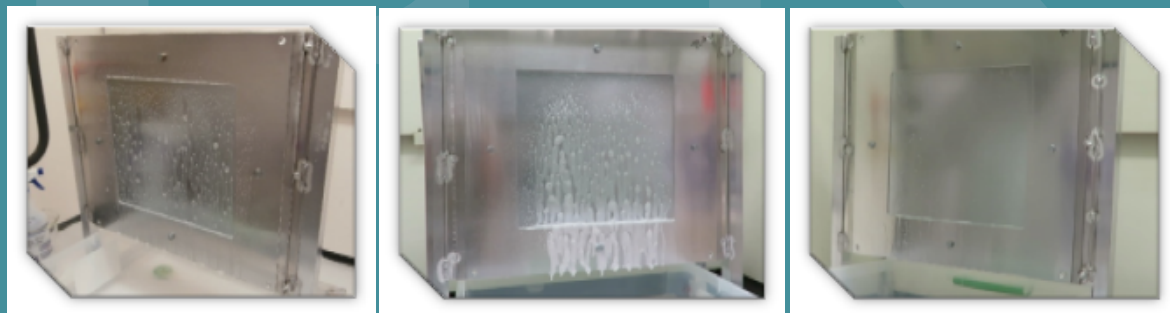


Water Rinses and Their Impact on Decontamination Efficacies of Surfaces Contaminated with Chemical Warfare Agent Simulants



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Disclaimer

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The Center for Environmental Solutions and Emergency Response (CESER) within the Office of Research and Development (ORD) conducts applied, stakeholder-driven research and provides responsive technical support to help solve the Nation's environmental challenges. The Center's research focuses on innovative approaches to address environmental challenges associated with the built environment. We develop technologies and decision-support tools to help safeguard public water systems and groundwater, guide sustainable materials management, remediate sites from traditional contamination sources and emerging environmental stressors, and address potential threats from terrorism and natural disasters. CESER collaborates with both public and private sector partners to foster technologies that improve the effectiveness and reduce the cost of compliance, while anticipating emerging problems. We provide technical support to EPA regions and programs, states, tribal nations, and federal partners, and serve as the interagency liaison for EPA in homeland security research and technology. The Center is a leader in providing scientific solutions to protect human health and the environment.

This report assesses the impact of pre- and post decontamination water rinses on the overall decontamination efficacy of a hydrogen peroxide-based decontamination product for the cleaning of clean or grimed surfaces that are contaminated with chemical warfare agent simulants. The study also investigates the presence of these simulants in the liquid runoff from these materials.

Gregory Sales, Director
Center for Environmental Solutions and Emergency Response

Acknowledgments

This research effort is part of the U.S. Environmental Protection Agency's (EPA's) Homeland Security Research Program (HSRP) to evaluate surface-applied liquid-based decontamination methodologies for decontamination of a persistent chemical agent that has (partially) absorbed into a permeable building material. The results of this work would inform responders, governments, and health departments in their guidance development for decontamination technology recommendations of building materials contaminated with toxic chemicals.

This effort was directed by the principal investigator from the Office of Research and Development's (ORD's) Homeland Security and Materials Management Division (HSMMD) within the Center for Environmental Solutions and Emergency Response (CESER). The contributions of the following individuals have been a valued asset throughout this effort.

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Executive Summary

Under Emergency Support Function (ESF) #10, the U.S. Environmental Protection Agency (EPA) coordinates, integrates, and manages the Federal effort to decontaminate and clean up infrastructure following releases of hazardous materials. Those hazardous materials include chemical, biological, radiological, and nuclear (CBRN) substances, whether accidentally or intentionally released. EPA's Homeland Security Research Program (HSRP) advances EPA's ability to carry out its homeland security responsibilities to respond to wide-area contamination. The HSRP has directed multiple research efforts that focused on liquid-based surface decontamination options using commercially available products that are expected to degrade various highly toxic chemical agents from various types of surfaces. These decontamination studies are typically limited to the measurement of efficacy of the decontamination product itself after a fixed contact time. This document reports on a study that was conducted to investigate a three-step pre-cleaning, decontamination, and post-rinse procedure that more realistically mimics possible field treatments of building surfaces contaminated with chemical warfare agents. This study also assessed whether this approach is advantageous in the presence of grime on a surface in improving overall efficacy.

A multistep decontamination procedure – consisting of detergent-water spray, followed by a spray application of a commercially available specialized decontaminant (EasyDECON® DF200) and a post-decontamination water rinse – was performed on selected nonporous, semi-porous, and porous building materials. Test materials were decontaminated in a horizontal and/or vertical surface orientation, depending on their most common use. The pre-decontamination treatment of dirty or grimed surfaces is a recommendation found in quick references guides and other remediation guidance documents as dirt and grime may interfere with the action of the decontaminant. In cases where the presence of residual decontaminant is undesirable, post-decontamination rinses are also recommended to remove residual decontaminant from the surface.

Materials were contaminated separately with malathion, an organophosphate pesticide, and a simulant for the VX nerve agent as well as 2-chloroethyl phenylsulfide (2-CEPS), a simulant for sulfur mustard (HD) blister agent. VX and HD are considered to be the most toxic and persistent chemical warfare agents (CWAs). Post-decontamination surface sampling of test surfaces was performed using dry cotton gauze to absorb residual rinse and decontaminant liquid and/or cotton twill wipes semi-saturated with acetone as the wetting agent. Liquid waste runoffs from each procedural step were collected as a composite sample (one per three test coupons). A mechanical removal of residual decontamination liquid using a squeegee was performed for selected surfaces tested in horizontal orientation. Decontamination efficacies for chemical-material-test orientation combinations were calculated using the means of chemical mass recovered from the surface of replicate test (decontaminated) coupons and the associated set of positive control (nondecontaminated) coupons through surface wipe sampling. Figures ES-1 and ES-2 show the measured decontamination efficacies.

Decontamination Results- Galvanized Metal

The decontamination efficiencies of the multistep decontamination procedure demonstrated that the tested procedure was suitable for decontamination of malathion and 2-CEPS from galvanized metal tested in horizontal and vertical orientations, with average decontamination efficacies ranging from a low of $49 \pm 14\%$ to $>99.9\%$ depending on chemical target and orientation of the material (Figure ES-1). The presence of surface grime reduced the average efficacy for malathion from galvanized metal tested in horizontal orientation to approximately 50% but increased efficacy to $>99\%$ in the vertical position (Figure ES-2).

Changes in test procedure by switching from detergent-water to DF200 in the first step (H1 and V1 data in Figure ES-2) did not change efficacies appreciably. The addition of a mechanical removal of the rinse and

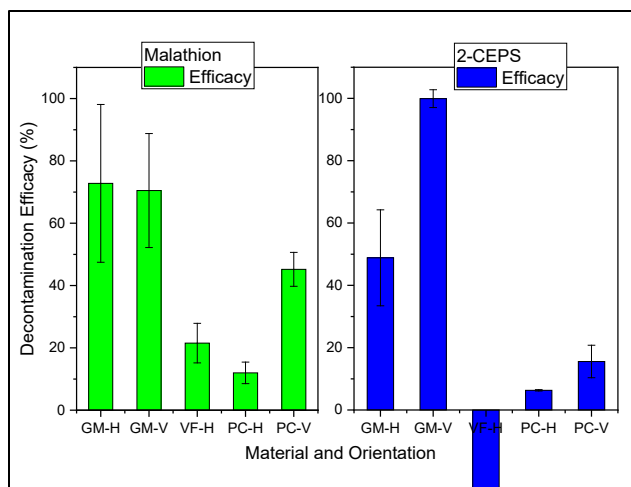


Figure ES-1. Average percent decontamination efficacies [% DE $\pm$ standard deviation (SD)] of malathion and 2-CEPS from different test materials/test surface orientations, without presence of surface grime. GM-H, VF-H, PC-H- galvanized metal, vinyl tile, and painted concrete (tested in horizontal (H) orientation); GM-V, PC-V- galvanized metal and painted concrete (tested in vertical (V) orientation).

decontamination liquid from horizontal grimed (applied manufactured grime) surfaces (H2) prior to wipe sampling rendered the residual surface concentration of malathion to below the limit of detection (LOD). The

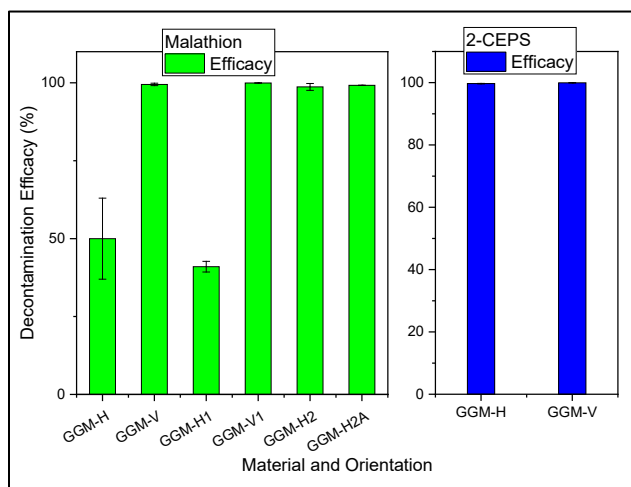


Figure ES-2. Average percent decontamination efficacies [% DE $\pm$ SD] of malathion and 2-CEPS from different test materials/test surface orientations, with a presence of surface grime. GGM-H, GGM-V- galvanized metal in horizontal (H) or vertical (V) orientation.

additional change in pre-rinse from detergent-water to DF200 (H2A) did not change efficacy.

Direct comparisons of efficacies for the cleaning of galvanized metal contaminated with malathion or 2-CEPS are convoluted by differences in solubility of these two chemicals, different affinity to adhere to the nonporous surface or grime, and actual degradation rate of the chemical by the decontaminant.

Decontamination Results- Porous/Permeable Materials

The reduced decontamination efficiency (DE) observed for semi-porous and porous building materials (Figure ES-1), with a maximum DE of 45% (malathion on painted concrete in vertical position) was linked to the permeation of the chemical into the test material, resulting in a limited availability of the chemical for perhydrolysis/oxidation by the DF200 decontaminant on the surface. Malathion and 2-CEPS recoveries from positive controls were also significantly impacted by the permeation into the materials, leaving less chemical (< 47% for malathion and < 20% for 2-CEPS) on the surface that is accessible during the wipe sampling.

Results - Liquid Wastes

Runoff collected and analyzed for residual chemical from vertically oriented materials showed a significant physical transfer/distribution of the applied chemical from the surfaces. Figure ES-3 illustrates the distribution of malathion across liquid wastes generated by each of the three steps in the decontamination procedure for a grimed galvanized metal surface. In (A), no runoff was collected, and all liquid remained on the surface until the wipe sampling of the surface. In (B), each fraction was collected by a skimming of the liquid off the surface. In (C), liquid waste for each fraction was collected as runoff due to the vertical position of the coupon. The slice that represents the degradation is derived from the difference between the positive control amount and the malathion that was otherwise unaccounted for in liquid wastes (as applicable). The liquid that remained on the horizontal surface contributed to the high recovery of malathion in the wipe sample (Figure ES-3A), whereas the wipe sample (Figure ES-3B) collected only residual malathion (less than 1%) from the surface with minimal residual liquid on it. This finding is consistent with what was observed for the vertically oriented coupon (Figure ES-3C). Absorption of the residual liquid on the surface

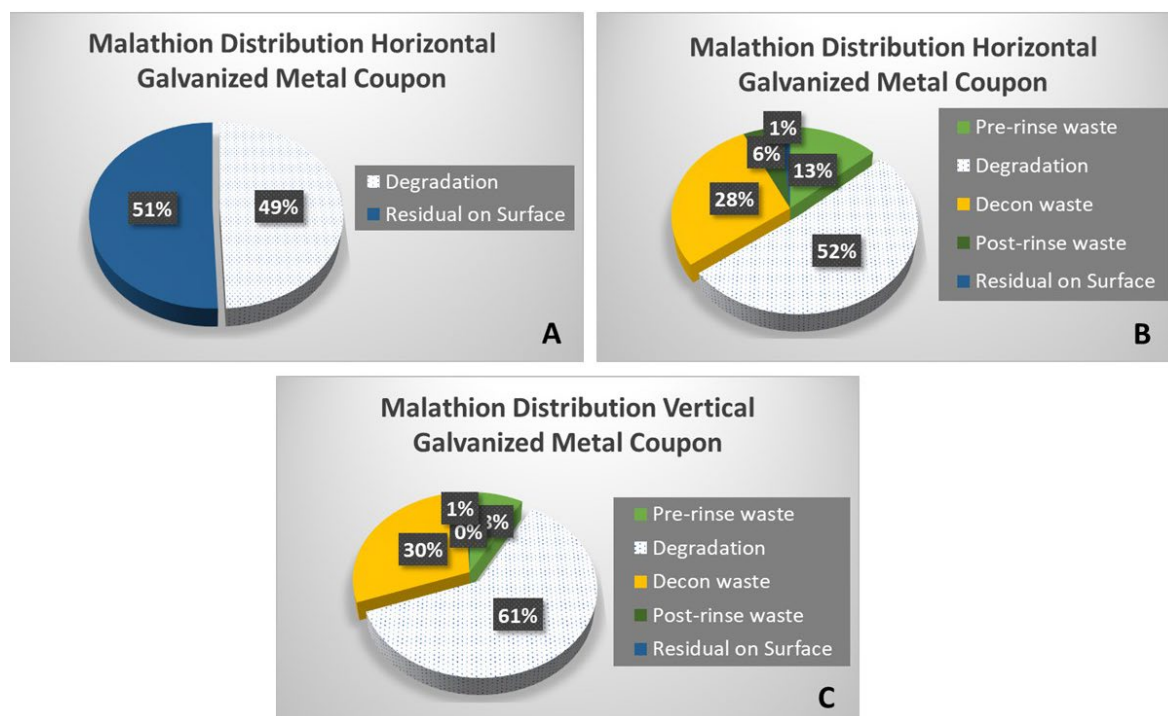


Figure ES-3. Relative mass distribution of malathion (normalized to positive control recovery) in liquid waste fractions associated with the three-step decontamination process using detergent-water in Step 1.

by the surface wipe may lead to the conclusion that the surface was not clean. However, the surface wipe facilitated in the physical transfer of unreacted chemical on the surface leaving much less on the surface. It is possible, as shown here, that unreacted chemical resides in the liquid on the surface, even in the presence of the decontamination solution, especially under more challenging conditions such as the presence of grime, higher initial contamination levels, or short contact time that lead to incomplete degradation. An investigation of potential toxic by-product formation would also be important but was not part of this study. The liquid waste generated was initially found to be contaminated with target chemicals at levels up to grams per liter [g/L]. However, residual decontaminant in the liquid waste resulted in a statistically significant degradation. Any treatment methods for contaminated waste were, however, not addressed in the present study.

