

## Technology Evaluation Report

# GE Analytical Instruments Sievers® 900 Portable Total Organic Carbon Analyzer



# **Technology Evaluation Report**

GE Analytical Instruments

Sievers<sup>®</sup> 900

Portable Total Organic Carbon (TOC)  
Analyzer

United States Environmental Protection Agency  
Cincinnati, Ohio, 45268

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## Notice

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## Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development (ORD) 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.

In September 2002, EPA announced the formation of the National Homeland Security Research Center (NHSRC). The NHSRC is part of the Office of Research and Development; it manages, coordinates, supports, and conducts a variety of research and technical assistance efforts. These efforts are designed to provide appropriate, affordable, effective, and validated technologies and methods for addressing risks posed by chemical, biological, and radiological terrorist attacks. Research focuses on enhancing our ability to detect, contain, and decontaminate in the event of such attacks.

NHSRC's team of world renowned scientists and engineers is dedicated to understanding the terrorist threat, communicating the risks, and mitigating the results of attacks. Guided by the roadmap set forth in EPA's Strategic Plan for Homeland Security, NHSRC ensures rapid production and distribution of security-related products.

The NHSRC has created the Technology Testing and Evaluation Program (TTEP) in an effort to provide reliable information regarding the performance of homeland security related technologies. TTEP provides independent, quality assured performance information that is useful to decision makers in purchasing or applying the tested technologies. It provides potential users with unbiased, third-party information that can supplement vendor-provided information. Stakeholder involvement ensures that user needs and perspectives are incorporated into the test design so that useful performance information is produced for each of the tested technologies. The technology categories of interest include detection and monitoring, water treatment, air purification, decontamination, and computer modeling tools for use by those responsible for protecting buildings, drinking water supplies and infrastructure, and for decontaminating structures and the outdoor environment. Additionally, environmental persistence information is important for containment and decontamination decisions.

The evaluation reported herein was conducted as part of the TTEP program. Information on NHSRC and TTEP can be found at <http://www.epa.gov/nhsrc/ttep.html>.

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## Abbreviations/Acronyms

BC	biological contaminant
BSL	biological safety level
cm	centimeter
%D	percent difference
EPA	U.S. Environmental Protection Agency
L	liter
m	meter
m/s	meter per second
mg/L	milligram per liter
NHSRC	National Homeland Security Research Center
PBS	phosphate buffered saline
PE	performance evaluation
PPL	portable pipe loop
QA	quality assurance
QMP	quality management plan
SCADA	supervisory control and data acquisition
SOP	standard operating procedure
T&E	testing and evaluation
TIC	toxic industrial chemical
TOC	total organic carbon
TSA	technical systems audit
TTEP	Technology Testing and Evaluation Program
UVS	ultraviolet spectrometers
%U	experimental uncertainty
µg/L	microgram per liter



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## Executive Summary

The U.S. Environmental Protection Agency's (EPA's) National Homeland Security Research Center (NHSRC) Technology Testing and Evaluation Program (TTEP) is helping to protect human health and the environment from adverse impacts resulting from acts of terror by carrying out performance tests on homeland security technologies. Under TTEP, the performance of several online total organic carbon (TOC) analyzers and ultraviolet spectrometers (UVS) was evaluated. The primary objective of this series of evaluations was to determine the response of the TOC analyzers and UVSs upon the introduction of contaminants such as toxic industrial chemicals and biological contaminants into drinking water. This report describes the evaluation of the Sievers® 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, Colorado), hereafter referred to as the 900 Portable. The 900 Portable was operated in conjunction with EPA's portable pipe loop (PPL), which was designed to simulate a drinking water distribution system. Investigators injected 14 different contaminants into both chlorinated and chloraminated water and observed the change in the TOC measurement. For the purposes of this study, a "response" (i.e., an anomalous change) was identified as a post-injection change in TOC measurement that must exceed at least three times the standard deviation of the baseline TOC level for the 30 minutes prior to and after the contaminant injection. Relatively low contaminant concentration levels (0.01 - 10 mg/L) were selected because many of the contaminants pose health risks at low drinking water concentrations. In addition, to evaluate the accuracy of the 900 Portable, measurements of TOC were made daily using a laboratory reference method and compared with the results from the 900 Portable. Deployment and operational factors were also documented and reported.

### 900 Portable Responses to Contaminant Injections

Investigators injected the contaminants aldicarb, carbofuran, colchicine, diesel fuel, disulfoton, mevinphos, nicotine, potassium cyanide, sodium fluoroacetate, *Bacillus globigii*, *Bacillus thuringiensis*, *Chlorella*, ovalbumin, and ricin for testing. The contaminant injection solutions were prepared within 24 hours (most within 8 hours) in the same water that was within the PPL. Since this water contained disinfectants it could cause degradation or transformation of the contaminants prior to injection. The 900 Portable responded to all three replicate injections of colchicine and nicotine at concentrations from 0.1 mg/L–10 mg/L in both chlorinated and chloraminated water. In chlorinated water, aldicarb was detected in two of three injections at 0.1 mg/L and carbofuran was detected in one of three injections at 0.1 mg/L. In chloraminated water, aldicarb and carbofuran were both detected in one of three injections at 0.1 mg/L. All of

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the toxic industrial chemicals were detected during every injection at 1 mg/L and above (if injections were performed) with the exception of potassium cyanide which was only once detected at 1 mg/L in chlorinated and in chloraminated water, but was detected in all the 10 mg/L injections into both water matrices. The 900 Portable did not respond to injections of *Bacillus globigii* or *Chlorella* at any injected concentration. *Bacillus thuringiensis* produced a response at  $10^7$  organisms/L for a mixture of spores and vegetative cells in both chlorinated and chloraminated water. Ovalbumin produced a response for all injections at 0.1 mg/L, 1 mg/L, and 10 mg/L in chlorinated water and in chloraminated water produced a response for one injection at 0.1 mg/L and all injections at 1 mg/L and 10mg/L. Disulfoton, diesel fuel, and ricin were analyzed only as discrete samples. For these contaminants, the 900 Portable detected a change in TOC in response to 0.1 and 1 mg/L of carbofuran in both water matrices. Although diesel fuel was insoluble, it was added to water and analyzed using the 900 Portable. The results, however, were inconsistent and difficult to interpret. Disulfoton caused a response at 1 mg/L in both water matrices and ricin caused a response at 1 and 10 mg/L. In addition to these measurements, limited experiments were performed to examine the effect of elevated TOC, ionic strength, and monochloramine concentrations on the 900 Portable TOC measurements.

### **Accuracy of 900 Portable Measurements**

The TOC measurements from the 900 Portable were compared with those from a commonly used reference method and instrument during all of the contaminant injections performed during the evaluation. These comparisons should be interpreted with the awareness that different TOC instruments and oxidation methods can respond differently to various contaminants. Overall, the average absolute value of the percent difference (%D) between the 900 Portable and the reference method for all the comparisons across the evaluation was 17% plus or minus ( $\pm$ ) a standard deviation (SD) of 7%. For toxic industrial chemicals (TICs) the %D averaged  $15\% \pm \text{SD } 5\%$  and  $14\% \pm \text{SD } 8\%$ , for chlorinated and chloraminated water, respectively. For the biological contaminants, the %D averaged  $19\% \pm \text{SD } 3\%$  and  $15\% \pm \text{SD } 6\%$ , for chlorinated and chloraminated water, respectively. For each individual comparison, the experimental error was propagated using the uncertainty of both measurements and is reported. Throughout the evaluation of the 900 Portable, the propagated experimental uncertainty was typically small with respect to %D. There were only a few instances when the %D did not result in a major difference between the 900 Portable and the reference method.

### **Operational Characteristics**

During the evaluation of the 900 Portable, general operational characteristics were observed. Installation and operation of the 900 Portable was straight forward and clearly articulated by the vendor during a one day visit. Operation of the 900 Portable using the touch screen on the front panel was simple and intuitive. Evaluation staff initiated tests by pressing one button, they downloaded data by following on-screen prompts, and they replaced reagents and the ultra-violet (UV) lamp by following the instruction manual.

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The front panel of the 900 Portable provided messages to prompt the user to initiate maintenance tasks. In this evaluation, where individual experiments lasted approximately one day, the data from the 900 Portable were easily retrieved and were provided in a text delimited format enabling export into a spreadsheet. This evaluation did not consider other possible data retrieval methods (e.g. supervisory control and data acquisition [SCADA]) that could be utilized with the 900 Portable.

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## 1.0 Introduction

The U.S. Environmental Protection Agency's (EPA) National Homeland Security Research Center (NHSRC) is helping to protect human health and the environment from adverse impacts resulting from intentional acts of terror. With an emphasis on decontamination and consequence management, water infrastructure protection, and threat and consequence assessment, NHSRC is working to develop tools and information that will help detect the intentional introduction of chemical or biological contaminants into buildings or water systems, the containment of these contaminants, the decontamination of buildings and/or water systems, and the disposal of material resulting from clean-ups.

NHSRC's Technology Testing and Evaluation Program provides high-quality information that is useful to decision makers in purchasing or applying the evaluated technologies. It provides potential users with unbiased, third-party information that can supplement vendor-provided information. The Technology Testing and Evaluation Program (TTEP) works in partnership with recognized testing organizations, with stakeholder groups consisting of buyers and users of homeland security technologies, and with the participation of individual technology developers, in carrying out performance testing. Stakeholder involvement ensures that user needs and perspectives are incorporated into the evaluation design so that useful performance information is produced for each of the evaluated technologies. The program evaluates the performance of innovative homeland security technologies by developing evaluation plans that are responsive to the needs of stakeholders, conducting tests, collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted with rigorous quality assurance (QA) protocols to ensure that data of known and high quality are generated and that the results are defensible.

Under TTEP, the performance of the Sievers<sup>®</sup> 900 Portable Total Organic Carbon Analyzer (GE Analytical Instruments, Boulder, Colorado), hereafter referred to as the 900 Portable was evaluated. The primary objective of this evaluation was to determine the ability of the 900 Portable to detect changes in the total organic carbon (TOC) concentration in response to the introduction of contaminants into drinking water. Two other objectives were to evaluate the accuracy of the TOC measurement and to document deployment and operational characteristics. This evaluation was conducted according to a peer-reviewed test/QA plan<sup>(1)</sup> that was developed according to the requirements of the TTEP quality management plan (QMP) and associated amendments.<sup>(2)</sup>

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## 2.0 Technology Description

This report provides results for the evaluation of the 900 Portable. A description of the 900 Portable based on information provided by the vendor follows.



**Figure 2-1. 900 Portable**

Figure 2-1 shows the 900 Portable as configured for this evaluation. The 900 Portable consisted of a portable analyzer with all analysis, control, data storage, and data visualization capabilities integrated into one package. The enclosure for the 900 Portable was 23 centimeters (cm) wide, 48 cm deep, and 36 cm tall.

The 900 Portable measures TOC and, while not used during this evaluation, has the capability to measure total inorganic carbon and total carbon. The 900 Portable oxidizes organic compounds using UV radiation and a chemical oxidizing agent, ammonium persulfate, to form carbon dioxide. Carbon dioxide is measured using a selective membrane-based conductometric detection technique. As configured for this evaluation, a separate inorganic carbon removal module was

included with the 900 Portable.

All data collection and storage is integrated into the 900 Portable package. Analysis results are displayed in a chart on the front panel as they are collected. Data can be downloaded using either an USB or serial connection. Data files from the 900 Portable are stored as comma delimited text.

The 900 Portable requires two reagents, an acid and an oxidizer. These reagents are housed within the enclosure and must be changed as needed (typically six months for the acid and three months for the oxidizer). The UV lamp must be replaced every six months. The total cost of the 900 Portable as configured for this evaluation is \$22,800. (There is a non-portable version of the same instrument that costs \$21,900 and has two customizable alarm outputs that can be triggered if the measured TOC exceeds a set value.) The estimated yearly non-labor operation and maintenance costs are expected to be approximately \$2,400 including such items as the reagents and the ultraviolet lamp.

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### 3.0 Experimental Details

The primary objective of this series of evaluations was to determine the capability of TOC analyzers and ultraviolet spectrometers (UVSs) to measure changes in TOC level due to the introduction of contaminants into drinking water. Four technologies, two TOC analyzers and two UVSs, were evaluated. Two drinking water matrices were used for all of the testing conducted in this evaluation: (1) finished drinking water from Columbus, Ohio (chlorinated and filtered surface water), and (2) water prepared to simulate water from a utility that uses chloramination as its primary means of disinfection. Eleven contaminants were injected using the EPA's portable pipe loop (PPL) and four contaminants were analyzed using a discrete analysis approach.

