CHALLENGE STUDIES OF THE PITTSBURGH DISTRIBUTION NETWORK PILOT CONTAMINATION WARNING SYSTEM

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The security and safety of the drinking water distribution system has recently generated concern. Accidental and intentional contamination by chemical, biological and radiological contaminants could cause major consequences for the consumer because clean water is critical to the nation's infrastructure. An attack on the water supply could disable an entire city. Therefore, it is necessary to develop a system to monitor the water quality to ensure the water is safe for consumption.

In an attempt to protect the water systems, Pittsburgh Water and Sewer Authority (PWSA) initiated research to test the various instruments within a Contaminant Warning System (CWS). The system measures water quality and triggers an alarm for deviation in the quality. The different methods of detection utilized in the study include turbidity, chlorine, pH, conductivity, TOC, Online gas chromatography-mass spectrometry, ultra violet transmittance, biomonitor, and a pathogen identification system.

The contaminants were pumped into the pilot distribution system CWS, and the responses of a variety of online monitors were evaluated. The contaminants range from fluorosilicic acid, which is used to increase the fluoride concentration of water, to a nonpathogenic species of *Bacillus,* which could serve as a model for *Bacillus anthracis*, the bacterial species that causes the disease anthrax. The system was connected to main transmission lines that feed downtown Pittsburgh with drinking water. While many of the monitors detected one or more contaminants, at least one of the devices used in the pilot distribution system CWS responded all of the contaminants.

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1.0 INTRODUCTION

Since the terrorist attacks of September 11, 2001, there has been an increased concern in the security of the drinking water infrastructure. As a result, the water industry and federal government have begun to demonstrate the development of a Contamination Warning System (CWS), in an effort to detect the sudden appearance of contaminants in public water supplies. In fact, Homeland Security Presidential Directive 9 (HSPD-9) directed USEPA, the lead agency for protection of drinking water and wastewater utilities, to "develop robust, comprehensive, and fully coordinated surveillance and monitoring systems…that provide early detection and awareness of disease, pest or poisonous agents" (Bush, 2004). The goal of the directive is to develop monitoring systems that not only enhance security against manmade events, but protect against 'All Hazards' by warning utilities of accidental contamination that may occur as a result of industrial spills into the source water, as well as from cross connections, back siphonages, and water main breaks that occur in the finished water distribution system. Additionally, it is hoped that multiple benefits can be derived from the deployment of online monitoring equipment that may provide useful information for utility regulatory compliance and process control.

The Pittsburgh Water and Sewer Authority (PWSA) provides drinking water treatment and distribution for the City of Pittsburgh and several surrounding municipalities. Average daily production of drinking water is approximately 75 mgd, with seasonal peaks of 100 mgd. Following the events of 9-11 Pittsburgh, like a number of other American cities, has been investing resources into increasing their online surveillance of water quality throughout the

finished water distribution system. The research reported herein was completed in cooperation with PWSA. Research was carried out to install and test a pilot contamination monitoring system located on a primary water distribution main going to downtown Pittsburgh.

This overall objective of installing, operating, evaluating and challenge testing a drinking water contaminant warning system can be divided into the following specific objectives:

- Observe changes in water quality parameters in response to an accidental or intentional contamination event;
- Analyze the detection of a contamination event by the contamination warning system instruments;
- Distinguish the difference from a true contamination event and normal back ground variation; and
- Scrutinize the usefulness, accuracy, and detection capabilities of the instruments in the pilot online monitoring system.
- Provide guidance to the water industry on the usefulness and accuracy of contaminant warning systems and their application in contaminant event detection.

The pilot CWS is located and connected to a water distribution main upstream of downtown Pittsburgh. The intention of the CWS is to identify contamination before the downtown population is affected. To monitor the water quality, a variety of equipment was used in the CWS including:

- Hach Distribution Panel and Event Sensor;
- Sievers TOC Analyzer;
- INFICON Online GC-MS;
- JMAR Biosentry Pathogen Identification System;
- Biosensor Fish Monitor; and
- Real Tech UVT 254 Online Monitor.

All the instruments continuously monitor the water quality. Changes in one or more monitored parameters could indicate a possible contamination. Once detected, the alarm should be evaluated and the appropriate action taken before the consumers are adversely affected. To test the system, select toxins related to accidental and intentional contamination were introduced

into the pilot system. The contaminants range from fluorosilicic acid, used to increase the fluoride concentration of water, to a nonpathogenic *Bacillus* species that serves as a model for the pathogenic *Bacillus anthracis*, the bacterium that causes anthrax. The next section discusses the background and literature associated with this research project.

2.0 BACKGROUND

The terrorist attacks on September 11, 2001 made it apparent that national infrastructure might be vulnerable to an attack. Water is a resource that affects every facet of life because it is not only used for drinking but also cooking, bathing, public health (hospitals), firefighting, and sanitation. The absence of clean water would negatively affect the economy. An attack on the water supply, downstream of a major treatment plant, could go undetected until individuals become ill and doctors/hospitals report cases. In the case of pathogens, days could pass before people become seriously ill. The potential to cause mass causalities is highly probable and detection needs to be available to protect against these events. An attack on a single metropolitan water supply would cause terror and national skepticism in water safety.

Accidental contamination is also a concern for the water sector. The possibilities of breakthrough of the filters or overdosing of treatment chemicals are events that could go unnoticed. The events although not deliberate could still cause widespread illness. Fire hydrants are of particular concern for intentional contamination. There are typically hundreds or thousands of hydrants within a municipality. A pump or pump truck large enough to overcome the hydrant pressure could be used to inject contaminants into the water supply.

Continuous monitoring of water within the distribution system could provide a rapid detection of changes in water quality. Quick detection could decrease cases of illnesses or even death. The distribution system is especially vulnerable due to the large geographic area and ease

of accessibility [Byer & Carlson, 2005]. The overall goal of the water sector is to provide clean water for the nation's population.

2.1 INTENTIONAL CONTAMINATION EVENTS

The possibility of a contamination event is real. Actions that would disrupt the system include [Bitton, 2005]:

- Physical destruction
- Chemical contamination
- Cyber attack
- Bioterrorist attack

Disruptions of the water supply by destroying treatment equipment would be an act of physical destruction. Chemical contamination would be done by deliberately injecting chemicals into the distribution system. Today, computers control many of the processes at the water treatment plant. A cyber attack could be done by a hacker disrupting the water operation via computer access. Lastly, a bioterrorist attack would be injection of microbes with the intent to cause harm to the consuming population. For this research, chemical and biological contamination will be the focus.

Contaminants can infect humans by adsorption through the skin, ingestion and inhalation. To have the greatest impact on a population, the ideal contaminants would have characteristic of [States, 2008]:

- Low infectious or toxic dose
- Chlorine resistant
- Stable in water
- Easily obtained
- Difficult for consumers to detect in water by appearance, odor, or taste
- Produces severe disease or results in death

Although a terrorist event affecting water supplies has not occurred within the US, vandals and disgruntled workers have caused problem for water utilities. Below is a summary of some accidental and intentional contamination events that have occur within the last 15 years.

2.1.1 Milwaukee, 1993

The largest outbreak of cryptosporidiosis occurred in Milwaukee, Wisconsin. It was caused by a combination of natural event and water treatment failure. The incident affected 403,000 residents with 4,400 people being hospitalize and 54 deaths.

2.1.2 Kosovo, 1998

In Kosovo, wells were poisoned with animal carcasses and hazardous material like paint, oil and gasoline by Yougoslav federal forces, or their allies. Seventy percent of the wells were contaminated. The events caused people to become ill and prevented the use of well water for an extensive period [Washington Post, 1998].

2.1.3 Ohio, June 2001

In Canton, Ohio, a former water department employee poisoned a pair of wells with organic trichloroethylene. Residents were warned not to drink, bathe or wash clothes for six days until home wells were inspected and cleared. “Preliminary samples showed levels of tetrachloroethane and trichloroethylene at 1,600 parts per billion, or about 400 times the safe limit set for drinking water by the Environmental Protection Agency” [Nation in Brief, 2001].

2.1.4 California, November 2001

In Portola, CA two locks to the city's one million gallon water storage tank were discovered missing. The city ordered a 'do not use' to thousands of consumers that rely on that water. The water was tested but no contamination was detected [Groover, 2005].

2.1.5 Rome, February 2002

The Italian police confiscated cyanide and maps of the city from four Moroccans. The arrested men were carrying 9 pounds of potassium ferricyanide and maps pinpointing the embassy and of the water distribution system of the city. The embassy was the suspected location for the attack [USA Today, 2002].

2.1.6 Iowa, May 2002

Juveniles were suspected in a case of vandalism at the water pumping station in Dawson, Iowa. Officials found chemicals splattered inside the building, and damaged computers.

2.1.7 Wisconsin, June 2002

In Janesville, WI, the barbed wire perimeter fence to a five million gallon storage tank was cut and the pad lock removed. The water department drained the tank and it was super chlorinated as a precaution. No evidence of contamination was found but the city added $150K in security improvements [Groover, 2005].

2.1.8 Florida, January 2003

In Debary, FL, the lock on the entry gate was broken and screens removed from the aerators. Introduction of a contaminant could have affected the water in more than 4,000 homes, but no contaminants were found. The officials suspect that the break in was a "professional job" beyond vandalism [Groover, 2005].

2.1.9 Jordan, April 2003

Iraqi agents were arrested before they executed their plotted plan to poison a water tank in Khao, Jordan. The tank supplied water to American Troops [New York Times, 2003].

2.1.10 Greenville, October 2003

In Greenville, South Carolina, the city's water supply was threatened with ricin poisoning unless demands were meet. The attacker wanted changes made in federal regulation pertaining to the number of hours that overland truckers were allowed to drive without rest. A vial of highly concentrated ricin was found in the local post office, but subsequent tests found no ricin in the water system [Greenville News, 2003].

2.1.11 China, 2003

In Henan Province, approximately 500 ml of pesticide was dumped into the city's reservoir that serves 9,000 homes. The act was carried out by a water purification device salesman in an effort

to promote sales. There were no deaths reported but 64 people became ill and 42 of them were hospitalized [BBC, 2003].

2.1.12 Pakistan, 2008

Five Sunni militants were arrested in a planned attempt to poison a water supply with cyanide powder. The target was the water distributed during a Shiite Muslim festival of Ashura in Karachi. Police recovered 500 grams of cyanide and concluded that the aim was to cause mass causalities [Wall Street Journal, 2008].

2.2 WATER CONTAMINATION INFORMATION TOOL (WCIT)

Introduced in late 2005, the online database provides information about chemical, biological and radiological contaminants of security concern. The password-protected database contains information on 93 different contaminants that are of concern to drinking water and wastewater. Unlike, other datasheets, WCIT provides water specific data about the contaminants. The United States Environmental Protections Agency (USEPA) operates the website. The site provides quick access to vital information about regulated and non-regulated contaminants.

Each contaminant is divided into a category defining the type of contaminant. The categories include organic, inorganic, biotoxin, pathogen, chemical warfare agent, radioisotope and radiochemical.

Each contaminant in WCIT includes information about [USEPA, 2007]:

- Name, chemical abstract service (CAS) ID;
- Physical or pathogen properties;
- Availability;
- Fate and transport;
- Medical and toxicity information;
- Field and laboratory methods;
- Drinking water and wastewater treatment;
- Environmental impacts; and
- Infrastructure decontamination.

Physical properties include information about solubility, vapor pressure, density, and Henry's law coefficient for each contaminant. For biological contaminants, size, shape and motility information is provided for the infective, reproductive, and resistant stages. The ease in which to obtain the substance, either by purchasing, harvesting or synthesizing is delineated in availability. Information about chlorine reactivity, adsorption, stability and reactivity in water, thermal inactivation, and half-life is found in the fate and transport. Under medical and toxicity, basic facts about adsorption, inhalation, and ingestion exposure are provided along with the lethal dose for 50 percent of a test population dies (LD_{50}). WCIT also, provides information on the effectiveness of drinking water and wastewater treatment processes in removing or inactivating a particular contaminant. For drinking water, alum coagulation, reverse osmosis, lime softening, carbon adsorption, and advance oxidation processes are evaluated for each contaminant. Activated carbon and multiple other disinfection possibilities are outlined for their effectiveness in removing the toxin. The section on infrastructure decontamination outlines the steps that should be taken if the contamination event were to occur.

The database is password protected and access is limited. Organizations that are eligible include [USEPA, 2007]:

- Drinking water and wastewater utilities;
- State drinking water primary agencies;
- Drinking water and wastewater associations partnering with EPA;
- State and local public health officials;
- Federal officials ; and
- State laboratories

2.3 RESPONSE TO A CONTAMINATION EVENT

Should an accidental or intentional contamination event occur, an emergency response plan is needed with clear concise steps. The EPA has developed the Response Protocol Toolbox, which outlines the steps to take during drinking water contamination event [USEPA, 2003]. The methods and steps do not guarantee that the contaminant will be identified, but a quick and safe evaluation of the water.

2.3.1 Site Characterization

EPA recommends that a field safety screening be conducted on a suspected site before the response team proceeds with testing and sampling [USEPA, 2003]. The three objectives of field-testing the water are to assess the credibility of the threat, to identify the possible contaminant and to determine if special precautions are needed during testing and sampling. The preliminary and presumptive contaminants will be justified by additional laboratory tests. For an assessment

of the level of threat, basic information about the water is needed. Therefore, tests need to be conducted on the water in question.

The first recommended step in a field safety screening is to examine the site for radiological hazards. Radiation detectors are an established technology. They are quick, easy to use and are capable of analyzing for alpha, beta and gamma radiation. In addition to ruling out a possible radiation contamination, the test is a safety screening for the response team. If radiation is detected, special personal protective equipment is needed for additional testing and sampling.

To proceed with further tests, baseline information about the water is necessary. Average distribution values for basic water quality are a valuable resource in interpreting results of general water quality. To ensure proper results, TOC, chlorine residual, or conductivity, among others, need to be compared against baseline values to determine if deviations have occurred. Parameters to consider for routine monitoring include:

- pH
- Conductivity
- TOC
- Chlorine/chloramines residual
- Total organic carbon (TOC)
- UV absorbance

With the exception of chlorine, the other parameters typically remain relatively stable throughout the distribution system [USEPA, 2003]. Although there will be slight variations of these due to changes in finished water quality. Chlorine concentration usually fluctuates with time and location and is a function factors such as of temperature, water usage, and distribution system residence time. Within many systems, there are also disinfectant booster stations to maintain the chlorine residual.

2.3.2 Rapid Analytical Field Testing

Once the site has been cleared, testing and sampling can begin. The flow chart for the field tests that need to be performed can be seen in Figure 1.

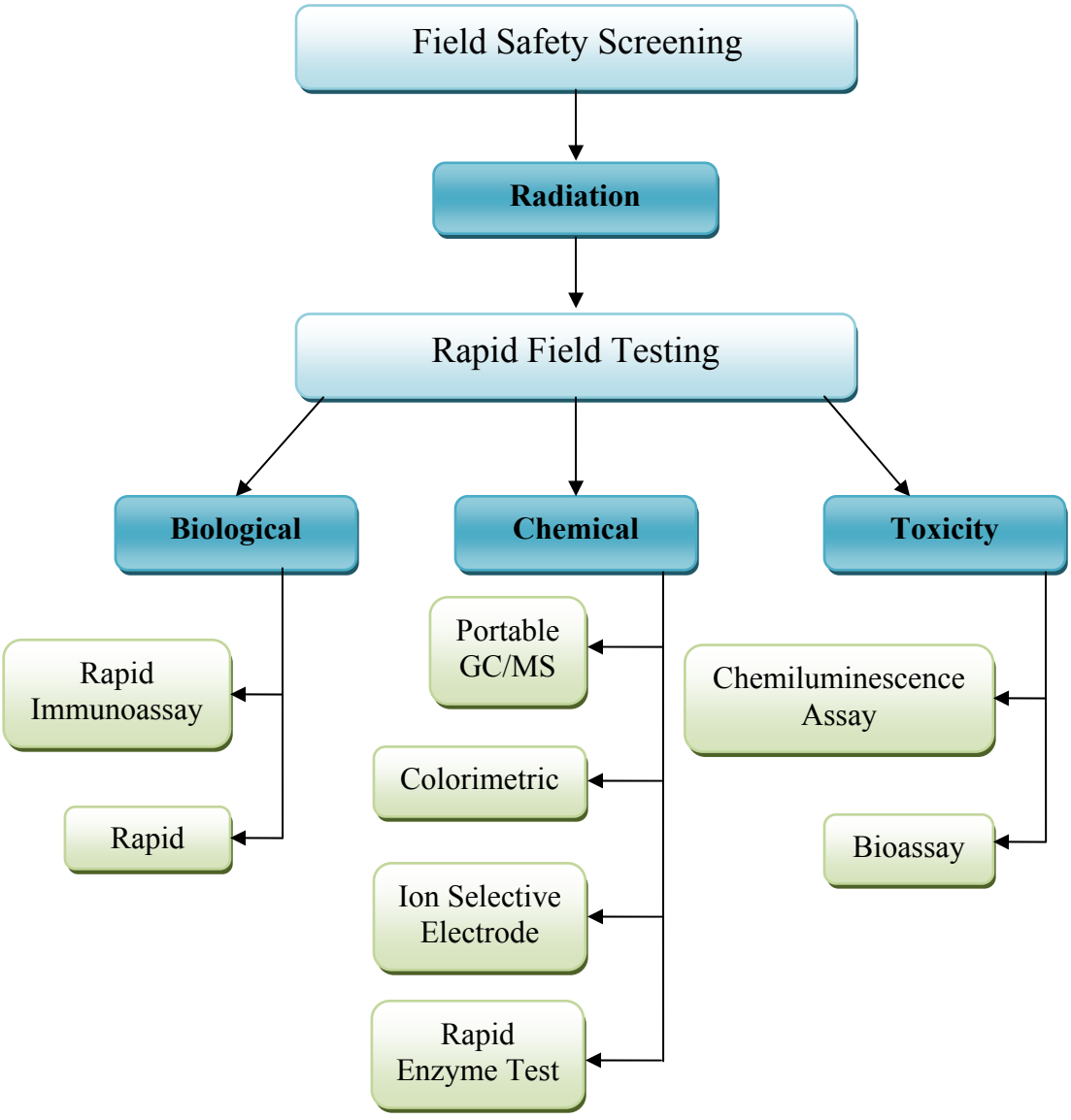

Figure 1. Flow Chart for Field Testing

2.3.2.1 Chemical Detection

Rapid testing of water should be done in a short amount of time at the site. “The underlying goal of rapid field testing is to produce results rapidly and accurately enough to help response officials make timely evaluations of the credibility of a threat, and initiate response actions that would reduce the impact of the contaminant and help protect the public, utility workers, infrastructure and private property, and the environment” [States, 2008]. During rapid testing, bacteria and chemical water quality should be evaluated along with toxicity. Chemical water quality analysis should include conductivity, pH, alkalinity, hardness, turbidity, TOC, UV absorbance, and chlorine demand.

Cyanide analysis is a quick field test and is recommended because it “has been one of the most commonly threatened intentional contaminants for drinking water” [States, 2008]. The technology for cyanide detection is based on either colorimetric or ion selective electrodes. Chlorine is easily measured using colorimetric testing. In addition, ion selective electrodes are established technologies for conductivity and pH monitoring.

The field deployable GC-MS detected for volatile hydrocarbons in water, soil, and air samples. The INFICON HAPSITE GC-MS utilizes a purge and trap system to collect samples for analysis. The system can identify and quantify the organic contaminant in the sample. Detection is in the range of low ppb and can detect compounds with molecular weight ranging from 45 to 300 grams per mole. Until laboratory analysis is conducted, the field GC-MS can analyze samples quickly.

The rapid enzyme test is used to identify pesticides and nerve agents in water samples. Inhibition of the enzyme cholinesterase provides a qualitative detection of toxins. For one minute, saturated cholinesterase membrane disk are exposed to the water sample. Next, the disk is attached to another disk containing ester for three minutes. A blue color is a negative result for

pesticide or nerve agents because cholinesterase hydrolyzes the bonded ester. Detections occurs when the cholinesterase is inhibited by the contaminant and the result is no color change.

2.3.2.2 Acute Toxicity

Broad-spectrum screening tests are used to measure for toxicity, where toxic substances include industrial chemicals, chemical weapons, and biotoxins. Three commercially available technologies include:

- Microtox
- Eclox
- IQ Toxicity Test

Microtox or Deltatox, the field version, is a broad-spectrum assay that follows Standard Methods 8050. Acute toxicity is determined by inhibition of bacterial bioluminescence. The test uses *Vibrio fischer*, a naturally luminescent marine bacteria, as test organisms.

Approximately one million bacteria are mixed into a water sample. At exposure duration of 5, 15, 30 minutes the resulting light from the bacteria is measured with a photometer. Positive toxic contamination should result in decease of bioluminescence compared to the negative control.

Eclox is a rapid chemiluminescence assay that utilizes plant enzymes combined with reagents to produce light. The amount of light is an indication of possible toxic substances in the water sample. The presence of toxins in the sample reduces the amount of luminescence by interfering with the reaction. The result is compared to negative control of distilled water. The samples are mixed with chemical luminal, a reaction enhancer, an oxidant, and the plant enzyme horseradish peroxidase.

IQ Toxicity Test utilizes the aquatic invertebrate *Daphnia magna* as an acute toxicity assay. In a series of 10 ml exposure compartments, six *Daphnia* are placed in each cavity and exposed for one hour. Some of the chambers contain contaminated water while others negative controls. After one-hour fluorogenically tagged sugar is added to the samples. Healthy Daphnia will metabolize the sugar (galactose) and release the tagged maker through the organism's circulatory system. The number of healthy organisms in the control chamber is compared to those in the sample water. Daphnia will not be illuminated when adversely affected by the water sample.

Toxicity screening test are just indicators for possible contamination. The tests are a broad-spectrum analysis that can detect toxicity for a wide range of contaminants. The exact contaminant cannot be determined from this detection method.

2.3.2.3 Rapid Immunoassay

The immunochromatographic assay is a qualitatively identification system. The test is able to detect chemical or biological agents by using antigen-antibody binding to form an indication color. For biological contamination, the test strips rely on antibodies targeting protein that are unique to that agent. Positive or negative results can visually be read by a color indicator. Electronic readers are available to enhance detection reading. The strips to indicate a possible contaminant but they are susceptible to false positives. For an electronic reader the contaminants and detection limits are [States, 2008]:

- Bacillus anthracis ($1x10^5$ cfu/mL)
- Yersinia pestis ($2x10^5$ cfu/mL)
- Francisella tularensis ($1.4x10^5$ cfu/mL)
- Botulinum toxin (10 μg/L)
- Staphylococcal Enterotoxin B (SEB) (2.5 μg/L)
- Ricin (50 μg/L)

Table 1 summarizes the tests that can be conducted, contaminants detected by each test, the difficulty performing the analysis and the time each test takes.

Table 1. Summary of Rapid Analytical Techniques [States, 2008]

Test/Assay	Contaminants Detected	Difficulty in Performing Analysis	Time (minutes)
Rapid Immunoassays	Pathogens: Anthrax, Plague, Cholera Biotoxins: Botulinum, Ricin, SEB	Simple	15
Rapid Enzyme Test	Insecticides: Organophosates, Carbamates, Thiophospates Nerve Agents	Simple	5
Rapid PCR	Pathogens: Anthrax, Plague, Campylobacter, E coli 0157, Salmonella, Cryptosporidium Biotoxins: Botulinum, Ricin	Moderately Difficult	90
Field Deployable GC or GC/MS	VOCs	Most Difficult	60
Acute Toxicity Screening Methods	Industial Chemicals, Weaponized Chemicals, Biotoxins	Simple to Moderately Difficult	Eclox - 5 Microtox - 45 IQ Toxicity - 90

The methods are tools for quick analysis of water during a possible contamination event. Additional testing is needed to confirm the field test. A quick examination of the water is needed for response and public health decisions. Additional information about commercially available detection technologies can be found in the EPA Environmental Technology Verification (ETV) program.

2.4 PREVIOUS STUDIES

There have been a few studies carried out related to CWS but the proposal to continuously monitor water for security reason is relatively new and not many works have been published. A few of the studies include a pilot system in Cincinnati, Ohio, and collaboration between the US Air Force and Colorado State University. Both of the pilot systems measured changes in water quality. Alternatively, the York City Department of Environmental Protection and the US Army conducted separate research on biomonitors utilizing fish. The research examined the changes in the behaviors of the fish related to possible contamination event.

2.4.1 Cincinnati, Ohio

A pilot study was completed in Cincinnati, Ohio at the Water Awareness Technology Evaluation Research and Security Laboratory within the USEPA Test and Evaluation Facility (T&E Facility) [Hall & et al, 2007]. The purpose of the research was to measure the changes in water quality parameters to indicate possible contamination.

To simulate a drinking water distribution system, the study used a recirculation pipe-loop distribution system simulator (DSS) which included 75 feet of pipe. The piping used was six-

inch diameter unlined cast-iron pipe and the looping piping system had a capacity of 150 gallons. Chlorine was added to the system to establish a baseline around 1mg/L. Potable water was added to the system at a rate of 0.16 gpm therefore the pilot takes 24 hours for the original water to be completely replaced. The DSS operated at a flow rate of 88 gpm.

Online chemical sensors were positioned 70 feet from the contaminant injection point. These monitors measured free chlorine, total chlorine, turbidity, pH, specific conductance, total organic carbon (TOC), dissolved oxygen (DO), oxygen reducing potential (ORP), temperature, ammonia, and nitrates. To test the sensors, contaminants were injected into the DSS. The contaminants used were: nonchlorinated secondary effluent from the local wastewater treatment plant, potassium ferricyanide, pesticide containing malathion, herbicide containing glyphosate, arsenic trioxide, nicotine, aldicarb and Escherichia coli K-12. From a tracer study, the time for the contaminant to reach the sensors 70 feet away was found to be 75 seconds. The results of the research can be seen in Table 2, which shows the differences from the baseline the different sensors for each contaminant injected. For the Cincinnati DSS biological sensors were not used because chlorine, which is present in distribution systems, is toxic to aquatic life.

Table 2. Sensor Response Following Introduction of Contaminant [Hall & et al, 2007]

	Sensor Response	
Contaminant	**Increase from Baseline**	**Decrease from Baseline**
Wastewater	Chloride Specific conductance Turbidity TOC	Free Chlorine ORP
Potassium ferricyanide	Free chlorine TOC Chloride Nitrate-nitrogen Ammonia-nitrogen ORP	
Glyphosate formation	TOC Chloride	Free Chlorine ORP
Malathion formation	TOC Turbidity	Free Chlorine ORP
Aldicarb	TOC Turbidity	Total chlorine Free chlorine ORP
Escherichia coli 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

2.4.2 US Air Force/ Colorado State University

The research carried out by David Byer and Kenneth Carlson used actual distribution water in the batch and pilot scale distribution system [2005]. The water in the pilot system was continuously monitored using real-time online instruments. Turbidity, conductivity, chlorine residual, TOC, and pH were the parameters monitored and data were collected once a minute. Baseline values were established 100 minutes before contaminants were injected. The four contaminants were selected based on [Byer & Carlson, 2005]:

1) Chemical is known to be a weapon
2) Readily available
3) Likely to cause illness or death
4) "Potential to cause public panic and social disruption"

The chemicals chosen for the research were sodium cyanide, sodium fluoroacetate, aldicarb and sodium aresenate. There were pumped using a peristaltic pump into a one-inch PVC piping network that had a volume of 4.2 l. The online monitoring instruments responded to all four of the contaminants. Sodium arsenate had the greatest impact on conductivity responded while sodium cyanide and sodium fluoroacetate also had measureable change. Sodium cyanide changed the baseline condition for pH and chlorine residual while aldicarb increased TOC and changed chlorine residual. Sodium fluoroacetate also increased the measured TOC. "Results from this study indicates that routine water quality instruments can detect chemical disturbances in drinking water distribution systems at relatively low concentrations" [Byer & Carlson, 2005].

2.4.3 Biomonitors

Research done by the New York City Department of Environmental Protection (NYCDEP) looked at online biomonitors, specifically bluegill fish (*Lepomis macrochirus*), in source waters.

Rapid changes in ventilatory patterns were observed in the fish that correlated with toxicity in the water. The research used eight fish in separate flow-through vessels, which had electrodes hanging above and below the fish. The electrodes recorded the electrical signals created by the fish's muscle movement, amplified the signal and sent the information to a computer. The fish's ventilatory rate, ventilatory depth (mean signal height), gill purge (cough), frequency, and whole body movement were monitored at 15-second intervals. The water flowing through the tanks was also monitored at 15-second intervals for pH, dissolved oxygen, and temperature [Mikol & et al, 2007]. Correlations between fish behavior and basic water quality were analyzed to identify the fish behaviors that indicate the presence of waterborne toxins.

A baseline was obtained by recording the movement of the fish for one day. For an alarm to be activated, the ventilation pattern of 70% of the fish needed to diverge from the baseline. Fish were used in the biomonitoring system for three weeks. During the second week, a new set of fish were added to the second monitoring tank to acclimate to water conditions. After acclimation, the second group of fish was placed online and the first group was returned to the holding tanks [Mikol & et al, 2007].

The biomonitoring system was used for two different case studies. First was a large system that served 17,000 residences and had an effluent average of 300 mgd. The second was a small system that discharged approximately 1.1 mgd of water [Mikol & et al, 2007].

The large system ran for 22 months during which the biomonitor was 96% operational. The biomonitor during that period detected an accidental oil spill were the water quality monitors (temperature, DO, pH, and conductivity) did not change. The spill was related to a construction site upstream. The fish increased their cough rate but no accident report was filed. Analysis of the sample from the auto sampler taken during the alarm event showed 47 μg/l of diesel oil in the sample [Mikol & et al, 2007].

The smaller system was located in Frederick County and draws water from the lower Monocacy River watershed. The biomonitor evaluated dechlorinated finished water and effluent water for the 8 months the system was operating. During that time, the monitor was operational 98% of the time [Mikol & et al, 2007]. An alarm event occurred during the case study when the fish in the effluent increased their cough rate and eventually all died. The fish in the finished water did not go into alarm and show no sign of being affected. This study concluded, that the treatment removed the toxin, which would have caused the fish to go into alarm.

In both case studies, there were alarms associated with nontoxic events such as changes in temperature, and flow interruptions. The study was a feasible method for determining toxicity in water but also detected nontoxic events.

The US Army Center for Environmental Health Research (USACEHR) conducted a similar study also using Bluegill fish to monitor water quality. Instead of using the system for existing water plants as the NYCDEP did, the USACEHR preformed their case study in a workshop. The USACEHR utilized tap water combined with different chemicals. The contaminants injected were sodium cyanide, malathion, sodium pentachlorphenate, phenol, 1,1,2,2-tetrachloroethane, tricaine methanesulfonate and zinc sulfate heptahydrate. Each fish was measured for coughing, amplitude of ventilation, rate, and whole body movement. The study is very similar to the NYCDEP in which eight fish were held in individual chambers and the temperature, pH, dissolved oxygen and conductivity were evaluated. The fish were given three days to acclimate and four days to determine a baseline for the parameters being assessed. Then, the contaminant was injected into three out of the four tanks. The fourth tank was the control. The influx of toxin continued for 96 hours and the bluegill's response was measured [Van der Schalie & et al, 2004].

Table 3 shows the correlation of the response time of the system to the concentration of toxins in the water. All of the control tanks indicated no response.

Table 3. Response of Bluegill Monitor on Injected Chemical Contaminants

Chemical	Concentration Tested (mg/L)	Bluegill 96-h LC_{50} (mg/L)	Concentration (fraction of LC_{50})	First alarm time (hr)
1,1,2,2-Tetrachloroethane	14.6	21	0.69	0.25
Zinc	2.80	4.5	0.62	0.25
Cyanide	0.06	0.11	0.55	0.50
Phenol	11.66	12	0.97	0.50
Tricaine methane sulfonate	60	64	0.94	1.25
Pentachlorophenol	0.25	0.40	0.62	12.25
Malathion	0.34	0.34	1	88.5

3.0 MATERIALS AND METHODS

Prior to beginning the experiment, a location for the CWS was selected. The site was selected due to its proximity to the drinking water transmission main serving the downtown portion of the city, and because PWSA owns a building at this location. The selected equipment for the CWS was installed within the building. Water from the distribution system continuously flows into the sentinel station and is screened by several monitors. PWSA has worked closely with a number of manufacturers of commercially available monitoring equipment. These vendors have been very cooperative in lending the PWSA their equipment for extended testing in the pilot station.

The following is a description of the experimental location for the sentinel system and the instruments used in the CWS. The contaminants used to challenge the system and experimental methods associated with those experiments are also described.

3.1 EXPERIMENTAL LOCATION

The sentinel station is located in a building owned by the PWSA that is adjacent to three major transmission mains supplying the downtown business area of the city of Pittsburgh. These transmission lines include two 36-inch mains and one 20-inch diameter main. A line that runs adjacent to the CWS interconnects the transmission mains. A service line was installed to bring water from this interconnect into the pilot station. A second service line allows the option of

feeding water into the pilot station from one of the transmission mains. Water from the distribution system continuously flows into the CWS. Figure 2 shows the location of the pilot system and the proximity to downtown Pittsburgh. The star indicates the location of the pilot sentinel system.

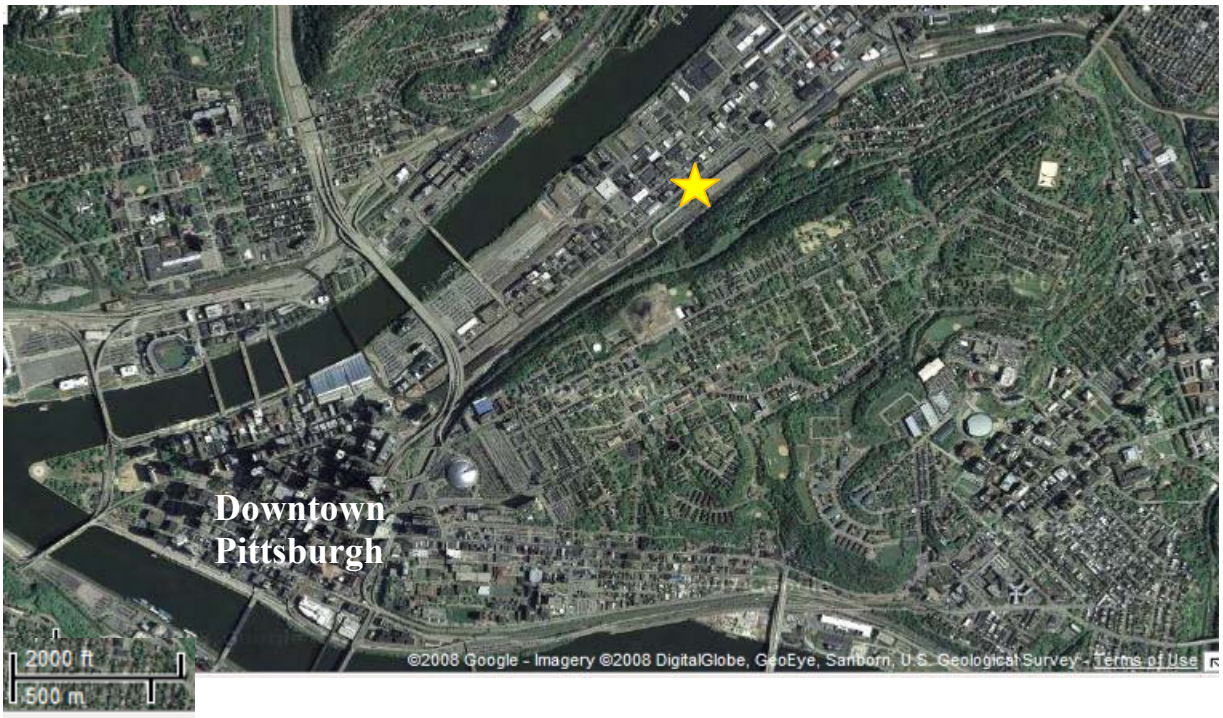

Figure 2. Arial View of the Location of the Pilot System

3.2 MONITORING EQUIPMENT

The distribution system CWS uses the following equipment for monitoring the water quality on a continuous basis and are described in the following sections.

- Hach Distribution Panel, Event Sensor, and Agent Library;
- Sievers 900 Online TOC Analyzer;
- INFICON Online GC-MS;
- JMAR Biosentry Pathogen Identification System;
- Biosensor Fish Monitor; and
- Real UVT 254 Online Monitor.

3.2.1 Hach Distribution Panel, Event Sensor and Agent Library

The instrument detects changes in water quality, alarms, and then attempts to identify the possible contaminant. The device consists of a 'Water Panel' containing several sensors that measure routine chemical parameters including TOC, chlorine, pH, turbidity, and conductivity. Measurements are taken at one-minute intervals. The system also includes an 'Event Monitor' that facilitates real-time analysis of data from the Water Panel. The Event Monitor integrates the readings for all of the chemical parameters into a composite value or vector. The Event Monitor alerts when one or more parameters deviate from a baseline range and exceeds the user-set threshold.

Additionally, Hach has developed an 'Agent Library', which contains a signature or fingerprint of the changes predicted to occur in multiple parameters when one of 80 different contaminants is introduced into the water. The goal of this 'Agent Library' is to be able to tentatively identify contaminants based on the chemical fingerprint produced by an 'unknown' substance.

The TOC Analyzer continuously monitors the water for total organic carbon using a chemical mechanism that is described in EPA method 415.1 and Standard Method 5310 C. The process used to measure TOC combines ultraviolet and chemical oxidation techniques. Acid is mixed with the sample in the first step to convert the total inorganic carbon (TIC) to CO_2. The CO_2 is then removed from the sample. The TIC free sample is combined with sodium persulfate and passed through the UV reactor. This process causes the TOC in the sample to be converted to CO_2 and the mixture is then sent into the gas-liquid separator (GLS). The gas is separated from the mixture and sent to the non-dispersive infrared (NDIR) CO_2 detector. The concentration of CO_2 is proportional to the concentration of TOC in the sample and results are displayed in mg/l TOC.

The Hach CL17 chlorine analyzer can measure either free chlorine or total chlorine. The CWS measured free chlorine which a measure of the concentration of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) in the water. The instrument samples every 2 ½ minutes and utilizes the DPD (N, N-diethyl-p-phenylenediamine) colorimetric method.

USEPA method 180.1 is used to measure turbidity in the 1720E Turbidimeter. Water continuously flows into the instrument where a beam of light is directed at the sample. Sensors positioned at a 90 degree angle to the photocell and measure the scattered light. The amount of turbidity in the water is proportional to the amount of scattered light. The results are recorded in nephelometric turbidity units (NTU).

Conductivity and pH are measured using probes. The pH sensor measures the acidity and caustic nature of a water sample, which is reported in pH units. Conductivity is measured in microsiemens per centimeter (µS/cm) by a two electrode conductivity sensor. The sensor measures the total ionic concentration in the water.

The Guardian Blue Early Warning System is shown in Figure 3. The Event Monitor and Agent Library are labeled A in the figure, B is the TOC analyzer, and C is the Water Panel.

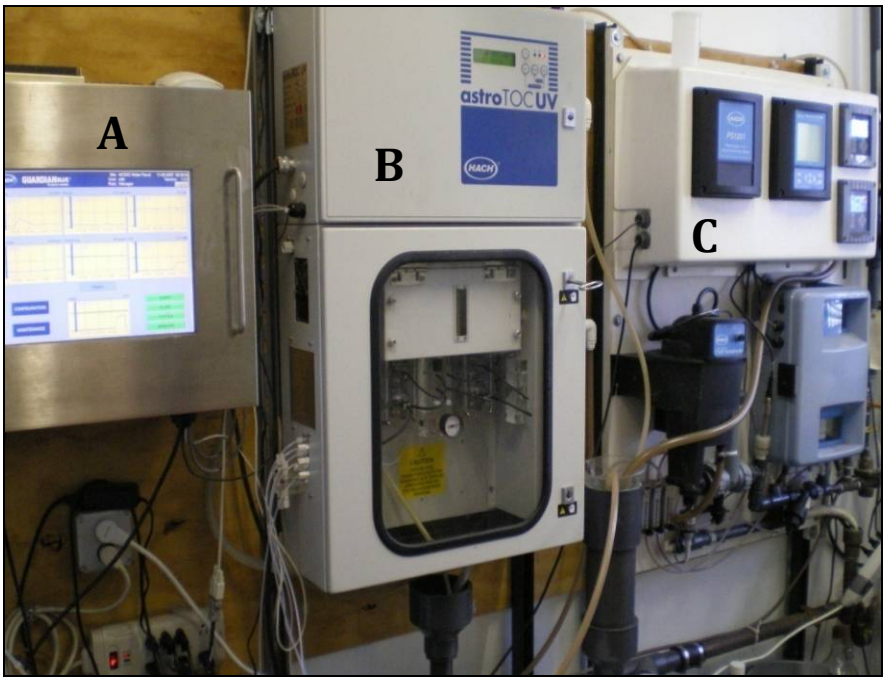

Figure 3. Hach Guardian Blue Early Warning System

3.2.2 GE Sievers 900 Online TOC Analyzer

The GE Sievers TOC analyzer utilizes UV/persulfate oxidation and membrane conductometric detection to measure the Total Organic Carbon (TOC) content of the water on a continuous basis. The analyzer utilizes the organic carbon in the sample and oxidizes the carbon to CO_2. Next, the CO_2 produced is measured. The process is similar to the Hach TOC analyzer but instead of the NDIR method, the Sievers TOC analyzer uses Membrane Conductometric Detection Technology. The method utilizes a selective membrane that allows CO_2 to permeate through the membrane. The CO_2 then travels to the conductive cell to ascertain the concentration of CO_2

where the detection of TOC ranges from 0.03 ppb to 50 ppm. The Instrument complies with the USEPA method 415.3 and Standard Methods 5310 C. Sievers 900 Online TOC analyzer in the pilot system can be seen in Figure 4.

Figure 4. Sievers 900 On-line TOC Analyzer

3.2.3 INFICON HAPSITE Online Smart Gas Chromatograph-Mass Spectrometer

This gas chromatograph-mass spectrometer utilizes a Situ-Probe purge and trap device to continually screen finished water for the presence of volatile organic compounds (VOC). Mass spectrometry is an analytical technique that uses mass-to-charge ratio to identify organic compounds in a sample. The mass spectrometric results are interpreted through use of AMDIS (Automated Mass Spectral Deconvolution and Identification System) and NIST (National Institute of Standards and Technology) databases.

The calibration library for the HAPSITE includes 68 analytes which samples are compared to for identification. To have a positive identified compound, the mass spectrometry qualitative fit must be greater than 75%. The detection limits of compounds range from the low ppb to part-per-trillion (ppt). Figure 5 shows the GCMS set up at the sentinel station.

Figure 5. Inficon HAPSITE Smart GCMS

3.2.4 JMAR Biosentry Pathogen Identification System

The Biosentry system is a commercial application of MALS technology. MALS (Multi-Angle Light Scattering) involves continual irradiation of a flowing column of water with a laser beam. Particles in a column of water, including microbes, scatter the laser beam. The dispersed beam produces a pattern, which is monitored by 16 detectors positioned on the opposite side of the water column. Microbes are identified by comparing the pattern of scattered light with a library of unique 'Bio-Optical Signatures' that have been developed by analyzing known microbes. The system analyzes for waterborne microorganisms without using consumable reagents and

analyzes approximately 1 mL/min of sample. The detection library for the instrument can be seen in Table 4. The detection library microorganisms are the pathogens which have known patterns of scattered light. If, the pattern does not match one of known Bio-optical Signature then the data is categorized as unknown. The instrument displays data every minute, which represents the average count from the last five minutes for unknown, rod, spore, and protozoan shape particles. Figure 6 shows the instrument used in the pilot study.

Table 4. JMAR pathogen detection library

Microbial Classification	Detection Library Microorganism	BioSentry Classification
Bacteria: Rod Shaped	• Pseudomonas • Legionella • E. coli • Salmonella • Shigella	Rod-shaped
Bacteria: Endospores	• Bacillus subtilis spores • Bacillus globigii spores • Bacillus cereus spores	Spore-shaped
Protozoa	• Cryptosporidium oocysts • Giardia cysts	Protozoa-shaped

Figure 6. JMAR Biosentry

3.2.5 Biosensor Fish Monitor

In this monitoring device, eight goldfish are maintained in individual chambers under continuous flow-through conditions. Electrical signals generated by respiratory muscle movements of individual fish are monitored, amplified, and sent to a personal computer for analysis. Ventilatory rate, ventilatory depth, gill purge (cough), and whole body movements are measured. Baseline behavior data is gathered during a one-hour initiation period to determine the average movements and ventilatory patterns of the fish.

Stress caused by the sudden appearance of a toxic substance in the water causes changes in ventilation and body movement. Deviation from the baseline causes the sensor to produce a warning signal. For normal behavior, the data are displayed as amplitude and frequency bar graphs for each fish. When the fish sensor goes into the warning mode, the bar graphs change from green to yellow. An alarm is triggered when six of the eight goldfish are in warning mode.

Because chlorinated drinking water is being passed through the Biosensor, and fish are sensitive to chlorine, a dechlorination system was installed. The dechlorinator pumps sodium thiosulfate into the influent where is mixes with the distribution system water before it is passed through the fish chambers. Figure 7 shows the biomonitor in the pilot CWS.

Figure 7. Biosensor Fish Monitor

3.2.6 Real Tech UVT 254 Online Monitor

The Real Tech UVT (ultra violet transmittance) measures the transmittance of UV light at a wavelength of 254 nm through a water sample. Water continuously flows through two rectangular quartz flow cells. On either side of the rotating cells, is a UV light source and UV sensor, which takes measurements at 90-degrees to the cells every 10 seconds [Real Tech Inc, 2008]. The system provides an instantaneous indication of natural organic matter (NOM) and

aromatic organics. Calibrating the system is simple and requires pure (distilled) water to be passed through the instrument as a reference sample. Fluctuation and drift can occur as a result of long time periods between calibrations and can give inaccurate readings.

The monitor has a baseline range, which depends on the water quality. An increase in NOM causes the measured transmittance value to decrease. In addition, an increase of turbidity may also cause the measured value to decrease. Figure 8 shows the UVT installed in the pilot CWS.

Figure 8. Real Tech UVT 254 Online Monitor

3.3 INJECTION SYSTEM AND METHOD

Water and contaminants of interest for a given study were pumped into the pilot station using a peristaltic pump. The arrangement of the contaminant, valve, and distribution water are depicted in Figure 9. A series of backflow preventers, check valves, and a manual shut off valve were installed to prevent contaminated water from flowing back into the distribution system.

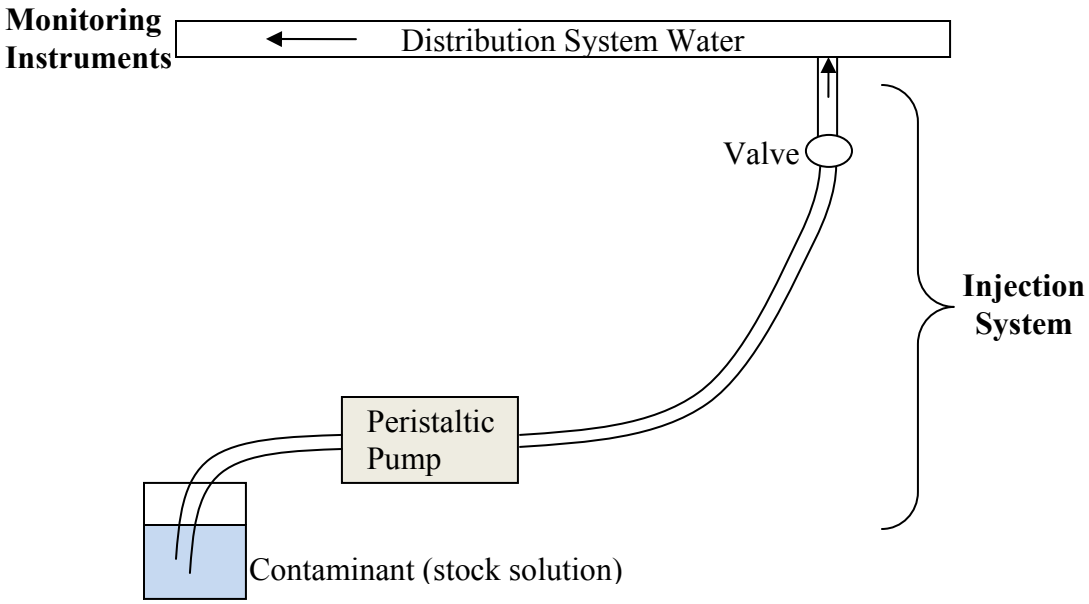

Figure 9. Pumping Set up

The online instruments, discussed above, continually monitor the distribution system water, which provides a baseline for the experiments. Contaminants were injected to stress and test the system. Normal monitoring conditions (no contaminant being injected) the valve, connecting the injection system, was in the closed position. To allow the substances to be pumped into the distribution water, the valve was opened to allow the contaminant to flow through the monitoring instruments. When the valve was initially opened, the monitoring instruments typically showed an increase in turbidity due to settled particulate matter in the

pipes. Water was then pumped through the injection system to allow the turbidity to stabilize and to regain a typical baseline. The time and flow rate to stabilize the system to the original turbidity differed for each run. Once the baseline was reestablished, a contaminant was pumped into the monitored water. The contaminants were measured using different water quality parameters and a variety of instruments. Water was then injected at the end of a run, to flush the monitoring system of injected contaminant. The contaminants used in the study included:

Hydrochloric Acid (HCl)	Sodium Fluoroacetate($NaFC_2H_2O_2$)
Nitric Acid (HNO_3)	Bug-B-Gone
Sodium Hydroxide (NaOH)	Fire Suppression Foam
Fluorosilicic Acid (H_2SiF_6)	Paint Thinner
Copper Sulfate ($CuSO_4$)	Toluene ($C_6H_5CH_3$)
Plastic Spheres	Carbon Tetrachloride(CCl_4)
E. coli	Bacillus Atrophaeus spores
Cryptosporidium oocysts	Giardia lamblia cysts

The chemical and biological contaminants were utilized for the challenge study to mimic an intentional or accidental contamination event in the finished drinking water system. The chemicals chosen for the study represent a variety of substance that could result from a spill, overdosing or a terrorist attack. Fire Foam was tested in the challenge study because an accidental contamination event had occurred in Pittsburgh several months earlier in the water distribution system by firefighters during a warehouse fire. The commercially available rodenticide and pesticide are of security concern for intentional contamination because they are easy to obtain. The E. coli and Cryptosporidium were used represent inadequately treated water from the water treatment plant. The microbes used are common organisms that are found in water that has not been treated properly. The intentional contaminates are chemicals and biological a person or group could possibly inject to cause harm to the consumer.

A summary of the concentration, volume, rate, and effluent concentration for the chemical contaminants is shown in Table 6 and a summary of the concentration, volume, rate, and effluent concentration for the microbes are depicted in Table 8.

3.3.1 Chemical Contaminants

3.3.1.1 Fluorosilicic Acid (H_2SiF_6)

Fluorosilicic Acid (HFS) is used in drinking water treatment plants to increase the concentration of fluoride in finished water. PWSA's fluoride concentration goal is 1.0 mg/l but can range from 0.05 to 1.45 mg/l in finished water according to the 2006 Water Quality Report for Pittsburgh. Samples are collected and analyzed daily to determine fluoride concentration and the dose of HFS is adjusted to meet the concentration goal. The maximum allowable concentration of fluoride in Pennsylvania drinking water is 2 ppm. Fluoride strengthens teeth against acids created by the bacteria in plague. At concentrations greater than 4 mg/l, fluoride causes mottling of teeth and a concentration greater than 15-20 mg/l causes fluorosis [MWH, 2005]. HFS was chosen as a contaminant in this study because of past instances of accidental fluoride overfeeds in Pennsylvania and other states.

Fluoride was introduced into the system using a 23.2% solution of fluorosilicic Acid, H_2SiF_6 (HFS). A volume of 12.5 ml of HFS was added to 12.5 l of distribution water to create the target concentration of contaminant. The actual measured concentration of the stock solution injection water was approximately 200 ppm of fluoride. The injection water was introduced into the system through a pump at a rate of 70 ml/min to the distribution line, which had an average flow of 2,200 ml/min. Four HFS contaminant trials were conducted with an average final concentration of 7.6 ppm F^-.

3.3.1.2 Hydrochloric Acid (HCl)

Hydrochloric acid is commonly used in drinking water treatment processes to reduce the alkalinity of the water. The chemical is a strong acid and for 0.1 N solution the pH is 1.1. The management of pH can control the formation of solids such as calcium carbonate and the corrosion of conduit material [MWH, 2005]. Because hydrochloric acid is used in some drinking water treatment processes, there is the possibility for accidental contamination to occur. Health issues associated with acute oral contact of HCl can include corrosion of the mucous membrane, esophagus and stomach [USEPA, 2007]. Swallowing excessive quantities may be fatal. In rabbits, the dose at which half of the test animals died, the oral LD_{50}, is 900 mg/kg.

Hydrochloric acid of 0.1 N was added to distribution water until the stock injection solution reached a pH of approximately 2.0. The stock solution was injected into the pilot monitoring system at a flow rate of 70 ml/min. Both run had an overall flow rate of 3.24 l/min with two liters of stock solution being injected during the two runs.

3.3.1.3 Nitric Acid (HNO_3)

Nitric Acid is used for many industrial applications for cleaning oxidizing or etching [NPI, 2005]. A common uses of nitric acid is to remove calcium carbonate buildup. Nitric acid reacts violently with many organic compounds and may cause fire and explosion [ILO, 2006]. The strong acid also reacts violently with bases and is corrosive to metal [NPI, 2005]. If exposed to the skin or eyes, the substance may cause serious burns. Ingesting the chemical may cause a sore throat, abdominal pains, vomiting, shock or collapse [ILO, 2006]. The lowest lethal does recorded for humans is 430 mg/kg.

The contaminant was created by mixing one normal nitric acid to the distribution water to achieve a pH of approximately 2. The stock solution was pumped into the system at a flow rate

of 70 ml/min. The first run, approximated 3.5 liter of stock solution with a pH of 1.91 was pumped into the system. The second run had a pH of 2.15 and 2.3 liter was pumped through the pilot system. The last run had a pH of 2.07 and a volume of 1.9 liter was used.

3.3.1.4 Sodium Hydroxide (NaOH)

Sodium Hydroxide is commonly known as caustic soda, lye, or sodium hydrate, and is often used in drinking water treatment. When there is insufficient carbonate hardness in the water, caustic soda can be used to decrease hardness instead of lime [MWH, 2005]. In addition to softening water, sodium hydroxide is used in drain cleaners, detergents and soaps. The chemical is corrosive when it comes in contact with skin and eyes. The lowest published LD_{50} for rabbits is 500 mg/kg [CHEMTREC, 2007]. In the presence of various metals, sodium hydroxide may produce flammable and explosive gases [CHEMTREC, 2007].

