

Detection of contamination in drinking water using fluorescence and light absorption based online sensors



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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of federal environmental laws, the Agency strives to formulate and implement actions leading to a balance between human activity and the ability of natural systems to support and nurture life. To meet this mandate, the Agency's Office of Research and Development provides data and scientific support needed to solve environmental problems and to build the scientific knowledge base needed to manage our resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks.

In September 2002, the Agency announced the formation of the National Homeland Security Research Center (NHSRC), which is part of the Office of Research and Development's Homeland Security Research Program. Guided by a roadmap set forth in the Agency's *Homeland Security Strategy*, NHSRC researchers manage, coordinate, support, and conduct research and provide technical assistance. The research is designed to provide appropriate, affordable, effective, and validated technologies and methods to address risks posed by chemical, biological, and radiological terrorist attacks. The EPA Homeland Security Research Program's water security research includes prevention, protection, detection, containment, treatment, and decontamination. Additional information on the program and its research products can be found at <http://www.epa.gov/nhsrc>.

Abbreviations and Acronyms

ADF	Airplane De-icer Fluid
ATCC	American Type Culture Collection
cfu	Colony Forming Unit
Ct	Concentration of Disinfectant Multiplied by Contact Time
CWA	Chemical Warfare Agent
DPD	N,N-diethylphenylenediamine
DSS	Distribution System Simulator
EPA	United States Environmental Protection Agency
FU	Fluorescence Units
HSPD	Homeland Security Presidential Directive
GCWW	Greater Cincinnati Water Works
gpm	Gallons per Minute
LED	Light Emitting Diode
NHSRC	National Homeland Security Research Center
NTU	Nephelometric Turbidity Units
ORP	Oxidation-Reduction Potential
PVC	Polyvinyl Chloride
RFU	Relative Fluorescence Units
S/N	Signal-to-Noise Ratio
T&E	Test and Evaluation
TOC	Total Organic Carbon
UV ₂₅₄	Ultraviolet Light at 254 nm Wavelength
UVAS _{sc}	Hach Ultraviolet Light Absorbance/Transmittance Sensor
UV-Vis	Ultraviolet and Visible light wavelengths
WIPD	Water Infrastructure Protection Division
WRF	Water Research Foundation (formerly known as American Water Works Association Research Foundation)
YSI	Yellow Springs Instruments (6920 Multi parameter sonde water quality logging system)

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Introduction

After the events of September 11, 2001, improving the security of our nation's water infrastructure became a priority. Research on water quality monitoring for drinking water distribution systems has increased in scope and importance. Homeland Security Presidential Directive 7 (HSPD-7), issued on December 17, 2003, established a national policy for federal departments and agencies to identify and prioritize the United States critical infrastructure and to protect the infrastructure from terrorist attacks. HSPD-9, issued on January 30, 2004, directed U.S. Environmental Protection Agency (EPA) to "develop robust, comprehensive, and fully coordinated surveillance and monitoring systems that provide early detection and awareness of disease, pest, or poisonous agents." EPA now plays a critical role as the lead federal agency for water security. In 2005, EPA released the peer-reviewed *Water Security Research and Technical Support Action Plan* [1], which identified high priority water security data gaps and outlined research and technical support projects to address these gaps. The technical support and action plan also identified research products that would summarize data and discuss how this data enhanced the

security of drinking water and wastewater systems.

The EPA's National Homeland Security Research Center's (NHSRC) team of scientists and engineers is dedicated to understanding the terrorist threat, communicating the risks, and mitigating the environmental impacts of attacks. The NHSRC's Water Infrastructure Protection Division (WIPD) performs research on contaminant detection, containment, mitigation, and decontamination in drinking water systems. This document focuses on fluorescence and light absorption based detection technologies that could be used to detect a contamination event within a water distribution system.

EPA has tested several sensors that relied on optical principles of operation in previous research at the Test and Evaluation (T&E) Facility. However, the past work was focused on measuring contaminant absorption of ultraviolet (UV) light alone, or UV-visible (UV-Vis) light as a surrogate measurement of total organic carbon (TOC), or on measuring turbidity changes due to contamination using optical devices [2-4]. Fluorometry is a mature technology and has

been used extensively for the detection of hydrocarbons in the oil and gas industry and for the detection of algae in source water. This established track record and the recent advances in light emitting diode (LED) technology, which can substantially lower the overall cost of ownership for these devices, prompted water security stakeholders and drinking water utility partners to propose this additional evaluation of online absorption and/or fluorescence-based monitoring devices for contaminant detection purposes. The fluorescent sensors were tested alongside conventional water quality monitors previously tested [5] at the Agency's Test and Evaluation (T&E) Facility in Cincinnati, Ohio.

Materials and Methods

Single Pass Pipe System

The drinking water distribution system simulator (DSS) used in this study has been described previously [4, 6]. A drinking water distribution pipe was represented using a once-through (or single pass) pipe. The pipe consists of 1,200 feet of 3-inch diameter fiberglass lined ductile iron. Experiments were conducted at 22 gallons per minute (gpm), which corresponds to an average velocity of 1 foot per second (ft/sec) in the pipe. This flow rate will produce turbulent flow (Reynolds number approximately 26,000) in the relatively smooth pipe. Although the pipe is lined with fiberglass, sections have chipped away, exposing ductile iron. These sections were heavily corroded and were more representative of an iron drinking water pipe than the lined sections. Note that English standard units, commonly used by the U.S. water utility personnel, have been used throughout this report. For example, volume is reported in U.S. gallons and velocity in feet per second (ft/s). However, in keeping with industry usage, contaminant concentrations are reported in metric units, in milligrams per liter (mg/L).