This series of evaluations took place between June 3, 2009 and September 24, 2009. The contractor and EPA provided QA oversight of this evaluation. The contractor QA staff conducted a technical systems audit (TSA) and an audit of data quality.

#### 3.1 Portable Pipe Loop and Experimental Setup

This series of evaluations was conducted using EPA's Portable Pipe Loop (PPL), which is shown in Figure 3-1. The PPL consists of: (1) an equipment rack that contains a 78 liter (L) stainless steel mixing tank, a recirculating pump, a peristaltic pump, and three contaminant injection ports; and (2) a piping rack that contains approximately 29 meters (m) of 7.6 cm diameter stainless steel pipe (316L grade). The two racks were connected for the evaluation. All four TOC analyzers and UVSs evaluated were connected to the PPL by one of the eight separate sample ports with 6.35 millimeter (mm) (or one quarter inch) inner diameter tubing.

The variable flow recirculating pump controlled PPL flow which allowed the operator to set flow rates from 44 to 440 liters/minute (L/min) in the PPL. For testing, the PPL contained approximately 250 L of water (including the mixing tank and pipe) with a flow rate of approximately 88 L/min (linear velocity of 0.33 m/s). Because of the addition of reagents to the water, the water sampled by the two TOC analyzers was discharged to a waste container after analysis.

When evaluating several technologies simultaneously, an adequate flow of water must be maintained to supply each of the technologies. The 900 Portable sampled a 2.5 milliliter sample from the flowing water every 4 minutes. Excess sample flow and waste from the 900 Portable were combined and then collected into a waste container.



**Figure 3-1. EPA's portable pipe loop**

### **3.2 Baseline Conditions**

Prior to the start of daily testing, investigators filled the PPL with drinking water using a hose (15.9 mm or 5/8" ID) and a hose-thread to sanitary-fitting coupler that connected the laboratory water supply to the PPL mixing tank. During the chlorinated water testing, this water was used with no alterations after the free chlorine level was measured using U.S EPA Method 330.5.<sup>(8)</sup> Over the course of the evaluation, free chlorine concentrations in the chlorinated water ranged from 1.0 to 1.6 mg/L with an average of 1.3 mg/L. The pH of the water was between 7.4 and 8.1.

The chloraminated test water matrix was prepared by mixing chlorine and ammonia in the proper ratio to yield approximately 2 mg/L monochloramine, following an EPA Testing & Evaluation (T&E) Facility standard operating procedure (SOP) for preparation of chloraminated water.<sup>(3)</sup> Investigators measured the total chlorine concentration and then added chlorine to the PPL to increase the total chlorine concentration to 2 mg/L. The total chlorine concentration was then measured again to confirm the total chlorine concentration was within 10% of 2 mg/L. Ammonia was then added to the PPL to form monochloramine at a concentration of 2 mg/L in the PPL. Prior to the injection of a contaminant, the monochloramine concentration was confirmed using Hach<sup>®</sup>

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Method 10200<sup>(8)</sup>. Throughout the evaluation, the monochloramine concentrations ranged from 1.8 to 2.3 mg/L with an average of 2.0 mg/L.

Once investigators completed the applicable chlorine measurement, they conducted a 30 minute baseline measurement using the 900 Portable. During this baseline measurement period, a reference sample was collected from an unoccupied PPL sampling port. The reference sample was collected by flushing approximately 500 mL of water from the sampling port into a waste container and then collecting two separate 40 mL vials of sample. The reference samples were immediately preserved by acidification with phosphoric acid. Reference samples were analyzed daily on the TOC reference instrument which was housed in the same laboratory as the PPL. The reference TOC results were used to evaluate the accuracy of the TOC measurements from the 900 Portable.

### 3.3 Portable Pipe Loop (PPL) Contaminant Injections

The toxic industrial chemicals (TICs) and biological contaminants (BCs) were injected into the PPL as concentrated 250 mL solutions. These solutions were prepared within 8 hours of injection (with the exception of the discrete samples which were prepared the day before) using the same water used to fill the PPL, either chlorinated or chloraminated. The preparation of contaminant injection solutions with water containing disinfectants could cause degradation or transformation of the contaminant. For example, the interaction of the cyanide ion with chlorinated water could have formed cyanogen chloride which continued to breakdown to the cyanate ion. These reactions are dependent on the water quality of the dissolution water so the results presented here should be interpreted carefully and not broadly extrapolated. However, the experimental plan was intended to simulate an actual contamination event during which the use of tap water as the dissolution solvent would be expected. In addition, degradation of organic carbon drinking water is not likely so, for the 900 Portable, the presence of a contaminant could still be measured.

Table 3-1 shows the sources of each TIC and toxin contaminants and their purity. The purity of the TICs varied substantially from 89% to 99%. Information about the content of the impurities for each contaminant was not available so the impurities could have contained organic carbon. In addition, aldicarb, carbofuran, and disulfoton were difficult to dissolve and required gentle heating to encourage them into solution. Heating these solutions could have favored transformations thereby preventing the stated contaminant (and instead transformational product) from being injected into the PPL.

Originally, the two *Bacillus* species were grown in nutrient broth while the *Chlorella* was grown in Bold INV Medium<sup>(9)</sup>. The final BC cultures were pelleted by centrifugation and washed in PBS three times. The washed pellet cake was then resuspended in phosphate buffered saline (PBS). The BC solution was enumerated and injection solutions were prepared by diluting the BC to the appropriate concentrations in PBS. The concentration of each injection solution was such that injection of 250 mL of the solution into 250 L of water in the PPL gave the desired steady-state concentration in the PPL.



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**Table 3-1 Source and Purity of Contaminants**

Contaminant	Supplier	Purity
Aldicarb	Ultra Scientific (North Kingston, RI)	99%
Carbofuran	Sigma-Aldrich (St. Louis, MO)	98%
Colchicine	Sigma-Aldrich (St. Louis, MO)	97%
Diesel	Marathon (Columbus, OH)	Retail-grade (from pump)
Disulfoton	Chem Service (West Chester, PA)	98.7%
Mevinphos	Ultra Scientific (North Kingston, RI)	89.4%
Nicotine	Acros Organics (Geel, Belgium)	98%
Ovalbumin	MP Biomedicals (Solon, OH)	98%
Potassium Cyanide	Sigma-Aldrich (St. Louis, MO)	96%
Ricin	Vector Laboratories (Burlingame, CA)	5 mg/mL (in phosphate buffered sodium azide)
Sodium Fluoroacetate	Sigma-Aldrich (St. Louis, MO)	99%
Sodium Fluoroacetate	Pfaltz & Bauer (Waterbury, CT)	95%

Upon establishing a steady response in the PPL and collecting a minimum of 30 minutes of baseline data, a series of single contaminant injections was made into the circulating water of the PPL. With each injection, the concentration of the contaminant at any point within the PPL changed until a steady-state concentration for the contaminant was reached. As the contaminant stock solution was introduced into the intake side of the recirculating pump of the PPL, the initial contaminant “slug” made a first pass by the 900 Portable intake. The contaminant concentration within the slug was higher than the eventual steady-state contaminant concentration within the PPL. As the contaminant slug flowed throughout the PPL, it entered the mixing tank, became greatly diluted, and then recirculated until, within about 10 minutes, a steady-state concentration was reached. This evaluation focused on the steady-state concentration reached in the PPL after mixing. The mixing time of approximately 10 minutes and the measurement frequency of 4 minutes prevented the initial contaminant slug through the PPL from being measured by the 900 Portable TOC. However, in an operational setting, the 900 Portable would be able to measure continuous changes in TOC as long as the changes being measured lasted for at least four minutes.

Starting with the lowest concentration level for each contaminant, the contaminant injection solution was pumped into the circulating water of the PPL at a rate that made the concentration of the contaminant 10 times greater than the eventual steady-state concentration in the water moving past 900 Portable. This injection lasted for 15-20 seconds, which at a flow rate of 88 L/min (linear velocity of 0.33 m/s) corresponds to approximately a 4.5 m long (~25 L) slug of injected contaminant at the desired concentration.

A steady-state TOC concentration was reached in the PPL approximately 10 minutes after the contaminant injection. To ensure that the contaminant concentration had reached steady-state, investigators allowed a 20 minute stabilization period after a contaminant injection. After this 20 minute stabilization period, 30 minutes of data from each instrument were collected at the post-injection steady-state concentration. In addition to being used to determine the steady-state response for each instrument, these

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30 minutes of data were used as the baseline for the next contaminant injection. The next higher concentration level of contaminant was introduced using an identical procedure. Therefore, a minimum of 50 minutes passed between contaminant injections. One reference sample was collected when the PPL reached the steady-state concentration following each contaminant injection. A duplicate sample was taken for one reference sample during each day of testing.

Each set of contaminant injections with increasing concentration levels (some contaminants had three concentration levels, some had four concentration levels) represented one replicate. Three replicate sets of injections were made for each contaminant. Between the replicate sets of injections, the PPL system was exchanged at least five times with contaminant-free water (from the laboratory supply). As this uncontaminated water filled the PPL, the online measurements returned to the original baseline. Once five water exchanges had been completed (approximately 30 minutes of water exchange) and the response from each technology steadied so it deviated from the average by less than 10% over 30 minutes, testing proceeded with the next replicate set of injections for that contaminant.

### **3.4 Discrete Sample Analysis**

Three contaminants (diesel fuel, disulfoton, and ricin) were analyzed with the 900 Portable solely as discrete samples rather than injections into the PPL. PPL use was precluded for ricin because it must be contained within a biosafety hood. Disulfoton was added to the experimental plan in the same test/QA plan amendment as ricin and was analyzed in the same fashion. Diesel fuel was analyzed discretely out of concern that it would contaminate the PPL. Carbofuran was analyzed discretely and also with the PPL so that one contaminant would be analyzed using both experimental approaches. For the discrete samples, investigators prepared 40 mL vials of chlorinated and chloraminated water contaminated to the desired concentration along with vials of uncontaminated water. In grab sample mode, the 900 Portable analyzed four samples from the same vial and reported the concentration as the average of the final three measurements. Following analysis of the uncontaminated water samples, the 900 Portable analyzed the vial containing the lowest contaminant concentration. This process was repeated for all concentrations measured. Three vials of each concentration were analyzed as discrete samples.

The 0.01 mg/L contaminant concentration was not evaluated by discrete analysis. In addition, due to poor solubility, disulfoton and carbofuran were not analyzed at 10 mg/L as discrete samples. Diesel fuel was insoluble in water and separated upon mixing with water, but discrete sample analyses at 10 mg/L were still performed.

### **3.5 Contaminant Concentrations**

Table 3-1 gives the injected contaminants and their corresponding concentrations. As described in the test/QA plan<sup>(1)</sup>, TIC injection concentrations were selected based on previous testing performed at EPA's Testing and Evaluation (T&E) Facility<sup>(4)</sup> BC injection concentrations were based on relevant toxicological data (e.g., infective dose)<sup>(5)</sup>

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as well as concentrations recommended by TTEP water security stakeholders. The 0.01 mg/L contaminant solutions were injected into the PPL during the evaluation and the results reported for the 900 Portable. However, 0.01 mg/L is very near the detection limit of the 900 Portable. Therefore, because the contaminants being injected contained both organic and inorganic carbon, detectable results for TOC were not necessarily expected for the 0.01 mg/L concentration level.

## **3.6 Data Analysis**

### ***3.6.1 Response***

During the evaluation, the 900 Portable made TOC measurements once every 4 minutes. The baseline concentration of TOC prior to injection is defined as the average concentration over the 30 minute baseline measurement period before each injection. Baseline measurement periods following injections began 20 minutes after the previous injection. For the purposes of this study, the 900 Portable was considered able to detect an anomalous change or “response” in TOC concentration following a contaminant injection if the absolute change ( $\Delta\text{TOC}$ ) in TOC concentration was at least three times the standard deviation of the baseline TOC concentration prior to the contaminant introduction and three times the standard deviation of the post-injection TOC concentration measurements. To simplify wording, in this report an anomalous change will be referred to as a “response” to the contaminant injection. The response threshold of three times the standard deviation was selected subjectively to indicate a change from baseline as part of this evaluation. Depending on operational parameters of a water system, a change in TOC that is at least three times the standard deviation of the baseline, may or may not be of concern in terms of a contamination event.

