

**On-line Water Quality Parameters as Indicators
of Distribution System Contamination**

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ABSTRACT

The safety and security of drinking water distribution systems have recently generated considerable interest because of the credible concern that they could be compromised with chemical, biological, and radiological contaminants. In order to protect public health, the United States Environmental Protection Agency (EPA) initiated a program to investigate how changes in water quality parameters, which potentially indicate contamination, may be detected by real- or near real- time sensors. The sensors investigated were off-the-shelf commercial products designed to monitor standard drinking water parameters such as pH, free chlorine, oxidation reduction potential (ORP), dissolved oxygen, specific conductance, turbidity, total organic carbon (TOC), chloride, ammonia, and nitrate. These sensors were mounted within a recirculating pipe loop and challenged with contaminants including secondary effluent from a wastewater treatment plant, potassium ferricyanide, a malathion insecticidal formulation, a glyphosate herbicidal formulation, nicotine, arsenic trioxide, aldicarb, and *E. coli* K-12 strain with growth media. Overall, the sensors that responded to most contaminants were those that monitored for free chlorine, TOC, ORP, specific conductance, and chloride. Generally, the technology used in sensor design or the particular manufacturer of the sensor did not affect the response characteristics. These results may help refine the role of water quality sensors in a contamination warning system (CWS) within a water distribution system.

DISCLAIMER

Any opinions expressed in this paper are those of the authors and do not necessarily reflect the official position and policies of the EPA. Any mention of products or trade names does not constitute recommendation for use by the Agency.

INTRODUCTION

The attacks of September 11, 2001 on the United States have raised concerns that critical elements of the infrastructure might be vulnerable to a terrorist attack. The public drinking water systems, which serve 90 percent of Americans (EPA, 2004), may be vulnerable at some locations. Accordingly, awareness has grown that drinking water is a critical and interdependent component of the nation's infrastructure. Homeland Security Presidential Directive 7 *Critical Infrastructure Identification, Prioritization, and Protection* (HSPD-7, 2003) specifically requires the United States Environmental Protection Agency (EPA) to address the needs of drinking water and water treatment systems. More recently, Homeland Security Presidential Directive 9 *Defense of United States Agriculture and Food* (HSPD-9, 2004) requires EPA to ensure public water quality through surveillance and monitoring initiatives.

There are several technological approaches for the surveillance and monitoring of drinking water. The detection and identification of specific substances in drinking water can involve the use of wet chemistry (such as colorimetric reactions), but generally rely on sophisticated analytical instruments such as gas chromatography/mass spectrometry, inductively coupled plasma techniques and ion chromatography. The expense of these sophisticated instruments makes them uncommon as continuous monitors of drinking water distribution systems. Nonetheless, laboratory analytical instruments can provide definitive confirmation of the presence of potential contamination in the drinking water and are routinely used for compliance monitoring. Because these instruments and associated analytical approaches are designed for compliance monitoring activities, the total analysis times when using them can be quite lengthy and may not be compatible with the goals of on-line monitoring during a water contamination emergency.

However, managing a water contamination threat or incident is not merely an exercise in analytical confirmation. Contamination threat management is discussed in more detail within the Response Protocol Toolbox (RPTB), recently released by EPA to address the complex, multi-faceted challenges of a water utility's planning and response to the threat or act of intentional contamination of drinking water (Magnuson, et al., 2005). The RPTB was developed in support of EPA's "Water Security Research and Technical Support Plan" (USEPA, 2004) through a consensus workgroup which included water utility professionals, officials from the American Water Works Association, and other major water supply organizations.

One step in the contamination threat management process is to understand various warnings that may indicate that contamination of the water has occurred. The RPTB describes eight such warnings, one of which is unusual water quality. Unusual water quality may serve as a warning of potential contamination if the data are available in real-time or near real-time (USEPA, 2003). This type of threat warning could come from on-line monitoring, grab sampling, or a contamination warning system (CWS).^{*} A variety of biological and chemical sensors are used for water quality monitoring. Biosensors use aquatic organisms such as water fleas, mollusks, algae, and fish to detect a sudden change of water quality (States, et al., 2004; States, et al., 2003). While these sensors respond rapidly to chemical and biological contaminants, their sensitivity to disinfectants and other treatment chemicals limits the use of biosensors in the drinking water distribution system. Chemical sensors include free chlorine, oxidation reduction potential (ORP), total organic carbon (TOC), turbidity, pH, dissolved oxygen, specific conductance, chloride, ammonia, and nitrate.

^{*}A CWS involves the active deployment and use of monitoring technologies/strategies and enhanced surveillance activities to collect, integrate, analyze, and communicate information to provide a timely warning of potential water contamination incidents and initiate response actions to minimize public health and economic impacts.

Water utilities have utilized water quality monitoring equipment for process control and compliance monitoring at water treatment plants for many years. The widespread use of these sensors within the distribution system is currently being considered. Prior studies have suggested that continuous turbidity and conductivity analyzers can be utilized to detect the intrusion of wastewater or surface runoff (Kessler, et al., 1998). The Portland Water Bureau in Oregon uses on-line chlorine analyzers to improve process control (Kirmeyer, et al., 2002). The Denver Water Department in Colorado has installed several remote on-line monitors in the drinking water distribution system (Kirmeyer, et al., 2002), such as chlorine, pH, turbidity and temperature detectors. The monitors are connected to a central Supervisory Control and Data Acquisition (SCADA) system. Changes in these parameters relate to treatment plant operation, and may also indicate potential water contamination if properly interpreted. For instance, on-line monitoring may help establish typical background levels of the monitored parameters. These established background levels can then be compared with levels recorded during a suspected contamination incident, such that when a water quality change is detected and is outside the expected range, an alarm will be triggered.

On-line monitors are a topic of much interest for water security applications, although there is a significant level of debate regarding their effectiveness as part of a CWS (ISLI, 1999). The American Water Works Association Research Foundation (AwwaRF) has published a report discussing on-line monitoring for drinking water utilities (Hargesheimer, 2002), which presents the cost-benefit analysis for on-line monitoring. Many of the costs and benefits are based on issues of general water quality, plant operations, and regulatory compliance. The reliability of using water quality sensors to detect intentional contamination has not been extensively investigated (States, et al., 2003). In summary, the use of on-line monitors may serve to increase

the quality of water in general, but there are unanswered questions regarding their applicability as components of a CWS.

The purpose of the current paper is to describe some of the investigations now underway at EPA. These investigations address two key questions surrounding the use of water quality sensors: 1) What types of water quality parameters respond to the greatest number of contaminants? 2) Are there significant differences between sensors for these parameters based on technology or manufacturer? To investigate, relevant response characteristics were compared among various water quality sensors based on different technologies and/or manufacturers. An evaluation of sensor performance, in terms of maintenance requirements, required calibration intervals, cost of operation, and failure rates, was also conducted. There are other related questions, many having to do with data interpretation, which will be the subject of a later publication.