Chlorinated tap water was introduced directly from the Greater Cincinnati Water Works (GCWW) distribution system into a 750 gallon storage tank from where it was fed by gravity into the 3-inch pipe system. An air gap was maintained between the GCWW system and this experimental setup to ensure that there was no back flushing of the injected contaminant. Free chlorine was generally 1.0 ± 0.1 mg/L, with temperature ranging from 10° to 30° C depending upon the season. Turbidity was 0.1 nephelometric turbidity units (NTU) or less throughout the year. The water fed from the 750 gallon overhead tank provided 10 to 12 pounds per square inch (psi) inside the pipe. Contaminant injections were performed for 20 minutes by injecting a 10 L mixture of contaminant and tap water at the rate of 0.5 L/min. Contaminant concentration in the pipe was varied by altering the amount of contaminant mixed in the 10 L volume. Control experiments were performed by injecting 10 L of tap water without the contaminant at the same injection rate.

Online Sensors

In order to cover a broad range of fluorometric sensors, two commercially available devices were chosen to represent

the low- and high-end of the cost and complexity spectrum. A Turner Designs (Turner Designs Hydrocarbon Instruments Inc., Fresno, California) online fluorometer (model TD1000C) with a single excitation and emission wavelength was utilized as an example of a relatively simple off-the-shelf fluorometric sensor. A multiple wavelength ZAPS LiquID™ unit (ZAPS Technologies Inc., Corvallis, Oregon) was used to represent a more complex instrument. Both instruments were inexpensive to operate and maintain (similar to the other optical sensors) but the capital cost of the ZAPS unit

was five times higher than the Turner sensor. However, the ZAPS unit also has the capability to perform absorbance measurements (i.e., spectrophotometry).

Sensors based on various detection principles are in continual operation at the T&E facility, and data were collected from them during testing of the fluorometric devices. Sensors used during testing, along with calibration procedures and principles of detection are summarized in Table 1, below.

Table 1: Sensors Used for Testing

Manufacturer	Parameter	Method Citation	Method Source	Reporting Units	Principle of Detection	Calibration Technique
YSI*	Specific conductance	2510 A	Standard methods[7]	mS/cm	4 nickel electrodes	1000 μ S/cm standard
YSI*	Oxidation-reduction potential	2580 A	Standard methods[7]	mV	Potentiometric, platinum electrode, Ag/AgCl reference electrode	Zobell solution, temperature-corrected, single point offset adjustment
YSI*	pH	150.1	EPA/600/4-79-020[8]	pH	Proton selective glass electrode (non-fouling version)	2-point - pH 7 and pH 10 buffers
YSI*	Temperature	170.1	EPA/600/4-79-020[8]	$^{\circ}$ C	Sintered metallic oxide thermistor	Not applicable
YSI*	Turbidity	180.1	EPA/600/4-79-020[8]	NTU	Nephelometric signal 860 nm LED (90 degrees) with integral wiper	2-point: zero and 20 NTU formazin
Hach® CL17	Free chlorine	4500-Cl G	Standard methods[7]	mg/L	Hach CL17 (DPD reaction) colorimetric	Factory calibrated
Hach CL10	Free chlorine	334.0	EPA/815/B/09/013[9]		Amperometric sensor with Cl ₂ permeable membrane (0- to 20-ppm)	Set to known value based on Hach DR2010 DPD colorimetric method
Hach	UVAS sc	DIN 38404 C3 and Standard Methods #5910	German Institute of Standardization and Standard Methods	UVA m ⁻¹	UV absorption measurement (2-beam technique), reagent-free. Determines the Spectral Absorption Coefficient (SAC) at 254 nm	Optical Filter - Lambda M 254 nm; Lambda R 550 nm
Hach Astro Model 4195/1030	TOC	415.1	EPA/600/4-79/020[8]	mg/L	UV-persulfate oxidation method coupled with the NDIR CO ₂ detection	25 ppm span calibration with Hach certified KHP. Zero calibration with Hach certified zero TOC standard. NDIR calibration

Manufacturer	Parameter	Method Citation	Method Source	Reporting Units	Principle of Detection	Calibration Technique
						with certified CO ₂ standards in nitrogen balance.
GE/Sieve rs On-line 900 Series Model 5310C	TOC	415.3	EPA/600/R-09/122 [10]	mg/L	UV-persulfate oxidation method coupled with conductometric detection of CO ₂	Single point calibration with KHP at 5 ppm with a single point sucrose verification at 2 ppm. Also required is a check of the inorganic carbon remover with Na ₂ CO ₃ .
RealUV2 54 (Hi-Pure) M4000	UV ₂₅₄	Standard Methods #5910	Standard Methods[7]	UVA m ⁻¹	UV absorption measurement (with anti drift compensation), reagent-free. Determines the spectral absorption coefficient (SAC) at 254 nm	Set to known water absorption at 254 nm
Turner Designs Hydrocarbon Instruments TD1000C , Oil in Water Monitor	fluorescence	No standard method	Not applicable	Relative fluorescence units (RFU)	Fluorescent hydrocarbons light absorption and emission. (ppm - ppb range)	Calibrated with a fluorescent dye to the oil equivalent of #6 fuel oil at 11.5 ppm
ZAPS LiquID Station **	carbon	Not specified	Not specified	Carbon Indicator (counts) Tryptophan (mg/L) UVA (m ⁻¹)	UV-Vis absorption, fluorescence and reflectance measurements	Factory calibration

Manufacturers' locations: GE Analytical Instruments, Boulder, Colorado; Hach Co., Loveland, Colorado; Real Tech Inc., Whitby, ON, Canada; Turner Designs (Fresno, California); YSI Inc., Yellow Springs, Ohio, ZAPS Technologies, Corvallis, Oregon

Acronyms: SAC, spectral absorption coefficient; TOC, total organic carbon; UV-Vis, ultraviolet and visible light wavelength

*YSI is the model 6920DW multi parameter sonde

** See specification sheet from ZAPS for other channel units at <http://www.zapstechnologies.com/wp-content/uploads/2012/05/LiquID-2012-Product-Brochure.pdf>

Contaminants

Contaminants were selected based on their widespread use by businesses, industry, and individuals, as well as input from the sensor manufacturers. Except for *Escherichia. coli* and sodium thiosulfate, there has been little online detection data available for these contaminants prior to this study.