In addition to the injection of the seven TICs, control injections of both chlorinated water and chloraminated water were performed to determine if the act of injecting water into the PPL caused a response for the 900 Portable. Water for control injections was removed from the PPL and then injected back into the PPL within 4 hours. Five such injections resulted in a standard deviation of 0.03 mg/L around zero TOC. Therefore, in addition to the requirement for a response described in this section, a second requirement for a response was that it must exceed the average and standard deviation of the blank injections. Following this criteria (in addition to a change in TOC being at least three times the baseline TOC), the threshold for detection was a change of 0.03 mg/L.

**Table 3-2. Contaminant List**

Type	Agent	Analysis Method	Concentrations	Medium
Toxic Industrial Chemicals	Aldicarb <sup>†</sup>	PPL	0.01, 0.1, 1 (mg/L)	Water
	Carbofuran	PPL, discrete	0.01, 0.1, 1, 10 (mg/L)	Water
	Colchicine	PPL	0.01, 0.1, 1, 10 (mg/L)	Water
	Cyanide	PPL	0.01, 0.1, 1, 10 (mg/L)	Water
	Diesel fuel	Discrete	0.1, 1, 10 (mg/L)	Water
	Disulfoton	Discrete	0.1, 1 (mg/L)	Water
	Mevinphos <sup>†</sup>	PPL	0.01, 0.1, 1 (mg/L)	Water
	Nicotine	PPL	0.01, 0.1, 1, 10 (mg/L)	Water
	Sodium Fluoroacetate	PPL	0.01, 0.1, 1, 10 (mg/L)	Water
Biological Contaminants	<i>Bacillus thuringiensis</i> (surrogate for <i>Bacillus anthracis</i> )	PPL	10 <sup>3</sup> , 10 <sup>4</sup> , 10 <sup>5</sup> , 10 <sup>6</sup> , 10 <sup>7</sup> (spores/L)	PBS and Nutrient Broth
	<i>Bacillus globigii</i> (surrogate for <i>Bacillus anthracis</i> )	PPL	10 <sup>3</sup> , 10 <sup>4</sup> , 10 <sup>5</sup> , 10 <sup>6</sup> , 10 <sup>7</sup> (spores/L)	PBS and Nutrient Broth
	<i>Chlorella</i> (surrogate for <i>Cryptosporidium</i> )	PPL	10 <sup>3</sup> , 10 <sup>4</sup> , 10 <sup>5</sup> (cells/L)	PBS and Bold 1NV Medium
Toxins	Ovalbumin (surrogate for botulinum toxin and ricin)	PPL	0.01, 0.1, 1, 10 (mg/L)	Water
	Ricin	Discrete	0.1, 1, 10 (mg/L)	Buffered sodium azide
Controls	Water	PPL	‡	Water
	PBS/nutrient broth	PPL	‡	Water
	PBS/Bold 1NV medium	PPL	‡	Water
	Buffered sodium azide	Discrete	‡	Water

PBS-phosphate buffered saline

<sup>†</sup>No 10 mg/L injections due to the response at 1 mg/L and the prohibitive cost of 10 mg/L injections.

‡ Concentrations (or volumes for water injections) equivalent to those present in contaminant injections.

The magnitude of a change in TOC concentration was calculated and expressed as  $\Delta\text{TOC}$ . The signal change of the 900 Portable as  $\Delta\text{TOC}$  for TOC was calculated using Equation 1:

$$\Delta\text{TOC} = \text{TOC} - \overline{\text{TOC}}_{\text{baseline}} \quad (1)$$

where TOC is the average post-injection TOC concentration measured by the 900 Portable (mg/L); and  $\overline{\text{TOC}}_{\text{baseline}}$  is the average baseline TOC concentration as determined by the 900 Portable (mg/L).

### 3.6.2 Accuracy

Results from the evaluation of the 900 Portable were compared to the results obtained from analysis of reference grab samples collected during the same period. The results for each sample are expressed in terms of the percent difference (%D) between the 900 Portable measurement and the reference measurements calculated from Equation 2:

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$$\%D = \frac{OC - OC_R}{1/2(OC + OC_R)} \times 100$$

(2)

where  $OC_R$  is the concentration determined by the reference method (mg/L) and  $OC$  is the average measurement from the 900 Portable when the reference sample was collected (mg/L). Ideally, if the results from the 900 Portable and reference method measurement are the same, %D would equal zero.

The combined experimental uncertainty (%U) of the %D was determined using the method of propagation of errors and is defined by Equation 3:

$$\%U = 100 \times \sqrt{16(OC + OC_R)^{-4} \times (OC_R^2 S_{OC}^2 + OC^2 S_{OCR}^2)} \quad (3)$$

where  $S_{OCR}$  and  $S_{OC}$  are the standard deviations of  $OC_R$  and  $OC$ , respectively.

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## 4.0 Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the program QMP<sup>(2)</sup> and the test/QA plan<sup>(1)</sup> for this evaluation.

### 4.1 Reference Method

EPA Method 415.3<sup>(6)</sup> was used to analyze reference samples for TOC concentration. The reference instrument was a Teledyne-Tekmar (Mason, OH) Fusion TOC Analyzer<sup>TM</sup>. Reference samples were collected immediately after contaminant injections as well as after the contaminant had become well-mixed in the PPL (steady-state). The analysis method is summarized in Table 4-1.

**Table 4-1. Summary of Total Organic Carbon Reference Method**

<b>Instrument</b>	<b>Method</b>	<b>Measurement Principle</b>	<b>Detection Limit</b>	<b>Maximum Holding Time</b>
Teledyne-Tekmar FusionTOC Analyzer <sup>TM</sup> (Mason, OH)	EPA 415.3 <sup>6</sup> (Standard Method 5310C)	UV/persulfate oxidation	0.2 µg/L	28 days with acidification to pH ≤2

### 4.2 Instrument Calibration

The contractor connected the 900 Portable to the PPL and the vendor representative verified the instrument was operating properly. The vendor calibrated the 900 Portable prior to shipment to the contractor and verified the calibration prior to testing using vendor-provided calibration verification standards. A single point calibration for total carbon and inorganic carbon was performed at 10 mg/L. Following the calibration, 5 mg/L verification standards were analyzed to verify the calibration.

The reference instrument was calibrated by the evaluation staff once prior to the start of the evaluation and once per month throughout the approximately three month duration of testing. Calibration check standards were analyzed with every batch of samples analyzed using the TOC reference instrument to ensure that the reference instrument calibration had not drifted. With the exception of one out of 56 days of analysis that occurred during that three month time period, all calibration check standard analysis results were within the required tolerance. Samples from that day were reanalyzed the next day, and the calibration check standards for the reanalysis were within the acceptable tolerance.

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## 4.3 Audits

### 4.3.1 Performance Evaluation (PE) Audit

A performance evaluation (PE) audit was conducted to assess the accuracy of the TOC reference method. A PE sample containing 5 mg/L organic carbon as potassium hydrogen phthalate was obtained (Pharmaceutical Resource Associates [Environmental Resource Associates], Arvada, CO) and analyzed. Accuracy of the TOC measurement was expressed in terms of the percent error (%E), as calculated from the following equation:

$$\% E = \frac{d - C_R}{C_R} \times 100$$

(3)

where  $C_R$  was the standard or reference concentration of the PE sample and  $d$  is the measurement obtained using the reference method. Ideally, if the reference value and the measured value are the same, there would be a percent error of zero. Table 4-2 shows that the results of the PE audit was below the maximum allowed %E for TOC.

**Table 4-2. Performance Evaluation Audit Results**

Reference Sample	Expected Result	Reference Method Result	%E	Maximum Allowed (%E)
TOC (Pharmaceutical Resource Associates, Arvada, CO)	5.00 mg/L	5.30 mg/L	6.0	20

TOC, total organic carbon

### 4.3.2 Technical Systems Audit (TSA)

The contractor QA manager conducted a technical systems audit (TSA) at the Columbus, Ohio testing location to ensure that the evaluation was performed in accordance with the test/QA plan<sup>(1)</sup> and the TTEP QMP<sup>(2)</sup>. As part of the audit, the contractor QA manager reviewed the reference sampling and analysis methods used, compared actual evaluation procedures with those specified in the test/QA plan<sup>(1)</sup>, and reviewed data acquisition and handling procedures. No adverse findings were noted in this audit. The records concerning the TSA are permanently stored with the contractor QA manager.

### 4.3.3 Amendments/Deviations

Investigators made one amendment to the test/QA plan for this evaluation. To accommodate the latest needs of EPA's homeland security mission the amendment changed the list of contaminants to be tested. The amendment removed cesium, as well as the chemical warfare agents VX, soman, and sarin from the contaminant list and added

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ricin, disulfoton, mevinphos, and sodium fluoroacetate, to the list of injected contaminants. The amendment stipulated that sodium fluoroacetate and mevinphos be evaluated in the PPL and that ricin and disulfoton be evaluated as discrete samples, and also changed the tests with diesel fuel from using the PPL to testing diesel as discrete samples.

Throughout the course of testing, there were a few instances of slight deviation from the test/QA plan.

- The PE sample for the reference method was analyzed after the first tests were conducted rather than before testing began. The first attempt at the PE audit was unsuccessful due to the use of PE audit samples that contained chemical constituents that interfered with only the reference TOC instrument. However, two TOC standards (one provided by the vendor) were measured accurately by the reference method during preparation for the evaluation. Therefore, the evaluation staff had a high degree of confidence in the accuracy of the reference method/instrument. Instead of holding up the evaluation, testing proceeded while interferent-free PE audit samples were being obtained.
- Investigators used an alternate test method for monochloramine. Rather than using the difference between total and free chlorine (EPA method 330.5)<sup>(7)</sup>, a test for monochloramine (Hach<sup>®</sup> Method 10200),<sup>(8)</sup> was used to determine the monochloramine level in the chloraminated water used for testing.
- In addition to the levels specified in the test/QA plan (0.1, 1, and 10 mg/L) for the TICs, injections at 0.01 mg/L were included in the test matrix. Some of the technologies being assessed were more sensitive than investigators had anticipated to the 0.1 mg/L injections. The injections at 0.01 mg/L were added to better understand the performance of the analyzers at the low end of their measurement range. In addition, because the 1 mg/L injections of aldicarb and mevinphos were detected by all the technologies and the injection of 10 mg/L would have been extremely expensive, the 10 mg/L tests were not performed.
- For the elevated TOC component of the testing, the TOC was elevated by approximately 1 mg/L rather than 2 mg/L because of the change in background TOC of the source water on the day of testing.
- Concentrations of the BCs were increased to include samples at 10<sup>6</sup> and 10<sup>7</sup> organisms/L to identify detectable levels.
- Percent difference was used to compare the reference method with the 900 Portable instead of percent error.



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#### ***4.3.4 Data Quality Audit***

At least 10% of the data acquired during the evaluation were audited. The contractor QA 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.

#### **4.4 Quality Assurance/Quality Control (QA/QC) Reporting**

Each assessment and audit was documented in accordance with the test/QA plan<sup>(1)</sup> and the QMP.<sup>(2)</sup> Once an assessment report was prepared by the contractor QA manager, it was routed to the EPA task order leader and the TTEP contract manager for review and approval. The contractor QA manager then distributed the final assessment report to the EPA task order project officer and the contractor QA manager.

