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A RESIDUAL CHLORINE REMOVAL METHOD TO ALLOW DRINKING WATER MONITORING BY BIOLOGICAL EARLY WARNING SYSTEMS

US Army Center for Environmental Health Research
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USACEHR TECHNICAL REPORT 0501

A RESIDUAL CHLORINE REMOVAL METHOD TO ALLOW DRINKING WATER MONITORING BY BIOLOGICAL EARLY WARNING SYSTEMS

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14. ABSTRACT

Aquatic biomonitors can provide continuous, real-time monitoring for toxicity in source water supplies, but they cannot be used to directly monitor chlorinated drinking waters because of aquatic organism sensitivity to residual chlorine. The threshold for a toxicity alarm by a biomonitor using bluegills (Lepomis macrochirus) was between 0.015 and 0.066 mg/L total residual chlorine (TRC). A portable dechlorinator that injected 6 mg/L sodium bisulfite into water containing 1.5 to 2.0 mg/L TRC was effective in removing TRC-related toxicity during a nine month evaluation at a water treatment plant. Three biomonitor alarms that occurred were not caused by dechlorinator malfunctions. In one-hour laboratory exposures to sodium bisulfite alone, the biomonitor did not respond until concentrations exceeded 48 mg/L. This study demonstrated the feasibility of using a biomonitor in conjunction with a portable dechlorinator for continuous monitoring of chlorinated drinking waters. Future studies should evaluate dechlorinator suitability in waters with total organic carbon levels exceeding 2 mg/L or that have been disinfected with chloramines.

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biomonitor, biological early warning system, residual chlorine, toxicity, sodium bisulfite, dechlorination, dechlorinator, bluegill, Lepomis macrochirus

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Preface

Increasing water security threats at military installations highlight a need for continual monitoring of drinking water for potential contaminants. Aquatic biomonitors such as the one developed by the U.S. Army Center for Environmental Health Research (USACEHR) can provide continuous, real-time monitoring of source water supplies, but cannot be used to directly monitor chlorinated drinking waters because of the sensitivity of the aquatic organisms used in the biomonitor to residual chlorine. This report documents the sensitivity of the USACEHR biomonitor to residual chlorine and evaluates the suitability of a portable dechlorination system to allow the biomonitor to monitor chlorinated product water produced at a water treatment facility. In addition, the portable dechlorination system may be suitable for use with other biomonitors using organisms with sensitivities to residual chlorine comparable to the bluegills (*Lepomis macrochirus*) used in the USACEHR biomonitor.

We are grateful for the assistance of Mr. David Grams and the staff of the Fort Detrick Water Treatment Plant in support of the field operation of the aquatic biomonitor.

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Research was conducted in compliance with the Animal Welfare Act, and other Federal statues and regulations relating to animals and experiments involving animals and adheres to principles stated in the Guide for the Care and Use of Laboratory Animals (NRC, 1996) in facilities that are fully accredited by the Association for the Assessment and Accreditation of Laboratory Animal Care, International.

Summary

Aquatic biomonitors can provide continuous, real-time monitoring of source water supplies and rapid response to a wide range of toxic chemicals, but they cannot be used to directly monitor chlorinated drinking waters because of the sensitivity of the aquatic organisms used in a biomonitor to residual chlorine.

This report documents the sensitivity of a biomonitor developed by the U.S. Army Center for Environmental Health Research (USACEHR) to residual chlorine and evaluates the suitability of a commercially-available dechlorinator (GEO-CENTERS, INC., Newton, MA) to allow the biomonitor to monitor chlorinated product water produced at the Fort Detrick (MD) Water Treatment Plant. The USACEHR biomonitor uses an expert system to identify abnormal ventilatory and movement patterns in the bluegill (*Lepomis macrochirus*).

The threshold for a toxicity alarm by the USACEHR biomonitor was found to be between 0.015 and 0.066 milligrams (mg)/Liter (L) total residual chlorine (TRC). A portable dechlorinator that injected 6 mg/L sodium bisulfite into chlorinated water containing 1.5 to 2.0 mg/L TRC was effective in removing TRC-related toxicity during a nine month evaluation of product water at a water treatment plant. Three biomonitor alarms during the nine-month monitoring period were related to operator error or equipment malfunctions unrelated to the dechlorinator. In one-hour laboratory exposures to sodium bisulfite alone, the biomonitor did not respond until concentrations exceeded 48 mg/L.

This study demonstrated the feasibility of using the USACEHR biomonitor in conjunction with a portable dechlorinator for continuous monitoring of chlorinated drinking waters. These findings should apply to biomonitors using other aquatic organisms whose sensitivities to TRC are similar to the bluegills as used in the USACEHR biomonitor. Applications of the dechlorinator in association with biomonitors include monitoring of water treatment plant product water or chlorinated water at strategic points in water distribution systems.

Dechlorinator operation could be improved through the addition of a flow controller to match sodium bisulfite pumping rates to chlorinated water flow rates. Additionally, a pressure switch could be used to shut off sodium bisulfite additions when chlorinated water flow is lost.

The suitability of the dechlorinator in chlorinated waters with total organic carbon levels exceeding 2 mg/L or that have been disinfected with chloramines was not determined. Biomonitor users with waters having these characteristics should evaluate the effectiveness of the dechlorinator before providing dechlorinated water to a biomonitor.

1. Introduction

Protecting Army drinking water sources from chemical contamination is an area of increased concern in recent years, but providing rapid identification of toxicity caused by potentially hundreds of diverse chemical contaminants is a difficult task. Instead of relying upon chemical by chemical analysis, biological early warning systems (BEWS) use changes in the responses of living organisms to rapidly identify potentially toxic conditions in water. To provide continuous, real-time monitoring for toxicity in drinking water supplies, the U.S. Army Center for Environmental Health Research (USACEHR) developed an aquatic biomonitor that evaluates changes in the ventilation and movement patterns of fish (van der Schalie et al., 2004). Other BEWS have been developed that monitor swimming movements and electrical organ discharges in fish (Blübaum-Gronau et al., 2000; Thomas, 2000), movement patterns of aquatic invertebrates (Gunatilaka et al., 2000; Lechelt et al., 2000; Gerhardt, 1999), valve movements of clams (Kramer and Foekema, 2000), and changes in algal fluorescence (Gunatilaka and Diehl, 2000) and bacterial luminescence (Gerhardt, 1999).

Although all BEWS can be used to monitor source waters (e.g., reservoir or river water), they are limited in their ability to monitor chlorinated drinking waters because of the high sensitivity of nearly all aquatic organisms to residual chlorine (U.S. EPA, 1986). While it is known that removal of residual chlorine is possible through the use of mild reducing agents such as sodium thiosulfate (Seegert and Brooks, 1978), this approach has seldom been used to allow BEWS to be used for monitoring chlorinated water in water distribution systems.

The possibility of using BEWS for monitoring chlorinated product water has been enhanced by the recent availability of a compact, portable dechlorinator for water. The dechlorinator was developed by GEO-CENTERS, INC. to remove residual chlorine from the discharge water of auxiliary seawater cooling systems on U.S. Navy ships and submarines. In order to evaluate the suitability of this dechlorinator for use with the USACEHR aquatic biomonitor, there is a need to determine the sensitivity of the biomonitor both to residual chlorine and the dechlorination chemical used and to evaluate ability of the portable dechlorinator to produce water suitable for long-term use with the biomonitor.

The purpose of this report is to document the sensitivity of the USACEHR biomonitor to residual chlorine and to evaluate the suitability of the GEO-CENTERS, INC. dechlorinator to allow the biomonitor to monitor chlorinated product water produced at a water treatment facility. This report describes the sensitivity of the USACEHR biomonitor to chlorine and to the dechlorination chemical used (sodium bisulfite) and provides performance-related information on the operation of the portable dechlorinator at an Army water treatment plant, where it was used in conjunction with the USACEHR biomonitor.