Airplane De-icer/Antifreeze: The ZAPS device has been used to detect airplane de-icer in runoff form airports. Accordingly, used airplane de-icer fluid was obtained from the Lunken airport (Cincinnati, OH) ground crew. The composition of the used de-icer was reported to be 60% propylene glycol and 40% water. Another commercial off-the-shelf antifreeze product (Prestone®, Prestone Products Corp., Danbury, Connecticut) containing ethylene glycol and diethylene glycol was also utilized. Finally, solutions of laboratory grade (99.8+%) ethylene glycol (Fisher Scientific, Thermo Fisher Scientific Inc., Waltham, Massachusetts) were investigated.

Herbicide: Basagran® herbicide (44% benazeton) (Southern Agricultural Insecticides, Inc., Palmetto, Florida) is a sedge-control herbicide. It was chosen since it represents the herbicide class of

chemicals. It also has a fluorescence emission wavelength similar to fuel oil #2 and the Turner device was calibrated to detect fuel oil #2. The ZAPS unit was not available during the Basagran herbicide injections.

Chlorine Bleach: Injection of chlorine bleach (Sno-Glo 10% Bleach, Brenntag Mid-South, Mulheim an der Ruhr, Germany) into the piping is meant to represent an increased level of free chlorine in a drinking water distribution system, similar to a decontamination scenario or accidental overdosing of chlorine.

Dechlorination Chemical: Sodium thiosulfate (ACS grade, 99+%, Fisher Scientific) is a common dechlorination chemical.

Biological agent: *E. coli* strain K-12 (ATCC™ 25204) represented a vegetative biological agent. *E. coli* cultures contain tryptophan, which has fluorescent properties and may be detectable by the ZAPS or Turner devices. *E. coli* would be quickly inactivated by free chlorine in the tap water flowing through the DSS; it could not be repeatedly injected and quantified without dechlorination. Thus, *E. coli* was always

injected with free chlorine. Sodium thiosulfate, described above, was chosen for dechlorination.

Diesel Fuel: Diesel fuel is an automotive fuel and was obtained from a local Sunoco® gas station in April 2011. The Turner equipment is used to detect hydrocarbons within the diesel fuel and the dispersant described below.

Dispersant: Polychem DISPERSIT® dispersant (U.S. Polychemical Corp., Chestnut Ridge, New York) was used as a model oil dispersant. The composition is proprietary, but it contains emulsifiers, dispersants and water soluble coupling solvents. Large amounts of dispersant could be used in an oil spill remediation and present a crossover hazard from source water to drinking water.

Toxin Surrogate: Pepsin dry powder (Acros Chemicals) was chosen as a surrogate for ricin because both have similar tryptophan contents.

Data Analysis

Sensor response to contamination was evaluated by calculating the change of the sensor output signal from a stable baseline

to the peak value recorded as the contaminant passed the sensor. Baseline values were calculated by averaging the sensor signal over a one-hour period before contaminant injection, with baseline noise represented by standard deviation. Absolute change was calculated as the difference between the peak sensor value recorded during contamination and the stable baseline value. Percent change was calculated by dividing the absolute change by baseline value and multiplying by 100. Calculating percent change yields the system specific response of water quality parameters to each contaminant; note that the same absolute change will yield different percent changes in drinking water systems with different baseline water quality values. Sensor response was also characterized as a signal-to-noise ratio (S/N). The absolute change recorded during injection was normalized by the baseline standard deviation. The S/N ratio accounts for baseline variation before contaminant injection.

Sensor response values provide metrics of sensor change after contamination, but whether sensor changes constitute a detection of the contaminant depends on how detection is defined. Often, the definition of detection will be drinking water

system specific and will depend on whether an event detection algorithm is used or if system-derived detection thresholds are determined. In practice, some degree of subjective data interpretation must be performed to define a detection threshold. In this report, the study contributors determined detection thresholds by manually examining sensor changes and, based on their experience with on-line sensor changes that have indicated contamination [4, 11], judging whether the change was large enough relative to the baseline to detect the contaminant. The detection thresholds are summarized in Table A1 (Appendix 1). A contaminant was considered detected if the absolute change, percent change, and S/N thresholds were surpassed. It is important to note that although these detection thresholds were determined by the contributors to this study; others could come to different conclusions.

Sensors were polled two every minutes during test runs, so 30 pre-injection data points were used to determine baseline mean and standard deviation. Contamination injections were performed in duplicate, and results are presented as the average of those duplicates. The time period when the injected contaminant was in contact with the

sensors was determined based on the flow rate and injection duration, and was confirmed through dye injections. Injections were 20 minutes long and flow velocity was 1 ft/sec, so the injection reached the 80 ft sampling point in 1.3 minutes after injection and continued passing the sensors for 20 minutes. Sensors typically responded to contamination 3-4 minutes after injection due to the time it takes water to travel from the sampling point to the sensor manifold. Sensor responses usually lasted longer than 20 minutes at this station due to dispersion, which elongated the contaminant plume in the pipe. Peak sensor responses were recorded from the time periods when the contaminants were in contact with the sensors.

