating statistically different results. This result did not appear to be driven by outlying temperatures; and the t-test, with a p-value of less than 0.05, also indicated that the results from each unit were, in fact, different. Note that the offsets in the conductivity and temperature results (or from any of the parameters) do not affect the performance of the identification algorithm because the baseline is removed and the identification is performed based only on deviations from baseline.

As discussed for turbidity, the inter-unit reproducibility results for each water quality parameter were confirmed through a visual evaluation of the figures throughout Chapter 6. As the statistical results indicated, all the parameters except temperature and conductivity (the two parameters that had been determined to be significantly different from one another) were nearly overlapping when plotted on the same axis, indicating that they were, indeed, extremely similar to one another.

6.6 Contaminant Identification

Thirteen contaminants were injected (in duplicate) during Stage 4 of this verification test. Section 3.2 describes the straight, single-pass pipe loop that was used. A total volume of 10 L of each contaminant solution was pumped into the flowing pipe for approximately 20 minutes, bringing the water to approximately 15 mg/L for each of the contaminants that were injected. After the leading edge of the injected slug of contaminant reached the WDMP, if the trigger signal (a proprietary combination of the monitored water quality parameters) exceeded a specified threshold (trigger event), the EMTS searched the agent library for possible matches. The EMTS produced an “agent alarm” whenever a trigger event occurred and the deviation in baseline water quality parameters matched an agent signature in the agent library. When these signatures were compared with the signatures from the agent library, the quality of the match was evaluated with a metric called the match angle, which was described in Section 5.4.

Table 6-8 shows the contaminant identification data for each injection that was performed, including the data from both units tested. A contaminant was never injected without the EMTS exceeding the trigger threshold and producing a corresponding agent alarm. For both units, the agent alarms occurred as few as eight times and as many as 79 times during the 20-minute injection periods. No agent alarms occurred outside of the 20-minute injection periods. As mentioned previously, each minute-by-minute search of the agent library can result in more than one agent being identified, which is why more than 20 agent alarms can occur during a 20-minute injection. If the EMTS recognized a deviation from baseline, but the signature did not match an agent in the library, the trigger event was identified and recorded as an “unknown” event. Because the leading and trailing edges of the injected contaminant are dynamic, it is possible that the injection event will generate alarms other than the injected contaminant.

In Table 6-8, the contaminants injected are presented in alphabetical order on left side, and across the top are the contaminants that were identified by the EMTS agent alarms. There are more contaminants across the top of the table because three contaminants were identified that had not been injected. At the time of this test, the EMTS library was populated with 22 contaminants. All except one of the 13 contaminants that were injected were among the contaminants in the EMTS library. The one exception was that pure glyphosate was used for the ETV test, while the EMTS library was developed using Roundup™, the commercial preparation of glyphosate.

