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# Decontamination of Malathion from Drinking Water Distribution System and Premise Plumbing Infrastructure



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# Decontamination of Malathion from Drinking Water Distribution System and Premise Plumbing Infrastructure

by

Jeffrey Szabo, John Hall, and James Goodrich Center for Environmental Solutions and Emergency Response Cincinnati, OH 45268

And

Sue Witt Aptim Federal Services Cincinnati, OH 45204

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and

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### **Disclaimers/Notices**

### 1.1 Disclaimers

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, funded and managed the research described herein under Contract 68HERC19D0009, Task Order 68HERC19F0172 with Aptim and Interagency Agreement DW-89-92381801 with the Department of Energy. It has been subjected to the Agency's review and approved for publication. Note that approval does not signify that the contents necessarily reflect the views of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the U.S. Government or EPA. The EPA does not endorse any commercial products, services, or enterprises. Contractor's role did not include establishing Agency policy.

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<u>On-site Field Support</u> Stephen Reese, Idaho National Laboratory

# **Abbreviations**

BWS CCC CFU cm CWA DC DPD EPA ft gal gpm h HDPE HSRP ICV INL L FB m MB MD mg µg/L min mL MSD NIST NTU PEX PVC QA QC RPD sec	bulk water sample continuing calibration check colony forming unit(s) centimeter(s) chemical warfare agent District of Columbia N,N-diethyl- <i>p</i> -phenylenediamine Environmental Protection Agency foot/feet gallon gallon(s) per minute hour(s) high-density polyethylene Homeland Security Research Program initial calibration verification Idaho National Laboratory liter(s) laboratory fortified blank meter(s) method blank matrix duplicate milligram(s) microgram per liter minute(s) milliliter(s) method reporting limit matrix spike matrix spike duplicate National Institutes of Standards and Technology nephelometric turbidity units cross-linked polyethylene polyvinyl chloride quality assurance quality control relative percent difference second
RPD	relative percent difference
0100	Water Security Test Ded

### **1** Executive Summary

The U.S. Environmental Protection Agency's (EPA's) Homeland Security Research Program partnered with the Idaho National Laboratory (INL) to build the <u>Water Security Test Bed (WSTB)</u> at the INL test site outside Idaho Falls, Idaho (USEPA, 2023). The WSTB was built using an 8-inch diameter cement-mortar-lined ductile iron drinking water distribution pipe that had previously been taken out of service. The pipe was exhumed from the INL grounds and used to create a small (450 feet long) drinking water distribution system. The WSTB can support drinking water distribution system research on a variety of topics, including biofilms, water quality, sensors, and homeland security-related contaminants. Since the WSTB is constructed of real drinking water distribution system pipes, research can be conducted under conditions that are representative of those in a drinking water distribution system (USEPA, 2016; USEPA, 2018).

This report summarizes the results of infrastructure decontamination experiments performed at the WSTB. These experiments focused on simulating contamination of drinking water distribution pipes with a commonly available insecticide formulation containing malathion. Malathion is used to control mosquitoes and a variety of insects that attack fruits, vegetables, landscaping plants, and shrubs. Large quantities of malathion containing insecticides can be purchased at a hardware store and later introduced into a water system. However, malathion is also an organophosphorus pesticide and is a surrogate for the chemical warfare agent (CWA) VX (Bartelt-Hunt et al., 2008). Thus, malathion can be used to assess CWA decontamination in water systems instead of VX, which would be prohibitively expensive to use at the full scale.

To assess infrastructure decontamination, common processes used by water utilities to clean their pipes were implemented. First, a fire hydrant in the 450-ft WSTB distribution pipe was opened, and the water was flushed at approximately 50 gpm (189 L/min, velocity of 0.32 ft/sec) for 20 minutes (min). Flow was reduced to 15 gpm (57 L/min) for an additional four hours, then to a 2.5 gpm (9.5 L/min) for an additional three days. Bulk water samples (BWS) and biofilm samples of the pipe interior were taken during each phase of the experiment to determine if contamination was removed from the distribution pipe. In addition, a premise plumbing system, which included a water heater, refrigerator, dishwasher, and washing machine, was contaminated with malathion. The system was flushed by opening taps or running the appliance.

These experiments were designed to provide water utility operators with realistic expectations of how effective standard decontamination processes like flushing would be for returning the distribution system to service. The following is a summary of the results:

- Malathion concentration in the 450 ft (137 m) pipe was 85,000 µg/L during contamination. Flushing at 50 gpm (189 L/min) for 20 min reduced the malathion concentration in the water by 84%. Subsequent flow at lower rates over the next four hours increased malathion removal to more than 99.99%. This level of removal was maintained over the next three days.
- Malathion adsorbed to inner pipe surface coupons (4 to 5 µg/cm<sup>2</sup>) sampled from the 450 ft (137 m) pipe during contamination. Except for one increase one day after contamination, malathion was not detected on pipe surface coupons after the pipe was flushed.

• Malathion contamination of the premise plumbing system achieved a concentration of 87,000 µg/L in the cold-water tap, with lower concentrations in the hot-water supply pipe, hot-water tank and appliances, likely due to dilution from the hot-water tank. One round of flushing the cold-water pipe removed 96% of the malathion, while emptying the hot-water tank and running the appliances removed at least 98-99% of the malathion. The exception was the refrigerator water dispenser, where 90% of the malathion was removed via flushing. Another round of flushing the next day increased malathion removal to 99.9%, except for the dishwasher and refrigerator water dispenser, where 99% was removed. Malathion was more persistent in the dishwasher and refrigerator water dispenser than the other pipes and appliances. This might be due to malathion adsorbing to the plastic components in these devices.