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## 5.0 Evaluation Results

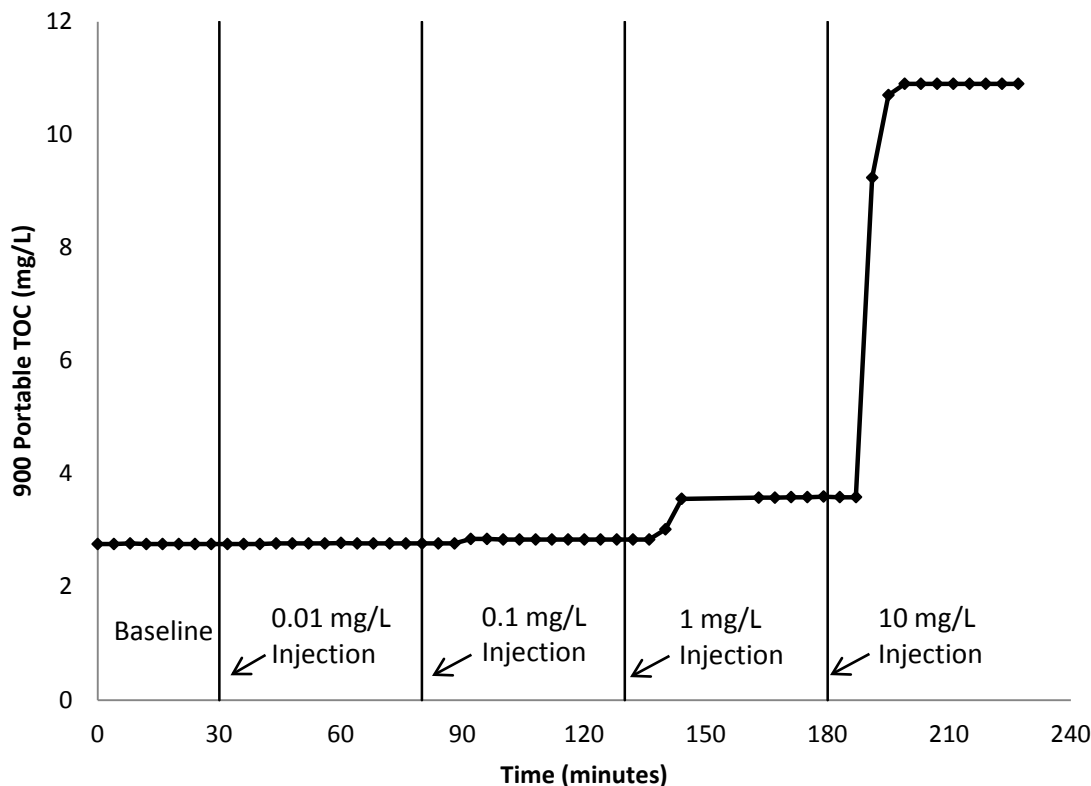
This section presents the evaluation results including the ability of the 900 Portable to measure changes in TOC concentrations in response to the injection of TICs, toxins, and BCs into drinking water. Also given are the accuracy of the 900 Portable TOC measurements and the operational characteristics of the 900 Portable that were observed during the evaluation.

### 5.1 Toxic Industrial Chemicals (TICs) in Drinking Water

#### 5.1.1 900 Portable Response to TIC Injections

A total of seven toxic industrial chemicals (TICs) were individually injected into the PPL at the concentration levels given in Table 3-2. As described in Section 3.3, contaminant injections were performed in sets. Each set consisted of sequential injections of increasing concentration to attain the target contaminant concentrations in the PPL. Three sets of injections were performed for each contaminant. Section 3.6.1 thoroughly describes the change in TOC concentration that was considered a “response” to a contaminant injection. After each set of TIC injections, the PPL was flushed with uncontaminated drinking water before the next set of injections was performed. The results presented in this report reflect the scenarios specific to those defined by the test/QA plan for this evaluation. As discussed in Section 3.3, it is possible that chemical transformations took place during the solution preparation prior to contaminant injections into the PPL.

Figure 5-1 shows an example of the 900 Portable response to one set of colchicine injections into chlorinated water. Injections of colchicine are marked on Figure 5-1 with vertical lines and labeled with the concentration level. The TOC concentration over the time period prior to the first injection was used as the baseline TOC concentration for the 0.01 mg/L injection. In the set of injections shown, the 900 Portable did not have a response to the 0.01 mg/L injection of colchicine but the 900 Portable did have a response to the 0.1, 1, and 10 mg/L injections. During the 1 and 10 mg/L injections, the 900 Portable concentration did not increase until the third measurement after the contaminant was injected into the PPL. This is because the 900 Portable only draws sample for analysis once every four minutes. Therefore, the first reported concentration (represented by the points on the line representing the TOC values in Figure 5-1) following the injection represented water that had been drawn into the 900 Portable before the contaminant injection and the second reported concentration represented water that was drawn into the 900 Portable prior to the time when the water in the PPL was well mixed. The data gap after the 1 mg/L injection was due to a reagent syringe fill cycle that occurs periodically during 900 Portable operation.



**Figure 5-1. Change in 900 Portable total organic carbon (TOC) in response to injections of colchicine.**

Table 5-1 presents the contaminant injected, the concentration of the injected contaminant, and the average and standard deviation of the measured change in TOC (as measured by replicate measurements of the 900 Portable) for each TIC injection. Those injections which were determined to produce a response (as defined previously) from the 900 Portable are highlighted in gray. The average change in TOC for reference samples collected for the three replicates and analyzed by EPA Method 415.3 is also included. Changes in TOC measured by the reference instrument were determined using the standard deviation of the check standard analyses. Investigators used these samples because the uncertainty of the reference method without the influence of the background TOC (which varied daily) could be determined. The check standard was always the same standard. Over the course of the evaluation, the standard deviation of reference analyses of 2 mg/L check standards was 0.04 mg/L with an average of 2.13 mg/L for 28 samples. Therefore, changes in TOC measured by the reference instrument greater than 0.12 mg/L (three times the standard deviation) are highlighted in gray as changes in response to contaminant injections.

The 900 Portable and the reference method measure the TOC concentration and not the contaminant concentration (which would include all non-organic carbon substituents). Therefore, the reference method and 900 Portable results would not be expected to be the same as the injected nominal contaminant concentration, but the changes in TOC as

**Table 5-1. Change in 900 Portable Total Organic Carbon (TOC) from Injections of Toxic Industrial Chemicals (TICs) into Chlorinated Water**

Contaminant	Injected Contaminant Conc. (mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Injection 1		Injection 2		Injection 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
Aldicarb	0.01	-0.05	-0.13	0.030	-0.02	0.021	0.02	0.020
	0.1	0.08	-0.11	0.030	0.05	0.008	0.08	0.020
	1	0.46	0.48	0.042	0.52	0.011	0.48	0.005
Carbofuran	0.01	-0.03	0.01	0.005	0.01	0.051	-0.05	0.021
	0.1	0.04	0.02	0.004	0.10	0.015	0.02	0.011
	1	0.52	0.45	0.004	0.68	0.021	0.60	0.109
	10	4.05	3.45	0.208	7.36	0.580	6.90	0.238
Colchicine	0.01	0.02	0.01	0.004	0.00	0.011	-0.02	0.013
	0.1	0.07	0.07	0.004	0.11	0.005	0.07	0.004
	1	0.66	0.75	0.007	0.71	0.008	0.75	0.000
	10	8.02	7.31	0.007	7.37	0.008	7.45	0.045
Mevinphos	0.01	-0.01	†	†	0.00	0.005	0.00	0.007
	0.1	0.04	0.04	0.005	0.04	0.005	0.04	0.004
	1	0.36	0.40	0.005	0.39	0.005	0.39	0.005
Nicotine	0.01	0.06	‡	‡	0.01	0.005	0.06	0.008
	0.1	0.03	0.08	0.005	0.09	0.005	0.08	0.005
	1	0.67	0.88	0.004	0.87	0.005	0.92	0.000
	10	7.01	8.16	0.000	7.68	0.035	8.02	0.049
Potassium Cyanide	0.01	0.03	-0.01	0.008	-0.02	0.012	-0.02	0.005
	0.1	0.02	0.01	0.005	0.01	0.005	0.00	0.005
	1	0.02	0.03	0.008	0.01	0.005	0.02	0.000
	10	0.34	0.08	0.021	0.06	0.019	0.05	0.005
Sodium Fluoroacetate	0.01	0.02	0.00	0.005	-0.01	0.011	0.00	0.005
	0.1	0.01	0.03	0.005	0.02	0.005	0.00	0.005
	1	0.25	0.25	0.017	0.27	0.005	0.19	0.029
	10	1.98	1.81	0.290	2.07	0.040	1.86	0.444
Water Controls	None	0.01	-0.03	0.00	0.00	0.00	0.01	0.00
			0.04	0.00	0.00	0.00	0.00 <sup>#</sup>	0.02 <sup>#</sup>

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

† 900 Portable had to be restarted immediately following this injection.

‡ Only two replicates of the 0.01 mg/L nicotine injections were performed.

<sup>#</sup> Average and standard deviation of water controls.

measured by the reference method should be similar to the changes in TOC measured by the 900 Portable. In this case, the 900 Portable is being compared with a UV-persulfate oxidation method and there may be inherent differences in how each method measure a particular compound. Therefore, the differences in results between the 900 Portable and the reference method may or may not indicate a deficiency in the 900 Portable.

In chlorinated water, with the exception of one injection of nicotine, the 900 Portable did not respond to any contaminants at 0.01 mg/L. Carbofuran produced a response from the

900 Portable for one of the three replicates at 0.1 mg/L. Aldicarb produced a response from the 900 Portable for two out of three replicates at the 0.1 mg/L injection level. Colchicine and nicotine produced a response from the 900 Portable for all replicates at 0.1 mg/L. Mevinphos was detected at both 0.1 and 1 mg/L. Potassium cyanide did not produce a response from the 900 Portable for any 0.1 mg/L injection. With the exception of two injections of potassium cyanide, all injections at 1 mg/L produced a response from the 900 Portable. The 900 Portable measured responded to the injection of 10 mg/L of each contaminant. For all the TIC injections into chlorinated water, the 900 Portable responded at or below all contaminant concentrations for which the reference method responded.

Table 5-2 presents the same information for injections made into the chloraminated water

**Table 5-2. Change in 900 Portable Total Organic Carbon (TOC) from Injections of Toxic Industrial Chemicals (TICs) into Chloraminated Water**

Contaminant	Injected Conc. (mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Injection 1		Injection 2		Injection 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
Aldicarb	0.01	-0.04	-0.11	0.031	-0.06	0.017	0.01	0.005
	0.1	0.15	-0.05	0.031	0.07	0.032	0.06	0.000
	1	0.39	0.51	0.006	0.51	0.032	0.50	0.000
Carbofuran	0.01	0.11	-0.03	0.014	-0.23	0.051	-0.04	0.027
	0.1	0.03	0.05	0.009	-0.06	0.051	0.06	0.031
	1	0.63	0.71	0.108	0.55	0.046	0.70	0.031
	10	4.88	8.21	0.185	9.80	1.031	8.78	0.348
Colchicine	0.01	-0.02	0.00	0.004	-0.06	0.052	0.00	0.004
	0.1	0.08	0.08	0.004	0.07	0.004	0.07	0.007
	1	0.69	0.67	0.012	0.66	0.022	0.72	0.007
	10	6.41	6.59	0.123	6.66	0.087	7.11	0.021
Mevinphos	0.01	0.01	0.00	0.000	0.01	0.004	0.00	0.004
	0.1	0.05	0.04	0.005	0.03	0.004	0.04	0.000
	1	0.36	0.39	0.011	0.36	0.033	0.41	0.004
Nicotine	0.01	0.03	0.01	0.000	0.01	0.004	0.01	0.005
	0.1	0.08	0.06	0.005	0.11	0.005	0.10	0.004
	1	0.68	0.86	0.012	0.95	0.005	0.85	0.004
	10	6.86	7.64	0.064	8.26	0.055	8.22	0.052
Potassium Cyanide	0.01	0.02	0.01	0.006	0.00	0.005	0.01	0.006
	0.1	0.01	0.02	0.005	0.02	0.006	0.01	0.005
	1	0.03	0.03	0.005	0.02	0.006	0.02	0.005
	10	0.37	0.11	0.026	0.10	0.015	0.07	0.035
Sodium Fluoroacetate	0.01	0.01	0.00	0.008	-0.01	0.005	0.00	0.005
	0.1	0.03	0.03	0.000	0.03	0.004	0.02	0.004
	1	0.30	0.27	0.000	0.28	0.004	0.25	0.041
	10	2.17	2.72	0.007	1.64	0.530	2.12	0.035
Water Controls	None	0.01	-0.03	0.00	0.00	0.00	0.01	0.00
			0.04	0.00	0.00	0.00	0.00 <sup>†</sup>	0.02 <sup>†</sup>

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

<sup>†</sup> Average and standard deviation of water controls.