Main findings

The main findings of this study are:

- Decontamination of permeable or porous materials remains problematic due to the fast permeation of some chemical agents into the surface. The presence of grime on the surface did not alter this observation.
- If a spray-based decontamination method is used but the residual liquid from the surface is not removed prior to wipe sampling, the calculated decontamination efficacy may be lower than expected because samples for such surfaces include unreacted chemicals present in the liquid on the surface.
- Tested decontamination methods resulted in physical transfer/distribution of chemical agent on the surface, yielding highly contaminated liquid waste which may degrade to lower concentrations due to the presence of residual decontaminant. Removing grime by pre-cleaning may result in physical transfer of the agent without degrading it.
- The addition of a mechanical removal of the remaining decontaminant on the surface after a specific dwell time may prove to be a promising aspect of surface decontamination.

Table of Contents

Disclaimer.....	i
Foreword	ii
Acknowledgments	iii
Executive Summary	iv
Acronyms and Abbreviations	xiii
1. Introduction	1
1.0. Project Objectives	1
2. Experimental Approach.....	2
2.1. Test Facility	2
2.2. Experimental Design	2
3. Materials and Methods.....	3
3.1. Preparation of Test Coupons	3
3.2. Preparation of Standard Grime	4
3.3. Application of Grime to Test Coupons	4
3.4. Chemical Agents and Contamination Procedure for Coupons	5
3.5. Decontamination of Building Materials.....	9
3.5.1. Preparation of decontamination solution	9
3.5.2. Preparation of detergent-water solution and water-only rinses	9
3.5.3. Decontamination procedure	9
3.5.4. Decontamination test matrix	11
3.6. Sampling and Analysis Method Development	13
3.6.1. Sampling methods	13
3.6.1.1. Surface wipe sampling and extraction of surface wipe samples	13
3.6.1.2. Sampling and extraction of decontamination samples	16
3.6.1.2.1. Liquid-liquid extraction of aqueous waste.....	19
3.6.1.2.2. Verification of quenching of decontamination reaction in wipe extracts	22
3.6.1.2.3. Verification of quenching of decontamination reaction in liquid waste	24
3.6.2. Decontamination process design for horizontal and vertical coupon testing.....	25
3.6.2.1. Surface sampling and extraction methods.....	28
3.6.2.2. Liquid waste sampling and extraction procedures.....	30
3.6.3. Preparation of extracts for analysis.....	31
3.6.4. Instrumental analysis	31
3.7. Data Reduction Procedures	36
3.7.1. Chemical concentration in extract calculations.....	36
3.7.2. Decontamination cleanup efficacy calculations	36
4. Results	37
4.1. Surface Decontamination Tests.....	37
4.1.1. Nongrimed coupons.....	37
4.1.2. Grimed coupons.....	41
4.2. Transfer to Liquid Waste – Vertical Coupons	44
4.3. Transfer to Liquid Waste – Horizontal Coupons	47
4.3.1 Direct extraction	47
4.3.1. Delayed extraction	49
5. Quality Assurance/Quality Control	50

5.1. Test Equipment Calibration.....	50
5.2. Data Quality Results for Critical Measurements	50
6. Summary	52
References	53
Appendices	55
Appendix A: Grime Application Procedure.....	55
Appendix B: Experimental parameters	57
Appendix C: Wipe sampling procedure.....	60

Figures

Figure ES-2. Average percent decontamination efficacies [% DE $\pm$ SD] of malathion and 2-CEPS from different test materials/test surface orientations, with a presence of surface grime. GGM-H, GGM-V- galvanized metal in horizontal (H) or vertical (V) orientation.	v
Figure ES-1. Average percent decontamination efficacies [% DE $\pm$ standard deviation (SD)] of malathion and 2-CEPS from different test materials/test surface orientations, without presence of surface grime. GM-H, VF-H, PC-H- galvanized metal, vinyl tile, and painted concrete (tested in horizontal (H) orientation); GM-V, PC-V- galvanized metal and painted concrete (tested in vertical (V) orientation).	v
Figure ES-3. Relative mass distribution of malathion (normalized to positive control recovery) in liquid waste fractions associated with the three-step decontamination process using detergent-water in Step 1.	vi
Figure 2-1. Decontamination procedure.	2
Figure 3-1. HVLP sprayer components: reservoir (a), reservoir cap (b), trigger (c) and hose connector (d).	5
Figure 3-2. Pattern for discrete droplet application of chemicals onto the 12-in x 12-in (a) and 8-in x 16-in test surfaces (b).	7
Figure 3-3. Application of chemical solution (a) and dried out (or post-weathering) chemical droplet pattern (b); the example shown is malathion on nongrimed galvanized metal.	7
Figure 3-4. Chemical contamination pattern on nongrimed test materials immediately after spiking onto vinyl (a), galvanized metal (b), painted concrete flooring (c), and painted concrete block (d).	8
Figure 3-5. Post-weathering chemical contamination pattern of malathion (a) and 2-CEPS (b) on grimed galvanized metal coupons.	8
Figure 3-6. Application of rinses or decontamination solution onto various coupon materials: pre-rinse detergent-water applications onto painted concrete (a), grimed galvanized metal (b) and nongrimed galvanized metal in a vertical position (c) and decontaminant application onto vinyl flooring (d), galvanized metal (e) and painted concrete block in a vertical position (f).	10
Figure 3-7. Mechanical removal of DF200 (A - at start; B - at end) and post-decontamination water rinse (C) from the grimed galvanized metal surface.	10
Figure 3-8. Malathion surface recovery from surface sampling and extraction method tests Round 1 (patterned bars) and results for Round 2 (solid bars) for nongrimed materials.	14
Figure 3-9. 2-CEPS surface recovery from surface sampling and extraction method optimization tests (patterned bars) and results for optimized method (solid bars) for nongrimed coupons.	14
Figure 3-10. Malathion surface recovery from surface sampling and extraction method tests Round 1 (isopropanol (IPA)) and results for Round 2 (acetone (ACE)) for grimed surfaces.	15
Figure 3-11. 2-CEPS surface recovery from surface sampling and extraction method tests using acetone as the wiping solvent for grimed surfaces; ACE - acetone.	16
Figure 3-12. Runoff of pre-decontamination rinse (left), decontaminant (middle) and post-decontamination rinse (right).	17
Figure 3-13. Experimental scheme for liquid waste extraction tests.	20
Figure 3-14. Extraction of liquid waste containing detergent collected from nongrimed surfaces. *: % ratio of recovery of malathion and 2-CEPS in nonpreserved versus preserved samples collected from nongrimed surfaces.	21
Figure 3-15. Optimization of extraction of liquid waste containing detergent collected from grimed surfaces. *: %ratio of recovery of malathion and 2-CEPS in nonpreserved samples collected from grimed surfaces.	22
Figure 3-16. Effect of decontamination solution in wipe extracts tests.	23
Figure 3-17. Recovery of malathion and 2-CEPS from sampling wipe containing residual DF200.	23

Figure 3-18. Effect of decontamination solution in liquid waste tests.	24
Figure 3-19. Recovery of malathion and 2-CEPS from DF200 runoff using extraction solvent only (ESN) and extraction solvent with sodium thiosulfate (STS).	25
Figure 3-20. Sample process design for horizontal coupon decontamination testing.	26
Figure 3-21. Sample process design for vertical coupon decontamination testing.	27
Figure 3-22. Sample process design for positive control testing.	28
Figure 3-23. Example of surface wipe sampling in horizontal orientation (left – cotton gauze sampling of galvanized metal; right – the follow-on cotton twill wipe sampling of galvanized metal)	30
Figure 3-24. Example of surface wipe sampling in vertical orientation (left – cotton twill wipe sampling of galvanized metal; right – cotton twill wipe sampling of painted concrete block).....	30
Figure 4-1. Recovered mass of (A) malathion and (B) 2-CEPS from test coupons and positive controls on nongrimed surfaces: GM-H, VF-H, PC-H: galvanized metal, vinyl tile, and painted concrete paver (tested in horizontal orientation); GM-V, PC-V: galvanized metal, and painted concrete block (tested in vertical orientation).	38
Figure 4-2. Galvanized metal coupon contaminated with 2-CEPS after application of the Step 1 water-detergent rinse.	40
Figure 4-3. 2-CEPS droplets on horizontal coupons and runoff of chemical contamination after turning galvanized metal in vertical orientation (30 minutes post-spiking).	40
Figure 4-4. Recovered mass of (A) malathion and (B) 2-CEPS from test coupons and positive controls on grimed surfaces: GGM-H, H1, H2: galvanized metal (tested in horizontal orientation); GGM-V: galvanized metal (tested in vertical orientation).	41
Figure 4-5. 2-CEPS spiking pattern on grimed galvanized coupons immediately after spiking, after weathering and readied for the vertical orientation testing.	44
Figure 4-6. Transfer of malathion contamination from galvanized metal (GM) in vertical position to different types of liquid waste from decontamination process. Grime* refers to the use of DF200 in the pre-rinse step.	45
Figure 4-7. Transfer of 2-CEPS contamination from galvanized metal (GM) in vertical position to different types of liquid waste from decontamination process.	45
Figure 4-8. Transfer of malathion contamination from galvanized metal (GM) in horizontal position to different types of liquid waste by physical removal from decontamination process. Grime* refers to the modified method that uses DF200 in the pre-rinse step.	48
Figure C-1. Folding wipe for sampling the first wiping pathway (horizontal).	60
Figure C-2. Horizontal wiping pathway.	61
Figure C-3. Folding wipe for sampling the second wiping pathway (vertical).	61
Figure C-4. Vertical wiping pathway.	61
Figure C-5. Folding wipe for sampling the third wiping pathway (diagonal).	62
Figure C-6. Diagonal wiping pathway.	62
Figure C-7. Folding wipe for sampling the fourth pathway (perimeter).	63
Figure C-8. Perimeter wiping pathway.	63

Tables

Table 3-1. Specifications of Building Materials	3
Table 3-2. Specifications of Grime Components.....	4
Table 3-3. Physical and Chemical Properties of Malathion and 2-CEPS.....	6
Table 3-4. Test Matrix for Decontamination Testing	12
Table 3-5. Characterization of Liquid Effluents from Step 1 of Simulated Decontamination Procedure	18

Table 3-6. Characterization of Liquid Effluents from Step 2 of Simulated Decontamination Procedure	18
Table 3-7. Characterization of Liquid Effluents from Step 3 of Simulated Decontamination Procedure	18
Table 3-8. Surface Sampling Parameters for Malathion and 2-CEPS	29
Table 3-9. Instrumental Parameters and Conditions for GC/MS Analyses of Malathion by EMSL Analytical, Inc.....	32
Table 3-10. Instrumental Parameters and Conditions for GC/MS Analyses of 2-CEPS by EMSL Analytical, Inc.....	32
Table 3-11. GC/MS Parameters for Analysis of Malathion by OSL	33
<i>df: film thickness</i>	33
Table 3-12. GC/MS Parameters for Analysis of 2-CEPS by OSL	33
<i>df: film thickness</i>	33
Table 3-13. QC Checks for Instrumental Analyses	34
<i>*re-calibrate when continuous calibration fails acceptance criteria and/or after system maintenance; RPD – relative percent difference</i>	34
Table 3-14. Laboratory Proficiency Results	35
Table 4-1. Material- and -Orientation-Specific Decontamination Test Results of Nongrimed Materials for Malathion and 2-CEPS.....	39
Table 4-2. Material- and Orientation- Specific Decontamination Test Results of Grimed Materials for Malathion and 2-CEPS.....	43
Table 4-3. Recovered Mass and Concentration of Malathion and 2-CEPS in Liquid Waste from Decontamination Procedures	46
Table 4-4. Recovered Mass and Concentration of Target Chemicals in Liquid Waste from Decontamination Procedures for Horizontal Grimed Galvanized Metal.....	48
Table 5-1. Instrument Calibration Frequency	50
Table 5-2. Acceptance Criteria for Critical Measurements	51
Table B-1. Characterization of DF200 Decontamination Solution	57
Table B-2. Characterization of Pre-decontamination Detergent-water Rinse Solution Application	57
Table B-3. Characterization of DF200 Decontamination Solution Application.....	58
Table B-4. Characterization of Post-decontamination Water Rinse Application	59