Flushing was an effective decontamination method for malathion in drinking water pipes and home plumbing pipes and appliances. Greater than 99.9% malathion removal was observed after flushing in most pipes and appliances. The exception was appliances in the premise plumbing system with plastic components. Additional flushing or remediation approaches beyond what was conducted in this study might be needed to effectively decontaminate these appliances.

### **2** Introduction

The U.S. Environmental Protection Agency's (EPA's) Homeland Security Research Program (HSRP) has partnered with the Idaho National Laboratory (INL) to build the <u>Water Security Test</u> <u>Bed (WSTB)</u> at the INL desert facility ~40 miles west of Idaho Falls, Idaho (USEPA, 2023). The centerpiece of the WSTB is an 8-inch (20 cm) diameter cement-mortar-lined ductile iron drinking water pipe that had been taken out of service. The pipe was exhumed from the INL grounds and used to create a small drinking water distribution system. The WSTB has been fitted with service connections, a premise plumbing and appliance system, fire hydrants, and removable coupons (excised sample materials) to collect samples from the pipe inner surface (USEPA, 2016; Szabo et al., 2017; USEPA, 2018).

Previously, experiments focused on decontamination of various contaminants that adsorbed to the inner surface of the 8-inch water pipe have been conducted at the WSTB (USEPA, 2016; Szabo et al., 2017; USEPA, 2018). In response to a contamination event, drinking water utilities will likely flush the distribution system using fire hydrants. This could include flushing water at high flow rates for short periods or allowing flow through hydrants or home and building taps at lower flows for longer periods of time.

Experiments described in this report focus on simulating contamination of drinking water distribution pipes with malathion, which is a commonly available organophosphorous insecticide. Malathion is a contaminant of interest for two reasons. First, it is commonly available in multiple commercial products at hardware and home improvement stores. Large quantities of malathion could be accumulated over time and used to contaminate a water system. Second, as an organophosphorus chemical, it shares chemical and physical properties with the chemical warfare agent (CWA) VX without its associated toxicological properties (Bartelt-Hunt et al., 2008; Rauglas et al., 2016). Therefore, malathion is a good surrogate for VX that can be used to study CWA contamination and decontamination of drinking water systems and home plumbing via flushing without using the actual agent. The experiments were designed to provide full scale data to utility operators considering using flushing to return a water distribution system to service after contamination with malathion.

### **3 WSTB System Description**

A primary feature of the WSTB is an 8-inch (20 cm) diameter cement-mortar-lined ductile iron drinking water pipe positioned to replicate a small drinking water distribution system. The WSTB contains ports for service connections and a 15 ft (5 m) removable coupon section designed to allow sampling of the pipe interior to examine contamination/decontamination of test agents deposited on the pipe wall. Figure 1 schematically depicts the main features of the WSTB, and Figure 2 shows an overhead view with major components labeled. Detailed discussion of the WSTB setup can be found in USEPA, 2016, USEPA, 2018 and USEPA, 2023.

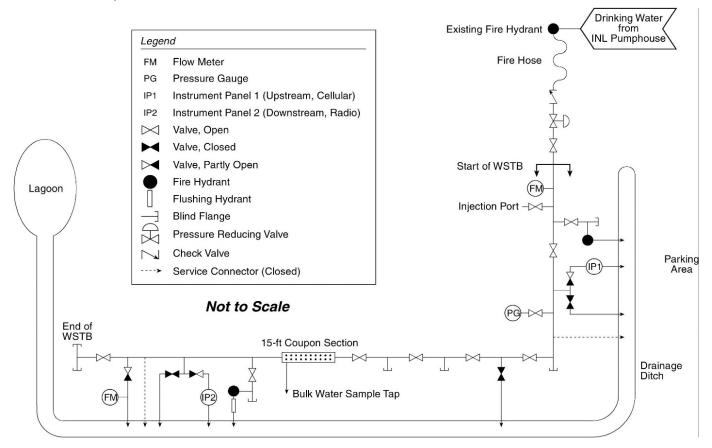


Figure 1: Schematic overview of the Water Security Test Bed (WSTB).

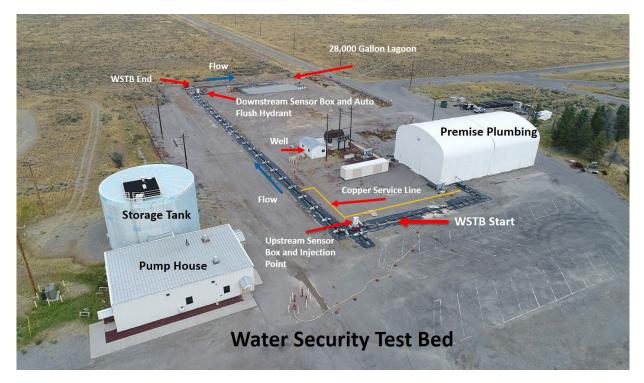


Figure 2: Aerial view of the Water Security Test Bed (WSTB).