Table 6-8. Contaminant Identification—Number and Quality of Matches

Injected Contaminant	Inj. #	Unit	Total # of IDs	Aldicarb			Arsenic Trioxide			Colchicine			Di-camba			Di-chlorvos			*E. coli*			Ferri-cyanide			Fluoro-acetate			Gly-phosate			Lead Nitrate			Mercuric Chloride			Methanol			Nicotine			Carbaryl			Malathion			Metha-midophos		
Quality of angle match				W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G	W	M	G
Aldicarb	1	1	33	9	4	0				1	0	0							2	1	0				1	0	0																15	0	0						
		2	42	2	4	12				1	0	0							2	2	0				1	0	0																18	0	0						
	2	1	20	6	2	0													3	2	0																						4	3	0						
		2	63	7	12	9													12	0	0																						8	2	0	1	3	5	2	0	2
Arsenic Trioxide	1	1	19				0	0	0																			16	3	0																					
		2	13				0	0	0																			9	3	0																1	0	0			
	2	1	10				0	0	0																			6	3	1																					
		2	18				0	0	0																			2	6	4																6	0	0			
Colchicine	1	1	56							1	1	17				1	3	14																			0	17	2												
		2	79							4	7	18				0	2	19																			2	23	4												
	2	1	65							1	7	17				1	1	16																			0	7	15												
		2	74							4	2	19				1	5	15																			5	17	6												
Dicamba	1	1	18							1	1	0	0	5	2	2	1	1																			2	1	2												
		2	10										1	3	4																						1	1	0												
	2	1	23							0			10	1	9	0	2	0																			0	1	0												
		2	25							2			18	0	0	4																		1	0	0	0	0	0												
Dichlorvos	1	1	53							7	3	0				16	1	0																			2	6	18												
		2	51							3	16	6				2	0	0																			1	16	7												
	2	1	41							9	9	0				2	0	0																			1	20	0												
		2	45							0	10	15				0	0	0																			5	15	0												
E. coli	1	1	33																3	2	0							1	6	0							1	0	0							14	2	0	2	2	0
		2	9																0	0	0																									1	2	6	0	0	0
	2	1	45																11	4	0							2	0	0							1	1	0				2	0	0	16	3	0	3	1	1
		2	16	0	0	3	0	0	0	1	1	0							0	0	0							0	0	0																2	6	1	2	0	0
Ferricyanide	1	1	19																			1	18	0																											
		2	23																			2	21	0																											
	2	1	17																			4	13	0																											
		2	18																			13	5	0																											
Fluoroacetate	1	1	19							1	0	0													11	5	1										0	1	0												
		2	23							2	0	0													10	10	0										1	0	0												
	2	1	10							1	1	0													3	1	1										0	1	0							1	0	0	1	0	0
		2	11							0	1	0													4	3	0										0	1	0							1	1	0	0	0	0
Glyphosate	1	1	9										0	0	1													1	1	1																4	0	0	1	0	0
		2	41	0	1	0							5	1	0													4	0	0				3	4	0										3	10	0	2	1	7
	2	1	13										2	0	0													0	0	0				9	0	0										2	0	0			
		2	24										8	0	0													0	0	0				9	5	0										1	1	0			
Lead Nitrate	1	1	22																												8	14	0																		
		2	19																												2	15	2																		
	2	1	24																												2	6	16																		
		2	19																												6	9	4																		
Mercuric Chloride	1	1	44										6	13	3																			4	13	5															
		2	44										4	17	1																			0	21	1															
	2	1	44										3	12	7																			0	11	11															
		2	40										0	15	5																			0	11	9															
Methanol	1	1	8							0	1	2				0	1	1																			0	0	3												
		2	10							1	0	3				0	1	1																			0	3	1												
	2	1	48							2	15	0				3	7	4																			5	3	9												
		2	17							3	5	0				1	5	1																			1	0	1												
Nicotine	1	1	29	5	11	0				2	1	1				0	0	2																						0	0	0	2	4	1						
		2	12	4	4	0				0	1	1				0	2	0																						0	0	0	0	0	0						
	2	1	30	14	5	0				1	0	1				0	1	0																						0	0	0	4	4	0						
		2	15																																																

W = weak, M = moderate, G = good.

In Table 6-8, for each injected contaminant, the total number of agent alarms is given for each replicate injection and for each unit. The three columns for each identified agent account for the quality of the match angle. For example, for the first injection of aldicarb, Unit 1 reported that nine of the agent alarms were considered weak matches to aldicarb, four were considered moderate, and there were no good matches. Moving to the right across the table, it can be seen that aldicarb was identified as colchicine, *E. coli*, fluoroacetate, and carbaryl by Unit 1 at some point during the injection. The agent alarms that correctly matched an injected contaminant are outlined with dark black; and the weak, moderate, and good matches are highlighted with tan, blue, and yellow, respectively.

The agent alarms resulting from injected contaminants provide an effective way of evaluating this data. The results for the injection of ferricyanide and lead nitrate clearly were distinct from the rest of the contaminant injections because, for both units during both injections, agent alarms were only attributed to those contaminants. The match angles for the ferricyanide alarm fell entirely in the moderate or weak match quality categories. For the first lead nitrate injection, 39 out of 41 agent alarms were also in the weak or moderate categories, with two in the good match category; however, for the second lead nitrate injection, 20 out of 43 agent alarms were in the good match category.