The primary audience for this report includes individuals responsible for Army water treatment plant and distribution system security who may wish to use the USACEHR biomonitor to evaluate chlorinated water in their system. In addition, the report is intended for users of other BEWS who

wish to monitor chlorinated waters and need a compact dechlorination system to facilitate the process.

2. Methods

This section describes the general procedures used in operating the USACEHR aquatic biomonitor as well as the specific methods used in laboratory tests of biomonitor responses to chlorine and sodium bisulfite. Procedures for evaluating dechlorinator operation and dechlorinator performance in field testing with the aquatic biomonitor are described.

2.1 Aquatic Biomonitor Operation

The aquatic biomonitor identifies potentially toxic events by continuously monitoring for abnormalities in the ventilatory and movement patterns of the bluegill (*Lepomis macrochirus*). Lengths and weights of bluegills used in testing are shown in Table 1. Fish were

Table 1. Size of Fish Used in Testing

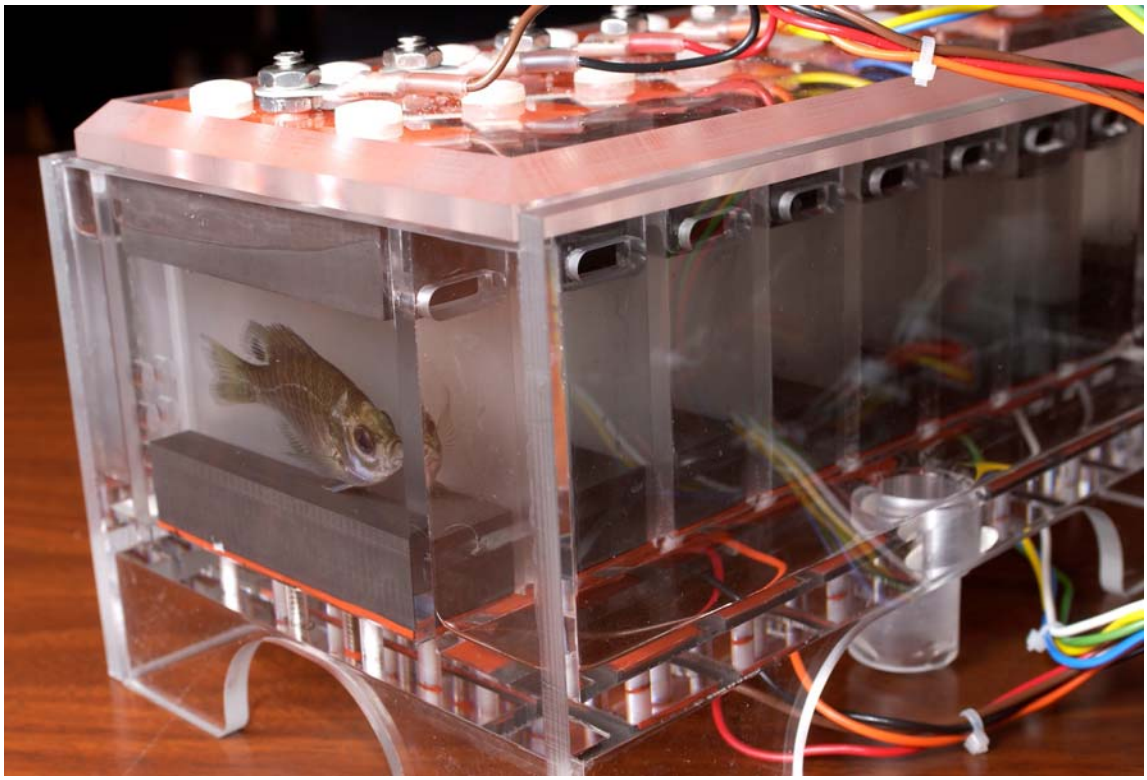
Test	Length (cm[1])	Weight (g[1])
Chlorine (high range)	5.5 – 7.8	4.4 – 14.8
Chlorine (low range)	5.0 – 8.0	3.4 – 15.1
Sodium bisulfite	5.5 – 7.7	4.5 – 11.9
Field Testing	3.8 – 8.2	2.4 – 17.8

[1] cm – centimeter; g - gram

acquired from local sources and acclimated on site in control water with continuous light (wide spectrum fluorescent bulbs) for a minimum of two weeks. Fish were held and tested under continuous light to eliminate diel changes in ventilatory patterns (Carlson, 1990). During acclimation, fish were fed commercial trout chow and frozen brine shrimp, but once placed in the ventilatory chambers for testing were not fed.

Eight fish are held in individual chambers under flow-through conditions (Figure 1). Electrical signals generated by muscle movements of individual fish are monitored by carbon block electrodes suspended above and below each fish. The electrical signals are amplified, filtered, and passed onto a personal computer for analysis. Each input channel is independently amplified by a high gain true differential-input instrumentation amplifier; signal inputs of 0.05-1 mV are amplified by a factor of 1000. Signal interference by frequencies above 10 Hz is attenuated by low-pass filters. The computer provides an additional factor of 10 signal amplification. Ventilatory parameters measured include ventilatory rate, ventilatory depth (mean signal height), gill purge (cough) frequency, and whole body movement (rapid irregular electrical signals). Each parameter is calculated at 15 second (s) intervals, and any interval containing whole body movement is excluded from calculation of the other three parameters. The 15 s intervals are summed to create a 15 minute (min) data record. Further details of specific algorithms are described elsewhere (Shedd et al., 2002). Test methods are similar to those described in van der Schalie, et al. (2001). In addition to fish ventilatory data, pH, temperature, dissolved oxygen, and conductivity are monitored every 15 min using a commercially-available water quality multiprobe (Hydrolab H2O® Submersible Water Quality Data Transmitter or a Yellow Springs Instrument (YSI) 600XL Multiparameter

Figure 1. Aquatic Biomonitor Chamber. The chamber contains eight cells, with one fish in each cell. Ventilatory and movement patterns are monitoring using the carbon block electrodes above and below each fish.



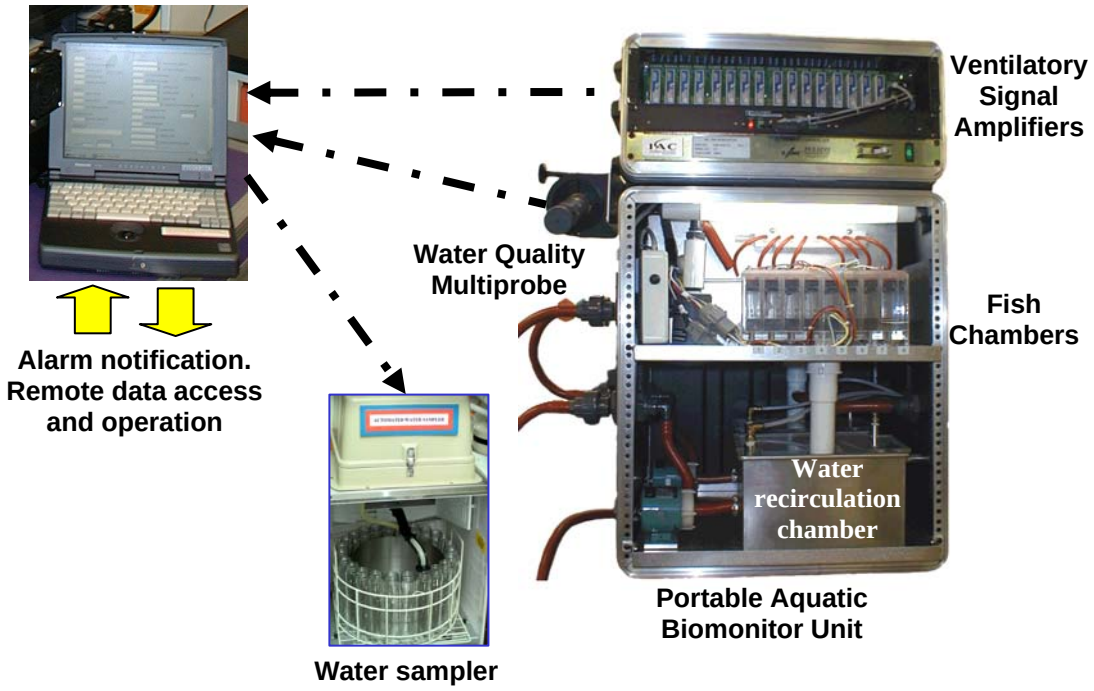
Water Quality Monitor). These data help determine whether fish responses are due to the presence of toxicants or to non-toxic water quality variations.