1 N Sodium hydroxide of was added to distribution water to create the stock injection solution. Two runs were performed with the contaminant. An average of 1.8 liters was pumped into the pilot system for about 30 minutes. Run one combined 28 ml of NaOH to 2500 ml of distribution water to create a pH of 12.17. The second run had a pH of 12.5 and used 50 mL of NaOH and 2500 mL of distribution water. Both runs were pumped into the system at 70 ml/min.

3.3.1.5 Copper Sulfate ($CuSO_4$)

Copper sulfate is commonly used as an herbicide, fungicide and pesticide. CuSO4 is commonly used in drinking water treatment to control algae [MWH, 2005]. Poisoning can occur from ingesting 1 to 12 grams of copper sulfate [Cornell University, 1994]. Some of the symptoms include metallic taste, burning pain in the chest and abdomen, nausea, vomiting, diarrhea, headache, sweating, and shock. The LD_{50} for ingestion of copper sulfate for rats is 30

mg/kg and the EPA drinking water limit concentration of copper sulfate is 1 ppm [Cornell University, 1994].

For the copper sulfate, three runs were performed. Each of the runs was pumped in the system at 70 ml/min for a period of 30 to 50 minutes. The non-dilution injection water consists of 0.44 g, 0.8 g and 1.25 g of $CuSO_4$ added to two liters of tap water. The two lower concentrations were added over flow rate of 1.89 ml/min. The higher concentration was pumped into an overall flow rate of 3.98 ml/min.

3.3.1.6 Bug-B-Gon

Ortho Bug-B-Gon Max Lawn and Garden Insect Killer is a common household insecticide that contains Bifenthrin (0.115%), $C_{23}H_{22}ClF_3O_2$. The chemical is highly toxic to aquatic organisms and moderately toxic to mammals when ingested. Acute contact with Bifenthrin can cause convulsions, tremors, and diarrhea, salivation, and irritability to sound and touch. The oral LD_{50} for female rats is 54 mg/kg [Cornell University, 1995].

Four different concentrations of Bug-B-Gon were pumped through the pilot system. Each stock injection solution was pumped into the system at a rate of 70 ml/min. Two liters of distilled water was combined with 1, 5, 10, and 20 ml of insecticide.

3.3.1.7 Sodium Fluoroacetate ($NaFC_2H_2O_2$)

Sodium fluoroacetate is an organic chemical that is used as a poison for vertebrate animals. Common animals that the poison is used to control include rabbits, pigs, foxes and wild dogs. The chemical is highly soluble in water and is considered very highly toxic. In drinking water, Sodium fluoroacetate is projected to increase conductivity and TOC. The oral LD_{50} is 0.1

mg/kg and ingesting the organic chemical can cause long-term cardiac damage. Vomiting, seizures, and coma are signs of exposure. Mortality is possible at high doses.

Two runs of sodium fluoroacetate were completed with a target effluent concentration of 0.5 ppm and 5 ppm based on a flow rate of 3.2 l/min. Distilled water was used instead of distribution water to make the stock injection solution. The experiments used 45.7 mg and 457.1 mg of sodium fluoroacetate and was added to two liters of distilled water.

3.3.1.8 Fire Foam

Fire is a commonly used substance to suppress fires, because combined with water the substance reduces the surface tension of water. Deceased surface tension allows water to penetrate surfaces where water alone might run off. In addition, the use of fire foam mixed with water decreases the amount of water need to extinguish a fire. The chemical components of Knockdown, one of the commercially available mixtures of fire fighting foam, can be seen in Table 5.

Table 5. The composition of Knockdown a fire fighting foam concentrate (Kidde Fire Fighting, 2007)

Components	% Weight
Water	48 -70%
Proprietary mixture of synthetic detergents	20 -30%
1,2 Propanediol	8- 12%
(2-methoxymethylethoxy) Propanol	2 -4%
Proprietary mixture of corrosion inhibitors	0 -6%

Ingestion of small amounts is not likely to cause injury but ingestion of large amounts may cause irritation. The LD_{50} for the concentration in Sprague-Dawley Rats is greater than 5000mg/kg [Kiddie Fire Fighting, 2007].

Dilutions of the fire suppression foam concentration were prepared to attain a final effluent concentration of 0.001% and 0.003% of foam. The final concentrations were achieved by adding 1 mL and 3 mL, respectively to two liters of distilled water. The typical concentration of foam for a structural fire would be 0.5% to 0.7%. The value used for the pilot is 500 times smaller than the actual value used to treat fire because of fear that a concentration that great would cause problems in the monitoring instruments. Approximately two liters of stock solution was pumped into the system at a flow rate of 70 ml/min.

3.3.1.9 Paint Thinner

The main components in paint thinner are mineral spirits or Stoddard solvent with trace amounts of benzene. Paint thinner contains about 95 to 100 percent Stoddard solvent and up to two percent benzene. The EPA MCL for benzene in drinking water is 5 ppb [USEPA, 2006]. The EPA classifies benzene as a human carcinogen. The oral LD_{50} observed in rats is 1800 mg/kg [Nova Chemicals, 2008]. When large quantities of paint thinner are ingested, vomiting, dizziness and convulsions could occur.

Two concentrations of paint thinner were pumped at a rate of 70 ml/min into the monitoring system. The first concentration was 2 ml of paint thinner added to 2 liters of distilled water and 1.5 liters was injected into the pilot distribution water. The second concentration was 5 ml of paint thinner added to 2 liters of distilled water and injected for 40 minutes and pumped 3 liters into the monitoring system.

3.3.1.10 Toluene ($C_6H_5CH_3$)

Toluene, also called methyl benzene, occurs naturally in crude oil and is a byproduct of gasoline production and coke from coal processes. The chemical is highly flammable and is

water insoluble. This aromatic hydrocarbon is used in manufacturing plastics, rubbers, disinfectants and is an additive to lead-free gasoline. The EPA MCL in drinking water is 1 ppm [USEPA, 2006]. When large quantities of Toluene are ingested, vomiting, dizziness and convulsions could occur. The lowest published lethal oral concentration (LDLO) for humans is 50 mg/kg [Oxford University, 2005].

Two concentrations of the stock injection solution was pumped through the system at a rate of 70 ml/min. The injection water was prepared by combining 1 µl and 5 µl of toluene to 2 liters of distilled water. Two liters of the stock solution were pumped through the pilot distribution system with an average flow rate of 3.25 ml/min.

3.3.1.11 Carbon Tetrachloride (CCl_4)

Carbon tetrachloride is an organic chemical that does not occur naturally. Fire extinguishers, dry cleaning agents, pesticides and manufacturing of nylon are common uses of the chemical. A large portion is used in the production of chlorofluorocarbon propellants and refrigerants. Due to harmful effects to the environments, a majority of the uses have been banned. The EPA MCL for drinking water is 5 ppb and it has been determined that carbon tetrachloride is a probable human carcinogen. Extended exposure can cause kidney, central nervous system, and liver damage. The oral LD for guinea pigs is 5760 mg/kg of carbon tetrachloride [Oxford University, 2004].

Three and five microliters were added to 2.4 liter and two liters of distilled water respectively. The stock injection solutions had a concentration of 2 ppm and 1.5 ppm. Both were pumped at a flow rate of 70 ml/min. The flow rate of the pilot system was about 3.2 ml/min.

Table 6. Summary of the chemical injected contaminants

Chemical	Evaluated Injection Solution	Volume (L)	System Flow Rate (L/min)	Calculated Effluent Concentration*
HFS	198 ppm	3.36	2.50	7.06 ppm F^-
	≈ 200 ppm	2.1	2.48	7.02 ppm F-
	192 ppm	2.66	3.15	9.77 ppm F-
	214 ppm	2.17	3.15	6.60 ppm F-
HCl	2.04 pH	1.75	3.24	1.5 pH drop
	2.09 pH	2.1	3.24	1.5 pH drop
HNO_3	1.91 pH	3.34	3.20	2.1 pH decrease
	2.15 pH	2.24	3.07	1.5 pH drop
	2.07 pH	1.89	3.22	1.5 pH drop
NaOH	12.17 pH	1.75	3.18	1 pH increase
	12.5 pH	1.89	3.55	1.2 pH increase
$CuSO_4$	220 ppm	2.24	1.89	8.1 ppm
	400 ppm	2.3	1.80	15.5 ppm
	625 ppm	2.52	3.98	11 ppm
Sodium Fluoroacetate	23 ppm	2	3.34	0.5 ppm
	230 ppm	2	3.34	5 ppm
Bug-B-Gone	500 ppm	3.64	3.18	10 ppm
	2500 ppm	3.5	3.29	50 ppm
	5000 ppm	2.17	3.79	100 ppm
	10,000 ppm	2.59	3.79	200 ppm
Fire Foam	500 ppm	2	3.30	0.001%
	1500 ppm	2	3.58	0.003%
Paint Thinner	1000 ppm	1.54	3.79	≈ 20 ppm
	2500 ppm	2.94	3.79	≈ 50 ppm
CCl_4	3.7 ppm	2	3.20	86 ppb
	2.8 ppm	2	3.15	62 ppb
Toluene	2.2 ppm	2	3.15	49 ppb
	0.4 ppm	2	3.34	9 ppb

* The calculated effluent concentration was based on the concentration of the stock solution, pumping flow rate, and system flow rate.

3.3.2 Biological Based Contaminants

3.3.2.1 Spheres

Two sizes of plastic spheres were injected into the monitoring system as models for microbes in the drinking water. For the two micron spheres, a count of 10 million and 100 million spheres were injected into the system. Similarly, 0.8 μ spheres were injected into the monitored water at counts of 10 million, 50 million and 100 million. All spheres were added to two liters of distilled water. A pumping rate of 140 ml/min was used for all the sphere runs. Duplicate runs were conducted for each concentration.

3.3.2.2 Cryptosporidium parvum

Cryptosporidium parvum is apathogenic protozoan that can cause gastrointestinal illness if ingested. For healthy people the minimum infective dose is 30 oocysts and a median infective dose is 132 oocyst [Bitton, 2005]. There are also studies that suggest that ingestion of as little as one oocyst may cause infection. *Cryptosporidium parvum* in intake water for drinking water are not always completely removed or inactivated by traditional process such as sand filtration and chlorination but the parasite can be partial inactivated by limewater softening. Due to the pathogen not being removed by traditional process breakouts do occur. "Compliance with U.S. EPA standards does not guarantee protection from infection with *Cryptosporidium*" [Bitton, 2005].

A single run of inactivated *cryptosporidium* was injected into the system at a rate of 140 ml/min. Ten million *cryptosporidium* oocyst were added to 2 liters of distilled water to create the stock solution for injection. The calculated effluent concentration *cryptosporidium* oocyst that passed through the monitoring system was calculated to be 200 oocyst/ml.

3.3.2.3 Giardia lamblia

Giardia lamblia is a flagellated protozoan parasite that is commonly found in domestic wastewater. Infection is caused by ingesting 25 to 100 cysts and the infection can cause abdominal pains, nausea, fatigue and weight loss [Bitton, 2005]. Giardiasis is rarely fatal but it is estimated in the United States that 2.5 million cases of giardiasis occurs annually [Bitton, 2005]. The most common case of outbreaks is due to consumption of water that was untreated or inappropriately treated, which could mean chlorinated but not filtered drinking water.

To create the stock injection solution, 10 million inactivated *Giardia lamblia* was mixed with two liters of distilled water. The concentrated was pumped into the monitoring system at 140 ml/min. A single run was conducted with *Giardia* cysts.

3.3.2.4 Escherichia coli

The facultative anaerobic bacterium Escherichia *coli* lives in the intestinal tract of warm blooded animals. The majority of E. coli strains are harmless and are common habitants of human gastrointestinal tract. A few groups are pathogenic and are related to waterborne disease outbreaks. These strains can be seen in Table 7. The infectious dose of the rod shape bacteria can range from 10^6 -10^9 organisms.

Table 7. Bacteria associated with waterborne disease(MWH, 2005)

Bacteria	Size, µm (diameter x length)	Health Effects in Healthy Persons
Enteropathogenic *E. coli* (EPEC)	0.3-0.5 x 1-2	Traveller's diarrhea
Enteroaggregative *E. coli* (EaggEC)	0.3-0.5 x 1-2	Childhood diarrhea and among immunocompromised
Enteroinvasive *E. coli* (EIEC)	0.3-0.5 x 1-2	Childhood diarrhea
Enterohemorrhagic *E. coli* (EHEC)	0.3-0.5 x 1-2	Bloody diarrhea, occasionally hemolytic uremic syndrome (HUS)
Enterotoxigenic *E. coli* (ETEC)	0.3-0.5 x 1-2	Traveller's diarrhea

Enterohemorrhagic *E. coli* (EHEC) has an infectious dose of less than 100 organisms which much lower than the other strains and the very young and very old are most susceptible by the pathogen. EHEC cause more than 20,000 infections and as many as 250 deaths each year in the United States [Bitton, 2005]. EPA does not require public water systems to monitor for *E. coli* but instead total coliform. When samples are positive for coliform bacteria, then the water facility must analyze for either *E. coli* or fecal coliform. Positive tests would indicate the presence of animal waste or human sewage in the water [EPA, 2006].

Four different concentrations of *E. coli* were pumped through the pilot monitoring system. Approximately 200 billion, 100 billion, 4 million and 3 million CFU were added to two liters of distilled water to create a stock solution for injection into the monitoring water. The *E. coli* was pumped into the system at a rate of 140 mL/min. The final concentration of *E. coli* passing through the monitoring system was 4.6 million, 2.7 million, 80, 67 CFU/ mL.

3.3.2.5 Bacillus atrophaeus

Bacillus anthracis spores were used as a surrogate for *Bacillus anthracis* spores (anthrax) which are non-flagellated, rod shape, facultative anaerobic, pathogenic bacteria. *Bacillus anthracis* is classified as a possible bioterrorism agent. The bacilli are about 1 μm wide and 3 μm long and usually straight. The estimated infectious dose from inhalation, which is the most deadly, is 6000 spores [Bitton, 2005]. Mortality rates exceed 80 percent for individual who inhale *B. anthracis* spores [MWH, 2005]. Signs of anthrax infection include influenza like symptoms followed by chest wall edema and hemorrhagic meningitis. Treatment delayed beyond 48 hours will result in death.

Two concentrations of *Bacillus atrophaeus* spores were injected into the system at a rate of 140 ml/min. The stock solution concentrations were prepared by combining 10 million and 30 million inactivated *Bacillus* spores to two liters of distilled water.

Table 8. Summary of injected biological based contaminants

Contaminant	Injection Solution	Injection System Flow Rate (mL/min)	Volume (L)	System Flow Rate (L/min)	Calculated Effluent Concentration *
Spheres (2µm)	$10x10^6$ spheres/2L	140	2	3.634	193 spheres/mL
	$10x10^6$ spheres/2L	140	2	2.753	254 spheres/mL
	$10x10^7$ spheres/2L	140	2	3.634	1926 spheres/mL
	$10x10^7$ spheres/2L	140	2	2.753	2543 spheres/mL
Spheres (0.8µm)	$10x10^6$ spheres/2L	140	2	3.723	188 spheres/mL
	$10x10^6$ spheres/2L	140	2	3.390	206 spheres/mL
	$5x10^7$ spheres/2L	140	2	3.268	1071 spheres/mL
	$5x10^7$ spheres/2L	140	2	3.268	1071 spheres/mL
	$10x10^7$ spheres/2L	140	2	3.723	1880 spheres/mL
	$10x10^7$ spheres/2L	140	2	3.390	2065 spheres/mL
Cryptosporidium	$10x10^6$ oocyst/2L	140	2	3.154	222 oocysts/mL
Giardia lamblia	$1x10^6$ CFU/2L	140	2	3.154	116 CFU/mL
E. coli	$2.11x10^{11}$ CFU/2L	140	2	3.154	$4.66x10^6$ CFU/mL
	$1.17x10^{11}$ CFU/2L	140	2	2.988	$2.74x10^6$ CFU/mL
	$3.9x10^6$ CFU/2L	140	2	3.441	80 CFU/mL
	$2.9x10^6$ CFU/2L	140	2	2.912	67 CFU/mL
Bacillus Atrophaeus	$10x10^6$ spores/2L	140	2	3.154	222 spores/mL
	$30x10^6$ spores/2L	140	2	3.154	666 spores/mL

* The calculated effluent concentration passing through the monitoring system was based on the concentration of the stock solution, pumping flow rate, and system flow rate.

3.4 NORMAL BACKGROUND VARIATION

Determining the difference between normal background variation and a contamination event is vital. Too many false alarms can cause "the boy who cried wolf" symptom where initially every alarm is evaluated with no water quality issues. After responding to many false alarms responders are less likely to react which could result in an actual contamination event affecting public health. The normal variation in water quality must be evaluated to set trigger level for the instruments. Numbers exceeding the value will indicate an alarm.

3.4.1 Detection Limit

Water quality in a public drinking water distribution system can vary as a result of a number of conditions including: source water quality, variation in the water treatment process, variations in hydraulic conditions in the distribution system, accidental back siphonage, and water main breaks. Consequently, pH, TOC, conductivity, turbidity, and chlorine are changing constantly and a single mean value cannot be calculated to represent a baseline for the values. To resolve this problem, a range of data will be used to represent normal water quality. The data sets are composed of continuous monthly readings of TOC, chlorine, conductivity, pH and turbidity.

The mean for each data was determined using Equation 1.

$$\bar{x} = \frac{x_1 + x_2 \ldots x_n}{n} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad \text{(Equation 1, [Devore, 2004])}$$

Where n is the number of samples in the data set. The mean is a useful representation of the average value of the data set but does account for variability. Standard deviation accounts for the data variability and was calculated for the data series using Equation 2.

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}} \qquad \text{(Equation 2, [Devore, 2004])}$$

Adding and subtracting the standard deviation to the mean offers a range for detection but in some cases only 60 percent of the data points will fall within the range. To encapsulate a majority of the data but still show contamination events, three standard deviations were chosen to represent normal variation. Values exceeding three standard deviations from the mean value were classified abnormal and possible indication of a contamination event. The detection limit was calculated by the mean value plus three standard deviations shown in Equation 3.

$$\text{Detection limits} = \bar{x} \pm 3\sigma \qquad \text{(Equation 3)}$$

Accord to Chebyshev inequality, at least 89% of the data set should fall within three standard deviations from the mean. For the TOC, chlorine, pH, conductivity and turbidity data sets, between 97.7 and 99.9 of the data point fell within the limits. Figure 10 shows the detection limits for TOC and an incidence of increase of TOC related to Giardia being injected into the pilot system.

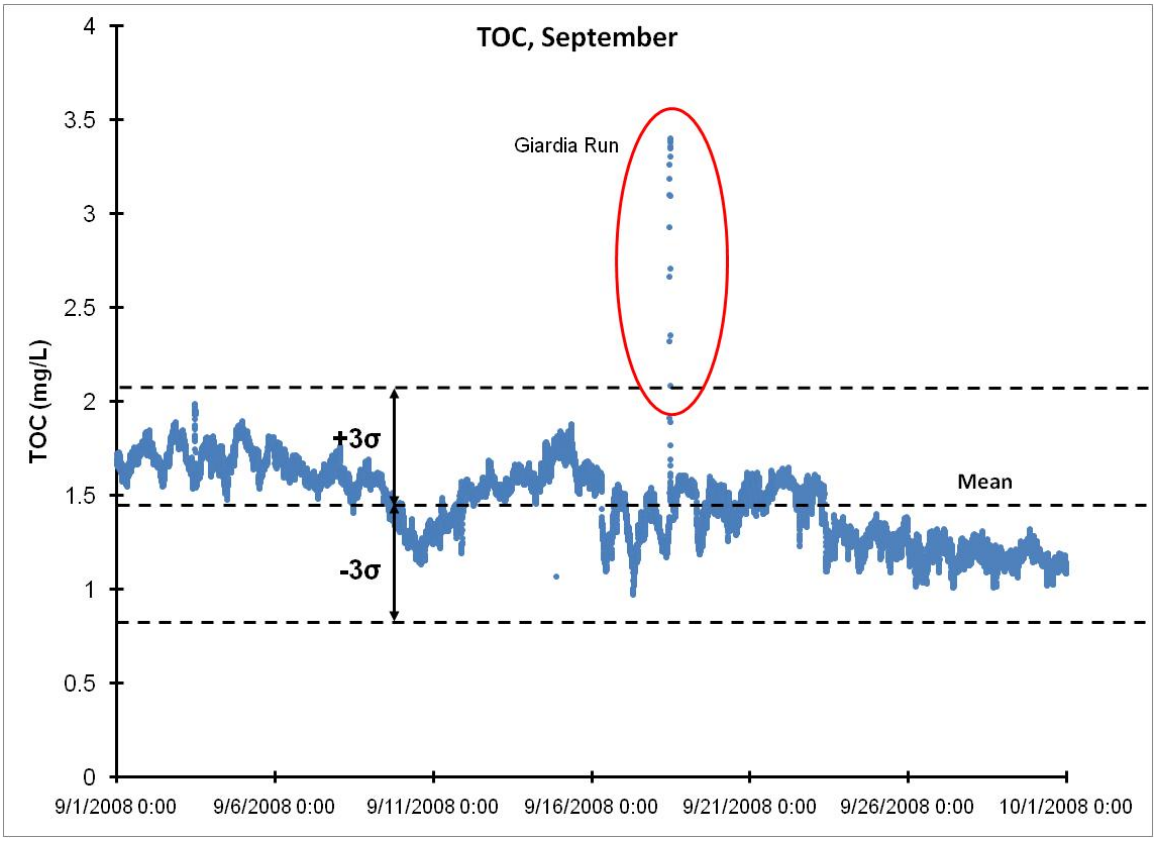

Figure 10. Detection limit for TOC during a injection trial analyzing Giardia cysts

The TOC responded to the inactivated agent, formalin, during the injected of *Giardia lamblia*. The organic solution, formalin is an aqueous solution of formaldehyde, H_2CO. Changes in water quality parameters, due to a toxin being injected, will be evaluated against the detection limit to determine if the chemical can be detected.

4.0 RESULTS AND DISCUSSION

Early warning monitoring of possible contaminants is necessary to protect the consumer from accidental or intentional contamination. Rapid detection instruments provide real time data about the water quality. If a contamination event were to occur, rapid detection would decrease the response time and possibly decrease the number of resulting illnesses or deaths.

There are five approaches used within the drinking water industry to monitor the quality of finished water and screen for signs of intentional or accidental contamination. They include:

- Monitoring routine chemical parameters;
- Real-time toxicity biomonitoring;
- Monitoring for radiation to detect the presence of radionuclides;
- Detecting, identifying, and quantifying specific chemical contaminants; and
- Detecting, Identifying, and quantifying specific pathogens.

This research did not address the use of radiation to detect radionuclides. However, the pilot CWS did utilize monitors for the other four approaches. To challenge the system, contaminants were pumped into the distribution line and deviations from baseline values were recorded. The contaminants used for this research included:

Hydrochloric Acid (HCl)	Sodium Fluoroacetate($NaFC_2H_2O_2$)
Nitric Acid (HNO_3)	Bug-B-Gon
Sodium Hydroxide (NaOH)	Fire Suppression Foam
Hydrofluosilic Acid (H_2SiF_6)	Paint Thinner
Copper Sulfate ($CuSO_4$)	Toluene ($C_6H_5CH_3$)
Plastic Spheres	Carbon Tetrachloride(CCl_4)
E. coli	*Bacillus Atrophaeus*
Cryptosporidium	*Giardia lamblia*

4.1 CHEMICAL CHALLENGE EXPERIMENTS

The chemicals mentioned previously were used to challenge the Hach Guardian Blue System, the Sievers TOC, and the Real Tech UVT. The Hach Panel measures turbidity, free chlorine, pH, conductivity, and TOC. The Real Tech UVT detects aromatic organics and NOM by measuring percent transmittance using 254 nm wavelength light. At the beginning of each run, a turbidity spike occurred as the valve connecting the injected system, shown in Figure 8, was opened. Water was pumped through the injection system until turbidity returned to the previous baseline. UVT was also affected as a result of the valve to the injection system being opened. After the baseline was regained, contaminants were introduced into the water supply by the injection system to stress the system and test the chemical detection instruments. The changes caused by the toxins were recorded and analyzed. For each toxin, changes in turbidity, free chlorine, pH, conductivity, TOC, and UVT were evaluated. A summary of the contaminants, concentration and the affected parameters are shown in Table 9[1].

[1] All of the biological trials had a decrease in conductivity as a result of the distilled water for preparation of the stock solution. *Cryptosporidium* and *Giardia* increased both the Sievers and Hach TOC as a results of the inactivation agent. The *Bacillus* spores induced a decrease concentration of chlorine

Table 9. Broad Spectrum Analysis for Chemical Contamination

	Theoretical Effluent Concentration	Trigger	Turbidity	Chlorine	pH	Conductivity	Hach TOC	Sievers TOC	UVT
HFS	7.06 mg/L F^-	X			X	X			
	7.02 mg/L F-	X			X	X			
	9.77 mg/L F-	X			X	X			
	6.60 mg/L F-	X			X	X			
HCl	1.1 pH decrease	X			x				
	1.5 pH decrease	X			X	X			
	1.5 pH decrease	X			X	X			
HNO_3	2.1 pH decrease	X			X	X			
	1.5 pH decrease	X			X	X			
	1.5 pH decrease	X			X	X			
NaOH	1 pH increase	X	X		X	X			
	1.2 pH increase	X	X		X	X			
CuSO4	8.1 mg/L		X		X	X			X
	15.5 mg/L	X	X		X	X			X
	11 mg/L	X	X		X	X			X
Sodium Fluoroacetate	0.5 mg/L					X		n/a	
	5 mg/L	X				X	X	n/a	
Bug-B-Gone	10 mg/L					X			
	50 mg/L					X			
	100 mg/L					X	X	X	
	200 mg/L			X	X	X	X	X	
Fire Foam	0.001%	X		X		X	X	X	
	0.003%	X		X		X	X	X	
Paint Thinner	20 mg/L					X			
	100 mg/L					X			
CCl_4	86 µg/L					X		n/a	
	62 µg/L					X		n/a	
Toluene	48 µg/L					X		n/a	
	9 µg/L					X		n/a	

Notes: X = Detected by Instrument n/a =Instrument not online during testing

The Hach Event Sensor did not alarm when exposed to various concentrations of Bug-B-Gon, paint thinner, carbon tetrachloride, or toluene in the distribution water. Toluene and carbon tetrachlorine concentrations were in the ppb range and were not predicted to be detected by routine chemical parameters. Bug-B-Gon at the highest concentrations had changes in chlorine, pH, conductivity, and TOC but still did not produce an alarm. The Hach Panel detected an increase in turbidity for copper sulfate, which could have been the result of solid copper sulfate that had not dissolved completely. In addition, sodium hydroxide induced an increase of turbidity. Fire foam and Bug-B-Gon were the only contaminants that caused changes in chlorine. As predicted, the acids and bases triggered either a decrease or increase in pH. Copper sulfate and the highest concentration of Bug-B-Gon also caused deviations in pH measurements. For all the chemicals besides the lower concentration of HCl, conductivity either decreased or increased. Running a blank sample of distilled water through the CWS resulted in a 20 μS/cm decrease in conductivity. Contaminants mixed with distilled water illustrated similar results in respect to conductivity. For the fire foam and the two highest concentrations of Bug-B-Gon, both were detected by Sievers and Hach TOC analyzers. Unfortunately, the Sievers TOC was not operational for the sodium fluoroacetate experiment because of routine maintenance. The Hach TOC did detect changes in TOC for the higher concentration of sodium fluoroacetate. The UVT only detected changes in transmittance for copper sulfate. As mentioned before, the change in transmittance could be correlated to the chemical not being completely dissolved.

Examples of the raw data from three sensors can be seen in Figure 11, Figure 12, and Figure 13. Figure 11 illustrates the response of the Hach Event Sensor Alarm to the injected contaminant HFS. Turbidity peaks were synonymous for each injected contaminant event. The actual effluent concentration of fluoride was 7 ppm as measured by an ion selective electrode. The initial response to the valve being opened can be seen in the first peak of Figure 11. The

second peak corresponds to deviation of pH which triggered the alarm. Trigger values greater than a warning threshold of 1.0, activate an alarm for the Hach Panel. This alarm value can be adjusted by the instrument operator. When the Plant Alarm is activated, the Hach Event Sensor begins to match the pattern of change in chemical parameters to the patterns recorded for various contaminants in the Event library. If a match is found, an agent alarm generates the possible contaminant(s) and the percent certainty for the identification. For the HFS run, the Hach Event Sensor matched fluorosilicic acid and mercuric chloride to the event.

Figure 12 shows turbidity related to the HFS run. An increase of turbidity, for HFS, only occurred when the valve to the injection system was opened. HFS did not affect the turbidity. The figure also shows that the pumping of HFS only commences once the turbidity regained the original baseline.

Figure 13 is the raw data for pH during the experiment. As predicted, there was a decrease in pH as a result of the acid being pumped into the pilot system. The result of the acid was a decrease in pH of 2 units. The water regained the original baseline value once injection of HFS stopped. This is an indication that the spike was a result of the acid.

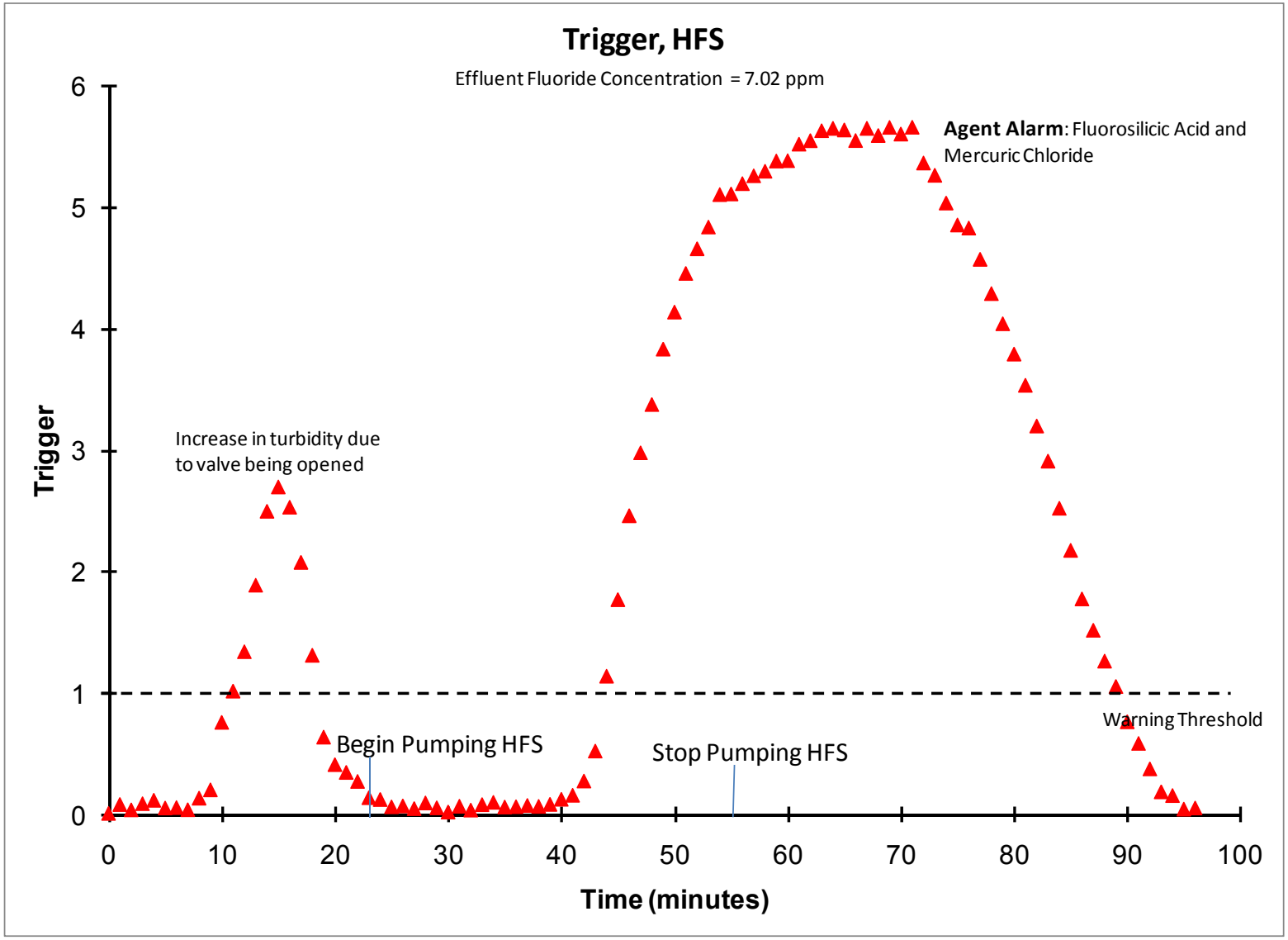

Figure 11. Trigger Graph for HFS Contamination Event

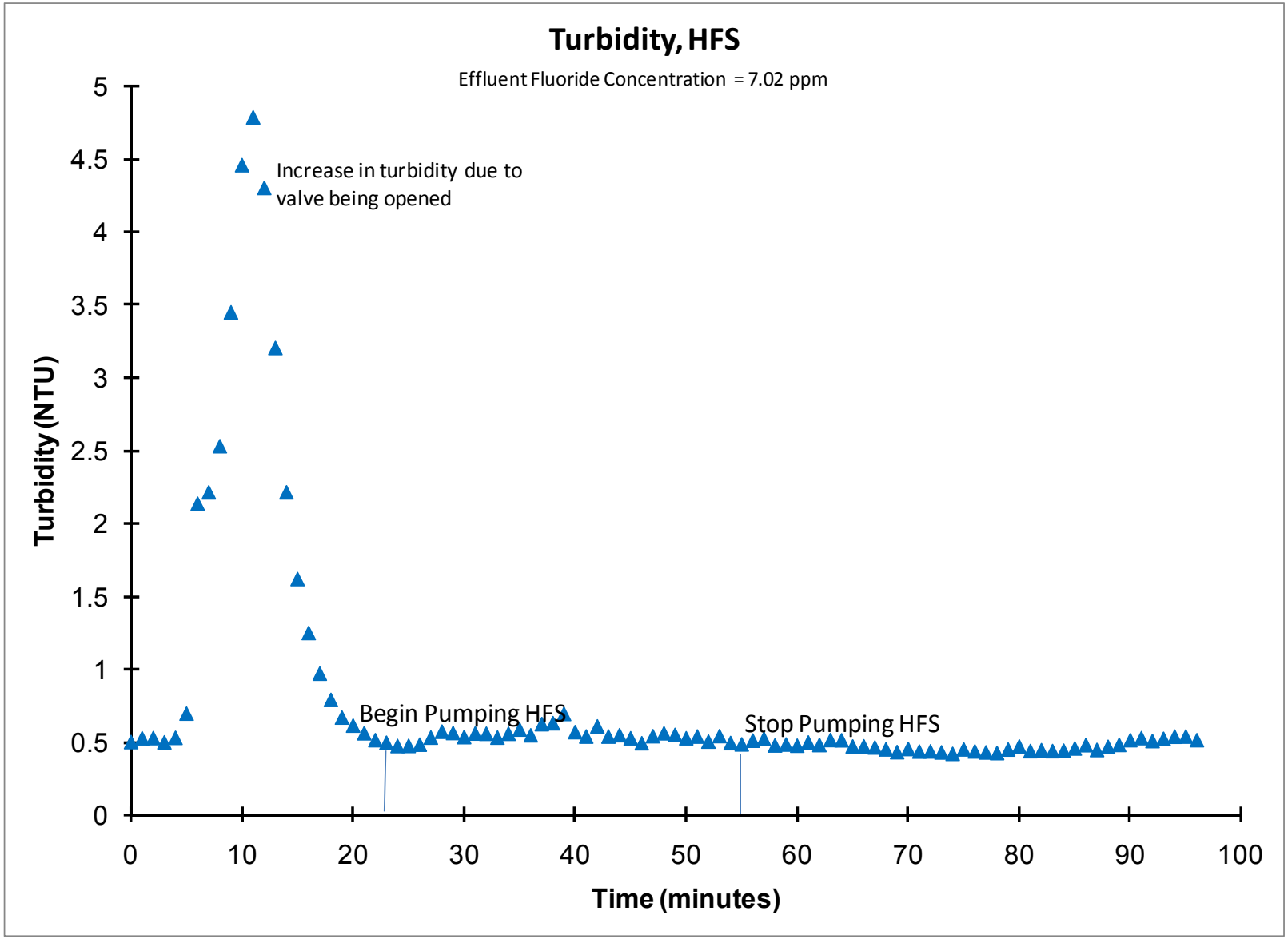

Figure 12. Turbidity Graph for HFS Contamination Event

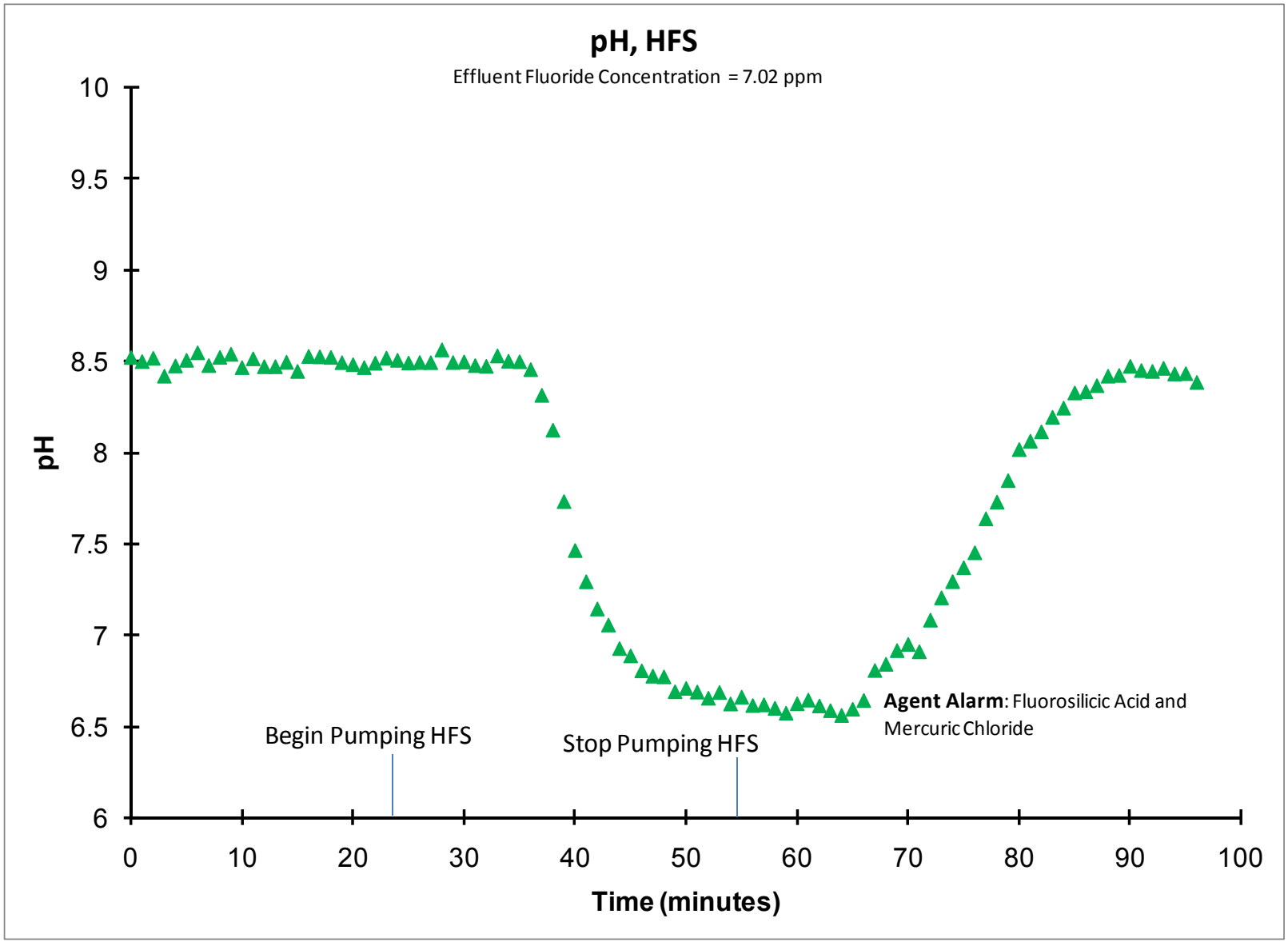

Figure 13. pH Graph for HFS Contamination Event

After each of the contaminants was injected into the pilot sentinel station, data were collected from the Sievers TOC analyzer and Hach Panel and analyzed. The values for TOC, conductivity, chlorine, pH, turbidity and the trigger were graphed on the vertical and time on the horizontal as shown in Figure 11, Figure 12, and Figure 13. Each of the graphs was studied to determine if detection occurred. The results were summarized using bar graphs. Maximums, minimums, and baseline values were calculated for each run. The difference between the maximum and minimum from the baseline was calculated. Next, the average of all the baseline values was calculated to give an overall baseline. The difference for each contaminant was added to or subtracted from the overall baseline to summarize the effects of the contaminants on each parameter. Figures 14 to 19 illustrate the response of each of the detectors to the battery of challenge contaminants. Individual bars in a cluster represent repeat trials.

Figure 14 depicts the response of the Hach Event sensor to various concentrations of contaminants. The Event Sensor trigger is a response of the five chemical sensors; turbidity, chlorine, pH, conductivity, TOC and temperature. The dashed line in the graphs represents the threshold of deviation for the five sensors. The alarm set point selected for the CWS research was one. Trigger values above one activate the plant alarm on the Hach Panel.

Bug-B-Gon, paint thinner, carbon tetrachloride, toluene, and the lowest concentration of copper sulfate and sodium fluoroacetate did not cause an alarm. The most significant response was HFS at a fluoride concentration of 9.77 ppm. As mentioned before, carbon tetrachloride and toluene concentrations were in the ppb range and not within the panels detection limit. Bug-B-Gon was predicted to trigger an alarm because multiple parameters changed due to the injection of the contaminant. Unfortunately, the changes were not significant enough to trigger a plant alarm.

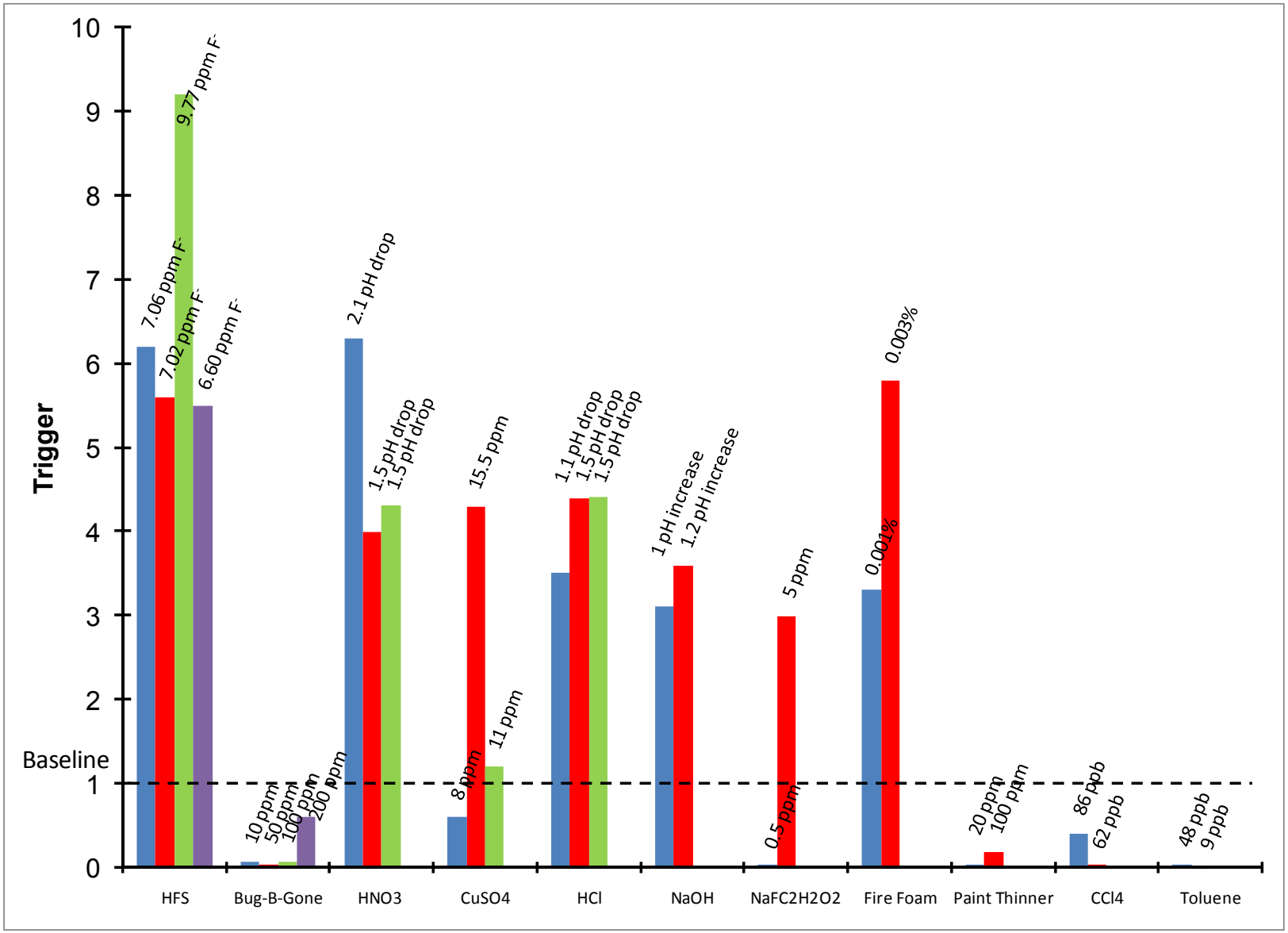

Figure 14. Summary of Runs for the Hach Event Sensor Trigger Alarm

Figures 15 to 20 show the response during the trials of the five individual chemical sensors that comprise the Hach Panel.

Figure 15 shows the changes in turbidity causes by the different contaminants. Sodium hydroxide and copper sulfate were the only contaminant that produced an increase in turbidity. Copper sulfate was predicted to increase the turbidity because of the color of the solution and the chemical was not completely dissolved. Conversely, sodium hydroxide was unpredicted. Speculation for the increase in turbidity was that the contaminant was removing matter from the pipes. The proposal was not tested for validity. For each run, the turbidity increased initially because of the valve to the pump being opened. Water was pumped into the sentinel system until the previous baseline was regained.

Figure 16 demonstrates the response the of the free chlorine analyzer to various contaminants. Chlorine was a difficult parameter to assess changes because the chlorine residual was constantly changing. Therefore, making the changes related to the injected contaminant difficult to assess. Example would be chlorine increasing throughout a run but not at a constant rate. Affects of the contaminant on the chlorine would be difficult to distinguish from the actual water quality. None of the contaminants caused an increase in chlorine concentration but the fire foam and the highest concentration of Bug-B-Gon decreased the chlorine residual. The changes in chlorine residual was difficult to determine due to variation in the distribution system show in Figure 38.

Figure 17 summarizes the change in pH responding to the different contaminants. As predicted, HFS, nitric acid, and hydrochloric acid, caused a decrease in pH. In addition, copper sulfate and Bug-B-Gon initiated a decrease in pH which were both unexpected. Exposure to sodium hydroxide produced an increase in pH due to the caustic nature of the contaminant.

The last column in Figure 18 shows the results of distilled water being injected into the system. Distilled water imposed a decrease of approximately 20 μs/cm. Similar changes can be seen with Bug-B-Gon, sodium fluoroacetate, Fire foam, paint thinner, carbon tetrachloride, and toluene because the stock solutions were prepared with distilled water. Additionally, the lowest concentration of copper sulfate had a decrease in conductivity. The lowest concentration of hydrochloric acid stayed the same while the rest of the toxins increased the conductivity. Sodium fluoroacetate was predicted to increase in conductivity but decreased for both trials. The possible explanation is that the distilled water used to produce the stock solution counterbalanced the increase. Toluene and carbon tetrachloride were not predicted to influence the conductivity because the concentrations were in the ppb range.