Arsenic trioxide and nicotine were two other contaminants whose data were distinct from the other contaminants. For these two contaminants, the agent alarms never corresponded to a correct identification for either unit. Arsenic trioxide was identified most of the time as glyphosate and less frequently as malathion. Nicotine was most often identified as aldicarb, but also was identified as colchicine, dichlorvos, and carbaryl. Following ETV test, the Hach Company updated its agent library with additional data for arsenic trioxide and nicotine to determine why the results were not as they had anticipated. A summary of their independent work is given in Appendix A.

The other nine contaminants were sometimes identified correctly and sometimes as another contaminant. Because of the subjective nature of evaluating the quality of the matches, no quantitative data analysis that accounts for the match angle will be performed here; but rather a general discussion of the results presented in Table 6-8. This approach to comparing the agent alarm results will focus on the data in the context of all the agent alarms that occurred across both injections and both units to provide an overview of how the EMTS performed.

During the injection of aldicarb, 67 agent alarms were attributed to aldicarb, 45 to carbaryl, and 21 to *E. coli.* Colchicine, fluoroacetate, malathion, and methamidophos were also identified. Of the alarms attributed to aldicarb, 21 had good match angles. The rest of the contaminants had weak or moderate match angles.

Agent alarms during the injection of colchicine were attributed to colchicine and methanol 98 times each and to dichlorvos 78 times. Of the colchicine alarms, 71 were good matches, while for the dichlorvos alarms, 64 were good matches. For the methanol alarms, 27 fell into that category.

For the dicamba injection, 51 agent alarms were correctly attributed to dicamba compared with 10 or fewer agent alarms attributed to colchicine, dichlorvos, mercuric chloride, and methanol. Fifteen of the 51 dicamba agent alarms were good matches.

During the dichlorvos injection, 21 agent alarms correctly identified the contaminant, while 78 identified the contaminant as colchicine and 90 as methanol. All but one of the dichlorvos alarms indicated weak matches, while several alarms for colchicine and methanol indicated good matches.

The *E. coli* injection was correctly identified 20 times with weak or moderate match angles, while it was identified as malathion 53 times, including seven good match angles. Also identified during the *E. coli* injection were arsenic trioxide, colchicine, glyphosate, methanol, carbonyl, and methamidophos between two and 11 times, mostly with weak and moderate match angles.

The fluoroacetate injection generated 49 correct agent alarms, with all but two in the weak or moderate match categories. Fluoroacetate was much less frequently (six or fewer times each) identified as colchicine, methanol, malathion, and methamidophos.

The injection of glyphosate generated seven correct agent alarms even though Roundup™, the commercial preparation of glyphosate that also includes other organic chemicals, rather than pure glyphosate, was included in the EMTS library. Because of this, Roundup™ has a different water quality parameter signature than pure glyphosate. This injection was also identified as aldicarb (one time), dicamba (17 times), mercuric chloride (30 times), malathion (20 times), and methamidophos (11 times). The only alarms that were good matches were for methamidophos. After the ETV test, Hach updated its agent library with data for pure glyphosate. A summary of Hach's independent work is given in Appendix A.

The mercuric chloride injection produced an almost equal number of agent alarms identifying it correctly and as dicamba. Eighty-seven agent alarms were for mercuric chloride, with 16 good matches and 56 moderate matches; and 86 alarms were attributable to dicamba, with 16 good matches and 57 moderate matches.

Methanol was correctly identified 26 times, with 14 good matches. However, it was identified as colchicine 32 times with five good matches and as dichlorvos 25 times with six good matches.

To summarize, the EMTS accuracy for detecting an injected contaminant was 100%; that is, in all cases, the injection of a contaminant caused a deviation from the baseline measurement of the water quality parameters significant enough to cause a trigger event resulting in an agent library search. For 11 out of 13 contaminants, at some time during the injection, the correct contaminant was identified during the search of the EMTS library. Two method blank injections of pipe loop water did not cause trigger events; and, therefore, no injection was detected.