To identify abnormal fish ventilatory and movement patterns, a radial basis function neural network trained as auto-associative memory is employed to perform the novelty detection. The neural network is trained to reproduce the normal patterns of normalized ventilatory parameters; i.e., the network outputs are equal to the inputs. The novelty is detected as an inability of the network to reproduce the input data and is quantified as the absolute value of the difference between the output and the input, averaged over all parameters (inputs/outputs) (Wroblewski, 2004). Temperature and dissolved oxygen data are incorporated into the neural network analysis to further assess abnormal fish behavior. The neural network was trained using data sets from hundreds of bluegills previously monitored under laboratory and field conditions.

For every 15 min monitoring interval, a toxicity index value is generated for each fish. If an individual fish has a toxicity index value greater than one, it is considered to be a novel event. If more than 70% of exposed fish have novel events in the same 15 min interval, an alarm response is generated.

The overall biomonitor system is shown in Figure 2. Water to be monitored flows through the water recirculation chamber and is pumped

Figure 2. Aquatic Biomonitor Diagram. Water to be monitored flows into the recirculation chamber and is pumped up to the fish chambers. The computer monitors fish ventilatory and movement patterns and water quality data from the multiprobe. See text for further explanation.



through the individual fish chambers. Each chamber receives 100-150 milliliters (mL)/min (field tests) or 200-300 mL/min (laboratory tests). The computer monitors fish ventilatory and movement patterns and water quality data from the multiprobe. If the fish alarm, the computer turns on the water sampler and provides alarm notification via autodialing or the Internet. Data examination and system operation can be performed remotely. In field operations, a second set of eight fish provided on the other side of the biomonitor (not visible) can provide for continuous, uninterrupted monitoring when the first set of fish is removed from the system (about every three weeks). For laboratory tests, the use of two biomonitors provides four treatments of eight fish each (a control plus three toxicant concentrations)

2.2 Laboratory Single Chemical Test Procedures

Three laboratory tests were conducted: a high concentration chlorine test, a low concentration chlorine test, and a sodium bisulfite test. In the chlorine tests, test solutions were supplied to four groups of eight fish (three toxicant concentrations plus a control); one group of exposed fish and one group of control fish were used in the sodium bisulfite test.

Endpoints monitored in each laboratory test included the time to first group alarm at each concentration and

Table 2. Water Quality Data During Laboratory Tests[1]					
Parameter	**pH**	**Conductivity (mS^2/cm)**	**Dissolved Oxygen (mg/L)**	**Alkalinity (mg/L as $CaCO_3$[2])**	**Hardness (mg/L as $CaCO_3$)**
Mean	7.9	0.63	7.8	125	191
Range	(7.6–8.6)	(0.51–0.89)	(6.4–8.8)	(102-130)	(140-208)
Number of Observations	96	96	96	61	61

[1] Includes chlorine tests and sodium bisulfite controls. See Figure 4 for water quality during sodium bisulfite exposure pulses

[2] mS – millisiemen; $CaCO_3$ – calcium carbonate

fish mortality. When mortality was high enough, a 96-hour (h) LC50 was determined using the trimmed Spearman-Karber method (Hamilton et al., 1977). Dilution water was a mixture of 60% well water obtained from a 150 meter (m) well adjoining the USACEHR facility at Fort Detrick, MD, and 40% dechlorinated, deionized tap water processed through a reverse osmosis system. Water quality data for the laboratory tests is summarized in Table 2. Temperature was maintained at 25±0.5° Celsius (C) using a thermoelectric unit (Electracool L-Chiller, Advanced Thermoelectric Corp., Nashua, NH).

2.2.1 Residual Chlorine

To initiate chlorine testing, appropriate amounts of stock solutions were added to the water recirculation chamber (Figure 2) for each group of eight fish. One liter of well water was removed from each recirculation chamber and replaced with the appropriate concentration of stock solution; controls received chlorine demand-free (CDF) well water only. Samples were taken 15 min and 60 min after each toxicant administration. After establishing this initial concentration, stock solutions of chlorine in water were delivered to the water recirculation chamber (Figure 2) using a peristaltic pump; sodium bisulfite was added in a stepwise fashion as described below.

Reagent-grade sodium hypochlorite was used in the chlorine tests (Chemical Abstracts Service (CAS) number 7681-52-9, 6 to 14% free available chlorine, Sigma-Aldrich Co., St. Louis, MO). Exposure levels in the high concentration range chlorine test were set to bracket the 96-h LC50 level reported in the literature. (The 96-h LC50 is the concentration lethal to 50% of exposed fish in 96 hours, a standard aquatic acute toxicity metric.) The ventilatory test continued for at least 96 h to permit calculation of a 96-h LC50, when there was sufficient mortality of fish exposed in the ventilatory system. The low concentration range chlorine test was conducted to estimate the lowest concentration of chlorine capable of eliciting a biomonitor alarm within the exposure period.

In both chlorine tests, chlorine test solutions were prepared daily by diluting sodium hypochlorite solution in CDF well water. CDF water preparation is described in APHA, 1992. Chlorine stock solutions were prepared daily in CDF water for each chlorine test, and stock solution concentrations were verified analytically.

Total residual chlorine (TRC) concentrations were the primary measure of chlorine exposure used. However, spot checks showed that over half the residual chlorine was present as free residual chlorine (FRC). The TRC concentrations in the high range chlorine test were analyzed using a Fisher Model 397 amperometric titrator, which had a detection limit of 0.10 mg/L TRC. Samples were taken at each concentration level at 15 min, 1 h, 4 h and 24 h after initiation of the test compound and measured immediately. Stocks were prepared and replenished daily and stock solution TRC concentrations were verified at 2 and 24 h after the new stock was introduced. Mean measured TRC concentrations in the three chlorine treatments were 0.08, 0.17, and 0.44 mg/L.

For the low concentration range chlorine test, test concentrations were analyzed using a Wallace and Tiernan amperometric titrator, with a detection limit of 0.001 mg/L TRC. The stock solution changeover and sampling schedules were similar to the first chlorine test. Mean measured TRC concentrations in the three chlorine treatments were 0.005, 0.015, and 0.066 mg/L. This test ended after 68 h because of a computer malfunction.

2.2.2 Sodium Bisulfite

Sodium bisulfite (CAS 7631-90-5, 99.9% purity) was obtained from Chem-Corr, Fredericksburg, VA. Because of the low toxicity of sodium bisulfite and the high concentrations required for continuous exposure, a step-wise incremental exposure was used to identify a threshold concentration for biomonitor response and provide an indication of acute toxicity.

The exposure was initiated in the same manner as the chlorine tests. One liter of water was drawn from the water recirculation chamber and replaced with 1 L of sodium bisulfite stock solution. The water then recirculated for 1 h with no additional dilution water added. After 1 h, dilution water flow started and continued for the next hour, providing a 99% reduction in test concentration. Progressively higher sodium bisulfite concentrations (3, 6, 12, 24, 48, and 96 mg/L) were then added in a similar manner 1 h exposure,1 h flushing) until a biomonitor response was achieved. After flushing out the highest concentration level for about 15 h, fish were again exposed at the next lower level for approximately 24 h to evaluate whether the biomonitor would respond at the lower concentration if the exposure time exceeded 1 h. For this continuous exposure, a stock solution of sodium bisulfite was delivered to the water recirculation chamber using a peristaltic pump, as was done for the chlorine tests.