Acronyms and Abbreviations

2-CEPS	2-chloroethyl phenyl sulfide
CBRN	chemical, biological, radiological, and nuclear
CC	continuous calibration
CESER	Center for Environmental Solutions and Emergency Response (US EPA)
cm	centimeter(s)
cm ³	cubic centimeter(s)
COC	chain of custody
CS	control spike
CT	contact time
CWA	chemical warfare agent
DE	decontamination efficacy
DI	deionized (water)
DQI	data quality indicator
DT	dwel time
DUP	duplicate
EC	end check (of calibration)
EMSL	Environmental Molecular Sciences Laboratory
EPA	U.S. Environmental Protection Agency
ESF	Emergency Response Function
ft	foot/feet
g	gram(s)
GC/MS	gas chromatography/mass spectrometry
GGM	grimed galvanized metal
GM	galvanized metal
GVF	grimed vinyl flooring (-material)
H ₂ O ₂	hydrogen peroxide
HD	sulfur mustard
HPLC	High Performance Liquid Chromatography
h	hour(s)
HSMMD	Homeland Security and Material Management Division (US EPA)
HSRP	Homeland Security Research Program (US EPA)
HVAC	heating, ventilation, and air conditioning
HVLP	High Volume Low Pressure

HWCL	hazardous waste control limits
ICAL	initial calibration
ICV	initial calibration verification
ID	identification
in	inch(es)
IPA	isopropanol (2-propanol)
IS	internal standard
ISO	International Organization for Standardization
L	liter
LB	laboratory blank
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LOQ	limit of quantitation
LSB	laboratory solvent blank
LW	liquid waste
LWD	liquid waste (from) decontaminant
m	meter(s)
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
ND	nondetect
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NRT	National Response Team
ORD	Office of Research and Development
OSL	Organic Support Laboratory (US EPA)
oz	(liquid) ounce(s)
PB	procedural blank
PC	positive control
PTFE	polytetrafluoroethylene
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control

QRG	Quick Reference Guide
R ²	coefficient of determination
RH	relative humidity
RLV	reporting limit verification
RPD	relative percent difference
RSD	relative standard deviation
RTP	Research Triangle Park
SB	solvent blank
SC	spike control
SD	standard deviation
sec	second(s)
STS	sodium thiosulfate
TC	test coupon
μL	microliter(s)
VX	Ethyl ({2-[bis(propan-2-yl)amino]ethyl}sulfanyl)(methyl)phosphinate

1. Introduction

A vital characteristic of any decontamination strategy is its ability to degrade a wide array of different chemicals using either specialized chemical decontamination treatments or commercial off-the-shelf products that would be widely available following a wide-area chemical (or biological) release. EPA's Homeland Security Research Program (HSRP) has directed multiple research efforts that focused on liquid-based surface decontamination options using commercially available products that are expected to degrade various highly toxic chemical agents from various types of surfaces [1-6]. These decontamination studies are typically limited to the measurement of efficacy of the decontamination product itself after a fixed contact time. Decontamination procedures using concentrated liquid formulations of hydrogen peroxide, and especially activated hydrogen peroxide are suggested to be effective decontaminants for various chemical agents, including chemical warfare agents (CWAs) and organophosphorus pesticides [3, 6-8].

Hydrogen peroxide-based (and other degradative) treatments can cause severe material incompatibilities, including permanent damage of the decontaminated material due to excessive corrosion or erosion post-treatment [6-7]. Some treatments also have well-known limitations for decontamination of chemical agents from semi-porous and porous materials due to permeation of target chemicals into inner layers of materials [9]. To address this problem, field decontamination procedures typically include a post-decontamination water rinse step to remove residual decontaminant and allow for better overall material compatibility. Another common problem that can limit decontamination efficacy is a high organic burden on the material surface. The presence of surface grime and dirt can lead to increased material-demand for the decontaminant, especially in comparison to materials with otherwise lower demand [10]. To mitigate the effect of organic burden, field decontamination procedures often suggest pre-decontamination detergent-based water rinses prior to deployment of core-decontaminant as indicated in, for example, the National Response Team's (NRT's) Quick Reference Guides (QRG) for CWAs [11]. The pre-treatment step is intended to remove (some of) the dirt/grime layer - that would otherwise be competing for decontaminant - and/or mobilize the chemicals that may be absorbed into the dirt/grime layer and therefore less accessible to the decontaminant.

This report discusses the investigation of a three-step cleaning and procedure for decontamination of surfaces contaminated with organophosphate pesticides and/or simulant CWAs and contributes to the understanding of the impact of water-based rinses on cumulative decontamination efficacy.

1.0. Project Objectives

The primary objective of this project is to provide responding agencies and field remediation specialists with more information on effectiveness of adding the pre- and post-decontamination water-based rinses for cleaning of various types of indoor surfaces contaminated with pesticides and/or CWAs (simulants). The secondary objective is to provide initial information on the contamination of liquid waste (runoff) generated, including determination of material-dependent chemical transfer rates to liquid waste.

Results from this project contribute to formation of guidelines for selection of the best standardized approaches for remediation of permeable, semipermeable, and nonpermeable surfaces contaminated with pesticides and CWAs, with and without presence of surface grime.

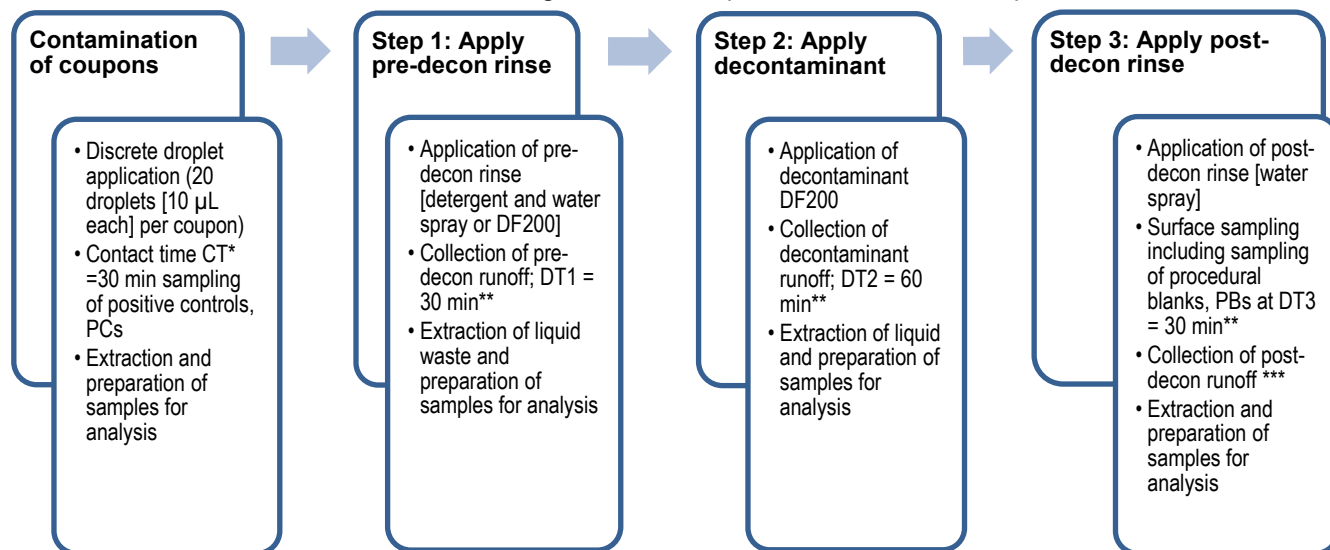
2. Experimental Approach

2.1. Test Facility

The experimental work was performed at the EPA's facilities in Research Triangle Park (RTP), NC. Instrumental analyses of the residual amounts of chemicals remaining on the coupons were performed initially by an external chemical analysis laboratory (Environmental Molecular Sciences Laboratory (EMSL) Analytical Inc., Cinnaminson, NJ, USA) and later by an on-site EPA laboratory.

2.2. Experimental Design

This study evaluated the cumulative decontamination efficacy of multistep cleaning procedures for degradation of selected organophosphate pesticides and/or simulant CWAs. After completion of a series of method demonstration tests (Section 3.6), a three-step decontamination procedure was tested on four types of surfaces (galvanized metal, painted concrete flooring, painted concrete blocks, and vinyl floor tile) in horizontal and/or vertical orientations (Section 3.1). Neat chemical (malathion or 2-CEPS) solutions in ethanol were applied using a discrete droplet application method (Section 3.4). After a contact time (CT) of 30 minutes (min) (i.e., a simulated weathering of the chemical on the surface) under room temperature conditions, the decontamination sequence was applied, which consisted of: (Step 1) pre-rinse of the surface with detergent in water solution; (Step 2) application of the decontaminant; and (Step 3) post-rinse of the surface with water to remove the residual decontaminant. At the conclusion of the decontamination sequence, a surface sampling was performed using a wipe-based surface sampling approach, followed by extraction of sampling media (wipes) and analysis of extracts via gas chromatography/mass spectrometry (GC/MS) (Sections 3.6.2.1, 3.6.3 and 3.6.4). The analysis of liquid effluents (volumes and chemical concentrations) for each step was performed as well (Sections 3.6.2.2, 3.6.3 and 3.6.4). The cleanup efficacy for each material was then determined using the total mass recovered of the contaminant from the test coupon and from the associated positive control (Section 3.7.2). The scheme and general timeline for each decontamination test are shown in Figure 2-1 with experimental details in Chapter 3.



* Contact time (CT) is the time the chemical (malathion/2-CEPS) is in contact with the material surface; ** Dwell time (DT) is the time the pre-rinse (DT1) or decontaminant (DT2) or post-decon rinse (DT3) is in contact with the contaminated material surface; *** for selected tests, a mechanical removal ('skimming') of liquid waste was performed for grimed surfaces tested in horizontal orientation.

Figure 2-1. Decontamination procedure.

3. Materials and Methods

3.1. Preparation of Test Coupons

Four building materials (galvanized metal, painted concrete flooring pavers, painted concrete blocks, and vinyl floor tile) were used for evaluation of cleanup procedures. Galvanized metal was a representative material for nonpermeable building surfaces and is used in heating, ventilation, and air conditioning (HVAC) systems. Vinyl flooring and concrete were selected as representative of a semipermeable and permeable building material, respectively. Selected sealers and paints for concrete paver and concrete blocks were based on their purpose to seal the open porous concrete and can be found in indoor environments as apposed to nonsealed or painted concrete in the outdoors. The building material specifications are given in Table 3-1.

Table 3-1. Specifications of Building Materials

Material	Description	Manufacturer/ Supplier Name/Location	Coupon Size, L x W (in) or D x H x W (in)	Material Preparation
Galvanized metal	24-in x 3-ft sheet galvanized metal, 30 gauge	Imperial 24-in x 3-ft sheet metal, Lowe's Item #50186, Model #GVL0108/ Lowe's, Morresville, NC, USA	12 x 12	Remove any lubricant/grease from shearing with acetone and wipe dry. Remove particles and dust by wiping clean with acetone and water and then wipe dry.
Vinyl flooring	3/32-in x 12-in x 12-in commercial vinyl tile	Tarkett 12-in x 12-in Cloudburst speckle pattern commercial vinyl tile, Lowe's Item #378985 Model #LO786-2/ Lowe's, Morresville, NC, USA	12 x 12	Remove particles by wiping clean with acetone and water and the wipe dry.
Concrete flooring (sealed)	12-in x 12-in Concrete paver and sealant	12 in x 12 in Pewter Concrete Step Stone. Home Depot Item # 556211 Model # 71200; Home Depot, Atlanta, GA, USA Valspar Solid Color Concrete Sealer Concrete Gray; The Valspar Corporation, Minneapolis, MN, USA; Lowes Item # 293575 Model # 024.0082020.007/ Lowe's, Morresville, NC, USA	12 x 12	Remove particles by wiping clean with acetone and water and then wipe dry.
Concrete blocks (painted)	8-in x 8-in x 16-in concrete block and sealant	Normal Weight/Standard Cored Concrete Block (8-x 8-x 16-in; actual: 7.625-in D x 7.625-in H x 15.625-in W); Lowe's Item # 10383 Model # 8008/ Lowe's, Morresville, NC, USA Loxon® Concrete & Masonry Primer; Sherwin Williams, P/N 6501-32646; Sherwin-Williams Company, Cleveland, OH, USA, and Cashmere® Interior Acrylic Latex in Ultra White; Sherwin Williams, USA; P/N 6504-06713; Sherwin-Williams Company, Cleveland, OH, USA	8 x 8 x 16	Remove particles by wiping clean with acetone and water and then wipe dry.

Galvanized metal coupons were prepared using heavy-duty powered hydraulic shears. The commercially available vinyl tiles and concrete blocks (concrete blocks) and concrete pavers did not require mechanical processing. Sealants and paints were applied onto concrete surfaces per manufacturer's instructions.

3.2. Preparation of Standard Grime

A standard grime formulation was prepared to simulate dirty surfaces in an urban indoor environment. The standard grime consisted of three classes of functional components: general dust, soot, and biological components (Table 3-2).