Drinking water supplied to the WSTB is chlorinated ground water that also supplies the surrounding INL facilities. The WSTB incorporates approximately 450 ft (137 m) of 8-in (20 cm) diameter cement-mortar-lined ductile iron pipe. The 8-in (20 cm) pipe system is constructed directly over the lined drainage ditch for spill/ leak containment (as shown in Figure 2). The total volume of the WSTB is estimated to be approximately 1,150 gallons (4,353 L). The effluent water from the WSTB system can be discharged to a lined lagoon (Figure 3) that has a total water storage capacity of 28,000 gallons (105,980 L).



Figure 3: Water Security Test Bed discharge lagoon.

The WSTB also includes a premise plumbing system that is connected to the 8-in (20 cm) diameter distribution main via a 1-in (2.5 cm) copper service connection (seen in Figure 2). Water flows through the service connection into a water meter, copper plumbing pipes, a removable pipe coupon section with copper, polyvinyl chloride (PVC), and cross-linked polyethylene (PEX) pipes, and appliances including a water heater, dishwasher, washing machine, and refrigerator with water dispenser. Water empties into a utility sink with hot- and cold-water taps and then drains to an exterior tank. All water from the tank eventually flows to the lagoon. These components are shown in Figure 4.



Figure 4: Premise plumbing setup at the WSTB: the water meter outside the building (top left), premise plumbing pipes (top middle), water heater (top right), dishwasher, washing machine and refrigerator (bottom left), utility sink (bottom middle) and exterior tank (bottom right).

## 4 Description of Malathion Contamination and Decontamination Experiments

### 4.1 Pipe Materials Tested

The distribution system-sized pipe used at the WSTB for decontamination experiments is constructed of 8-in (20 cm) diameter cement-mortar-lined ductile iron and was previously excavated from the INL property. This piping had been used for water distribution for over 30 years prior to excavation and installation at the WSTB. Visual inspection of the cement-mortar lining indicated that the lining was in good condition. The interior and exterior view of this pipe is shown in Figure 5. Removable coupons of the cement mortar lined pipe are shown in Figure 6, as is the section of pipe where they are located.

Pipe in the premise plumbing system is mostly 1-in (2.5 cm) diameter copper, with coupon sections made of copper, PVC and PEX (Figure 4, top middle).



Figure 5: External and internal view of the cement-mortar lined pipe.



Figure 6: Removable pipe coupon section and images of the coupons.

### 4.2 Contamination and Decontamination Procedures

Contamination and decontamination took place in the 450-ft (137 m) distribution pipe, home plumbing and short individual sections of pipe. The following sections describe those processes.

#### 4.2.1 Distribution System Pipe

Before contamination, biofilm formation was accomplished by passing local INL tap water through the pipe continuously for four weeks. After initial flushing to remove any debris, the 450-ft (137 m) WSTB pipe was set to 2.5 gpm (9.5 L/min) for the four-week biofilm formation period. This procedure has been used to form biofilms in the pipe during previous experiments, resulting in biofilm levels of 10<sup>4</sup> to 10<sup>5</sup> CFU/cm<sup>2</sup> (USEPA, 2016; USEPA, 2018). These biofilm levels have been consistent between past experiments, so the same formation conditions were used for this experiment.

Contamination of the pipe occurred by first diluting a commercially available malathion formulation in multiple 6.5 gallon (24.6 L) buckets. The pesticide formulation was 50% malathion (by weight) in a 1-quart bottle, which contains 1.07 lb (485.78 g, or 485,780 mg) malathion. The contents of the 1-quart bottle were diluted to 40 L using local tap water from the INL site. This solution was pumped using a gear pump into the INL pipe at 0.667 L/min, which resulted in the 40 L being pumped in 1 hour. Flow in the pipe was 15 gpm (56.8 L/min), which theoretically resulted in 142 mg/L malathion in the contaminant slug. This setup is depicted in Figure 7.



Figure 7: Malathion contaminant injection setup in the 450 ft pipe.

After the 1-hour contaminant injection, the first decontamination step was to flush the system through the downstream fire hydrant. Flushing is shown in Figure 8. A fire hose was attached to the downstream fire hydrant (Figure 8, left) with the outlet placed in the lagoon and braced with sandbags and cement blocks (Figure 8, right). The hydrant was opened so that flow through the hose was estimated to be 50 gpm (189 L/min). Flushing in this manner took place for 20 min. After 20 minutes, the hydrant was closed, and flow was set to 15 gpm (57 L/min) using the flowmeter at the end of the pipe for the next four hours. After the four-hour period, flow through the flowmeter was set to 2.5 gpm (9.5 L/min), where it remained for the rest of the experiment.



Figure 8: Flushing contaminated water from the WSTB distribution pipe via the downstream fire hydrant. The left image is the fire hydrant with the hose connected, and the hose in the lagoon with sandbags is on the right.

#### 4.2.2 Premise Plumbing System

Before contamination, tap water continuously flowed through the premise plumbing system for four weeks to allow biofilm and deposits to form on the inner surfaces of the pipes and appliances. During this pre-contamination phase, total flow though the plumbing system was set to 138 gallons per day (0.096 gpm or 363 mL/min), which is the typical usage in many households (DeOreo et al., 2016). Water flowed through the utility sink taps, with equal flows through the hot- and cold-water taps. Flow was regulated by a set of flowmeters downstream from the utility sink (Figure 9). The dishwasher and washing machine were operated for one cycle once per week, and the refrigerator water dispenser was opened for 10 minutes once per week.



Figure 9: Flow meters downstream from the utility sink used to control flow through the premise plumbing system.