Sodium bisulfite stock solutions were prepared daily in deionized water and verified using a Hach sulfite test kit (method 8216) and a Hach Digital Titrimeter (Hach Corporation, Loveland, CO). Although sodium bisulfite was stable in deionized water, it degraded in well water, so test results are reported as nominal concentrations.

2.3 Dechlorinator Testing

This section describes the procedures used to modify the GEO-CENTERS, INC. dechlorinator to make it suitable for use with the USACEHR biomonitor and the methods used to evaluate dechlorinator performance in a field application of the biomonitoring system.

Table 3. Water Quality Data During Field Testing[1]				
Parameter	**pH**	**Turbidity (NTU[2])**	**Alkalinity (mg/L as $CaCO_3$)**	**Hardness (mg/L as $CaCO_3$)**
Monthly Mean	7.9	0.051	74	125
Range	7.1 – 8.2	0.018 – 0.483	36 - 110	78 - 164
Number of Observations	276	276	276	276

[1] Data from the period May 2004 through Jan 2005. Source: Grams, D., personal communication, Fort Detrick Water Treatment Plant, Fort Detrick, MD.
[2] NTU – Nephelometric turbidity unit

2.3.1 Dechlorinator Operation

Removal of residual chlorine was achieved using a commercially-available portable continuous flow dechlorinator (Dechlorination Unit, Model AN/PSQ-11(V), GEO-CENTERS, INC., Newton, MA). This system was originally designed for dechlorination of large volumes of chlorinated seawater originating from cooling systems on U.S. Navy ships. Except as noted below, procedures follow those recommended in the operation manual (GEO-CENTERS, INC. 2004).

The dechlorination system (Figure 3) includes a pumping unit and a 20 L jerrican that serves as a reservoir for sodium bisulfite solution. An in-line static mixer (Ko-Flo #1/2-4OC-4-6-2) was added to ensure thorough mixing of the sodium bisulfite solution with the pressurized chlorinated water to be monitored (Figure 3c). An additional 20 L jerrican is useful for mixing the sodium bisulfite solution prior to addition to the reservoir. Jerrican modifications required for dechlorinator operation with the jerrican are described in Appendix A. The jerrican was placed at least 0.3 m above the pump to ensure a flooded suction line, which is necessary for proper pump operation.

The sodium bisulfite solution was pumped at 1 mL/min into a chlorinated water flow volume of approximately 1 L/min (2 mL/min into 2 L/min from 28 JUN 04 through 20 SEP 04). A 1 mL/min pump rate was achieved with a manual pump setting of 22% stroke length and 15% stroke rate.

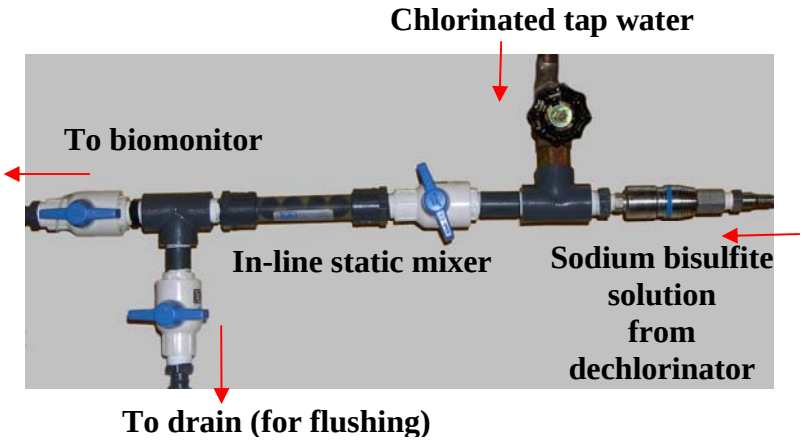
To help ensure residual chlorine removal, the sodium bisulfite concentration should be set at 1.46 times the TRC concentration (GEO-CENTERS, INC. 2004). Although a maximum TRC concentration of 2 mg/L was anticipated in the Fort Detrick Water Treatment Plant product water, 6 mg/L of sodium bisulfite was maintained to allow for unanticipated variations in incoming flow rate or pumping rate. Stock solutions were prepared in deionized water because it was found the sodium bisulfite degraded more rapidly in tap water. To help ensure proper operation, dechlorinator pumping rates and stock solution utilization rates were checked periodically. The Fort Detrick Water Treatment Plant monitors FRC in their product water, and these values were periodically compared with the FRC levels in the dechlorinated tap water provided to the biomonitor using a Hach Pocket Colorimeter, using Hach method 8167.

2.3.2 Field Test Procedures

Dechlorinator operation was evaluated in conjunction with biomonitor operation at the Fort Detrick Water Treatment Plant.

Figure 3. Dechlorinator System.

a. Pumping Unit



c. Mixing System

b. Modified Jerrican

The water supply for Fort Detrick is drawn from the lower Monocacy River watershed (Frederick County, MD), which covers approximately 304 square miles (788 square kilometers) of predominantly agricultural land (MD DNR, 2003). Water treatment includes flocculation followed by sedimentation, sand bed and carbon filtration, and chlorination. Water usage is approximately 1.1 million gallons/day (4.2 million L/day). Treated water quality is summarized in Table 3. Turbidity was uniformly low in the treated water, but pH, alkalinity, and hardness varied, as might be expected in a water taken from a river system. Summer temperatures were as high as

about 30°C; winter temperatures were no lower than 13°C in winter because of the use of a thermoelectric unit.

Both source water and dechlorinated product water were evaluated using the biomonitor; only dechlorinated product water data are reported here. The biomonitor received chlorinated product water from the clear well, which was dechlorinated prior to the biomonitor as described in the previous section.

One set of eight fish is used in the biomonitor for at least three weeks at a time. In this application, only one of the two sets of eight fish was available for dechlorinated water monitoring, so after three weeks, the original set of fish was removed and a second set of fish was put on-line in the same monitoring chamber. Approximately 4-6 h was required for the new set of fish to acclimate sufficiently so that routine water monitoring could resume.

When a group of fish alarms, the computer turns on a refrigerated water sampler (ISCO, Inc.) and uses a Sensaphone autodialer to notify appropriate individuals; email notification is possible using the expert system software. Data examination and system operation can be done remotely via PC Anywhere® using a phone connection or via the Internet. Other aspects of biomonitor operation are as described in Section 2.1.

The dechlorinator was tested in conjunction with continuous biomonitor testing of chlorinated product water at the Fort Detrick Water Treatment Plant product water over a nine month period between May 2004 and January 2005. The primary performance criterion was whether the biomonitor alarmed as a result of TRC exposure.

3. Results and Discussion

3.1 Laboratory Single Chemical Biomonitor Tests

3.1.1 Residual Chlorine

Results for the two biomonitor chlorine tests are shown in Table 4. The threshold for a biomonitor response was between 0.015 and 0.066 mg/L, with complete mortality occurring at TRC concentrations of 0.17 mg/L and above. The calculated 96-h LC50 for fish in the high range chlorine study was 0.12 mg/L. This is somewhat lower than reported bluegill 96-h LC50s, which ranged from 0.18 to 0.80 mg/L (Roseboom and Richey, 1977a, b).