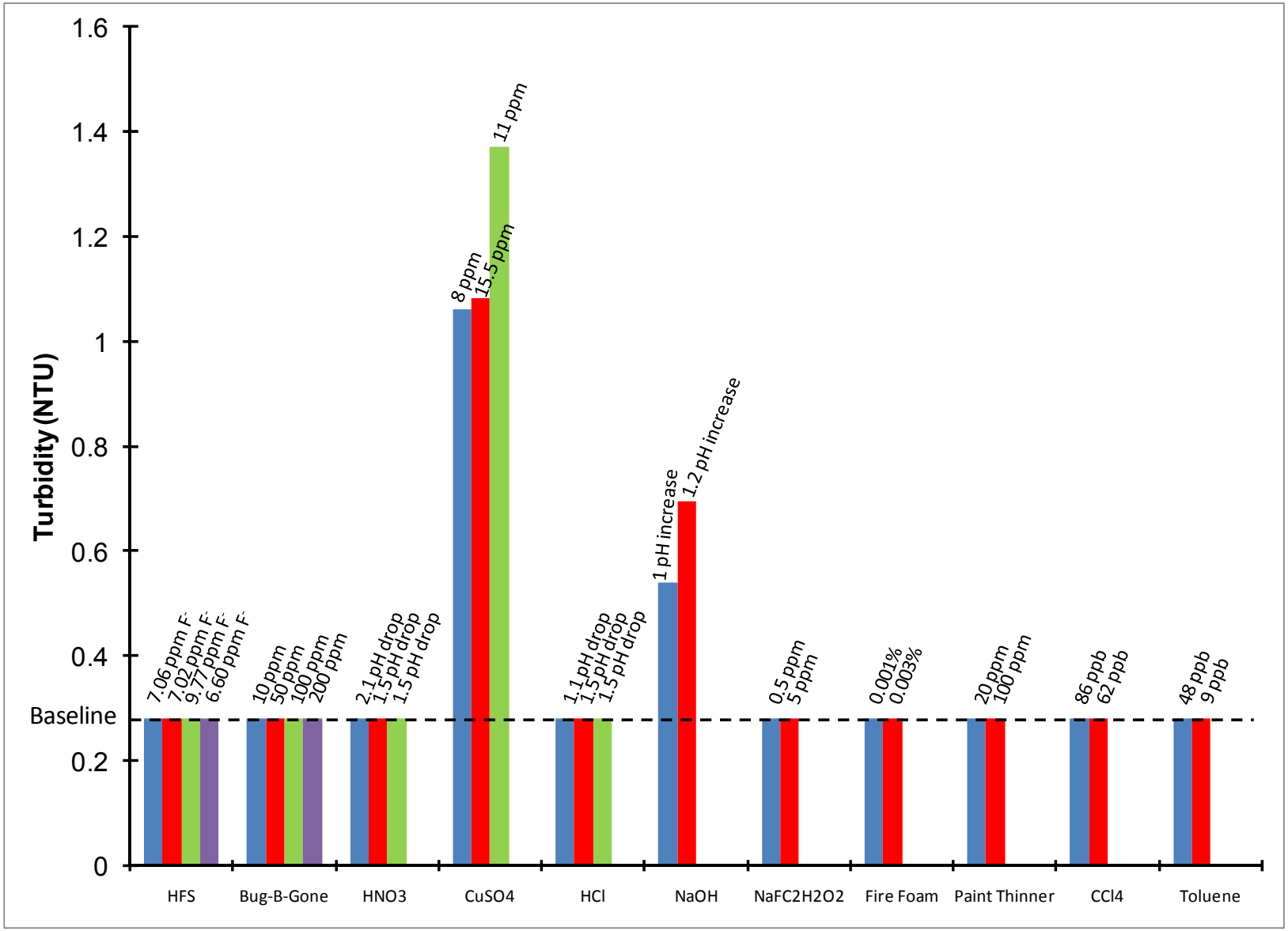

Figure 15. Summary of Runs for the Hach Turbidity

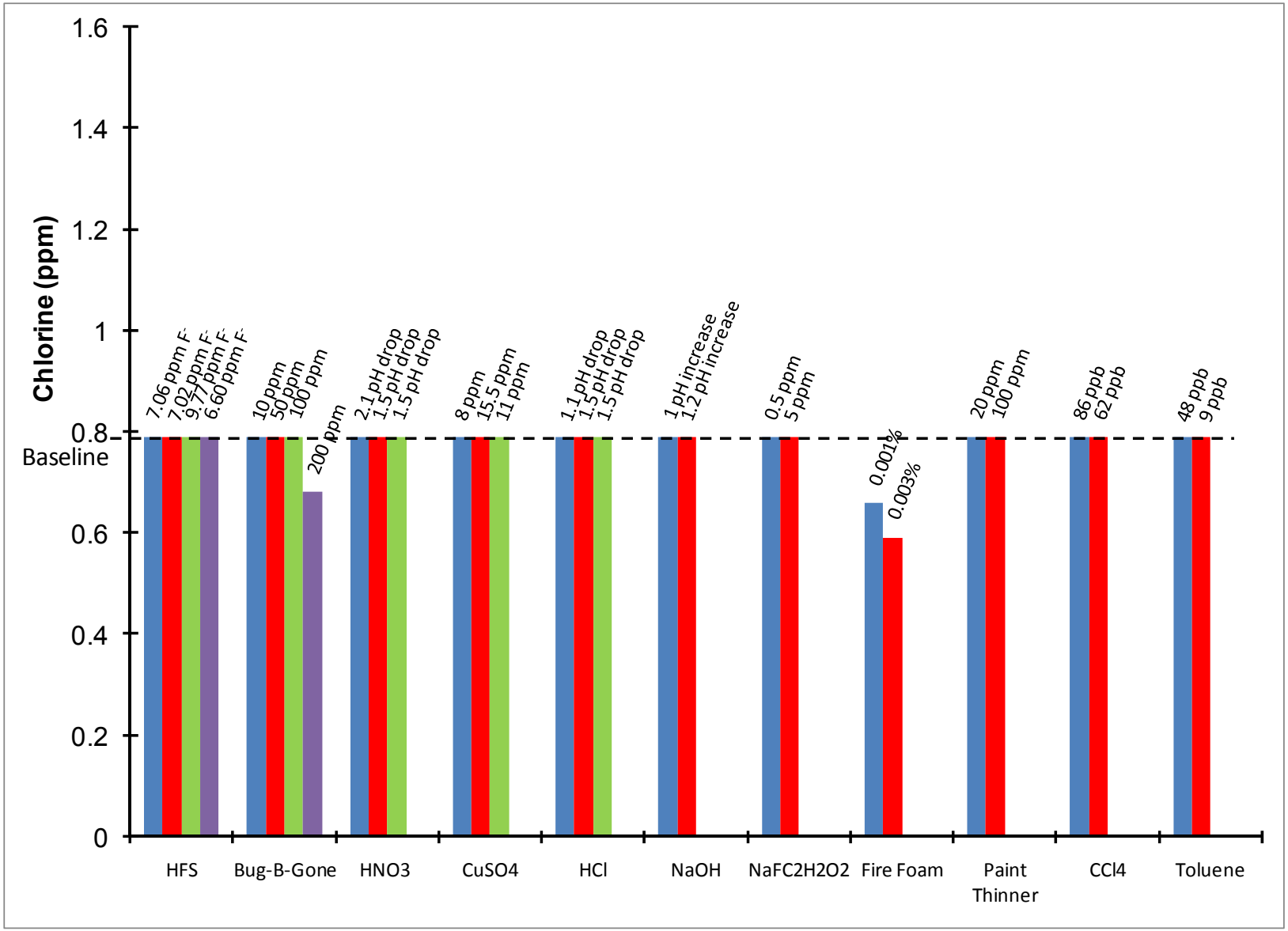

Figure 16. Summary of Runs for the Hach Chlorine Analyzer

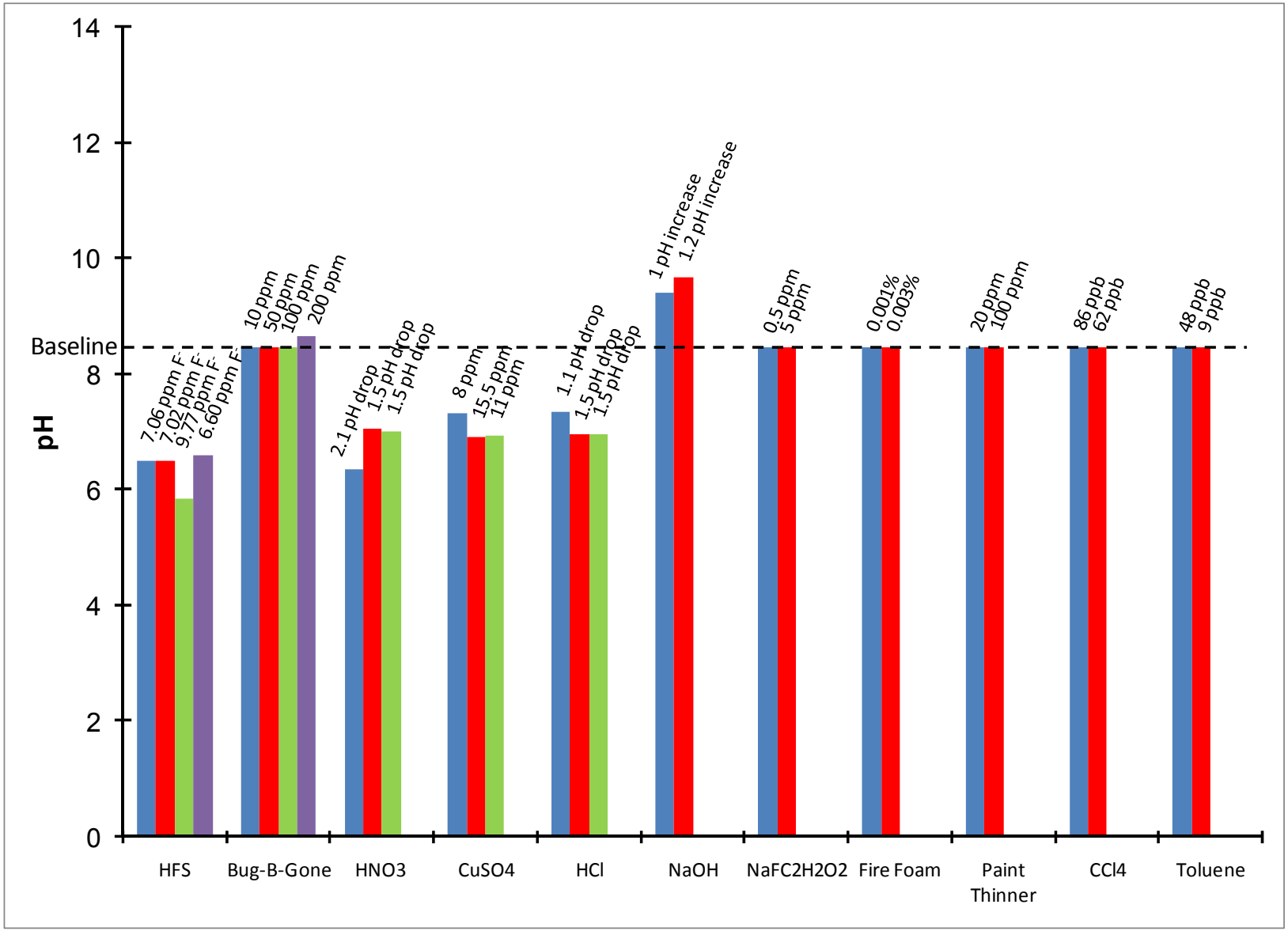

Figure 17. Summary of Runs for the Hach pH

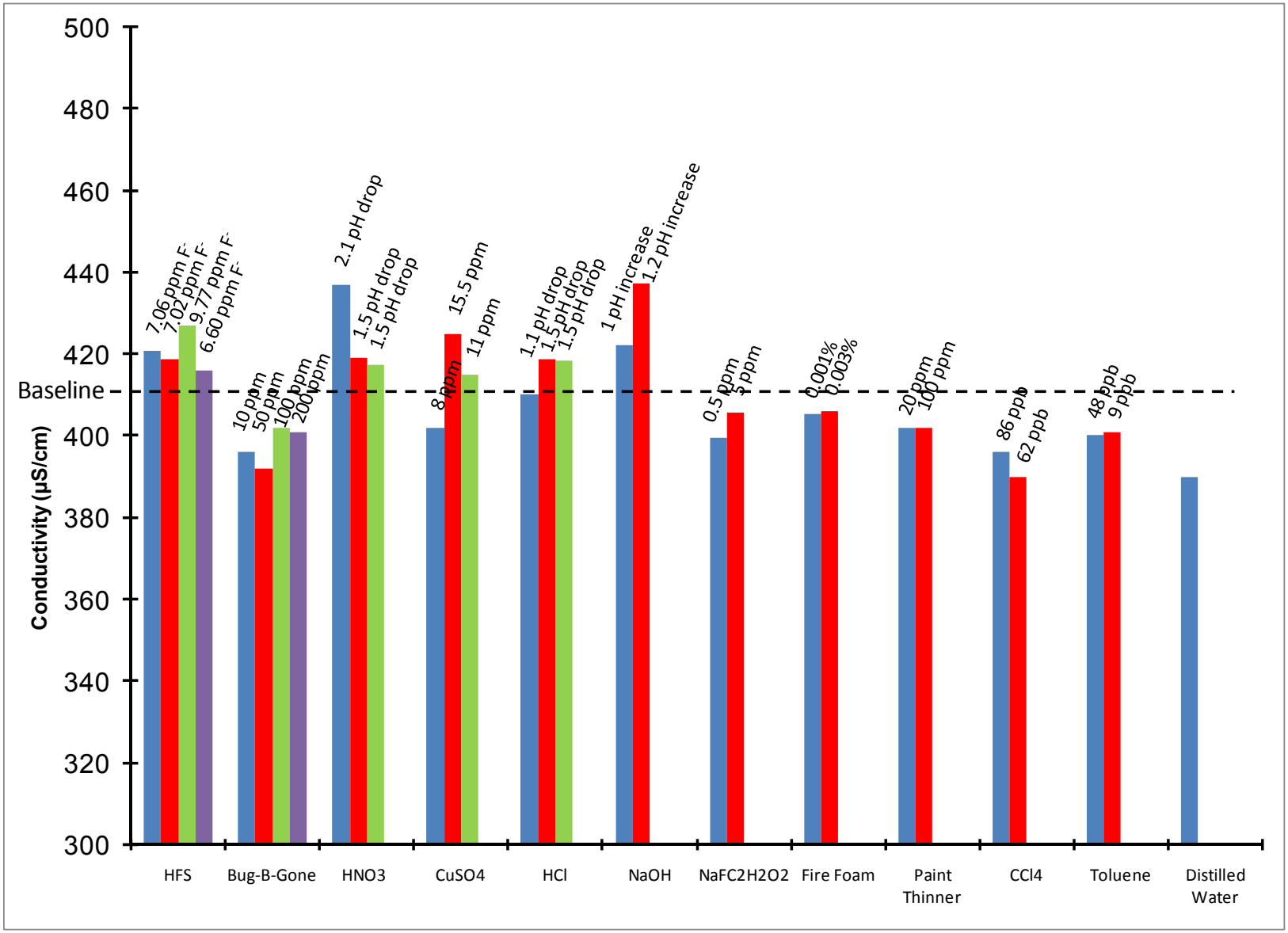

Figure 18. Summary of Runs for the Hach Conductivity

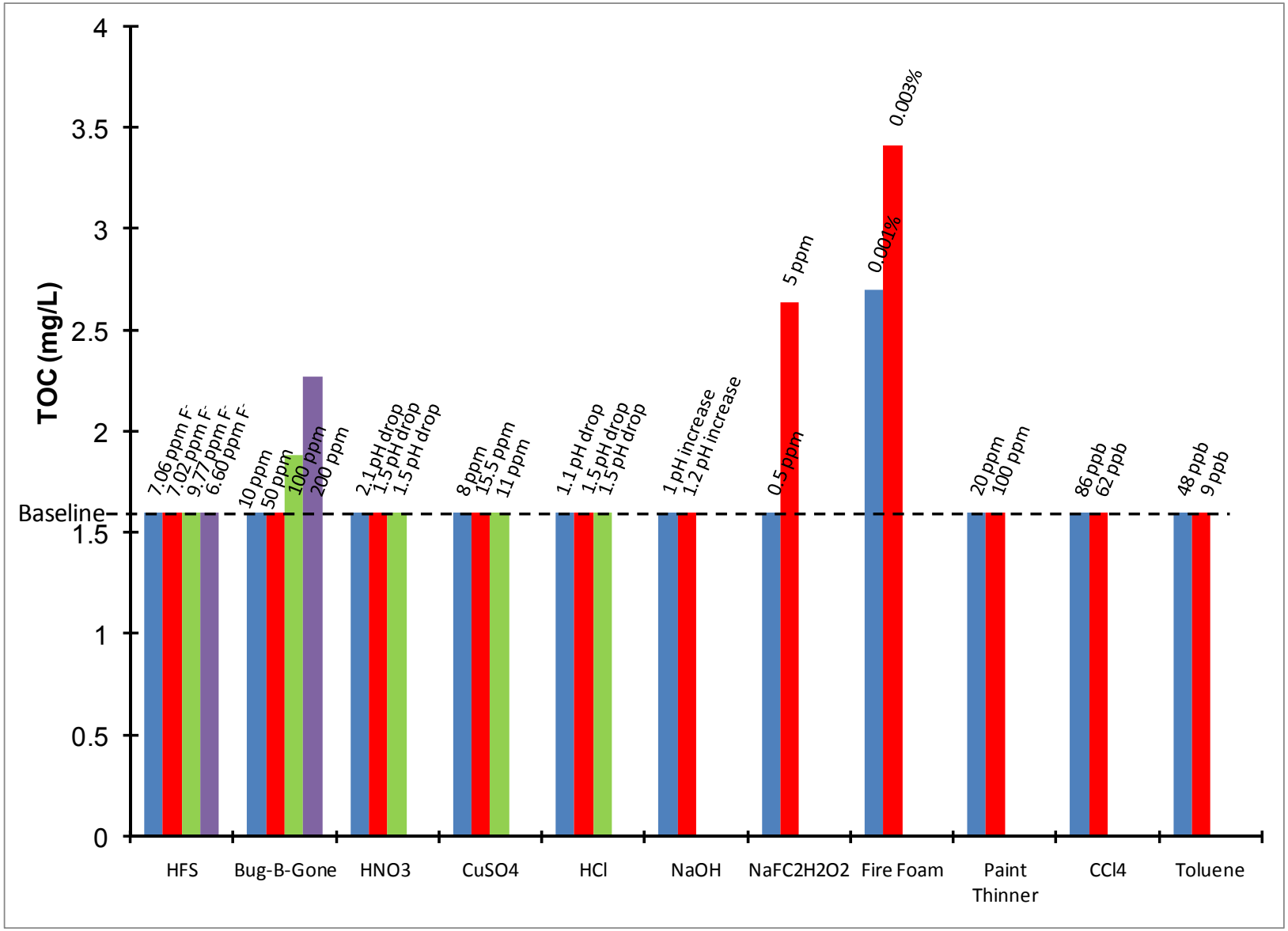

Figure 19. Summary of Runs for the Hach TOC

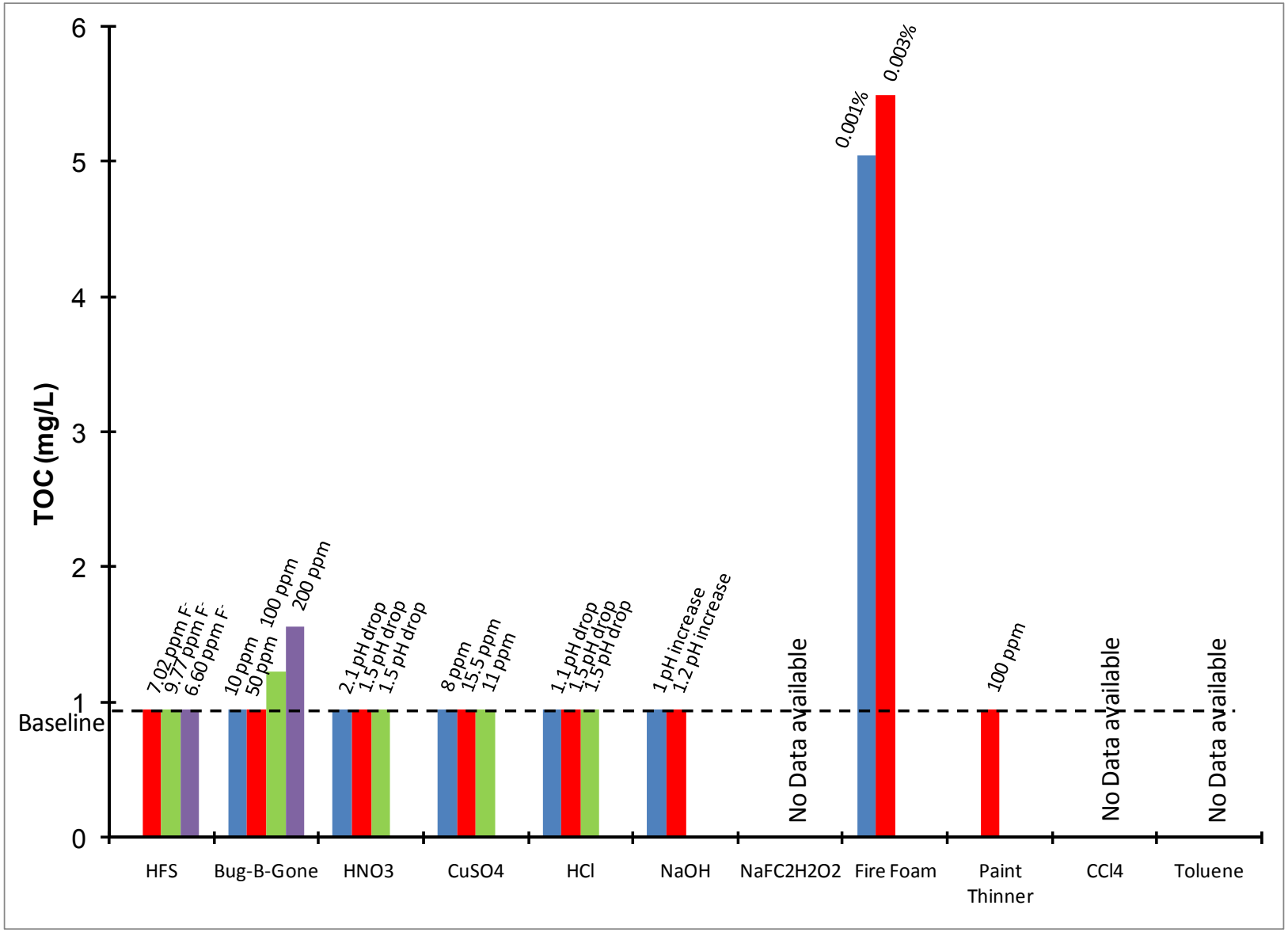

Figure 20. Summary of Runs for the Sievers TOC

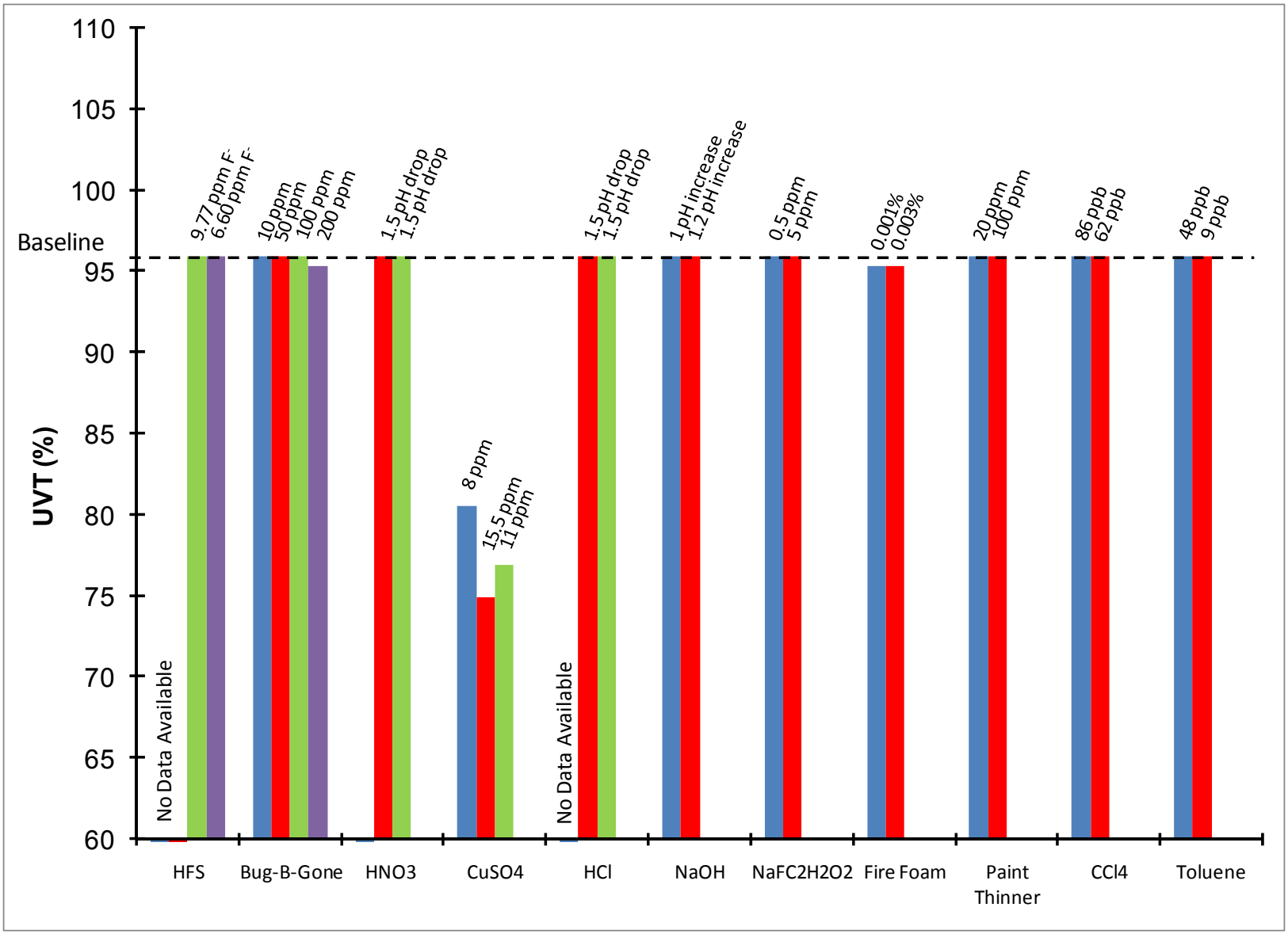

Figure 21. Summary of Runs for the Real UVT

Figure 19 depicts the results of TOC changes due to the injected contaminants. For the Hach TOC analyzer, the two higher concentrations of Bug-B-Gon, the highest concentration of sodium fluoroacetate, and both concentrations of fire foam caused increases in TOC. Sodium fluoroacetate, fire foam, and Bug-B-Gon were predicted to increase the TOC. Toluene and carbon tetrachloride were also predicted to increase the TOC but as mentioned before the concentration was too low. Paint thinner was predicted to increase the TOC because the contaminant is composed of saturated aliphatic and alicyclic hydrocarbons (C7 – C12) and aromatic hydrocarbons (C7 – C12) but did not change. A possible explanation was the concentration was below the detection limits.

Figure 20 shows the Sievers TOC outcomes. Similar to the Hach results, the two higher concentration of Bug-B-Gon, and both concentrations of fire foam caused an increase in TOC. The only difference was that data were not available for the sodium fluoroacetate, toluene and carbon tetrachloride runs because the instrument was not operational. Therefore detection is unknown for those runs. Similar results as the Hach TOC were projected.

The changes in UVT due to the contaminants being pumped through the CWS are shown in Figure 21. Copper sulfate was the only contaminant that caused a significant change in transmittance. Fire foam and the highest concentration of Bug-B-Gon caused a slight deviation from the baseline but not significant enough to be labeled a detection. Because the UVT monitor detects the presence of NOM and aromatic organics, paint thinner and toluene should have been detected. Again, a possible reason was they were not within the detection limit of the instrument.

The result from the agent identification from the parameters that deviated can be seen in Table 11. All the acid had the match of fluorosilicic acid, sarin, and mercuric chloride. The base, sodium hydroxide, did not produce an agent match. Copper sulfate had a similar response to the acids with the agent identification being fluorosilicic acid and mercuric chloride. Bug-B-Gon,

paint thinner, carbon tetrachloride, and toluene did not trigger a plant alarm. The Hach Agent library could not match sodium fluoroacetate but found multiple matches for fire foam. Dichlorvos, oxamyl, difenzoquate, dicotopho, and colchicine were all matches for fire foam.

For the injection of HFS, the Hach Event Monitor designated the event as fluorosilicic acid, mercuric chloride, and sarin. Due to the injection of HFS, the water quality increased in pH and conductivity. The agent library was able to correctly identify the contaminant but also had two other possibilities. Mercuric chloride when added to water should only cause an increase in conductivity making it a probable match. Sarin introduced to a water supply is likely to increase the TOC, but should not affect pH or conductivity, making it an unlikely candidate for the contamination. Sarin is an unusual choice for events where only the pH and conductivity changed. Similar results occurred for hydrochloric and nitric acid.

Copper sulfate was identified as fluorosilicic acid and mercuric chloride. The contaminant produced a pH decrease, and conductivity and turbidity increase once injected into the pilot monitoring system. Mercuric chloride is likely to increase conductivity and fluorosilicic acid has the potential to increase conductivity and decrease pH making both contaminants a possible candidate for the event.

The fire foam had better matches than the fluorosilicic acid and copper sulfate but was not identified correctly. The contaminant was not predicted to be identified correctly because many different types of fire suppression foams are on the market and could have different results. Table 10 summarizes the possible matches for fire foam and the likely affects when added to a water source.

Table 10. Agent library results for fire foam injection and changes to water quality parameters

Contaminants	Chlorine	pH	Conductivity	TOC
Fire Foam	↓		↓	↑
Dichlorvos				↑
Oxamyl		↑	↑	↑
Dicrotophos	↓	↑	↑	↑
Colchicine	↓	↓		↑

Notes: ↑ = increase

↓ = decrease

With the exception of conductivity, the parameters changed during the injection are similar to the characteristic of the four identified agents. Conductivity might have increased, but because it was mixed with distilled water, they balanced each other. The decrease in conductivity was about 6 μS/cm.

Table 11. Hach Agent Identification

Contaminant	Agent Alarm
HFS	Fluorosilicic Acid
	Sarin
	Mercuric Chloride
HCl	Fluorosilicic Acid
	Sarin
	Mercuric Chloride
HNO_3	Fluorosilicic Acid
	Sarin
	Mercuric Chloride
NaOH	No Agent Alarm
$CuSO_4$	Fluorosilicic Acid
	Mercuric Chloride
Sodium Fluoroacetate	No Agent Alarm
Bug-B-Gon	No Plant Alarm
Fire Foam	Dichlorvos (Organo phosphate)
	Oxamyl (Carbamate)
	Difenzoquate (Herbicide)
	Dicotopho (Organo phospate)
	Colchicine (Poison)
Paint Thinner	No Plant Alarm
CCl_4	No Plant Alarm
Toluene	No Plant Alarm

4.2 BIOLOGICAL CHALLENGE EXPERIMENTS

The JMAR Biosentry was used to detect microorganisms in the drinking water distribution system. To test the instrument, plastic spheres, *E. coli*, *cryptosporidium*, *Giardia lamblia*, and *Bacillus atrophaeus* spores were pumped through the pilot system to measure response.

4.2.1 Baseline

A baseline for the JMAR Biosentry needed to be established before the data could be analyzed. The deviation from the baseline would provide the count of microbes detected by the instrument during a run. As mentioned before, opening the valve to begin the injection process induces a large increase of turbidity and results in a significant increase in count per min for the Biosentry. Due to the increase of turbidity, the baseline average was taken before the valve was opened for a run. A problem was encountered in the Spore and Rod shape readings. The spore and rod shape channels steadily increase throughout the day, which makes detection difficult shown in Figure 39. For this reason, baselines mean needs to be taken close to the initiation of pumping to ensure an accurate value.

Figure 22 shows an average contamination event for spheres being injected. A spike occurred around 140 minutes, due to the valve and water being introduced into the pilot system. The second peak corresponds to the contamination event of 2μ spheres being injected into the water. The end of the baseline value will be the beginning of pumping (opening the valve).

To determine the best average, five averages were calculated using the duration of 20, 30, 40, 50, and 60 minutes before the opening of the valve. The value for the averages can be seen in Table 12.

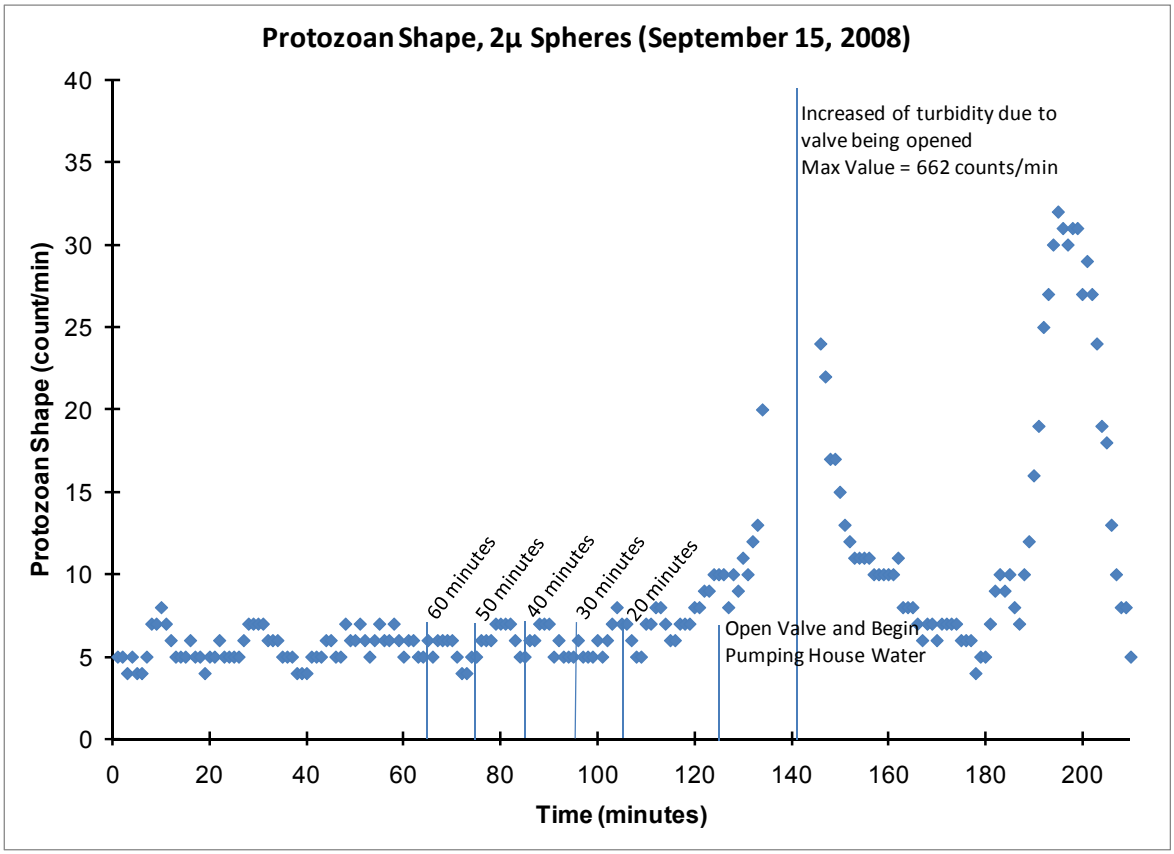

Figure 22. Determination of baseline duration

Table 12. Average values of count/ml for determination of a baseline before opening the valve

Minutes before Pumping	Average
20 min	6.67
30 min	6.26
40 min	6.27
50 min	6.1
60 min	6.03

The duration of 40 minutes before the beginning of pumping was chosen for the time taken to determine the baseline. The duration is long enough before the opening of the valve to

establish a beneficial baseline but not too long, that baseline is not similar as the actual contamination event. The average for the five values in Table 11 was 6.27, which corresponds to 40 minutes. Baseline values were calculated for each run performed.

4.2.2 Detection Analysis for the Biosentry

To determine the total count detected by the Biosentry a left Riemann's sum was used which is shown in Equation 4. For the case of the Biosentry, data of intervals of one minute was taken for Δx.

$$A \approx f(x_1)\Delta x + f(x_2)\Delta x + \ldots + f(x_n)\Delta x \qquad \text{(Equation 4)}$$

The data were normalized by subtracting the baseline value from the value records by the instrument. Highlighted in Figure 23 was the increased count per min caused by injecting 2μm spheres. The area under the curve will provide the total count of spheres during the injection period. Figure 24 is an enlarged graph of Figure 23. In addition, Figure 24 shows the left Riemann's sum being applied to the curve.

The area under the curve was calculated for each contamination event that created an increase in counts per minutes. The procedure was used for the rod, spore, protozoan shape, and unknown data.

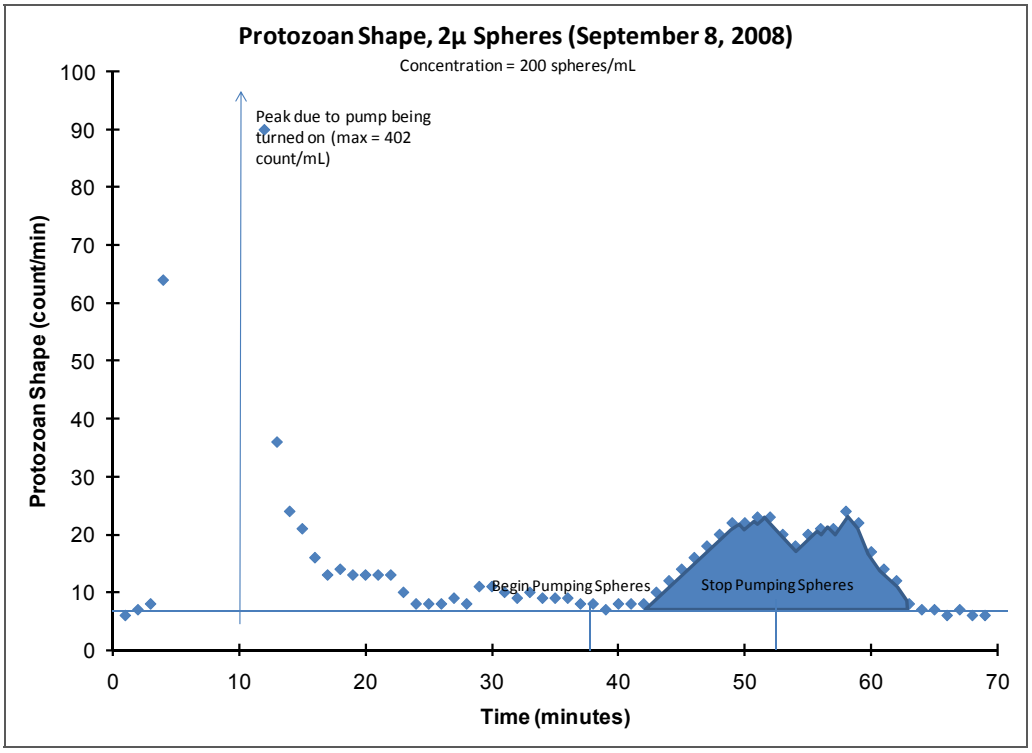

Figure 23. Spheres Contamination Event with Baseline and Area Highlighted

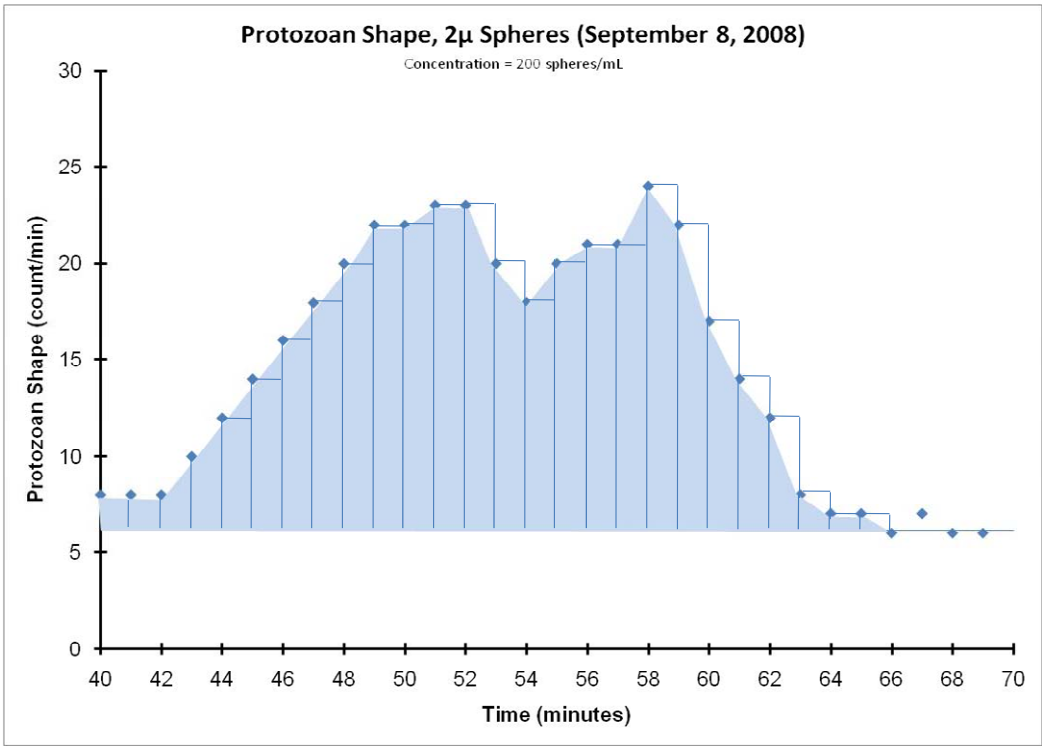

Figure 24. Left Riemann's Sum Being Applied to Calculate the Total Number of Spheres

4.2.3 Conductivity

All the microbes and spheres injected caused a decrease in conductivity which was detected by the Hach panel. Distilled water was used to create the stock solution for all the biological contaminants. The distilled water verified the spheres and microbes being pumped through the system because it could be seen on the Hach panel as shown in Figure 25.

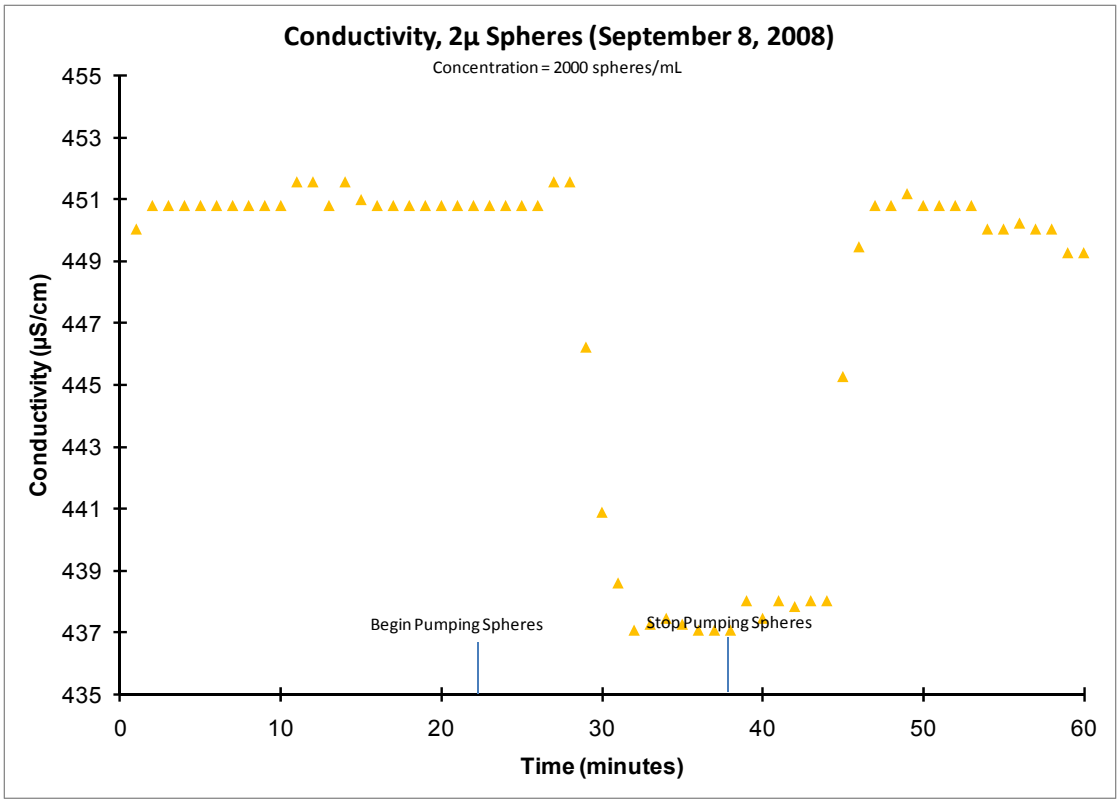

Figure 25. Change in conductivity due to distilled water

4.2.4 Contamination Events

For each of the spheres and microbes injected, data were recorded and analyzed for the Biosentry. The Biosentry organizes the data into four different channels:

- Rod- smallest particles (0.4 to 4 μm)
- Spore- ovoid-shaped particles with more rigid walls/cases (1 to 3μm)
- Protozoa- ovoid-shaped (3 to 10 μm)
- Unknown

The data from the Rod shape, spore shape, and protozoan shape counts were plotted against time to determine if an increase occurred.

The summary of detection for the biological contaminants can be seen in Table 13. The two-micron spheres were detected as protozoan shape at all four concentrations. This was predicted because the 2 μm spheres are supposed to represent protozoan microorganisms. At concentrations of 2000 and 2500 spheres/mL, the Biosentry also classified the spheres as spore shapes. The large concentration could have caused disturbance in the readings and the size of the sphere also falls within the spore channel. The 0.8 micron spheres with a concentration of 200 spheres/mL were not detected by the instrument but a concentration of 1000 and 2000 spheres/mL were detected and both were classified as spore shape. As predicted, because 0.8 μm spheres are suppose to represent a contamination of spores.

A single concentration of *cryptosporidium* oocysts was injected into the pilot system. The pathogen caused an increase in count for the unknown, spore, and protozoan shapes. As classified by the manufacture, Table 4, *cryptosporidium* belongs in the protozoan channel. Therefore, an increase in unknown and spore counts was not projected. This could be due to the use of inactivated *cryptosporidium* instead of living oocysts.

Giardia lamblia was injected into the system at a concentration of 100 colony forming units (CFU) per mL. The Biosentry recorded an increase in unknown and protozoan shape count. The protozoan was predicted to increase but not the unknown. Unknown could be related to turbidity or dead parasites.

E coli were only detected at the highest concentration. For the highest concentration, $4.66x10^6$ CFU/mL, there was an increase count for unknown, rod, and spore shapes. Similar to the highest concentration, $2.74x10^6$ CFU/mL was seen in the same channels and was also seen in the protozoan. According to the manufacture, the rod channel should have only increased. The system could have been bombarded with particles because the high concentration injected.

The Biosentry only detected *Bacillus atrophaeus* spores at a concentration of 660 count/mL, which was anticipated.

Table 13. Contaminant Specific Monitoring for Biological Contaminants

	Detection Category				
Contaminant	**Concentration**	**Unknown**	**Rod**	**Spore**	**Protozoan**
Plastic Sphere (2μ)	200 spheres/mL				X
	250 spheres/mL				X
	2000 spheres/mL			X	X
	2500 spheres/mL			X	X
Plastic Sphere (0.8μ)	200 spheres/mL				
	200 spheres/mL				
	1000 spheres/mL			X	
	1000 spheres/mL			X	
	2000 spheres/mL			X	
	2000 spheres/mL			X	
Cryptosporidium oocysts	200 oocysts/mL	X		X	X
Giardia lamblia cysts	100 CFU/mL	X			X
E. coli cells	4.66×10^6 CFU/mL	X	X	X	
	2.74×10^6 CFU/mL	X	X	X	X
	80 CFU/mL				
	67 CFU/mL				
Bacillus Atrophaeus spores	200 spores/mL				
	660 spores/mL			X	

Notes:
X = Detection by Instrument

Table 14 exhibits the summary of baseline values, maximum values, area under the curve, and percent recovery. Baseline values are the average count per minute 40 minutes before the opening of the valve. Maximum values are the peak number reached during the experiment. The numbers in the table are normalized by subtracting the baseline value. Area under the curve was calculated using a left Riemann's sum. Percent recovery was calculated by dividing the maximum values for each contaminant by the actual concentration. Counts per minute is equivalent to counts per milliliter because the Biosentry analysis one mL of water a minute.

Percent recovery ranged from 8% to 63%, excluding percent greater than 100.

For *Giardia* cysts, the infectious does is 25 to 100 cysts and the concentration injected was 100 CFU/mL. The concentration injected for cryptosporidium was 200 oocysts/mL and the infectious dose is 1 to 30 oocysts. The concentration detected for E. coli was greater than $2.74x10^4$ CFU/mL and the infectious does is between 10^6 and 10^9 organisms. At the concentration injected for the three contaminants, only one to two mL of water would need to be ingested to be infected.

Notes for Table 14:
Unk = Unknown
Spo = Spore
Prot = Protozoan
- = Undetected change in the Biosentry

Table 14. Summary of Detection for the Biosentry

		Baseline (counts/mL)				Max Values (count/mL)				Area (Count)				% Recovery			
	Concentration	Unk	Rod	Spo	Prot	Unk	Rod	Spo	Prot	Unk	Rod	Spo	Prot	Unk	Rod	Spo	Prot
Sphere (2µm)	200 spheres/mL	-	-	-	6.5	-	-	-	18	-	-	-	242	-	-	-	9
	250 spheres/mL	-	-	-	6	-	-	-	26	-	-	-	335	-	-	-	10
	2000 spheres/mL	-	-	325	6	-	-	207	213	-	-	3334	3319	-	-	10	11
	2500 spheres/mL	-		375	5	-		192	289	-		3005	4124	-		8	12
Sphere (0.8µm)	200 spheres/mL	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	200 spheres/mL	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	1000 spheres/mL	-	-	281	-	-	-	141	-	-	-	1968	-	-	-	14	-
	1000 spheres/mL	-	-	281	-	-	-	151	-	-	-	2010	-	-	-	15	-
	2000 spheres/mL	-	-	411	-	-	-	340	-	-	-	5033	-	-	-	17	-
	2000 spheres/mL	-	-	1,092	-	-	-	465	-	-	-	5539	-	-	-	23	-
Crypto-sporidium	200 oocyst/mL	7,790	-	202	9	950	-	125	21	14,829	-	2254	545	475	-	63	11
Giardia lamblia	100 CFU/mL	5,350	-	-	4.5	554	-	-	18	4,495	-	-	197	554	-	-	15
E. coli	$4.66x10^6$ CFU/mL	5600	377	170	-	24,612	5,788	1093	-	$3x10^5$	71,889	12,702	-	0.53	0.12	0.02	-
	$2.74x10^6$ CFU/mL	4300	296	150	8	4490	877	75	17	81,774	13,521	1170	105	0.16	0.03	0.00	
	80 CFU/mL	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	67 cfu/ml	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Bacillus Atrophaeu	200spores/mL	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	660 spores/mL	-	-	103	-	-	-	80	-	-	-	1010	-	-	-	15	-

For each of the spheres and microbes injected, data was recorded and analyzed from the Biosentry. The data from the Rod shape, spore shape, and protozoan shape counts were plotted against time to determine if an increase occurred. Figure 26 and Figure 27 demonstrate raw data for the injection of 0.8μm spheres and *cryptosporidium*.

The spore shape count increased as a result of 0.8μm spheres being injected into the pilot system seen in Figure 26. From the baseline, the count increased by 151 count per minute. The area under the curve was 2100 spore shaped 'organisms'. Five million spheres were injected for analysis. The instrument detected 0.04% of the total amount injected.

Figure 27 was the increase of protozoan shapes as a result of *cryptosporidium* being injected into the CWS. The theoretical concentration of organisms in the effluent was 200 oocysts per ml, which caused an increase of 21 protozoan shaped organisms. The total number under the curves was 545 *oocysts*. Compared to the one million injected, only 0.05% was detected by the protozoan channel. For this run, the unknown and spore shapes also increased. The total number of organisms detected by the Biosentry was 1.8%.

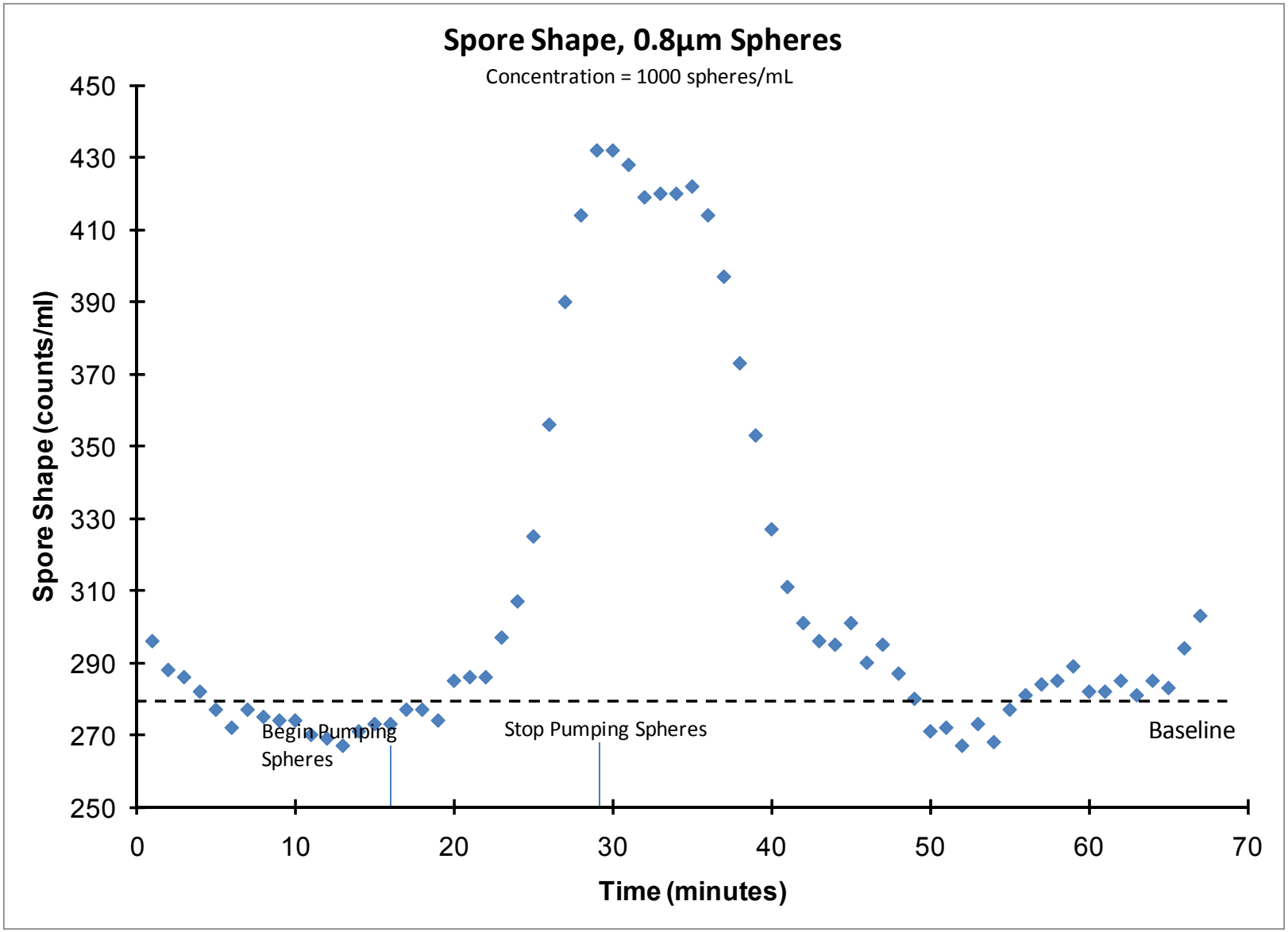

Figure 26. Increase in Spore concentration as a result of 0.8µm spores

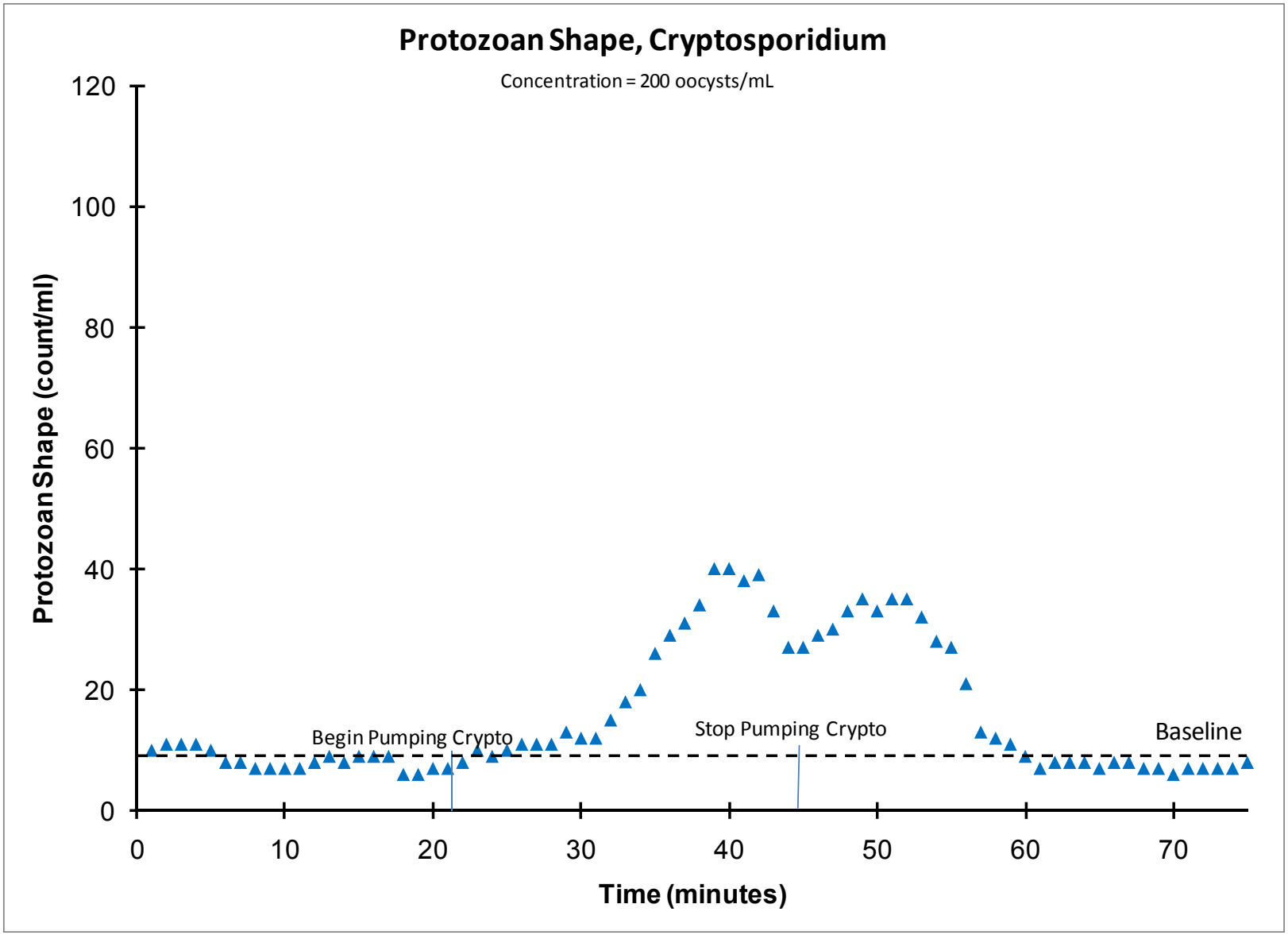

Figure 27. Increase in Protozoan concentration as a result of Cryptosporidium

The data from the unknown, rod shape, spore shape, and protozoan shape counts was summarized by sorting the information into bar graphs. Figures 28 to 31 show each detection category in the Biosentry.

Figure 28 summarizes the unknown results from all the experiments when the optical pattern could not be matched to a pattern in the library. The E. coli at two higher concentrations significantly increased the unknown count. Cryptosporidium and Giardia also increase the unknown count for the Biosentry. None of the other contaminants had an impact on the count.

Figure 29 shows the detection of organisms in the rod shape category. The two higher concentrations of E. coli caused an increase in the rod shape count. This was predicted because E. coli is one of the known patterns in the detection library and it is classified as a rod shape. None of the other contaminants caused an increase in count.

Figure 30 shows the changes in spore count. The spore count did not change for the 200 to 250 count per ml for the 0.8µm and 2µm plastic spheres and *Bacillus* spores. All the other contaminants had an increase in spore count other than the lower concentrations of *E. coli* and *Giardia*. The 0.8µm spheres and *Bacillus* spores are the only contaminants that should have increased the spore count.