MATERIALS and METHODS

Sensors investigated. Several water quality sensors were investigated in terms of their response following exposure to a contaminant that could be intentionally introduced into water. The sensors identified for evaluation are continuous on-line monitoring devices. Such monitors were selected because response time is critical for achieving the project objective of contamination warning. Table 1 presents a list of the manufacturers and the parameters of the associated sensors. Table 2 lists the sensor technologies evaluated for each parameter. The monitors in which the sensors are incorporated consisted of multi-parameter sondes and single-parameter process monitors presented in Table 1. In general, the measurement technologies employed by the multi-parameter sondes are very similar; the one exception is a sonde that

utilizes planar sensor technology. In this technology, all of the six sensors (Table 1) are engineered to fit on a printed circuit board approximately 1 square inch (6.5 square centimeters) in size.

Pilot Scale Distribution System Simulator. The pilot-scale system used for this test program is a recirculating, pipe-loop distribution system simulator (DSS) located at the Water Awareness Technology Evaluation Research and Security Laboratory within the EPA Test and Evaluation Facility (T&E Facility) in Cincinnati, Ohio. A process flow schematic of the pilot-scale pipe loop DSS system used for these tests is presented in Figure 1. The pipe-loop is constructed from approximately 75 feet (23 m) of 6-inch diameter (15-cm diameter) unlined cast-iron pipe having a total capacity of around 150 gallons (570 liters). The DSS was operated in recirculation mode for the sensor tests. In this mode, the feed tanks and the 100-gallon (379-liter) recirculation tank are in line with the pipe-loop. Operation in this mode effectively increases the volume of water in the system by 85 gallons (322 liters) to a total of approximately 240 gallons (910 liters). When operating in recirculation mode, potable water is added to the system from the 30-gallon (114-liter) feed-water tank at a rate of 0.16 gallons per minute (gpm) or 0.61 liters per minute (lpm). At this rate, the entire volume of water in the loop is replaced every 24 hours. However, due to mixing in the system, the time required to completely exchange the contents of the pipe-loop via dilution is considerably longer. Dye tests have shown that up to several days may be required to completely purge an injected contaminant from the DSS.

Two feed tanks are part of the DSS. One is a 10-gallon (38-liter) chemical feed tank. This feed tank is used to add chlorine to establish baseline conditions prior to the addition of contaminants. For this study, chlorine was added at a rate sufficient to maintain a concentration

of 1 milligram per liter (mg/L) during baseline conditions. The other feed tank is a 50-gallon (190-liter) tank with a delivery line to the intake side of the recirculation pump. This tank was used to introduce contaminants into the DSS. The sensors were installed at approximately 70 feet downstream from the injection point, in a sensor-loop manifold fabricated for the purpose of diverting water flow to the continuous monitors under evaluation.

With the pipe-loop DSS operating at a flow rate of 88 gpm (333 lpm), dye testing revealed that contaminants reach the sensors in approximately 75 seconds after entering at the injection point and rapidly become fully mixed with the 240 gallons (910 liters) of water in the loop. The generated response profiles for injected contaminants reflect this design. The response persists as the contaminant becomes dispersed in the loop followed by a period of recovery associated with dilution or potential destruction of the injected material via reaction with water (hydrolysis) or free chlorine.

Contaminants investigated. Specific quantities of various contaminants were injected into the DSS. The contaminants injected into the loop included non-chlorinated secondary effluent (wastewater) from the Metropolitan Sewer District (MSD) Mill Creek Plant (Cincinnati, Ohio), potassium ferricyanide, a pesticide (malathion) formulation, a herbicide (glyphosate) formulation, arsenic trioxide, nicotine, aldicarb, and *E.coli* K-12 strain grown in Terrific Broth nutritional media. Control samples consisted of injections of uncontaminated pipe-loop water. These control experiments were designed to determine if the sensor response to contaminants could be attributed to the physical disturbance of the injection process.

SCADA system. To facilitate data collection, a SCADA system was installed at the DSS. This system incorporated the electronic hardware and custom software interfaces

necessary for the monitoring devices selected for study. The SCADA system collected, archived, and displayed data from the continuous monitoring devices and the traditional sensors. Software algorithms were used to display historical data and compare any combination of water quality parameters.

Experimental Procedure. Prior to the introduction of contaminants, the water quality sensors were monitored to establish baseline conditions. Sensors were calibrated in accordance with the manufacturer's recommendations and were verified with a calibration check standard. Sensor responses were recorded after establishing stable baseline conditions within the pipe-loop and for at least 4 hours after the introduction of contaminants. Sensor data were collected continuously and archived electronically to establish stable baseline conditions and to record sensor responses to injected contaminants.

After the baseline was stable, either 2.0 gallons (7.8 liters) or 5.0 gallons (19.5 liters) of each contaminant solution were separately injected in the DSS. Each contaminant injection was completed in less than one minute. To investigate reproducibility of the data, sensor responses to each contaminant were evaluated in three separate test runs, using the same volume of solution, but not necessarily using the same quantities of dissolved contaminant. After injection, data from the various sensors were monitored and recorded for a period of 4 hours. The polling frequency of the on-line monitors was every 2 minutes during the 4-hour test run. The sensor data were complemented by the analysis of grab samples taken from the DSS at discrete intervals. (ORP grab samples were generally inconclusive due to problems associated with making this measurement in the experimental set-up.) A series of test runs was conducted by injecting known quantities of potential contaminants into the DSS. Sensor response profiles were generated to identify responses for each water quality parameter versus the contaminant

injected. Grab samples were collected periodically before and after injection of contaminants to evaluate the validity of sensor results. Grab samples were taken prior to injection and post-injection at 3 minutes, 15 minutes, 40 minutes, 60 minutes, 2 hours, 3 hours, and 4 hours.

Sensor response profiles to contaminants for each drinking water parameter were plotted along with associated grab sample results. These plots allowed for 1) the detection of changes in baseline conditions caused by contaminant introduction, 2) comparison of sensors using different technologies to measure the same parameter, and 3) comparison of unexpected responses of the sensors to the contaminant solutions to the grab-sample data. These unexpected responses are referred to as false negative/false positive responses because the sensor did not respond as anticipated based on the chemical properties of the contaminants involved. However, even in the case of false positives/false negatives, the sensor may still have value in helping to detect contamination. Quantitative analysis of these results is warranted, and is the subject of future research. Accordingly, the data analysis discussed below is largely qualitative and is based on whether the sensor response shown on the plots was visually greater than the fluctuations in the baseline.

RESULTS AND DISCUSSION OF SENSOR RESPONSES

Control samples. Experimental controls were used to check for sensor response resulting from the introduction of the control, uncontaminated loop water, into the DSS using the same injection system used for the contaminants described below. Introduction of the control resulted in changes in sensor response in the ammonia-nitrogen ($\text{NH}_3\text{-N}$) and turbidity sensors. However, visually, the magnitude of the changes in both of these sensors were similar to the variations in the baseline.

Wastewater. Nonchlorinated secondary effluent from the Cincinnati MSD Mill Creek Plant was used to investigate sensor response to wastewater. The physical and chemical characteristics of the wastewater (turbidity ORP, ammonia-nitrogen, chloride, etc.) varied considerably during the three wastewater injection runs because the wastewaters were collected at different times. Figure 2 is a representative plot of the response of the in-line free chlorine sensors to a wastewater injection run. Free chlorine, along with ORP levels (not shown), decreased due to the increased chlorine demand. The intensity of the free chlorine demand changed with the variability in the composition of the MSD wastewater between runs. Chloride, specific conductance, turbidity, and TOC exhibited positive deviations from the baseline (not shown). These observations were confirmed by the grab sample results. The responses of sensors can be understood in terms of the differences in characteristics of drinking water compared to that of wastewater, as well as reactions of wastewater with chlorine.