The data in Table 6-8 are difficult to interpret, but give a complete report of EMTS performance, including total number of agent alarms, agent alarms that were attributable to the injected contaminant (correct identification), and those that were not. Table 6-8 also shows the quality of match that the agent alarms represented. To provide a more concise way of presenting the data, the fraction of agent alarms attributable to the injected contaminant (correct identification) was calculated for each injection. This fraction was called the classification rate and is defined in Section 5.4. (Note that this approach does not take into consideration the match angle of each agent alarm.) To present the data succinctly, the classification rates were divided into five levels, which are shown in Table 6-9. Level 5 represents a classification rate of greater than 70%, Level

4 between 31% and 69%, Level 3 between 1% and 30%, Level 2 indicates that the injected contaminant was not correctly identified but other contaminants were identified, and Level 1 was reserved for instances when no injections were detected. During this verification test, the Level 1 conditions were met only when two method blanks of pipe loop water were injected. Contaminants with mostly Level 4 and 5 classification rates included dicamba, ferricyanide, fluoroacetate, and lead nitrate. Those with mostly Level 4 classification rates included aldicarb, colchicine, mercuric chloride, and methanol. Glyphosate, dichlorvos, and *E. coli* each had a mixture of Level 2, 3, and 4 classification rates. Arsenic trioxide and nicotine had classification rates of 2, which indicates that those two contaminants were not correctly identified during their injection. As mentioned above, see the appendix to this report for additional data on glyphosate, arsenic trioxide, and nicotine.

Table 6-9. Classification Rate Levels

Injected Contaminant	Injection 1		Injection 2	
	Unit 1	Unit 2	Unit 1	Unit 2
Aldicarb	4	4	4	4
Arsenic trioxide	2	2	2	2
Colchicine	4	4	4	4
Dicamba	4	5	5	5
Dichlorvos	4	3	3	2
E. coli	3	2	4	2
Ferricyanide	5	5	5	5
Fluoroacetate	5	5	4	4
Glyphosate	4	3	2	2
Lead nitrate	5	5	5	5
Mercuric chloride	4	4	4	4
Methanol	4	4	4	3
Nicotine	2	2	2	2

Level 5 = >70% correctly identified
Level 4 = 31-70% correctly identified
Level 3 = 1-30% correctly identified
Level 2 = 0%, other contaminants identified
Level 1 = 0%, no contaminant identified

Evaluating the differences between the performance of individual EMTS units in accurately identifying injected contaminants is difficult because any differences between the two units are a result of the monitoring data that is input to the algorithm. Repeatability of that data was discussed previously. Presumably, because this is a software application, if identical data were input, identical results would be generated.

6.7 Ease of Use and Data Acquisition

Hach Company staff performed all maintenance on the WDMP and EMTS units. They recorded any maintenance activity they performed on either of the units in a logbook. The WDMPs did not require daily operator attention. Throughout the verification test, Hach Company staff periodically adjusted the flows on the turbidity and total chlorine meters as needed to keep them at the required levels and rebooted the EMTS when the real-time display was not displaying data properly.

Reinitialization (i.e., rebooting the EMTS) occurred almost daily for Unit 2 for the first week or so of Stage 3, but thereafter, it only was necessary one or two times. This was required when the real-time display was not functioning properly. The sample cuvettes within the chlorine monitors were cleaned four times throughout the verification test (twice during extended deployment) to maintain accurate measurement. This process took approximately 15 minutes. The TOC analyzers were calibrated three times throughout the test, the reagents were changed out once, and the TOC manifold was cleaned two times: once after nitrogen flow had actually been blocked and once after the nitrogen supply had run out. According to the maintenance records, Hach Company staff cleaned the turbidimeter lines and checked its calibration two times throughout the verification test. The conductivity data from one contaminant injection was lost because of an air bubble. This was remedied by opening the conductance meter to release the bubble.

The data were downloaded from the EMTS using a USB port. The data were in a comma-delimited format that was easily opened into a spreadsheet. Overall, some of the regular maintenance such as cleaning the chlorine meter cuvette and turbidimeter and calibrating the TOC analyzer would have to be performed regularly if this system was placed in a remote location, requiring periodic site visits.