Figure 31 shows the results for the impact of the contaminants on the protozoan count. All the 2µm spheres caused an increase in the protozoan count. The 0.8µm spheres did not increase the protozoan count during the experiments as anticipated. *Cryptosporidium*, *Giardia*, and *E. coli,* at a concentration of 2.74 million cfu/ml, had an increase in protozoan count. An increase should have occurred for the 2 µm spheres, *Cryptosporidium* oocysts, and *Giardia* cysts but not the *E. coli* cells.

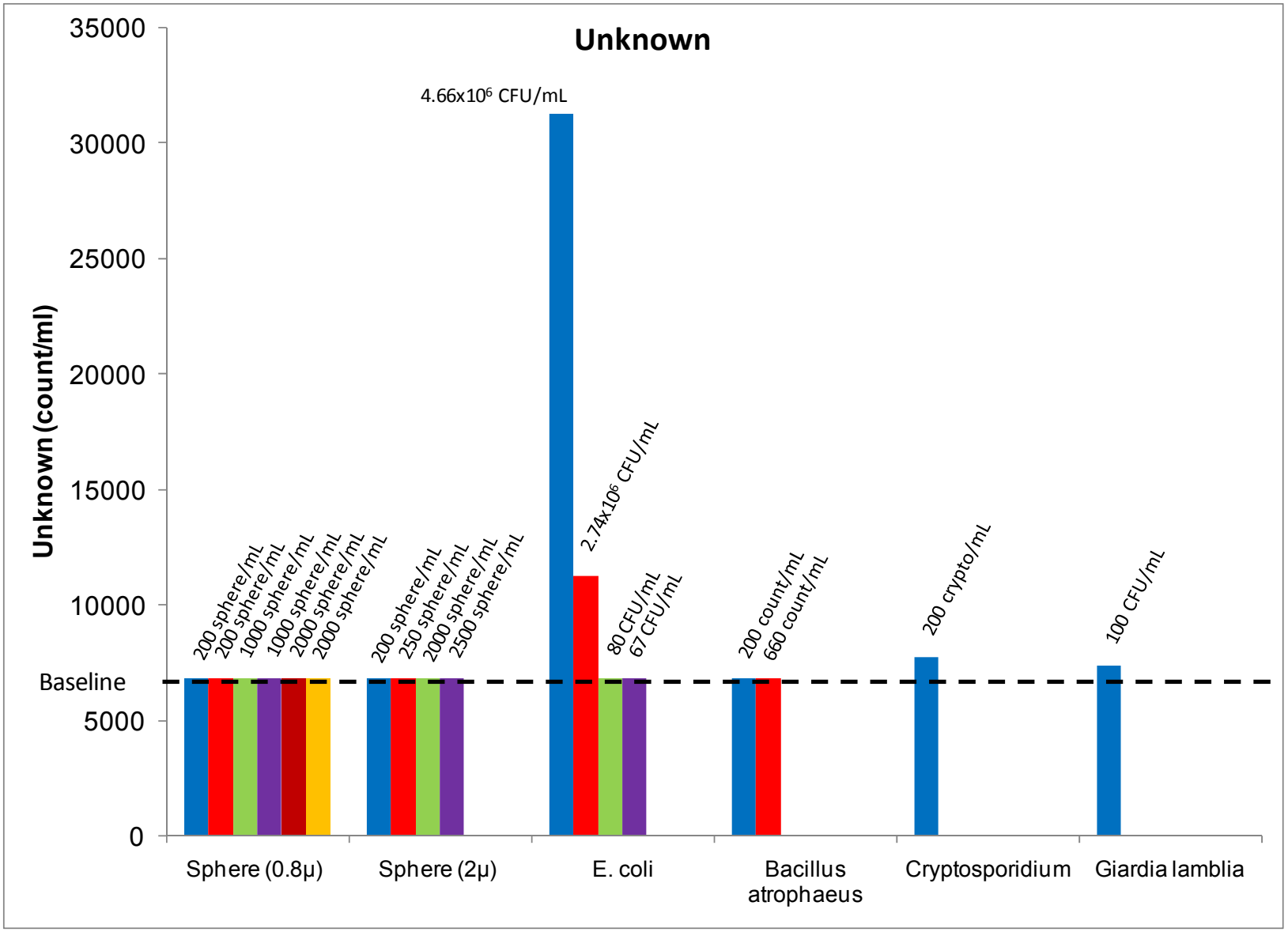

Figure 28. Unknown Biosentry Results

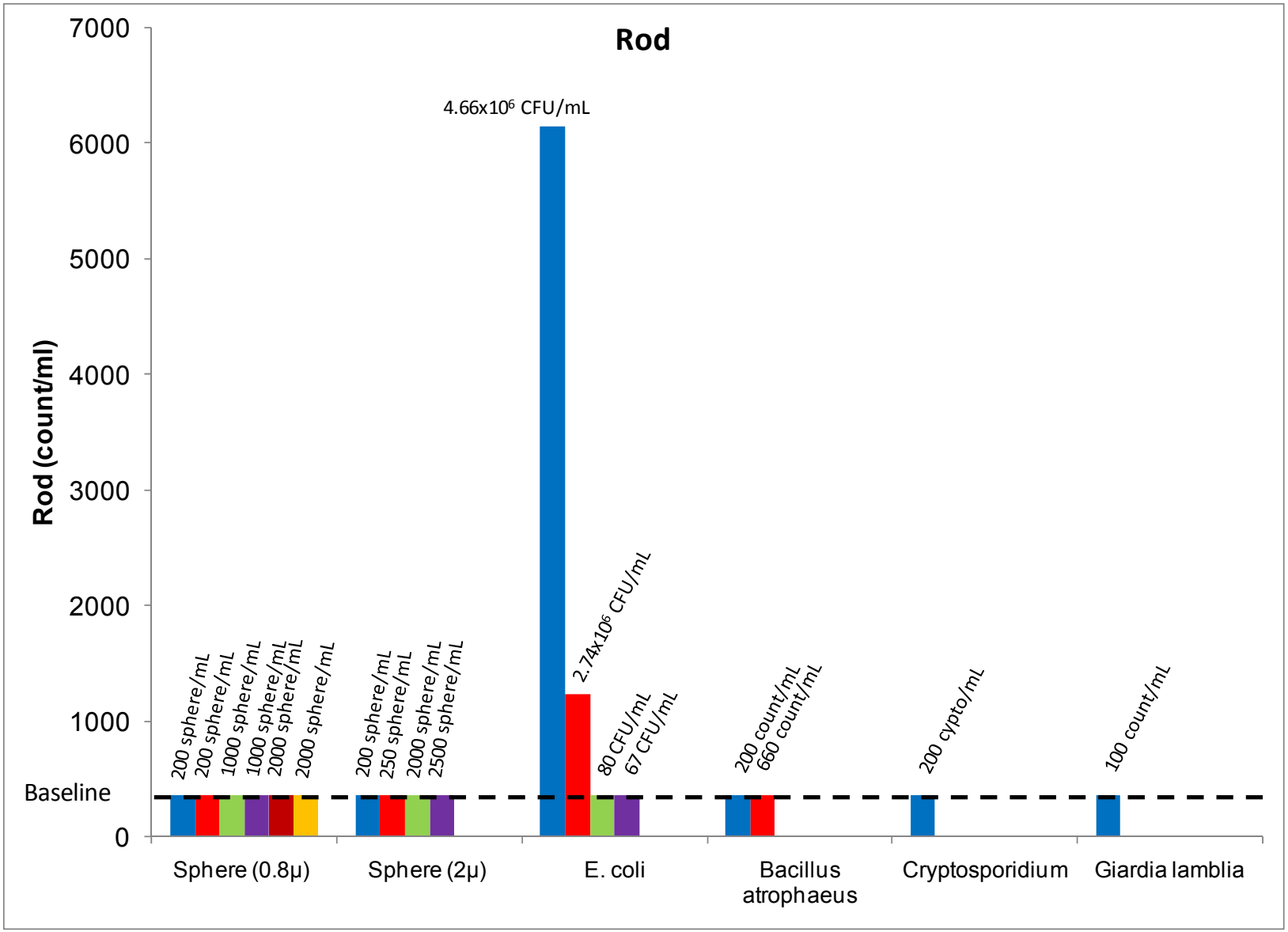

Figure 29. Rod Biosentry Results

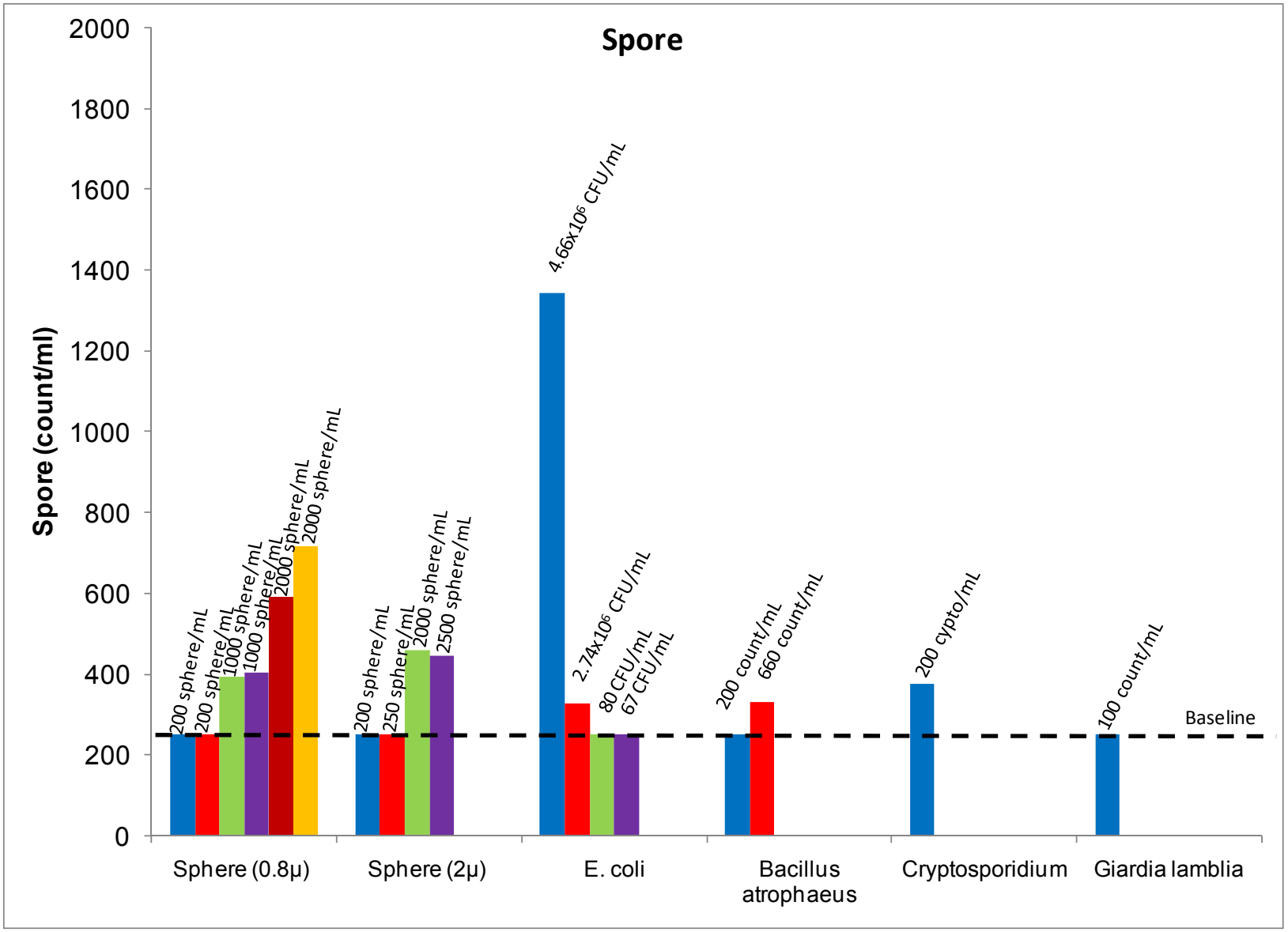

Figure 30. Spore Biosentry Results

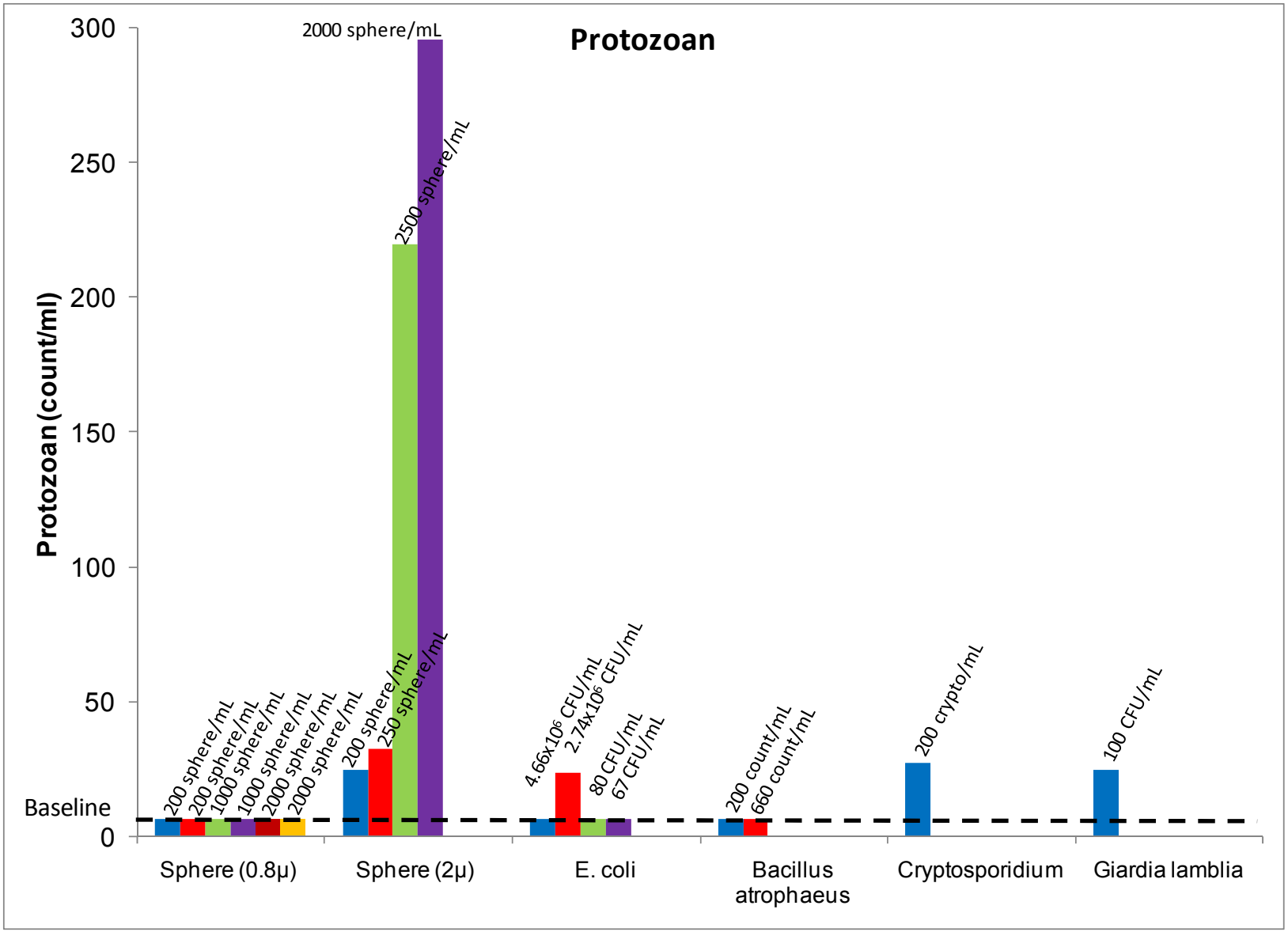

Figure 31. Protozoan Biosentry Results

The injected chemical contaminants did not have an impact on the Biosentry. There were no noticeable changes in the instrument during the chemical injection. The Biosentry did increase in count for all of the channels when the valve to the injection system was opened. This is the result of an increase of turbidity through the system.

4.3 CHEMICAL CONTAMINANT SPECIFIC MONITORING – GC-MS

The gas chromatography-mass spectrometry was tested by injecting paint thinner, toluene and carbon tetrachloride in the pilot system. Every 15 minutes a sample was taken for analysis. The instrument records a concentration of contaminants but it is based on the library calibration.

To quantify the concentration detected average chloroform concentration at the drinking water plant was compared to recorded values by the GC-MS. Table 15 summarizes the concentration of chloroform detected by the GC-MS during the each of the experiments. The average value of chloroform was divided by the GC-MS value of chloroform to produce a scalar. The concentration of contaminants quantified by the GC-MS is then multiplied by the scalar.

Table 15. Concentration Scalar Based on Average Chloroform Concentration

	GC-MS Chloroform Concentration (ppb)	Actual Ave. Chloroform Concentration (ppb)	Scalar
Paint Thinner	11.37	9	0.792
	18.65	9	0.483
CCl4	2.536	9	3.549
	2.078	9	4.331
Toluene	2.369	9	3.799
	2.352	9	3.827

The drinking water normally has low concentrations of disinfection byproducts (DBPs). For Pittsburgh water, the common byproducts are chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBR_2Cl$), and bromoform ($CHBr_3$) which are all trihalomethanes.

4.3.1 Paint thinner

Paint thinner was injected into the pilot system at calculated effluent concentrations of 20 and 200 mg/l . Concentration of 20 mg/l was not detected by the GC-MS, but the 200 mg/l was detected. Figure 32 shows the baseline of the water quality for the day that the paint thinner was injected. The four peaks correspond to the four DBPs mentioned above. Figure 33 shows the detection of paint thinner in the water. The multiple peaks are a result of the many organics within the injected solution.

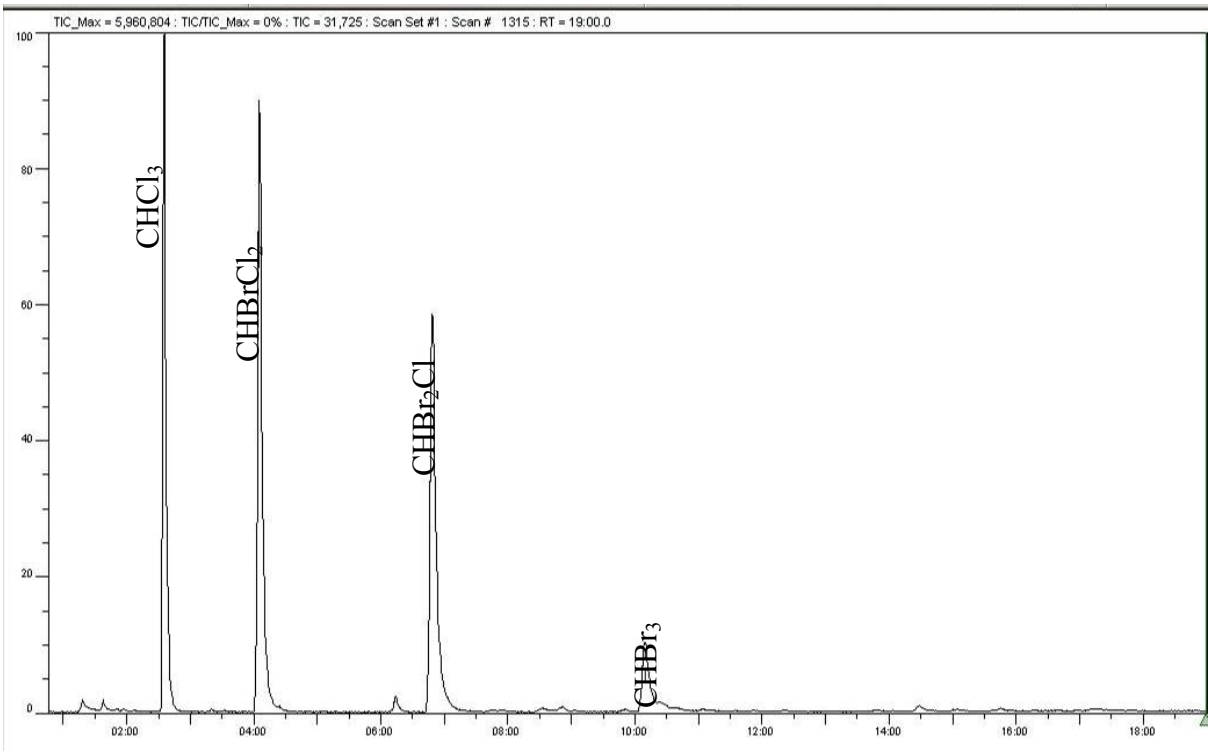

Figure 32. Baseline Values for the GC-MS before Paint Thinner was Injected

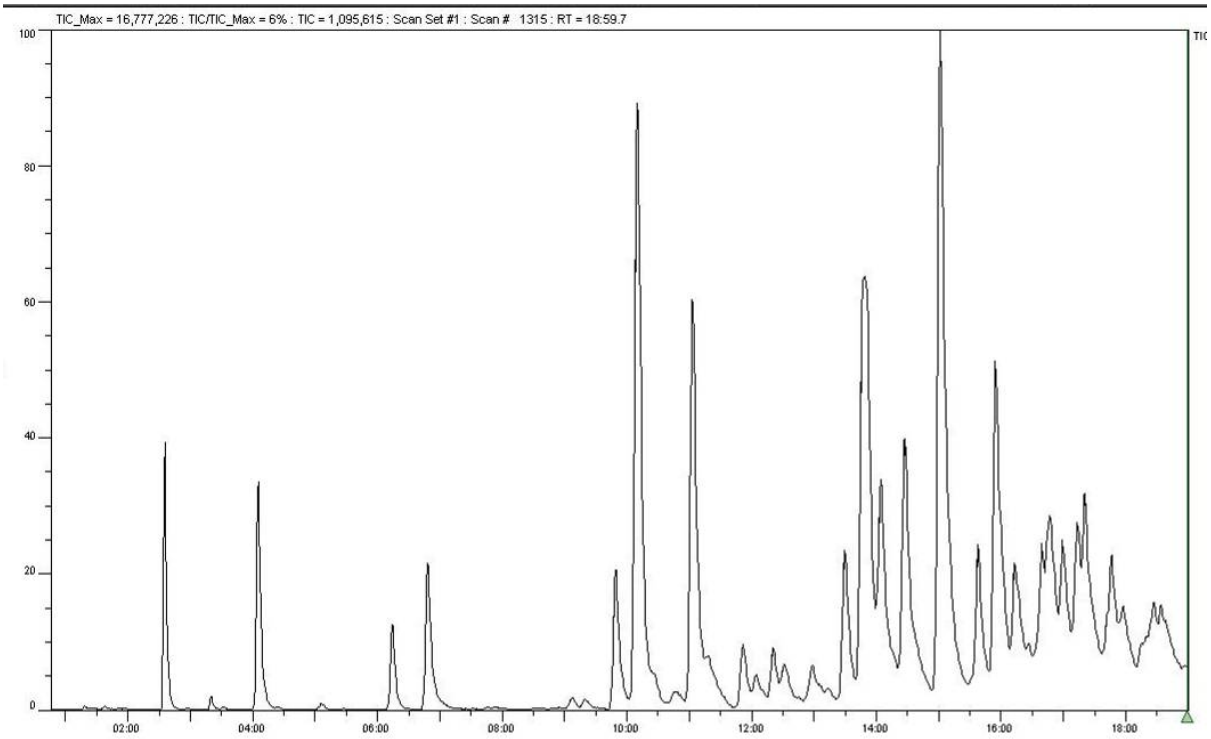

Figure 33. Detection of Paint Thinner by the GC-MS

4.3.2 Carbon Tetrachloride

Concentrations of 86 and 62 µg/l carbon tetrachloride were injected into the pilot system. Both runs were detected by the GC-MS. Figure 34 shows the baseline values before carbon tetrachloride was injected into the pilot system. The four peaks represent the four DBPs in the drinking water. Figure 35 shows the detection of carbon tetrachloride by the GC-MS. The peak occurs between chloroform and bromodichloromethane.

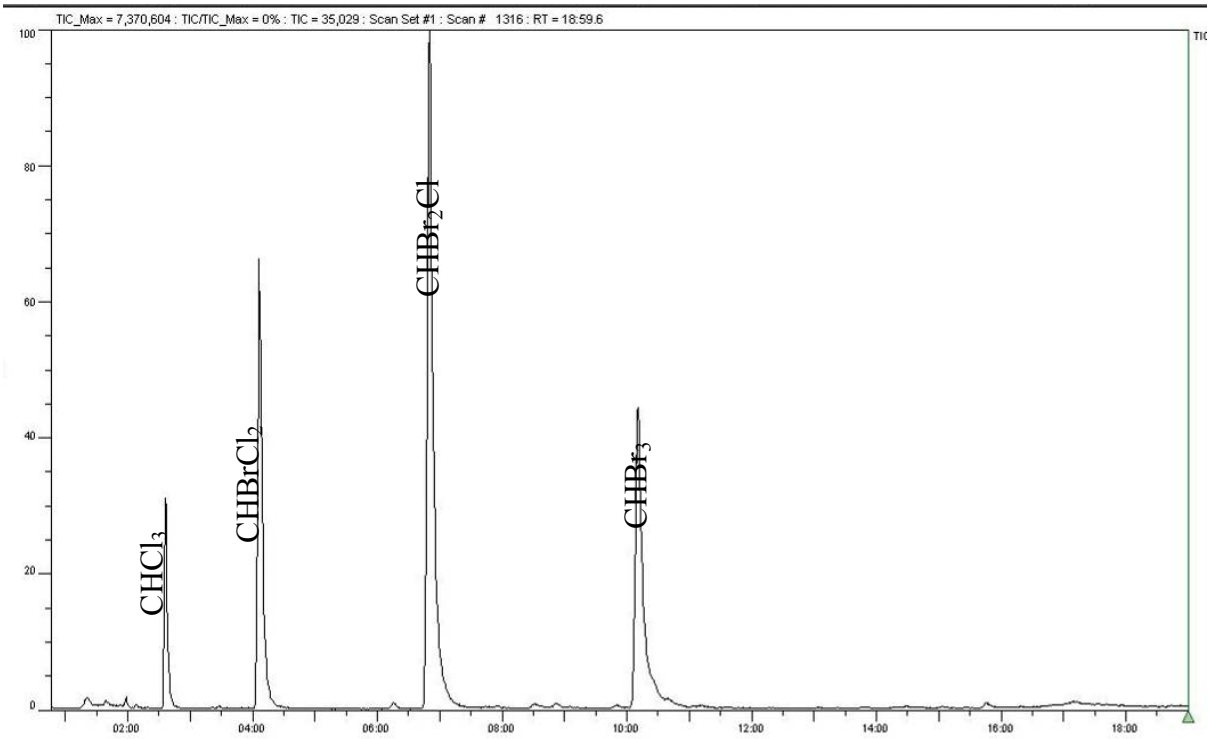

Figure 34. Baseline Values for the GC-MS before Carbon tetrachloride was Injected

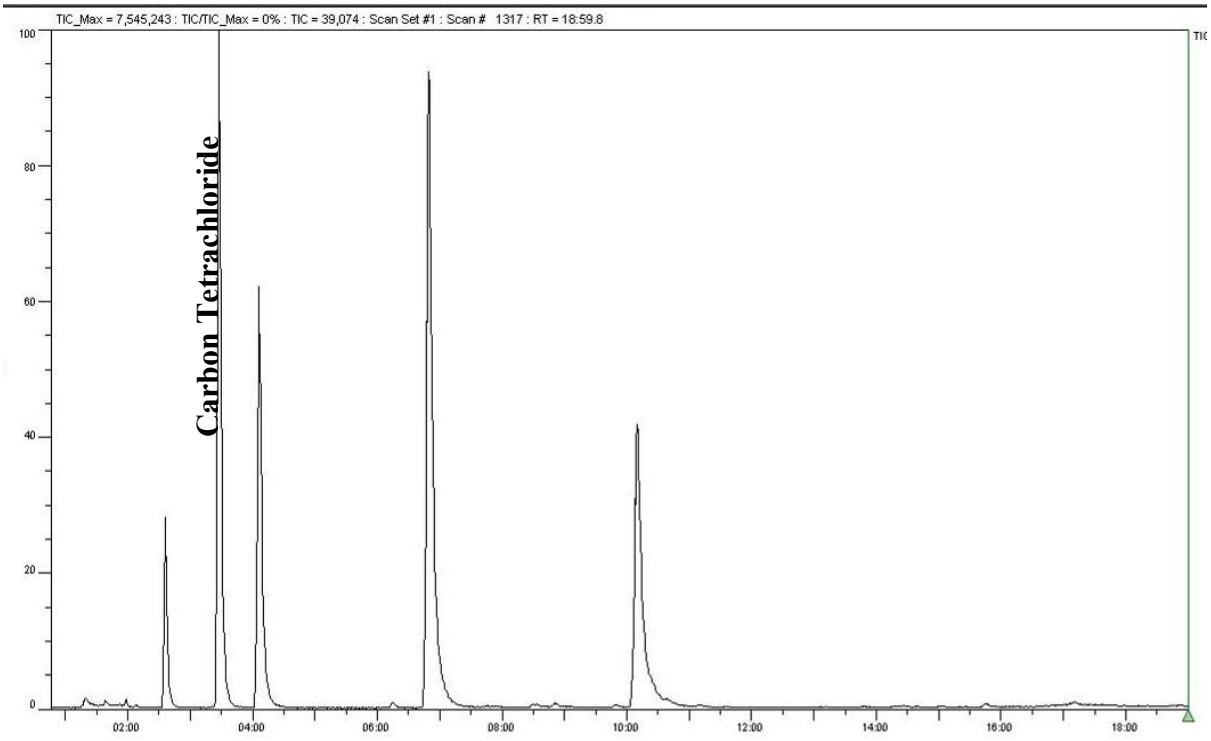

Figure 35. Detection of Carbon Tetrachloride 86 µg/L by the GC-MS

The concentrations detected by the GC-MS for the two runs were 9.9 and 1.8 ppb. The number was estimated based on the concentration of chloroform detected by the instrument, as represented in Table 16. The percent difference is the absolute value of the theoretical effluent concentration minus the MC-MS concentration that quantity divided by the theoretical concentration. Table 16 shows the data for the two runs of carbon tetrachloride. Neither of the estimated values was close to the calculated value. Accurate results were not predicted because the instrument was not calibrated for carbon tetrachloride. During an actual contamination event, the contaminant will be unknown and the GC-MS would not be properly calibrated for the detected contaminant.

Table 16. Concentration of Detected Carbon Tetrachloride

Theoretical Effluent Concentration (ppb)	GC-MS CCl_4 Concentration (ppb)	Scaled Concentration (ppb)	% Difference
86	9.879	35.060	40.77%
62	1.792	7.761	87.48%

4.3.3 Toluene

Toluene was injected into the pilot system with effluent concentrations of 9 and 48 µg/l. The baseline conditions for the distribution water before toluene was injected can be seen in Figure 36. The GC-MS detected both concentrations of toluene. Figure 37 shows the detection of 48 µg/l of toluene and the peak occurs between bromodichloromethane and dibromochloromethane.

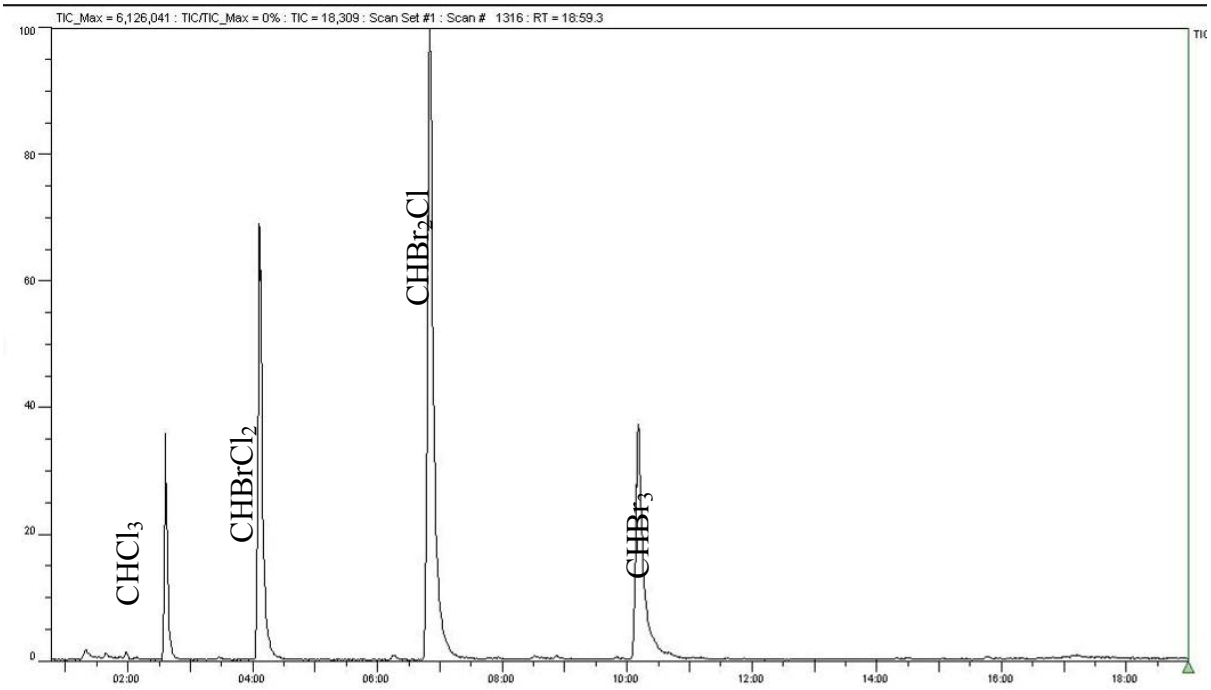

Figure 36. Baseline Values for the GC-MS before Toluene was Injected

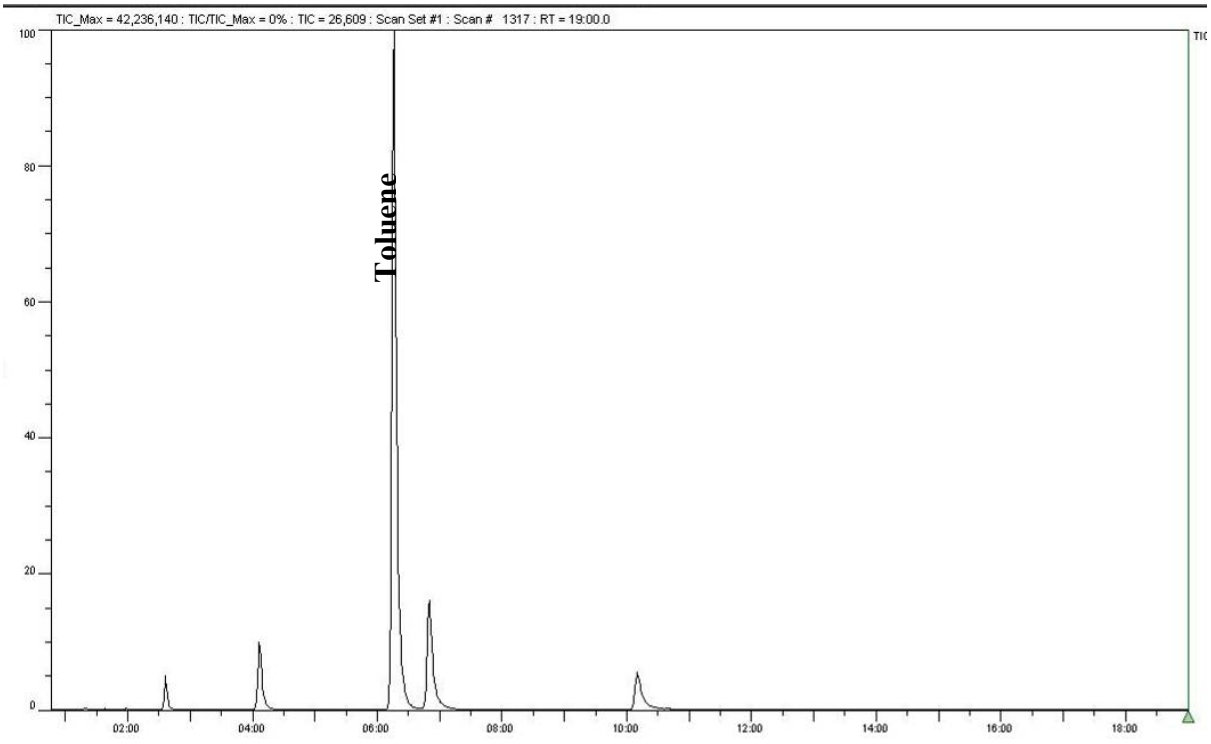

Figure 37. Detection of Toluene 48 µg/L by the GC-MS

Table 17 compares the theoretical effluent concentration to the scaled concentration detected by the GC-MS. The higher concentration of toluene was close to the estimated value but the lower concentration was not close. As mentioned before, the GC-MS was not calibrated for toluene because during an actual event the instrument would not be calibrated.

Table 17. Concentration of Detected Toluene

Theoretical Effluent Concentration (ppb)	GC-MS Toluene Concentration (ppb)	Scaled Concentration (ppb)	% Difference
48	17.45	66.294	38.11%
9	0.5076	1.942	78.42%

From Table 16 and Table 17 the comparisons of the theoretical concentrations to the scaled concentrations were not similar. Therefore, the GC-MS should be used more as a qualitative instrument instead of quantifying the concentration detected for the CWS because calibration is impossible for unknown contaminants during an event. Lab analysis with a calibrated GC-MS would be able to give a more accurate concentration of hydrocarbons. The GC-MS for the field is more for detection and classification of possible contaminants.

4.4 REAL-TIME TOXICITY BIOMONITORING

Chemical parameters in a continuous monitoring system utilize TOC, pH, chlorine, conductivity, temperature, and turbidity to detect changes in the water, but these parameters cannot report the toxic effects associated with the combination of chemicals. Biomonitoring systems detect changes in the in behavioral and physiological responses of aquatic organisms and provide rapid detection and continuous real time monitoring.

Biomonitors are sensitive to toxicity associated with an expansive array of organic and inorganic compounds. They provide near real-time evidence of the presence of toxins through their biological reactions to the water supply. The major disadvantage of biological systems are that they do not specify the contaminant, only that the water could be harmful and can respond to water conditions not harmful to humans. Also, a major issue with biomonitors are that chlorine is toxic to aquatic life. Therefore, finished water needs to be dechlorinated before flowing to the aquatic life.

To dechlorinate the water, Sodium thiosulfate was added to distribution water before flowing through the fish chambers. Daily variations of chorine create difficulties for proper dosing of the dechlorinator. Therefore, the fish reacted to changes in concentration of chlorine.

The following contaminants were injected into the water to evaluate the detection possibilities of the biomonitor:

- Hydrochloric Acid (HCl)
- Nitric Acid (HNO_3)
- Sodium Hydroxide (NaOH)
- Hydrofluosilic Acid (H_2SiF_6)
- Copper Sulfate ($CuSO_4$)
- *E. coli*
- *Cryptosporidium*
- Sodium Fluoroacetate($NaFC_2H_2O_2$)
- Bug-B-Gon
- Fire Suppression Foam
- Paint Thinner
- Toluene ($C_6H_5CH_3$)
- Carbon Tetrachloride(CCl_4)
- *Bacillus Atrophaeus*
- *Giardia lamblia*

The fish monitor did not produce a warning for the biological contaminants (*E. coli*, *Cryptosporidium*, *Bacillus*, and *Giardia*). A possible reason that the fish did not respond to the bacteria is that fish are accustom to living with biological contaminants in the wild. The summary of the fish response to the injected chemical toxins can be seen in Table 18.

For HFS, the fish did not react to the toxin. The LD_{50} for trout was greater than the concentration of contaminant in the water. In addition, the dechlorinator neutralized the pH, therefore a pH drop did not occur in the fish monitor. This was verified by a sample taken from the effluent of the fish monitor and the pH measured with a handheld pH meter.

HCl is slightly toxic to fish. The injected acid caused a pH decrease of 1.1 to 1.5 on the distribution water. The fish sensor did alarm 4 hours after the contaminant was injected into the pilot system. Other factors could have influenced the fish going into alarm; therefore a non-detect was designated for the acid. For the other two runs, the behaviors of the fish were unaltered.

The nitric acid experiments initiated a 1.5 to 2.5 decrease in pH. Two runs of a 1.5 pH decrease were performed and neither had an effect on the fish. The third caused at least six of the eight fish to go into warning, thus triggering the alarm. The fish possibly reacted to the change in pH rather than the increase in nitric acid. This was the only run that had a pH drop this large.

The fish did not detect the presence of sodium hydroxide in the distribution water. The concentration in the water exceeded the LD_{50} for fish but the fish did not go into alarm. Sodium hydroxide is only moderately toxic to aquatic life and maybe the duration was not long enough to have major effects on the fish behavior.

Copper sulfate is extremely toxic to fish and for the three concentrations the fish went into alarm. A concentration of 8.1 mg/l triggered an alarm less than an hour after the toxin was injected into the pilot system. For the concentrations of 15.5 and 11 mg/l of copper sulfate, the

alarm for the biomonitor was triggered one hour after injecting a contaminant. The three concentrations exceeded the LC_{50} of 0.1 mg/L.

Fire foam, sodium fluoroacetate, and paint thinner were not detected by the fish monitor. In addition, the fish did not go into alarm for either toluene or carbon tetrachloride. The concentration of the toxins in the water was below the LD_{50} for the substances.

The Bug-B-Gon at concentrations of 11.5 and 57.5 µg/l were not detected by the fish monitor. For the two high concentrations, the biosensor did not alarm during the experiment. Data for the time after water was injected through the monitor was not available. The fish should have gone into alarm because the concentration of bifenthrin, which is highly toxic to aquatic life, exceeded the LD_{50} for fish.

Table 18. Chemical, Lethal Concentration, Concentration Feed and Fish Response

Chemical	Toxic to Fish	LD_{50} (fish)	Concentration Feed	Fish Detection
HFS	Moderately	96 hr LC_{50} (Salmo gairdneri) = 51 mg/L [CSBP, 2005]	7 mg/L F- for 48 min	
			7 mg/L F- for 30 min	
			9.77 mg/L F- for 46 min	
			6.6 mg/L F- for 30 min	
HCl	Slightly	96 hr LC_{50} (Bluegill) pH 3.0 to 3.5 [Fisher Scientific, 2000]	1.5 pH decrease	
			1.5 pH decrease	
HNO_3	Slightly	5 hr LCL 750 mg/L [Terra, 2006]	2.1 pH decrease	**X**
			1.5 pH decrease	
			1.5 pH decrease	
NaOH	Moderately	43 mg/L for 96 hr [TCI, 2008]	250 mg/L for 30 min	
			440 mg/L for 30 min	
$CuSO_4$	Highly	96 hr LC_{50} (Goldfish) 0.1 mg/L [J.T. Baker, 2008]	8.1 mg/L for 32 min	**X**
			15.5 mg/L for 33 min	**X**
			11 mg/L for 36 min	**X**
Sodium Fluoroacetate	Low	n/a	0.5 mg/L for 30 min	
			5 mg/L for 30 min	
Bug-G-Gone (Bifenthrin)	Highly	0.0038 - 17.8 µg/L [Scotts, 2001]	11.5 µg/L	
			57.5 µg/L	
			115 µg/L	
			230 µg/L	
Fire Foam	Moderately	96 hr LC_{50} (Rainbow Trout) 28 mg/L [Kidde Fire Fighting, 2007]	10 µg/L for 30 min	
			30 µg/L for 30 min	
Paint Thinner		n/a	20 mg/L for 22 min	
			50 mg/L for 42 min	
Toluene	Moderately	96 hr LC_{50} 10 to 100 mg/L [J.T. Baker, 2007]	49 µg/L for 30 min	
			9 µg/L for 30 min	
Carbon Tetrachloride	Moderately	96 hr LC_{50} (Fathead Minnow) 43.1 mg/L [Matheson Tri-Gas, 2004]	86 µg/L for 30 min	
			62 µg/L for 30 min	

Notes:
X = 6 out of the 8 fish went into warning
n/a = information is not available

5.0 SUMMARY AND CONCLUSIONS

The pilot Contamination Warning System was used to help detect accidental or intentional contamination in the drinking water distribution. The pilot was set up within the actual distribution system which was connected to main transmission lines that feed downtown Pittsburgh. To help detect changes in the water various technologies were used. The instruments included chemical and biological monitors:

- Hach Distribution Panel;
- Sievers 900 Online TOC Analyzer;
- Online GC-MS;
- JMAR Biosentry Pathogen Identification System;
- Biosensor Fish Monitor; and
- Real UVT 254 Online Monitor.

To test the instruments, contaminants relating to accidental and intentional contamination were injected into the pilot. The toxins include:

Hydrochloric Acid (HCl)	Sodium Fluoroacetate($NaFC_2H_2O_2$)
Nitric Acid (HNO_3)	Bug-B-Gone
Sodium Hydroxide (NaOH)	Fire Suppression Foam
Hydrofluosilic Acid (H_2SiF_6)	Paint Thinner
Copper Sulfate ($CuSO_4$)	Toluene ($C_6H_5CH_3$)
Plastic Spheres	Carbon Tetrachloride(CCl_4)
E. coli	Bacillus Atrophaeus
Cryptosporidium	Giardia lamblia

Data were collected for each run, and then analyzed. The summary of each instrument's response to the different contaminants injected can be seen in Table 19. Each instrument responded to at least one toxin.

Table 19. Contaminant and Response

Contaminant	Concentration	Hach Panel	Real Tech UVT	Sievers TOC	JMAR Biosentry	INFICON HAPSITE GC-MS	Biosensor Fish Monitor
Hydrofluosilicic Acid	6.6 to 9.8 mg/l F-	**X**					
Hydrochloric Acid	1.1 and 1.5 pH drop	**X**					
Nitric Acid	1.5 and 2.1 pH drop	**X**					
Sodium Hydroxide	1 and 1.2 pH increase	**X**					
Copper Sulfate	8.1 to 15.5 mg/l	**X**	**X**				**X**
Fire Suppression Foam	0.001% and 0.003%	**X**		**X**			
Sodium Fluoroacetate	0.5 and 5 mg/l	**X**		**n/a**			
Bug-B-Gon	100 to 200 mg/l			**X**			
Paint Thinner	100 mg/l					**X**	
Toluene	9 and 48 µg/l			**n/a**		**X**	
Carbon Tetrachloride	62 and 86 µg/l			**n/a**		**X**	
E. coli	$2.74x10^6$ and $4.66x10^6$ cfu/ml				**X**		
Cryptosporidium	200 crypto/ml	**X**			**X**		
Bacillus Atrophaeus	660 count/ml				**X**		
Giardia lamblia	100 cfu/ml	**X**			**X**		
Spheres (0.8µ and 2µ)	200 to 2500 spheres/ml				**X**		

Note:
X = Detection by Instrument
n/a = Data Not Available

5.1 HACH GUARDIAN BLUE

The instruments detected change in water quality and triggered an alarm for all the chemicals with the exception of Bug-B-Gon, paint thinner, toluene, and carbon tetrachloride. The concentrations of toluene and carbon tetrachloride were in the ppb range, which did not cause changes in the water quality parameters (i.e. chlorine concentration, pH, TOC, turbidity, and conductivity). For the biological contaminants, cryptosporidium and Giardia triggered an alarm because of an increase of TOC. The inactivation agent, formalin, used for the pathogens, explains the increase in TOC.

Hach Guardian Blue System attempted to identify contaminants for five of the seven detected chemicals. Only Fluorosilicic was identified correctly. In addition, HFS was also identified as sarin and mercuric chloride by the agent library. The same identification transpired for each contaminant that had a pH change. HFS, when introduced into the distribution water, produced an increase in pH and conductivity, which was predicted. The agent library correctly identified the substance as fluorosilicic acid but also identified sarin and mercuric chloride. According to WCIT, water tainted with sarin is likely to increase the TOC but is unlikely to affect pH and conductivity. This is an unusual match for HFS because only pH and conductivity were matches. TOC for the injection run was unaffected. Mercuric chloride was also identified as a possible match. When introduced into a water supply, mercuric chloride will commonly increase the conductivity but not alter the pH. This is a more reasonable match to HFS than mercuric chloride because at least one of the parameters was predicted to change coincides with the actual run.

Hydrochloric and nitric acids had the same response as HFS when injected in the pilot system. Therefore, the agent identification was the same. The pH and conductivity increases were predicted changes for the two contaminants.

The results for the Agent identification system are erroneous. Some of the results could be possible but others are not even close. Sarin had none of the same indicators as HFS but was a possible match. The system might be better off without the agent detection. To identify contaminants based only on the five water quality parameters would be difficult because combination of chemicals would alter the identification results.

Beneficial detection methods for the Hach Guardian Blue System were conductivity and turbidity. A disruption within a system will produce an increase in turbidity. Increase in turbidity not related to a known water main breaks or routine repairs could possibly be an indicator of a contamination event. In addition, conductivity changed for all the contaminants injected. The change was small but a peak in a system with relatively stable baseline conditions could be an indication of a contamination event. These two instruments had little to no maintenance problems during the research.

The chlorine analyzer was difficult to detect changes. Figure 38 shows the monthly variation from the free chlorine monitor. Water quality was constantly changing as a result of source water quality, variations in the treatment process, variation in hydraulic conditions in the distribution system, accidental back siphonage and water main breaks. In Pittsburgh, some of the chlorine variation is related to the booster stations. The method is not precise thus having daily variations. The instrument itself, worked properly and had little maintenance problems but created many false alarms.

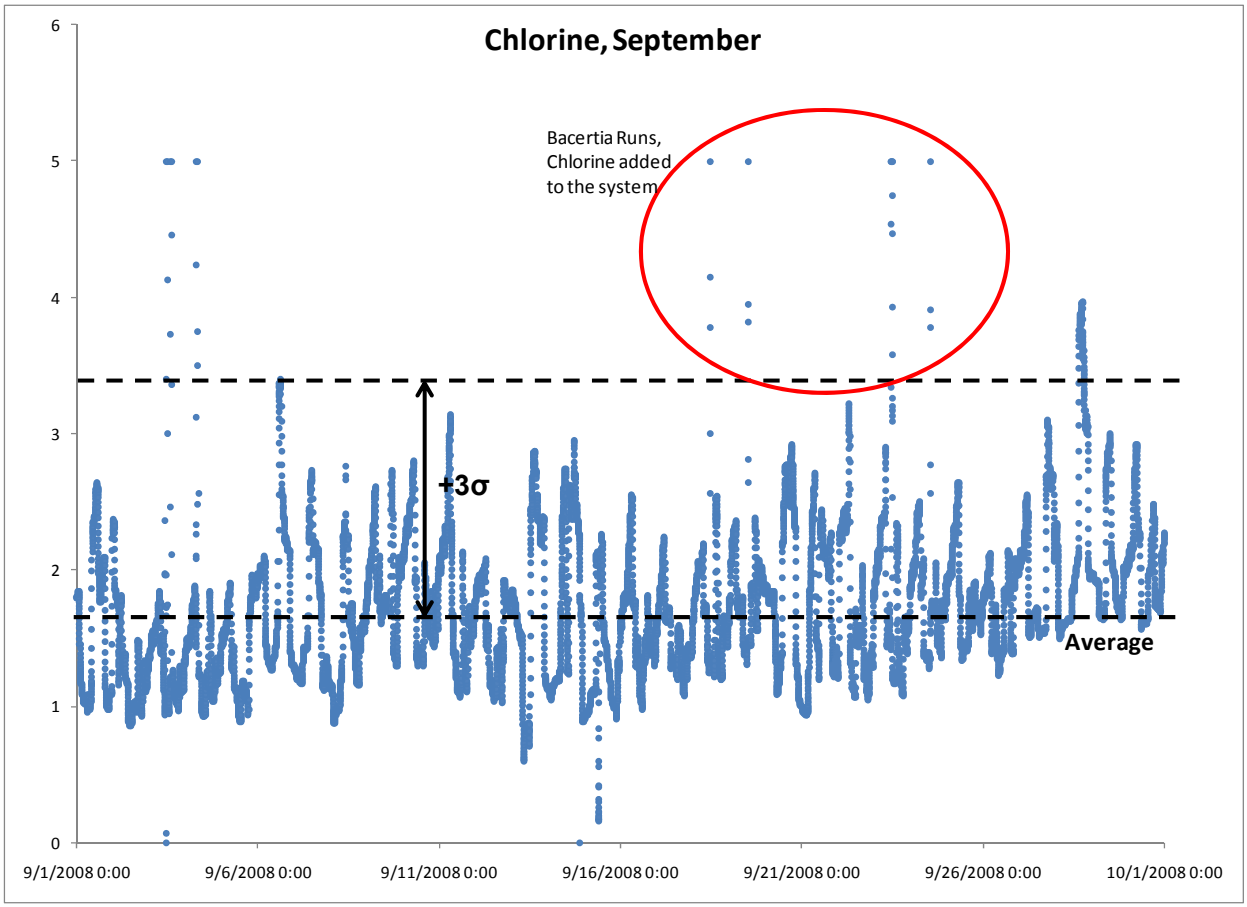

Figure 38. Chlorine variations for a Duration of One Month

The TOC analyzer produced the majority of the problem for the Hach Distribution panel. The instrument malfunctioned often and required a great deal of maintenance. It was difficult to maintain a constant flow through the TOC analyzer, which produced inaccurate readings. The purge gas generator is loud and bulky and initially we had problems with the connection of the air generator to the analyzer. Overall, the footprint of the system is large, had many maintenance problems and compared to the Sievers TOC the results were less accurate.

One advantage is that the Event monitor contains all the data for each instrument and is very easy to use. Data can be easily retrieved via a UBS port. The exported data were easily downloaded into a spreadsheet. In addition, this instrument detects the widest range of

contaminants. For the instrument to be better, I would remove the Agent Identification system and install a better TOC analyzer.

5.2 SIEVERS TOC

. Unlike, the Hach TOC analyzer, the Sievers TOC analyzer worked very well for all the studies performed. Bug-B-Gon, paint thinner, and fire foam were predicted to increase the TOC. A TOC increase was detected for fire foam and Bug-B-Gon but not the paint thinner. A possible explanation was that the concentration was not large enough for the contaminant to be detected. Near the end of the research, routine maintenance caused erroneous readings. Therefore, data are not available for sodium fluoroacetate, toluene and carbon tetrachloride. Little maintenance was required and the monitor gave accurate readings. The system operated soundly for one year with just only minor problems near the end of the study. The ideal situation would be that the Sievers TOC replaces the Hach TOC in the HACH Guardian Blue. The system is much smaller than the Hach and produced more accurate results.