Contamination of the premise plumbing system was accomplished by pumping diluted malathion from a bucket into the flow meter (Figure 10). A 10 L solution of 3,976 mg/L malathion was made by diluting 39.76 g (0.088 lbs, or 77 ml of the 50% malathion solution) up to 10 L in a bucket. The 10 L solution was injected into the premise plumbing system at 0.167 L/min for 1 hour, with the premise plumbing system flow set to 1.6 gpm (6.06 L/min), split equally between cold and hot water. The resulting concentration of malathion was theoretically 110 mg/L. The refrigerator flow, dishwasher and washing machine were started 20 min after the injection started.



# Figure 10: Malathion contamination of the premise plumbing system. Diluted malathion is pumped from a bucket into a flow meter, where it flows into the copper pipe.

Decontamination was performed based on the findings of the Water Research Foundation report 4572 titled "Flushing Guidance for Premise Plumbing and Service Lines to Avoid or Address a Drinking Water Advisory" (WRF, 2016). In this report, suggestions for how to flush household plumbing and appliances were derived from an expert panel of water industry professionals. The specific suggestions summarized in the report are as follows (reproduced verbatim from the report):

#### Flushing Cold-Water Taps

- Begin by running the cold-water faucet closest to where water enters the house. Starting from the point closest to where water enters the house, open all the other cold-water taps and allow the water to run for 20 minutes.
- Next, flush toilets at least once. If a bathtub has a spout and showerhead, direct flow through the spout.
- Flush all outside spigots for 10 minutes.
- After flushing all cold taps, direct the flow from the bathtub spout to the showerhead, if applicable.

#### Flushing Hot-Water Taps and Water Heater

- Run the hot-water tap closest to the water heater and proceed to open all hot-water taps.
- If a bathtub has a spout and shower head, direct flow through the shower head first.
- Allow the water to run for at least 75 minutes and then turn off the faucets.
- If applicable, direct shower head flow to bathtub tap for 2 minutes.

#### Flushing Appliances

- Run empty dishwasher and washing machine once on rinse cycle.
- Replace all water filters (e.g., whole-house filter, refrigerator filter, etc.) and empty ice from ice maker bin; run ice maker and discard 2 additional batches of ice.

Based on the suggestions given in the report, the premise plumbing system was flushed in stages. First, the utility sink hot-water tap was closed, the valve to the water heater was turned off, and the cold-water tap on the utility sink was fully opened. Simultaneously, the cold-water dispenser on the refrigerator was opened to its maximum setting. Cold water was flushed for 20 min. The cold-water pipes were turned off after they were flushed. The water heater tank was then drained and filled with tap water, and the hot-water tap in the utility sink was fully opened for 75 min. At the conclusion of the hot-water flushing, the dishwasher and washing machine were operated for one cycle.

At the conclusion of decontamination, the premise plumbing system was operated at an average flow rate of 138 gallons per day (0.096 gpm or 363 ml/min) overnight. Samples were collected the morning after the contamination/decontamination on the previous day. Cold water, hot water and appliance decontamination was performed a second time to remove any residual contaminant from the plumbing. Once this second round of decontamination was complete, additional samples were collected to determine the efficacy of decontamination.

#### 4.2.3 Experimental Methods

#### Malathion

Malathion was analyzed using EPA Method 8270D (USEPA, 2014). Coupon and bulk water sampling methods are described below.

#### Extraction of biofilm and adsorbed malathion from coupon surfaces

Removable cement-mortar coupons in the WSTB pipe were sampled by shutting off water flow to a small section of the pipe containing the coupons, draining water to relieve pressure, and unscrewing the coupons. The coupons were scraped with a sterile scalpel (Thermo Scientific, Waltham, MA) into a sterile sample bottle (Thermo Scientific, Waltham, MA) containing sterile buffer (Sigma Aldrich, St. Louis, MO) while periodically rinsing the scalpel with sterile buffer. Samples were scraped five times.

The extracted material was collected in a sterile sample bottle with a sodium thiosulfate tablet (Thermo Scientific, Waltham, MA) (for dechlorination of the water) and 100 mL of pre-filled carbon-filtered water. The extracted sample was transferred to a cooler with ice to maintain temperatures of  $4 \pm 2$  °C. The samples were shipped overnight to thelaboratory and analyzed within the sample hold time.

#### Bulk Water Sampling

The bulk water samples (BWS) for malathion and other water quality parameters were collected using the grab sampling technique in 100 mL sterile sample bottles. The bulk water sampling port in the WSTB coupon section was opened and the water was drained for 15 seconds prior to collection of 100 mL of water from the WSTB. The same procedure was used for taps in the premise plumbing system. Samples were shipped to a lab on ice (4 ±2  $^{\circ}$ C) and analyzed within the holding time of the analyte.

#### Free Chlorine

Free chlorine samples were analyzed immediately in the field using the Hach Method 10102 using N,N-diethyl-*p*-phenylenediamine (Hach, 2022). Samples were diluted in distilled water as needed.

#### Turbidity, Conductivity, pH and Temperature

These parameters were analyzed immediately in the field. Turbidity was measured using a Hach 2100P Portable Turbidimeter (Hach Corp., Loveland, CO), and all analyses and calibration followed the manufacturer's instructions. Conductivity, pH, and temperature were measured by a YSI 556 multiprobe sonde (Xylem, Rye Brook, NY). All analyses and calibrations followed the manufacturer's instructions.