Chapter 7
Performance Summary

Evaluation Parameter			Total Chlorine	Turbidity	Temperature	Conductivity	pH	TOC
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		-47.4 to 4.5 (-3.9)	-53.9 to -1.3 (-34.1)	-3.0 to 44.3 (-0.2)	-15.5 to 8.1 (2.2)	-6.6 to 3.1 (0.9)	-64.7 to 147.5 (-14.8)
Stage 2—Response to Injected Contaminants	Nicotine	Reference	–	[a]	NC	NC	NC	+
		WDMP	–	+	NC	NC	NC	+
	Arsenic trioxide	Reference	–	[a]	NC	+	+	NC
		WDMP	–	+	NC	+	+	NC
	Aldicarb	Reference	–	[a]	NC	NC	NC	+
		WDMP	–	+	NC	NC	NC	+
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-15.9 to 6.9 (-3.2)	-81.1 to 245.5 (-21.3)	-7.4 to 8.5 (-0.1)	-1.8 to 9.6 (4.8)	-2.7 to 0.5 (-0.9)	-47.3 to 103.0 (-6.9)
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		-4.9	-5.9	-0.2	6.7	-2.2	-20.5
	Unit 2, %D		-4.9	-11.8	4.6	0.3	0.2	3.4
Stage 3—Response to Injected Contaminants	*E. coli*	Reference	–	+[b]	NC	+	–	+
		WDMP	–	+	NC	+	–	+
	Aldicarb	Reference	–	+[b]	NC	NC	–	+
		WDMP	–	+	NC	NC	–	+
Injection Summary	Total chlorine and TOC were dramatically affected by injections of nicotine, *E. coli,* and aldicarb; and turbidity, pH, and conductivity were affected by some or all of the injections, but not as consistently as total chlorine and TOC. Aldicarb altered the pH during Stage 3, but not Stage 2.							
Inter-unit Reproducibility (Unit 2 vs. Unit 1)	Slope (intercept)		0.98 (0.03)	0.97 (0.005)[c]	0.72 (7.68)	0.92 (4.19)	1.06 (-0.40)	0.97 (0.31)
	r^2		0.994	0.881[c]	0.758	0.961	0.919	0.991
	p-value		0.779	0.884[c]	5.5×10^{-6}	0.006	0.517	0.374
	With the exception of temperature and conductivity, both units generated similar results.							
Stage 4—Contaminant Identification	Each time a contaminant was injected, the EMTS detected a deviation in baseline conditions, causing a "trigger event." Eleven of 13 contaminants were correctly identified at some point during the injection time. Ferricyanide and lead nitrate were identified correctly 100% of the time. The rest of the injected contaminants were identified as a contaminant other than themselves at some point throughout the duration of the injection. Only nicotine and arsenic trioxide were never correctly identified.							
Ease of Use and Data Acquisition	Neither the WDMPs nor the EMTSs required daily operator attention. Hach Company staff adjusted the flows on the turbidity and total chlorine meters as needed to keep them at the required levels and rebooted the EMTS when it was not displaying data properly. The chlorine sensors and turbidimeters needed periodic cleaning, and the TOC analyzer was calibrated three times.							

[a] Relatively large uncertainty in the reference measurements made it difficult to detect a significant change.

[b] Magnitude of change different between duplicate injections.

[c] Outlier excluded.

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

NC = No change in response to the contaminant injection.

Chapter 8
References

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3. American Public Health Association, et al., SM 2510, Conductivity*,* in *Standard Methods for the Examination of Water and Wastewater.* 19th Edition, Washington, D.C., 1997.

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5. U.S. EPA, EPA Method 415.1, Total Organic Carbon, in *Methods for Chemical Analysis of Water and Wastes,* EPA/600/4-79/020, March 1983.

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7. U.S. EPA, EPA Method 180.1, Turbidity, in *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, March 1983.

8. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.

Appendix A
Hach Company Review

The following text summarizes the results acquired by the Hach Company after review of the ETV test results. This work was performed at its facility without EPA or Battelle QA oversight. The results should not be considered part of the ETV testing. Questions about these results should be directed to representatives of Hach Company.