Potassium Ferricyanide. Two tests were conducted using 15 grams of potassium ferricyanide dissolved in 2 gallons (7.8 liters) of loop water, and one test was conducted with 2 grams dissolved in the same volume of solution. The specific conductance of the loop water in the DSS increased with the introduction of the ionic compound (potassium ferricyanide), as expected. ORP sensor response decreased upon injection of ferricyanide, which may be expected because ferricyanide is a mild oxidant (O'Neil, et al., 2001). In comparison to the colorimetric method described below, the free chlorine sensors, based on the membrane electrode method, did not indicate any additional chlorine in the DSS as a result of the introduction of ferricyanide.

The responses of other sensors to potassium ferricyanide were dominated by false positive responses, i.e., responses not consistent with the chemical properties of the contaminant,

which can largely be attributed to interference of potassium ferricyanide with the measurement principle, as explained below. These effects were experienced at both potassium ferricyanide concentrations, and probably also caused a non-linear response of the sensors with respect to concentration.

Figure 3 provides a good illustration of the response of the in-line chloride sensors to a potassium ferricyanide injection. Although confirmed by the grab sample results, the chloride response may also be considered a false positive because the sample was not composed of chloride. The only other potential source of chloride would be via reduction of free chlorine; however, no reducing agents should have been present in sufficient quantities to produce the observed increase in chloride sensor response (equivalent to >10 mg/L). The measurement principle of the grab method is identical to that employed by the continuous monitors, namely a membrane-based ion-selective electrode (ISE). Therefore, one possible conclusion is that the ferricyanide ion is a positive interfering species for chloride at the ISE membrane.

The response of the free chlorine sensors based on the colorimetric process monitor indicated a large positive deviation from baseline conditions after injection. This result was also reflected in the grab sample measurements, which were also based on the same principle. These results may be due to the oxidant properties of potassium ferricyanide, in that it may react directly with the N-N-diethyl-p-phenylenediamine (DPD) reagent in the colorimetric method, mimicking the response to chlorine.

The TOC monitor did indicate an increase in TOC above the baseline which would be consistent with the presence of carbon in the ferricyanide. However, the TOC instrument is based on the persulfate oxidation of organic matter, so the presence of additional oxidant in the form of ferricyanide may interfere with the TOC monitor's response.

Malathion formulation. Two tests were conducted using 1 gram of malathion formulation dissolved in 2 gallons (7.8 liters) of loop water, and one test was conducted with 0.04 grams dissolved in the same volume of solution. Three injection runs were conducted using 2 gallons (7.8 liters) each of malathion formulation to test sensor response to a pesticide (malathion). The malathion formulation selected for this study contains approximately 50 percent of the active malathion ingredient; the remaining fraction contains other proprietary ingredients. Only four sensors responded to the presence of the malathion formulation in the DSS greater than the fluctuations in the baseline: free chlorine, ORP, turbidity (at the higher dose only), and TOC. Chlorine demand is reflected by a decrease in free chlorine concentration and ORP. Turbidity increases might be caused by a suspension formed when the malathion formulation is injected. TOC levels increase as a result of the addition of an organic species in the form of malathion and other inert ingredients in the formulation. An example plot, which shows the response of the TOC analyzer to a malathion injection, is presented in Figure 4.

Glyphosate formulation. One gram quantities of glyphosate formulation were used to investigate sensor response to this formulation, which contained 8 percent of glyphosate along with other proprietary ingredients. Only 4 parameters responded to the introduction of glyphosate formulation into the DSS: free chlorine, ORP, TOC, and chloride. Grab sample results confirm these observations. The glyphosate formulation reacted readily with free chlorine, and the decrease in ORP mirrors the consumption of free chlorine (Figure 5). The positive change observed in the chloride sensor response could be largely due to the proprietary ingredients in the formulation, although chloride could also be formed as a product of the reduction of free chlorine.

Nicotine. TOC and free chlorine were most responsive to 10-gram nicotine injections. The initial baseline values for TOC increased over 100% within 15 minutes of the injection (Figure 6). There was a notable difference between total and free chlorine response. Virtually all of the free chlorine (essentially 100% change in signal) was depleted while only half (around 50% change in signal) of the total chlorine decreased within the first 15 minutes of injection. This change is consistent with the formation of an N-chloro compound by reaction between the nicotine and the free chlorine. Because this reaction is not expected to result in significant reduction of the free chlorine to chloride, no change in the chloride sensor response was expected or observed. Similarly, the specific conductance monitors tested were not affected by this contaminant.

Arsenic Trioxide. All of the free and total chlorine (100% change in signal) was depleted within 15 minutes of the injection of 10 grams of arsenic trioxide, a known reducing agent. An example plot, which shows the response of the free and total chlorine analyzers to an arsenic trioxide injection, is presented in Figure 7. The TOC monitor did not respond to the injections greater than the fluctuation in the baseline. The arsenic trioxide was difficult to dissolve in tap water due to low solubility which, combined with mixing effects upon injection, may account for the response of the turbidimeter to this contaminant. The response of the ammonia-nitrogen and ORP sensors was greater than baseline variation, which was unexpected.

Aldicarb. All of the free and total chlorine was depleted within 15 minutes of injection of 10 grams of aldicarb, which is known to react rapidly with chlorine. The response from the TOC monitor increased relative to the baseline TOC value within 15 minutes of the injection. An example plot, which shows the response of the TOC analyzer to an aldicarb injection, is

presented in Figure 8. The specific conductance monitors tested were not responsive to this contaminant.

***E. coli* in Terrific Broth Growth Medium.** Each test run was conducted using 10 grams wet cell weight of *E. coli* K-12 strain in 1 liter of Terrific Broth growth medium. The concentration of *E. coli* within the loop was approximately 1.6×10^5 cells/milliliter. Three additional test runs were also performed using 1 liter of the growth medium only without *E. coli*. The free chlorine sensor response indicated essentially quantitative depletion by the combination of *E. coli* and the Terrific Broth growth medium. Some of the free chlorine evidently was not oxidized but formed combined chlorine, resulting in a smaller change in total chlorine response. The TOC sensor response also showed an expected increase (Figure 9). Increases in turbidity response were primarily observed for the test runs involving *E. coli* with Terrific Broth, but not for the test runs using growth medium only. With the exception of response to turbidity, it was also observed that the experimental results for the other sensors were similar whether *E. coli* was present or not. This suggests that the sensors are responding primarily to the growth medium instead of the *E. coli*.

OBSERVATIONS REGARDING SENSOR OPERATION

The following summarizes some salient, operational features of the water quality sensors investigated. These features involve qualitative observations regarding the various types of technologies used in these sensors. Other observations involve their maintenance and relative cost. Some of these features were based on experience gathered during this investigation while others are based on the historic operation of and industry experience with the sensors. It should be noted that some of these observations apply only to the specific units used in this test (Tables

1 and 2). While these types of sensors are potentially subject to revolutionary developments by the manufacturers, improvements in the designs of subsequent models of these technologies to date appear to be generally incremental, so the following general observations may be more valuable for current models.