5.3 REAL TECH UVT

The detection limit for the instrument is within the ppm range therefore, concentrations in the ppb range were not detected. Modifications can be made by the company to increase the sensitivity of the instrument and detect in the ppb range. The Real UVT was easy to maintain. A calibration does need to be performed regularly or the baseline value will drift. Calibrating the instrument is easy and only requires pure water to be pushed through the monitor. For the

research, the UVT only detected copper sulfate. The aromatic hydrocarbon toluene was injected at too low of a concentration to be detected by the UVT. The instrument is limited in the detection capabilities and should be used in conjunction with other monitoring devices.

5.4 JMAR BIOSENTRY

The biosentry detected all the biological contaminants injected except for the 200 spheres/ml of the 0.8µm spheres, 200 spores/ml *Bacillus atrophaeus*, and the two lower concentrations of *E. coli*. For the detected pathogens, the percent recovery was mediocre. The total count detected by the JMAR was not close to the concentration injected and for the concentration injected, one would only have to consume one to two ml to receive the infectious dose. The greatest percent of detected pathogens was Giardia. Only 0.5% of the total concentration injected was detected. Detection at the 200 count/ml did not occur for the spore and rod channel. Therefore, not being an effective tool for spore and rod microbial that have a low effective dose.

One of the main problems is turbidity in the water. An unstable baseline, which made interpreting data difficult, was due to natural changes of turbidity in the distribution water. The system would be more accurate if the water was considerably less turbid. Figure 39 shows the daily variation for the Bacillus injection. The baseline slightly increases throughout the day until 700 minutes (midnight) where the system goes through self-cleaning. The actual contamination event is difficult to distinguish from naturally occurring variance. For the system to be more useful, detection at a lower concentration is necessary to prevent the consuming population from becoming ill.

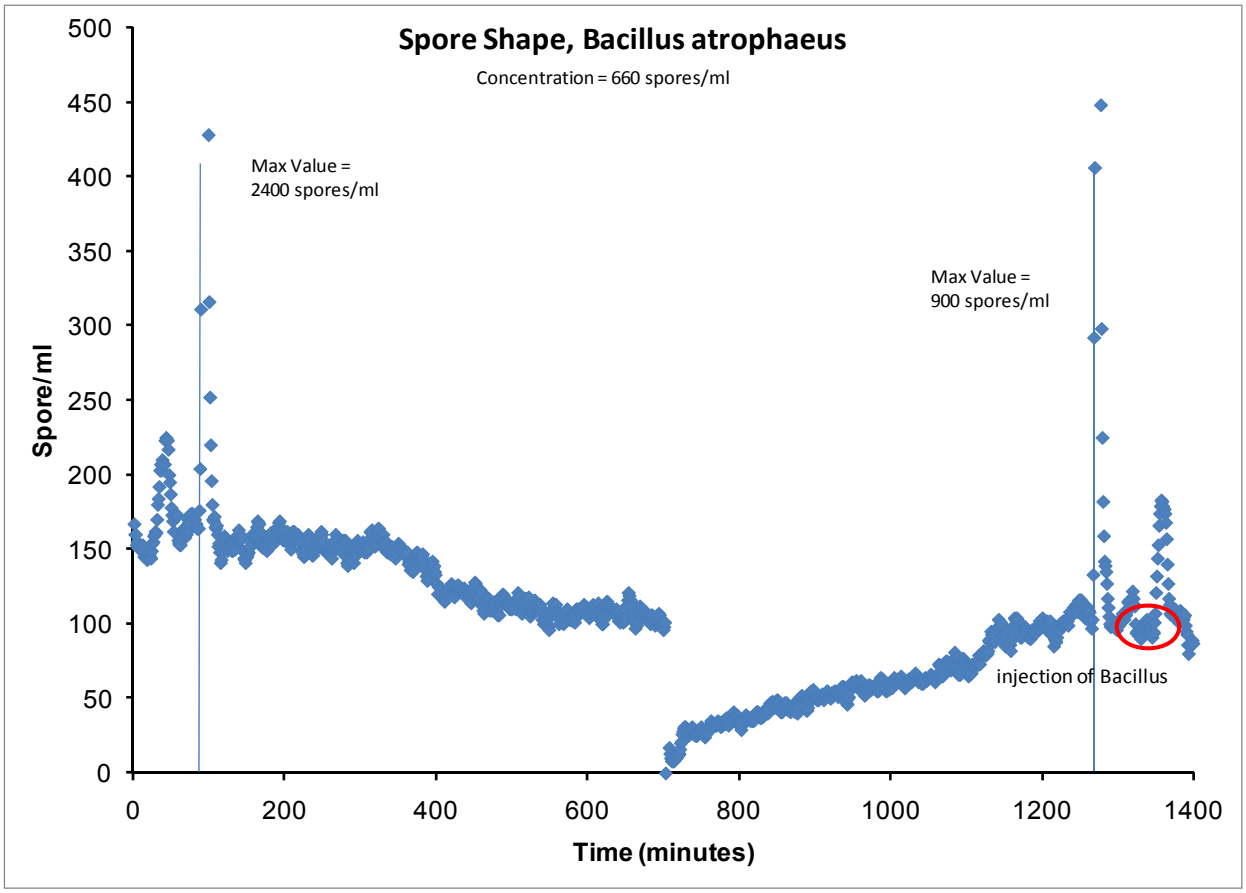

Figure 39. Daily variation of spore count for the Bacillus run

5.5 INFICON HAPSITE GC-MS

No problems were experienced during the study for the CG-MS. Toluene, paint thinner, and carbon tetrachloride were injected into the water for analysis. The instrument detected them all and worked seamlessly. But, the online GC-MS should be used more qualitatively than analyzing the concentration because the instrument will not be calibrated during an event. The contaminant during an event will most likely be unknown and proper calibration impossible. Therefore, the instrument should be used more for detection and classification instead of concentration. A disadvantage is that the instrument is expensive. Therefore, having multiple

GC-MS throughout the distribution system would be difficult in terms of cost. Out of the six instrument used for this study, this was the best instrument. It detected all the predicted chemicals and had little maintenance problems. An issue is the limited number of contaminants that can be detected and should be used with other monitoring instruments.

5.6 BIOSENSOR FISH MONITOR

The fish only detected the presence of copper sulfate in the water. The instrument was very difficult to maintain. The fish had to be checked, replaced in the monitor, or the baseline had to be recalibrated on a daily basis. For monitoring purposes, a positive alarm was hard to distinguish. Alarms for some of the contaminants would occur hours after the contaminant was injected and there could be multiple reasons for the alarm therefore a non-detect would be issued for the toxin.

Fluctuations of chlorine residual in the distribution system made it difficult to dechlorinate the water before flowing through the fish chamber. Chlorine is highly toxic to fish and excessive chlorine can affect the monitoring data. The pump for the dechlorinator malfunctioned often and it was hard to tell if sodium thiosulfate was actually being pumped into the monitor. In addition, the flow through instrument was never consistent and fluctuation transpired daily. In general, the instrument may better serve intake water than distribution water. This was the most difficult of the instruments to maintain and the results were difficult to interpret. I would not include this system within a CWS.

At least one of the monitors used detected each contaminant injected. In general, the pilot CWS worked well but required a great deal of maintenance. Natural variations in water quality would cause false alarms by the monitors. To decrease the false alarms, an appropriate range of

safe concentrations needs to be determined before the start of a CWS. In addition, multiple systems would be needed throughout the distribution system because a contamination event could occur downstream or another part of the system. If that were to happen, the system would not detect or alert changes in the water, therefore making it ineffective. The CWS showed realistic results of performance in an actual distribution system. The research provided valuable data for the development of an accurate monitoring system to protect against contamination events.