## **5** Quality Assurance

### 5.1 Quality Control

Quality control (QC) samples for the contaminant reference method included continuing duplicate samples, controls, and laboratory blanks and spikes. The data quality objectives for each of these quality control samples are provided in Table 1. The acceptance criteria limit the error introduced into the experimental work. All analytical methods operated within the QC requirements for controls and laboratory blanks, and unless otherwise noted in the Deviations (Section 5.3), all data quality objectives in Table 1 were met. Note that duplicate samples refer to a duplicate analysis of one sample.

			Acceptance	
Measurement	QA/QC Check	Frequency	Criteria	Corrective Action
Malathion	Multilevel calibration	Initially	Analysis of standard solutions should result in a linear coefficient of determination (r <sup>2</sup> ) of 0.99 or greater, using a minimum of six independent concentrations that bracket the sample analysis.	Recheck the standard and if necessary, repeat calibration
	Second Source Standards for Initial calibration verification (ICV)	Immediately after calibration	ICV ±30% of expected value	Recheck ICV standard and reanalyze. Repeated failure warranted recalibration
	Initial and Continuing Calibration Checks (CCC)	Initially, after every 10 samples and at the end of sample sequence	80-120% of expected value	Investigate problem, re-analyze affected samples
	Method Blanks (MB)	One with each set of extracts	<mrl< td=""><td>Investigate problem, re-analyze method blank</td></mrl<>	Investigate problem, re-analyze method blank
	Laboratory Fortified Blank (LFB)	Each extraction batch of 20 samples	The analyses are considered acceptable if the calculated concentrations are ±30% of the expected values.	If the LFB results do not meet these criteria for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. Repeat extraction.
	Surrogate	Each sample	Limits based	When SG recovery

#### Table 1: QA/QC criteria for methods used during malathion decontamination tests.

		_	Acceptance	
Measurement	QA/QC Check Standard (SG)	Frequency and standard prior to extraction	Criteria upon statistical study (rounded to 0 or 5) for the target compound analyses. Generally, acceptable SG recovery is 50 – 150%.	<b>Corrective Action</b> from a sample is less than 60% or greater than 140%, check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. Correct the problem and reanalyze the extract.
	Matrix Spikes/ Matrix Spikes Duplicate	10% of samples	±30% Recovery for MS or MD/MSD RPD ≤ 30%	If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.
Free Chlorine	Manufacturer DPD color standards kit	Once per experiment	As specified by the color standards kit	Clean the colorimeter measuring cell. Clean the DPD standards vials and recheck.
Turbidity	Check standard set for 2100 P	Once per day	Deviation of ± 0.2 NTU	If it fails, repeat calibration
Specific Conductivity	Initial calibration	Once per day	Deviation of ± 5%	If it fails repeat calibration
рН	Initial calibration Calibration check	Once per day	±0.1 pH units ±0.1 pH units	Check standard buffers for contamination, check electrode for electrolyte, replace probe if required
Temperature	NIST calibration Source	When purchased	Pass	NA

### 5.2 Data Quality

At least 10% of the data acquired during the evaluation were audited. These data include the biofilm malathion measurements, BWS and water quality measurements. The data were traced from the initial acquisition, through analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked. No significant adverse findings were noted in this audit.

### 5.3 Deviations

When scraping the surface of the pipe coupons, the sampling method calls for the scraping to be conducted five times and for the scrapings to be placed into sterile water. The same person performed the scraping for the same number of times to ensure consistency between scrape samples. However, there is inherent variation in how much pressure is applied to each scrape. It was not possible to precisely quantify this variation.

# 6 Experimental Results

### 6.1 Water Quality

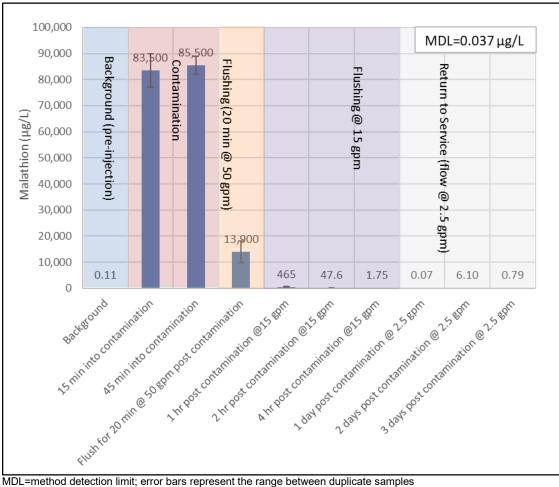
Water quality samples were taken from the sample port in the coupon section of the 450 ft (137 m) WSTB pipe. Before contamination, free chlorine ranged from 0.15-0.20 mg/L; turbidity was 0.24 NTU; conductivity was 404  $\mu$ s/cm; pH ranged from 6.8 to 6.9 and temperature ranged from 19-22° C. Parameters returned to these ranges and values during the "return to service" period of the experiment (see figures in the next section). Free chlorine dropped to zero during contamination, but other parameters were not monitored during contamination.

### 6.2 Decontamination of Malathion from the 450 ft pipe

Figure 11 and Figure 12 show the phases of the decontamination experiment in the 450 ft (137 m) WSTB pipe. Background is the baseline malathion concentration in the water or on the pipe surface before contamination. The contamination phase is when the insecticide containing malathion was injected into the pipe. The flushing phase (20 min @ 50 gpm or 189 L/min) is when the downstream fire hydrant was opened for 20 min at a flowrate of approximately 50 gpm (189 L/min). Flushing at 15 gpm (57 L/min) took place immediately after the 50-gpm (189 L/min) flush and lasted for 4 hours. Return to service occurred after the flushing phases. The flow was lowered to 2.5 gpm (9.5 L/min) for the next three days, which represented a baseline level of flow, or return to normal service.