Ion-selective electrodes. Based on an examination of the raw data plots, there is no discernible difference in the operating characteristics among vendors of the chloride, nitrate, and ammonium ISE analyzers. There are several characteristics of ISE analyzers that affect their operation. For instance, the nitrate electrodes could not be calibrated properly after they were exposed to chlorinated water, perhaps because chlorine alters the function of the ion-selective membrane, causing debilitating drift and long response times. Therefore, long term use of nitrate electrodes in chlorinated water would not seem possible. Although not as dramatic as the nitrate electrode failure, under continuous use in chlorinated water, the chloride and ammonium sensors fail at the rate of once every 3 to 6 months. Replacement electrodes cost approximately \$370. Additionally, calibration of these sensors was required approximately every 2 weeks, in order to remain within manufacturers' drift specifications (± 20 percent). Calibration solutions were purchased from the vendors, at an average cost of \$50 and \$80 per liter, and it was found that the integrity of these solutions was not compromised if reused four or five times. For the best accuracy, three-point calibrations were used, i.e., a two-point calibration with the addition of one calibration point repeated at low temperature, are recommended. While this procedure compensates for drift associated with temperature change, two-point calibrations may suffice if deviation from baseline conditions is the relevant criterion.

Specific conductance monitors. There are no substantial differences in the operating characteristics among the different specific conductivity cell designs and manufacturers.

Operationally, calibration is very easy with a single-point offset using a commercially-available calibration solution, and the sensors were all viable over the course of the experiment. In fact, they are generally expected to last for years if properly maintained. The required maintenance consists of brushing debris from the sensing surfaces. Care must be exercised with the annular-ring carbon electrodes to avoid wearing down the surface during cleaning.

The electrodes tested were composed of a variety of materials, e.g., noble metals, stainless steel. In the current study, the choice of material did not affect baseline stability. However, it is well known that some substances will “plate” onto certain metals; thus, baseline stability could vary with source water and potential contaminants to which the electrode is exposed.

Turbidity monitors. The turbidity sensors, all based on different designs (Table 2) by different manufacturers, behaved similarly to each other. The presence or absence of an integral wiper did not affect performance in potable water. Calibration requires good operator skill and practice. When calibrated and properly serviced (clean optical surface), these devices are very stable.

Free/total chlorine monitors. Three different principles of detection by three different manufacturers were tested: DPD colorimetric, polarographic, and voltametric. The single parameter free chlorine monitors (colorimetric and polarographic) cost between \$3,000 and \$5,000, while the five-parameter planar (voltametric) technology costs approximately \$10,000. Each of these systems exhibited very different operating characteristics, and a fundamental difference relates to how these monitors are placed in service within the water system. The DPD colorimetric system withdraws a discrete sample from the flowing pipe and then performs a wet chemistry analysis, including the addition of reagents which cannot be returned to the

distribution system, although manual disposal does not involve particularly hazardous materials. The discrete sample analysis results in a sampling interval of approximately 3 minutes. Sensors operating on non-colorimetric detection do not add reagents and provide essentially continuous monitoring because they are placed within a slip-stream of the water pipe.

The failure rate of the equipment for colorimetric methods is historically low when properly serviced (monthly and quarterly scheduled maintenance). The polarographic technique is also very reliable if membranes are replaced on an average of every 2 months. These devices must be periodically checked because the electrolyte slowly bleeds out through the membrane and must be recharged if the resulting air bubbles become large enough to expose the internal electrodes.

Every 6 months, rigorous (acid) cleaning of the polarographic electrodes is required, and calibration intervals averaged approximately 2 weeks to achieve a drift specification of ± 20 percent. A reference method, such as the one used for grab samples, must be available on site to calibrate the polarographic membrane electrode method. The planar measurement technology required frequent calibration weekly or more often. The planar sensor calibration also requires the availability of a reference method.

TOC monitor. The TOC monitor tested performs a sophisticated wet chemistry analysis and costs between \$19,000 and \$29,000 per unit. A qualified technician can perform calibration and reagent preparation. However, an experienced operator with extensive training should be available to properly service the system in accordance with the recommendations of the manufacturer. Such service includes tubing and pump maintenance because this is a wet chemical system. The system uses reagents which cannot be returned to the distribution system, although manual disposal does not involve particularly hazardous materials.

ORP monitors. Electrode detection technologies of various materials of construction provided by three manufacturers were tested. The ORP levels dropped along with the free/total chlorine levels, as a result of the contaminant injections. The ORP baseline values showed less fluctuation and were more stable than the free/total chlorine values, but the magnitude of the change was not as pronounced as it was for free/total chlorine perhaps because the ORP value results from a combination of redox-active species.

CONCLUSION

One important caveat to the results presented here is that the characteristics of distribution system water used in this type of investigation can significantly impact the results. Thus, while there are many observations that may be possible from the data generated by these experiments, the following discussion involves those results that seem most applicable to distribution system waters in general.

No single chemical sensor responded to all of the contaminants used in this study, yet some sensors responded to the introduction of a larger number of contaminants than others. Table 3 summarizes the response of the sensors in terms of which sensors showed a response of greater magnitude than baseline fluctuations. The table also indicates whether the value of the response was greater than or less than the baseline value. Table 3 does not indicate the absolute magnitude of the change. While the absolute magnitude may be part of a detailed quantitative analysis, qualitative observations were the focus of this study. When performing a quantitative analysis, it is not only the absolute magnitude of the change that is important, but also the magnitude relative to the size and fluctuations in the baseline along with the slope of the change (i.e., to determine if the changes occur over several hours or several minutes). Thus, quantitative

evaluation makes use of principles of signal to noise, which is difficult to generalize and is location-specific.

An examination of Table 3 reveals that there were several sensors that responded to a large number of contaminants. These were specific conductivity, TOC, free chlorine, chloride, and ORP. The chlorine sensors appear to respond to all contaminants, although it is well known that some potential contaminants do not react significantly with chlorine. The TOC responded to all the organic (carbon-containing) compounds; the TOC monitor, however, has a higher capital cost when compared to other sensors. The calibration requirements for the sensors in these systems vary from weekly to monthly. Each sensor has a reagent and maintenance cost of several hundred dollars per month.

This group of sensors provided consistent changes in response to contaminant injections. In general, the magnitude of these sensor responses was dependent upon the concentration of the contaminant injected, chemical and physical phenomena which occurred as a result of contaminant injection into the DSS water, and dilution effects. The baseline stability of the sensors over 15-minute intervals in actual field conditions warrants further investigation.

While only a handful of contaminants were tested, the results presented here demonstrate that selected on-line sensors, regardless of their technological basis or manufacturer, may be able to detect the presence of contaminants in a dynamic water supply. All of the contaminants injected at the T&E Facility caused at least one or more water quality parameters to change significantly in response to the injection. Further studies are planned to determine the threshold of such systems relative to toxicity and nuisance effects for real and surrogate contaminants of concern in the field. Studies, similar to the ones described above, with chemical and biological

warfare agents have been initiated by another organization, along with research to determine the minimum contaminant dose required to trigger a sensor alarm.