Although water quality sensors typically respond within seconds of water quality change, the Hach CL17 and TOC analyzers had run cycles of 2.5 and 8 minutes, respectively. These instruments were polled every two minutes, but only returned new values at the end of their cycles. Still, new values were returned frequently enough that the changes in water quality were seen for both devices while the contaminant was passing the sampling point.

Results and Discussion

Table 2 (located at the end of the report) summarizes the detection test results in terms of whether the contaminant was detected or not. As discussed in the Materials and Methods section, detection of contamination is determined by calculations of absolute change, percent change and S/N, and whether all three values surpass detection thresholds. The detection threshold values that define detection of contamination are in Table A1. The results of absolute change, percent change and S/N are included in Tables A2-A4 in the appendices.

Online Water Quality Sensors Detection

As determined in past studies, free chlorine and TOC are the most effective widely used online water quality parameters for detection of contamination [4, 5, 11-13].

Antifreeze/ethylene glycol, de-icer, dispersant, pepsin, and Basagran herbicide all have organic components and were detected by online TOC analyzers. Diesel fuel was not introduced into the TOC analyzers since it would have permanently contaminated their complex plumbing systems. Diesel fuel is organic, but it is not miscible with water, so whether the TOC analyzers would have detected it is

uncertain. The Sievers and Hach Astro TOC analyzers detected the same contaminants at the same concentration except for Basagran herbicide at 1 mg/l, which the Hach unit did not detect. The Sievers and Hach TOC analyzers both detected absolute changes of 0.41 and 0.44 mg/L and percent changes of 57.5 and 73.2, respectively. The main difference was in S/N, which was 74.8 and 7.0 for the Sievers and Hach units, respectively. The difference comes from noise in the baseline of the Hach unit.

As expected, the free chlorine analyzer values increased when chlorine bleach was injected at 5 mg/L. Dispersant, pepsin, and Basagran herbicide have organic components that react with free chlorine to lower the free chlorine levels in the water flowing through the DSS. Thiosulfate is a common dechlorinating agent and reduced free chlorine to zero when injected at 9 mg/L. *E. coli* co-injected with 9 mg/L thiosulfate also reduced free chlorine to zero. This reduction was due to the thiosulfate and not *E. coli*. Previous work established that *E. coli* and *Bacillus* spores were not detected by free chlorine or TOC sensors at 10^3 - 10^4 colony forming units (cfu)/ml, and that more sophisticated online

sensors were required to detect biological agents at these levels [4].

The only discrepancy between the Hach CL17 and Hach CL10 analyzers' capabilities was with Basagran herbicide. The Hach CL17 detects free chlorine through a color change reaction between free chlorine and N,N-diethylphenylenediamine (DPD), and is an online version of the laboratory method. The CL17 signal did not decrease when Basagran herbicide was injected. The Hach CL10 analyzer is an amperometric electrochemical sensor, and its output signal did decrease when Basagran herbicide was injected. The Basagran solution (either benazon or other ingredients) may have interfered with the CL10 sensor and gave the appearance of free chlorine changing even though it did not. Even though this is not a true free chlorine change, it is interesting to note that the presence of Basagran herbicide can be detected with an amperometric free chlorine sensor.

The remaining online water quality sensors did not detect the wide range of contaminants that free chlorine and TOC parameters indicated, which is consistent with past research [4, 5, 11-14]. Specific

conductivity increased when bleach and sodium thiosulfate were injected due to the high concentration of ions in these solutions. The oxidation-reduction potential (ORP) decreases when free chlorine decreases since the oxidation potential of the water decreases. Thiosulfate with and without *E. coli* depleted the free chlorine in the tap water, which was enough of a change to trigger a detection with ORP. Bleach increased free chlorine, and pepsin and dispersant reacts with and decreases free chlorine, but not enough to detect either with ORP. The pH increased when bleach was injected since chlorine bleach typically has a pH between 11.0-11.5.

Turbidity sensors were effective at detecting de-icer, diesel fuel, dispersant and pepsin. The used de-icer fluid has particulate matter which contributed to the turbidity increase. Diesel fuel does not dissolve in water and turbidity increased due to the bubbles and drops of diesel circulating in the water column.

UV-Vis Spectrophotometric Sensor Detection

The same contaminants were detected by the Real UVT and the Hach UVAS sensors, and each sensor detected the same

concentrations. Results were the same for the UV₂₅₄ absorption channel on the ZAPS, except for dispersant at 1 mg/L. Antifreeze (commercial Prestone®) was detected at 10 mg/L, but ethylene glycol, which is a component of commercial antifreeze products, was not detected, suggesting another component in the commercial product is responsible for the detection. According to the MSDS, the other component of Prestone antifreeze is diethylene glycol [15]. Thus, the detection observed by devices utilizing UV light absorption at 254 nm may have come from diethylene glycol or perhaps a dye added to the formulation. Bleach was also detected by both sensors. Hypochlorous acid and hypochlorite ion have UV absorption peaks at 236 and 292 nm, but enough absorption occurs at 254 nm for detection to take place. Similarly, dispersant, thiosulfate, *E. coli*/thiosulfate, pepsin, and Basagran herbicide also have sufficient absorption at 254 nm to be detected. De-icer fluid and diesel fuel did not exhibit sufficient absorption at 254 nm at the concentration used in this study to be detected.

UV₂₅₄ and UV-Vis (ultraviolet and visible light wavelength) sensors have been examined as possible replacements for TOC

analyzers in water security applications. One study showed that UV based sensors detected five out of sixteen contaminants (inorganic, culture media, organics), while traditional online TOC analyzers detected ten out of sixteen [16]. Fewer contaminants are detected since some organic compounds do not have an absorption peak at 254 nm or in the UV-Vis range. However, sensors based on light absorption are simpler in design and have significantly lower maintenance costs than online TOC analyzers.