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matrix. In general, the results are similar for chlorinated and chloraminated water. The differences were as follows: the 900 Portable did not respond to any injections at 0.01 mg/L with chloraminated water, gave two responses with chloraminated water (instead of one with chlorinated water) to injections of 0.1 mg/L carbofuran, and gave two responses (instead of one with chlorinated water) with chloraminated water to 0.1 mg/L sodium fluoroacetate. With the exception of potassium cyanide, all of the TICs caused approximately a linear increase in TOC with increasing concentration. The 900 Portable response to potassium cyanide was never larger than 0.11 mg/L, even for injections at 10 mg/L of potassium cyanide. The 900 Portable responded at or below the lowest concentration producing a response with the reference method for all TIC injections except for two injections of aldicarb at 0.1 mg/L.

### ***5.1.2 900 Portable Accuracy during Toxic Industrial Chemical (TIC) Testing***

Table 5-3 and Table 5-4 compare the steady-state TOC measurements obtained for PPL reference samples by the 900 Portable to the measurements obtained by the reference method. In addition to the steady-state contaminant concentrations in the second column, the actual TOC concentrations and standard deviations measured by the reference method and the 900 Portable are shown in the middle columns. These measurements include the background TOC concentration of the drinking water used for the testing in addition to any contribution of TOC from the injected contaminant. The last column includes the percent difference (%D) between the average 900 Portable TOC measurement and the average reference TOC measurement. This %D can be used to assess the accuracy of the 900 Portable measurements. As mentioned before, TOC instruments and methods can provide different responses to contaminants. In most cases, the average and standard deviation reported are based on three replicate measurements, however, in some cases, the results are based on four replicates. The propagated experimental uncertainty of the %D is shown in the same column as %D in Table 5-3 and 5-4.

The average %D between the 900 Portable and the reference method was typically less than 20% with the only exceptions being data collected for carbofuran (28-46%), mevinphos (21-23%), and sodium fluoroacetate (20%). The data for carbofuran show that there is a larger %D for samples collected after the 10 mg/L injections. The absolute value of the %Ds between the 900 Portable and the reference method for all the comparisons across the evaluation was 14% plus or minus ( $\pm$ ) a standard deviation (SD) of 7%. For TICs in chlorinated and chloraminated water, the absolute value of the %Ds averaged  $15\% \pm 5\%$  and  $14\% \pm 8\%$ , respectively. In general, the standard deviations generated by the reference instrument were similar to the 900 Portable. The propagated experimental uncertainty was typically small with respect to %D. There were only a few instances when the %D did not result in a statistically significant difference between the 900 Portable and the reference method.

**Table 5-3. 900 Portable Accuracy for Toxic Industrial Chemicals (TICs) in Chlorinated Water**

Contaminant	Injected Contaminant Concentration (mg/L)	Reference TOC		900 Portable TOC		Percent Difference (%D)
		Average (mg/L)	Std. Dev. (mg/L)	Average (mg/L)	Std. Dev. (mg/L)	
Aldicarb	Pre-Injection	2.52	0.14	2.95	0.40	16 ± 14
	0.01	2.47	0.15	2.91	0.32	16 ± 12
	0.1	2.55	0.20	2.91	0.22	13 ± 10
	1	3.01	0.24	3.40	0.21	12 ± 9.3
Carbofuran	Pre-Injection	2.45	0.07	2.96	0.23	19 ± 8.0
	0.01	2.51	0.16	2.95	0.20	16 ± 8.6
	0.1	2.55	0.15	3.00	0.20	16 ± 8.3
	1	3.07	0.24	3.57	0.29	15 ± 10
	10	7.12	1.54	9.47	2.42	28 ± 30
Colchicine	Pre-Injection	2.41	0.05	2.77	0.03	14 ± 2.1
	0.01	2.43	0.05	2.76	0.05	13 ± 2.6
	0.1	2.50	0.04	2.84	0.07	13 ± 2.8
	1	3.16	0.06	3.58	0.05	13 ± 2.2
	10	11.19	0.16	10.96	0.05	-2.1 ± 1.5
Mevinphos	Pre-Injection	1.38	0.00	1.71	0.00	21 ± 0.0
	0.01	1.37	0.01	1.72	0.01	23 ± 0.8
	0.1	1.42	0.03	1.76	0.01	21 ± 1.8
	1	1.77	0.04	2.15	0.01	19 ± 1.9
Nicotine	Pre-Injection	2.54	0.10	2.89	0.06	13 ± 4.0
	0.01	2.55	0.03	2.90	0.07	13 ± 2.6
	0.1	2.63	0.03	3.01	0.06	14 ± 2.2
	1	3.29	0.06	3.90	0.08	17 ± 2.5
	10	10.05	2.06	11.53	0.88	14 ± 19
Potassium Cyanide	Pre-Injection	2.37	0.06	2.72	0.07	14 ± 3.4
	0.01	2.41	0.06	2.70	0.07	11 ± 3.4
	0.1	2.43	0.06	2.71	0.08	11 ± 3.7
	1	2.45	0.08	2.72	0.07	10 ± 3.9
	10	2.79	0.06	2.79	0.09	0.0 ± 3.9
Sodium Fluoroacetate	Pre-Injection	1.60	0.16	1.95	0.16	20 ± 12
	0.01	1.55	0.12	1.86	0.13	18 ± 9.4
	0.1	1.55	0.10	1.88	0.11	19 ± 7.8
	1	1.81	0.08	2.12	0.08	16 ± 5.3
	10	3.66	0.21	3.96	0.15	7.9 ± 6.5

† Standard deviation is of the replicates on which the average TOC concentration is based.

In addition to the accuracy data presented in Tables 5-3 and 5-4, the standard deviation data presented represents not only the precision of the baseline measurements, but the precision of the resulting TOC concentration due to the injections themselves. This measure of precision could be used to calculate the amount of change that would be required to detect a contamination event. For example, if the TOC measurements for a set of replicate injections are precise (e.g., 1 mg/L mevinphos) and therefore, has a low standard deviation, a small change would be detectable. Conversely, if the TOC measurements for a set of replicates (e.g. 10 mg/L carbofuran) are imprecise and, therefore, have a larger standard deviation, a relatively larger change in TOC would be

**Table 5-4. 900 Portable Accuracy for Toxic Industrial Chemicals (TICs) in Chloraminated Water**

Contaminant	Injected Contaminant Concentration (mg/L)	Reference TOC		900 Portable TOC		Percent Difference (%)
		Average (mg/L)	Std. Dev. (mg/L)	Average (mg/L)	Std. Dev. (mg/L)	
Aldicarb	Pre-Injection	2.01	0.36	2.40	0.52	18 ± 26
	0.01	1.92	0.32	2.27	0.56	17 ± 28
	0.1	2.07	0.45	2.30	0.50	10 ± 29
	1	2.46	0.40	2.81	0.51	13 ± 23
Carbofuran	Pre-Injection	1.95	0.18	2.60	0.60	29 ± 24
	0.01	2.06	0.30	2.50	0.50	19 ± 23
	0.1	2.09	0.24	2.52	0.45	19 ± 20
	1	2.72	0.30	3.17	0.38	15 ± 15
	10	7.60	0.16	12.10	1.16	46 ± 9.2
Colchicine	Pre-Injection	1.80	0.09	1.94	0.14	7.5 ± 8.6
	0.01	1.79	0.05	1.91	0.09	6.5 ± 5.4
	0.1	1.88	0.05	1.98	0.09	5.2 ± 5.2
	1	2.59	0.11	2.67	0.04	3.0 ± 4.4
	10	9.04	0.09	9.56	0.28	5.6 ± 3.1
Mevinphos	Pre-Injection	1.43	0.02	1.77	0.02	21 ± 1.6
	0.01	1.44	0.03	1.77	0.01	21 ± 1.8
	0.1	1.49	0.02	1.81	0.02	19 ± 1.5
	1	1.85	0.03	2.19	0.04	17 ± 2.3
Nicotine	Pre-Injection	1.92	0.12	2.08	0.12	8.0 ± 8.1
	0.01	1.95	0.11	2.09	0.12	6.9 ± 7.8
	0.1	2.03	0.09	2.18	0.10	7.1 ± 6.2
	1	2.71	0.08	3.06	0.10	12 ± 4.2
	10	9.56	0.35	11.10	0.29	15 ± 4.1
Potassium Cyanide	Pre-Injection	1.91	0.05	2.14	0.03	11 ± 2.7
	0.01	1.93	0.05	2.15	0.03	11 ± 2.7
	0.1	1.94	0.03	2.17	0.03	11 ± 1.9
	1	1.97	0.04	2.19	0.04	11 ± 2.6
	10	2.34	0.03	2.28	0.06	-2.6 ± 2.9
Sodium Fluoroacetate	Pre-Injection	1.56	0.10	1.89	0.10	19 ± 7.4
	0.01	1.50	0.05	1.81	0.02	19 ± 2.9
	0.1	1.53	0.05	1.84	0.02	18 ± 2.9
	1	1.83	0.14	2.10	0.02	14 ± 6.7
	10	3.86	0.45	4.19	0.58	8.2 ± 18

<sup>†</sup>Standard deviation is of the replicates on which the average TOC concentration is based.

necessary to attain a detectable concentration. These data are also useful for evaluating the precision of the 900 Portable versus the reference method. In many cases, the precision data are rather similar. In this instance, the precision is not only dependent on the instrument, but also on experimental factors having to do with the PPL operation. However, similar variables may exist in the context in an operational setting.

As is evident from the preinjection TOC levels, the water in the laboratory did show some variation over the course of the evaluation. The average pre-injection baseline TOC in the water ranged from 1.38 mg/L to 2.54 mg/L during the TIC evaluation period.

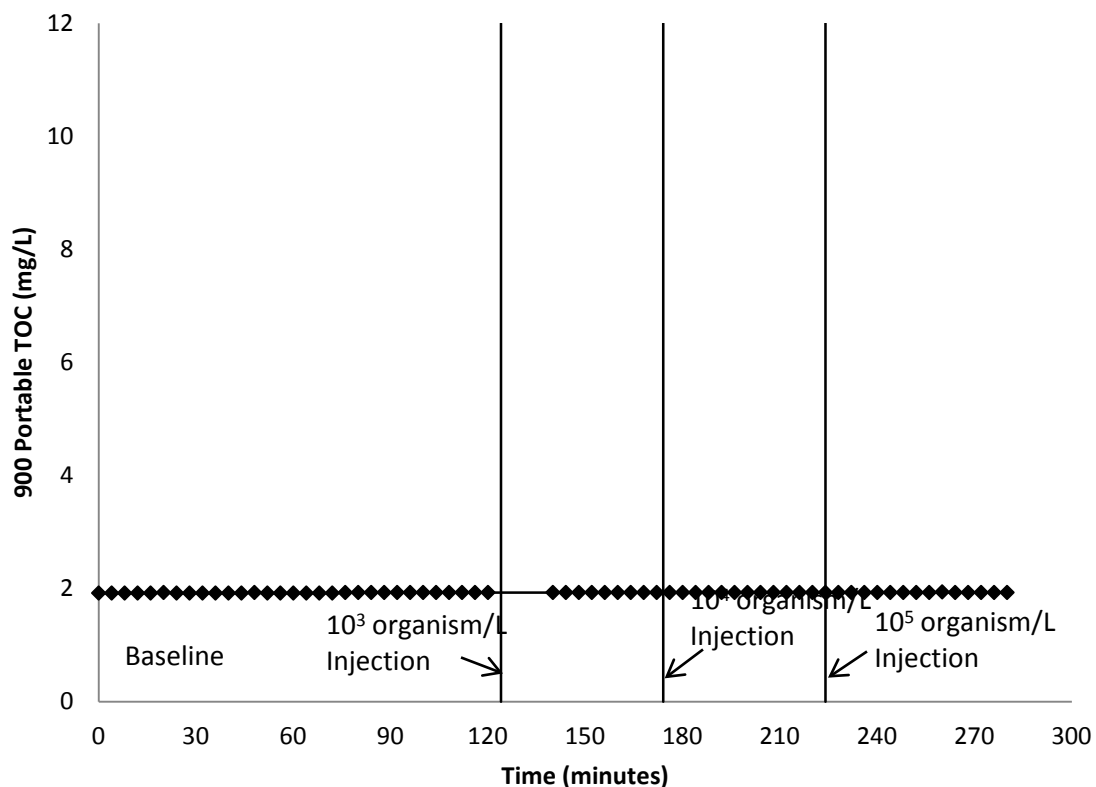


However, during the course of each set of replicate contaminant injections, the background TOC was steady because the same water was used for each contaminant injection.