Clearly, very careful quantitative analysis of the sensor data is required to establish the relationship between the identity of a specific contaminant, concentration of the contaminant, and the responses of various sensors, used separately or in combination. It is important in this regard to emphasize that unusual water quality data, from sensors or other sources, should be evaluated against an established baseline that captures normal variability in the system, both temporally and spatially. Deviations from an established water quality baseline may serve as a threat warning and should be investigated to determine whether or not the results are indicative of potential contamination. In the absence of a baseline, it will be difficult to discriminate between normal variability and legitimate threat warnings; this situation could lead to unacceptable false alarms.

Based on complex statistical arguments, the value of such quantitative analysis of sensor data and baseline values is not clear (Hrudey, et al., 2004; Hrudey, et al., 2003). Accordingly, on-line water quality monitors may provide data to help protect the drinking water supply against contaminants, although such data might not be solely used in response to an emergency. Rather, sensor data might be used to complement other sources of data for an effective surveillance and monitoring program, leading to an emergency response that is protective of public health and other societal interests.

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Table 1: Sensors Evaluated

Probe type	Model (water quality parameters sensed)
Single Parameter	ATI A/S (free chlorine) Hach Cl-17 (free/total chlorine)* Hach 1720 D (turbidity)* GLI Model PHD (pH)* GLI Model 3422 (specific conductance)* Hach Astro TOC UV Process Analyzer (TOC)
Multiparameter	Dascore Six-Sense Sonde (specific conductance, DO, ORP, pH, temp, free chlorine) YSI 6600 Sonde (specific conductance, DO, ORP, pH, temp, ammonia-nitrogen, chloride, nitrate-nitrogen, turbidity) Hydrolab Data Sonde 4a (specific conductance, DO, ORP, pH, temp, ammonia-nitrogen, chloride, nitrate-nitrogen, turbidity)

*These sensors were contained within the same panel (Aquatrend)

Table 2: Parameters measured and principles of detection for the sensors used in this study

Water Quality Parameter	Detection Principle	
	On-line Sensor	Grab Sample
Ammonia - nitrogen	NH ₄ ⁺ ion-selective electrode in sonde (NH ₃ is calculated)	Colorimetric
Chloride	Ion-selective electrode	Ion-selective electrode
Dissolved oxygen	Membrane electrode method in sonde (without low-flow technology; circulator available)	Membrane electrode method
	Membrane electrode method in sonde (low-flow technology; no circulator)	
	Membrane electrode method; solid-state reference electrode	
	Three-electrode volt-a-metric technique (planar sensor technology)	
Free chlorine	(DPD) colorimetric	Colorimetric
	Three-electrode volt-a-metric technique (planar sensor technology)	
	Polarographic with Cl ₂ permeable membrane	
Nitrate-nitrogen	Ion-selective electrode	Colorimetric
Oxidation-reduction potential	Potentiometric, platinum electrode	Potentiometric platinum electrode, Ag/AgCl reference electrode
	Potentiometric, flat platinum sensing surface	
	Noble metal sensors (planar sensor technology)	
pH	Proton-selective glass electrode (sonde)	Glass combination electrode
	Proton-selective glass electrode in sonde (non-fouling version)	
	Flat surface proton-selective glass combination electrode	
	Proton-selective glass combination electrode	
	Proton-selective metal oxide (planar sensor technology)	
Specific conductance	Annular-ring carbon electrodes (sonde)	Platinum electrode method
	4 nickel electrodes (sonde)	
	Noble metal sensors (planar sensor technology)	
	Titanium and stainless steel electrodes	
Temperature	High-stability thermistor (sonde)	precision thermistor
	Sintered metallic oxide thermistor (sonde)	
	Platinum thermistor	
	Platinum thermistor (planar sensor technology)	
Total organic carbon	UV-persulfate oxidation, NDIR detection of carbon dioxide	UV-persulfate oxidation, NDIR detection of carbon dioxide
Turbidity	Nephelometric signal at 880 nm LED (90 degrees); shutter technique (sonde)	Ratio nephelometric signal (90 degrees) scatter light ratio to transmitted light
	Nephelometric signal 860 nm LED (90 degrees) with integral wiper (sonde)	
	Nephelometric signal, tungsten filament (90 degrees)	

DPD: N-N-diethyl-p-phenylenediamine LED: Light emitting diode NDIR: Non-dispersive infrared

Table 3: Sensor response following introduction of contaminant

Contaminant	Sensor Response	
	increase from baseline	decrease from baseline
Wastewater	Chloride Specific conductance Turbidity TOC	Free chlorine ORP
Potassium ferricyanide	Free chlorine (DPD) * TOC Chloride Nitrate-nitrogen Ammonia-nitrogen ORP	
Glyphosate formulation	TOC Chloride	Free chlorine ORP
Malathion formulation	TOC Turbidity	Free chlorine ORP
Aldicarb	TOC Turbidity	Total Chlorine Free chlorine ORP
<i>E. coli</i> in Terrific Broth	TOC Ammonia-nitrogen Turbidity	Total chlorine Free chlorine
Terrific Broth	Turbidity TOC	Total chlorine Free chlorine ORP
Arsenic trioxide	Turbidity Ammonia-nitrogen	Total chlorine Free chlorine Nitrate-nitrogen ORP
Nicotine	TOC Ammonia-nitrogen Chloride	Free chlorine Nitrate-nitrogen ORP

*Potassium ferricyanide injected which was yellow in color may have masked the DPD colorimetric method creating an increased reading from the baseline.