In this study, UV₂₅₄ and TOC analyzers both detected Basagran herbicide, pepsin, dispersant and antifreeze. UV₂₅₄ sensors detected bleach because its components have absorption wavelengths, but it is inorganic so it is not detectable with TOC sensors. Airplane de-icer fluid (ADF) was detected using the TOC parameter since it has a large organic concentration. However, like antifreeze, a significant component of ADF is ethylene or propylene glycols, which do not have absorption peaks at 254 nm. Interestingly, the Real UVT, Hach UVAS and ZAPS-UVA channel sensors detected *E. coli* with 9 mg/L sodium thiosulfate present. It has been previously shown that UV-Vis and UV₂₅₄ sensors do not detect *E. coli* at

10^3 - 10^4 cfu/ml or the associated growth media, so sodium thiosulfate was being detected [3, 4]. However, *E. coli* will survive in disinfected tap water if the water is dechlorinated, and a common, effective dechlorinating agent is sodium thiosulfate. So, sensors based on light absorption may be an effective way to detect biological contamination that includes sodium thiosulfate, which is not the case for traditional online TOC analyzers.

Fluorometric Sensor Detection

Fluorescence was evaluated as a contaminant detection tool by using the Turner fluorometer and the ZAPS unit (tryptophan channel) in DSS contamination experiments. The Turner and ZAPS sensors were calibrated to detect fluorescence excitation emission wavelengths for fuel oil #2 and tryptophan, respectively. This is important to consider since neither of these units was calibrated to detect specific contaminants used in this study. In practice, calibrating a fluorometric (or UV-Vis) sensor to a specific contaminant may not be useful since there are numerous contaminants that could be introduced into a drinking water system and contaminant specific excitation and fluorescence wavelength may vary. The standard

fluorescence setup/configuration as provided by the vendor was used during testing.

Compared to TOC, free chlorine and UV₂₅₄ sensors, the fluorometric sensors detected fewer contaminants. This is somewhat expected as only a subset of the contaminants will fluoresce. However, fluorescence measurement is more specific than a simple absorption measurement, which can reduce signal-to-noise ratios. Dispersant, *E. coli* with thiosulfate, and thiosulfate alone were detected by both sensors at the same concentrations.

Basagran herbicide was detected by the Turner fluorometer, but the ZAPS instrument was not available for testing during these injections. The ZAPS unit detected diesel fuel and pepsin through the channel selected to detect the fluorescence from tryptophan. The ZAPS unit was not optimized for these contaminants, but the fluorescence response in the tryptophan channel was large enough to detect them.

Fluorescence has been used as a detection method for microbiological agents such as *E. coli* and *Bacillus* spores in previous research studies [17-19]. These studies were laboratory and field based experiments that used microbial concentrations that ranged

from 10^7 - 10^9 cfu/ml. This concentration range is likely higher than what would be experienced in a microbial contamination event in a drinking water system, which precludes the direct detection of these microorganisms. More advanced sensor-based technology needs to be developed that could detect contaminants as well as the various concentration levels of the microbial agents [20]. As noted, if thiosulfate were in a preparation of microbiological agents used for intention injection, the preparation could be detected because thiosulfate has UV absorption and fluorescence emission signals, which could be detected by fluorescence and UV based detectors.

A limited number of contaminants were detected via fluorescence in either the ZAPS or Turner units. The ZAPS device has numerous “channels” utilizing UV-Vis absorption, fluorescence and reflectance that can be used for detection. If multiple channels are used for contamination detection simultaneously, the number of detectable contaminants increases. Thus, if a UV₂₅₄ and carbon indicator channel had been included in these tests, all of the contaminants might have been detected except for de-icer. According to the manufacturer, the ZAPS unit has been used

to detect deicing fluid at airports [21]. The concentration was likely too low for detection in drinking water in the experiments described in this report, although variations in de-icing fluid composition, particularly the presence of dyes, may have influenced the results, too.

An alternative to utilizing multiple detection channels with different detection principles is utilizing more fluorescence emission wavelengths (note the Turner unit only utilizes one). Currently, the monitoring of specific excitation and emission wavelengths are the basis of detecting contamination using fluorescence-based sensor. Simultaneous detection with multiple absorption wavelengths in a UV-Vis sensor may also be beneficial. Further adoption of fluorescence based sensors for water security applications could require employing a single or several discrete wavelengths that are useful for detection and using inexpensive light emitting diodes (LED) as excitation source(s). Future research could include determining the key fluorescence emission wavelengths for priority contaminants, then assessing whether a manageable number of wavelengths could be used to detect a wide range of contaminants.

Costs

Capital and maintenance costs for online TOC, free chlorine, pH, ORP, conductivity and turbidity detectors are well documented [5]. The Real UVT sensor “as tested” capital cost was \$7,000 and the Hach UVAS sensor was \$15,000. Little maintenance is needed for either sensor and would likely not exceed \$200/yr, which would include labor and disposable items such as new tubing. The ZAPS unit was leased for one month during this testing for \$3,000. The ZAPS capital cost was quoted at \$60,000. No maintenance was performed on this unit during that time period. The Turner device cost \$12,000 and maintenance is estimated to be \$200/yr based on labor costs and replacement of disposable items such as tubing.