Table 4. Biomonitor Responses to Chlorine

Test	TRC (mg/L)	Response Time (h)	Mortality (96-h)
Low range	0.001	>68[1]	0
Low range	0.005	>68[1]	0
High range	< 0.01	>96	0
Low range	0.015	>68[1]	0
Low range	0.066	1.75	0
High range	0.08	2.5	0
High range	0.17	0.75	100
High range	0.44[2]	0.25	100

[1] Test duration was 68 h
[2] The measured concentration at the 0.25-h response was 0.33 mg/L

Bluegill ventilatory responses to TRC in the biomonitor were characterized by a decrease in ventilatory depth, increases in cough rate and percent movement, and an initial spike in ventilatory rate followed by a

decrease. Miller et al. (1980) exposed bluegills to a pulse of chlorine, noting initially depressed ventilatory rates (which, with their method of monitoring, may have reflected very low ventilatory depths) within 15 min at a concentration of 0.03 mg/L, followed by increased ventilatory rates as the concentration rose to 0.21 mg/L and greatly reduced ventilatory rates above that level..

If chlorinated drinking water supplies are to be evaluated with the aquatic biomonitor, TRC concentrations should be maintained below 0.01 mg/L to ensure that biomonitor responses do not occur. When biomonitor responses do occur in dechlorinated water, an initial evaluation should be conducted to ensure that the dechlorinator is functioning properly and that residual chlorine is not present.

3.1.2 Sodium Bisulfite

No mortality occurred during exposure. This is consistent with the low toxicity reported for sodium bisulfite; the 96-h LC50 for the western mosquitofish (*Gambusia affinis*) is reported as 240 mg/L (Wallen et al., 1957).

Results of the sodium bisulfite test are shown in Figure 4. One-hour pulses of sodium bisulfite caused decreased pH and dissolved oxygen levels, as reported by others (Ryon et al., 2002). The reductions were particularly noticeable at concentrations of 48 or 96 mg/L; conductivity increased at these same levels. Minor temperature variations associated with the dosing protocol did not cause any apparent biomonitor responses (Figure 4d).

No biomonitor responses were detected during the static 1 h exposures at 3, 6, 12, 24, and 48 mg/L. The 96 mg/L concentration elicited a response after 0.75 h of exposure. During the 24-h continuous exposure at 48 mg/L, a biomonitor response was observed after 1.75 h of exposure. It is unclear whether the observed biomonitor responses at 48 and 96 mg/L were due to the changes induced in pH, dissolved oxygen, and conductivity or to some other property of the sodium bisulfite. In both responses, the primary effect was a dramatic increase in ventilatory rate. Ventilatory depth increased slightly at 96 mg/L and decreased slightly during the extended 48 mg/L exposure.

It appears that concentrations of sodium bisulfite far in excess of the 6 mg/L used to dechlorinate the Fort Detrick Water Treatment Plant product water during field testing would be necessary to cause biomonitor alarms; such concentrations should occur only in the event of a dechlorinator malfunction. Dechlorinator performance is discussed in the next section.

3.2 Dechlorinator Testing

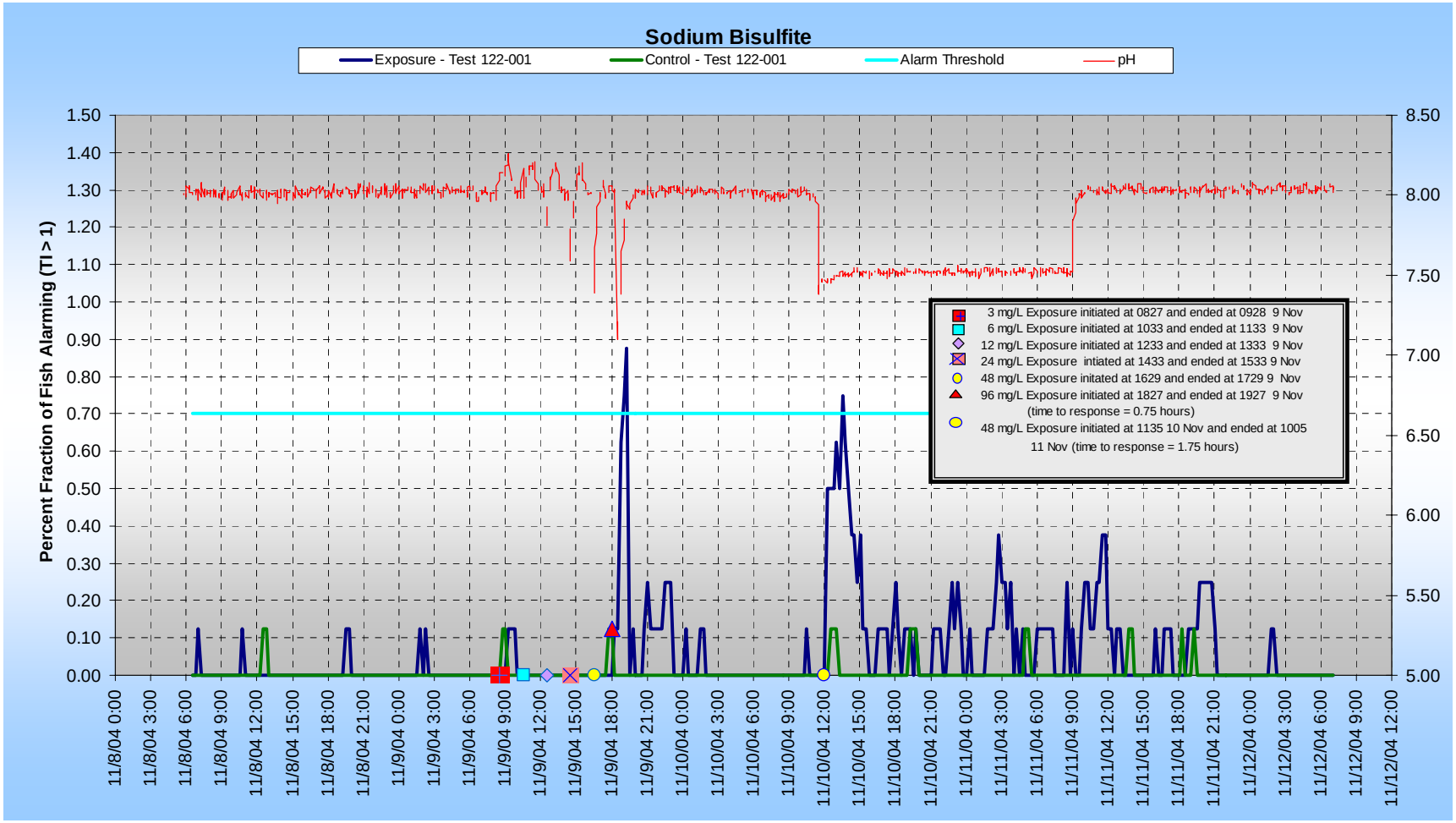
Dechlorinator performance was evaluated by monitoring pumping operation, measuring TRC levels in treated water, and by recording biomonitor alarms in the Fort Detrick Water Treatment Plant product water.