Table 3-2. Specifications of Grime Components

Grime Component	Weight %*	Manufacturer/Product number
General dust component		
Arizona fine dust	94%	Powder Technology Inc. Arden Hills, MN USA; P/N PP2G4 A2 fine
Soot-related components		
Black carbon	2.5%	Powder Technology Inc. Arden Hills, MN USA; P/N Raven 410
Diesel particulate matter	0.25%	National Institute of Standards and Technology (NIST) Gaithersburg, MD USA; P/N SRM 2975
10W30 motor oil	0.125%	O'Reilly Auto Parts Springfield, MO; P/N10-30
Biological components		
Alpha-pinene (neat)	0.125%	Fisher Scientific Waltham, MA USA; P/N AC1646-0050
Lycopodium powder	1%	Fisher Scientific Waltham, MA USA; P/N S25396
Ragweed pollen	1%	Polysciences Warrington, PA USA; P/N 7673
Paper mulberry mixture	1%	Polysciences Warrington, PA USA; P/N7670

**in the finished grime mixture*

It is expected that the dust in the grime may absorb some of the decontaminant leading to a lower mobility for the decontaminant to reach the contaminant. The soot related components in the grime may degrade the decontaminant (an increased "material demand" by the grime) while the biological components are likely not of critical importance here considering their small weight percentage in the grime.

The grime mixture was prepared by mixing of standard components using the recipe in Table 3-2. The components were weighed and added to a 500-milliliter (mL) polypropylene bottle, and the bottle was capped and placed in a laboratory tumbler overnight (18 hours [h]) to mix the grime components. After tumbling the mixture, the standard grime was stored at room temperature in a capped 500-mL plastic bottle until use.

3.3. Application of Grime to Test Coupons

Coupon surfaces were grimed with standard grime dissolved in analytical grade ethanol (Fisher Scientific, Fair Lawn, NJ, USA) and applied to the surface with a high-volume low pressure (HVLP) sprayer (Transtar Autobody Technologies Inc., Brighton, MI, USA; P/N 6618) connected to the pressurized house

air supply via an air hose connector. The main structural components of the HVLP sprayer are shown in Figure 3-1. The method for applying grime to the test coupon surface is detailed in Appendix A.

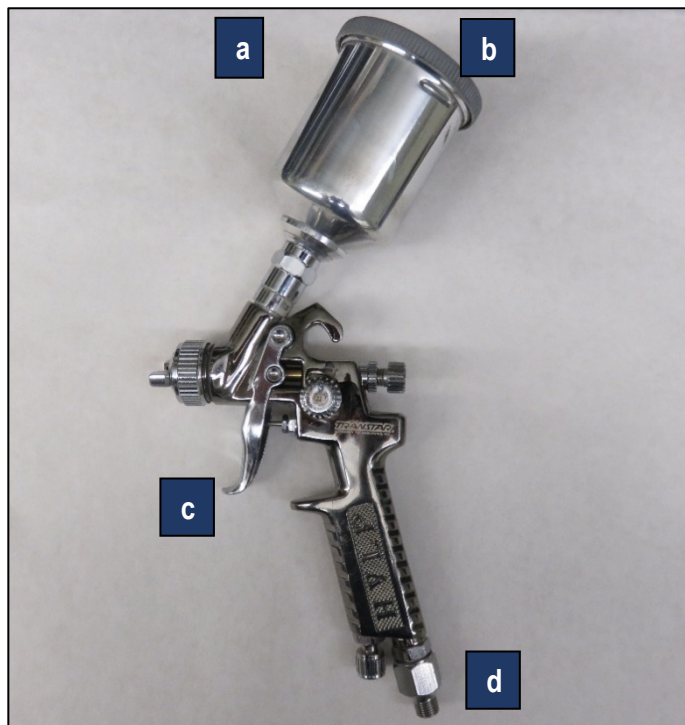


Figure 3-1. HVLP sprayer components: reservoir (a), reservoir cap (b), trigger (c) and hose connector (d).

3.4. Chemical Agents and Contamination Procedure for Coupons

The relevant physical and chemical properties of the target chemicals are summarized in Table 3-3. Malathion is an organophosphate insecticide widely used in applications such as agriculture, outdoor pest control, and residential landscaping. It is also considered a simulant for the CWA nerve agent VX [12]. The second chemical is 2-chloroethyl phenyl sulfide (2-CEPS). Based on chemical similarity, 2-CEPS is considered a valid simulant for sulfur mustard (HD) CWA [12]. The malathion analytical standard was purchased from Chem Service (Chem Service, Inc., West Chester, PA, USA; P/N N-12346-100MG; purity: 99.5%). The 2-CEPS analytical standard was purchased from Sigma-Aldrich (Sigma-Aldrich Co. LLC, St. Louis, MO, USA; P/N 417602-25ML; purity 98%).

Table 3-3. Physical and Chemical Properties of Malathion and 2-CEPS

Property	Malathion*	2-CEPS**
CAS	121-75-5	5535-49-9
Molecular weight	330.4	172.67
Formula	C ₁₀ H ₁₉ O ₆ PS ₂	C ₈ H ₉ ClS
Density (g/cm ³) at 20 °C	1.23	1.17
Physical form at 20 °C	Liquid	Liquid
Vapor pressure	3.3E-6 mm Hg at 25 °C	1.86E-2 mm Hg at 25 °C
Solubility in water	0.143 g/L	0.084 g/L
Log K _{ow}	2.36–2.89	3.58

*: See <https://pubchem.ncbi.nlm.nih.gov/compound/Malathion>

**:: See <https://pubchem.ncbi.nlm.nih.gov/compound/2-Chloroethyl-phenyl-sulfide>

The target surface chemical concentrations in this study were approximately 1 gram/square meter (g/m²). The test area of each 12-in × 12-in coupon (total surface area of 929 centimeter² [cm²]) were contaminated with twenty 10 µL-droplets of 500 milligrams (mg) per mL (mg/mL) solutions of the target chemical agents, yielding contamination levels of 100 mg/coupon, equivalent to 1.1 g/m².

Solutions were prepared using procedures developed in previous research efforts [5] by dissolution of neat chemicals in organic solvents. Briefly, neat chemicals were dissolved in High Performance Liquid Chromatography (HPLC) grade ethanol to produce a 500 mg/mL concentration, then mixed using a vortex mixer and then via sonication for approximately 30 seconds (sec). The accuracy and precision of preparation of spiking solution was tested along with each experimental batch, by analysis of control spike (CS) samples (see Section 5.2 for results of analysis of control spikes).

Chemical solutions were applied onto test coupons using a discrete droplet micro-application of chemicals. Prior to application, each 12-in × 12-in test coupon was placed in an individual, pre-cleaned test box (sliding storage box, IRIS USA, Inc., Surprise, AZ USA; P/N 491530). Chemical solutions were then applied to the coupons under ambient room temperature conditions in a chemical safety hood using a separate tip-programmable electronic repeatable pipette (Eppendorf Repeater Plus Single Channel Repeater Pipette, Eppendorf AG, Hamburg, Germany; P/N 22260201) and pre-cleaned stainless steel spiking template standing over the coupon surface. The 20 discrete droplets were applied following the pattern shown in Figure 3-2.

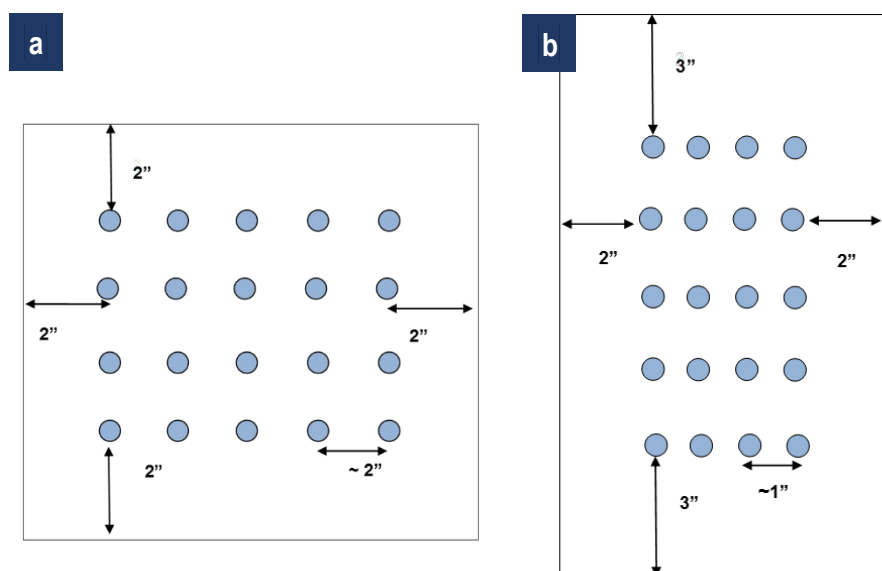


Figure 3-2. Pattern for discrete droplet application of chemicals onto the 12-in x 12-in (a) and 8-in x 16-in test surfaces (b).

After application of chemical, the boxes were closed to allow a 30-min long simulated weathering to ensure that the ethanol had evaporated. This weathering was performed under ambient laboratory conditions of 22 °C and 25% relative humidity (RH) (uncontrolled; averages typical for indoor laboratory in early winter/spring months when testing was performed). Figure 3-3 shows an example of the sampling template placed over a coupon and the weathered/dried out (CT=30 min) chemical droplet pattern.

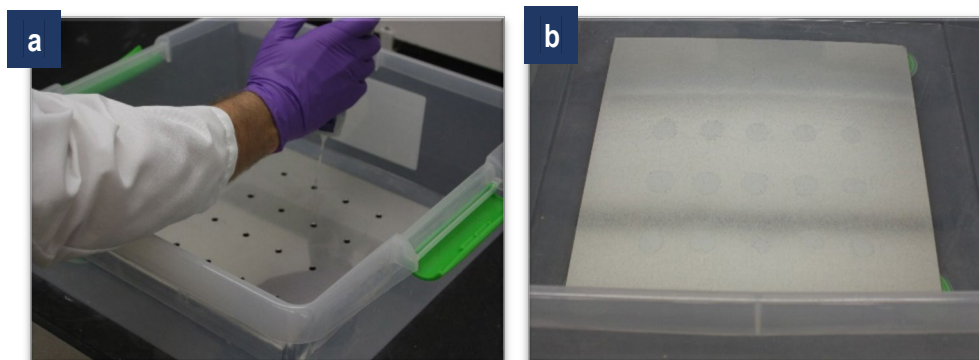


Figure 3-3. Application of chemical solution (a) and dried out (or post-weathering) chemical droplet pattern (b); the example shown is malathion on nongrimed galvanized metal.

The chemical contamination pattern for other nongrimed materials is shown in Figure 3-4. Weathering was always performed with materials in the horizontal position. A subset of galvanized metal and all concrete block coupons were positioned in the vertical orientation immediately after contamination.

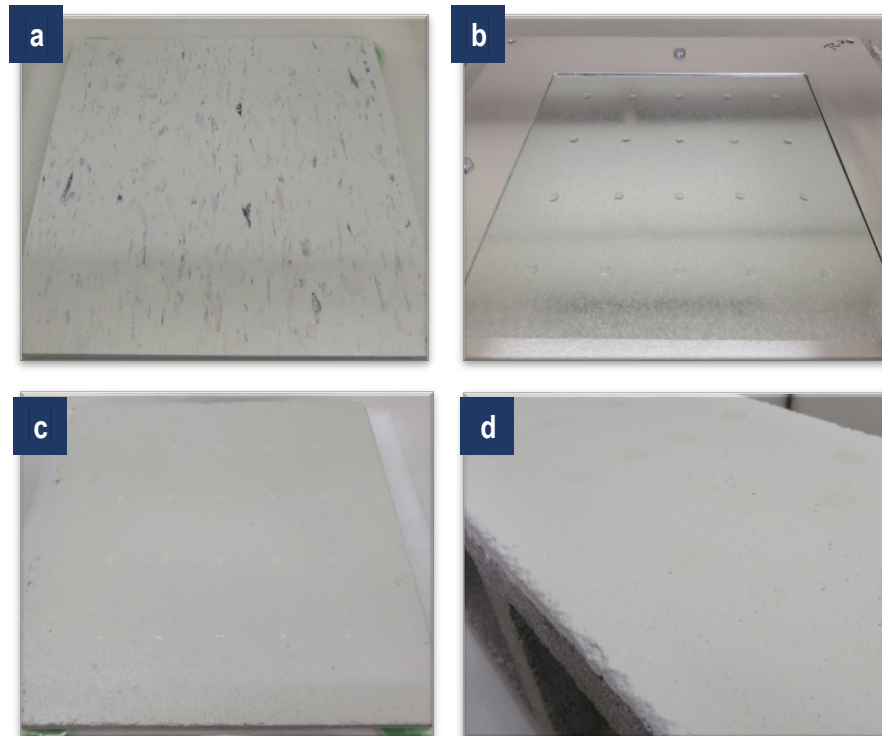


Figure 3-4. Chemical contamination pattern on nongrimed test materials immediately after spiking onto vinyl (a), galvanized metal (b), painted concrete flooring (c), and painted concrete block (d).

Figure 3-5 shows examples of post-weathering malathion and 2-CEPS chemical contamination pattern as visible on the grimed galvanized metal surface.