Figure 11 shows that a small amount of malathion (0.11  $\mu$ g/L) was detected in the water before contamination. It's possible that low levels of malathion could be present due to local insecticide use, but there could also be interference from constituents in the local tap water or external contamination. During contamination, malathion increased to 83,500 to 85,500  $\mu$ g/L in the contaminant injection pulse. Flushing at 50 gpm (189 L/min) for 20 min reduced the malathion concentration by 84% to 13,900  $\mu$ g/L. The flushing period was designed to remove one pipe volume, which is approximately 1,000 gallons (3,785 L). Residual malathion in the pipe after the 20 min flush can be attributed to malathion persistence in dead leg portions of piping (i.e., pipe sections that are isolated from the normal flow of water). These sections are difficult to flush and could be a source of the residual malathion detected in this study post-flushing. Additionally, the slug dosing of the contaminant could have resulted in an elongated longitudinal dispersion of the malathion (e.g., a U-shaped pattern of dispersion) (Yang et al., 2008), where the tail ends of the dispersed contaminant were still in the pipe at the end of the 20 min flush period.

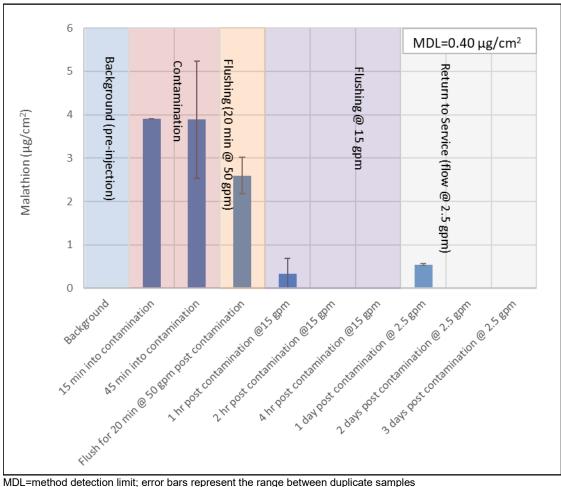
Malathion concentration continued to decrease at the one-, two-, and four-hour time points postcontamination during flushing at a flow rate of 15 gpm (57 L/min). At the four-hour time point, malathion concentration was reduced by over 99.99%. Malathion samples taken 1, 2, and 3 days after contamination with flow at 2.5 gpm (9.5 L/min) showed that malathion concentration was close to background levels (Figure 11). The one exception was day two postcontamination, when concentration spiked to 6.1  $\mu$ g/L. While external contamination of the sample can't be ruled out, this spike might have come from malathion hung up in a dead end or fixture in the pipe. If flushing is used in practice to mitigate a malathion contamination incident, contamination trapped in dead ends should be considered when designing a flushing strategy.



MDL=method detection limit; error bars represent the range between duplicate samples

#### Figure 11: Contamination and decontamination of malathion from the bulk water phase using flushing in the 450 ft WSTB pipe.

Coupons containing the pipe interior material of construction (cement-mortar) were also sampled for any adsorbed malathion. Results are shown in Figure 12. No malathion was detected on the coupons before contamination. During contamination, adsorbed malathion increased to nearly 4 µg/cm<sup>2</sup>. After flushing for 20 min at 50 gpm, adsorbed malathion levels dropped to 2.6 µg/cm<sup>2</sup>, or a decrease of 33%. As noted earlier, malathion was still present in the water during this sample point, and this likely contributed to the presence of malathion on the interior pipe surface. Malathion levels on the pipe material further decreased to 0.34 µg/cm<sup>2</sup> (91% reduction) one hour after contamination when the flow was at 15 gpm (57 L/min). This value is below the MDL. At two and four hours after contamination (flow at 15 gpm/57 L/min), no malathion was detected on the pipe coupons. In the days after contamination when flow was at 2.5 gpm (9.5 L/min), malathion was detected on the 1-day sample, but not at days 2 and 3. Little malathion was in the water at the 1-day sample point, so the presence of malathion on this sample was likely due to variation in adsorption between coupons. Still, the amount of adsorbed malathion on the 1-day coupon sample was 86% less than during contamination.



MDL=method detection limit; error bars represent the range between duplicate samples

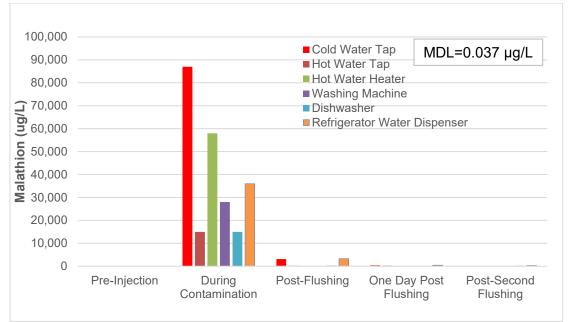
#### Figure 12: Contamination and decontamination of malathion from the pipe coupons using flushing in the 450 ft WSTB pipe.