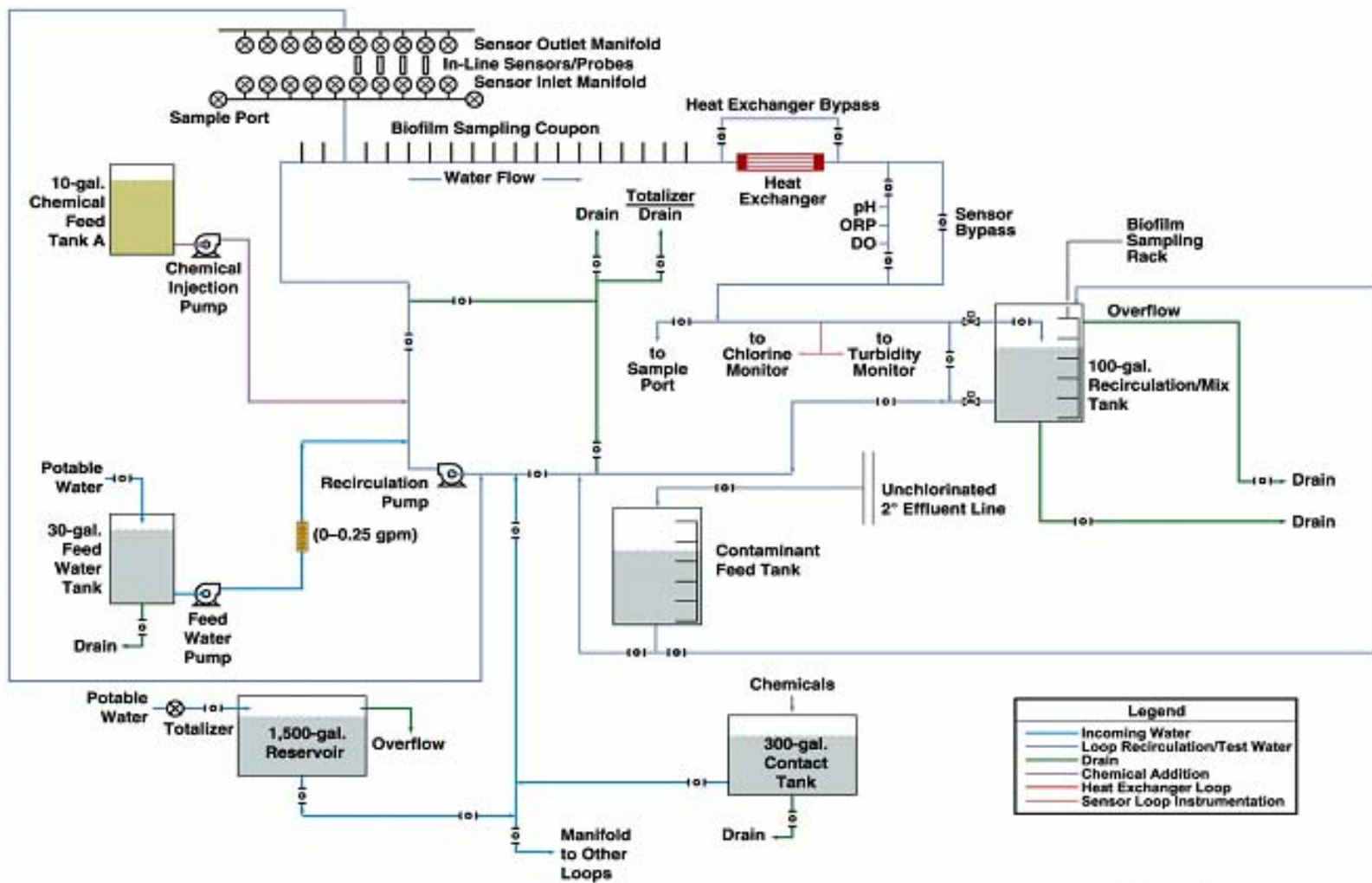


Figure 1.
Configuration of Pipe Loop for Sensor Study.

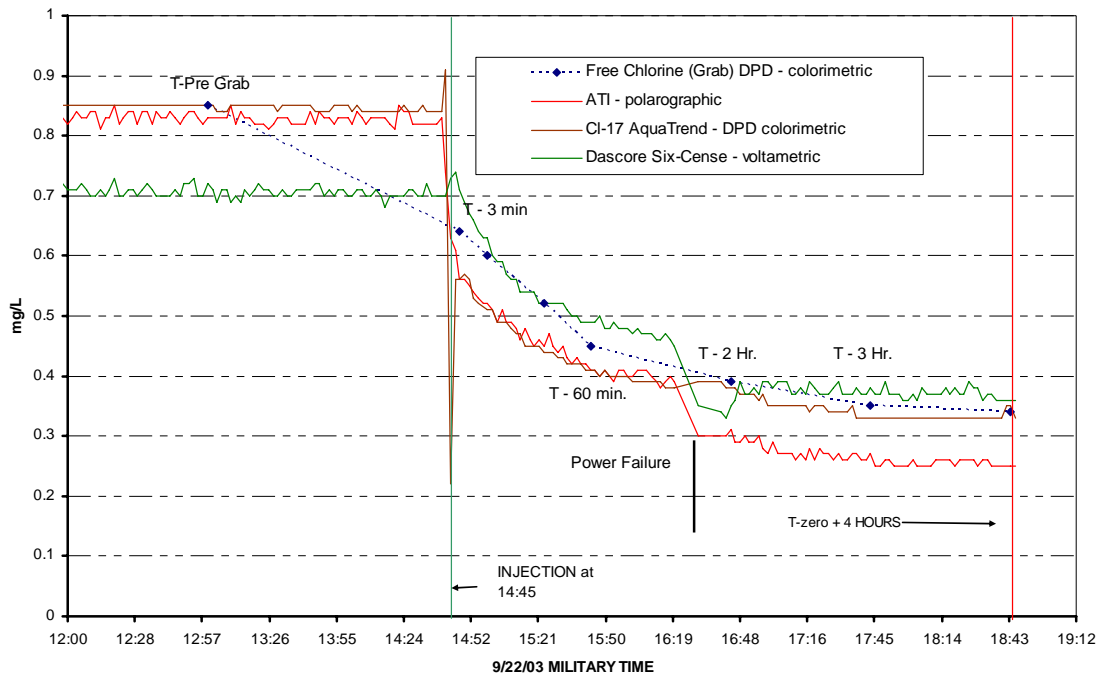


Figure 2: Free Chlorine Sensor Responses Upon Injection of Wastewater

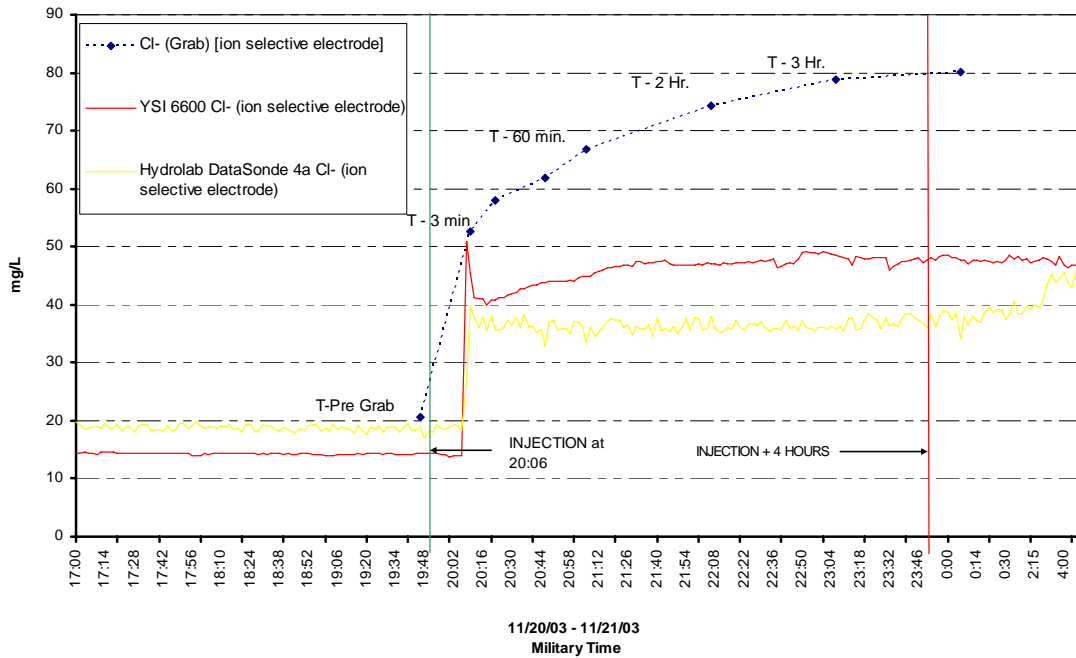


Figure 3: Chloride Sensor Responses Upon Injection of Potassium Ferricyanide Solution