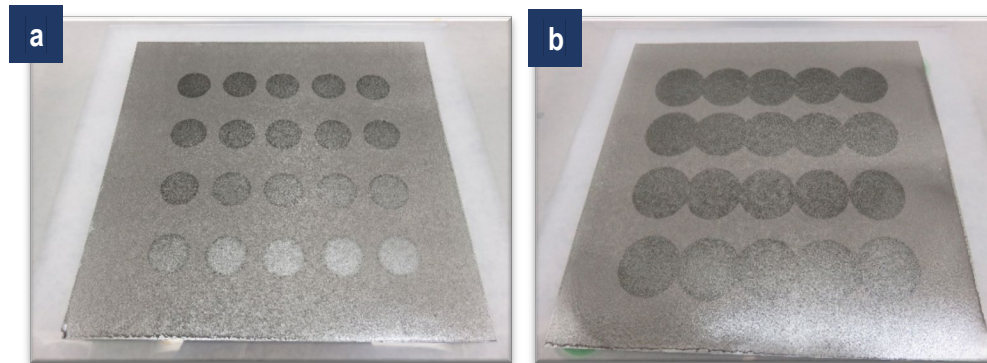


Figure 3-5. Post-weathering chemical contamination pattern of malathion (a) and 2-CEPS (b) on grimed galvanized metal coupons.

3.5. Decontamination of Building Materials

3.5.1. Preparation of decontamination solution

The decontamination product that was used in this study was EasyDECON® DF200 (hereafter, DF200) manufactured by Envirofoam Technologies/Intelagard (Lafayette, CO, USA). The manufacturer markets the DF200 formulation as 100% effective for decontamination of HD (1-hour dwell time, challenge ratio 1:200) [13]. The active ingredient of DF200 is hydrogen peroxide (H_2O_2), and its pH range is 9.6–9.7. The liquid-based results for malathion suggest full decontamination (nondetectable in test samples) at 1-hour dwell time (challenge ratio not provided) [14].

Fresh batches of DF200 solution were prepared daily through proportional mixing as per the manufacturer's instructions. After mixing, the manufacturer recommends the use of the EasyDECON® Fortifier Test Kit to test the stability of the DF200 final blend. This test (a "Go/No Go" test) measures the percentage of active ingredient and instills confidence that the decontamination solution is effective and ready to use. The ongoing evaluations that occurred prior to use also included pH and temperature measurements of the finished blend. Results are shown in Appendix B (Table B-1).

3.5.2. Preparation of detergent-water solution and water-only rinses

The pre-rinse detergent-water solution was prepared by adding 1 part of Dawn Ultra Dishwashing Liquid Original Scent (Procter & Gamble, Cincinnati, OH, USA) to 50 parts of deionized (DI) water followed by thorough mixing. The solution was mixed by hand shaking for 10 sec prior to application of this decontamination solution to the coupon. No evaluation of the detergent solution was performed. DI water was used for post-decontamination rinses.

3.5.3. Decontamination procedure

Pre- and post-decontamination rinses and decontamination solution DF200 were applied using commercially available cleaning-grade spray bottles. A durable industrial sprayer bottle was used (32-ounce (oz) plastic spray bottle, Lowe's Item #366843, Model #LOAPS30; as shown in use on Figure 3-6). This type of bottle is equipped with a trigger sprayer with no adjustable spray pattern and is recommended by the manufacturer of the sprayer bottle for general household cleaning purposes, including application of concentrated formulas. Bottles were rinsed with DI water prior to use.

DF200 was sprayed onto each coupon using a pre-filled bottle. The pre- and post-decontamination water rinses were applied using separate spray bottles. The surface of the coupon was always sprayed using horizontal (left to right) overlapping strokes, that were applied from top to bottom of each coupon. Fill volumes - measured by use of a graduated cylinder - were $20 \text{ mL} \pm 1 \text{ mL}$. The actual volumes of decontaminant and water rinses sprayed onto each coupon were $20 \text{ mL} \pm 4 \text{ mL}$ (20% of surface target) across all testing and were determined gravimetrically by weighing each test box before and after application. Accuracy of the scale was sufficient to measure an absolute mass change of 1 g (an equivalent of approximately 1 mL of liquid decontaminant). Test-specific results are given in Tables B-2 and B-3 (Appendix B). Figure 3-6 shows application of rinses or decontamination solution onto various coupon materials.

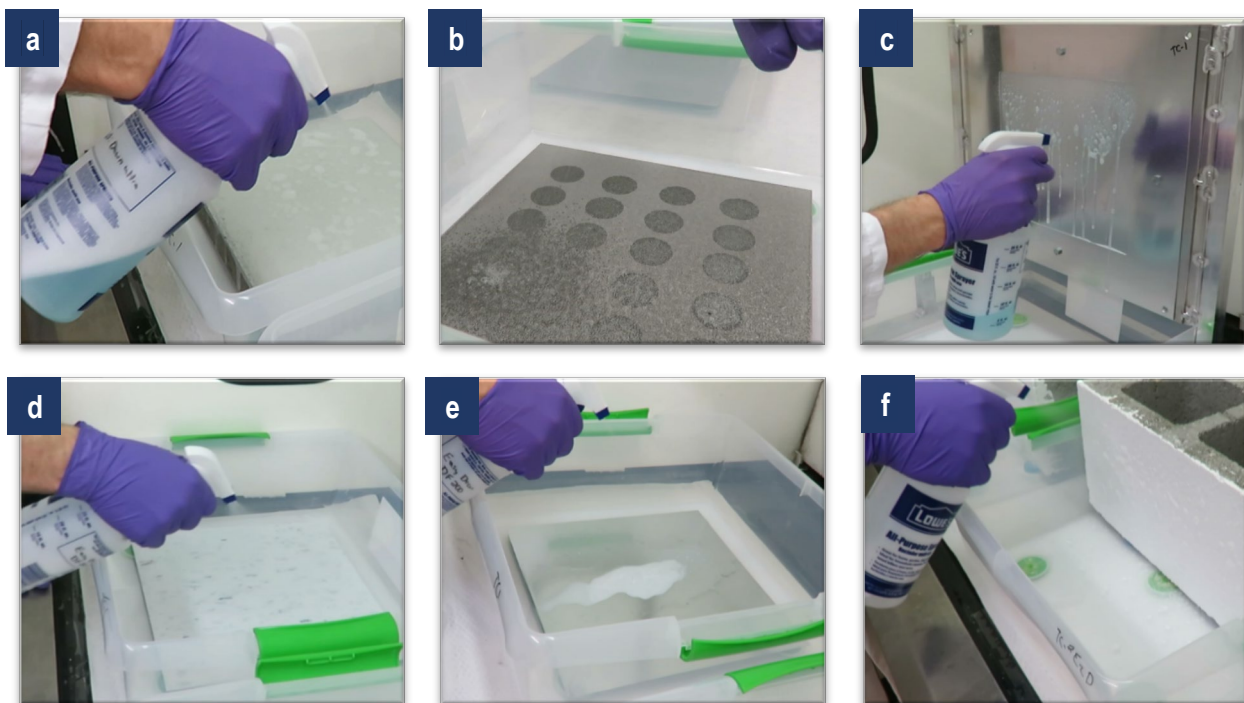


Figure 3-6. Application of rinses or decontamination solution onto various coupon materials: pre-rinse detergent-water applications onto painted concrete (a), grimed galvanized metal (b) and nongrimed galvanized metal in a vertical position (c) and decontaminant application onto vinyl flooring (d), galvanized metal (e) and painted concrete block in a vertical position (f).

For selected tests on grimed surfaces (Table 3-4), the pre-rinse, decontaminant and post-rinse fractions were mechanically removed using a small hand-held cleaning device equipped with a rubber blade (Polypropylene-Thermoplastic Rubber Home Squeegee, Walmart, Inc., Bentonville, AR, USA; P/N 564493773). The mechanical removal step was not intended to scrub the chemical contamination of the horizontal surface, but rather to gently skim the pre-rinse liquid, processed decontaminant liquid, or water rinse fraction of the test coupon surface. Figure 3-7 shows the mechanical removal of the DF200 and post-decontamination water rinse from a horizontal grimed galvanized metal surface. The recovered liquid waste was split equally, and the two aliquots were extracted at 0 and 24 h to assess whether the liquid waste contained residual decontaminant that would reduce the malathion concentration.

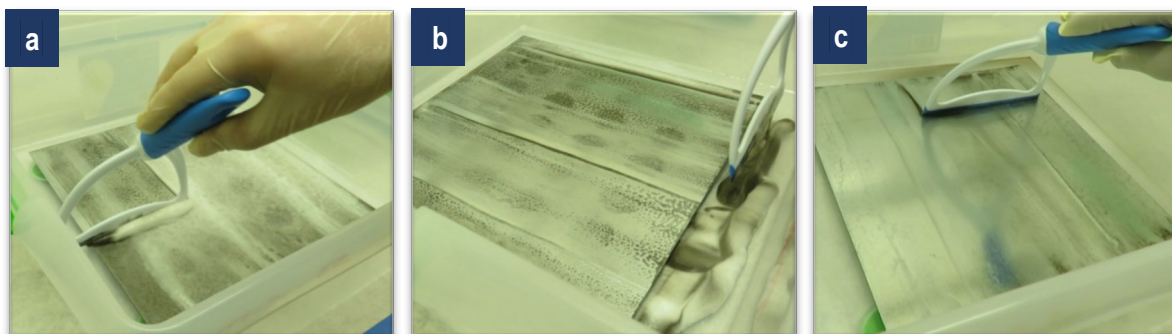


Figure 3-7. Mechanical removal of DF200 (A - at start; B – at end) and post-decontamination water rinse (C) from the grimed galvanized metal surface.

3.5.4. Decontamination test matrix

The complete decontamination test matrix is shown in Table 3-4. Results from the nongrimed coupon decontamination tests (Test ID 1M - 5M for malathion; 1C - 5C for 2-CEPS) were used to determine the test conditions and materials for the grimed coupon testing (Test ID 6M – 11M for malathion; 6C - 7C for 2-CEPS). For example, low recoveries of both malathion and 2-CEPS from permeable materials resulted in excluding these types of materials in further testing to focus on the facets of the three-step decontamination procedure. Test ID 1M - 7M and 1C - 7C were conducted with malathion (M-series) and 2-CEPS (C-series) as the contaminants. Test ID 8M - 9M were related to modifications of the default decontamination procedure (Mod1) by replacing the initial detergent and water rinse with an initial application of the DF200 decontaminant. The purpose was to assess whether any demand of the grime on the surface could be overcome with a pre-decon application of the actual decontaminant (instead of the detergent-water pre-rinse). These tests were executed only in the presence of malathion. The last two tests (Test ID 10M-11M) included the use of a physical removal of excess liquid from the horizontal surface using a squeegee; one with detergent-water as the first step (Mod2) and one test with the DF200 as the first step (Mod2A).

Each test consisted of three decontaminated test coupons for each chemical in horizontal and/or vertical orientation (depending on material tested), three positive controls per test day per material (coupons contaminated with chemical that did not undergo decontamination), and one procedural blank (coupon not spiked with chemical but did undergo decontamination in the horizontal orientation). Additionally, one composite sample of liquid waste (LW) per set of three test coupons – pre-decontamination composite rinse, decontamination composite rinse, and post-decontamination composite rinse runoffs were collected for vertical orientation testing. The horizontal orientation testing did not result in appreciable liquid waste volumes. One control spike sample was prepared per test day to check for nominal concentration of spiking solution as well as for ongoing laboratory proficiency testing. The sample was prepared as a direct spike of chemical solution into hexane at a level corresponding to 100% of the target surface concentration of the chemical expected in the final extract. Types of samples resulting from decontamination testing are summarized in Table 3-4. The decontamination test results are provided in Section 4.1.

Table 3-4. Test Matrix for Decontamination Testing

Test ID	Test Material	Material Orientation	Pre-rinse	Decontaminant	Post-rinse	Mechanical Removal	Method ID	Types of Samples
Target chemical: Malathion								
1M	Galvanized Metal	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
2M	Galvanized Metal	Vertical	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS, LW
3M	Vinyl Tile	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
4M	Painted [sealed] concrete flooring	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
5M	Painted [sealed] concrete block	Vertical	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS, LW
6M	Grimed galvanized Metal	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
7M	Grimed galvanized Metal	Vertical	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS, LW, LWD
8M	Grimed galvanized metal	Horizontal	DF200	DF200	Water	No	Mod1	PC, TC, PB, LB, CS
9M	Grimed galvanized metal	Vertical	DF200	DF200	Water	No	Mod1	PC, TC, PB, LB, CS, LW, LWD
10M	Grimed galvanized metal	Horizontal	Soapy water	DF200	Water	Yes	Mod2	PC, TC, PB, LB, CS, LW, LWD
11M	Grimed galvanized metal	Horizontal	DF200	DF200	Water	Yes	Mod2A	PC, TC, PB, LB, CS, LW, LWD
Target chemical: 2-CEPS								
1C	Galvanized metal	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
2C	Galvanized metal	Vertical	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS, LW
3C	Vinyl tile	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
4C	Painted [sealed] concrete flooring	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
5C	Painted [sealed] concrete block	Vertical	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS, LW
6C	Grimed galvanized metal	Horizontal	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS
7C	Grimed galvanized metal	Vertical	Soapy water	DF200	Water	No	UM	PC, TC, PB, LB, CS, LW

UM – unmodified (default) method, Mod1- Modified method 1; Mod2 – Modified method 2; Mod2A – Modified method 2A; PC –positive control, TC –test coupon, PB –procedural blank, LB –laboratory blank, CS – control spike, LW – liquid waste, LWD – liquid waste of decontaminant

3.6. Sampling and Analysis Method Development

Method development was required to: (1) demonstrate that the surface wipe sampling and subsequent extraction of the wipe(s) met the minimal requirements (higher than 70% recovery); (2) assess whether the presence of grime was impacting the data quality; (3) establish acceptable methods to extract malathion or 2-CEPS from the liquid waste extracts through liquid-liquid extraction; (4) verify that residual decontaminant in the wipe extract or liquid waste extract was adequately quenched to assure that the sample itself was inactive; and (5) determine whether samples were preserved adequately. The method development established the final protocol for the decontamination tests including the sampling and analysis of all generated extracts. This section addresses these elements and was executed prior to the decontamination testing.