### 6.3 Decontamination of malathion from the home plumbing system

Figure 13 shows the results from the background, contamination, and decontamination sampling phases in the home plumbing system. Background is baseline level of malathion coming out of the water taps or water in the appliances before contamination. The contamination phase is when malathion contaminated water was introduced into the pipes and appliances. The flushing phase is when the taps were flushed, the water heater drained and refilled, and the appliances run for one cycle with water. The system of pipes and appliances was sampled the next day after the previous day's flush with flow overnight. The system was flushed again and sampled. The full flushing procedure is described detail in section 4.2.2. Note that since lower concentration samples are difficult to see in Figure 13, the data and percent removal of malathion compared to the contamination concentration are summarized in Table 2.

Figure 13 shows that malathion levels spiked during contamination, with 87,000 µg/L in the cold tap, and lesser amounts in the hot water, water heater and appliances. Contaminated water was diluted in the hot-water tank, which reduced the malathion concentration in the downstream

pipes and appliances. After flushing, malathion in the cold-water line and refrigerator water dispenser (fed directly from the cold-water line) still contained 3,100 and 3,300  $\mu$ g/L (96 and 91% removal), respectively, which suggests that 20 minutes was not long enough to completely remove the contaminant pulse from the pipe. Malathion has been found to bond with copper materials in water infrastructure, and this adhesion might have played a role in the elevated levels after a round of flushing (Harper et al., 2017).



MDL=method detection limit

# Figure 13: Contamination and decontamination of malathion from the bulk water phase using flushing in the premise plumbing system.

Draining the water heater, refilling it and flushing for 75 min reduced malathion concentration to 24  $\mu$ g/L, or a 99.9% reduction. Malathion levels in the hot-water line were higher at 180  $\mu$ g/L, or a 98.8% reduction. This result is unusual since water in the hot-water line was coming from the tank and suggests that some adsorption of malathion to the copper pipe took place. It is also possible that malathion was hung up in a dead space in the hot-water plumbing and was slowly desorbing. Malathion levels in the washing machine dropped to 11  $\mu$ g/L, which was a 99.9% reduction from the contamination phase. Dishwasher malathion levels remained elevated at 220  $\mu$ g/L, or a 98.5% reduction from the contamination phase.

Following flow overnight (363 ml/min), malathion concentrations were collected in the hot and cold taps, water heater, and the refrigerator water dispenser. Levels in cold tap water and refrigerator samples dropped by nearly an order of magnitude. Water heater malathion levels were stable, while malathion concentration increased in the hot-water pipe. After another round of flushing, samples in the cold-water line and washing machine had returned to near baseline levels and decontamination was greater than 99.99%. The hot-water pipe and water heater levels remained elevated at 18 and 22  $\mu$ g/L, but decontamination was still 99.9%. Some residual malathion could have remained in the hot-water tank, which could be alleviated by draining and refilling the tank again.

The highest levels of malathion remaining after two rounds of flushing were in the refrigerator

water dispenser and the dishwasher (335 and 150  $\mu$ g/L, respectively). A possible reason for this is because both appliances have large surface areas made of plastic components. Past research has found that malathion can adsorb to and persist on polyvinyl chloride (PVC) and high-density polyethylene (HDPE) (Hermosillo-Nevarez et al., 2020). It is possible that more than two rounds of flushing/running the appliance or use of surfactants might increase the level of decontamination. However, replacement of these devices might be preferable if numerous rounds of flushing and amended flush water (e.g., addition of a surfactant) are needed for effective decontamination.

Table 2: Contamination and decontamination data from the premise plumbing system. Malathion values from each phase of the experiment are in the top portion, and percent removal is in the bottom portion.

Sample Point	Pre- Injection (μg/L)	During Contamination (µg/L)	Post- Flushing (µg/L)	One Day Post Flushing (µg/L)	Post- Second Flushing (µg/L)
Cald Water Ter					
Cold-Water Tap	0.07	87,000	3,100	370	1.8
Hot-Water Tap	1.4	15,000	180	260	18
Water heater	ND	58,000	24	28	22
Washing Machine	ND	28,000	11	*	2.2
Dishwasher	ND	15,000	220	*	150
Refrigerator Water Dispenser	ND	36,000	3,300	460	335
	Pre-	During	Post-	One Day Post	Post- Second
Sample Point	Injection	Contamination	Flushing	Flushing	Flushing
Sample Point	Injection	Contamination	Flushing	Flushing	Flushing
Sample Point Cold-Water Tap	Injection	Contamination	Flushing 96.44%	Flushing 99.57%	Flushing 99.998%
· · · · · · · · · · · · · · · · · · ·	Injection	Contamination			
Cold-Water Tap	Injection	Contamination	96.44%	99.57%	99.998%
Cold-Water Tap Hot-Water Tap	Injection	Contamination	96.44% 98.80%	99.57% 98.27%	99.998% 99.88%
Cold-Water Tap Hot-Water Tap Water heater	Injection	Contamination	96.44% 98.80% 99.96%	99.57% 98.27% 99.95%	99.998% 99.88% 99.96%

\*Samples were not taken one day post flushing for the washing machine and dishwasher.

# 7 Conclusions

The following points summarize the results of the malathion decontamination experiments performed at the WSTB. Water utility employees and personnel who respond to water contamination events can use this summary to devise a decontamination strategy if malathion or a CWA with similar chemical and physical properties to malathion contaminate a water system.