APPENDIX A

CHEMICAL CONTAMINANTS

A.1 FLUOROSILICIC ACID

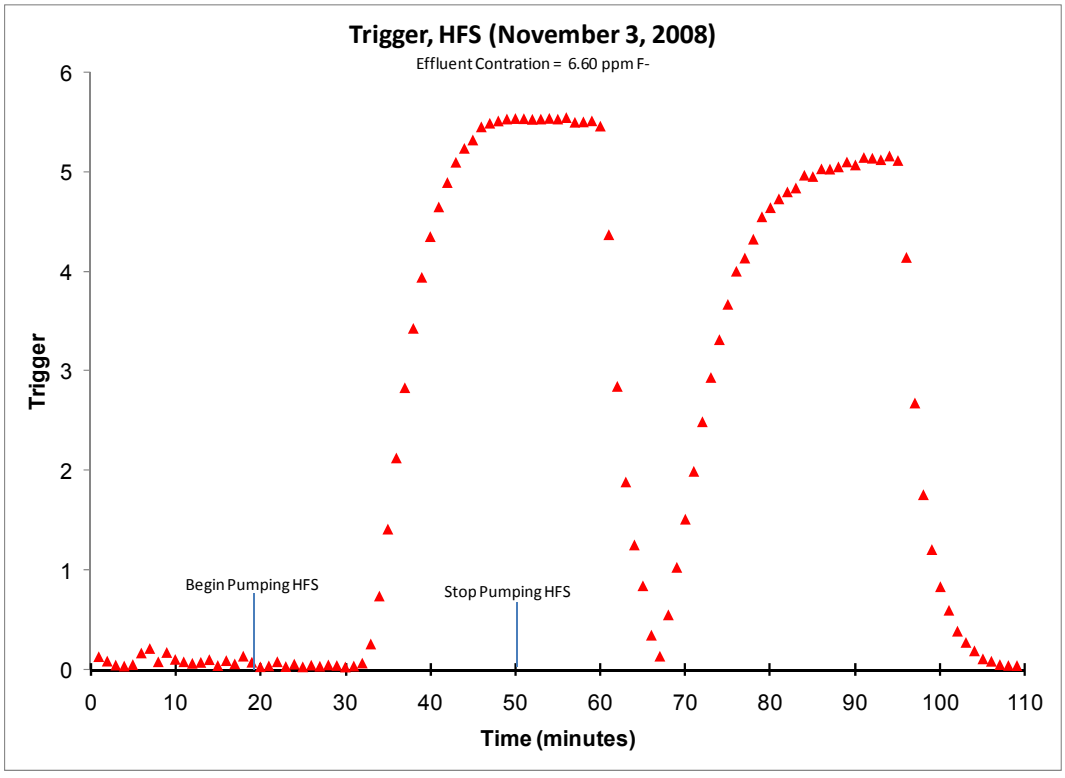

Figure 40. HFS Trigger Graph for 6.60 ppm F-

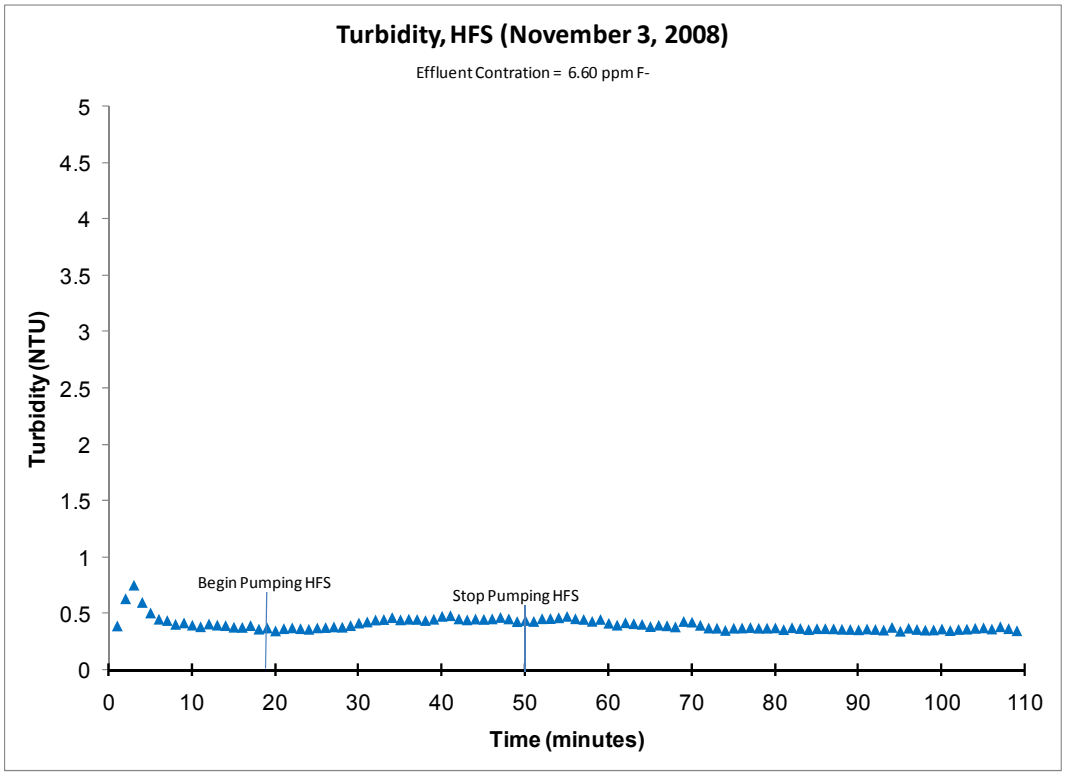

Figure 41. HFS Turbidity Graph for 6.60 ppm F-

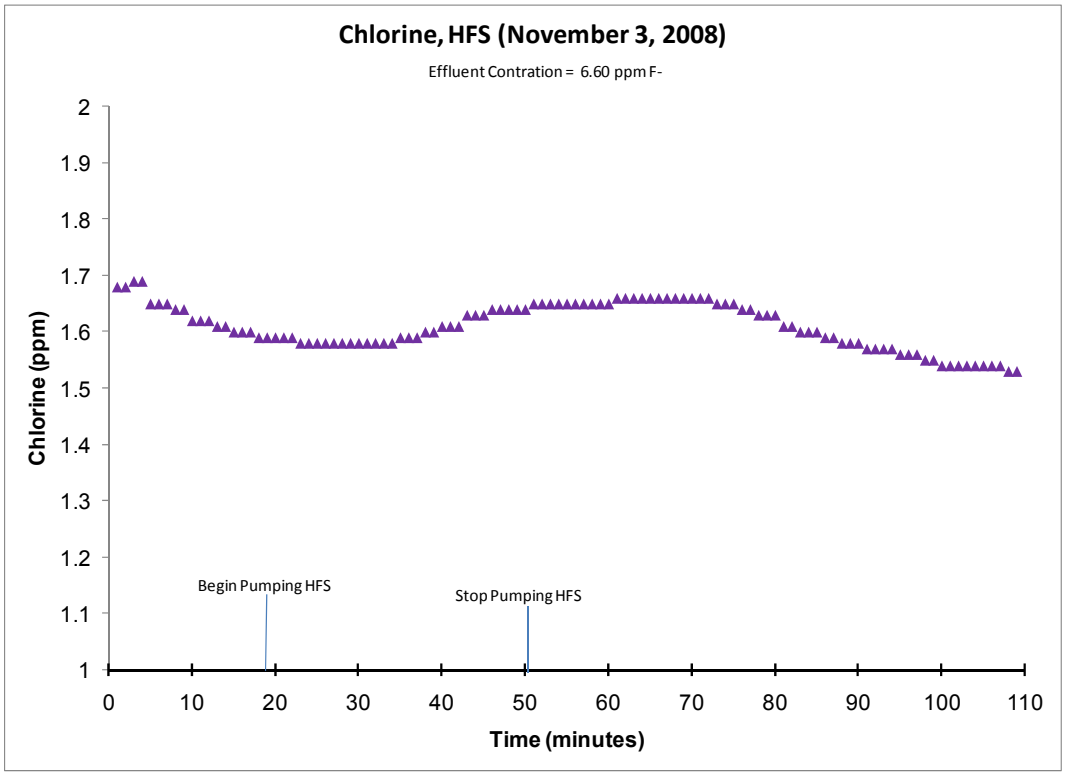

Figure 42. HFS Chlorine Graph for 6.60 ppm F-

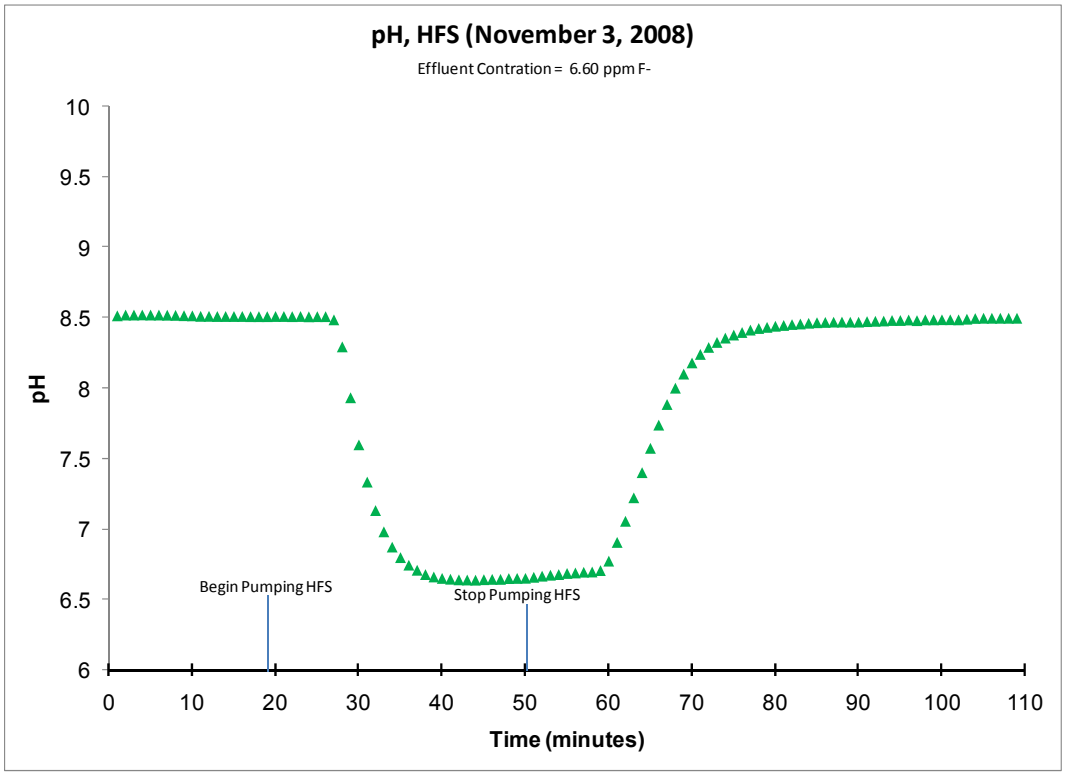

Figure 43. HFS pH Graph for 6.60 ppm F-

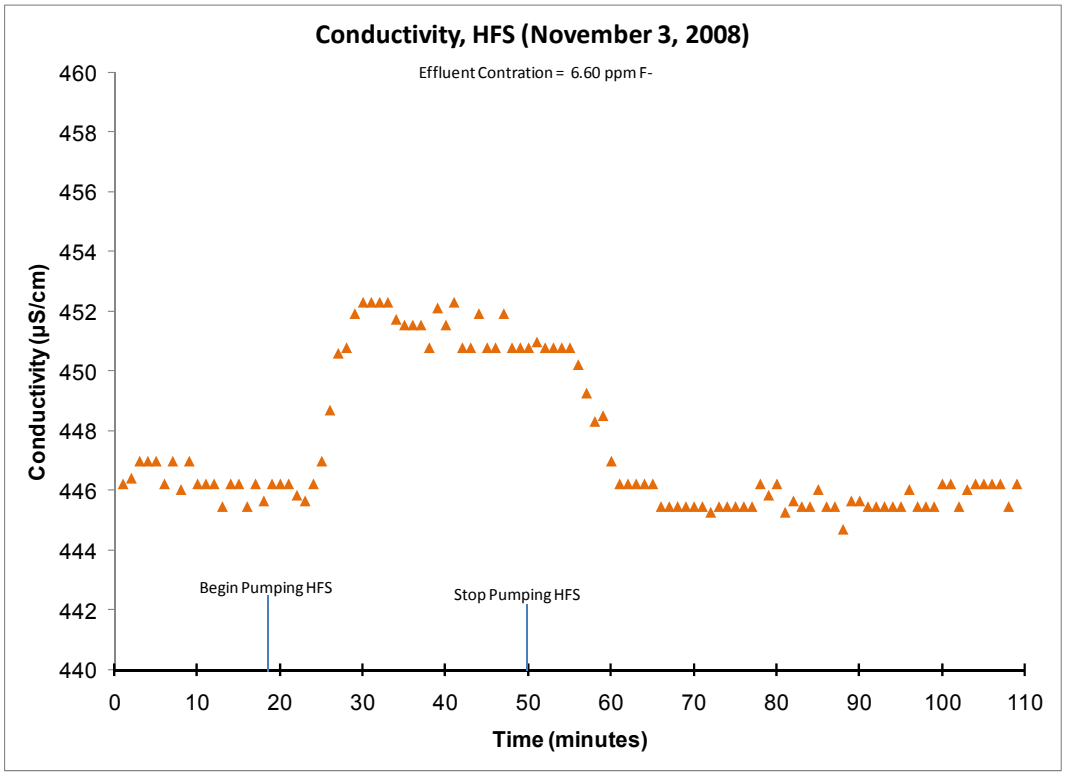

Figure 44. HFS Conductivity Graph for 6.6 ppm F-

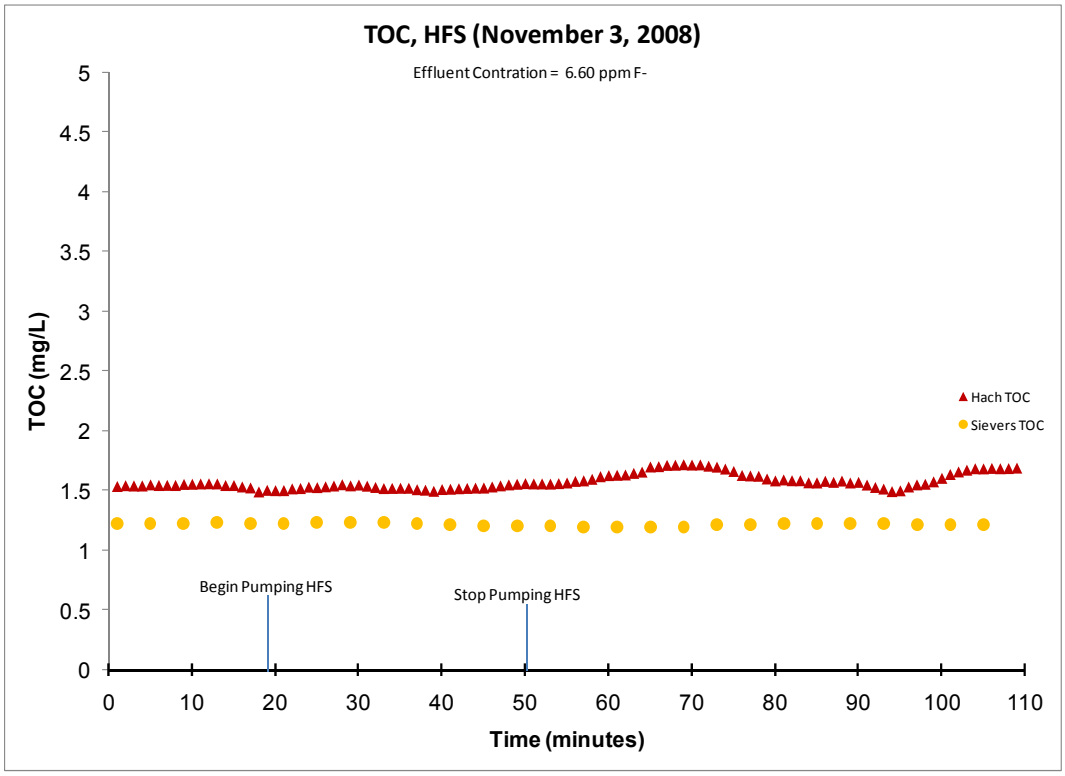

Figure 45. HFS Conductivity Graph for 6.6o ppm F-

A.2 HYDROCHLORIC ACID

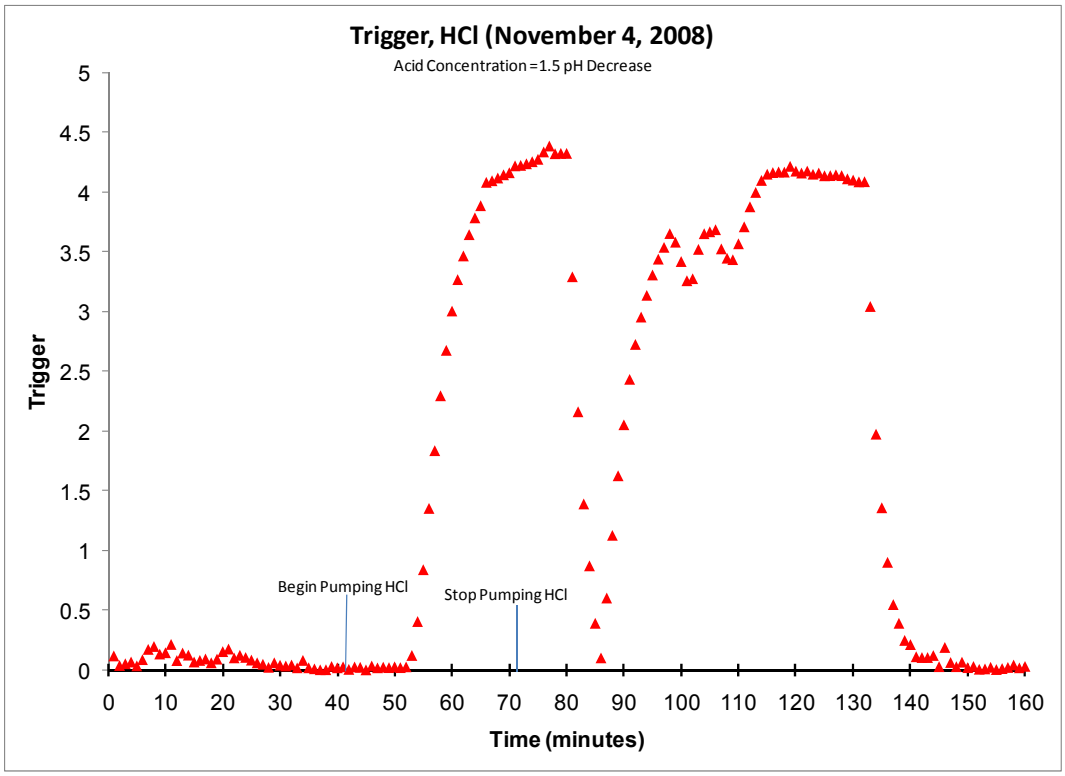

Figure 46. HCl Trigger Graph for 1.5 pH Decrease

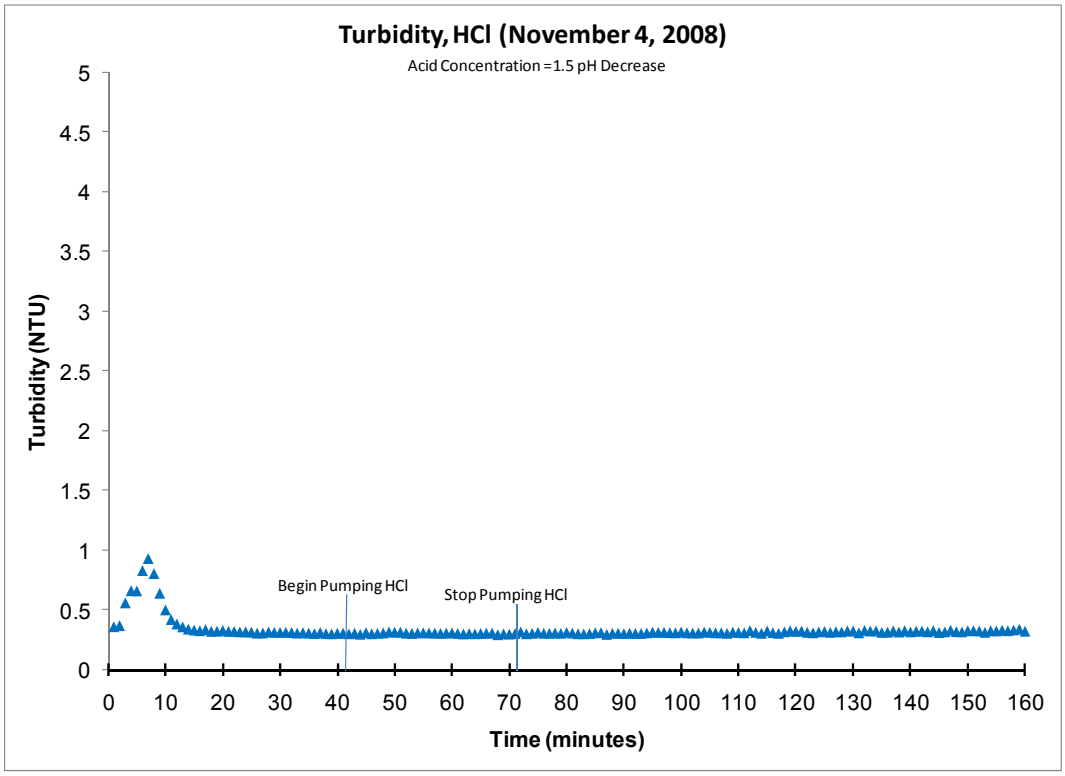

Figure 47. HCl Turbidity Graph for 1.5 pH Decrease

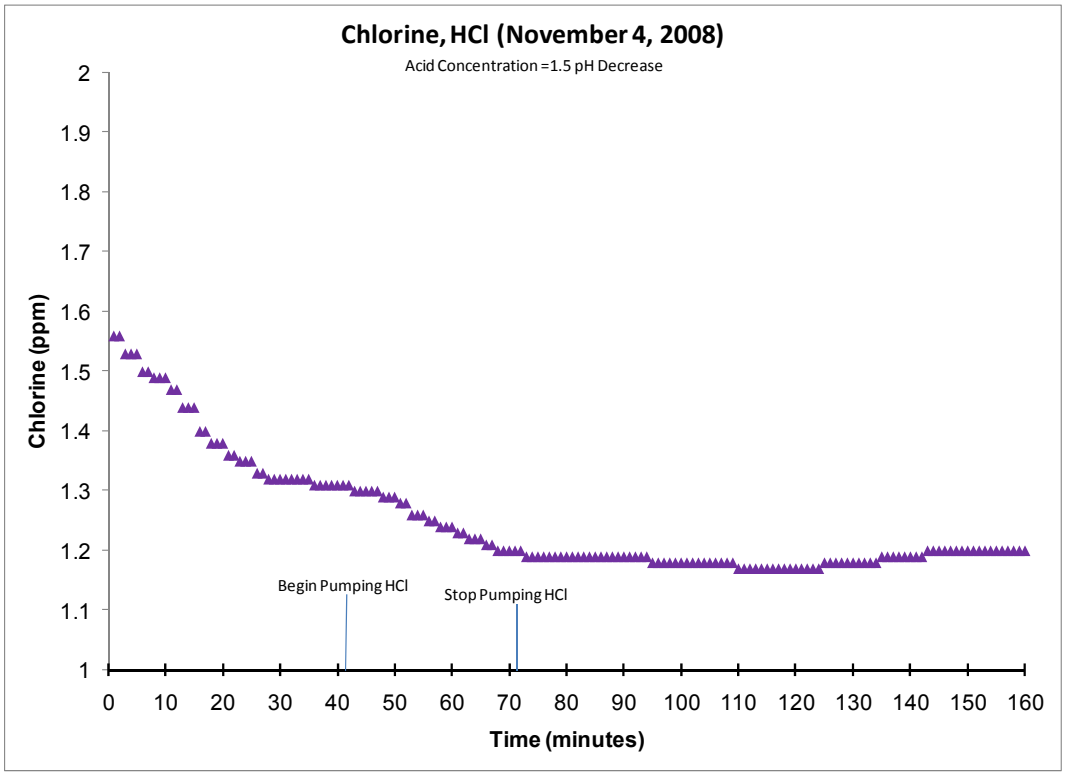

Figure 48. HCl Chlorine Graph for 1.5 pH Decrease

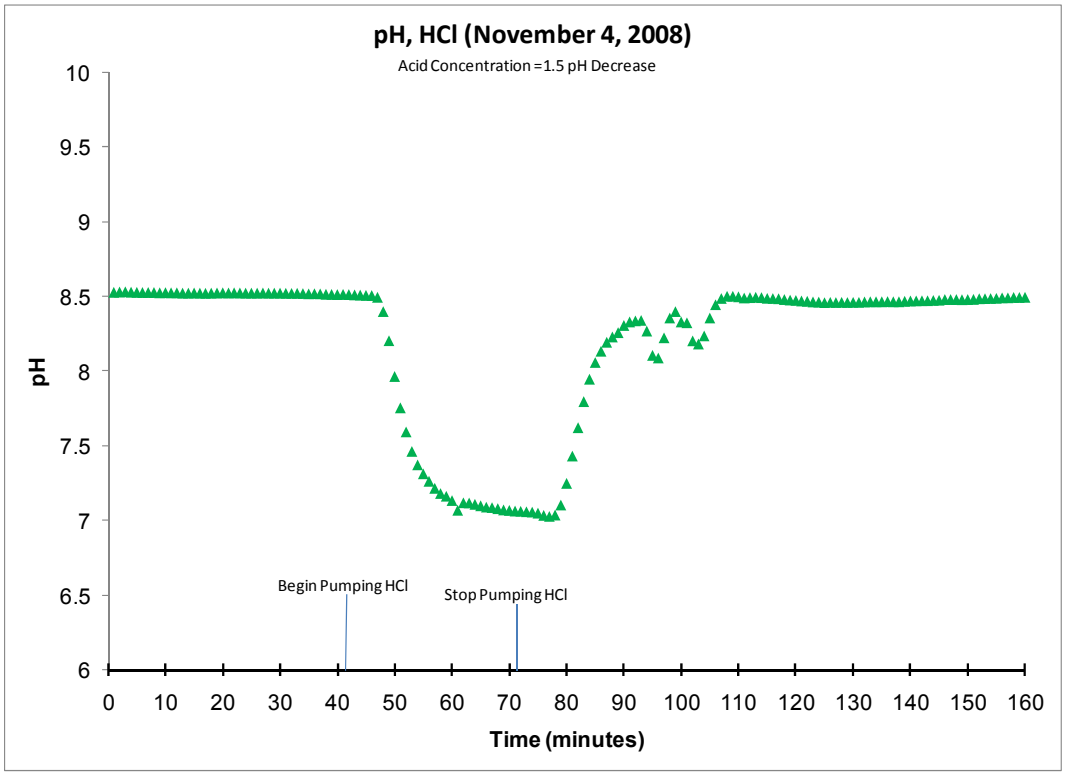

Figure 49. HCl pH Graph for 1.5 pH Decrease

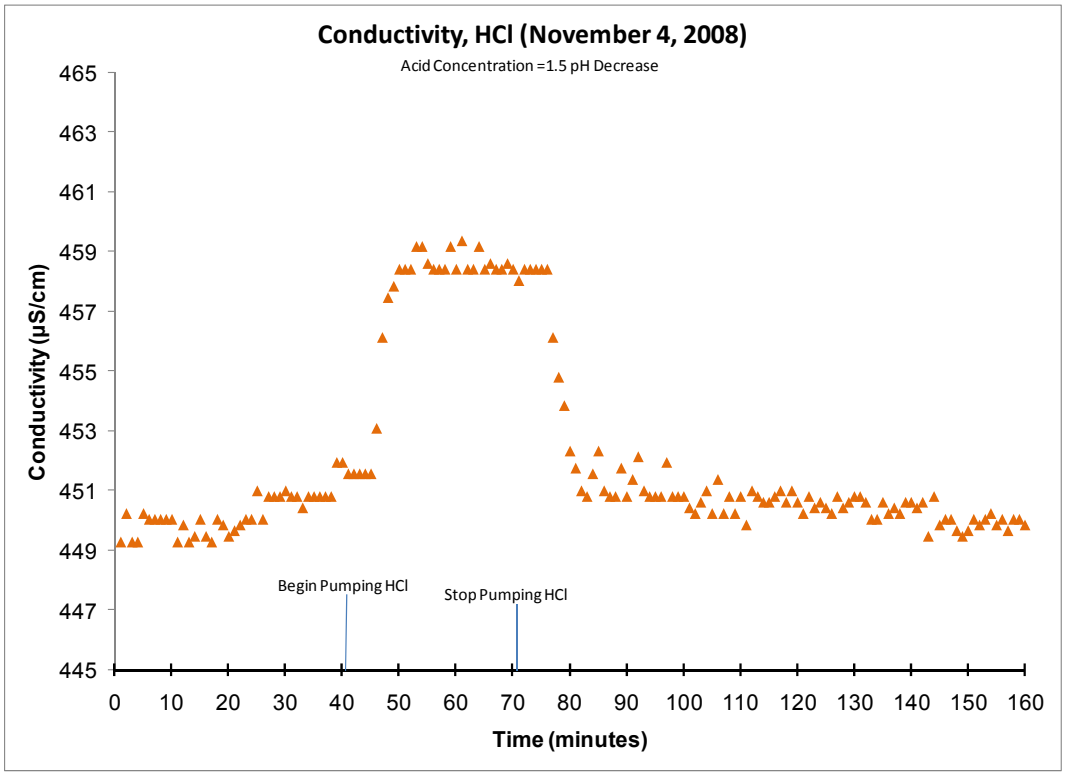

Figure 50. HCl Conductivity Graph for 1.5 pH Decrease

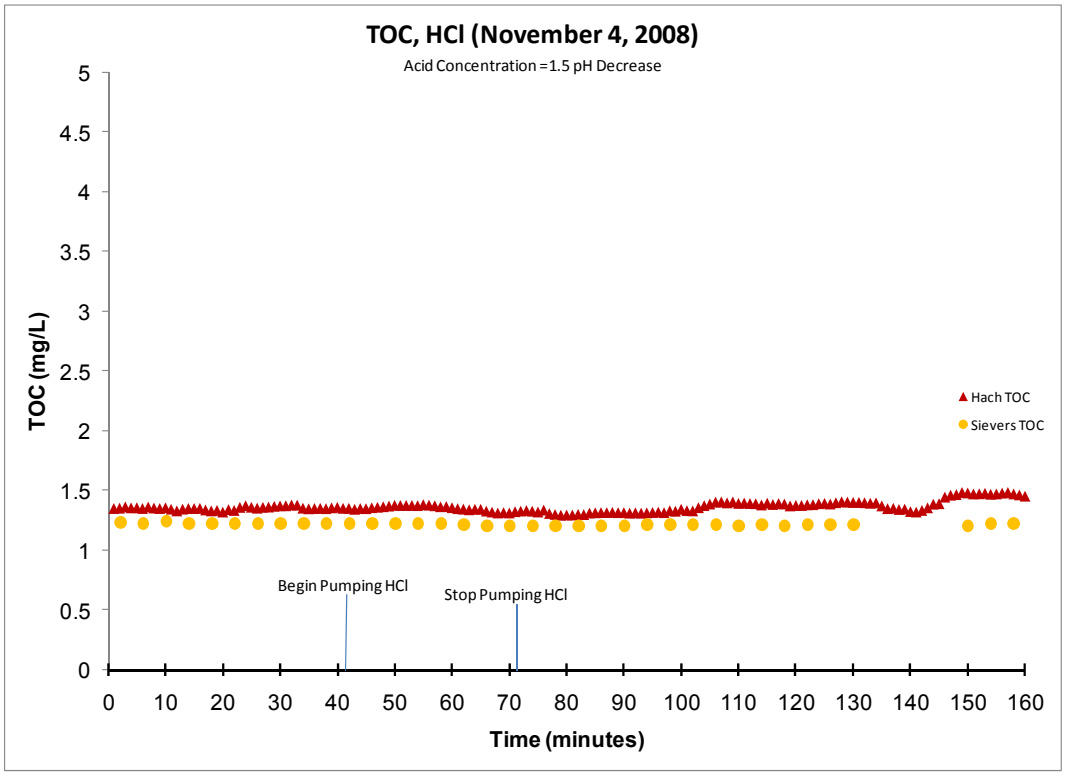

Figure 51. HCl TOC Graph for 1.5 pH Decrease

A.3 NITRIC ACID

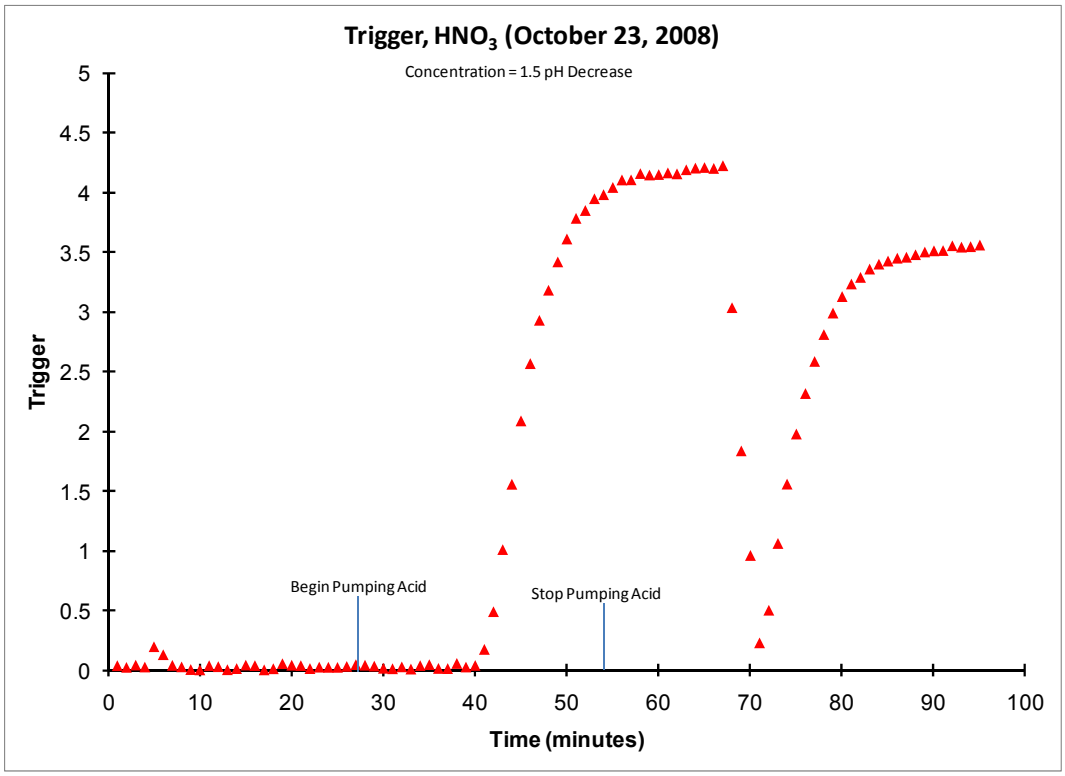

Figure 52. HNO_3 Trigger Graph for 1.5 pH Decrease

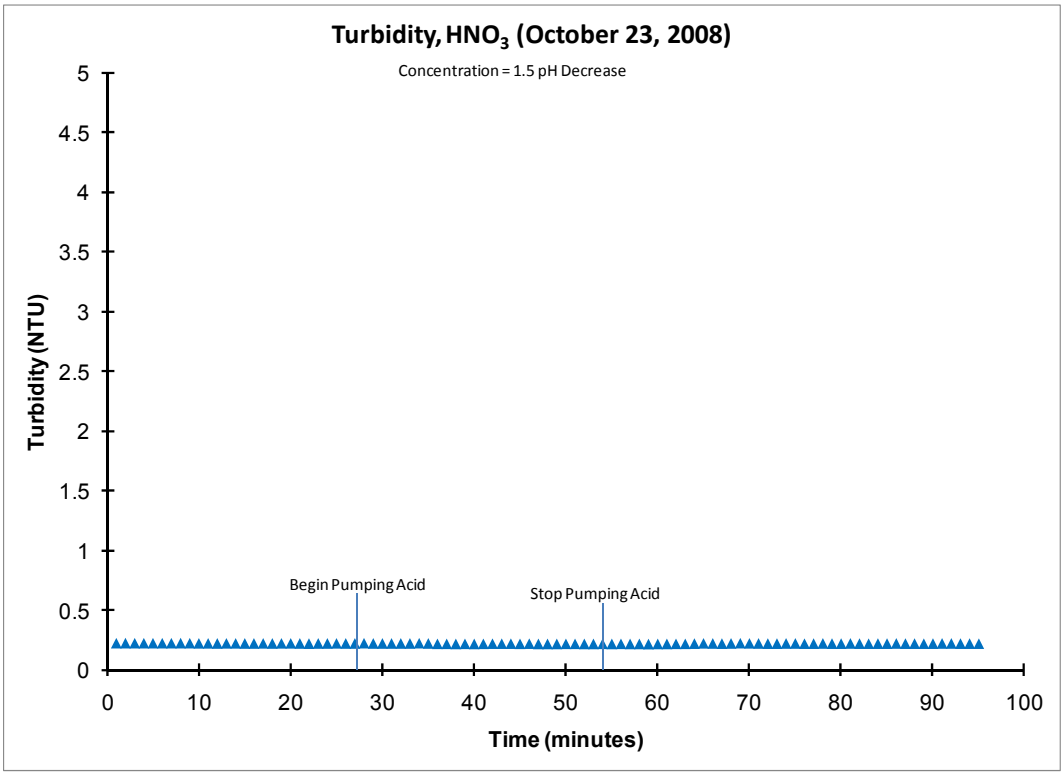

Figure 53. HNO_3 Turbidity Graph for 1.5 pH Decrease

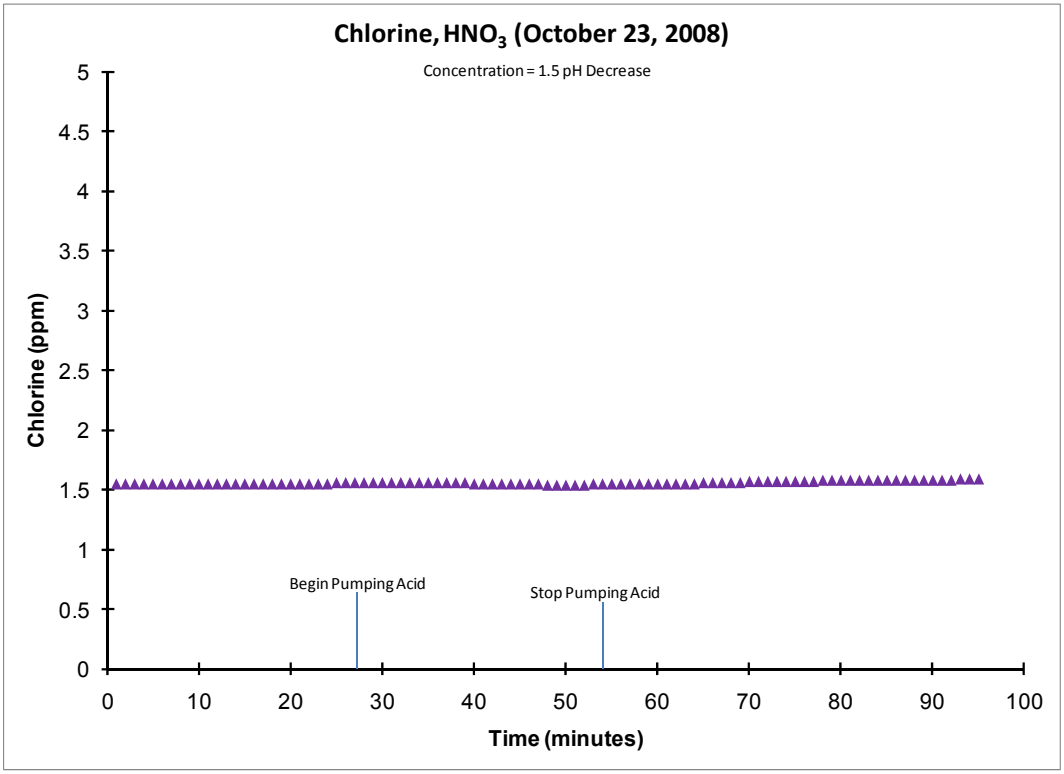

Figure 54. HNO_3 Chlorine Graph for 1.5 pH Decrease

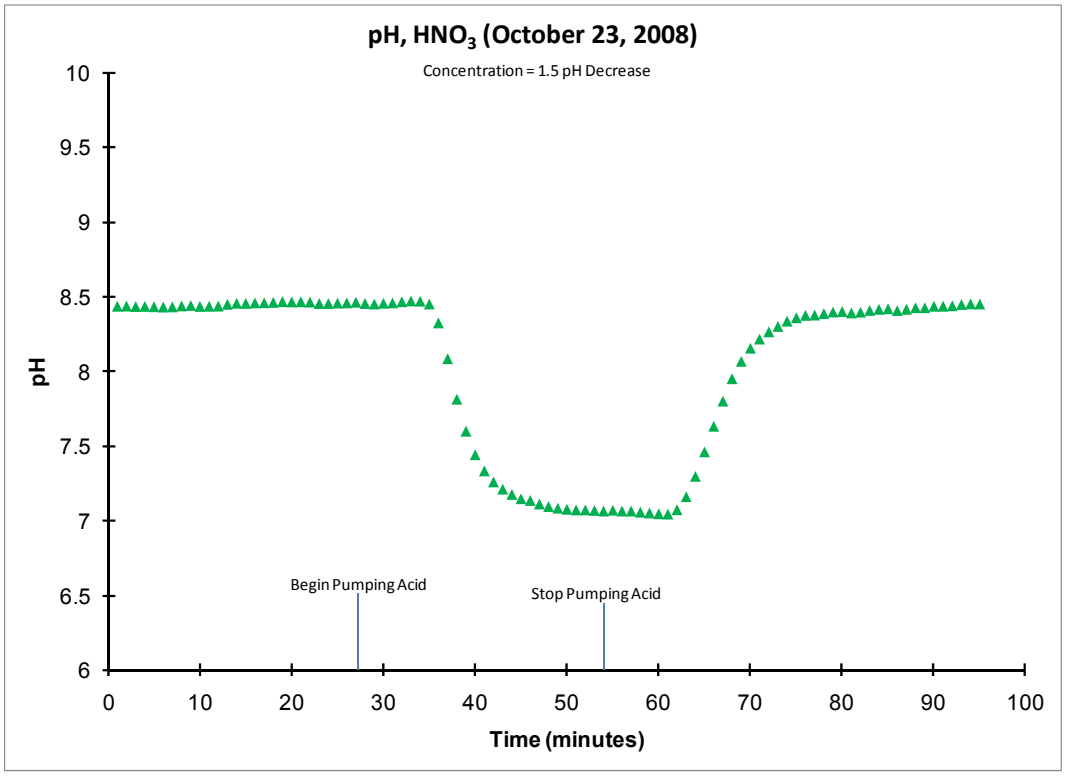

Figure 55. HNO_3 pH Graph for 1.5 pH Decrease

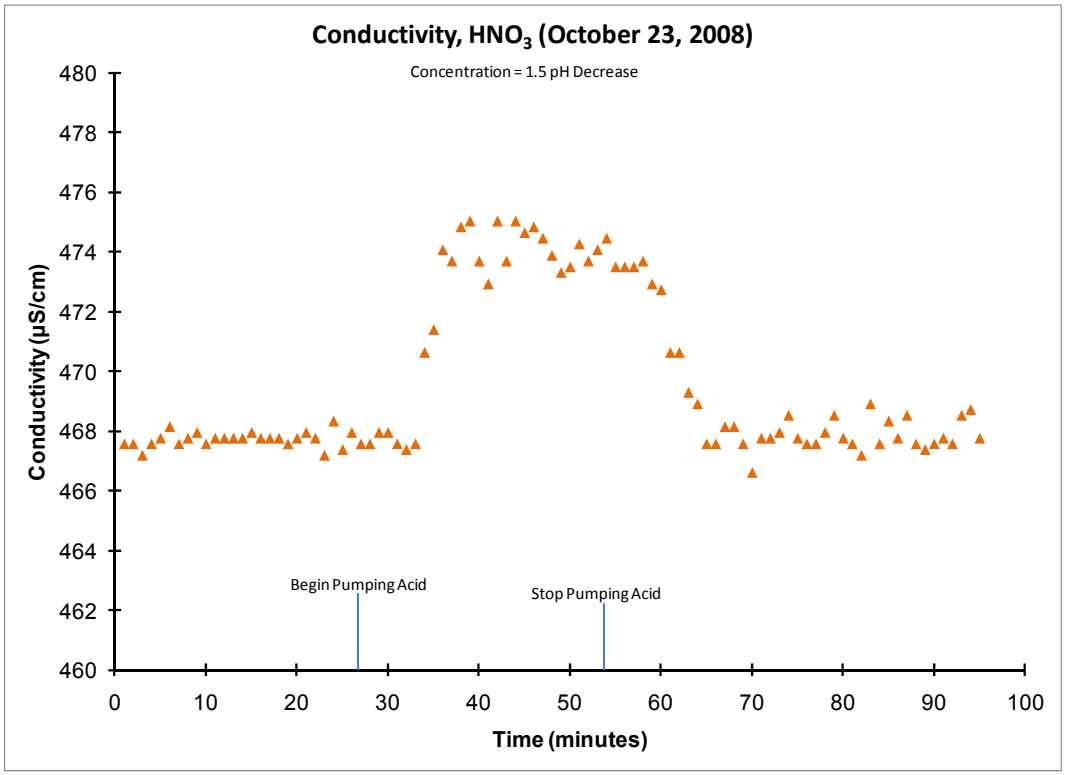

Figure 56. HNO_3 Conductivity Graph for 1.5 pH Decrease

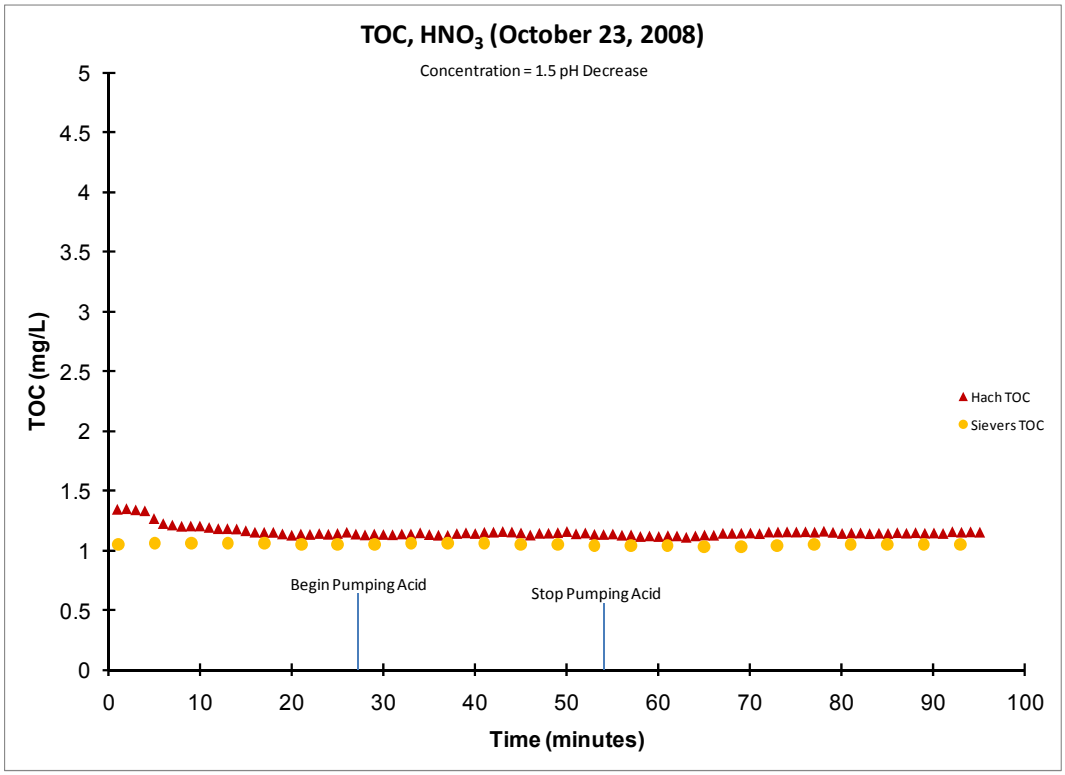

Figure 57. HNO_3 TOC Graph for 1.5 pH Decrease

A.4 SODIUM HYDROXIDE

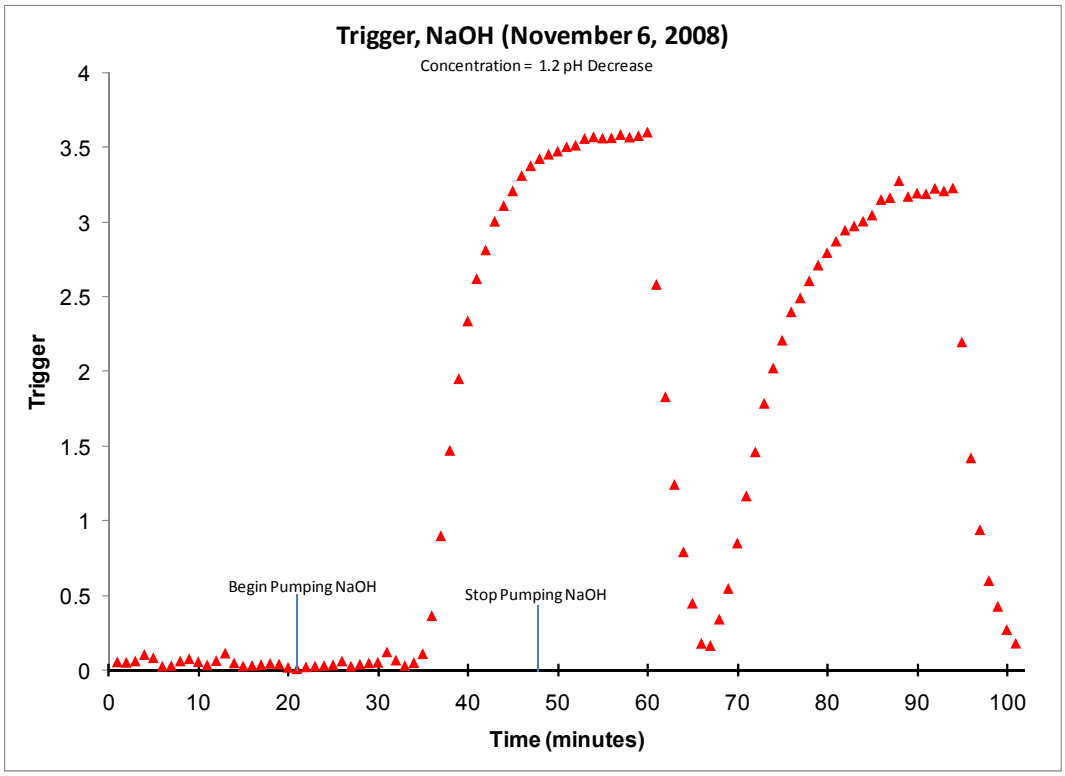

Figure 58. NaOH Trigger Graph for 1.2 pH Decrease

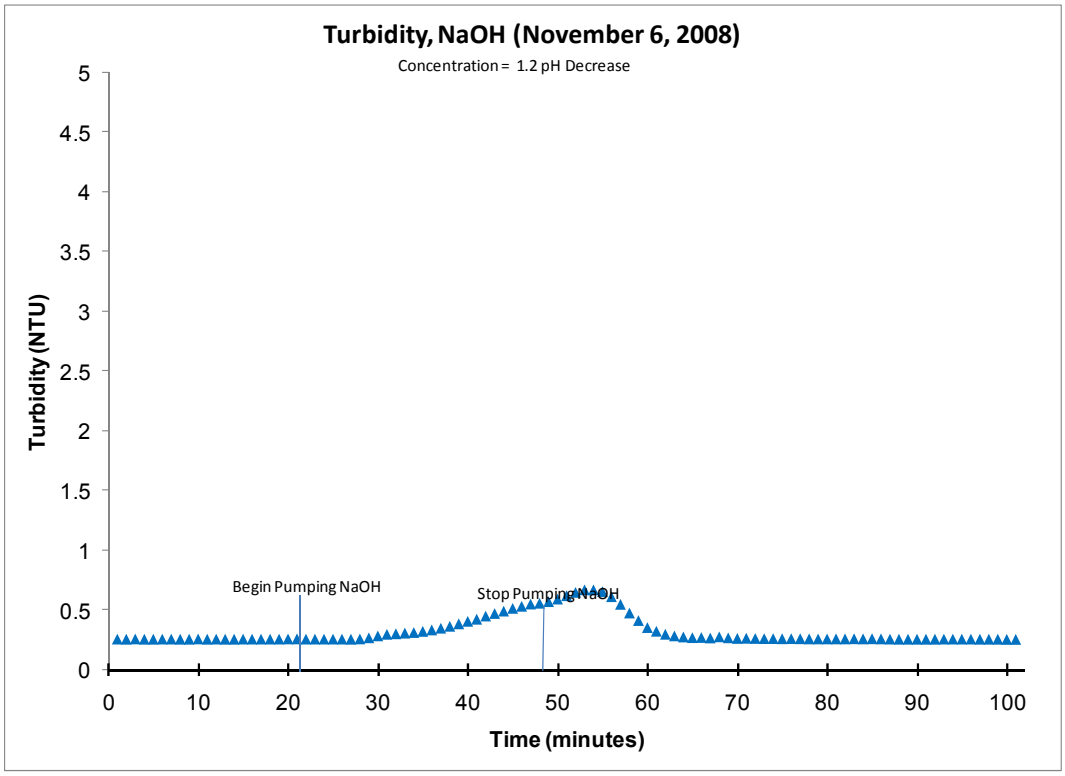

Figure 59. NaOH Turbidity Graph for 1.2 pH Decrease

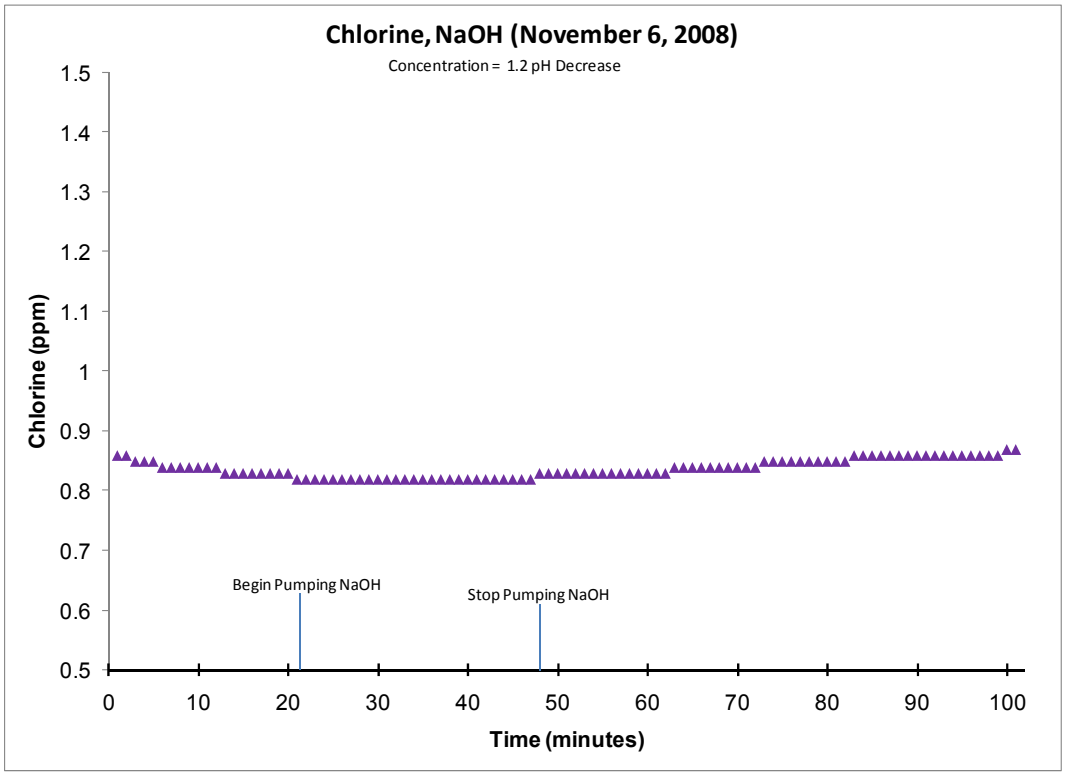

Figure 60. NaOH Chlorine Graph for 1.2 pH Decrease

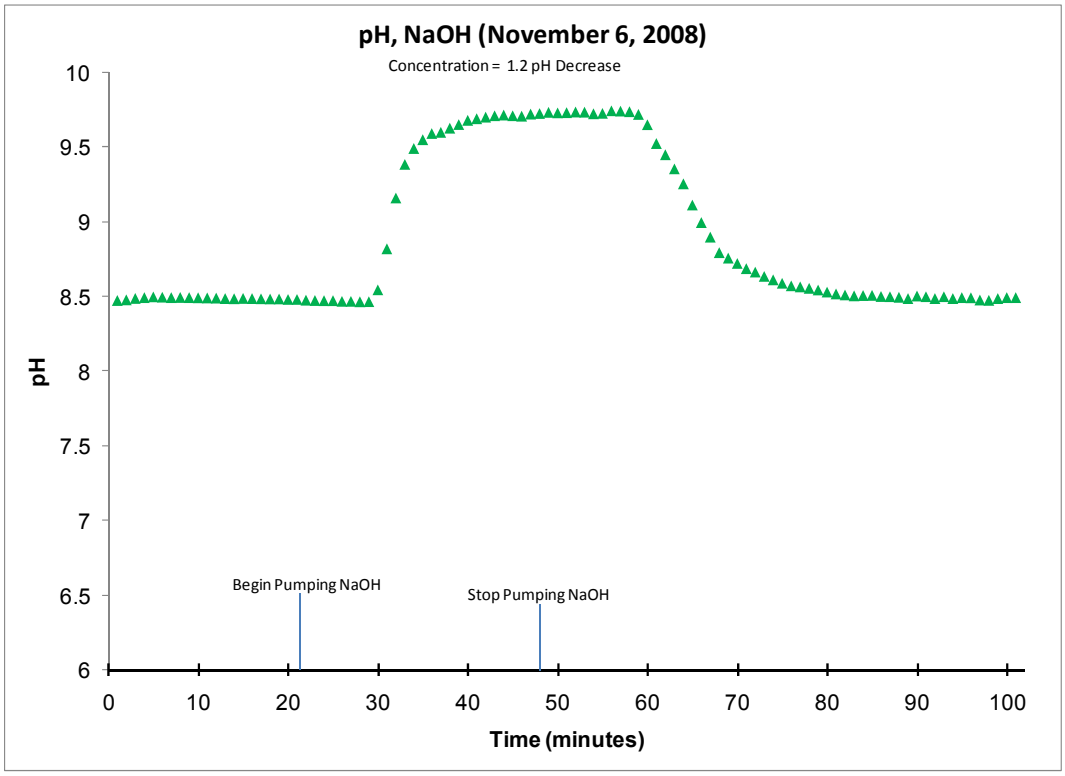

Figure 61. NaOH pH Graph for 1.2 pH Decrease

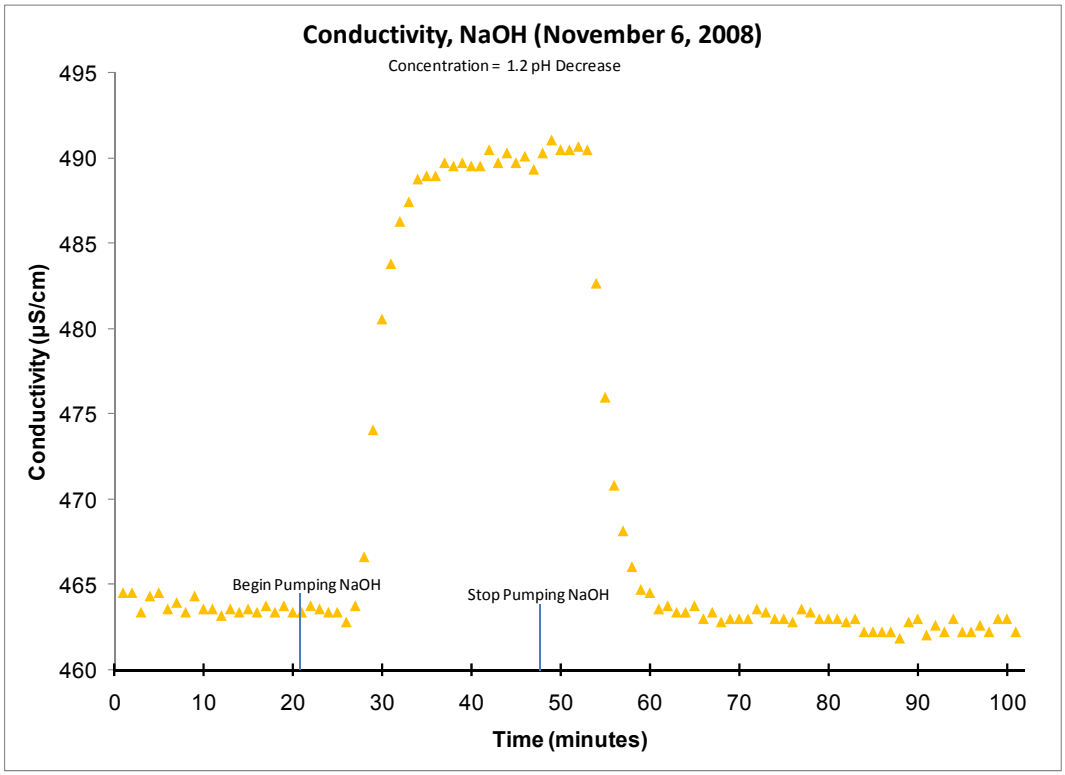

Figure 62. NaOH Conductivity Graph for 1.2 pH Decrease

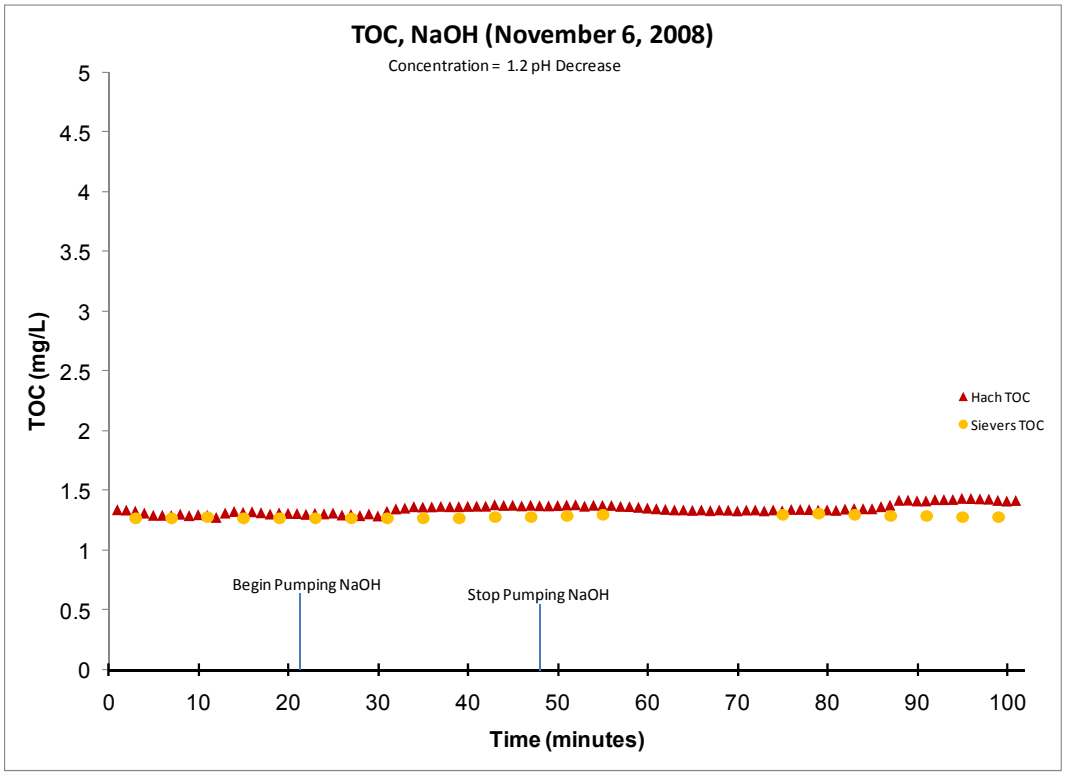

Figure 63. NaOH TOC Graph for 1.2 pH Decrease

A.5 COPPER SULFATE

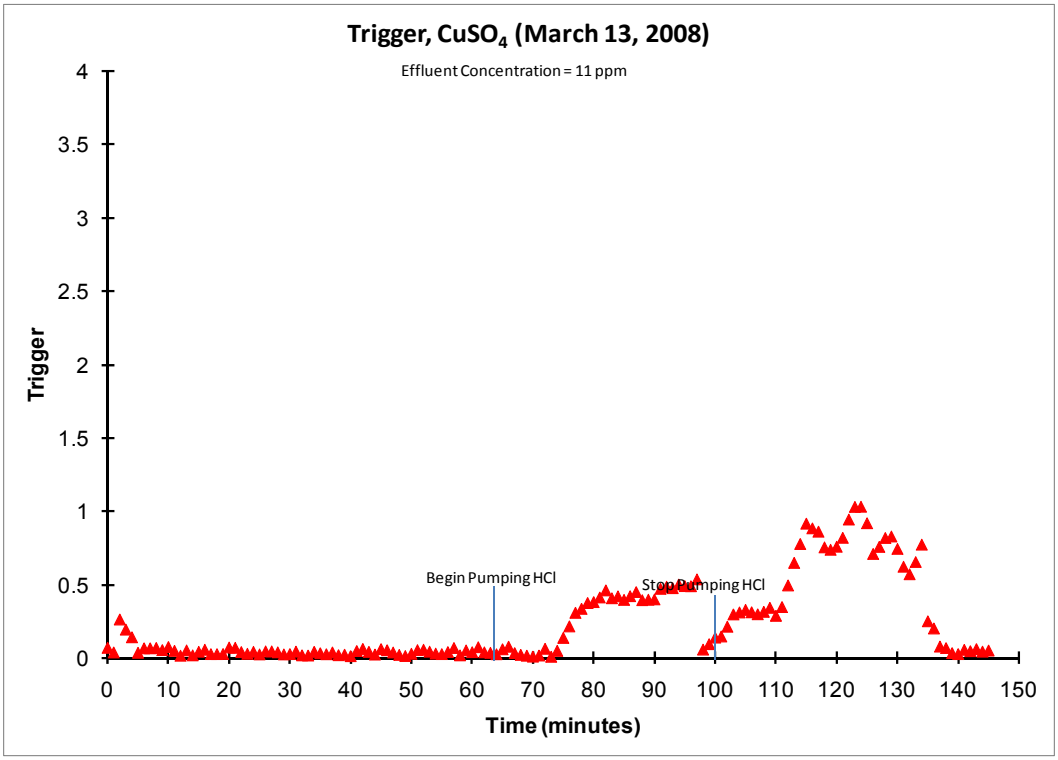

Figure 64. $CuSO_4$ Trigger Graph for 11 ppm Concentration

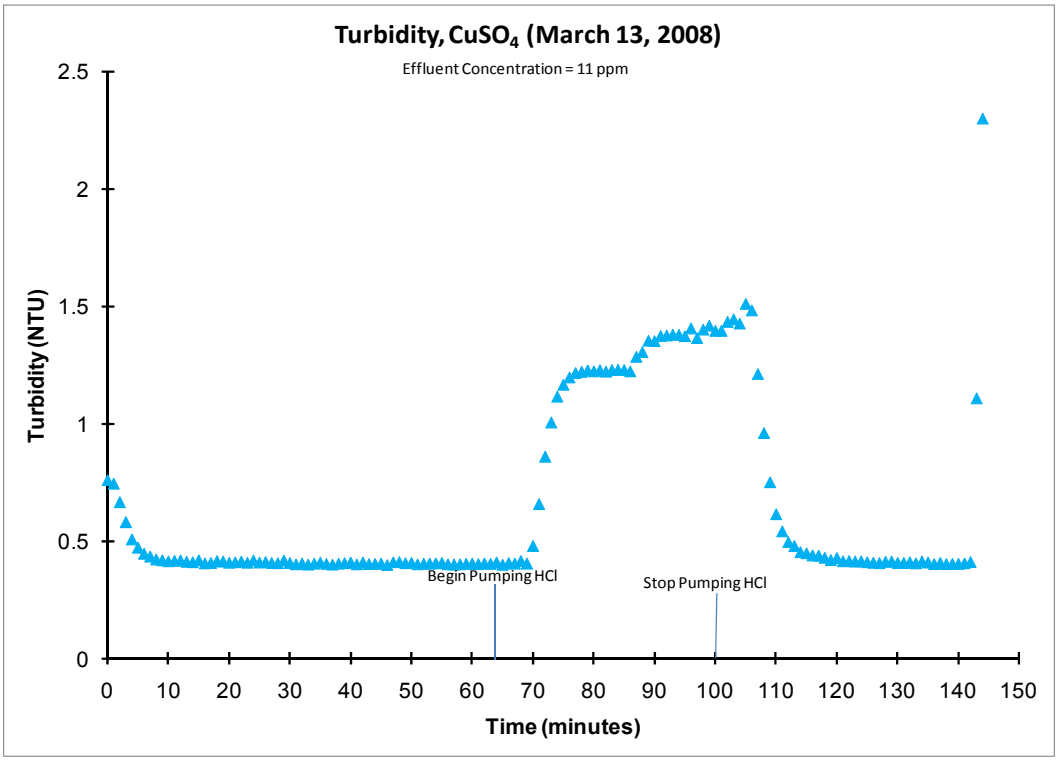

Figure 65. $CuSO_4$ Turbidity Graph for 11 ppm Concentration

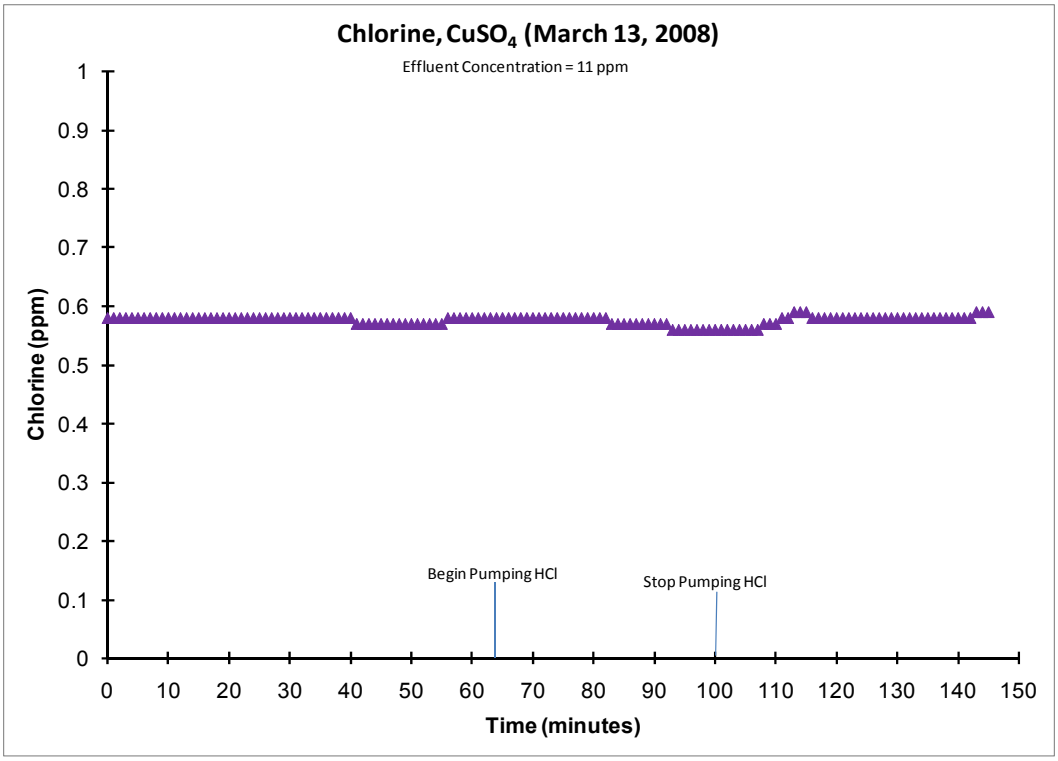

Figure 66. $CuSO_4$ Chlorine Graph for 11 ppm Concentration

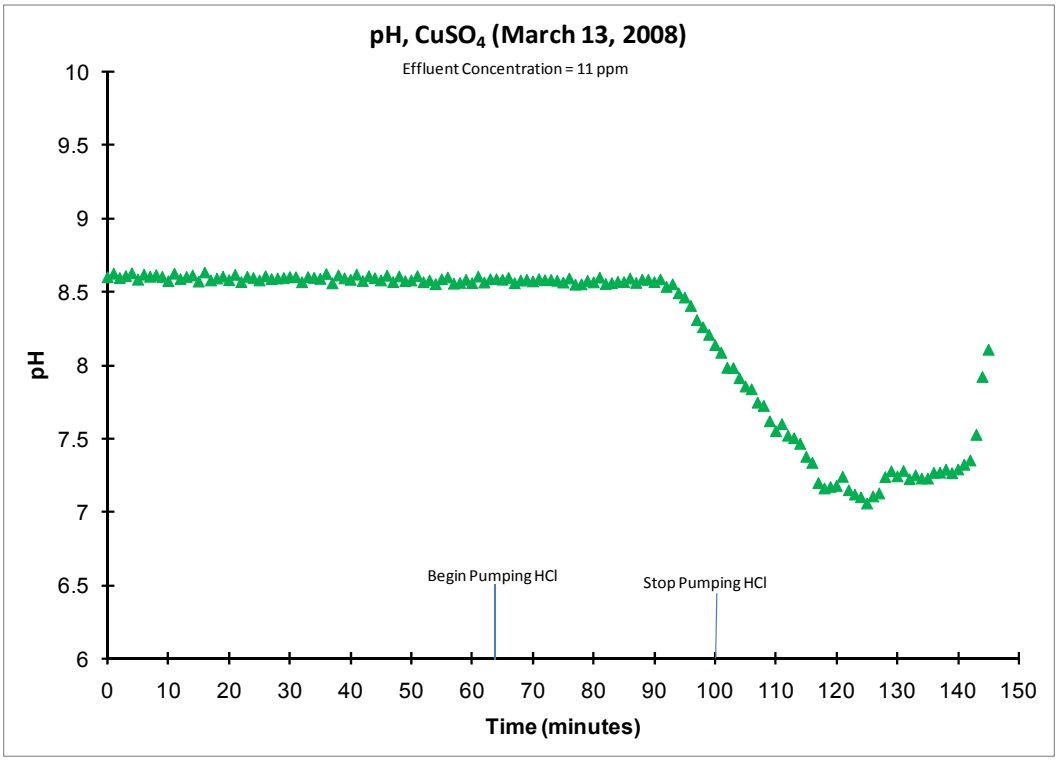

Figure 67. $CuSO_4$ pH Graph for 11 ppm Concentration

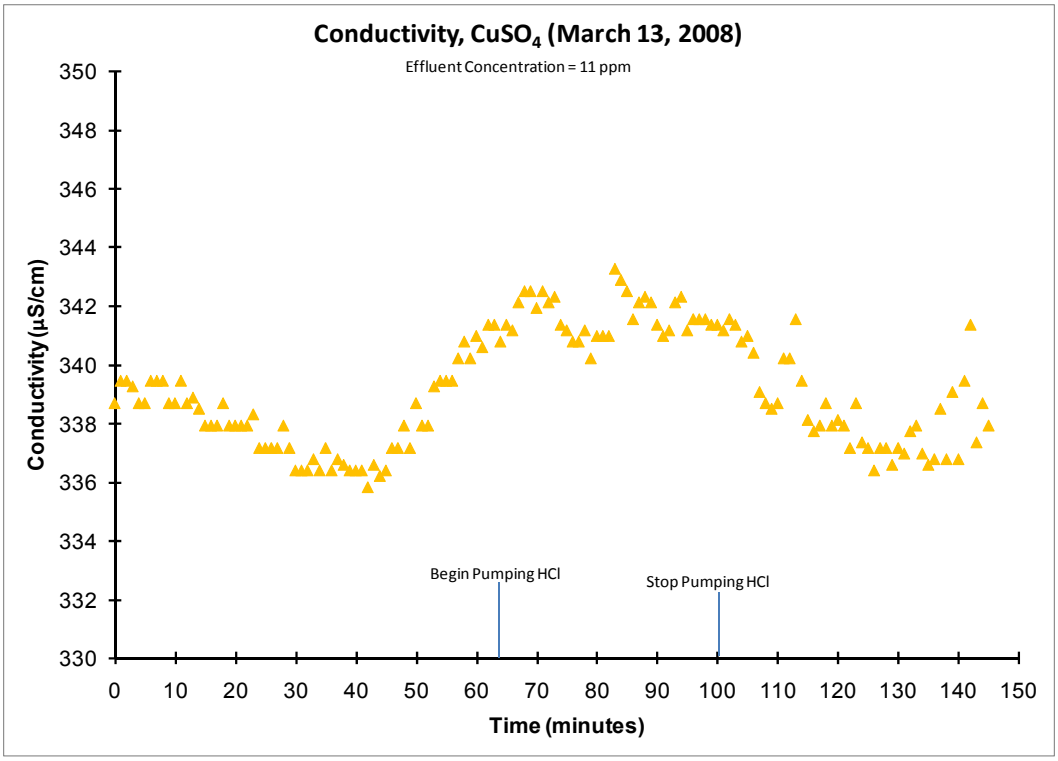

Figure 68. $CuSO_4$ Conductivity Graph for 11 ppm Concentration

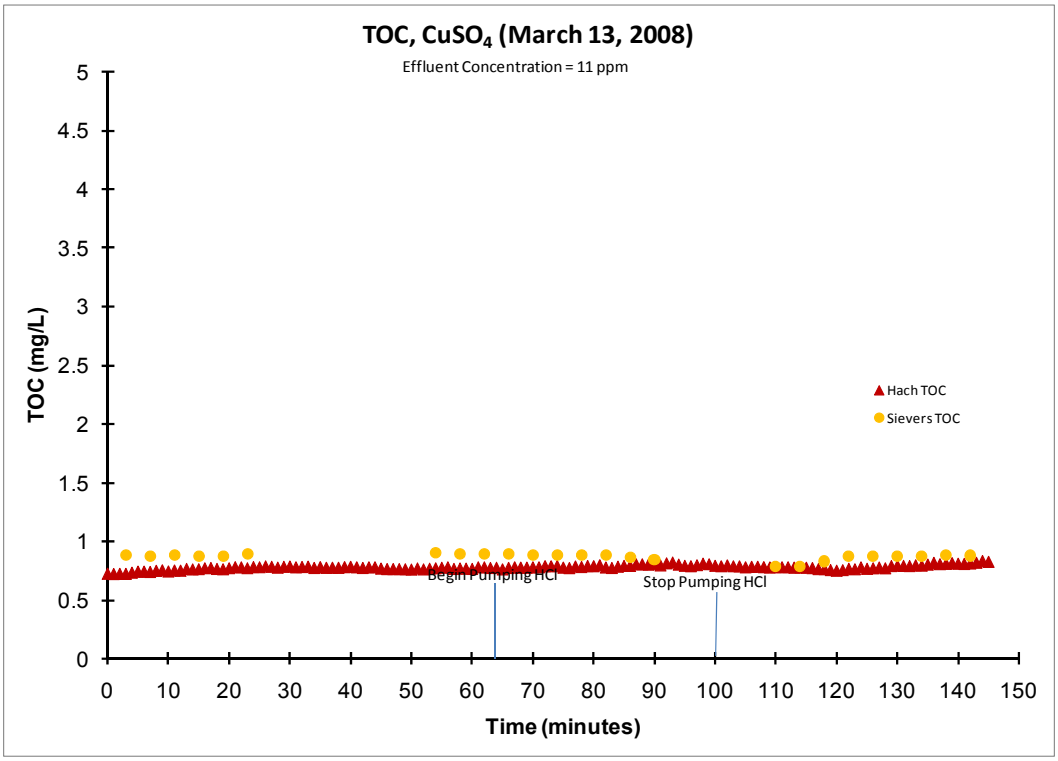

Figure 69. $CuSO_4$ TOC Graph for 11 ppm Concentration

A.6 SODIUM FLUOROACETATE

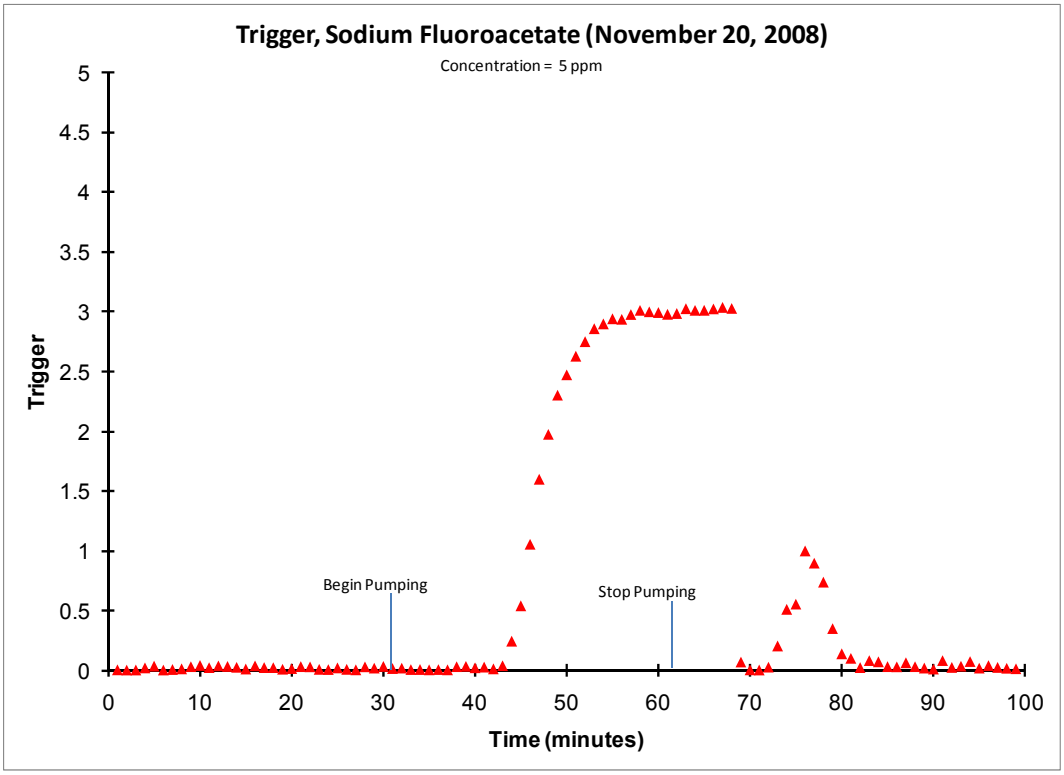

Figure 70. Sodium Fluoroacetate Trigger Graph for 5 ppm Concentration

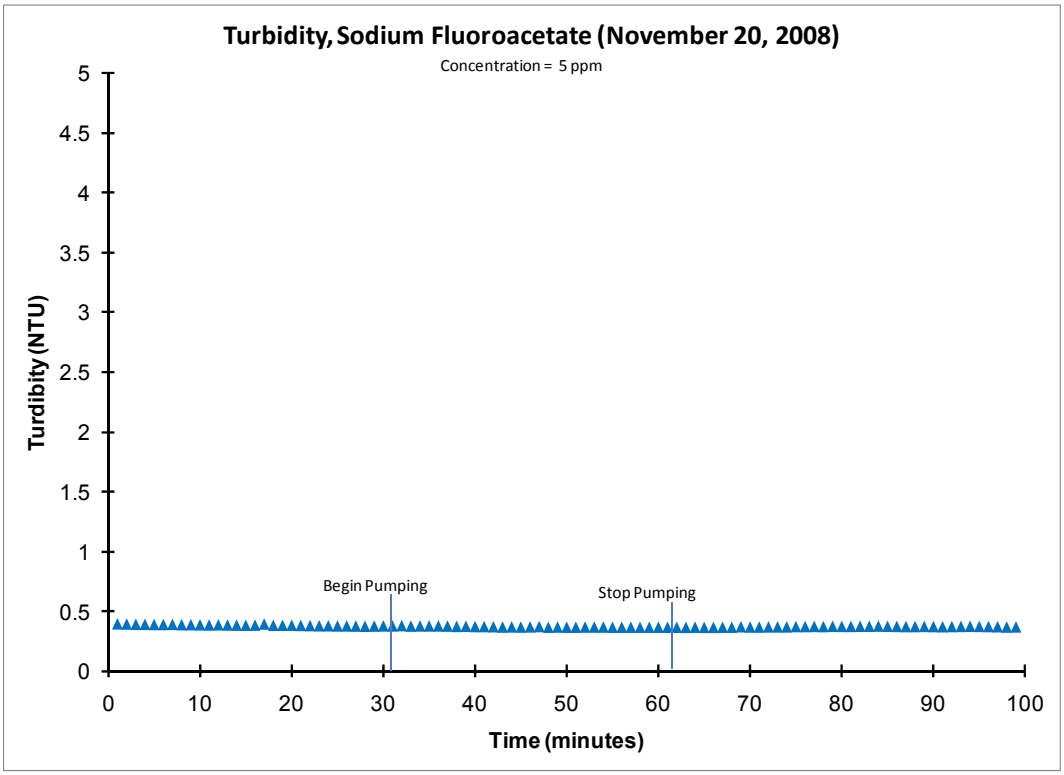

Figure 71. Sodium Fluoroacetate Turbidity Graph for 5 ppm Concentration

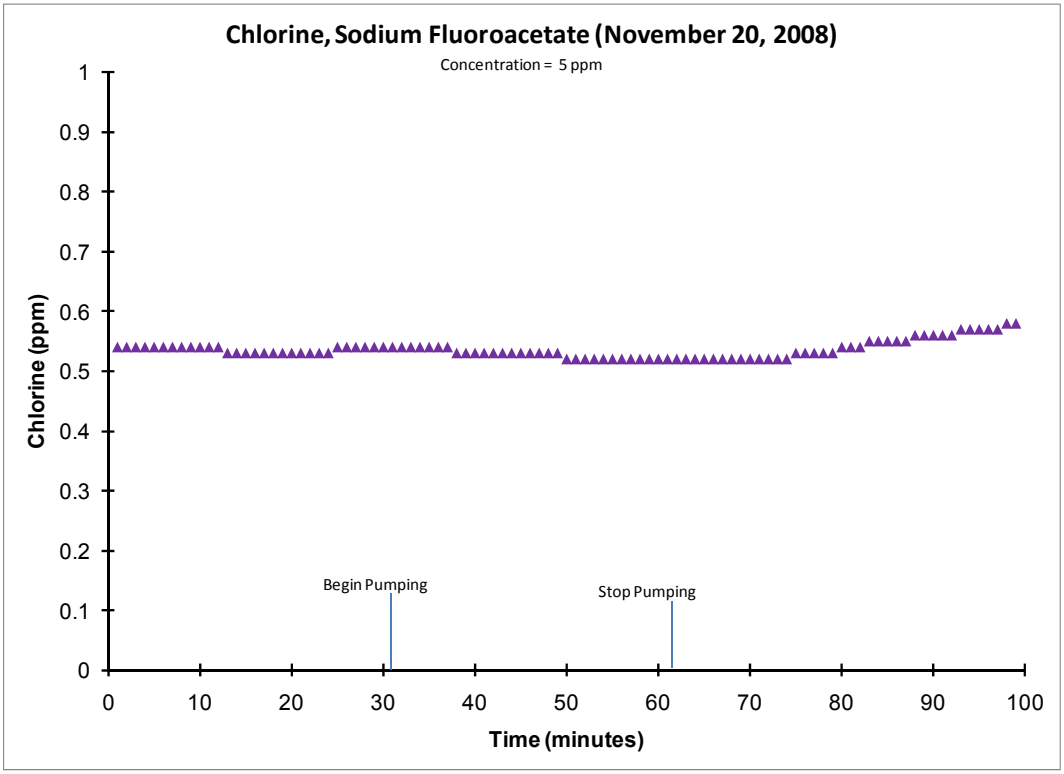

Figure 72. Sodium Fluoroacetate Chlorine Graph for 5 ppm Concentration

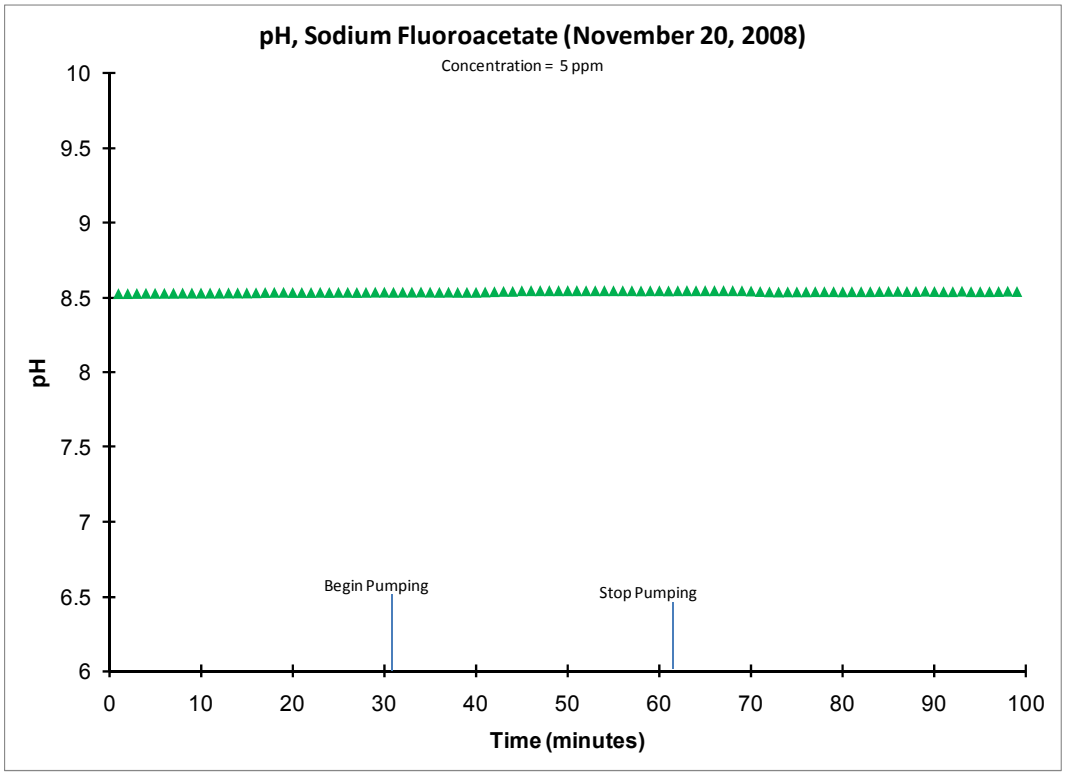