## 5.2 Biological Contaminants (BCs) in Drinking Water

### 5.2.1 900 Portable Response to Biological Contaminant (BC) Injections

Three types of BCs and one toxin surrogate were injected into the PPL. These injections were performed in the same manner as the TIC injections with a concentrated solution injected into the PPL over approximately 15-20 seconds. The same injection and flush procedures were used and response determination (as defined in Section 3.6.1) was performed in the same way. Figure 5-2 shows that the 900 Portable did not respond to any of the injected concentrations ( $10^3$ ,  $10^4$ , and  $10^5$  organisms/L) of *Bacillus globigii*. Initially, concentrations of  $10^3$ ,  $10^4$ , and  $10^5$  organisms/L were injected into the PPL for each organism. After the results of the initial injections showed no response, the concentrations were increased to include a maximum concentration of  $10^7$  organisms/L for *Bacillus globigii* and *Bacillus thuringiensis*. This increased concentration of *Bacillus thuringiensis* was a mixture of spores and vegetative cells while the other concentrations were spores only. Limitations on the amount of stock solution available prevented increasing the concentrations of *Chlorella* in a similar manner.



**Figure 5-2. Change in 900 Portable Total Organic Carbon (TOC) response to injections of *Bacillus globigii*.**

Table 5-5 presents the contaminant injected, the concentration of the injected contaminant, and the average and standard deviation of the measured change in TOC (as measured by replicate measurements of the 900 Portable) for each BC injection into chlorinated water. Those injections which the 900 Portable responded are highlighted in gray. The 900 Portable “response” is defined as described in Section 3.6.1.

**Table 5-5. Change in 900 Portable Total Organic Carbon (TOC) from Injections of Biological Contaminants (BCs) into Chlorinated Water**

Contaminant	Injected Contaminant Conc. (organism/L or mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Injection 1		Injection 2		Injection 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
<i>Bacillus globigii</i>	$10^5$	-0.09	0.00	0.000	0.00	0.004	0.00	0.000
	$10^6$	0.01	-0.01	0.007	-0.01	0.005	0.00	0.005
	$10^7$	-0.03	-0.01	0.007	0.01	0.005	0.00	0.005
<i>Bacillus thuringiensis</i>	$10^5$	-0.03	-0.02	0.012	0.00	0.000	0.00	0.013
	$10^6$	-0.02	0.01	0.000	0.00	0.000	0.00	0.004
	$10^7$	-0.02	0.07	0.004	0.05	0.005	0.03	0.013
<i>Chlorella</i>	$10^3$	-0.04	-0.01	0.006	0.01	0.000	0.01	0.005
	$10^4$	-0.04	0.00	0.004	-0.01	0.000	0.02	0.010
	$10^5$	-0.04	0.00	0.005	0.00	0.000	0.00	0.010
Ovalbumin	0.01	0.01	0.02	0.000	-0.01	0.006	0.03	0.007
	0.1	0.02	0.04	0.021	0.03	0.006	0.03	0.008
	1	0.09	0.31	0.041	0.32	0.016	0.35	0.013
	10	1.10	4.75	0.081	4.48	0.047	4.60	0.125
Water controls	None	0.01	-0.03	0.00	0.00	0.00	0.01	0.00
			0.04	0.00	0.00	0.00	0.00 <sup>†</sup>	0.02 <sup>†</sup>
PBS/nutrient broth	Equivalent to $10^7$ <i>Bacillus</i>	-0.02	-0.01	0.00	0.02	0.01	-0.01	0.00
			-0.00	0.00	0.01	0.02	-0.01	0.00
PBS/Bold 1NV medium	Equivalent to $10^7$ <i>Chlorella</i>	-0.01	0.00	0.01	0.00	0.00	0.01	0.00
			-0.01	0.01	0.02	0.00	-0.01	0.00

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

<sup>†</sup> Average and standard deviation of water controls.

None of the injections of *Bacillus globigii* or *Chlorella* resulted in a response from the 900 Portable at the concentrations injected. All three injections of *Bacillus thuringiensis* at  $10^7$  organisms/L including spores and vegetative cells resulted in a response from the 900 Portable. The reference method responded to none of the BCs. Ovalbumin, a protein surrogate for biological toxins such as ricin or botulinum, produced a response from the 900 Portable for all three 0.1 mg/L, 1 mg/L, and 10 mg/L injections. The reference method measured a response in TOC only for the 10 mg/L injections of ovalbumin.

Table 5-6 presents the response to injections of the BCs and ovalbumin into chloraminated water. Initial injections of *Bacillus globigii* were performed at  $10^3$ ,  $10^4$ , and  $10^5$  organisms/L. One injection of  $10^7$  organisms/L was included with the final

**Table 5-6. Change in 900 Portable Total Organic Carbon (TOC) from Injection of Biological Contaminants (BCs) into Chloraminated Water**

Contaminant	Injected Conc. (organism/L or mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Injection 1		Injection 2		Injection 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
<i>Bacillus globigii</i>	10 <sup>3</sup>	-0.01	0.01	0.005	-0.02	0.005	-0.02	0.005
	10 <sup>4</sup>	-0.03	0.00	0.000	0.00	0.005	0.00	0.005
	10 <sup>5</sup>	-0.01	0.00	0.003	0.00	0.005	0.00	0.004
	10 <sup>7</sup>	-0.05	†	†	†	†	0.01	0.004
<i>Bacillus thuringiensis</i>	10 <sup>3</sup>	-0.03	-0.01	0.007	-0.02	0.010	†	†
	10 <sup>4</sup>	-0.03	0.00	0.004	-0.01	0.005	†	†
	10 <sup>5</sup>	-0.02	0.03	0.004	0.03	0.005	-0.01	0.004
	10 <sup>6</sup>	-0.04	†	†	†	†	0.00	0.000
	10 <sup>7</sup>	-0.01	†	†	†	†	0.05	0.000
<i>Chlorella</i>	10 <sup>3</sup>	-0.05	-0.01	0.006	0.00	0.005	-0.07	0.044
	10 <sup>4</sup>	-0.04	0.01	0.000	0.00	0.005	0.00	0.000
	10 <sup>5</sup>	-0.02	0.00	0.000	0.00	0.000	0.01	0.005
Ovalbumin	0.01	-0.01	-0.02	0.008	0.02	0.005	0.00	0.005
	0.1	0.04	0.01	0.005	0.02	0.005	0.03	0.000
	1	0.29	0.32	0.036	0.45	0.057	0.47	0.039
	10	1.34	5.41	0.045	5.24	0.057	5.02	0.054
Water controls	None	0.01	-0.03	0.00	0.00	0.00	0.01	0.00
			0.04	0.00	0.00	0.00	0.00 <sup>#</sup>	0.02 <sup>#</sup>
PBS/nutrient broth	Equivalent to 10 <sup>7</sup> <i>Bacillus</i>	-0.02	-0.01	0.00	0.02	0.01	-0.01	0.00
			-0.00	0.00	0.01	0.02	-0.01	0.00
PBS/Bold 1NV medium	Equivalent to 10 <sup>7</sup> <i>Chlorella</i>	-0.01	0.00	0.01	0.00	0.00	0.01	0.00
			-0.01	0.01	0.02	0.00	-0.01	0.00

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

† Fewer than three replicates performed at this concentration.

<sup>#</sup> Average and standard deviation of water controls.

replicate set of injections to confirm the results determined during the chlorinated water injections. The final set of injections of *Bacillus thuringiensis* was also performed at 10<sup>5</sup>, 10<sup>6</sup>, and 10<sup>7</sup> organisms/L. Injections which produced a response in the 900 Portable TOC concentration and the reference method are highlighted in gray.

In chloraminated water, none of the *Bacillus globigii* or *Chlorella* injections resulted in a response from the 900 Portable. The only BC injection that resulted in a response from the 900 Portable was of *Bacillus thuringiensis* at 10<sup>7</sup> organisms/L including spores and vegetative cells. The reference method did not respond to any of the organism injections. The 900 Portable and the reference method both measured a response to ovalbumin for all of the 1 and 10 mg/L injections.

In addition to the injections of BCs, control injections of freshly prepared growth media handled in the same manner as the stock solutions of the BCs, but without organisms added, were injected into the PPL. Triplicate sets of injections of the washed growth

media for both the *Bacillus* organisms and *Chlorella* were made into chlorinated and chloraminated water. None of the 12 injections produced a change in TOC that was detectable by the 900 Portable or the reference method.

### 5.2.2 900 Portable Accuracy during Biological Contaminant (BC) Testing

Table 5-7 and Table 5-8 summarize the comparisons of the steady-state TOC measurements from the 900 Portable to the results obtained from the reference method through analysis of reference samples from the PPL for chlorinated and chloraminated water, respectively. In addition to the steady-state contaminant concentrations in the second column, the reference TOC concentrations and standard deviations measured by the 900 Portable and the reference method are shown in the middle columns. These measurements include the background TOC concentration of the drinking water used for the testing in addition to any contribution of TOC from the injected contaminant. The last column includes the %D between the average 900 Portable measurement and the average reference measurement. This %D can be used to assess the accuracy of the 900 Portable measurements. In most cases, the average and standard deviation reported are based on three replicate measurements, but in some instances there were four replicates.

The average % D between the 900 Portable and the reference method was typically less than 25% with the only exceptions being  $10^7$  organisms/L of *Bacillus thuringiensis* in chloraminated water (27%), and 10 mg/L of ovalbumin (73-75%). In general,

**Table 5-7. 900 Portable Accuracy for Biological Contaminants (BCs) in Chlorinated Water**

Contaminant	Contaminant Concentration (mg/L or organisms/L)	Reference TOC		900 Portable TOC		Percent Difference (%)
		Average (mg/L)	Std. Dev. (mg/L)	Average (mg/L)	Std. Dev. (mg/L)	
<i>Bacillus globigii</i>	Pre-Injection	1.61	0.09	1.86	0.10	14 ± 7.2
	$10^5$	1.52	0.10	1.86	0.10	20 ± 7.5
	$10^6$	1.54	0.06	1.86	0.09	19 ± 5.8
	$10^7$	1.51	0.06	1.85	0.09	20 ± 5.8
<i>Bacillus thuringiensis</i>	Pre-Injection	1.54	0.08	1.86	0.08	19 ± 6.0
	$10^5$	1.50	0.09	1.86	0.06	21 ± 5.7
	$10^6$	1.48	0.11	1.86	0.06	23 ± 6.6
	$10^7$	1.49	0.07	1.90	0.09	24 ± 5.9
<i>Chlorella</i>	Pre-Injection	1.66	0.02	1.92	0.02	14 ± 1.5
	$10^3$	1.62	0.02	1.93	0.02	18 ± 1.5
	$10^4$	1.58	0.01	1.93	0.00	20 ± 0.5
	$10^5$	1.54	0.03	1.93	0.00	22 ± 1.5
Ovalbumin	Pre-Injection	2.38	0.02	2.74	0.02	14 ± 1.0
	0.01	2.39	0.01	2.76	0.02	14 ± 0.8
	0.1	2.41	0.02	2.79	0.02	15 ± 1.0
	1	2.50	0.04	3.12	0.04	22 ± 1.8
	10	3.59	0.31	7.73	0.14	73 ± 3.8

†Standard deviation is of the replicates on which the average TOC concentration is based.

**Table 5-8. 900 Portable Accuracy for Biological Contaminants (BCs) in Chloraminated Water**

Contaminant	Contaminant Concentration (mg/L or organisms/L)	Reference TOC		900 Portable TOC		Percent Difference (%)
		Average (mg/L)	Std. Dev. (mg/L)	Average (mg/L)	Std. Dev. (mg/L)	
<i>Bacillus globigii</i>	Pre-Injection	1.76	0.02	1.94	0.02	9.7 ± 1.5
	10 <sup>3</sup>	1.75	0.01	1.93	0.01	9.8 ± 0.7
	10 <sup>4</sup>	1.72	0.03	1.93	0.01	12 ± 1.6
	10 <sup>5</sup>	1.71	0.04	1.93	0.01	12 ± 2.1
	10 <sup>7</sup>	1.62	‡	1.93	‡	18
<i>Bacillus thuringiensis</i>	Pre-Injection	1.63	0.14	1.84	0.07	12 ± 8.5
	10 <sup>3</sup>	1.68	0.01	1.87	0.01	11 ± 0.8
	10 <sup>4</sup>	1.65	0.01	1.87	0.01	12 ± 0.8
	10 <sup>5</sup>	1.56	0.12	1.85	0.07	17 ± 7.5
	10 <sup>6</sup>	1.38	‡	1.76	‡	24
	10 <sup>7</sup>	1.38	‡	1.81	‡	27
<i>Chlorella</i>	Pre-Injection	1.46	0.08	1.74	0.03	18 ± 4.9
	10 <sup>3</sup>	1.41	0.07	1.71	0.07	19 ± 5.7
	10 <sup>4</sup>	1.37	0.07	1.72	0.07	23 ± 5.7
	10 <sup>5</sup>	1.36	0.08	1.72	0.06	23 ± 5.7
Ovalbumin	Pre-Injection	1.80	0.04	1.95	0.06	8.0 ± 3.7
	0.01	1.78	0.03	1.95	0.06	9.1 ± 3.4
	0.1	1.83	0.04	1.97	0.07	7.4 ± 4.1
	1	2.12	0.28	2.38	0.15	12 ± 13
	10	3.46	0.20	7.60	0.08	75 ± 2.4

† Standard deviation is of the replicates on which the average TOC concentration is based.