Conclusions

As seen in past studies, free chlorine and TOC sensors responded to the widest range of contaminants compared to other online water quality sensors. UV₂₅₄ instruments responded to many of the contaminants detected by traditional online TOC. Sodium thiosulfate as part of the biological suspension was detected by the UV₂₅₄ sensors, but not by online TOC sensors, although the response is related to thiosulfate itself. The low capital and maintenance costs of UV₂₅₄ sensors coupled with their contaminant detection ability may increase their potential for long-term deployment in the field.

In general, the tested fluorometers alone were not as effective at detecting contaminant injections as traditional water quality sensors such as free chlorine and TOC sensors, mainly due to the need to optimize the fluorometer settings to the

contaminant of interest. There were several positive outcomes from this study. First, the ZAPS unit that employed multiple detection principles and absorption/fluorescence wavelengths detected eight out of nine contaminants. Using only a single wavelength, the Turner device was limited to detecting eight out of ten contaminants that fluoresce similarly to fuel oil #2, which is what the unit was designed to detect. Future fluorescence and absorption-based detection research in water could focus on lower ranges of wavelengths capable of being produced by LEDs (i.e., capable of emitting between 200 and 400 nm) and/or several key excitation and emission wavelengths that can detect a wide range of contaminants. Developing lower capital cost LED fluorometer and/or UV-Vis absorption-based optical devices with several robust wavelengths would enhance the contaminant detection capability of online TOC and free chlorine sensors.

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Table 2. Contamination Detection Results (DET = detect; nd = no detect)

Contaminant	Concentration mg/L	Parameter/Instrument/Units of Measurement													
		Free Chlorine	Free Chlorine	Specific Conductivity	Fluorimeter	ORP	pH	TOC	TOC	Turbidity	Absorbance	UVAS	Carbon Indicators	Tryptophan	UVA
		CL10	CL17	YSI	Turner	YSI	YSI	Sievers	Astro	YSI	RealUVT	Hach	ZAPS	ZAPS	ZAPS
		mg/L	mg/L	µS/cm	mg/L	mV	pH	mg/L	mg/L	mNTU	m ⁻¹	m ⁻¹	counts	mg/L	m ⁻¹
Antifreeze	1	nd	nd	nd	nd	nd	nd	DET	DET	nd	nd	nd	nd	nd	nd
	10	nd	nd	nd	nd	nd	nd	DET	DET	nd	DET	DET	nd	nd	DET
Bleach	5	DET	DET	DET	nd	nd	DET	nd	nd	nd	DET	DET	nd	nd	DET
De-icer	1	nd	nd	nd	nd	nd	nd	DET	DET	nd	nd	nd	nd	nd	nd
	10	nd	nd	nd	nd	nd	nd	DET	DET	DET	nd	nd	nd	nd	nd
Diesel Fuel	1	nd	nd	nd	nd	nd	nd	n/a	n/a	DET	nd	nd	nd	nd	nd
	5	nd	nd	nd	nd	nd	nd	n/a	n/a	DET	nd	nd	nd	DET	nd
Dispersant	1	DET	DET	nd	nd	nd	nd	DET	DET	DET	DET	DET	nd	nd	nd
	10	DET	DET	nd	DET	nd	nd	DET	DET	DET	DET	DET	nd	DET	DET
<i>E. coli</i> with thiosulfate (9 mg/L)	1150 (cfu/ml)	DET	DET	nd	DET	DET	nd	nd	nd	nd	DET	DET	nd	DET	DET
	11500 (cfu/ml)	DET	DET	nd	DET	DET	nd	nd	nd	nd	DET	DET	nd	DET	DET
Sodium Thiosulfate	9	DET	DET	DET	DET	DET	nd	nd	nd	nd	DET	DET	nd	DET	DET
Ethylene Glycol	1	nd	nd	nd	nd	nd	nd	DET	DET	nd	nd	nd	DET	nd	nd
	10	nd	nd	nd	nd	nd	nd	DET	DET	nd	nd	nd	DET	nd	nd
Pepsin ^a	1	DET	DET	nd	nd	nd	nd	DET	DET	DET	DET	DET	nd	nd	nd
	10	DET	DET	nd	nd	nd	nd	DET	DET	DET	DET	DET	nd	DET	DET
Basagran ^b	1	DET	nd	nd	DET	nd	nd	DET	nd	nd	DET	DET	n/a	n/a	n/a
	10	DET	nd	nd	DET	nd	nd	DET	DET	nd	DET	DET	n/a	n/a	n/a

Acronyms: **DET**, detect; **n/a**, not available; **nd**, no detect; **ORP**, oxidation-reduction potential; **TOC**, total organic carbon; **UVAS**, a, surrogate for ricin; b, surrogate for #2 fuel oil

Appendix 1

Table A1: Detection Thresholds

Threshold Criteria	Free Chlorine (CL10) (mg/L)	Free Chlorine (CL17) (mg/L)	Specific Conductivity ($\mu\text{S}/\text{cm}$)	Turner Fluorimeter (mg/L)	ORP (mV)	pH	TOC (Sievers) (mg/L)	TOC (Astro) (mg/L)	Turbidity (mNTU)	Absorbance (RealUVT) (m^{-1})	Hach UVAS (m^{-1})	ZAPS Carbon Indicator (counts)	ZAPS Tryptophan (mg/L)	ZAPS UVA (m^{-1})
Absolute Change	0.1	0.1	5	0.05	5	0.1	0.1	0.1	1	0.005	0.005	0.1	3	0.005
Percent Change	5%	5%	2%	10%	4%	1%	10%	10%	10%	8%	10%	2%	N/A	10%
Signal to Noise	5	5	5	4	10	10	10	10	10	10	5	2	N/A	4