- Flushing was an effective method to remove malathion from the bulk water phase and pipe surface in the 450 ft (137 m) WSTB pipe. In the water phase, malathion concentration decreased by 99.99+% from the contamination peak to near baseline levels. Malathion was undetectable on most pipe surface coupon samples after two hours of flushing.
- While flushing was an effective decontamination method for malathion, the data did indicate two areas to consider when designing a flushing strategy. First, malathion concentration did increase by a small amount two days after contamination when flushing was complete. Although the cause is uncertain, the increase could be due to malathion trapped in a dead-end reemerging into the 450 ft (137 m) pipe. Second, malathion was detected on a coupon sample one day after contamination when flushing was complete, and previous samples showed no detection. This data suggests that variations in pipe surface could lead to malathion adhering to some portions of the pipe surface more than others.
- Malathion was effectively removed from the home plumbing system using flushing and running the appliances, with removal in all pipes and appliances over 99%. Two rounds of flushing were needed for malathion levels in the cold-water pipe and washing machine to approach pre-contamination baseline levels. Levels of malathion ranged from 18-22 µg/L even after two rounds of flushing in the hot-water line and water heater. This may have been due to malathion being trapped in the water heater and could be alleviated by emptying the water heater more than twice. Malathion levels remained elevated in the refrigerator water dispenser and dishwasher (335 and 150 µg/L, respectively) after flushing. This may be due to adsorption to the plastic components in these appliances. Additional flushing could result in further malathion removal, but replacement might be preferable if extensive flushing is needed. Further research on this subject is needed to determine the various mechanisms of contaminant persistence in home appliances. This would help to inform and implement appropriate and effective decontamination procedures.
- The level of malathion contamination in the 450 ft (137 m) pipe and the cold-water pipe in the home plumbing setup was between 85,000 and 90,000 µg/L. If malathion containing insecticide was introduced into a water system, this concentration is high enough that tap water consumers would detect odors from the commercial product and the water would look cloudy. This level of contamination would likely be hard to achieve over a wide area in a real water system. Since flushing was an effective decontamination method at the high concentrations used in this study (which represented a worse-case scenario), the flushing strategies employed here should also be effective at lower contaminant levels. Any effects of adsorption to pipe or appliance surfaces would be

less, and less would be trapped in pipe dead ends or areas of low flow.

### 8 References

- APHA (American Public Health Association) (2005). Standard Methods for the Examination of Water and Waste Water, Method 9222D, 21st edition. Washington, DC: American Public Health Association.
- Bartelt-Hunt, S.L., Knappe, D.R.U, and Barlaz, M.A. (2008). A review of chemical warfare agent simulants for the study of environmental behavior. *Critical Reviews in Environmental Science and Technology*, 38(2): 112-136.
- DeOreo, W.B., Mayer, P.W., Dziegielewski, B., and Kiefer, J.C. (2016). Residential Uses of Water 2016. Water Research Foundation. Denver, CO.
- Hach (2022). Chlorine, Free and Total, High Range. <u>https://cdn.bfldr.com/7FYZVWYB/at/xtn3qr6g6gzrvfgr3c7kg43/DOC3165301449\_7ed.pd</u> <u>f</u>. Last Accessed Feb. 25, 2022. Hach Corporation, Loveland, CO.
- Harper WF Jr., Flemings W, Bailey K, Lee W, Felker D, Gallardo V, Magnuson M, and Phillips R. (2017). Adsorption of Malathion onto Copper and Iron Surfaces Relevant to Water Infrastructure. J Am Water Works Assoc. 109(11): 494-502.
- Hermosillo-Nevárez JJ, Bustos-Terrones V, Bustos-Terrones YA, Uriarte-Aceves PM, and Rangel-Peraza JG. (2020). Feasibility Study on the Use of Recycled Polymers for Malathion Adsorption: Isotherms and Kinetic Modeling. *Materials,* 13(8): 1824.
- Rauglas, E., Martin, S., Bailey, K., Magnuson, M., Phillips, R., and Harper, W.F. (2016). The effect of malathion on the activity, performance, and microbial ecology of activated sludge. *Journal of Environmental Management*, 183: 220-228.
- Szabo, J.G., Hall, J., Goodrich, J. and Ernst, H. (2017). Full scale drinking water system decontamination at the Water Security Test Bed. *Journal of the American Water Works Association*, 109(12): E535-E547.
- USEPA (U.S. Environmental Protection Agency), 2014. Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry. <u>https://19january2017snapshot.epa.gov/sites/production/files/2015-</u> <u>12/documents/8270d.pdf</u>
- USEPA, 2016. Water Security Test Bed Experiments at the Idaho National Laboratory. EPA/600/R-15/146, Washington, DC: U.S. Environmental Protection Agency.
- USEPA, 2018. Decontamination of Bacillus Spores from Drinking Water Infrastructure with Physical Removal (Pigging). EPA/600/R-18/078, Washington, DC: U.S. Environmental Protection Agency.
- USEPA, 2023. Water Security Test Bed. <u>https://www.epa.gov/emergency-response-research/water-security-test-bed</u>. Accessed Dec. 1, 2023.
- WRF (Water Research Foundation), 2016. Flushing Guidance for Premise Plumbing and

Service Lines to Avoid or Address a Drinking Water Advisory. Report #4572. Denver, CO.

Yang, Y.J., Goodrich, J.A., Clark, R.M., and Li, S.Y. (2008). Modeling and testing of reactive contaminant transport in drinking water pipes: Chlorine response and implications for online contaminant detection. *Water Research*, 42(6-7): 1397-1412.



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