3.2.1 Dechlorinator Operation

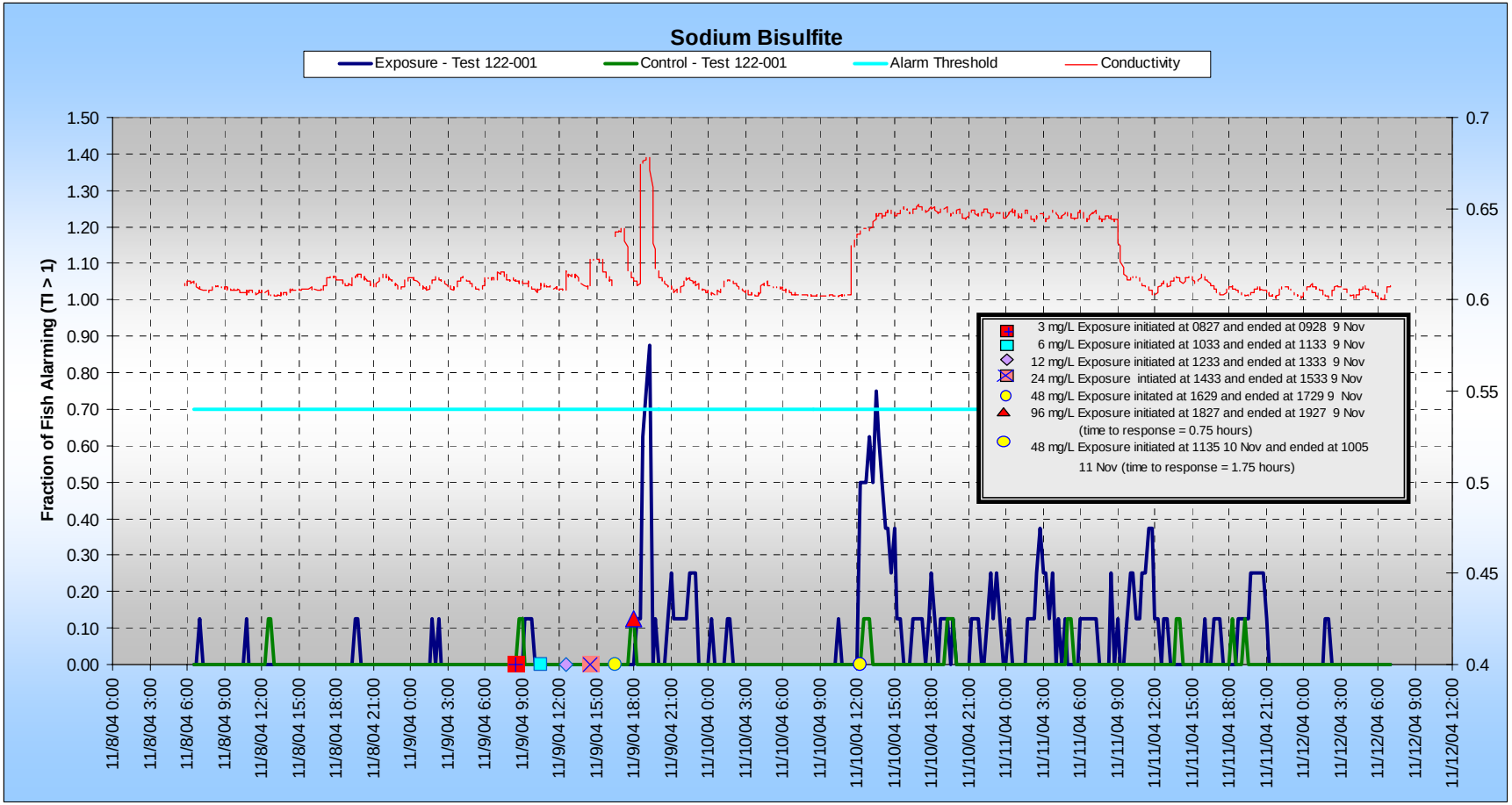
In continuous use over a nine-month period, the dechlorinator operated very reliably. The manual pump settings required to achieve a 1 mL/min injection rate were virtually unchanged; stroke length increased from 22% to 24%; stroke rate changes from 15% to 17%. At this rate of use, about 10 L/week of sodium bisulfite stock solution was required.

No pump maintenance was required, although a monthly check of the pumping rate is recommended. There

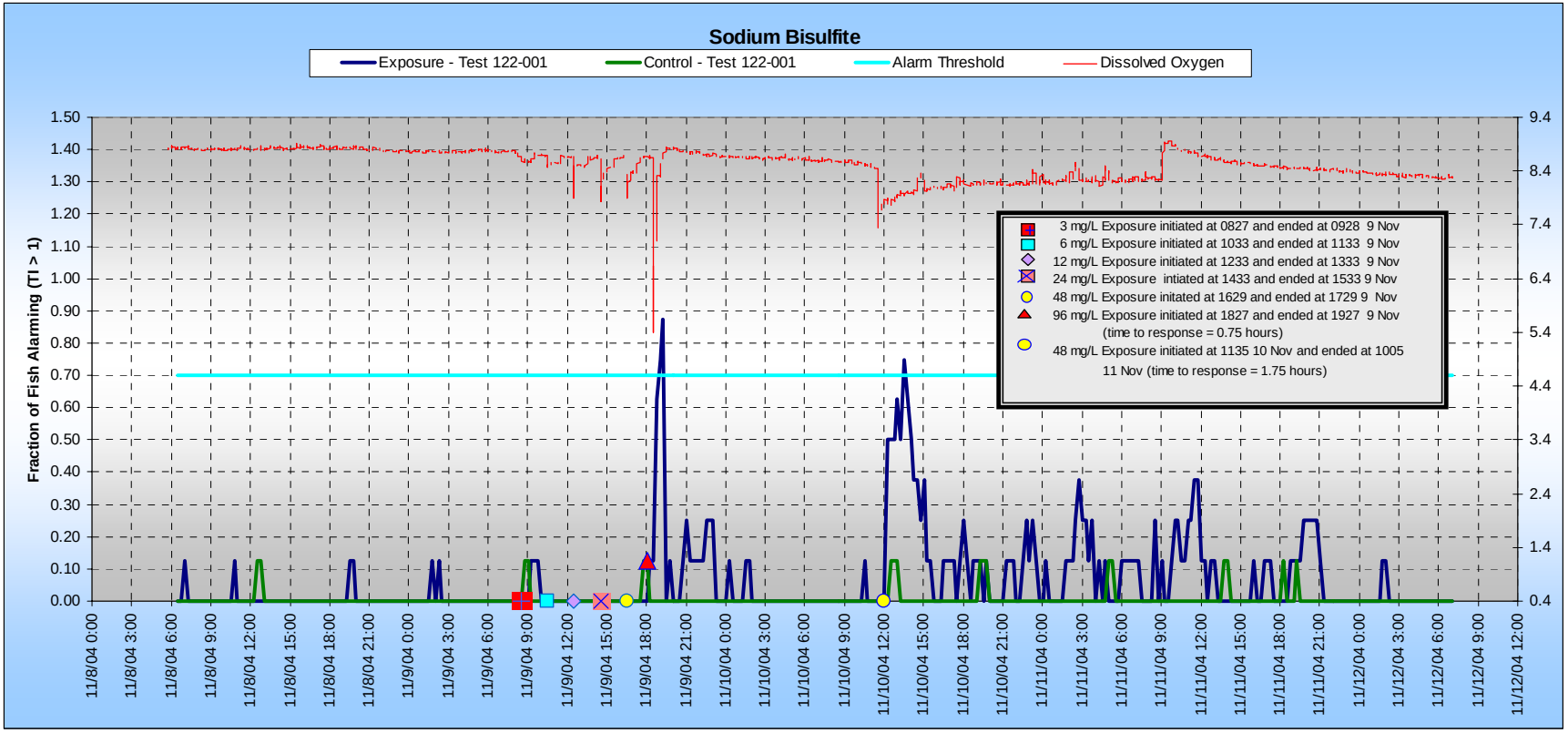
Figure 4. Sodium Bisulfite Response Data