Table A2: Absolute Change Results

Contaminant	Concentration (mg/L)	Free Chlorine (CL10) (mg/L)	Free Chlorine (CL17) (mg/L)	Specific Conductivity ($\mu\text{S}/\text{cm}$)	Hydrocarbon (Turner Fluorimeter) (mg/L)	Oxidation Reduction Potential (mV)	pH	TOC (Sievers) (mg/L)	TOC (Astro) (mg/L)	Turbidity (mNTU)	Absorbance (RealUVT) (m^{-1})	Hach UVAS (m^{-1})	ZAPS Carbon Indicator (counts)	ZAPS Tryptophan (mg/L)	ZAPS UVA (m^{-1})
Antifreeze	1	0.04	0.00	0.47	0.04	0.29	0.01	0.72	0.59	1.15	0.02	0.03	0.76	0.00	0.00
	10	0.08	0.05	2.26	0.04	1.00	0.02	7.31	7.42	2.22	0.14	0.11	0.09	0.00	0.20
Bleach	5	3.06	3.64	30.29	0.06	21.12	0.16	0.00	0.05	1.53	0.26	0.23	14.45	0.82	0.66
De-icer	1	0.01	0.01	1.27	0.04	0.78	0.02	0.77	0.76	0.87	0.01	0.03	0.17	0.00	0.30
	10	0.01	0.01	0.78	0.04	0.38	0.01	7.62	7.51	19.03	0.04	0.06	1.01	0.00	0.31
Diesel Fuel	1	0.01	0.01	0.50	0.04	0.11	0.02	N/A	N/A	14.00	0.03	0.03	0.63	0.87	0.07
	5	0.01	0.00	0.07	0.07	0.58	0.02	N/A	N/A	38.24	0.05	0.03	0.15	3.31	0.04
Dispersant	1	0.16	0.12	0.34	0.04	3.37	0.01	0.61	0.58	49.26	0.08	0.14	0.36	2.29	0.13
	10	0.90	0.91	0.00	0.20	7.82	0.04	6.29	5.42	438.36	0.89	1.65	0.77	50.42	0.49
<i>E. coli</i> with thiosulfate	1150 (cfu/ml)	1.12	1.06	5.21	0.10	67.00	0.09	0.05	0.04	0.62	0.83	1.19	0.45	17.74	0.33
	11500 (cfu/ml)	1.21	1.14	3.10	0.11	49.23	0.09	0.04	0.04	0.58	0.82	1.22	1.02	16.01	0.22
Sodium Thiosulfate	9	1.05	1.00	7.09	0.09	32.68	0.06	0.05	0.11	0.77	0.81	1.21	0.72	14.14	0.29
Ethylene Glycol	1	0.00	0.00	0.22	0.04	0.60	0.01	0.74	0.74	0.80	0.00	0.02	1.81	0.00	0.51
	10	0.01	0.02	0.67	0.03	0.27	0.01	7.26	7.25	2.13	0.00	0.02	1.45	0.00	0.07
Pepsin	1	0.17	0.14	0.81	0.04	1.07	0.03	0.38	0.31	8.74	0.12	0.14	0.10	0.00	0.24
	10	1.02	1.10	1.57	0.06	9.95	0.06	3.83	3.46	49.13	1.00	1.06	0.43	19.57	0.76
Basagran	1	0.13	0.02	0.15	0.74	0.50	0.00	0.41	0.44	1.12	2.22	2.27	N/A	N/A	N/A
	10	0.65	0.03	2.70	7.85	0.63	0.00	4.93	4.34	1.32	3.23	21.64	N/A	N/A	N/A

Table A3: Percent Change Results

Contaminant	Concentration (mg/L)	Free Chlorine (CL10) (mg/L)	Free Chlorine (CL17) (mg/L)	Specific Conductivity (µS/cm)	Hydrocarbon (Turner Fluorimeter) (mg/L)	Oxidation Reduction Potential (mV)	pH	TOC (Sievers) (mg/L)	TOC (Astro) (mg/L)	Turbidity (mNTU)	Absorbance (RealUVT) (m ⁻¹)	Hach UVAS (m ⁻¹)	ZAPS Carbon Indicator (counts)	ZAPS Tryptophan (mg/L)	ZAPS UVA (m ⁻¹)
Antifreeze	1	4.4%	0.3%	0.2%	34.6%	0.0%	0.1%	98.2%	82.6%	5.8%	1.8%	4.3%	1.38%	0.00%	0.11%
	10	8.5%	4.7%	0.8%	29.7%	0.1%	0.2%	1068.7%	1221.0%	9.0%	16.1%	16.3%	0.16%	0.00%	40.05%
Bleach	5	282.5%	334.8%	9.7%	72.3%	2.8%	1.9%	0.6%	0.6%	6.6%	28.3%	29.1%	24.19%	#DIV/0!	1259.21%
De-icer	1	1.6%	1.5%	0.5%	25.4%	0.1%	0.3%	103.2%	102.2%	3.9%	0.6%	4.1%	0.30%	0.00%	13.63%
	10	1.0%	1.5%	0.3%	33.7%	0.1%	0.1%	1008.5%	1076.7%	90.8%	3.9%	8.2%	1.82%	0.00%	8.61%
Diesel Fuel	1	0.6%	1.0%	0.2%	31.0%	0.0%	0.2%	N/A	N/A	66.7%	3.1%	4.8%	1.12%	#DIV/0!	2.67%
	5	0.7%	0.1%	0.0%	49.7%	0.1%	0.2%	N/A	N/A	184.1%	5.8%	3.9%	0.26%	#DIV/0!	1.33%
Dispersant	1	16.8%	11.2%	0.1%	28.7%	0.5%	0.1%	84.4%	75.8%	237.4%	8.8%	18.3%	0.64%	#DIV/0!	9.71%
	10	100.0%	87.5%	0.0%	150.1%	1.1%	0.5%	840.8%	720.1%	2122.2%	104.8%	220.2%	1.37%	#DIV/0!	31.64%
<i>E. coli</i> with thiosulfate	1150 (cfu/ml)	100.0%	99.1%	1.8%	81.1%	9.4%	1.1%	5.6%	3.7%	2.4%	84.4%	139.8%	0.91%	#DIV/0!	20.90%
	11500 (cfu/ml)	100.0%	99.1%	1.1%	80.0%	7.5%	1.0%	4.3%	3.8%	2.5%	83.5%	141.9%	2.03%	#DIV/0!	18.46%
Sodium Thiosulfate	9	99.5%	98.0%	2.6%	58.2%	4.7%	0.7%	6.6%	15.3%	3.8%	93.5%	168.4%	1.25%	546.68%	17.94%
Ethylene Glycol	1	0.5%	0.3%	0.1%	52.2%	0.1%	0.1%	100.8%	75.6%	3.5%	0.4%	2.3%	3.18%	0.00%	11.36%
	10	0.9%	1.4%	0.2%	43.9%	0.0%	0.1%	1014.1%	838.3%	8.8%	0.6%	3.5%	2.48%	0.00%	1.17%
Pepsin	1	17.0%	12.9%	0.3%	46.8%	0.2%	0.4%	48.4%	35.5%	36.0%	13.7%	19.0%	0.18%	#DIV/0!	11.68%
	10	100.0%	94.8%	0.6%	57.2%	1.4%	0.7%	496.0%	388.3%	198.4%	110.8%	142.7%	0.75%	#DIV/0!	91.33%
Basagran	1	11.3%	1.3%	0.0%	421.6%	0.1%	0.0%	57.5%	73.2%	4.5%	289.9%	143.8%	N/A	N/A	N/A
	10	57.4%	2.6%	0.7%	4329.5%	0.1%	0.0%	669.2%	789.7%	5.3%	422.6%	1425.2%	N/A	N/A	N/A