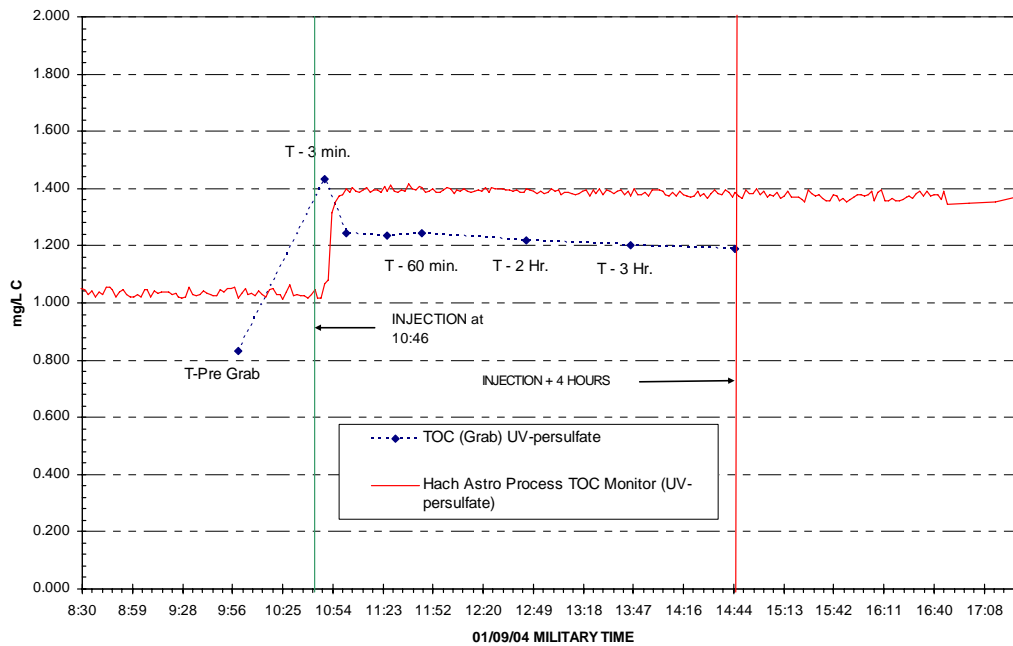


Figure 4: TOC Analyzer Response Upon Injection of a Pesticide (Malathion) Solution

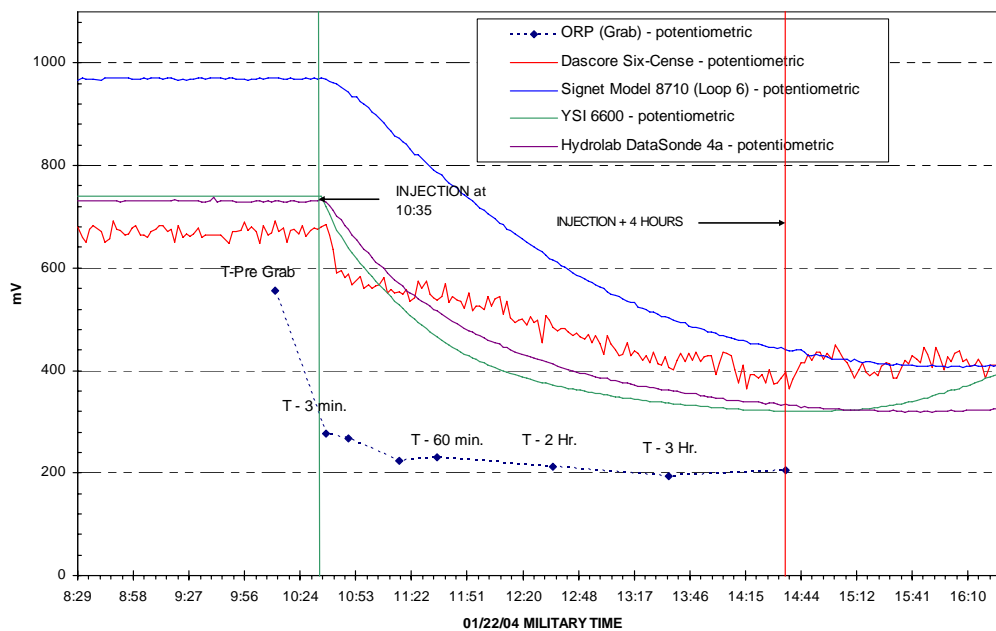


Figure 5: ORP Sensor Responses Upon Injection of a Herbicide (Glyphosate) Solution