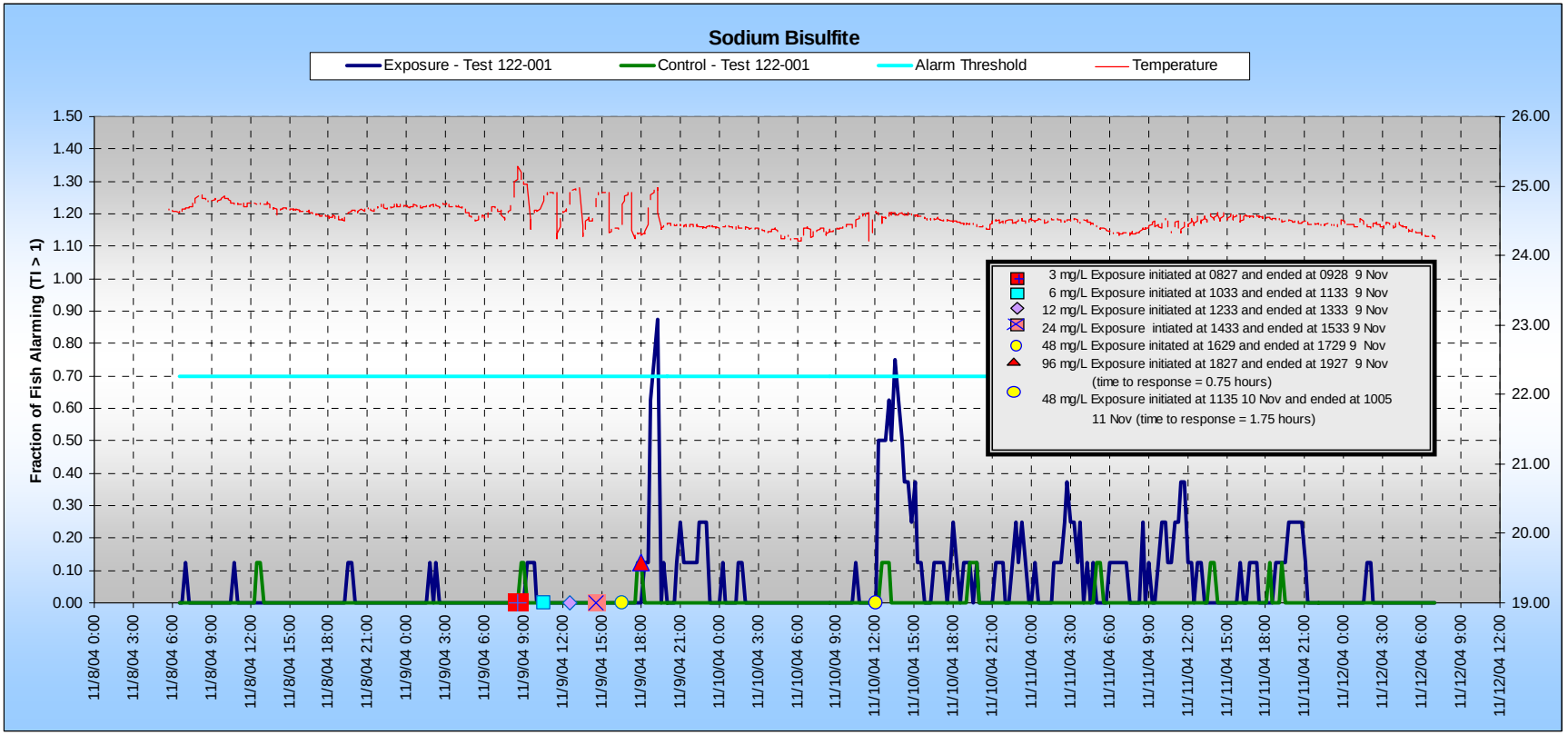
a. Biomonitor responses to sodium bisulfite, showing pH data.



b. Biomonitor responses to sodium bisulfite, showing dissolved oxygen data.



c. Biomonitor responses to sodium bisulfite, showing conductivity data.



d. Biomonitor responses to sodium bisulfite, showing temperature data.

Table 5. Fort Detrick Water Treatment Plant FRC Measurements

Date	Product Water FRC (mg/L)	Dechlorinated Water FRC (mg/L)	Comment
5/20/04	1.5	<0.01	
5/21/04	1.6	<0.01	
5/24/04	1.6	0.03	
5/26/04	1.6	<0.01	
5/27/04	1.6	0.01	
6/8/04	1.8	<0.01	
6/12/04	1.7	0.08	Biomonitor alarm
6/14/04	1.4	<0.01	
6/16/04	1.8	0.01	
6/28/04	1.7	<0.01	
7/2/04	1.7	<0.01	
7/13/04	1.7	<0.01	
7/16/04	1.9	0.01	
7/27/04	1.7	0.03	
8/17/04	1.7	0.00	
9/8/04	1.9	0.04	
9/14/04	1.8	0.04	Biomonitor alarm
9/16/04	1.6	<0.01	
9/22/04	1.8	0.02	Biomonitor alarm
9/30/04	1.5	0.01	
1/10/04	1.6	0.01	
Average	**1.7**		
Minimum	**1.4**	**<0.01**	
Maximum	**1.9**	**0.04**	

were no leaks from the pump housing; a small leak from the bulkhead on the jerrican was fixed by providing support for the weight of the stainless steel connections into the bulkhead.

3.2.2 Field Biomonitor Tests

In nine months of operation monitoring the dechlorinated product water from the Fort Detrick Water Treatment Plant, the biomonitor alarmed very infrequently. A malfunctioning dissolved oxygen probe reported false low dissolved oxygen readings that caused alarms even though fish behavior was normal. Excluding this problem, only three biomonitor alarms were recorded.

Table 5 shows the FRC measurements for the product water at the Fort Detrick Water Treatment Plant along with corresponding FRC levels found in the dechlorinated water

delivered to the biomonitor. As might be expected, FRC levels in the product water are closely regulated at between 1.5 and 2.0 mg/L.

Although the dechlorinator operated effectively throughout the nine-month test period, operational issues were responsible for three biomonitor alarms during the evaluation. The alarm on 12 JUN 04 occurred when the valve regulating the flow of dechlorinated water to the biomonitor (Figure 3c) was opened to flush the biomonitor recirculating chamber without increasing the pumping rate of sodium bisulfite solution. This caused an elevated chlorine level (measured at 0.08 FRC) and a biomonitor alarm. Fish responses returned to normal after the normal flow rate of dechlorinated water was restored and chlorinated water was diluted.

On 14 SEP 04, the chlorinated tap water valve malfunctioned, allowing an excess flow of chlorinated water that exceeded the sodium bisulfite dechlorination capacity. About a week later (22 SEP), tap water flow was lost, but sodium bisulfite flow continued, eventually causing a biomonitor alarm. The concentration of sodium bisulfite at the time of the alarm is unknown.

Based on nine months of experience, the dechlorination system has been extremely reliable and effective in reducing residual chlorine levels to the point that the aquatic biomonitor can be used. Nevertheless, some caution in using sodium bisulfite to dechlorinate water to be used in biomonitoring systems like the USACEHR biomonitor is warranted. Although Yonkos et al. (2001) found sodium bisulfite to be effective in reducing the acute residual chlorine toxicity to the aquatic invertebrate *Daphnia magna* in well water with low (< 1 mg/L) total organic carbon (TOC), it was not nearly as effective in pond water with elevated TOC (17 mg/L).

Since the TOC levels of the Fort Detrick Water Treatment Plant product water was low (between 1 and 2 mg/L during the nine month study period; D. Grams, personal communication), use of the dechlorinator for waters having higher TOC levels may require high concentrations of sodium bisulfite or longer contact times to achieve the necessary reduction in residual chlorine levels.

It is more difficult to remove residual chlorine from water disinfected with chloramines. In testing with a rapid toxicity test that uses *Daphnia magna*, James et al. (2003) found that sodium thiosulfate was ineffective in removing residual chlorine toxicity associated with a chloraminated municipal tap water. Helz and Newke (1995) found that sulfur (IV) compounds such as sodium bisulfite removed 87 to 98% of residual chlorine from chlorinated wastewater but that a reduction-resistant fraction of residual chlorine remained that included chlorinated secondary amines and peptides. Further testing of the dechlorinator in chloraminated water is advisable.

4. Conclusions

This research supports the following conclusions:

- The threshold for USACEHR biomonitor alarms in response to TRC is between 0.015 and 0.066 mg/L.
- The threshold for USACEHR biomonitor alarms in response to sodium bisulfite is between 24 and 48 mg/L (nominal concentrations).
- Use of a commercial dechlorinator in-line prior to the USACEHR

biomonitor allowed chlorinated water to be continuously monitored for extended periods of time.