Table A4: Signal to Noise Results

Contaminant	Concentration	Free Chlorine (CL10)	Free Chlorine (CL17)	Specific Conductivity	Hydrocarbon (Turner Fluorimeter)	Oxidation Reduction Potential	pH	TOC (Sievers)	TOC (Astro)	Turbidity	Absorbance (RealUVT)	Hach UVAS	ZAPS Carbon Indicator	ZAPS Tryptophan	ZAPS UVA
	(mg/L)	(mg/L)	(mg/L)	(µS/cm)	(mg/L)	(mV)		(mg/L)	(mg/L)	(mNTU)	(m ⁻¹)	(m ⁻¹)	(counts)	(mg/L)	(m ⁻¹)
Antifreeze	1	8.7	0.0	0.8	2.3	0.4	1.6	158.0	11.1	2.6	7.34	2.2	1.7	0.0	0.1
	10	9.2	2.6	2.9	1.9	1.2	1.7	1039.2	66.6	1.8	20.29	8.0	0.2	0.0	4.0
Bleach	5	337.4	733.6	64.7	2.7	5.7	22.5	1.8	0.9	1.9	132.04	17.6	1.5	#DIV/0!	6.4
De-icer	1	1.5	2.4	1.7	2.0	2.5	2.4	355.0	28.5	0.8	3.03	2.1	0.4	0.0	3.0
	10	0.6	1.6	1.9	2.2	0.8	1.4	2956.8	276.4	29.3	8.84	4.5	2.0	0.0	3.4
Diesel Fuel	1	0.7	1.4	2.0	2.1	0.2	2.3	N/A	N/A	54.1	17.58	2.1	1.2	#DIV/0!	2.4
	5	0.8	0.3	0.4	3.3	0.8	2.1	N/A	N/A	92.3	25.11	1.9	0.4	#DIV/0!	1.1
Dispersant	1	34.5	40.8	0.7	1.7	6.7	0.8	50.2	26.5	95.9	23.18	8.6	0.8	#DIV/0!	3.2
	10	148.0	317.8	0.0	9.3	10.5	7.3	1176.4	521.6	730.8	498.21	55.3	2.4	#DIV/0!	16.0
<i>E. coli</i> with thiosulfate	1150 (cfu/ml)	227.2	75.7	11.3	6.2	60.3	7.1	8.3	1.8	0.6	362.90	84.2	1.1	#DIV/0!	9.3
	11500 (cfu/ml)	181.0	52.0	5.7	4.4	27.6	6.5	14.3	3.6	1.0	329.24	63.9	1.9	#DIV/0!	6.5
Sodium Thiosulfate	9	128.5	111.7	18.5	4.6	59.9	10.5	9.6	2.4	1.6	372.35	73.4	1.9	23.0	6.8
Ethylene Glycol	1	0.5	0.6	0.5	1.9	0.8	1.0	576.6	31.8	1.7	1.54	1.0	3.4	0.0	2.6
	10	1.0	1.9	1.0	1.5	0.6	1.1	4389.0	321.9	3.8	2.37	1.7	3.8	0.0	0.7
Pepsin	1	17.7	35.3	1.2	2.3	1.2	3.4	88.1	26.3	22.5	74.38	6.7	0.3	#DIV/0!	3.3
	10	72.9	180.8	2.7	3.2	18.4	6.2	2208.6	143.5	125.6	192.19	55.7	1.0	#DIV/0!	6.5
Basagran	1	23.1	3.6	0.4	29.7	1.0	0.4	74.8	7.0	2.7	1029.6	143.9	N/A	N/A	N/A
	10	134.2	6.3	6.3	415.9	0.4	0.5	915.0	77.5	2.6	1561.4	1342.1	N/A	N/A	N/A

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