‡ Only one replicate conducted at these concentrations.

the standard deviations generated by the reference instrument were similar to the 900 Portable. For the biological contaminants (excluding the 10mg/L ovalbumin measurements), the average of the absolute values of the %D was 19% ± SD 3% and 15% ± SD 6% for chlorinated and chloraminated water, respectively. For each individual comparison, the experimental error was propagated using the uncertainty of both measurements and is reported. In most cases the differences between the 900 Portable results and the reference method results are larger than the experimental uncertainty. In general, the 900 Portable measured higher TOC than the reference method for BC samples. Injections of 10 mg/L of ovalbumin resulted in 73 to 75 percent difference with the 900 Portable measuring higher TOC concentrations than the reference method. There is no definite explanation for this, although the data suggests that the 900 Portable responds more linearly to ovalbumin than does the reference method.

As is evident from the pre-injection TOC levels, the water in the laboratory did show some variation over the course of the testing. The average pre-injection baseline TOC in the water ranged from 1.46 mg/L to 2.38 mg/L during the BC evaluation period. However, during the course of each set of replicate contaminant injections, the background TOC was steady because the same water was used for each contaminant injection.

## 5.3 Discrete Sample Analyses

### 5.3.1 900 Portable Response for Discrete Sample Analyses

Three contaminants were analyzed as discrete samples to minimize the volume used for injection of some of the contaminants. Carbofuran was analyzed in discrete samples as well as in the PPL. For the PPL tests, water was continuously flowing through the 900 Portable inlet whereas for the discrete tests, the 900 Portable was operated in grab sample analysis mode with samples drawn from a static 40 mL vial containing the solution to be tested. In grab sample mode, the 900 Portable drew four samples from the vial and reported a concentration as the average of the final three measurements. The reported concentration is the average of the measurements collected from one vial. The discrete samples were analyzed in a similar manner to the tests in the PPL increasing from drinking water to the highest concentration analyzed. Three vials of each concentration were analyzed in both chlorinated and chloraminated water for each contaminant.

Table 5-9 and Table 5-10 give the contaminant tested, the concentration of the contaminant, the measured change in TOC, and the standard deviation for each contaminant concentration in chlorinated and chloraminated water, respectively. The 900 Portable responded to the concentrations highlighted in gray. Results of the ricin and sodium azide phosphate buffer samples are included in both tables.

**Table 5-9. Change in 900 Portable Total Organic Carbon (TOC) for Discrete Sample Analyses in Chlorinated Water**

Contaminant	Solution Contaminant Conc. (mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Vial 1		Vial 2		Vial 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
Carbofuran	0.1	†	0.06	0.000	0.05	0.000	0.05	0.000
	1	†	0.27	0.000	0.29	0.000	0.30	0.006
Diesel fuel	0.1	0.12	0.19	0.012	0.13	0.015	0.11	0.015
	1	0.00	0.11	0.000	0.11	0.015	0.10	0.015
	10	-0.02	0.43	0.010	0.54	0.015	0.53	0.015
Disulfoton	0.1	-0.01	0.02	0.006	0.00	0.006	0.02	0.006
	1	-0.23	0.19	0.006	0.16	0.000	0.17	0.006
Ricin	0.1	‡	0.04	0.000	-0.06	0.042	0.11	0.000
	1		0.30	0.010	0.28	0.042	0.40	0.000
	10		4.47	0.050	4.56	0.042	4.65	0.012
Sodium azide/phosphate buffer (ricin blank)	0.1		-0.07	0.006	*			
	1		-0.05	0.006				
	10		-0.11	0.006				

Responses (indicated by shading) must be at least three times standard deviation.

† Reference samples not analyzed for discrete analyses of carbofuran in chlorinated water.

‡ Reference instrument could not be placed within the biosafety hood so ricin and corresponding azide blanks reference analyses were not performed.

\* One set of blank replicate samples were analyzed.

**Table 5-10. Change in 900 Portable Total Organic Carbon (TOC) for Discrete Sample Analyses in Chloraminated Water**

Contaminant	Solution Contaminant Conc. (mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Vial 1		Vial 2		Vial 3	
			$\Delta$ TOC (mg/L)	Std. $\dagger$ Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. $\dagger$ Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. $\dagger$ Dev. (mg/L)
Carbofuran	0.1	0.07	0.11	0.006	0.05	0.006	0.04	0.006
	1	0.30	0.38	0.000	0.77	0.006	0.52	0.006
Diesel fuel	0.1	0.00	-0.01	0.006	-0.05	0.020	0.01	0.015
	1	0.03	0.27	0.006	0.15	0.020	0.22	0.015
	10	0.05	1.13	0.021	0.37	0.020	0.31	0.015
Disulfoton	0.1	-0.01	0.02	0.006	0.04	0.000	0.05	0.006
	1	0.29	0.30	0.006	0.32	0.000	0.32	0.006
Ricin	0.1	$\ddagger$	0.01	0.000	0.00	0.012	0.03	0.010
	1		0.43	0.006	0.41	0.012	0.44	0.010
	10		4.81	0.021	4.77	0.021	4.77	0.010
Sodium azide/phosphate buffer	0.1		0.00	0.006	*			
	1		0.00	0.006				
	10		-0.01	0.006				

Responses (indicated by shading) must be at least three times standard deviation.

$\ddagger$  Reference instrument could not be placed within the biosafety hood so ricin and corresponding azide blanks reference analyses were not performed.

\* One set of blank replicate samples were analyzed.

The ricin was stored in the sodium azide phosphate buffer so, along with each measurement of ricin, the sodium azide phosphate buffer was analyzed at the concentration at which it was present in the ricin solutions. The diesel fuel, disulfoton, and carbofuran were insoluble or only partially soluble in water making interpretation of the 900 Portable and reference method results for these discrete samples difficult.

#### 5.3.1.1 Carbofuran

Discrete analyses of carbofuran at 0.1 and 1 mg/L were conducted. No analysis of discrete 10 mg/L carbofuran samples was conducted due to the limited solubility of carbofuran. During the discrete analyses, the 900 Portable responded to both the 0.1 and 1 mg/L concentration levels in both chlorinated and chloraminated water. The 900 Portable responded to all of the discrete samples of carbofuran except for one of the 0.1 mg/L tests in chloraminated water. The 0.1 mg/L injections of carbofuran into the PPL produced responses for two of three injections in chlorinated water and one of three injections in chloraminated water (see Table 5-2, 5-3, respectively). For the discrete analyses, the reference method responded to only the 1 mg/L injections of carbofuran into chloraminated water. The discrete samples produced TOC readings that were about half the PPL analyses readings. The reason for this difference in results between the experimental setups was not obvious.

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#### **5.3.1.2 Diesel fuel.**

Discrete analysis of diesel fuel samples was conducted at 0.1, 1, and 10 mg/L. The solubility of diesel was such that diesel was insoluble in water at any of the concentrations evaluated. For each sample, two phases were visible with diesel on top of water. Prior to each analysis, the samples were mixed, but over the course of the analysis period the samples began to separate into a distinct diesel (organic) phase and an aqueous phase. The 900 Portable responded to all diesel samples in chlorinated water and for 1 and 10 mg/L of diesel in chloraminated water. With similar inconsistency, only the lowest concentration diesel was detected by the reference method. These inconsistent results can be explained by the lack of solubility of diesel fuel. Without a homogeneous solution, results from any chemical measurement, including TOC, is problematic.

#### **5.3.1.3 Disulfoton.**

Discrete analysis of disulfoton samples was conducted at 0.1 and 1 mg/L. No analysis of discrete 10 mg/L disulfoton samples was conducted due to the limited solubility of disulfoton. The 900 Portable responded to 1 mg/L of disulfoton in both chlorinated and chloraminated water and for one test of 0.1 mg/L in chloraminated water. The reference method did not respond to the 1 mg/L of disulfoton in chlorinated water, but respond to 1 mg/L in chloraminated water. There was not a clear reason for the response differences between the two water matrices.

#### **5.3.1.4 Ricin.**

Ricin tests were carried out inside a hood in a biological safety level 2 (BSL-2) laboratory. Discrete analysis of ricin samples was conducted at 0.1, 1, and 10 mg/L. The 900 Portable responded to all of the 1 and 10 mg/L samples. As mentioned above, the sodium azide phosphate buffer solution was analyzed at the same concentrations at which it was present in the ricin solutions to determine whether the 900 Portable responded due to the sodium azide phosphate buffer. The 900 Portable responded to 0.1 mg/L for one test in chlorinated water but to none of the tests in chloraminated water. The phosphate buffered sodium azide solution did not cause any change in TOC in either water matrix, therefore, the change in TOC concentration due to ricin was considered to be anomalous. Analysis of ricin by the reference method would have required relocation of the reference instrument into a BSL-2 hood, which was not logistically possible.

### **5.3.2 900 Portable Accuracy during Discrete Sample Analyses**

Table 5-11 and Table 5-12 summarize the comparison of the TOC measurements from the 900 Portable to the results obtained from the reference method through analysis of samples prepared in the same manner as the test samples analyzed by the 900 Portable in chlorinated and chloraminated water, respectively.

The average %D of the 900 Portable compared to the reference method was typically less than 25% for discrete sample analyses. The only exceptions were diesel fuel (38-41%) and carbofuran (17-27%). Overall, the absolute value of the %D for the chlorinated water was  $21\% \pm \text{SD } 8\%$ , for chloraminated water  $23\% \pm \text{SD } 7\%$ , for an overall average absolute %D of  $22\% \pm \text{SD } 8\%$ .



**Table 5-11. 900 Portable Accuracy for Discrete Sample Analyses in Chlorinated Water**

Contaminant	Contaminant Concentration (mg/L)	Reference TOC	900 Portable TOC		Percent Difference (%D)
		Average (mg/L)	Average (mg/L)	Std. Dev. (mg/L)	
Carbofuran	Water	†	1.65	0.02	†
	0.1	†	1.70	0.01	†
	1	†	1.93	0.01	†
Diesel fuel	Water	1.64	1.87	0.03	13 ± 1.9
	0.1	1.76	2.01	0.01	13 ± 1.1
	1	1.64	1.98	0.03	19 ± 1.8
	10	1.62	2.37	0.09	38 ± 3.8
Disulfoton	Water	1.33	1.68	0.01	23 ± 1.3
	0.1	1.36	1.70	0.01	22 ± 1.3
	1	1.56	1.86	0.01	18 ± 1.2

†Reference samples not analyzed for this concentration.

**Table 5-12. 900 Portable Accuracy for Discrete Sample Analyses in Chloraminated Water**

Contaminant	Contaminant Concentration (mg/L)	Reference TOC	900 Portable TOC		Percent Difference (%D)
		Average (mg/L)	Average (mg/L)	Std. Dev. (mg/L)	
Carbofuran	Water	1.41	1.69	0.01	18 ± 1.3
	0.1	1.48	1.76	0.05	17 ± 3.0
	1	1.71	2.25	0.19	27 ± 8.3
Diesel fuel	Water	1.89	2.34	0.06	21 ± 2.7
	0.1	1.88	2.33	0.04	21 ± 1.9
	1	1.92	2.56	0.01	39 ± 0.9
	10	1.94	2.95	0.41	41 ± 13
Disulfoton	Water	1.57	1.93	0.01	21 ± 1.1
	0.1	1.62	1.97	0.01	20 ± 1.1
	1	1.85	2.24	0.01	19 ± 1.0

## 5.4 Additional Tests

### 5.4.1 Effect of Elevated TOC Concentration on 900 Portable Response

A minor component of this evaluation was undertaken as a control to determine if the background TOC level had any effect on the ability of the 900 Portable to detect a change in response to a contaminant injection. Three sets of nicotine solutions at 0.1 and 1 mg/L were injected into chlorinated water which had been fortified with quinine to raise the background TOC level. Quinine was added to the PPL to increase the background TOC concentration by approximately 1 mg/L. Table 5-13 presents the response determinations from the elevated TOC injections as well as those from the injections of nicotine at the same levels without elevated background TOC.