3.6.1. Sampling methods

3.6.1.1. Surface wipe sampling and extraction of surface wipe samples

For surface sampling and wipe extraction efficacy tests, all test surfaces were spiked with target chemicals using the procedure described in Section 3-4 and placed in the same type of pre-cleaned test boxes that were used during the decontamination testing. After weathering of the chemical (CT = 30 min), gauze-wipe (DukaTM HoneywellTM NorthTM, 2" x 2" 12-ply sterile cotton gauze pads; Fisher Scientific Waltham, MA USA; P/N 17986468) samples were collected and extracted using procedures described in Section 3.6.2.1. The initial wetting solvent used for the first round of sampling method development (Round 1) was isopropanol (IPA), and the volume used was 3 mL per wipe, resulting in the semi-saturation of the wipe material. IPA was selected as a solvent as it would be compatible with painted surfaces. Post-sample collection wipes were extracted in *n*-hexane and prepared for analysis as per Section 3.6.4. Each test set consisted of three TCs complemented by one PB; there was one solvent blank (SB) and one control spike (CS) sample per test day per chemical. Initial optimization of surface sampling was performed for materials in the horizontal orientation only.

After the first round of surface wipe sampling tests, malathion and 2-CEPS extraction efficacy from the galvanized metal was within project-specific acceptance criteria of 60-140% of theoretical surface target (average recovery of 68% and 86%, as shown on Figures 3-8 and 3-9 below, for malathion and 2-CEPS, respectively). The average recoveries of malathion from other materials ranged from nondetect (ND; <2.4%) for painted concrete block to 46% (Figure 3-8) for painted concrete paver, and from below 1% (painted concrete block) to less than 5% (painted concrete paver) for 2-CEPS (Figure 3-9).

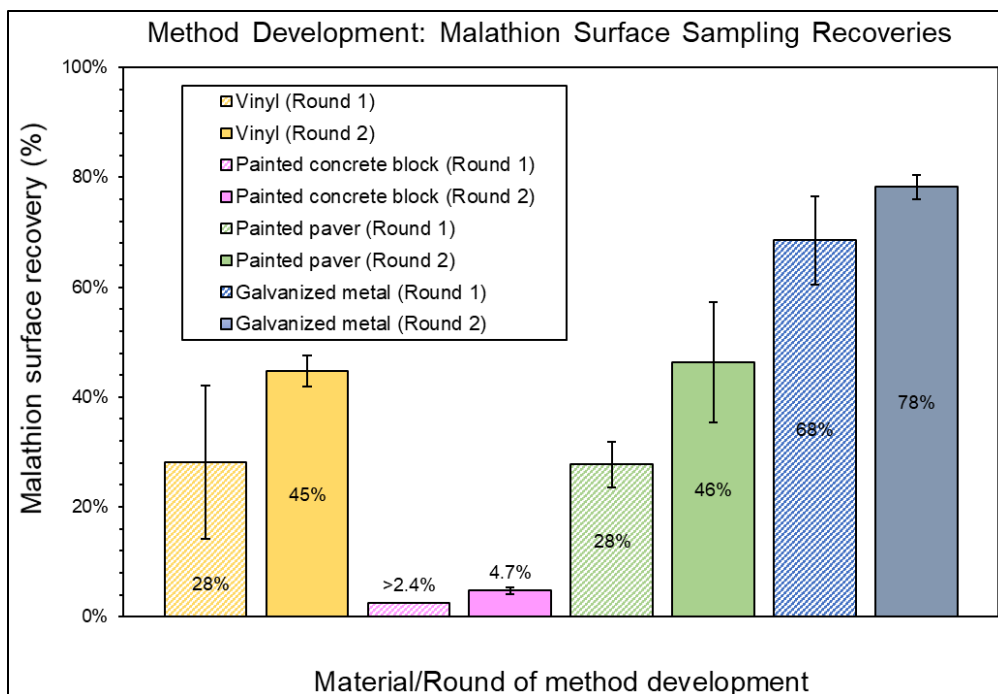


Figure 3-8. Malathion surface recovery from surface sampling and extraction method tests Round 1 (patterned bars) and results for Round 2 (solid bars) for nongrimed materials.

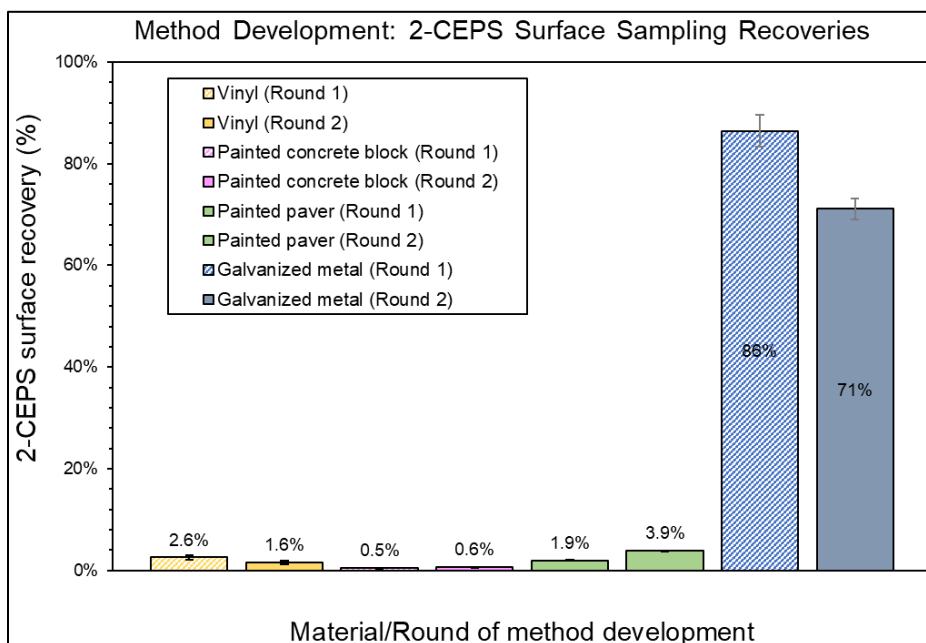


Figure 3-9. 2-CEPS surface recovery from surface sampling and extraction method optimization tests (patterned bars) and results for optimized method (solid bars) for nongrimed coupons.

Based on these initial results, the sampling method was repeated by introduction of an additional wiping medium (Cotton twill wipe, 4 x 4 in., MG Chemicals; Surrey, BC, Canada; P/N 829-4X4) for sampling of all surfaces and the use of acetone instead of IPA as wetting solvent (Round 2). Cotton Twill wipes

resulting from each coupon underwent composite extraction (i.e., placed in the same sample extraction jar as the wipe and co-extracted together). The multiwipe method offered improved recovery of malathion from challenging porous surfaces (5-45% across painted concrete materials), but no major improvement of 2-CEPS recovery (less than 5% across vinyl and painted concrete surfaces). The 2-CEPS sampling method could not be further optimized likely due to high permeation rates of 2-CEPS into these permeable materials, even after only a 30-min contact time.

A similar improvement in changing from IPA to acetone as the wetting solvent was observed when grimed surfaces were sampled. Figure 3-10 shows the wipe sampling recoveries for malathion from grimed galvanized metal and vinyl.

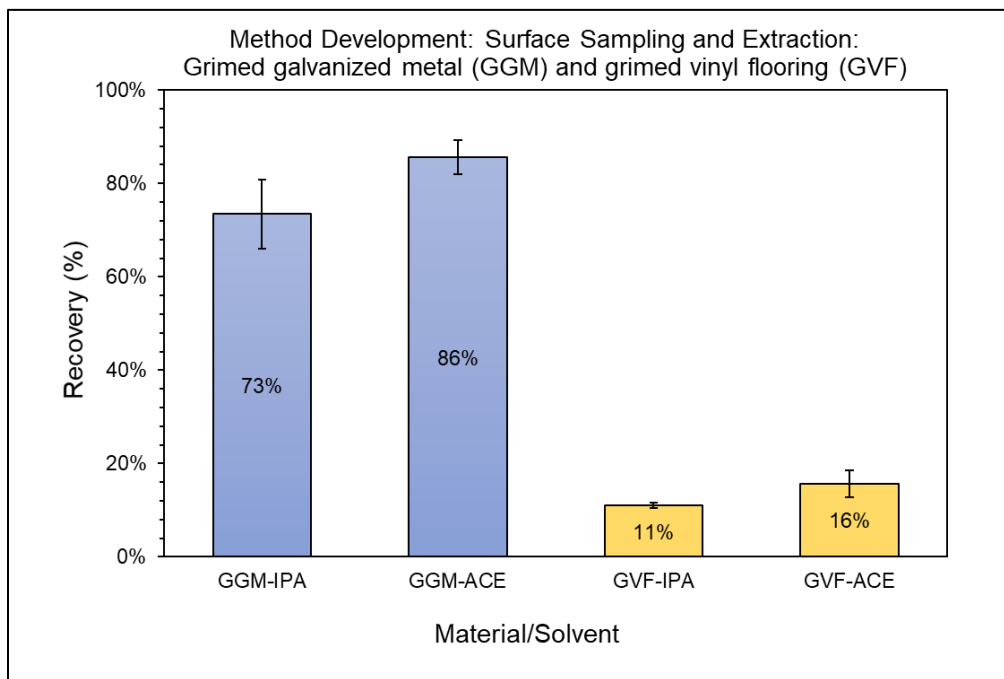


Figure 3-10. Malathion surface recovery from surface sampling and extraction method tests Round 1 (isopropanol (IPA)) and results for Round 2 (acetone (ACE)) for grimed surfaces.

High recovery (>80%) of malathion from the grimed galvanized metal material was observed when acetone was used as the wipe-wetting solvent. These results were comparable to the results for the nongrimed galvanized metal, indicating that the presence of surface grime does not negatively affect the performance of the sampling and analytical methods. However, wipe-sampling efficacies for the grimed vinyl were noticeably lower (11-16%) than for nongrimed surfaces (28–45%). Based on the repeated improvement for acetone, only acetone was verified as the wetting solvent for the wipe sampling of 2-CEPS from grimed surfaces. Figure 3-11 shows that the average 2-CEPS recoveries were high (80%) for grimed galvanized metal and below 5% (2.1%) for grimed vinyl. Further surface sampling method development for the grimed vinyl or other semi-porous and porous materials was beyond the scope of this study and was not performed. Similarly, for nongrimed materials, low recoveries from these types of surfaces were attributed to the permeation-related transport of chemicals into subsurface layers [9] despite the presence of a layer of grime that could have made the surface effectively less permeable.

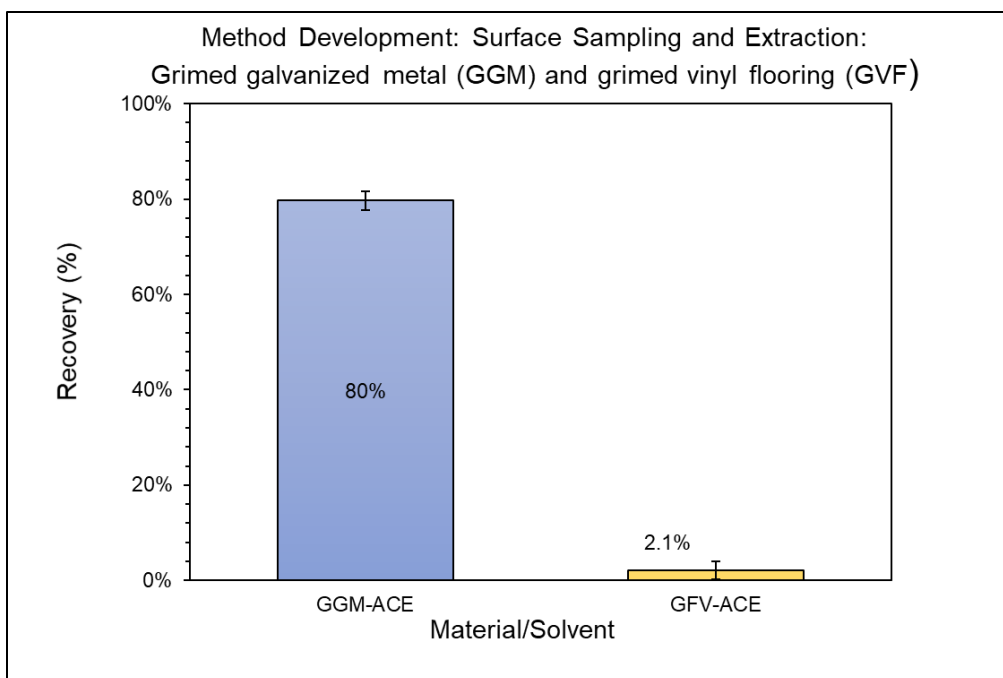


Figure 3-11. 2-CEPS surface recovery from surface sampling and extraction method tests using acetone as the wiping solvent for grimed surfaces; ACE – acetone.