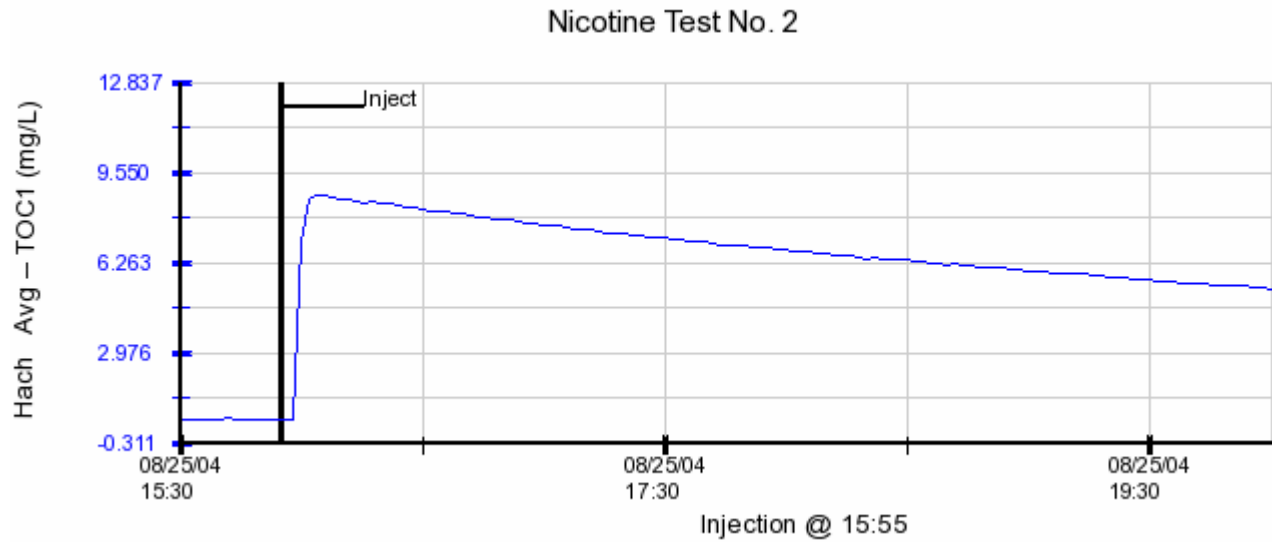


Figure 6: TOC Analyzer Response Upon Injection of Nicotine*

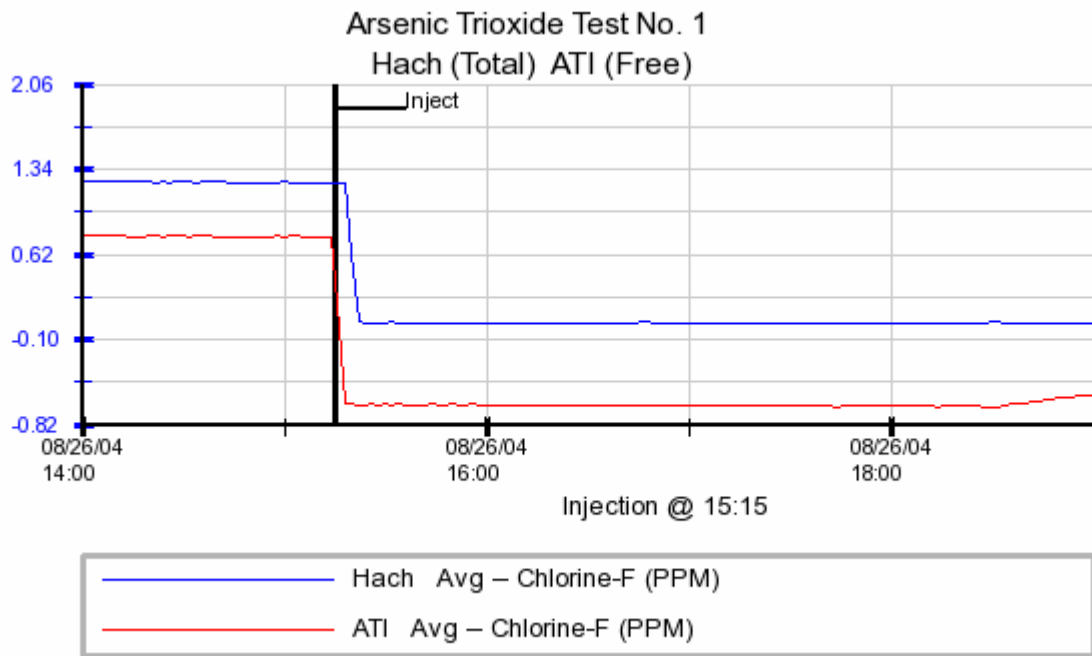


Figure 7: Free & Total Chlorine Sensor Responses Upon Injection of Arsenic Trioxide

* In the process of conducting the studies, the graphing software was replaced resulting in a difference in appearance of the later graphs

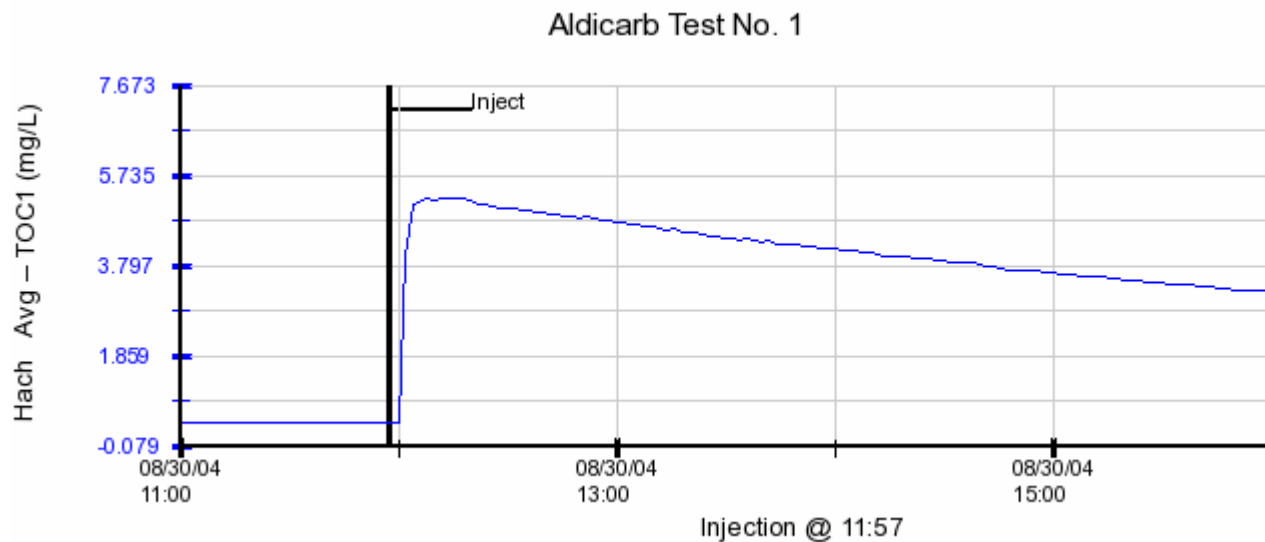


Figure 8: TOC Analyzer Response Upon Injection of Aldicarb

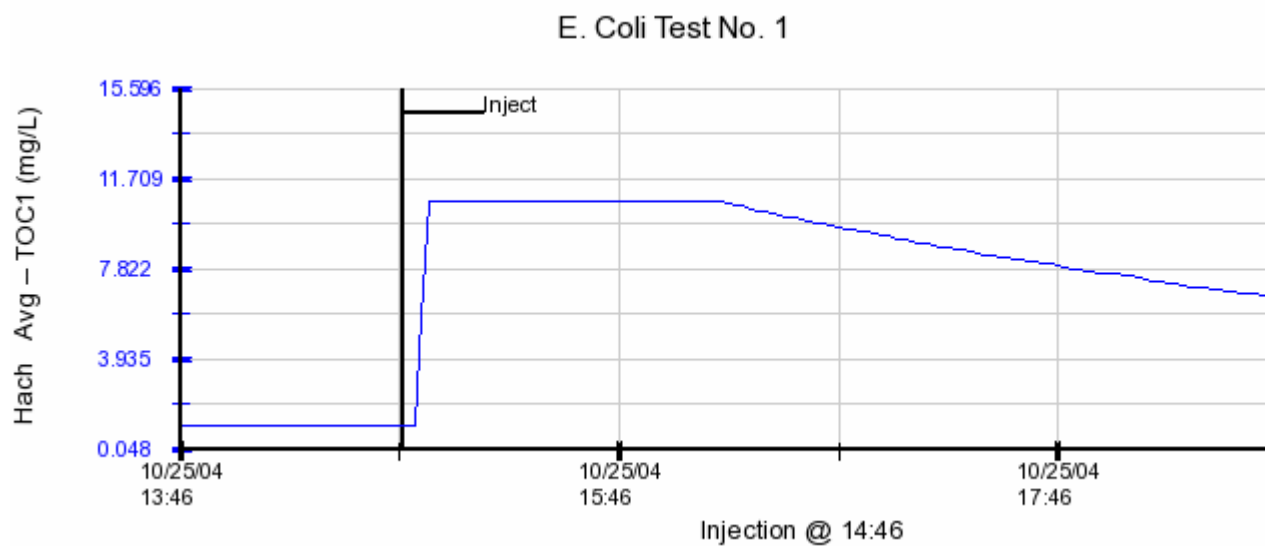


Figure 9: TOC Analyzer Response Upon Injection of E. coli in Terrific Broth