**Table 5-13. Change in 900 Portable Total Organic Carbon (TOC) with Elevated Total Organic Carbon (TOC) Concentrations**

Contaminant	Injected Contaminant Conc. (mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Injection 1		Injection 2		Injection 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
Nicotine (background TOC)	0.1	0.03	0.08	0.005	0.09	0.005	0.08	0.005
	1	0.67	0.88	0.004	0.87	0.005	0.92	0.000
Nicotine (elevated TOC)	0.1	0.11	0.08	0.011	-0.01	0.017	0.04	0.031
	1	0.65	0.80	0.007	0.80	0.007	0.77	0.040

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

The addition of quinine was observed to possibly affect the response from the 900 Portable. Without addition of quinine, all three injections at 0.1 mg/L showed a response while, after the addition of quinine, only one of the three injections showed a response. However, the level of the response at 1 mg/L was only slightly lower for the injections made into the elevated background TOC water. The reference method measured a change in TOC at 1 mg/L, but not at 0.1 mg/L.

#### 5.4.2 Effect of Elevated Ionic Strength on 900 Portable Response

A minor component of this evaluation was undertaken as a control. Three replicate sets of nicotine solutions at 0.1 and 1 mg/L were injected into chlorinated water which had been fortified with calcium chloride to raise the calcium cation concentration from approximately 42 mg/L to 126 mg/L. Grab samples collected before and after the addition of the calcium chloride were analyzed to confirm that the calcium chloride addition tripled the background calcium concentration.

**Table 5-14. Change in 900 Portable Total Organic Carbon (TOC) with Elevated Ionic Strength**

Contaminant	Injected Contaminant Conc. (mg/L)	Average Reference Method $\Delta$ TOC (mg/L)	Injection 1		Injection 2		Injection 3	
			$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)	$\Delta$ TOC (mg/L)	Std. Dev. (mg/L)
Nicotine (background Ionic Strength)	0.1	0.03	0.08	0.005	0.09	0.005	0.08	0.005
	1	0.67	0.88	0.004	0.87	0.005	0.92	0.000
Nicotine (elevated Ionic Strength)	0.1	0.01	-0.01	0.010	0.08	0.012	0.08	0.008
	1	0.23	0.76	0.010	0.80	0.012	0.78	0.007

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

Additional experiments would need to be performed to draw conclusions, but Table 5-14 presents the response determinations from the elevated ionic strength injections as well as those from the injections of nicotine at background ionic strength.

The 900 Portable performed similarly at both ionic strengths. The only difference was that one of the injections of nicotine at 0.1 mg/L did not produce a response in water with elevated ionic strength. However, high concentrations of chloride interfered with the reference measurements so a decreased reference result was obtained. The 900 Portable was apparently less affected by the increased calcium chloride concentration while the reference method was inhibited.

#### 5.4.3 Effect of Monochloramine Level on 900 Portable Response

Lastly, a minor experiment was included to determine whether the level of monochloramine had an effect on the TOC measurement from the 900 Portable. The 900 Portable was used to monitor water with three different concentrations of monochloramine. Table 5-15 presents the 900 Portable and reference TOC measurements for the PPL testing at monochloramine concentrations of 1.92, 5.72, and 7.54 mg/L. At the lowest monochloramine concentration of 1.92 mg/L, the baseline 900 Portable TOC concentration was 1.97 mg/L. For the reference method, the TOC baseline was 1.74 mg/L. Neither the 900 Portable nor the reference method responded with changes in monochloramine concentration from 1.92 mg/L to 7.54 mg/L.

**Table 5-15. Change in 900 Portable Total Organic Carbon (TOC) with Varying Monochloramine Concentrations**

Monochloramine Concentration (mg/L)	Reference Method TOC (mg/L)	Reference Method $\Delta$ TOC (mg/L)	900 Portable TOC (mg/L)	900 Portable Std. Dev. (mg/L)	900 Portable $\Delta$ TOC (mg/L)
1.92	1.74	Baseline	1.97	0.000	Baseline
5.72	1.69	-0.05	1.98	0.004	0.01
7.54	1.69	-0.00	1.99	0.003	0.01

Responses (indicated by shading) must be at least three times the baseline standard deviation (in table) and the average and standard deviation of the background injection result by exhibiting a response of at least 0.03 mg/L.

## 5.5 Operational Characteristics

Operational characteristics of the 900 Portable that were encountered during this evaluation are organized into the following categories:

- Training/Education Material
- Installation
- Operation
- Maintenance/Consumables/Waste
- Software/Data Collection

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### ***5.5.1 Training/Educational Material***

The training for operation and maintenance of the 900 Portable was a combination of vendor provided in-person training and printed instructional material. A vendor representative set up the 900 Portable and gave an overview of the operation, calibration, and maintenance of the instrument. Instruction in operation of the instrument through the front panel display was also provided.

A printed instruction manual contained information on calibration and verification procedures as well as data retrieval and instrument operation. The manual contained instructions for performing both scheduled and unscheduled maintenance tasks. The manual was well organized and easy to follow. All needed test procedures were clearly articulated in the instruction manual.

### ***5.5.2 Installation***

Installation of the 900 Portable was straight-forward. At the contractor's lab the vendor made all necessary connections and installed the inorganic carbon removal module. Once the instrument was up and running, the vendor performed diagnostic checks to verify the operation of the 900 Portable. The waste line from the 900 Portable was routed to a waste container where the waste was collected. Calibration verification was performed by the vendor upon completion of the installation procedures.

### ***5.5.3 Operation***

After the evaluation staff had become familiar with using the 900 Portable, operation was straight-forward. The 900 Portable was left on during periods of inactivity (overnight and on weekends) to minimize start-up time each day. At the start of each day of testing, the syringes were flushed prior to running tests. At the end of each day of testing, analysis was stopped and the data file from the day was transferred to a dedicated computer. The experimental design required these daily activities; they would not be required in an operational setting.

### ***5.5.4 Maintenance/Consumables/Waste***

The 900 Portable required two reagents, an acid and an oxidizer, for operation. These reagents were housed within the 900 Portable enclosure in specially constructed reagent cartridges provided by the vendor. The acid typically lasts for six months and was not replaced during the testing. The oxidizer has a stability of three months and was changed once throughout the 56 days of testing. The procedure for changing the oxidizer was clearly articulated in the instruction manual. Replacement of the oxidizer cartridge took less than 30 minutes to complete.

The only other maintenance performed on the instrument during testing was the replacement of the UV lamp. The lamp was provided by the vendor and replacement

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took approximately 15 minutes. Following replacement of the UV lamp, the 900 Portable was left on overnight and calibration was performed the following day.

All maintenance activities performed were initiated due to warning messages displayed on the instrument's front panel. For reagents, installation and expiration dates are entered when reagents are changed and the instrument automatically generates a message prompting the user to change the reagent when the reagent is nearing the end of its useful lifetime. The same process applies to replacement of the UV lamp. An automated message was displayed on the front of the instrument prompting the user to replace the UV lamp.

Waste from the 900 Portable was combined with the excess flow and collected in a dedicated waste container and then disposed of. The waste and excess flow amounted to approximately 10 L of liquid per hour of operation. During normal operation, the waste and excess flow would be routed directly to drain without collection in a waste container.

#### ***5.5.5 Software/Data Collection***

The 900 Portable software is integrated into the instrument and operated via a touch screen on the front face. The software controls the instrument, displays the data graphically, and stores the data for download. Data collection was initiated and stopped using the touch screen. A separate data tab from the touch screen allowed data to be downloaded to a USB flash drive daily. Downloaded data files were automatically named and were saved as comma delimited text.

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## 6.0 Performance Summary

Summary results from evaluation of the 900 Portable are presented below for each performance parameter evaluated. Discussion of the observed performance can be found in Section 5 of this report.

### 6.1 900 Portable Response to Contaminant Injections

Contaminant injections were performed for aldicarb, carbofuran, colchicine, diesel fuel, disulfoton, mevinphos, nicotine, potassium cyanide, sodium fluoroacetate, *Bacillus globigii*, *Bacillus thuringiensis*, *Chlorella*, ovalbumin, and ricin. The contaminant injection solutions were prepared within 24 hours (most within 8 hours) in the same water that was within the PPL. Since this water contained disinfectants it could cause degradation or transformation of the injected contaminants prior to injection. The 900 Portable responded to all three replicate injections of colchicine and nicotine at concentrations of 0.1 mg/L-10 mg/L in both chlorinated and chloraminated water. In chlorinated water (Table 5-1), aldicarb was detected in two of three injections at 0.1 mg/L and carbofuran was detected in one of three injections at 0.1 mg/L. In chloraminated water (Table 5-2), aldicarb and carbofuran were both detected in one of three injections at 0.1 mg/L. All of the TICs were detected during every injection at 1 mg/L and above with the exception of potassium cyanide which was detected at 1 mg/L only once each in chlorinated and chloraminated water, but was detected in all the 10 mg/L injections. The 900 Portable did not respond to injections of *Bacillus globigii* or *Chlorella* at any injected concentration (Tables 5-5, 5-6). *Bacillus thuringiensis* produced a response at  $10^7$  organisms/L for a mixture of spores and vegetative cells in both chlorinated and chloraminated water. Ovalbumin produced a response for all injections at 0.1 mg/L, 1 mg/L, and 10 mg/L in chlorinated water and in chloraminated water produced a response for one injection at 0.1 mg/L and all injections at 1 mg/L and 10 mg/L. Disulfoton, diesel fuel, ricin, were analyzed only as discrete samples. For these contaminants, the 900 Portable detected a change in TOC in response to 0.1 and 1 mg/L of carbofuran in both water matrices. Although diesel fuel was insoluble, it was added to water and analyzed using the 900 Portable. The results, however, were inconsistent and difficult to interpret. Disulfoton caused a TOC response at 1 mg/L in both water matrices and the 900 Portable detected a response in TOC for ricin at 1 and 10 mg/L. In addition to these measurements, limited experiments were performed to examine the effect of elevated TOC, ionic strength, and monochloramine concentrations on the 900 Portable TOC measurements.

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## 6.2 Accuracy of 900 Portable Measurements

The TOC measurements from the 900 Portable were compared with those from a commonly used reference method and instrument during all of the contaminant injections performed during the evaluation. These comparisons should be interpreted with the awareness that different TOC instruments and oxidation methods can respond differently to various contaminants. Overall, the average absolute value of the %Ds between the 900 Portable and the reference method for all the comparisons across the evaluation was  $17\% \pm \text{SD of } 7\%$ . For TICs in chlorinated and chloraminated water, the %Ds averaged  $15\% \pm 5\%$  and  $14\% \pm 8\%$ , respectively. For the BC, the %D averaged  $19\% \pm \text{SD } 3\%$  and  $15\% \pm 6\%$  for chlorinated and chloraminated water, respectively. For each individual comparison, the experimental error was propagated using the uncertainty of both measurements and is reported. Throughout the evaluation of the 900 Portable, the propagated experimental uncertainty was typically small with respect to %D.

## 6.3 Operational Characteristics

During the evaluation of the 900 Portable, general operational characteristics were observed. Installation and operation of the 900 Portable was straight forward and clearly articulated by the vendor during a one day visit. Operation of the 900 Portable using the touch screen on the front panel was simple and intuitive. Tests were initiated by pressing one button and data was downloaded by following a series of on-screen prompts. Replacement of the reagents and UV lamp were easily accomplished using the instructions in the manual. Messages prompting the user to initiate maintenance tasks were provided on the front panel of the 900 Portable. In the context of this evaluation, where individual experiments lasted approximately one day, the data from the 900 Portable were easily retrieved and in a text delimited format that allowed easy transition into a spreadsheet. This evaluation did not consider other possible data retrieval methods (e.g. SCADA) that could be utilized with the 900 Portable.

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