Figure 73. Sodium Fluoroacetate pH Graph for 5 ppm Concentration

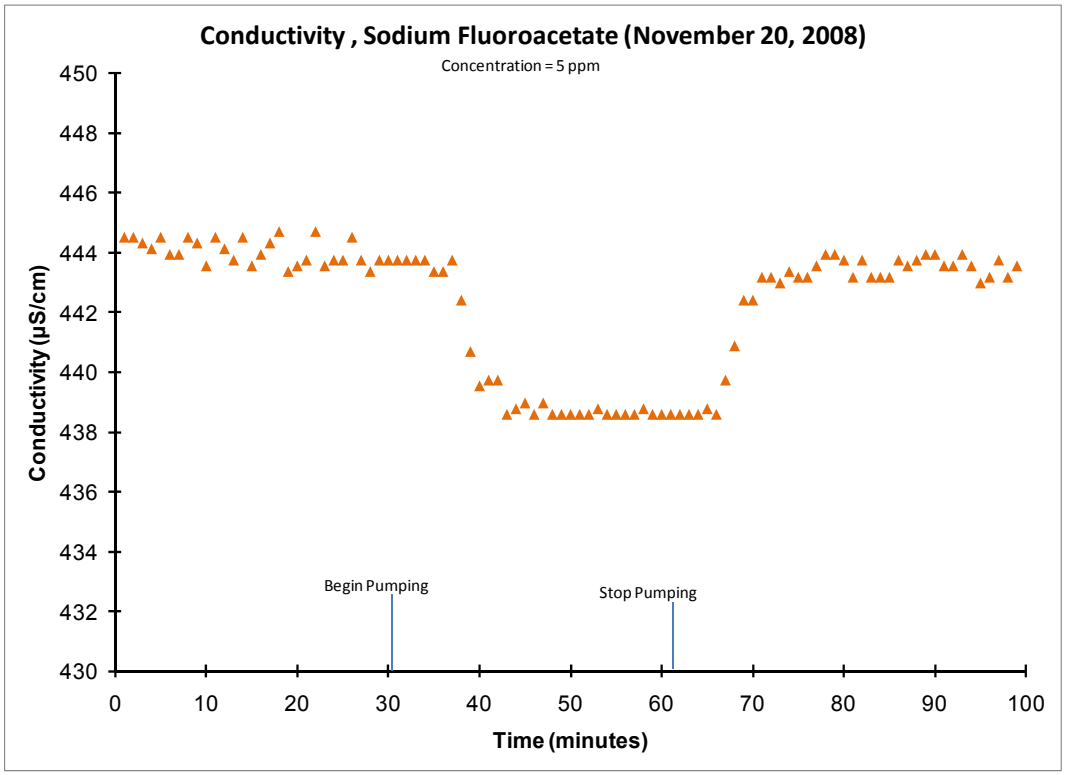

Figure 74. Sodium Fluoroacetate Conductivity Graph for 5 ppm Concentration

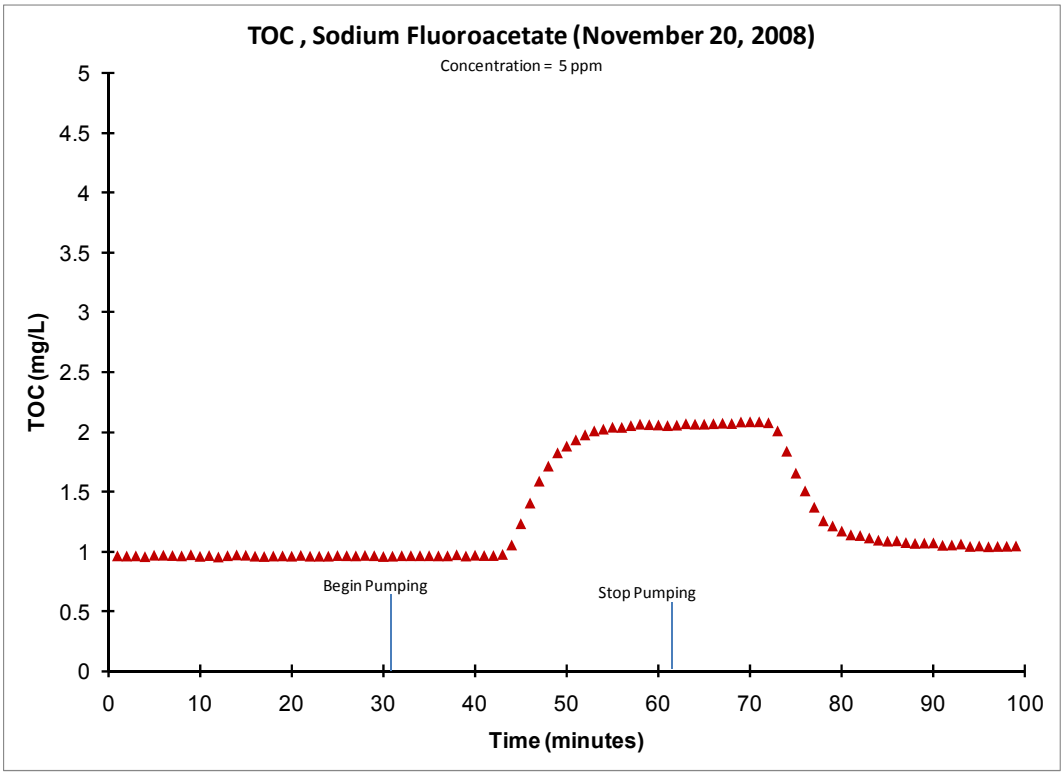

Figure 75. Sodium Fluoroacetate TOC Graph for 5 ppm Concentration

A.7 BUG-B-GON

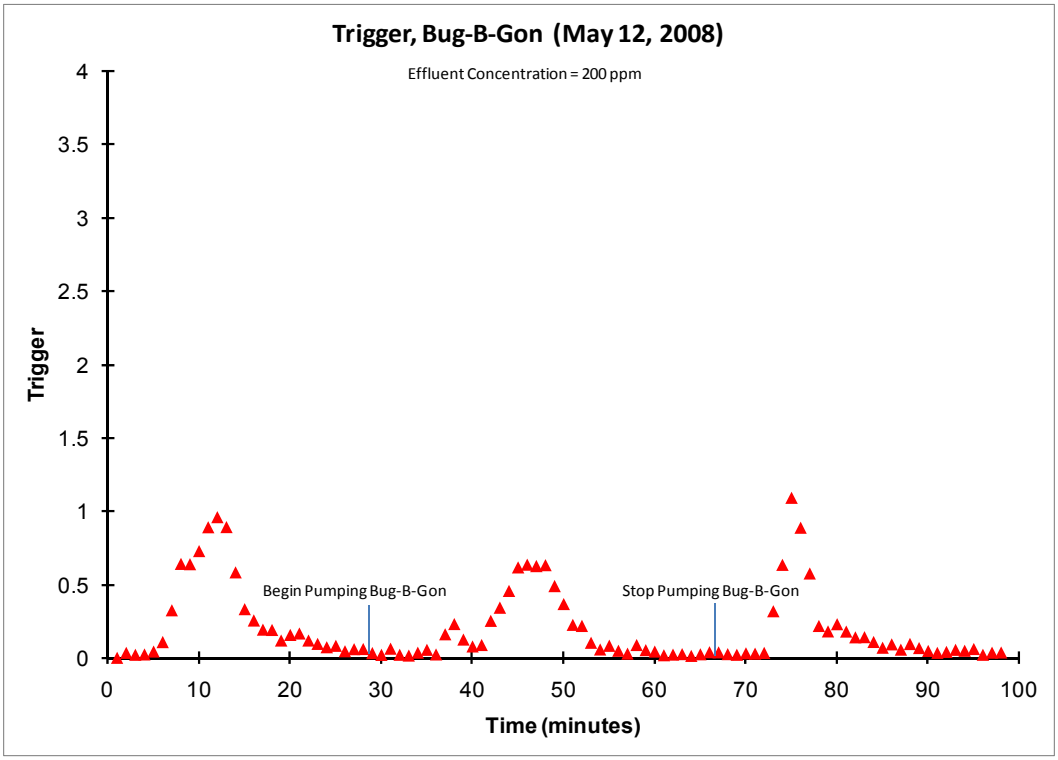

Figure 76. Bug-B-Gon Trigger Graph for 200 ppm Concentration

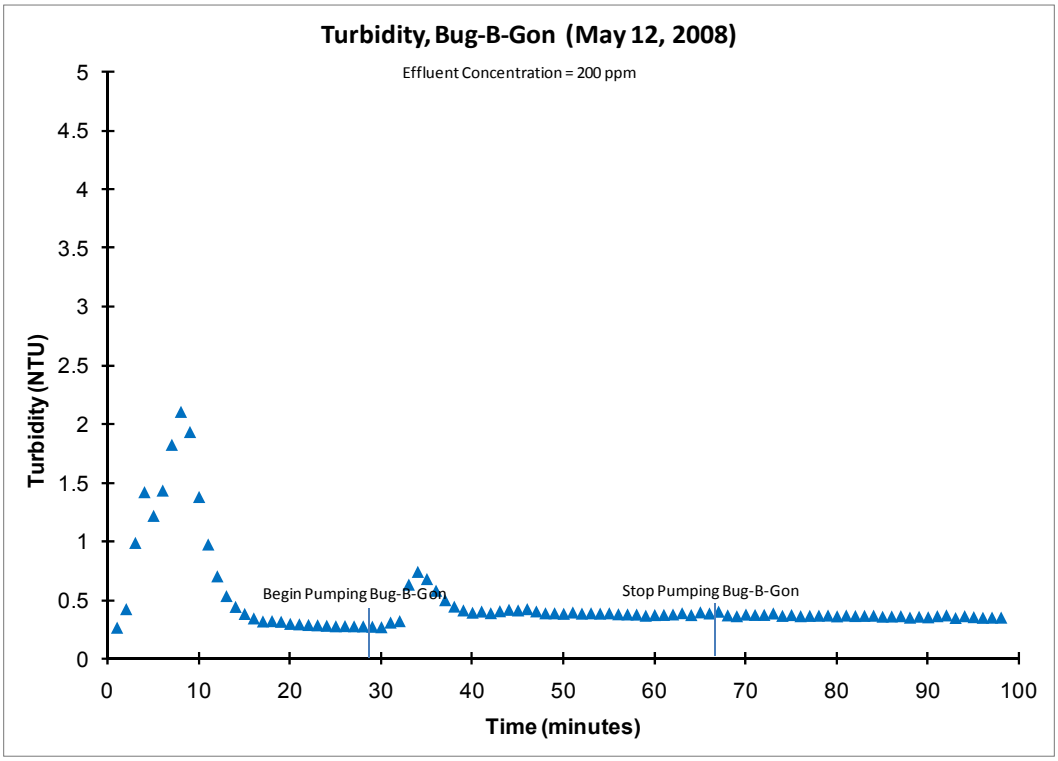

Figure 77. Bug-B-Gon Turbidity Graph for 200 ppm Concentration

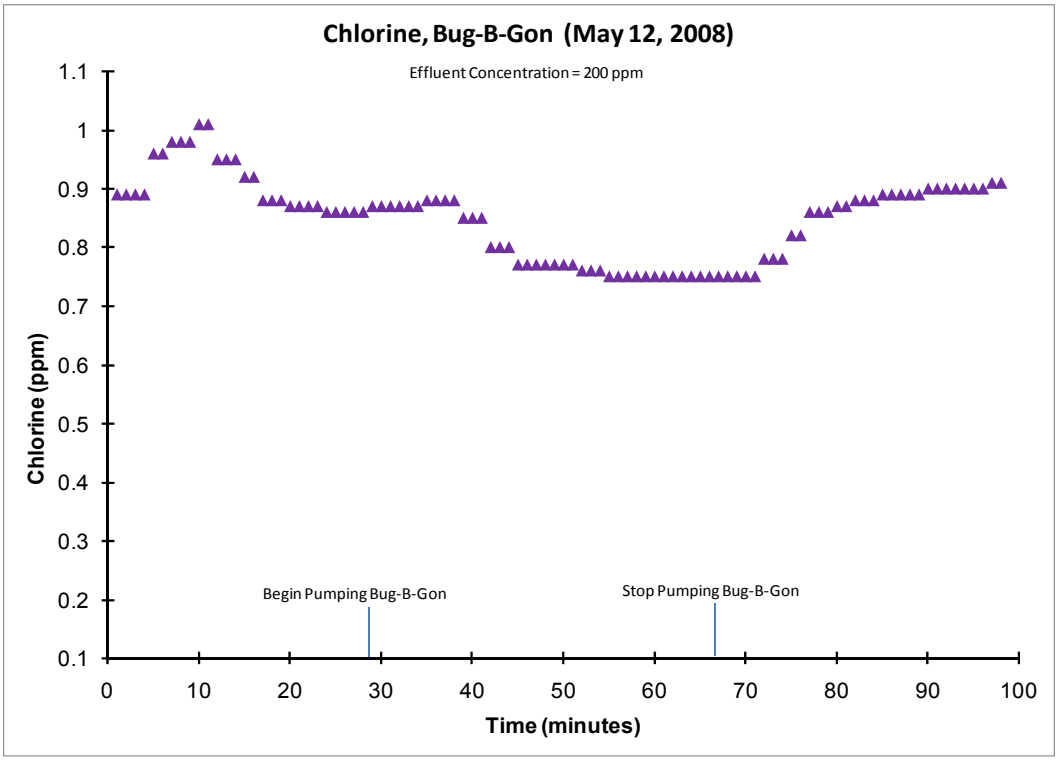

Figure 78. Bug-B-Gon Chlorine Graph for 200 ppm Concentration

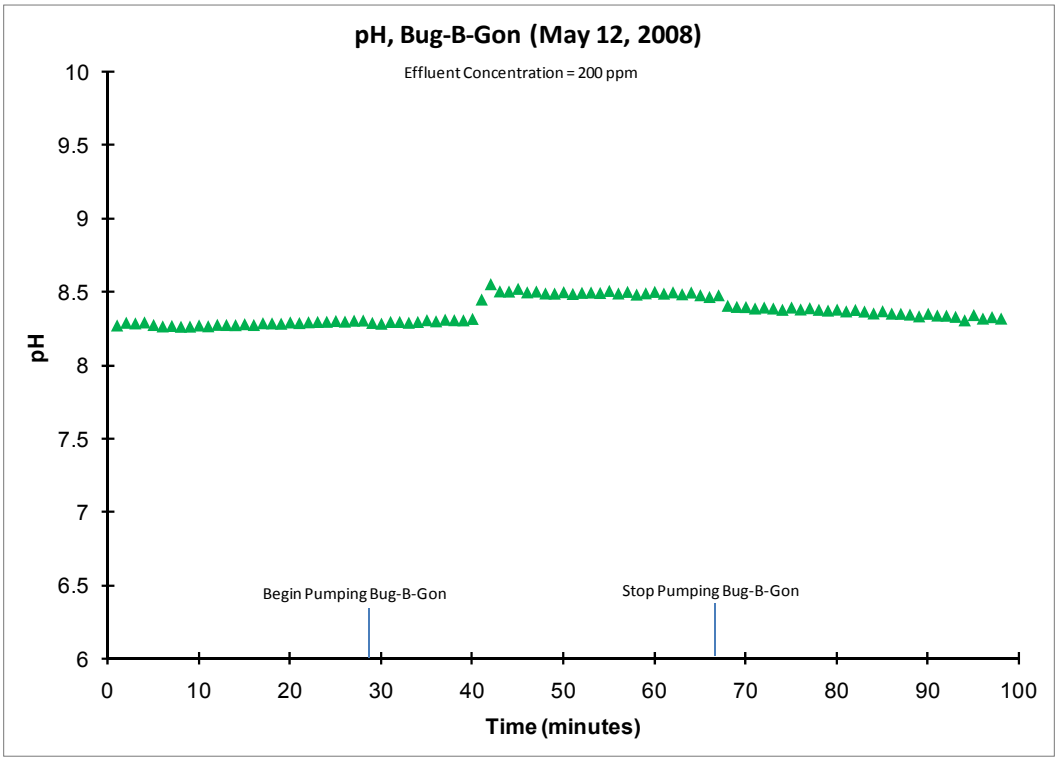

Figure 79. Bug-B-Gon pH Graph for 200 ppm Concentration

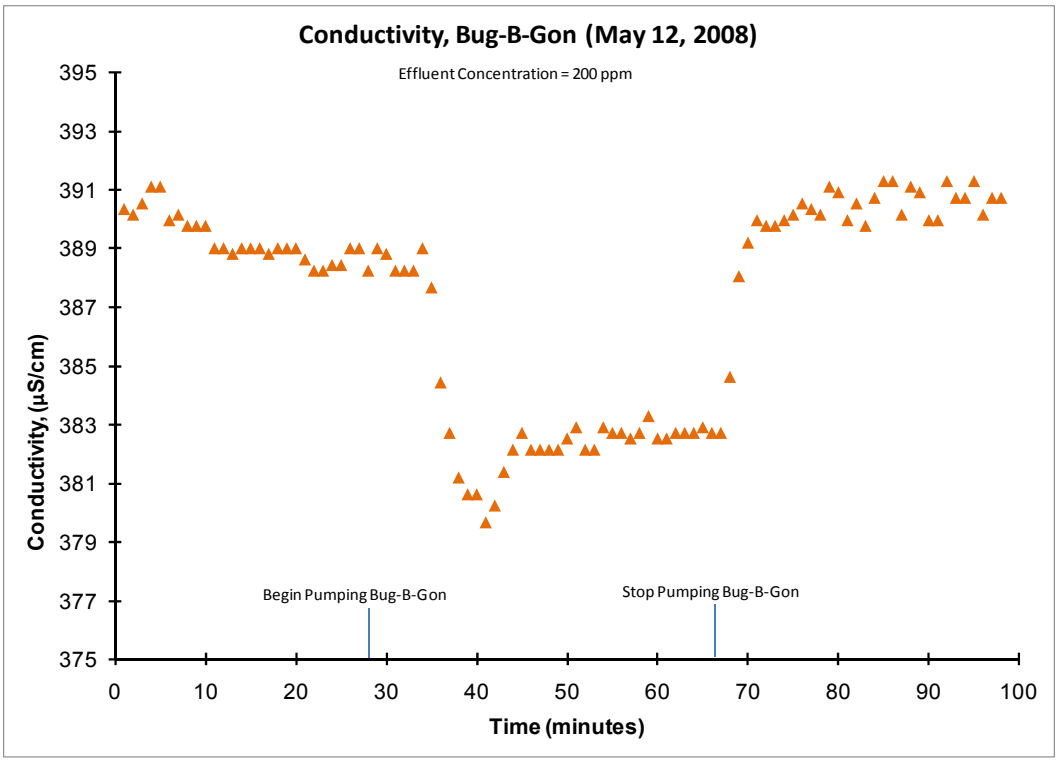

Figure 80. Bug-B-Gon Conductivity Graph for 200 ppm Concentration

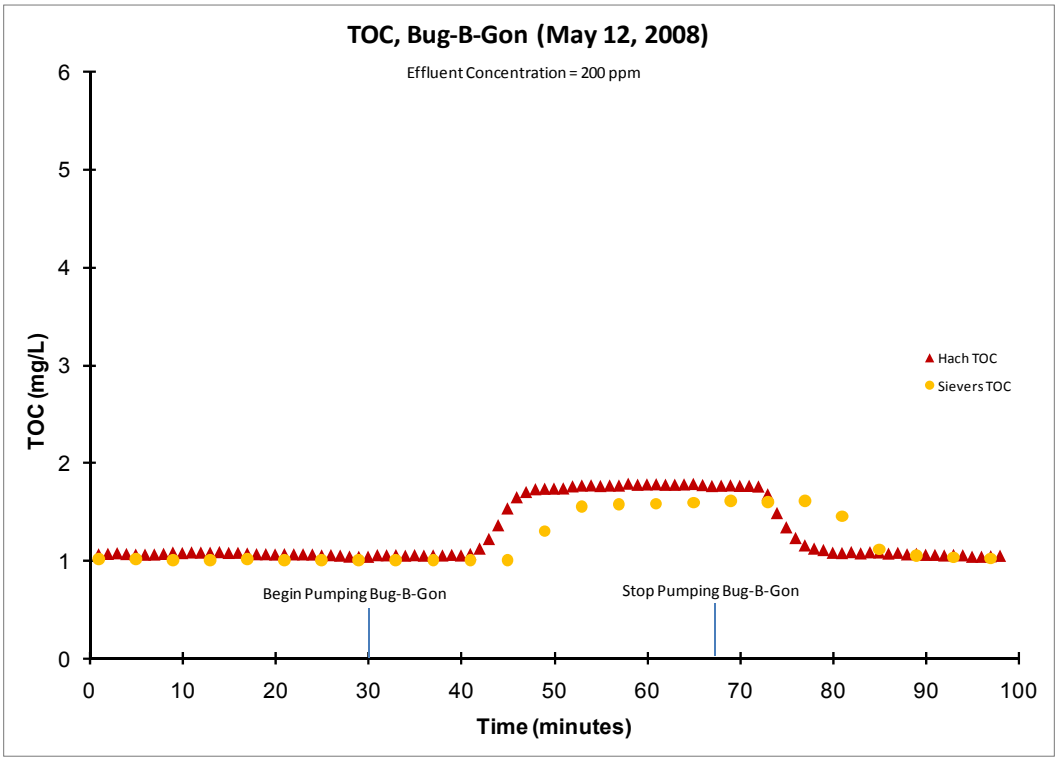

Figure 81. Bug-B-Gon TOC Graph for 200 ppm Concentration

A.8 FIRE FOAM

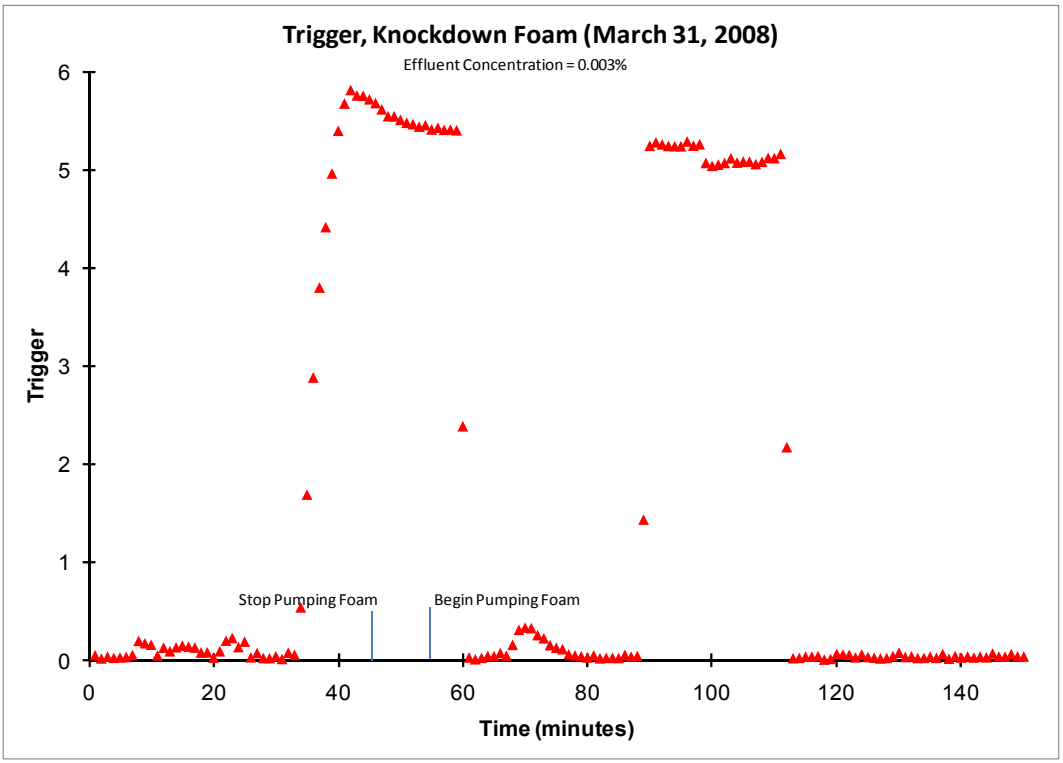

Figure 82. Fire Foam Trigger Graph for 0.003% Concentration

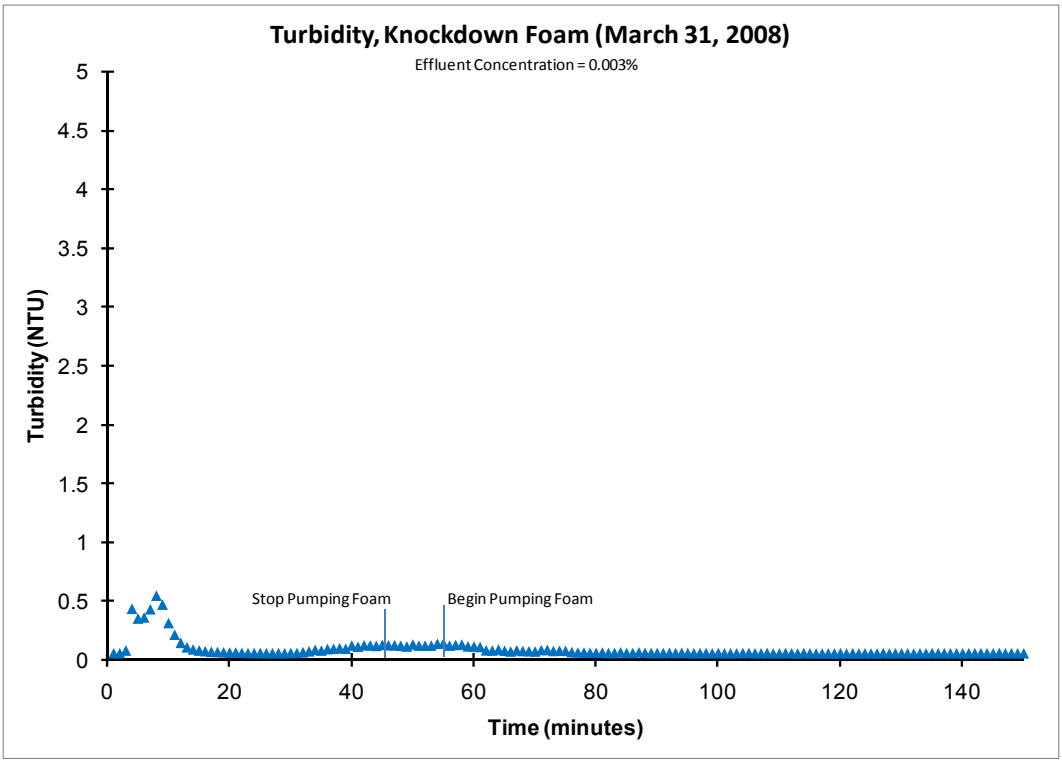

Figure 83. Fire Foam Turbidity Graph for 0.003% Concentration

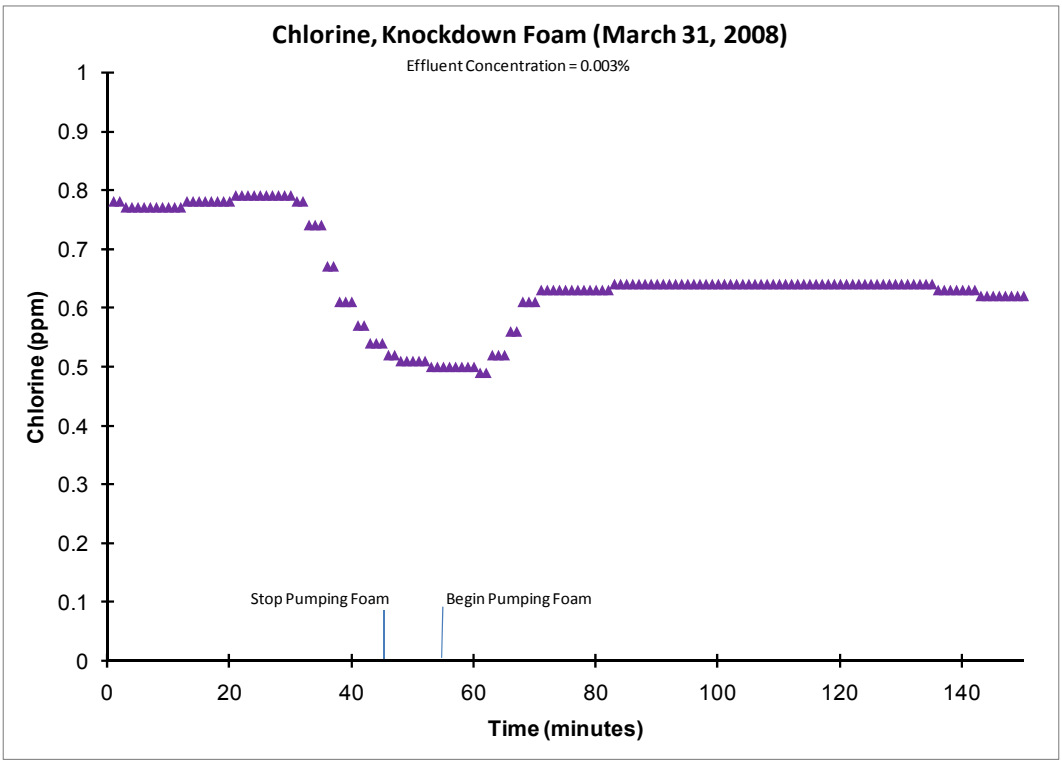

Figure 84. Fire Foam Chlorine Graph for 0.003% Concentration

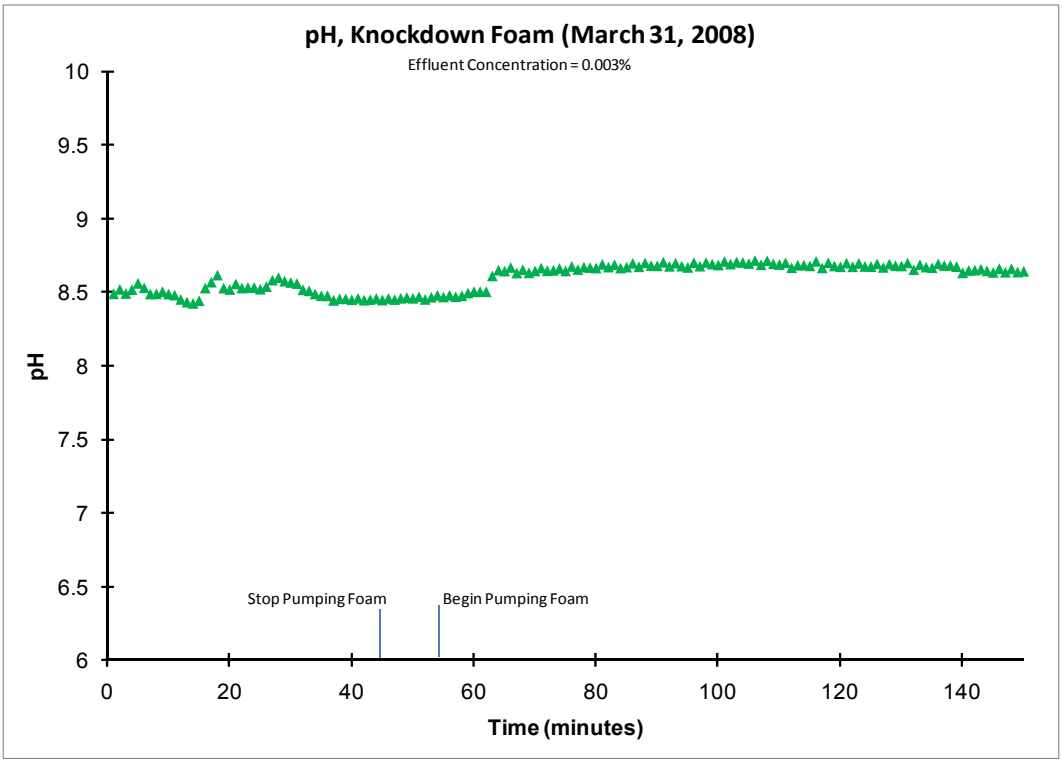

Figure 85. Fire Foam pH Graph for 0.003% Concentration

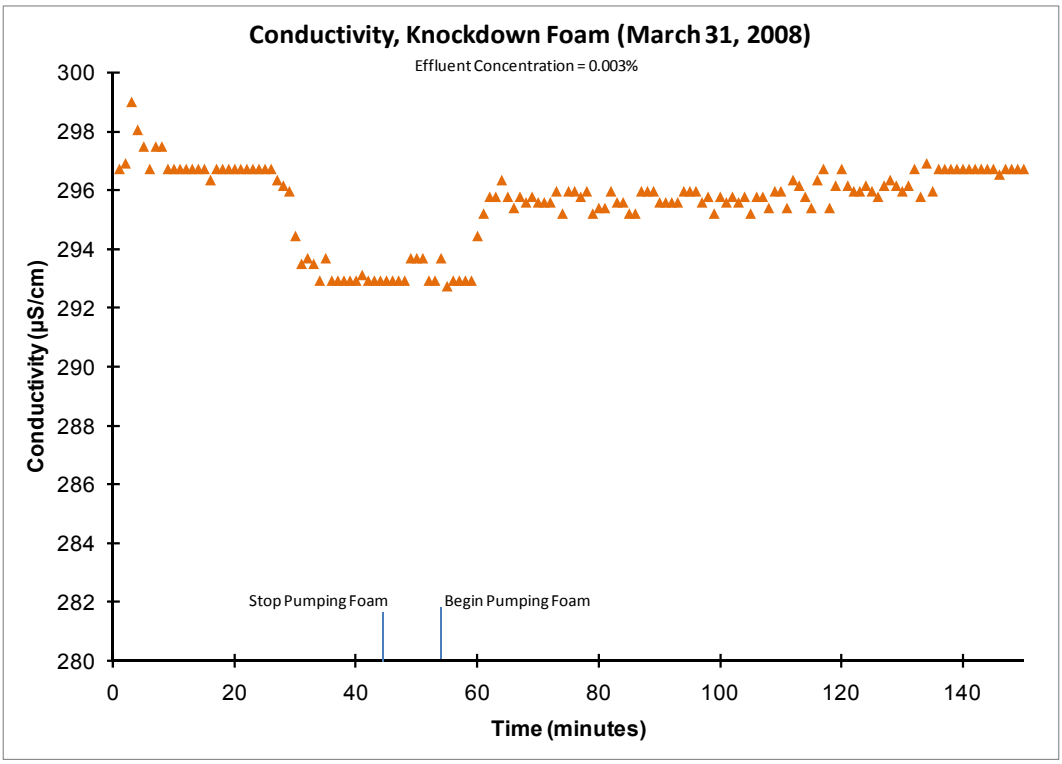

Figure 86. Fire Foam Conductivity Graph for 0.003% Concentration

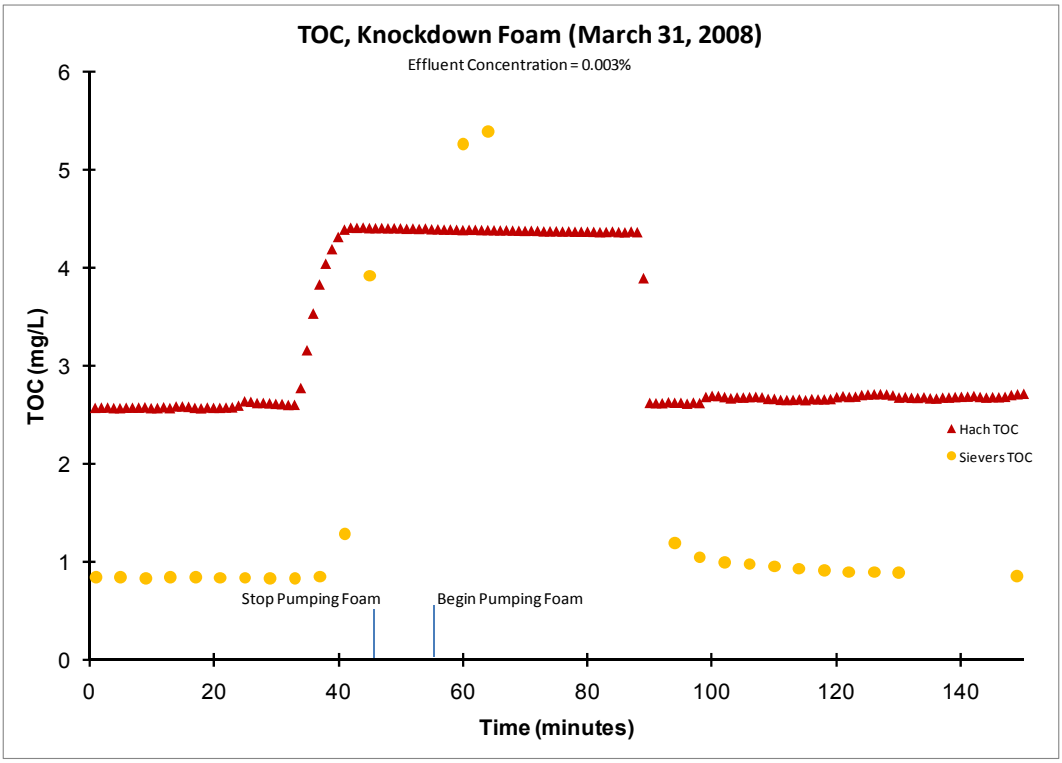

Figure 87. Fire Foam TOC Graph for 0.003% Concentration

A.9 PAINT THINNER

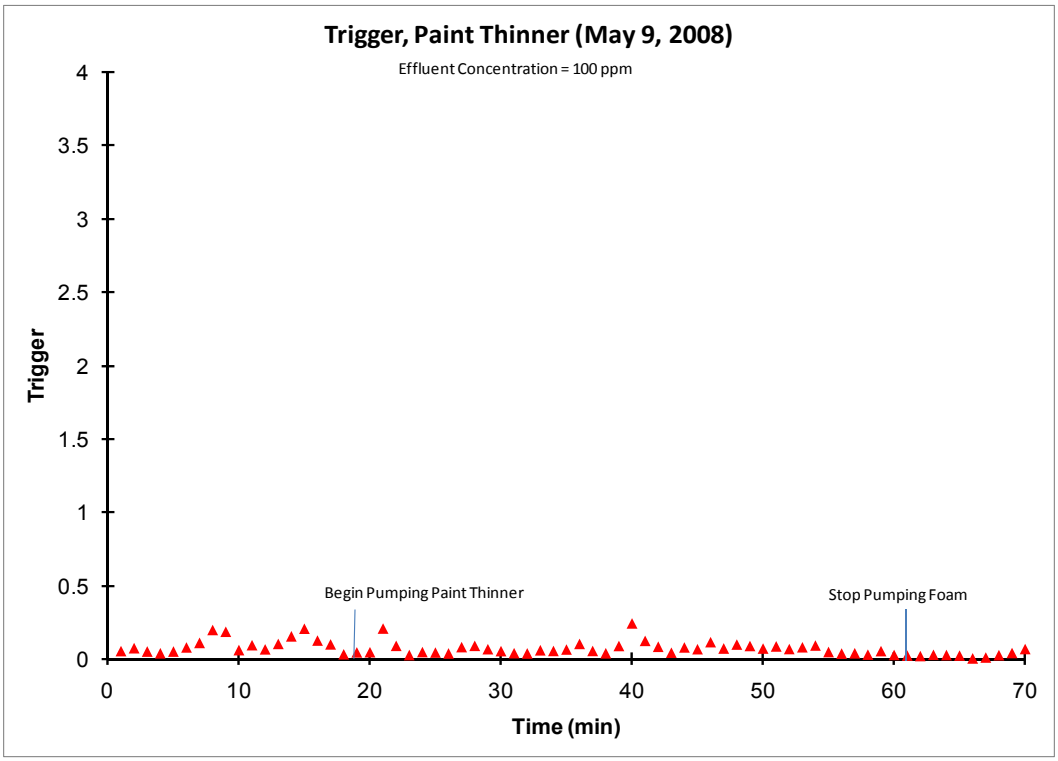

Figure 88. Paint Thinner Trigger Graph for 100 ppm Concentration

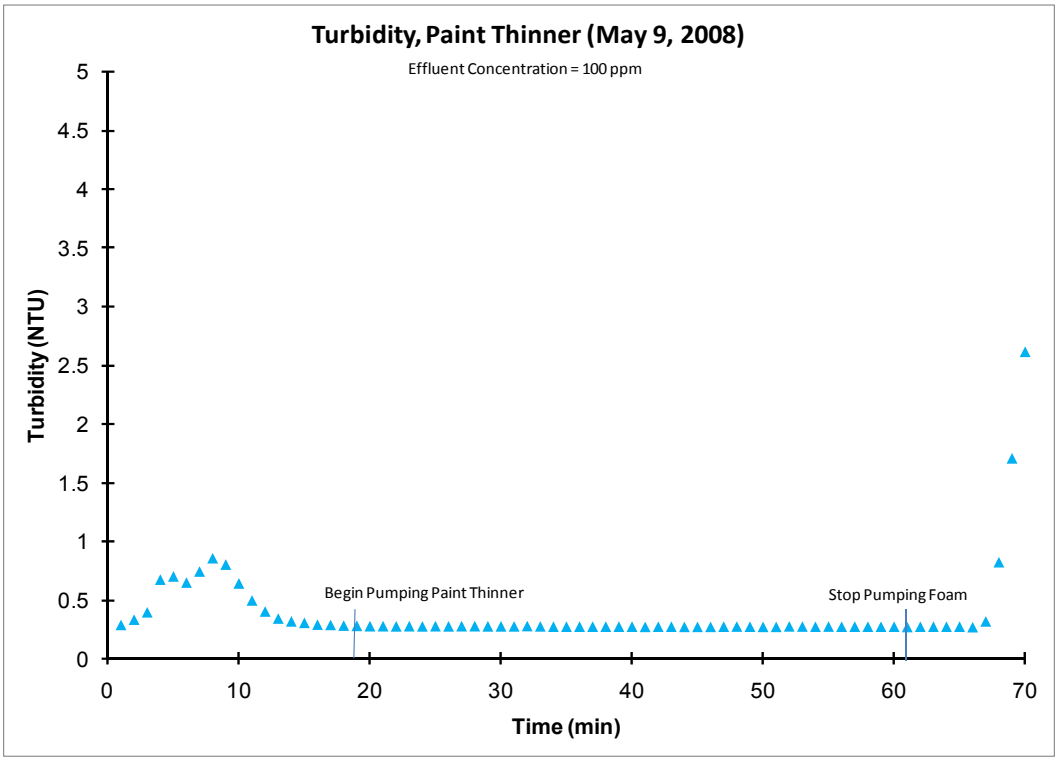

Figure 89. Paint Thinner Turbidity Graph for 100 ppm Concentration

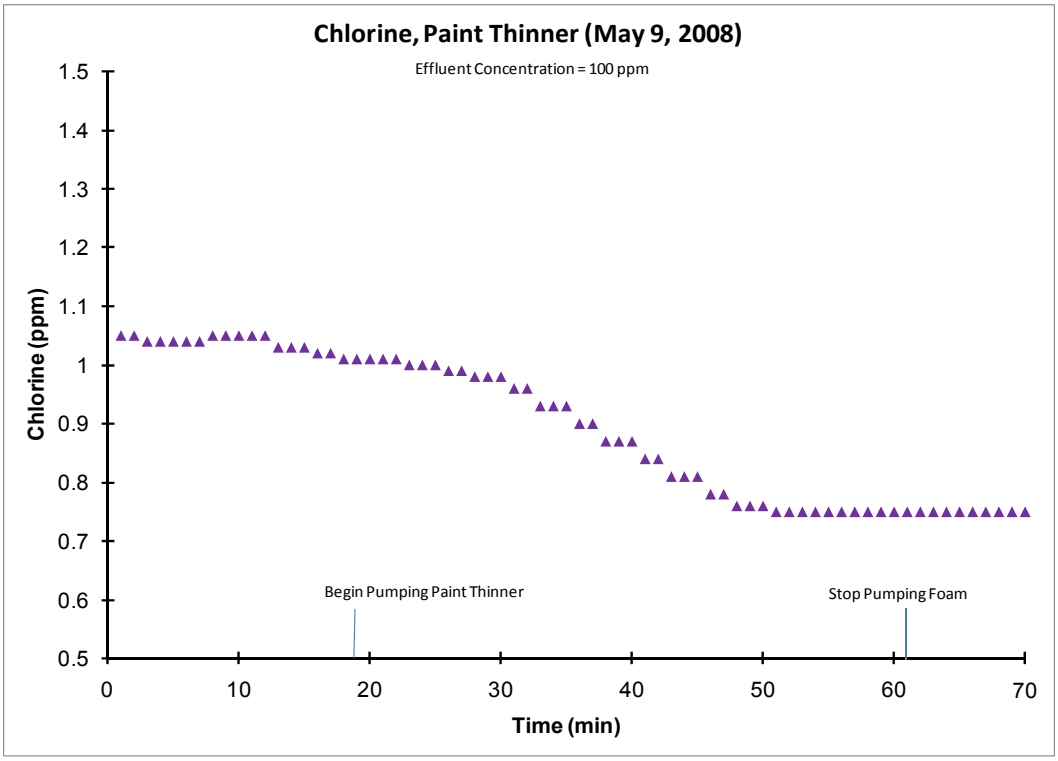

Figure 90. Paint Thinner Chlorine Graph for 100 ppm Concentration

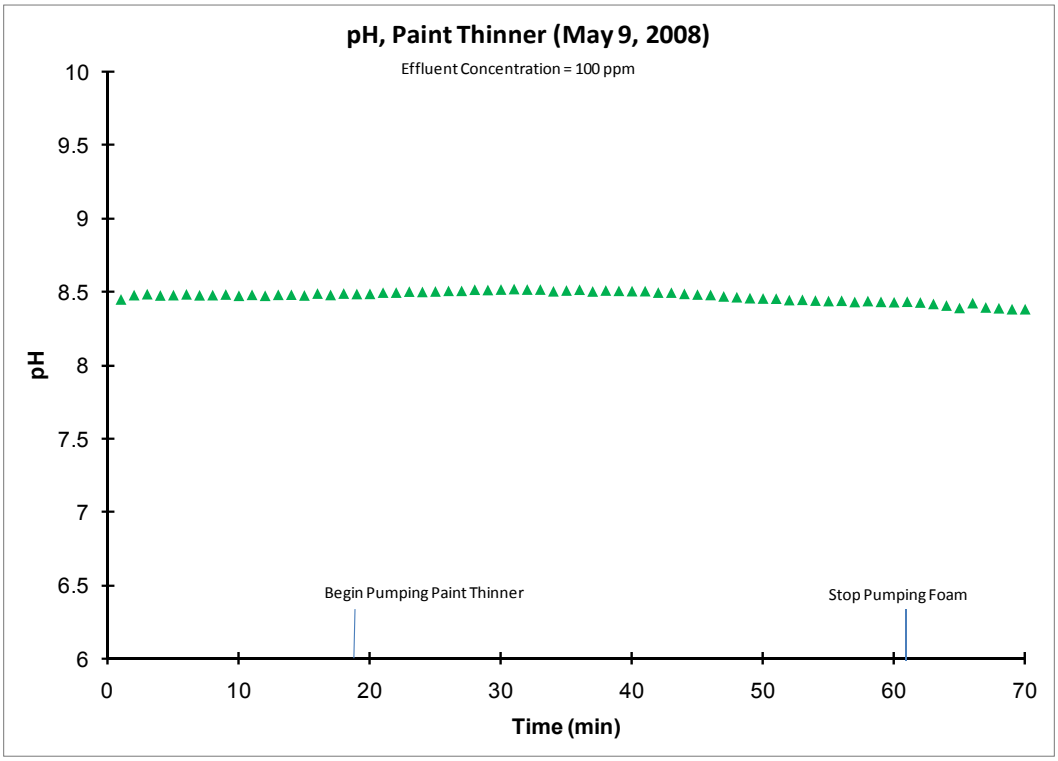

Figure 91. Paint Thinner pH Graph for 100 ppm Concentration

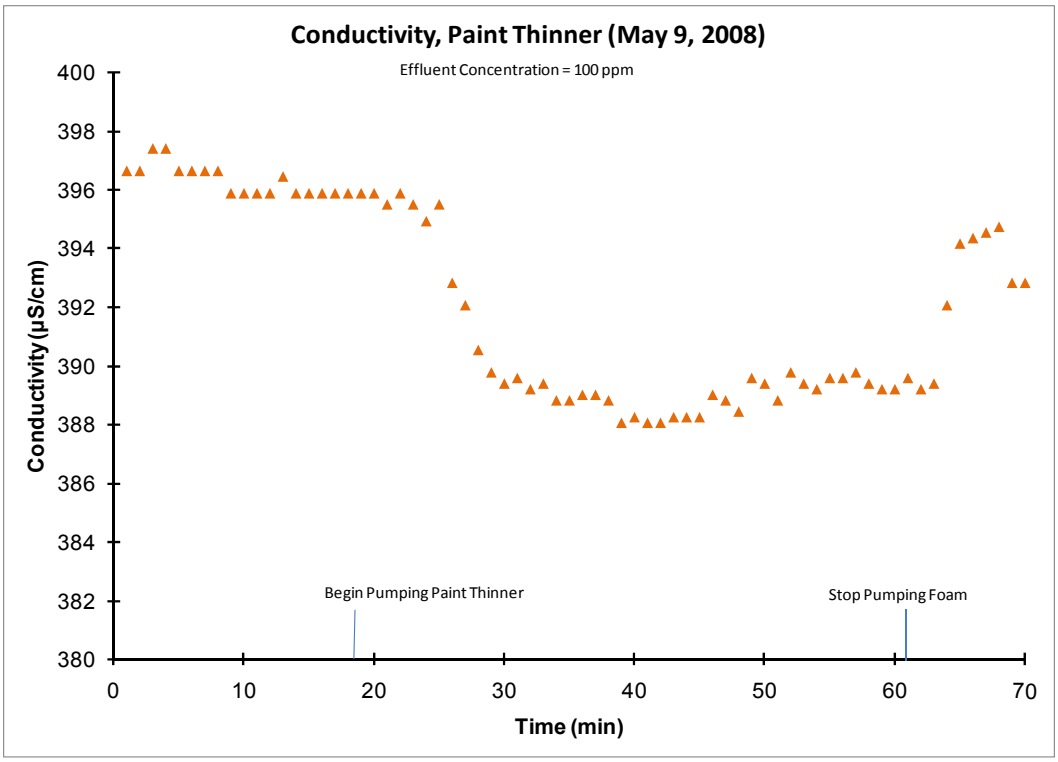

Figure 92. Paint Thinner Conductivity Graph for 100 ppm Concentration

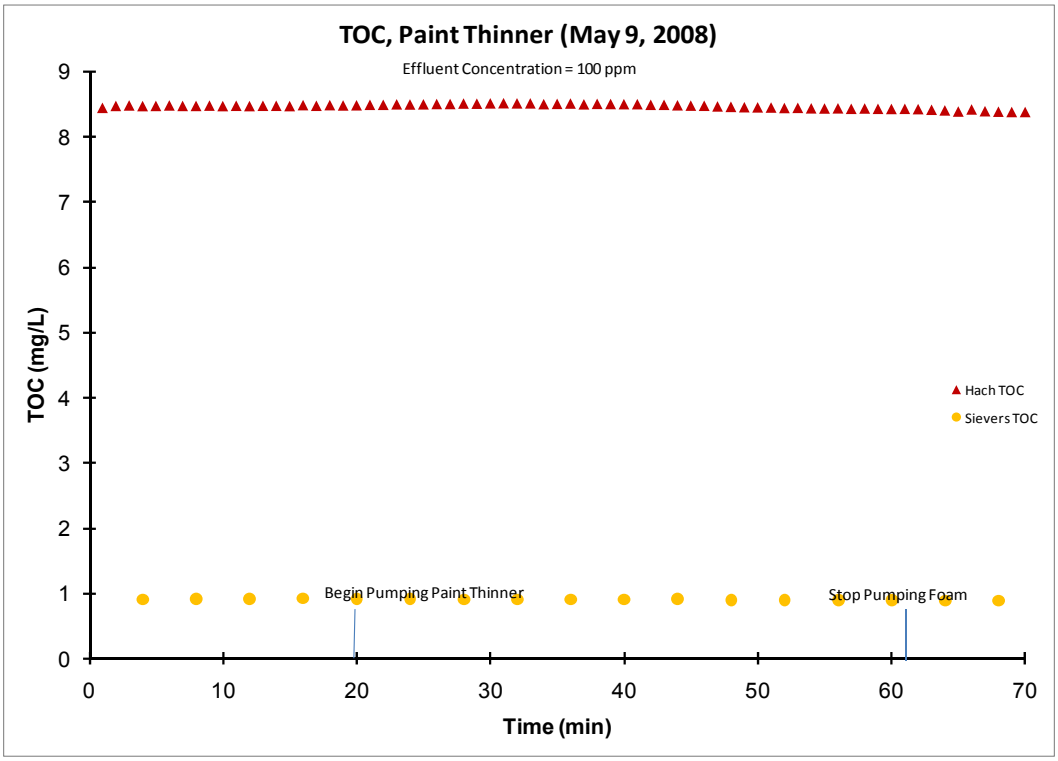

Figure 93. Paint Thinner TOC Graph for 100 ppm Concentration

APPENDIX B

BIOLOGICAL CONTAMINANT

B.1 TWO MICRON SPHERES

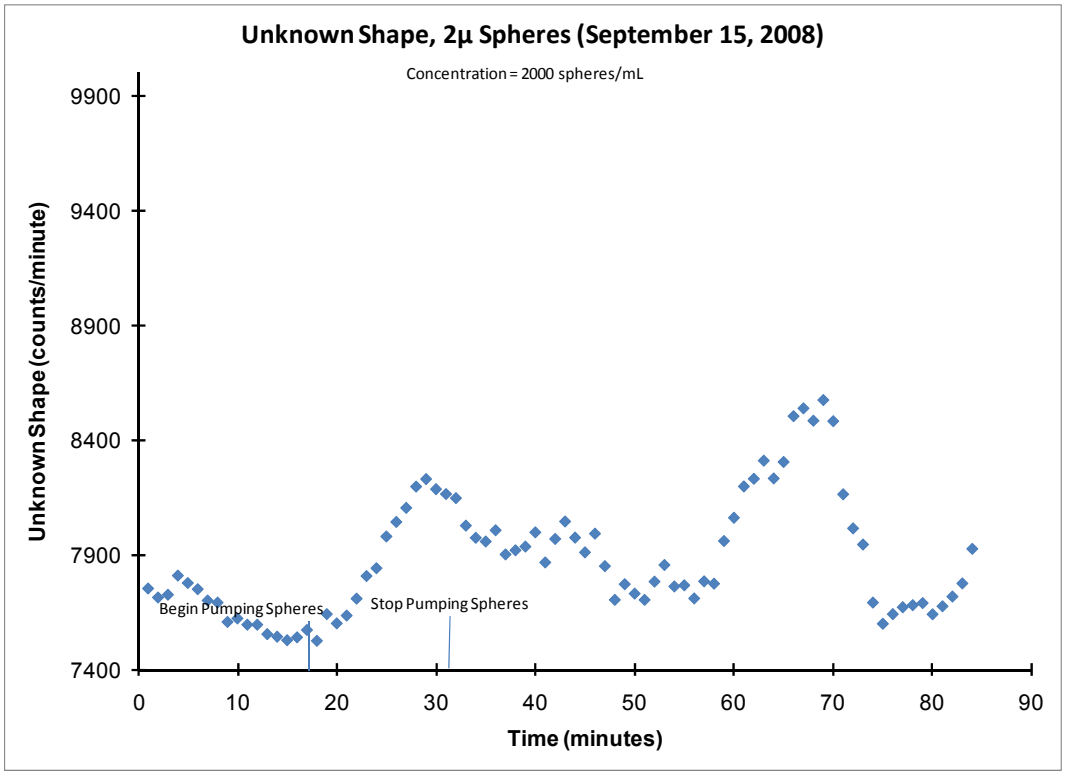

Figure 94. 2µ Spheres Unknown Graph for 2000 spheres/ml

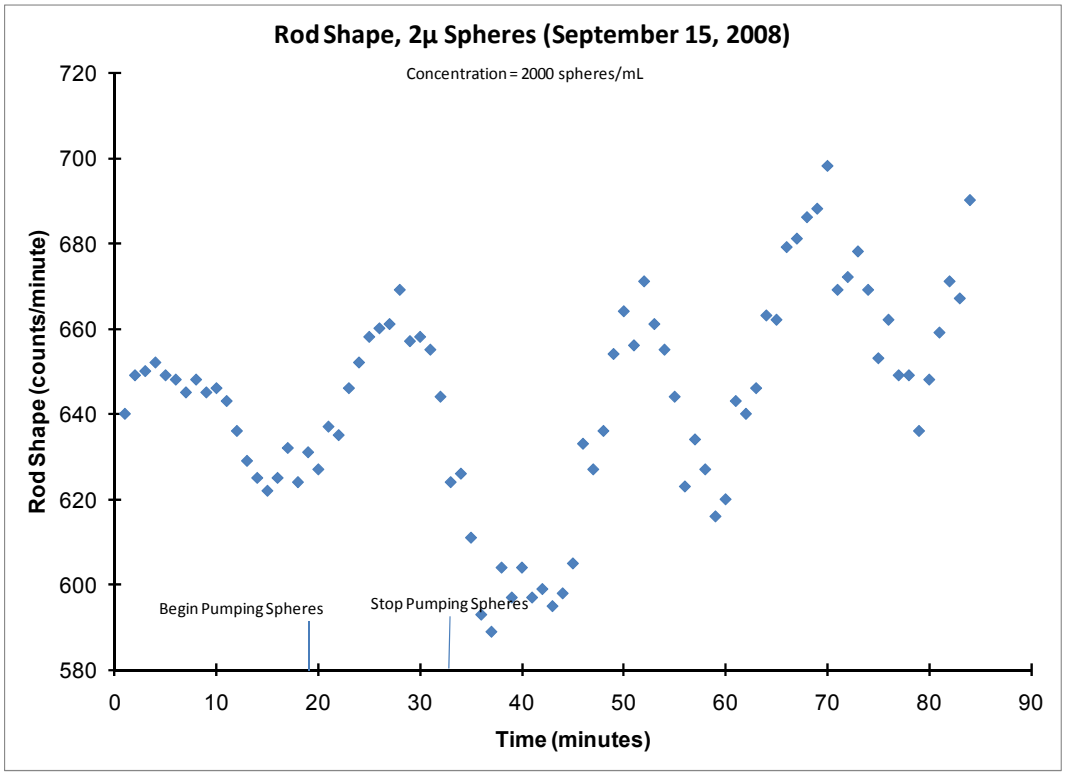

Figure 95. 2µ Spheres Rod Graph for 2000 spheres/ml

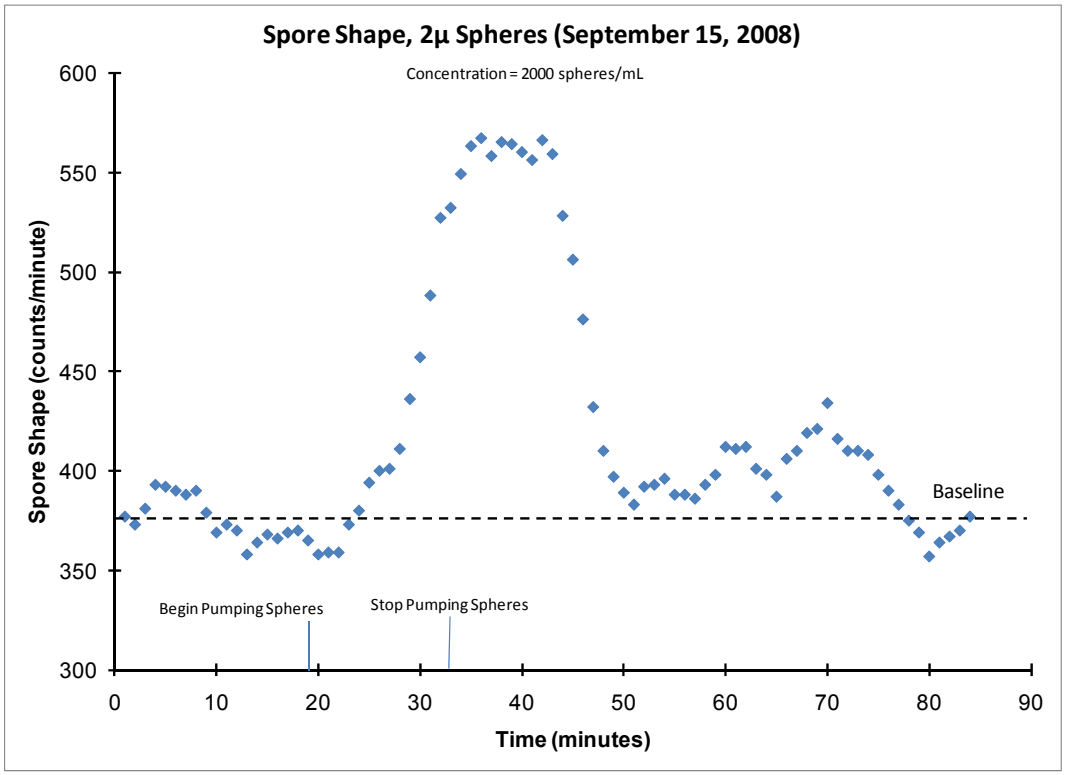

Figure 96. 2µ Spheres Spore Graph for 2000 spheres/ml

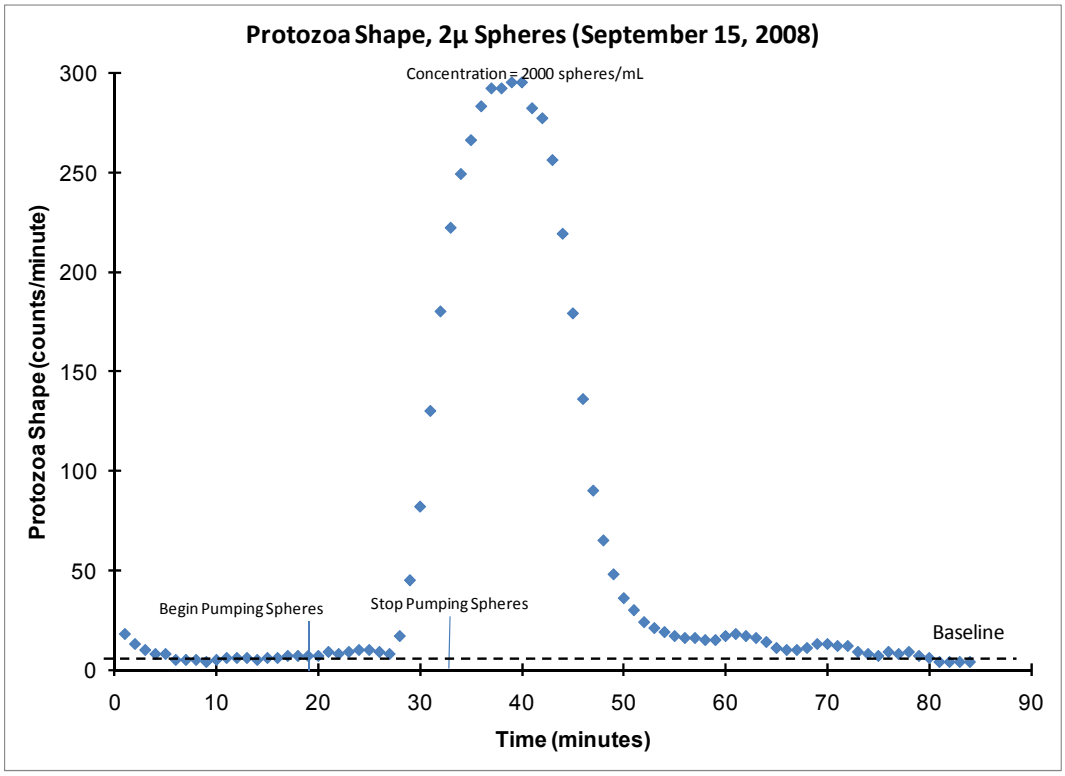

Figure 97. 2µ Spheres Protozoa Graph for 2000 spheres/ml

B.2 0.8 MICRON SPHERES

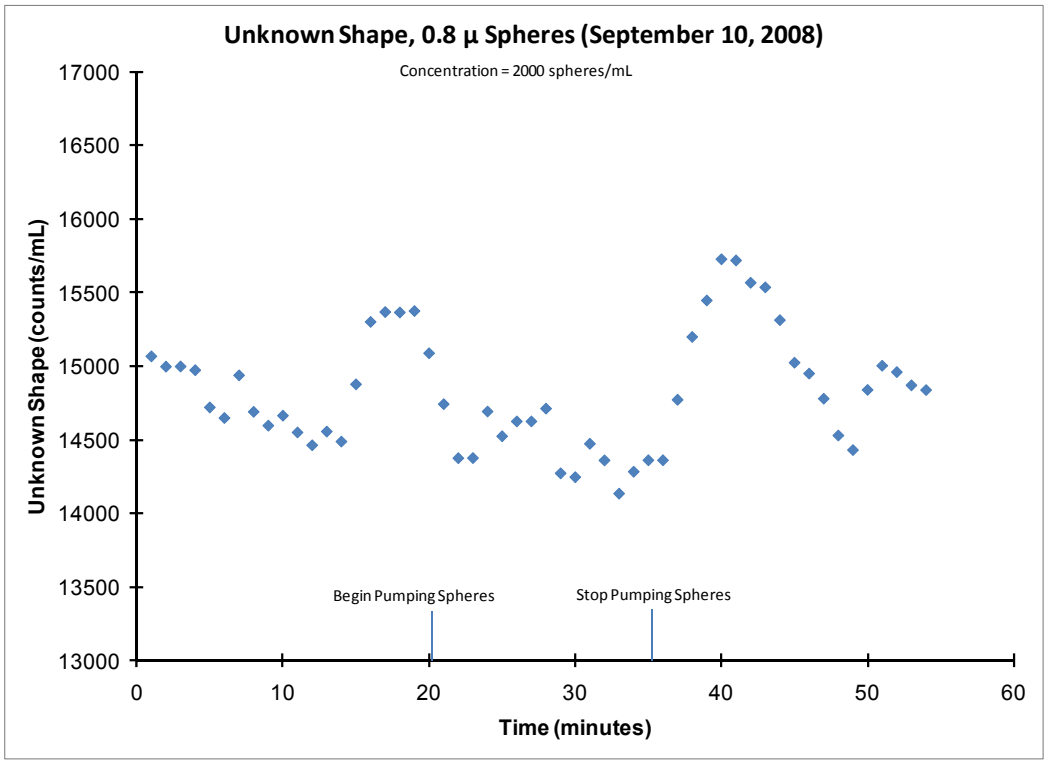

Figure 98. 0.8µ Spheres Unknown Graph for 2000 spheres/ml

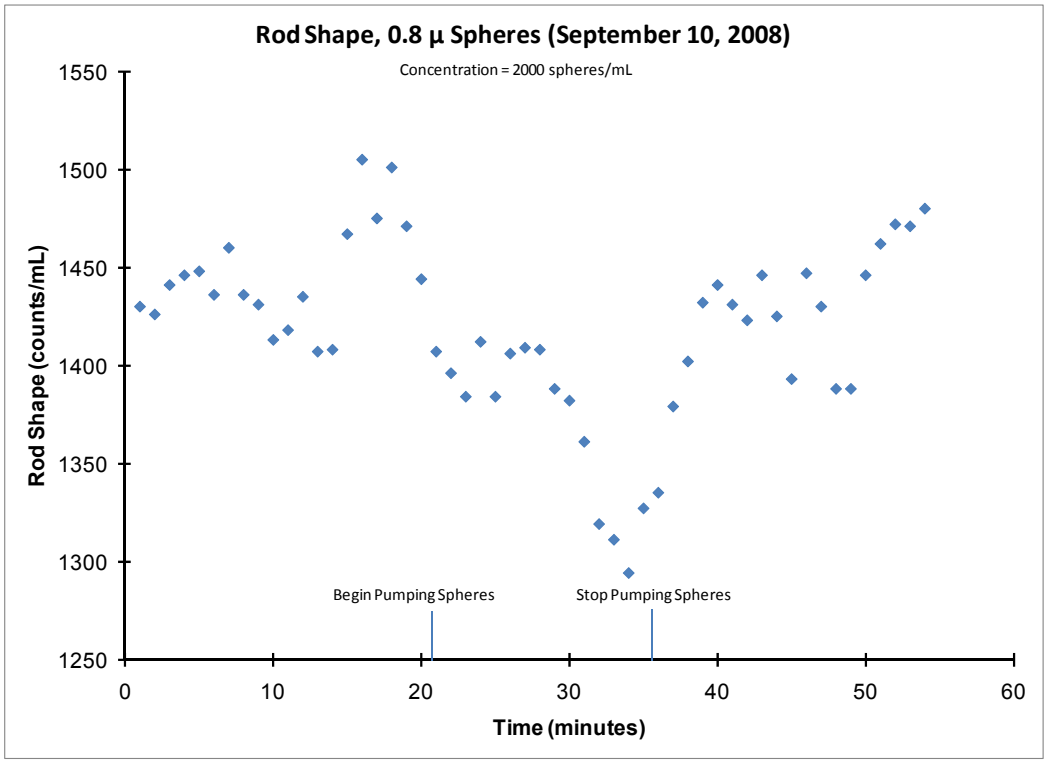

Figure 99. 0.8µ Spheres Rod Graph for 2000 spheres/ml

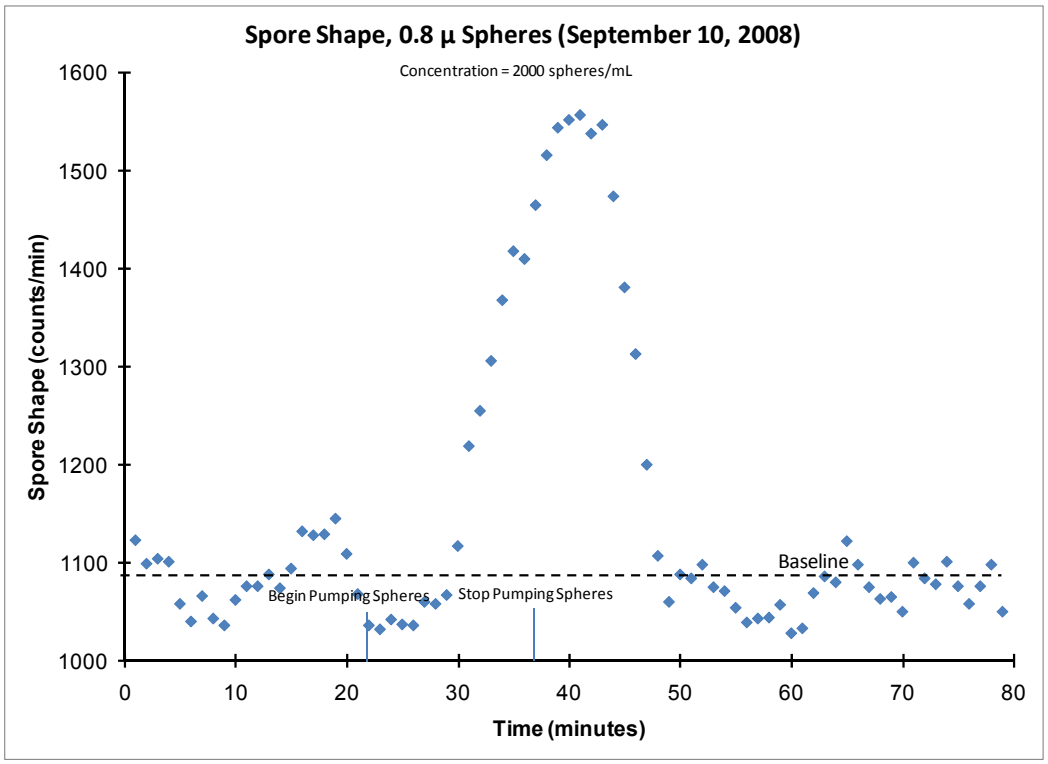

Figure 100. 0.8µ Spheres Spore Graph for 2000 spheres/ml

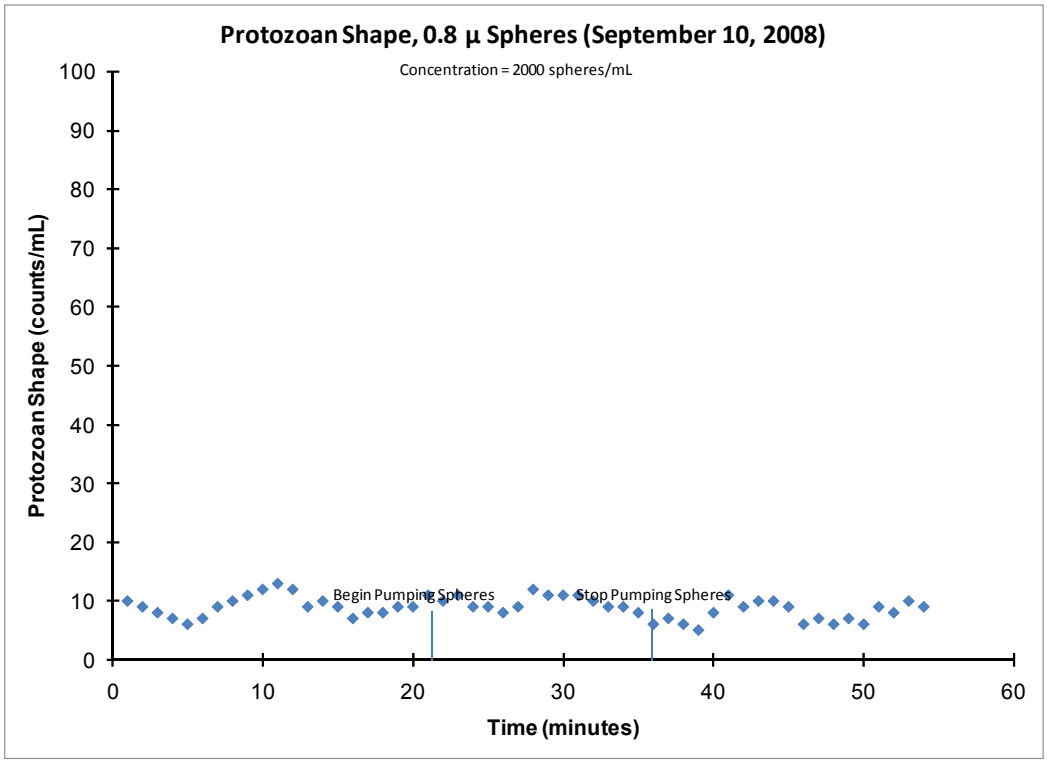

Figure 101. 0.8µ Spheres Protozoan Graph for 2000 spheres/ml

B.3 CRYPTOSPORIDIUM

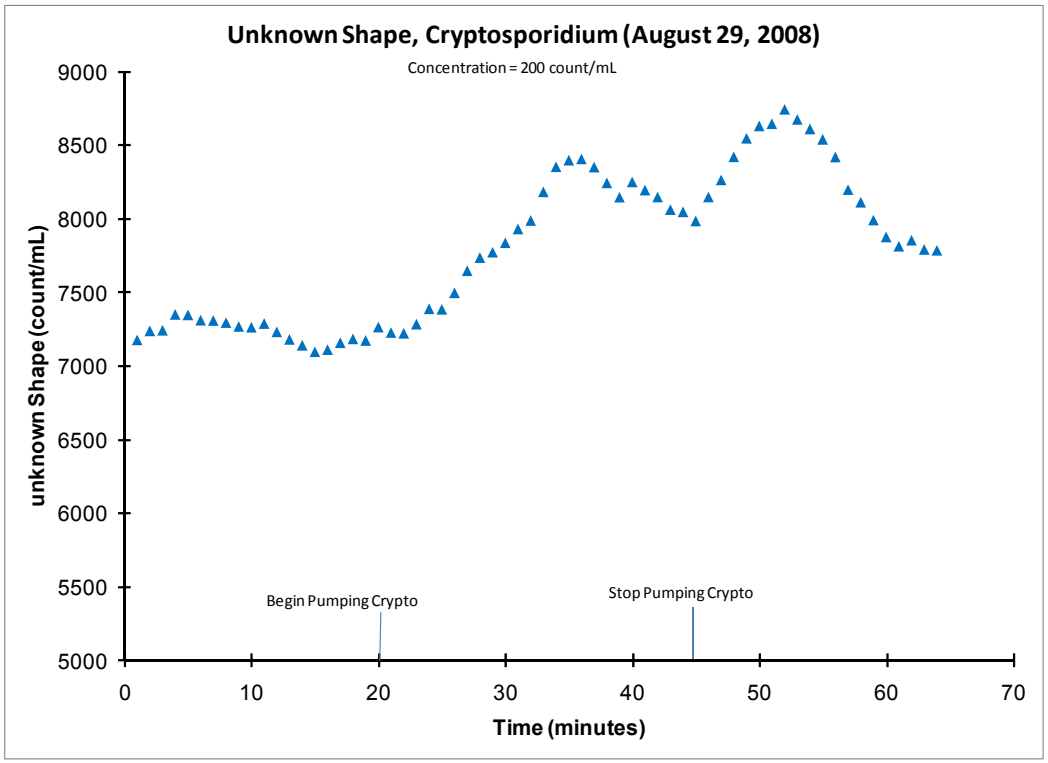

Figure 102. Cryptosporidium Unknown Graph for 200 crypto/ml

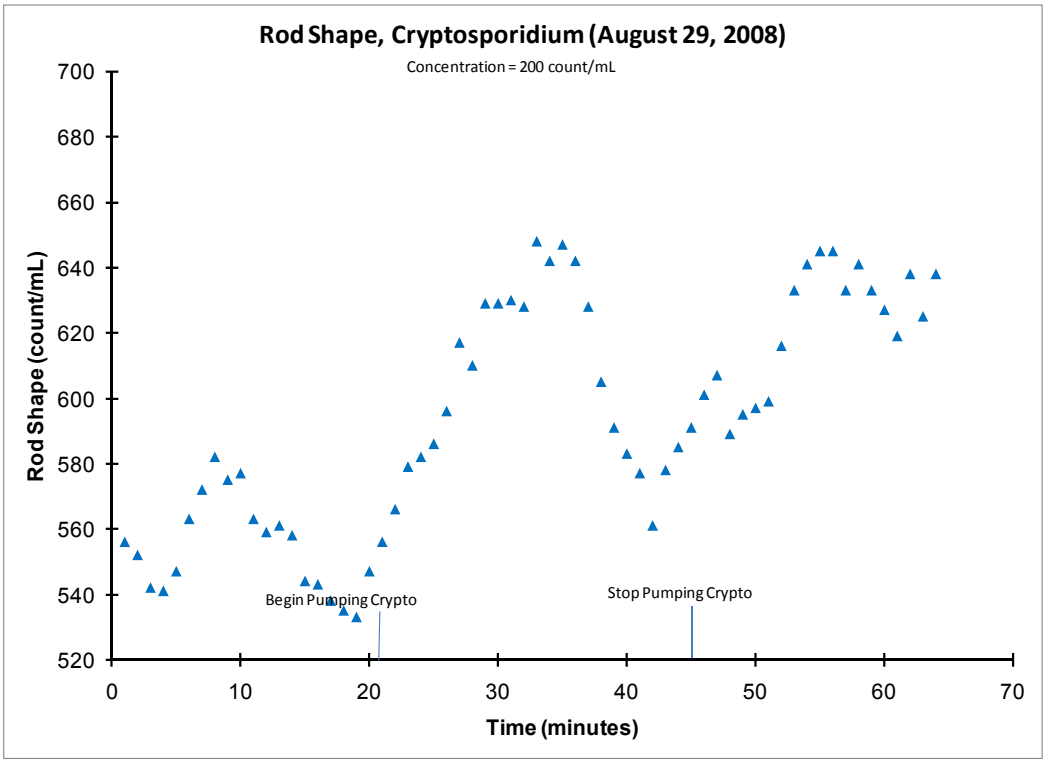

Figure 103. Cryptosporidium Rod Graph for 200 crypto/ml

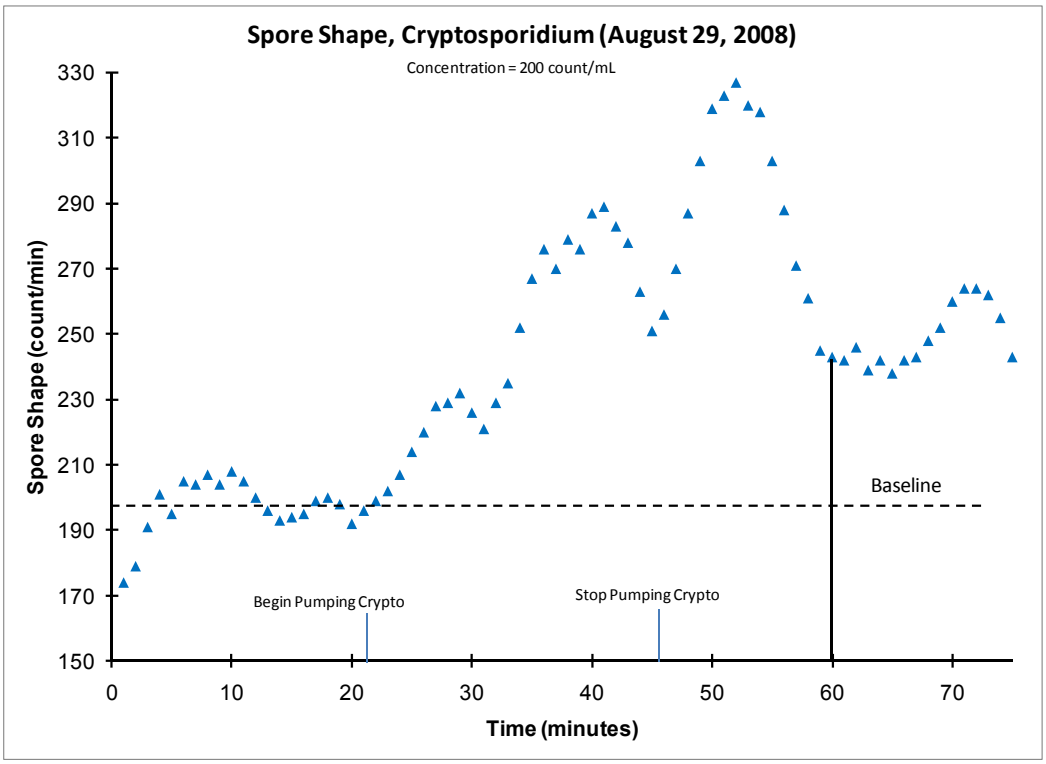