3.6.1.2. Sampling and extraction of decontamination samples

Liquid sample characterization tests were designed to determine the volumes of effluents collected for each of the three decontamination procedure steps (Step 1 pre-rinse; Step 2 decontamination; and Step 3 post-rinse). Concentration of the residual active ingredient (H_2O_2) was determined in liquid waste samples from Step 2 and 3 of a simulated decontamination process (i.e., in the DF200 runoff and in the post-decontamination water rinse runoff, respectively). This information was needed to determine the need for a quenching of H_2O_2 and/or preservation of post-decontamination liquid waste (see Section 3.6.1.2.1 and 3.6.1.2.3 for details). H_2O_2 concentration in the liquid waste samples was measured via permanganate (potassium permanganate, KMnO_4) titration. The H_2O_2 concentrations were recorded only for the liquid samples associated with the grimed surfaces. In addition, surface wipes were collected and extracted to confirm that the extraction into a nonpolar solvent (hexane) is a satisfactory approach to halt further reaction of residual decontaminant in the extract which may occur if most of the active ingredient, H_2O_2 , remained in the aqueous layer and not in the hexane layer containing the extracted chemical (see Section 3.6.1.2.2).

The method development test procedure started with the preparation and assessments of DF200 decontaminant and detergent-water solution (using procedures described in Section 3.5.1 and 3.5.2). Four clean galvanized metal coupons (labeled A through D) were placed in vertical coupon holders and positioned in clean test boxes used to secure test surfaces in the vertical orientation. Each box was weighed, and the mass was recorded in the laboratory notebook. Spray bottles were filled with detergent-water and DF200 solutions and pre-weighed. A pre-decontamination detergent solution rinse was first applied to all four coupons (target application rate of 20 ± 4 mL per coupon), and the post-application mass of the spray bottle was recorded. After $\text{DT1} = 30$ min, each test box was weighed, and the results were recorded in the laboratory notebook. The detergent-water rinse runoffs were then composited into clean

beakers for pH and temperature measurements. After conclusion of Step 1, the decontamination solution was applied to all four coupons (target application rate of 20 ± 4 mL per coupon), and gravimetric measurements were recorded. After DT2 = 60 min, each box was weighed, and the results were recorded. Any changes in weight between the start and end of the decontamination application period (60 min) can be attributed to decontamination solution evaporation losses. Coupon D was sampled using the wipe procedure described in Section 3.6.1, and the wipe used was placed into hexane for immediate extraction. The individual post-decontamination runoffs were composited into clean beakers for pH, temperature and H₂O₂ concentration measurements. Lastly, the spraying procedure was repeated for the application of the post-decontamination water rinse to coupons A through C, followed by 30 minutes of processing (DT3 = 30 min), and a final determination of pH, temperature and hydrogen peroxide concentration in the water rinse composite sample. After completion of the entire effluent characterization procedure, liquid samples were refrigerated for liquid-liquid extraction and decontamination efficacy of aqueous waste tests.

Figure 3-12 shows Steps 1 through 3 processing with the visible runoff of pre-decontamination rinse, decontaminant, and post-decontamination rinse, respectively.

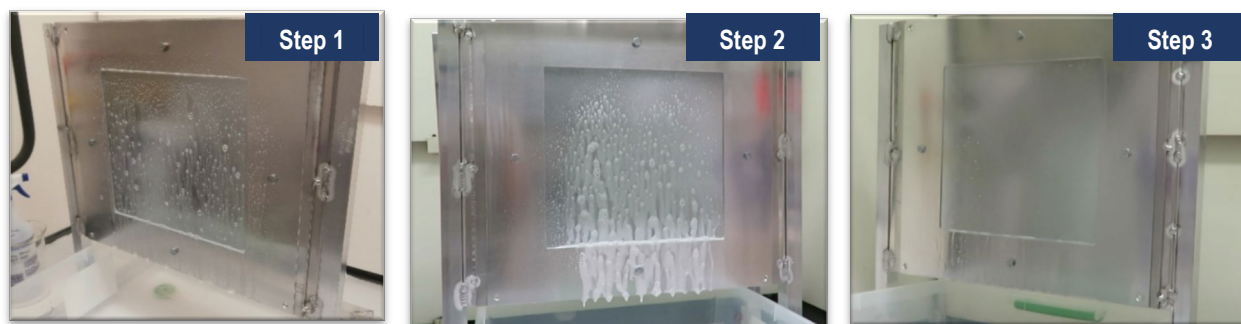


Figure 3-12. Runoff of pre-decontamination rinse (left), decontaminant (middle) and post-decontamination rinse (right).

No contaminant chemicals were applied during these method development tests. The results from this characterization of simulated liquid effluents from nongrimed surface testing are given in Tables 3-5 through 3-7.

Table 3-5. Characterization of Liquid Effluents from Step 1 of Simulated Decontamination Procedure

Coupon	Spray bottle initial mass [g]	Test box initial mass [g]	Spray bottle final mass [g]	Test box final mass [g]	Step 1 rinse applied [g]	Mass of runoff from Step 1 [g]	Composite sample Measurements*			
							Mass [g]	Volume [mL]	T [°C]	pH
A	368.2	785	348.5	793	19.7	7	23.6	23.6	22.3	8.41
B	348.5	814	321.9	824	26.6	8.5				
C	321.9	802	301.7	807	20.2	3.7				
D	301.7	800	281.6	806	20.1	4.4				

*composite sample collected from four coupons

Table 3-6. Characterization of Liquid Effluents from Step 2 of Simulated Decontamination Procedure

Coupon	Spray bottle initial mass [g]	Test box initial mass [g]	Spray bottle final mass [g]	Test box final mass [g]	Step 2 decontaminant applied [g]	Mass of runoff from Step 2 [g]	Composite sample Measurements*				
							Mass [g]	Volume [mL]	T [°C]	pH	H ₂ O ₂ [%]
A	254.7	799	234.5	807	20.2	3.9	19.1	23.6	22.4	9.8	3.2
B	234.3	810	214.6	820	19.7	7.2					
C	214.5	784	194.3	791	20.2	4.7					
D	194.2	799	173.2	808	21	6.8					

*composite sample collected from four coupons

Table 3-7. Characterization of Liquid Effluents from Step 3 of Simulated Decontamination Procedure

Coupon	Spray bottle initial mass [g]	Test box initial mass [g]	Spray bottle final mass [g]	Test box final mass [g]	Step 3 rinse applied [g]	Mass of runoff from Step 1 [g]	Composite sample Measurements*				
							Mass [g]	Volume [mL]	T [°C]	pH	H ₂ O ₂ [%]
A	439.2	784	418.9	791	20.3	5.1	15.5	15.5	21.7	9.9	0.20
B	418.9	785	398.8	792	20.1	5.7					
C	398.8	806	379.8	813	19	4.7					

*composite sample collected from three coupons

Measured weight gains in test boxes for each of the three steps are noticeably lower than the weight of the applied spray volume. This difference can be explained by evaporative losses of the applied liquid in any of the three steps and some spray volume that does not reach the surface. The relative weight of the recovered liquids was 81%, 66%, and 74% of the weight gain of the test boxes for Step 1, Step 2, and Step 3, respectively. The H₂O₂ concentration in the Step 2 effluent (3.2%) is only slightly lower than the 4% (or higher) concentration based on the Go/No-Go test that was conducted for this solution. The H₂O₂ concentration in the Step 3 effluent (0.2%) is significantly lower due to the dilution of decontaminant runoff with the post-rinse water.

3.6.1.2.1. Liquid-liquid extraction of aqueous waste

Liquid waste in this study was extracted using the modified extraction procedure described in EPA SW-846 Method 3571 (Extraction of Solid and Aqueous Samples for Chemical Agents) [15]. The method recommends an extraction solvent of 10% IPA/dichloromethane that was replaced with 100% *n*-hexane. Method performance with *n*-hexane was demonstrated to be equivalent to or better than the recommended solvent using the simulated liquid waste samples collected in tests to characterize liquid effluents as described in Section 3.6.1.2. The 0.5- to 0.6-mL aliquots of simulated liquid waste samples from Step 1 (pre-decontamination detergent solution rinse) were spiked with malathion or 2-CEPS solutions prepared per Section 3.4. The Step 1 effluents were chosen for the liquid-liquid extraction tests as they are representative of the matrix but do not contain any decontaminant (i.e., they will not require quenching) but do contain surfactants (detergent).

Two target concentrations were tested in these matrix spike samples (1% and 100% of the maximum concentration) that could be expected in a composite sample of liquid waste, i.e., target concentrations of 0.05 mg/mL and 5 mg/mL, respectively. There were six samples for each target chemical and concentration combination, three with preservative added and three without preservative, accompanied by one procedural blank (Step 1 liquid effluent aliquot that was not spiked). There was one solvent blank sample (*n*-hexane) per test per chemical. The preservation of samples varied depending on the analyte:

1. Six samples, three at 1% and three at 100% for analysis of 2-CEPS, were preserved through addition of 0.5 mL of glacial acetic acid/NaCl for each 0.5 mL of aqueous sample containing 2-CEPS immediately after spiking. Acidic conditions (pH within a range of 3.5 to 5) are expected to slow the decomposition rate of 2-CEPS like that of HD (hydrolysis to thiodiglycol and other compounds). The presence of chloride ion would reduce the effects of metal cations. Six samples, three at 1% concentration and three at 100% concentration, were prepared without preservatives. In this study, preserved and unpreserved liquid samples were extracted with 5 mL of hexane immediately after collection to avoid losses of target chemicals.
2. Six samples, three at 1% and three at 100% for analysis of malathion, were preserved with L-ascorbic acid, ethylenediaminetetraacetic acid, and pH-adjusted with trisodium salt potassium dihydrogen citrate to pH 3.8 to slow alkaline hydrolysis of malathion [16]. Preserved samples were each spiked with 30 μ L of concentrated L-ascorbic acid, ethylenediaminetetraacetic acid, and pH-adjusted with trisodium salt potassium dihydrogen citrate solutions. Six samples, three at 1% concentration and three at 100% concentration, were prepared without preservatives. In this study, preserved and unpreserved liquid samples were extracted with 5 mL of hexane immediately after collection to avoid losses of target chemicals.

Samples were prepared for analysis per Section 3.6.3. In addition, CS samples were prepared by direct spiking of the chemical solution into hexane. Figure 3-13 shows the experimental scheme for the liquid waste extraction optimization tests.

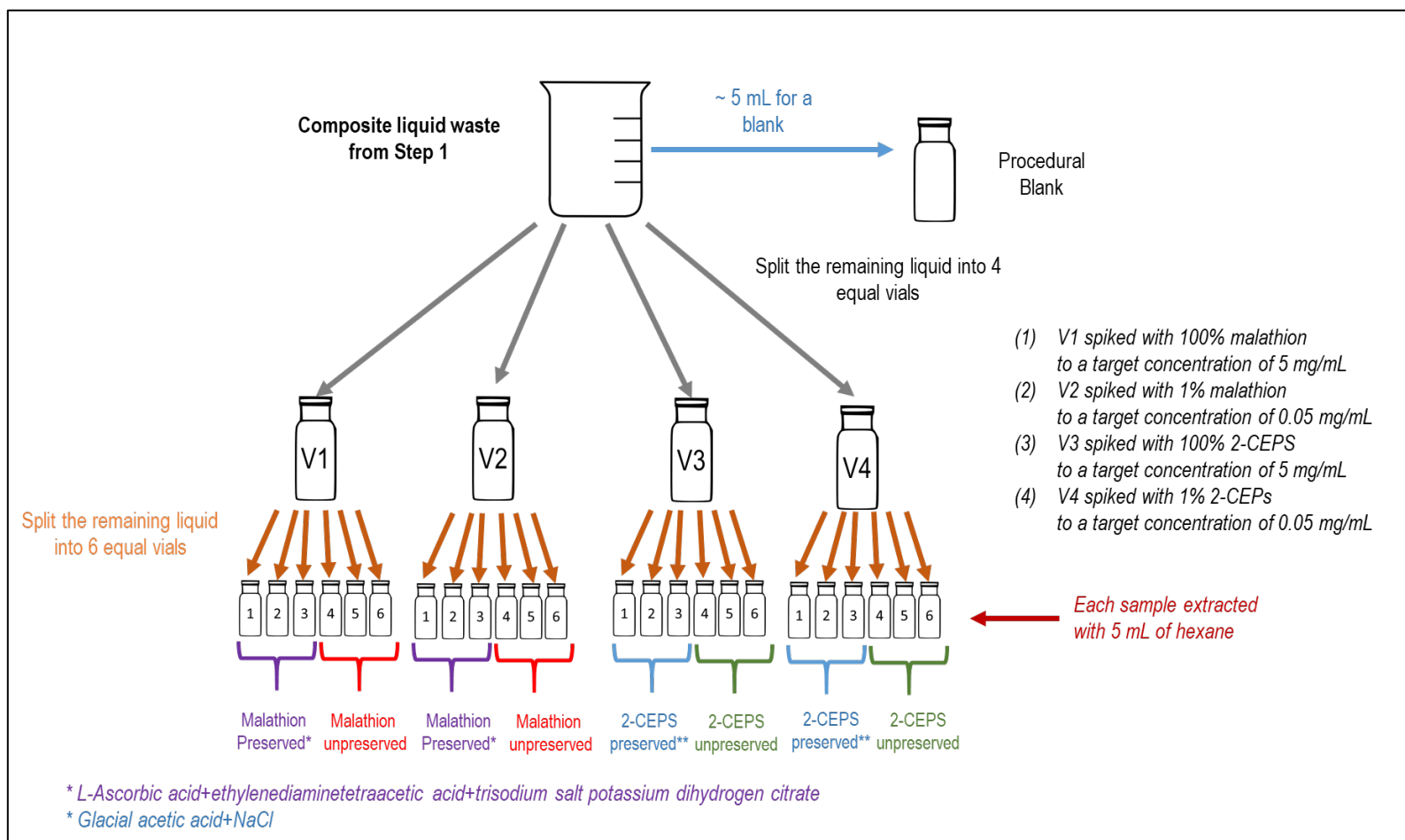


Figure 3-13. Experimental scheme for liquid waste extraction tests.