To test whether the EMTS would identify pure glyphosate if it had been populated with data attained during the injection of that chemical, the water quality parameter fingerprint of pure glyphosate was added to the EMTS agent library; the contaminant previously called glyphosate was renamed Roundup™; and the identification algorithm was reapplied to the original ETV data. Table A-1 shows that, during the original ETV evaluation, very few of the agent alarms during the injection of glyphosate were reporting glyphosate; and, if they did, the match angles were typically weak. After Hach's update, the vast majority of alarms were reported as glyphosate, with mostly strong match angles.

In response to the results of the ETV test, The Hach Company updated the EMTS agent library by including additional arsenic trioxide data and then reanalyzed the original ETV test data. Table A-1 shows that, during the ETV evaluation, arsenic trioxide was never identified during its injection, while glyphosate (renamed Roundup™ for this reanalysis) was identified frequently. The updated data from Hach show that some agent alarms were reported as arsenic trioxide, but typically with low match angles. Also, Roundup™ was still identified frequently. The difficulty in identifying arsenic trioxide may be due to its partial solubility in water, making it difficult to maintain a consistent level during the injections into a pipe. The Hach Company noted that it also had difficulty in maintaining a consistent suspension for its agent library development.

The Hach Company previously (during non-ETV testing) identified nicotine with the EMTS rather successfully. It was noted that one difference between the nicotine solution used during the ETV test and that used during the agent library development was how vigorous the stirring had been during solution preparation. For ETV testing, the solution was stirred with a stirring attachment on an electric drill as opposed to a small stir bar used by the Hach Company during library development. The Hach Company performed an experiment both with and without vigorous mixing and determined that the vigorous mixing caused the basic form of nicotine to react with atmospheric carbon dioxide to form the neutralized form of nicotine, which had a lower characteristic pH than the basic form of nicotine. The EMTS agent library signature was updated to include the vigorously mixed nicotine, and the ETV data was reanalyzed as previously described for glyphosate and arsenic trioxide. The Hach Company did not provide the raw data for these results, but they did indicate that nicotine was identified with strong match angles during their independent testing.

Table A-1. Comparison of ETV Data and Data Updated by Hach

Injected Contaminant	Inj. #	Unit	Total # of IDs	Aldicarb			Arsenic Trioxide			Dicamba			Glyphosate			Mercuric Chloride			Malathion			Metha-midiphos			Roundup		
Quality of angle match				**W**	**M**	**G**	**W**	**M**	**G**	**W**	**M**	**G**	**W**	**M**	**G**	**W**	**M**	**G**	**W**	**M**	**G**	**W**	**M**	**G**	**W**	**M**	**G**
Glyphosate (ETV results)	1	1	9							0	0	1	1	1	1				4	0	0	1	0	0	NA		
		2	41		1	0	0			5	1	0	4	0	0	3	4	0	3	10	0	2	1	7			
	2	1	13							2	0	0	0	0	0	9	0	0	2	0	0						
		2	24							8	0	0	0			9	5	0	1	1	0						
Glyphosate (Hach Update)	1	1	40				3	3	2				3	4	17				4	0	0	1	0	0	0	2	1
		2	44				1	2	1	2	0	0	4	3	20	9	0	0	2	0	0						
	2	1	60	0	0	3	1	0	0	5	1	0	4	7	9	3	4	0	2	9	0	2	2	6	2	0	0
		2	59				5	1	0	8	0	0	2	7	20	9	5	0	1	1	0						
Arsenic Trioxide (ETV results)	1	1	19				0	0	0				16	3	0										NA		
		2	13						0				9	3	0				1	0	0						
	2	1	10						0				6	3	1												
		2	18						0				2	6	4				6	0	0						
Arsenic Trioxide (Hach Update)	1	1	24				4	2	0																5	7	6
		2	20				6	0	0																8	6	0
	2	1	25				0	1	1				1	5	0				1	0	0				5	6	5
		2	18				1	3	0																3	6	5

NA = Contaminant not injected during the ETV test.