Figure 104. Cryptosporidium Spore Graph for 200 crypto/ml

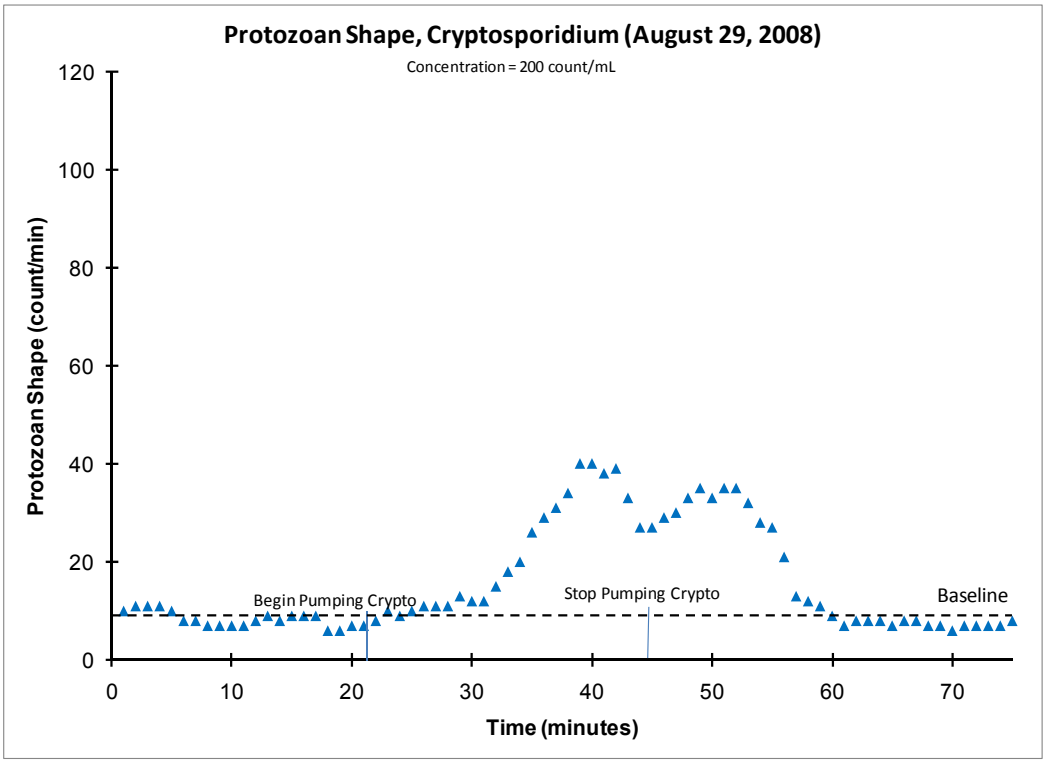

Figure 105. Cryptosporidium Protozoan Graph for 200 crypto/ml

B.4 GIARDIA LAMBLIA

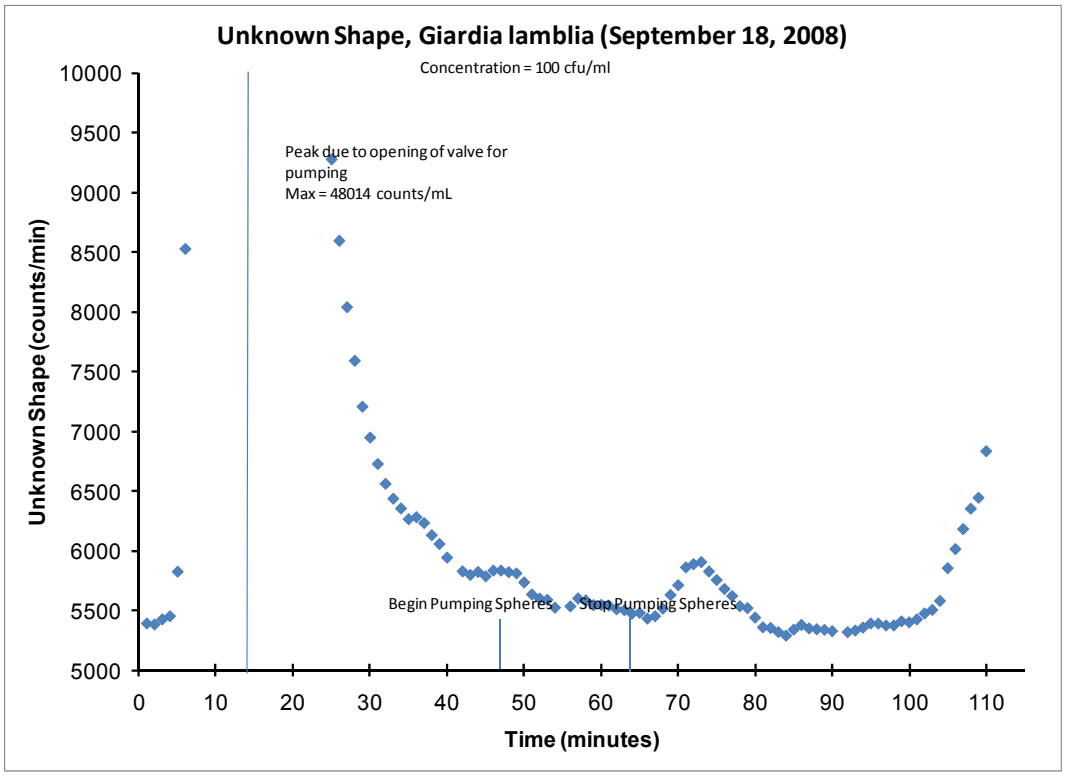

Figure 106. Giardia lamblia Unknown Graph for 100 cfu/ml

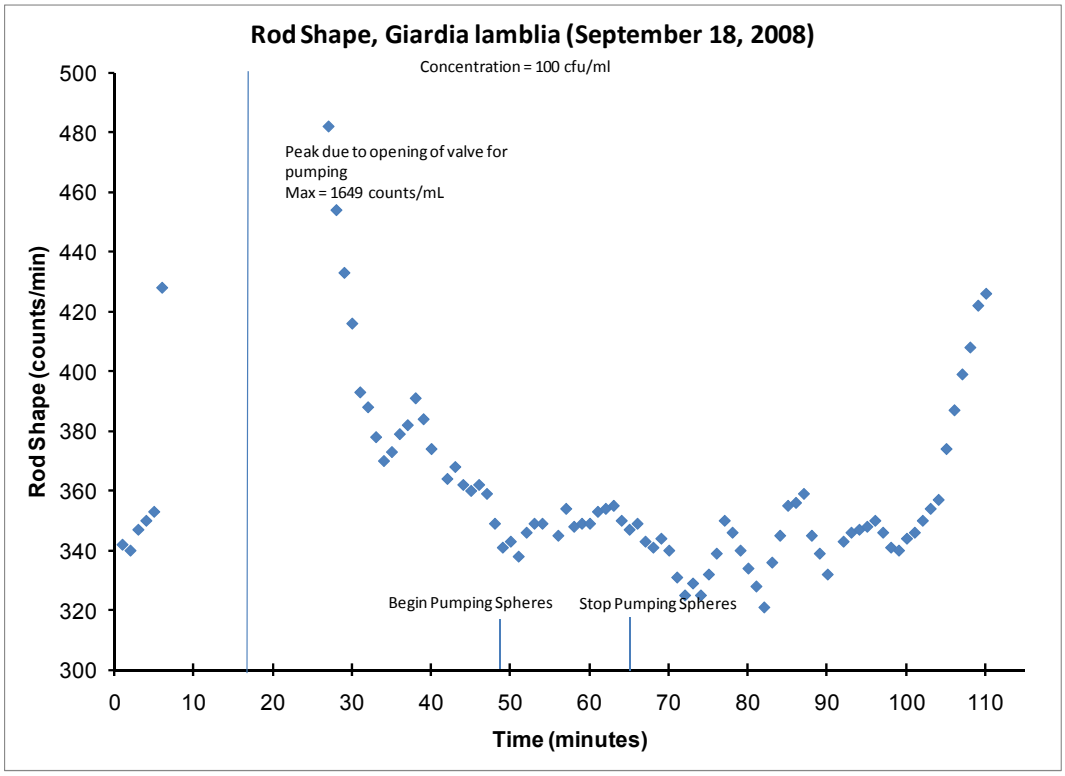

Figure 107. Giardia lamblia Rod Graph for 100 cfu/ml

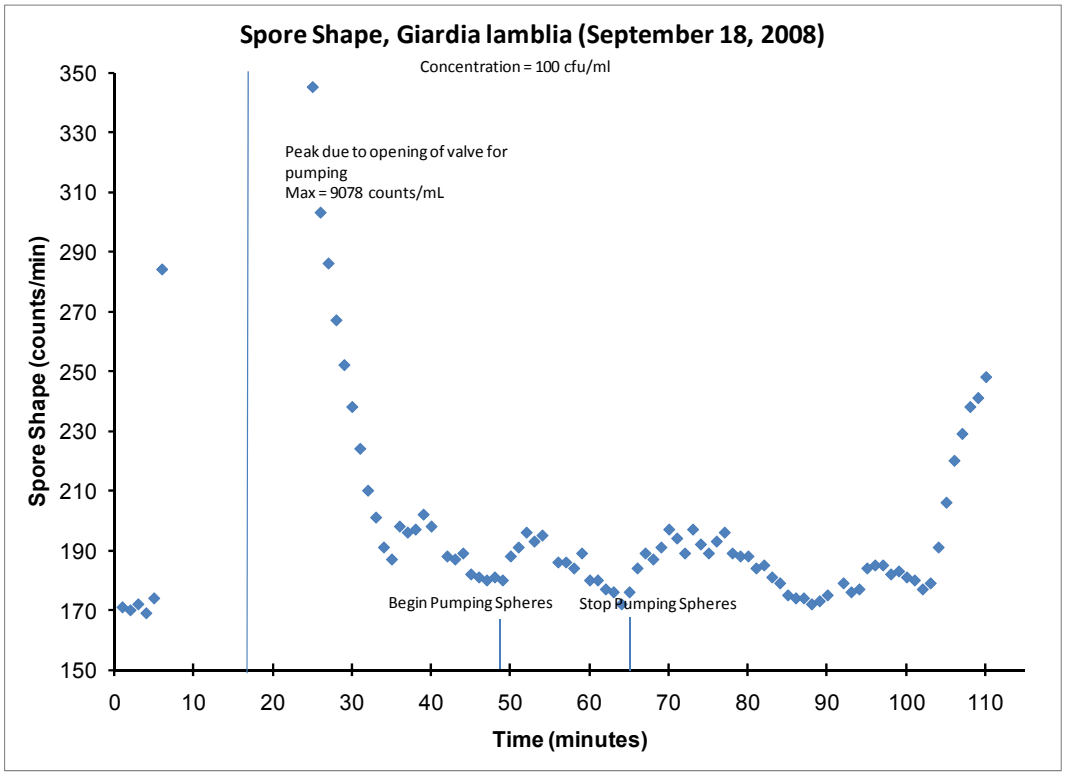

Figure 108. Giardia lamblia Spore Graph for 100 cfu/ml

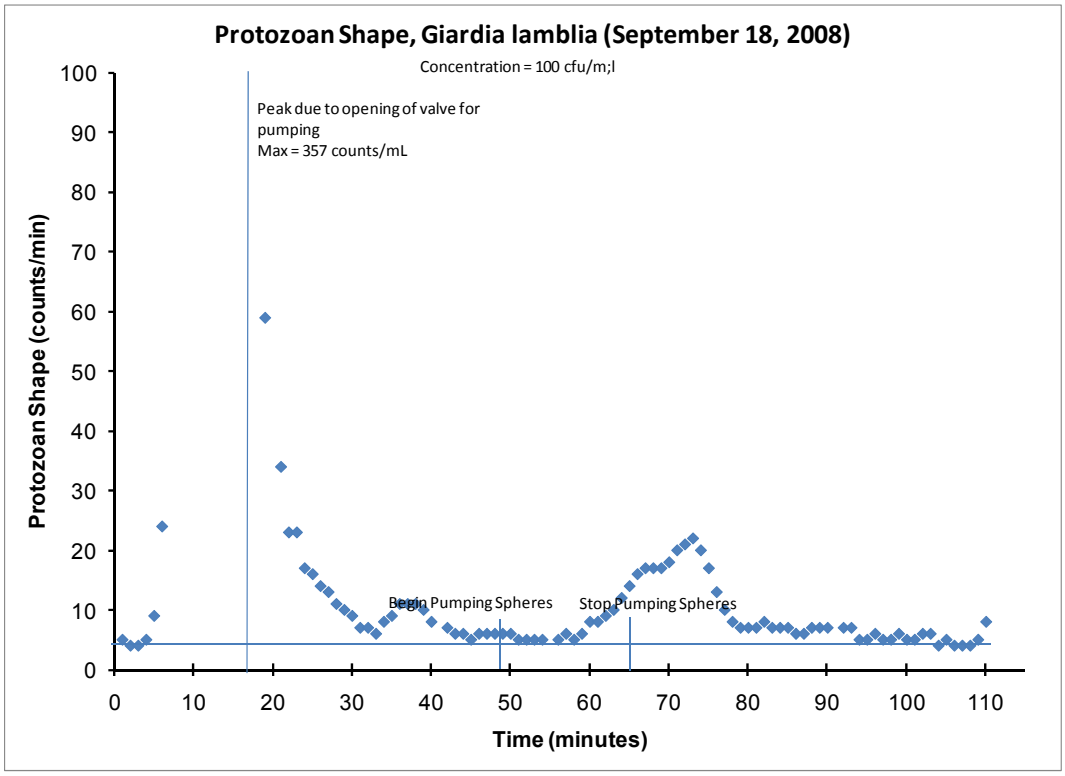

Figure 109. Giardia lamblia Protozoan Graph for 100 cfu/ml

B.5 ESCHERICHIA COLI

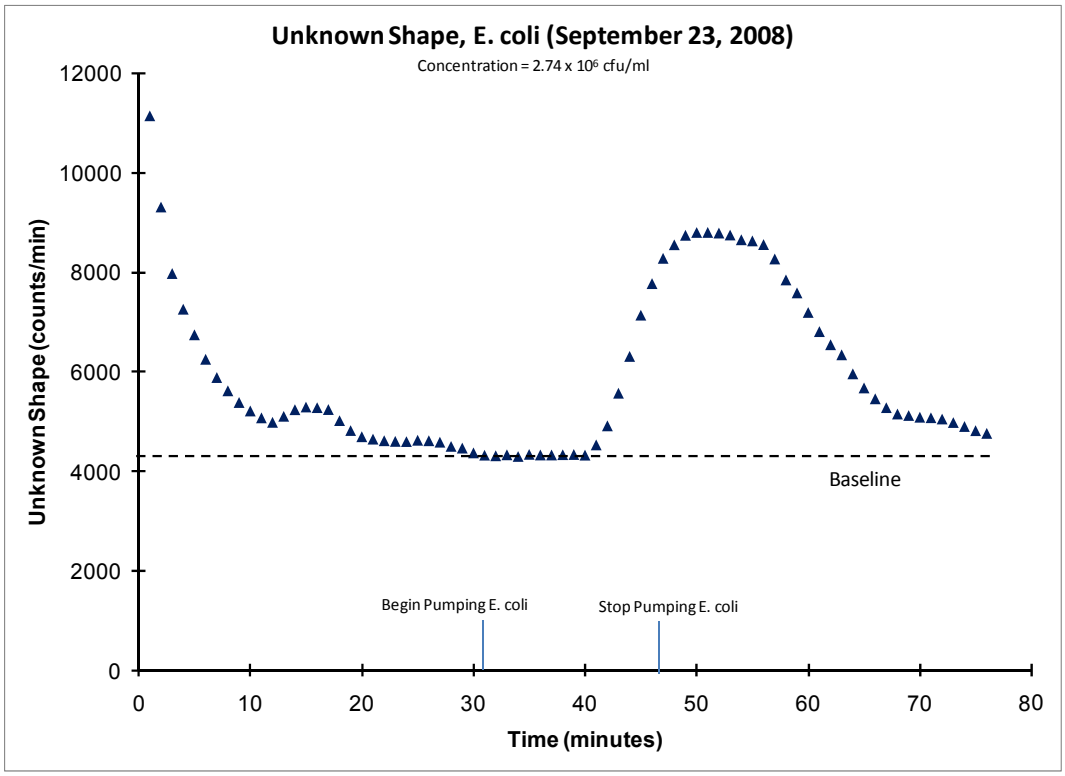

Figure 110. Escherichia coli Unknown Graph for 2.74 x10^6 cfu/ml

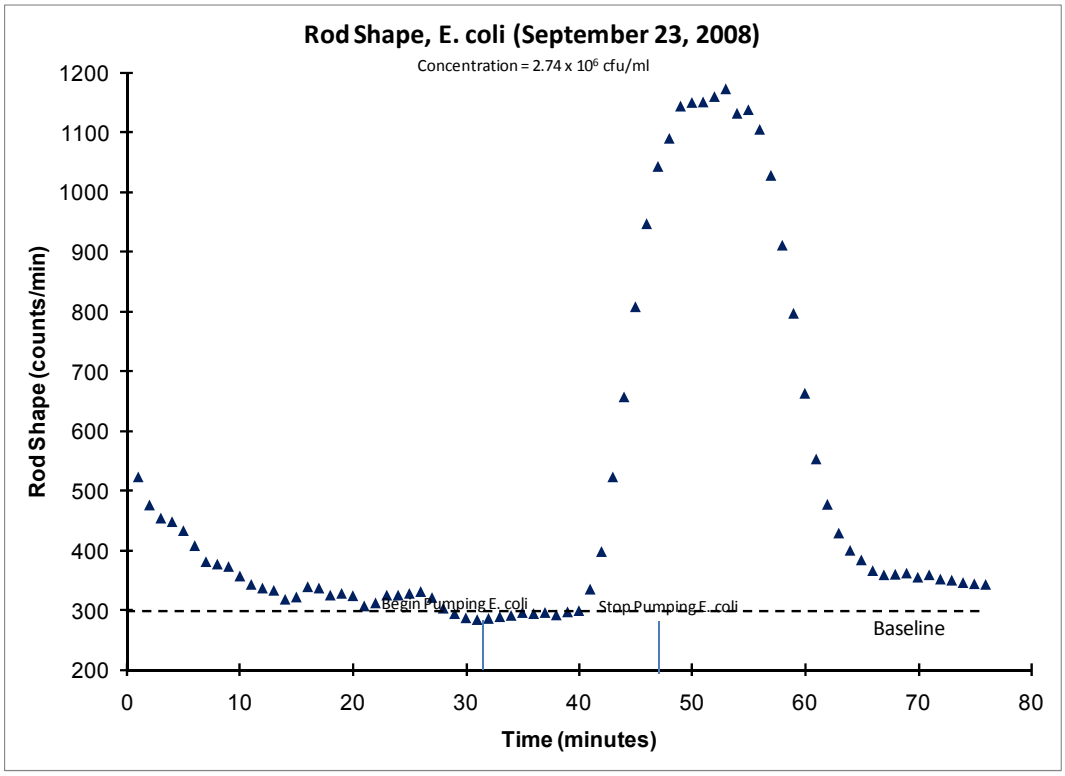

Figure 111. Escherichia coli Rod Graph for 2.74 x10^6 cfu/ml

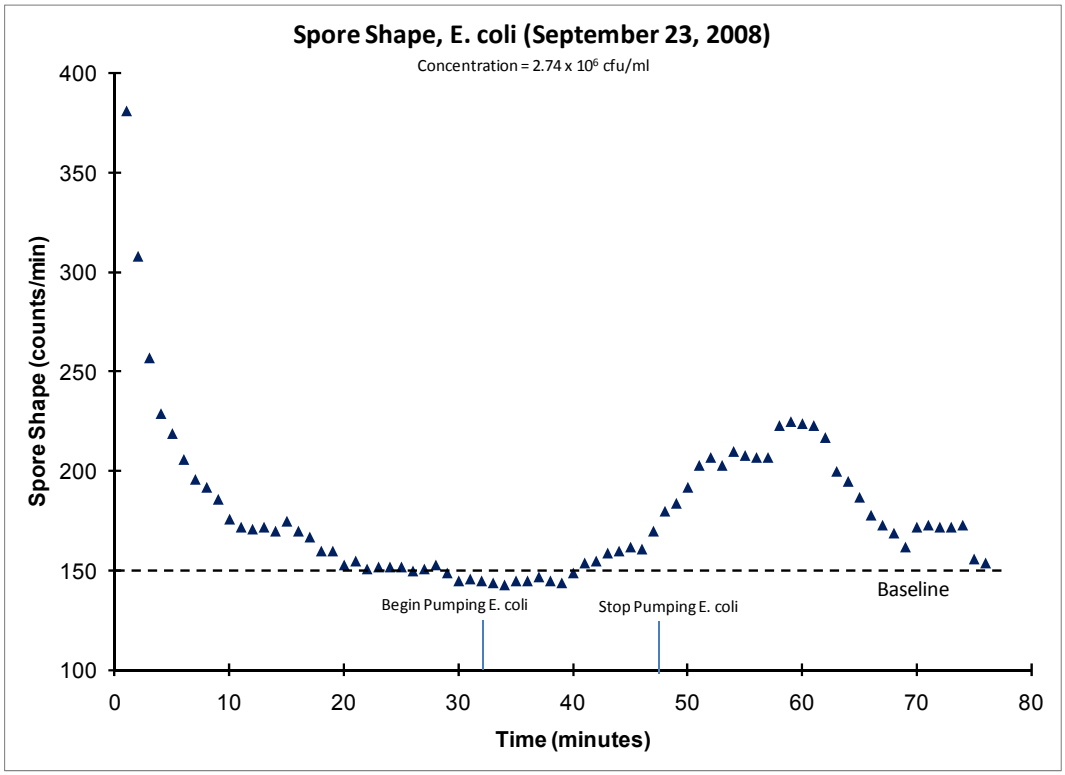

Figure 112. Escherichia coli Spore Graph for 2.74 x10^6 cfu/ml

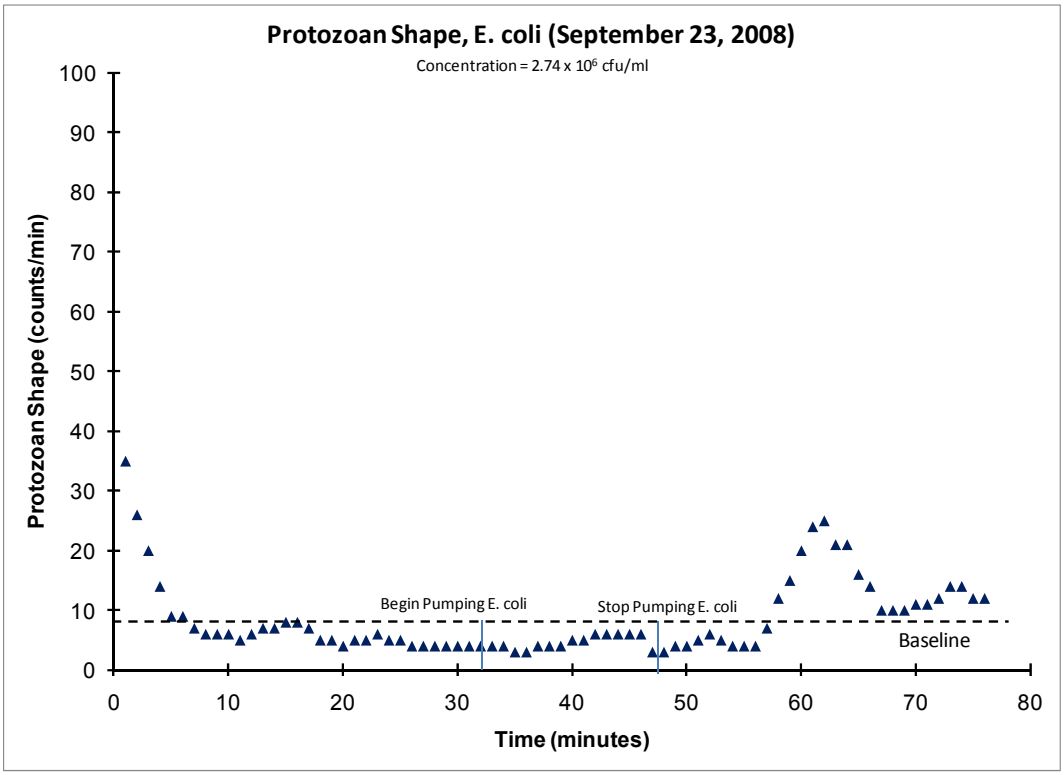

Figure 113. Escherichia coli Protozoan Graph for 2.74 x10^6 cfu/ml

B.6 BACILLUS ATROPHAEUS

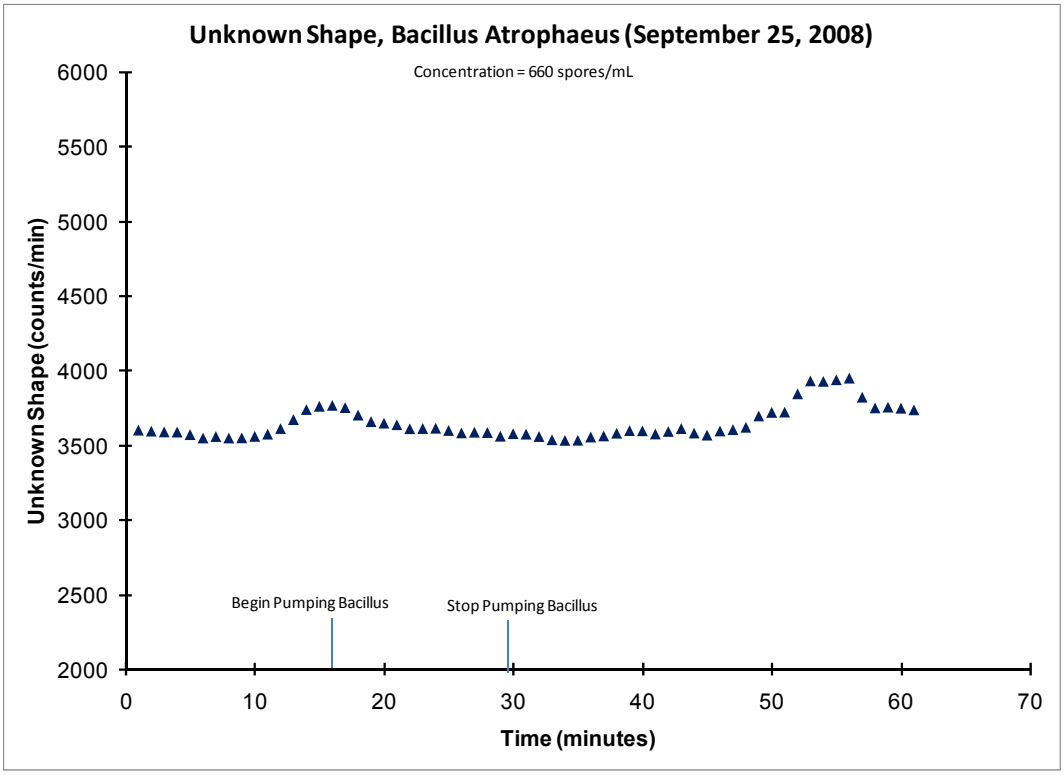

Figure 114. Bacillus atropaeus Unknown Graph for 660 count/ml

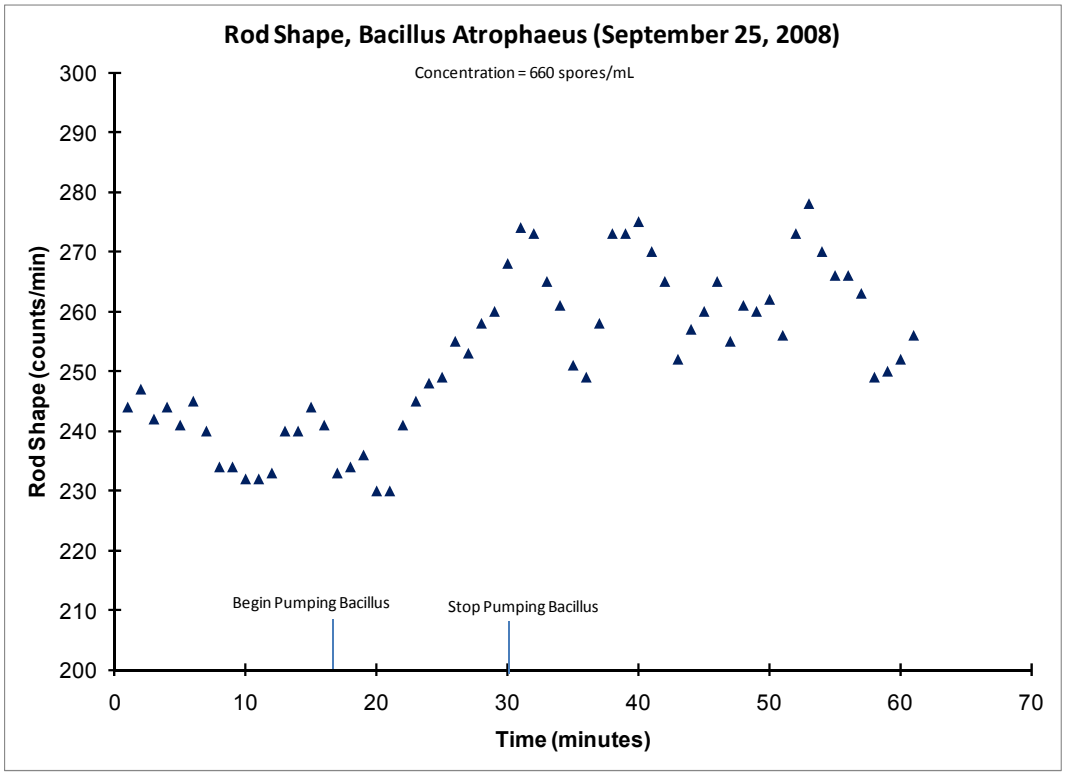

Figure 115. Bacillus atropaeus Rod Graph for 660 count/ml

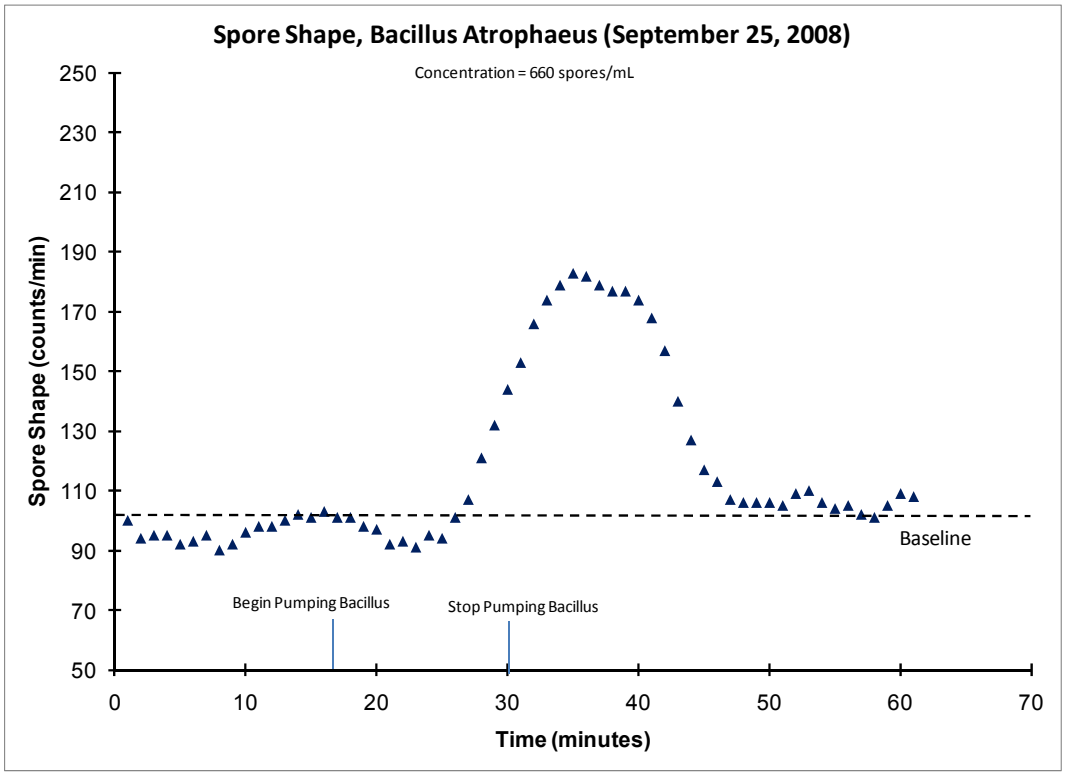

Figure 116. Bacillus atropaeus Spore Graph for 660 count/ml

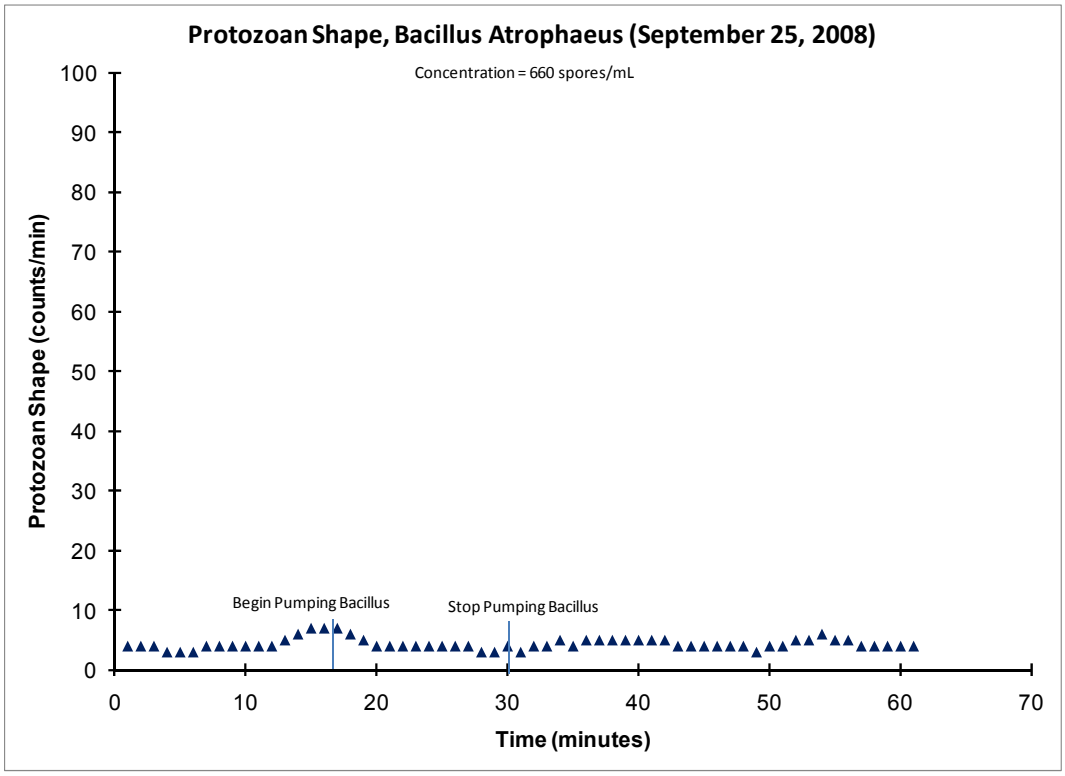

Figure 117. Bacillus atropaeus Protozoan Graph for 660 count/ml

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ABBREVIATIONS

AMSDIS	Automated Mass Spectral Deconvolution and Identification System		HSPD-9	Homeland Security Presidential Directive 9
CAS	Chemical Abstract Service		kg	kilograms
cfu	Colony Forming Units		L	Liter
CWS	Contamination Warning System		LC50	Lethal concentration where 50 percent of the test population dies
DBPs	Disinfection by-products		LD_{50}	Lethal Dose where 50 percent of the test population dies
DI	De-ionized		MALS	Multi-Angle Light Scattering
DO	Dissolved oxygen		MCL	Maximum contamination level
DPD	N, N-diethyl-p-phenylenediamine		mg	Milligram
DSS	Distribution system simulator		mgd	Million gallons per day
EHEC	Enterohemorrhagic *E. coli*		min	Minute
EIEC	Enteroinvasive E. coli		ml	milliliter
EPEC	Enteropathogenic E. coli		N	Normal
ETEC	Enterotoxigenic E. coli		NDIR	Non-dispersive infrared
ETV	Environmental Technology Verification		NIST	National Institute of Standards and Technology
g	Gram		NOM	Natural organic matter
GC-MS	Gas chromatography-mass spectrometry		NTU	Nephelometric turbidity units
GLS	Gas-liquid separator		NYCDEP	New York City Department of Environmental Protection
gpm	Gallons per minute		N	Normal
HFS	Fluorosilicic Acid		NDIR	Non-dispersive infrared
hr	Hour		NIST	National Institute of Standards and Technology

NOM	Natural organic matter		TIC	Total inorganic carbon
NTU	Nephelometric turbidity units		TOC	Total Organic Carbon
NYCDEP	New York City Department of Environmental Protection		USACEHR	US Army Center for Environmental Health Research
ORP	Oxygen reducing potential		USEPA	United State Environmental Protection Agency
PCR	Polymerase Chain Reaction		UV	Ultra violet
ppb	Part per billion		VOC	Volitile organic compounds
ppm	Part-per-million		WCIT	Water Contamination Information Tool
ppt	Part per trillion		µ	Micron
PWSA	Pittsburgh Water and Sewer Authority		µg	Micrograms
			µS/cm	Microsiemens per centimeter