- It should be possible to use the dechlorinator with other types of biomonitors if the monitored aquatic organism's sensitivity to residual chlorine is similar to that of the bluegills used in the USACEHR biomonitor.
- Applications of the dechlorinator in association with the biomonitor include monitoring of water treatment plant product water or chlorinated water at strategic points in water distribution systems.
- The utility of the dechlorinator has been demonstrated in chlorinated water with relatively low TOC levels. Dechlorinator use with water having high TOC levels or with chloraminated water has not been demonstrated. Further research should be conducted to evaluate dechlorinator effectiveness in waters that have TOC levels exceeding 1 – 2 mg/L or that have been disinfected with chloramines.

5. Recommendations

The USACEHR aquatic biomonitor can successfully monitor chlorinated drinking water when used as described in this report. However, based on experience gained with this application, the following suggestions are offered for improving overall operation:

- Adding a flow controller would help ensure a consistent chlorinated water flow rate so that the correct concentration of sodium bisulfite is maintained. Output from a flow meter could provide a feedback loop to the distribution pump of the dechlorinator.
- A pressure switch could be added to shut off sodium bisulfite additions if chlorinated water flow is lost. This would have eliminated the overdosing of sodium bisulfite associated with one of the biomonitor alarms.

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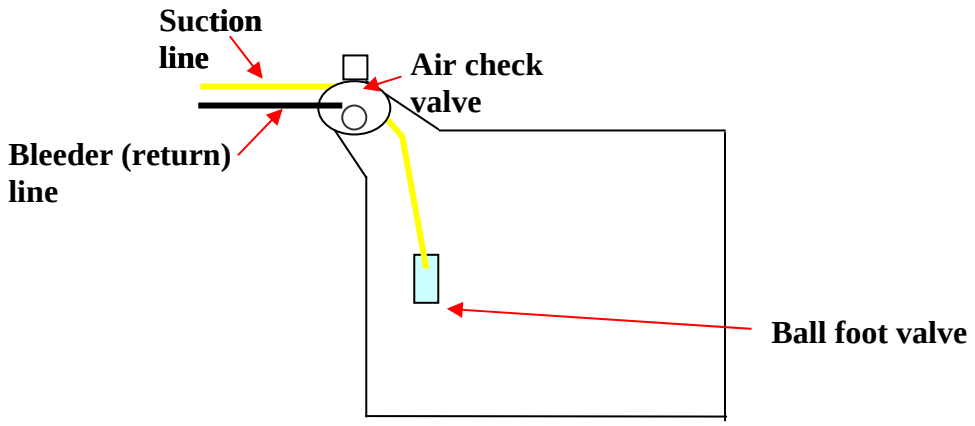
Appendix A. Jerrican Modification Procedures

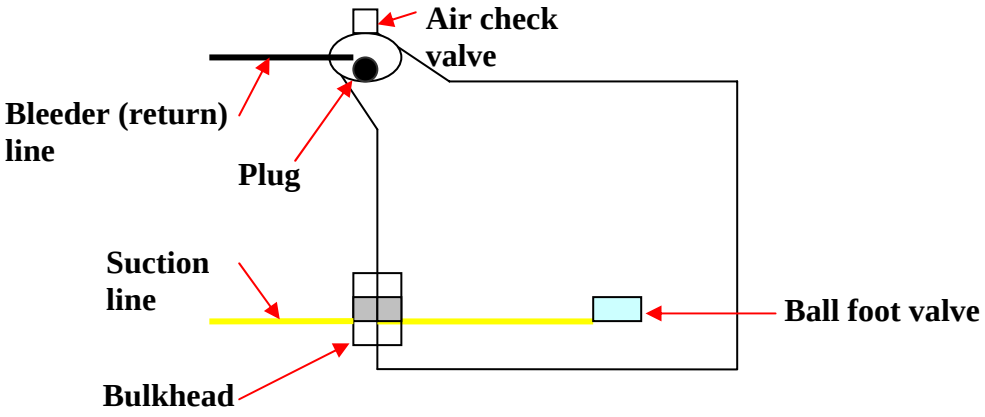
The jerrican required significant modification for use with the biomonitoring system (Figure A1a). The original jerrican had the suction line exiting the jerrican at the cap opening, which occasionally led to the loss of pump priming. This also meant that the dechlorinator had to be turned off when sodium bisulfite solution was added. The jerrican was modified to include a bulkhead fitting (Figure A1b) to ensure that the suction line remained submerged. The jerrican should be located above the pump to avoid the loss of pump priming and must be tightly capped to prevent loss of sodium bisulfite. A modified jerrican that has a suction line installed in the bottom of the jerrican in may be available for purchase from GEO-CENTERS, INC. the near future. The availability is dependent on the frequency of dechlorination unit applications with low volume pumping needs. In any case, procedures for modifying the original jerrican are described below.

Figure A1. Jerrican Configurations.

A1a. Original Configuration.



A1b. Modified Configuration.



The flooded suction configuration shown in Figure A1b was achieved as follows. To modify the cap assembly, the yellow suction line tubing and Swage-lock connection on both sides of the cap assembly were removed. A ¼" threaded plug was placed into the threaded opening where the suction lines were (Figure A2). The bleeder return line and air-check valves were still needed in

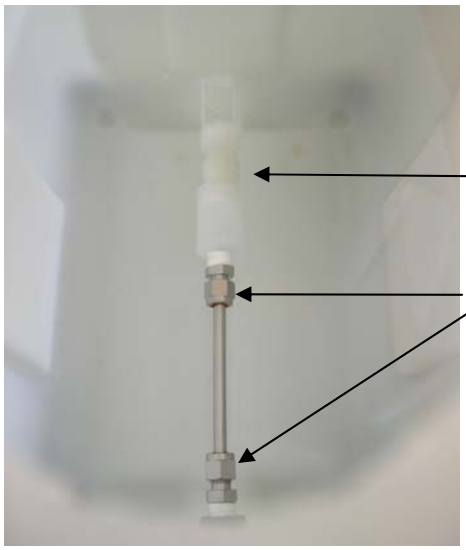
Figure A2. Modified Cap Assembly

their configuration. Next, the suction line was modified (Figure A3). A 20 L Nalgene jerrican with a ¾" spigot (US Plastics #67015) was purchased for use as the reservoir for the dechlorination unit. The ¾" spigot was removed. The ball foot-valve was modified to be placed through the ¾" hole by removing it from the cap assembly and attaching it to approximately 6 inches of steel tubing using compression fittings. The end compression fitting was attached to a threaded ¼" nipple and was then screwed into a ¼" to ¾" bushing.

This assembly was dropped into the empty jerrican through the upper opening. Using two unraveled coat hangers in a forceps-like motion, the assembly was pulled through the ¾" hole so that the ½" nipple was barely protruding from the hole. At this point, a ½" to ¾" threaded coupling was screwed to the assembly to keep it from falling back into the jerrican. Then ½" to ¼" bushings were screwed into the originally-provided Swage-lock steel fitting.

Figure A3. Suction Line Modifications

A3a. View Inside Jerrican



A3b. External View

List of Symbols, Abbreviations, and Acronyms

BEWS	Biological early warning systems
CAS	Chemical Abstracts Service
CDF	Chlorine demand free
d	Day
FRC	Free residual chlorine
g	Gram
h	Hour
LC50	Concentration of a chemical lethal to 50% of exposed organisms in a specified period of time
L	Liter
m	Meter
mg	Milligram
mL	Milliliter
mS	Millisiemen
min	Minute
NTU	Nephelometric turbidity unit
s	Second
TOC	Total organic carbon
TRC	Total residual chlorine
USACEHR	U.S. Army Center for Environmental Health Research
YSI	Yellow Springs Instrument