Results for the extraction of nonpreserved as compared to preserved liquid waste matrix spike samples for malathion and 2-CEPS are shown in Figure 3-14.

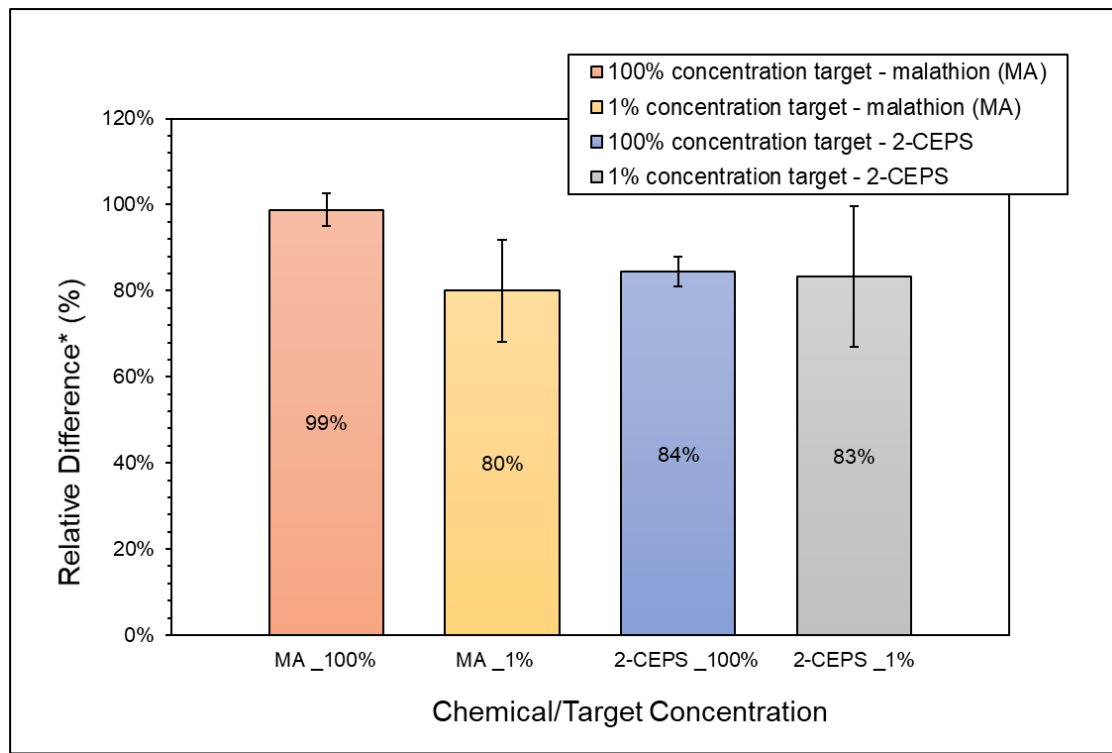


Figure 3-14. Extraction of liquid waste containing detergent collected from nongrimed surfaces.
*: % ratio of recovery of malathion and 2-CEPS in nonpreserved versus preserved samples collected from nongrimed surfaces.

The relative percent difference in recoveries of malathion and 2-CEPS between preserved and nonpreserved liquid waste was less than 20%, while at least 80% of the amount of chemical (with a coefficient of variance less than 30%) was recovered from all samples processed using the reference versus modified method [15]. Based on the relatively small (within experimental error) differences between nonpreserved and preserved liquid waste samples, the modified method that did not include the preservation step was deployed in the follow-on testing, including testing of grimed surfaces. Results from the extraction efficacy testing of liquid samples collected from the grimed surfaces are shown in Figure 3-15.

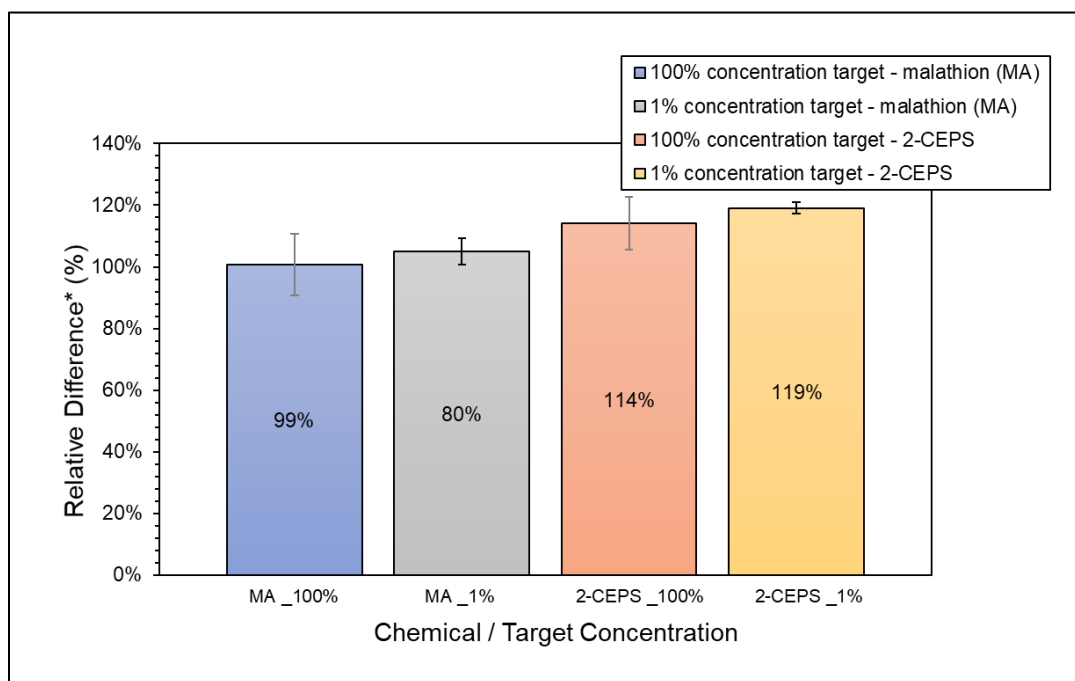


Figure 3-15. Optimization of extraction of liquid waste containing detergent collected from grimed surfaces. *: %ratio of recovery of malathion and 2-CEPS in nonpreserved samples collected from grimed surfaces.

Recoveries from the spiked liquid waste from a grimed surface using the modified extraction procedure without preservation step were found to be better than 80%, which indicated that any grime that was present in the extract did not impact the analysis of the liquid waste. This procedure was therefore deployed in the actual decontamination testing of nongrimed and grimed surfaces.

3.6.1.2.2. Verification of quenching of decontamination reaction in wipe extracts

Verification tests were performed to verify whether the use of a nonpolar wipe extraction solvent (here, hexane) is a satisfactory approach to halt degradation of the contaminant in the wipe extract in the presence of residual decontamination solution. This approach is based on the affinity of both malathion and 2-CEPS to move from an aqueous decontamination layer to the nonpolar solvent layer based on their high log K_{ow} values (see Table 3.3). These verification tests were solution-based tests (i.e., no coupon material or wipe was present). For wipes, extracts were used from the Step 2 wipe sampling performed during waste characterization tests described in Section 3.6.1.2. Six samples were generated (for each chemical-material combination); three test vials (Vials 1 - 3) received 5 mL of wipe extract, three vials (Vials 4 - 6) received solvent only (hexane). Wipe extracts were then spiked with chemical solutions corresponding to 100% of the target chemical concentration on the coupon surface (Figure 3-16).

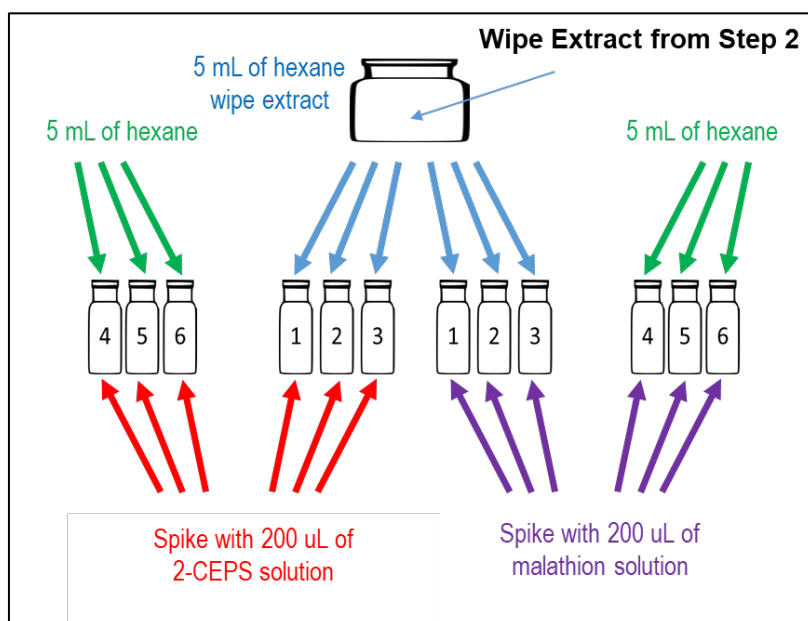


Figure 3-16. Effect of decontamination solution in wipe extracts tests.

Samples were prepared for analysis per Section 3.6.3. In addition, CS samples were prepared by direct spiking of chemical solution into hexane. Results from avoiding oxidant reaction in the wipes through use of the nonpolar extraction solvent are summarized in Figure 3-17.

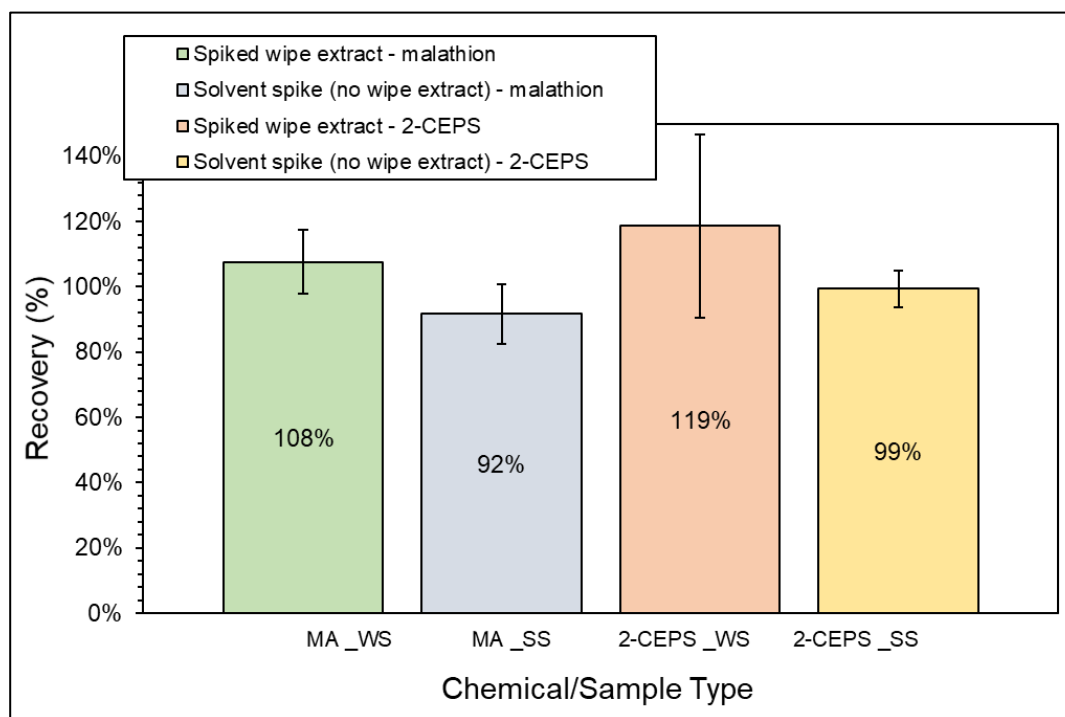


Figure 3-17. Recovery of malathion and 2-CEPS from sampling wipe containing residual DF200.

Recovery of malathion and 2-CEPS in wipe extract matrix spikes ($108 \pm 10\%$; relative standard deviation (RSD) = 9% and $119 \pm 28\%$; RSD = 24%, respectively) was within QAPP acceptance criteria of 60 – 140% with an RSD less than 30%. Hence, the extraction-solvent-based avoidance of further reaction in a sample by residual H_2O_2 present in the sampling wipes was considered sufficient. No additional chemical quenching (e.g., through the addition of sodium thiosulfate [STS]) to the extract was required for these wipe extracts.

3.6.1.2.3. Verification of quenching of decontamination reaction in liquid waste

The solution-based test approach used for the verification of quenching of decontamination solution in liquid waste was similar to one described in Section 3.6.1.2.2 for wipes. The quenched and nonquenched Step 2 liquid waste extracts were extracted using the procedure described in Section 3.6.3. Since the amount of residual decontaminant was expected to be higher than in a wipe extract, the quenching tests included samples that were extracted with and without an additional quenching chemical (here, STS). Six test samples (for each chemical) were generated: three test vials (Vials 1 - 3) received extracts that were not treated with STS, three vials (Vials 4 - 6) received extracts that were quenched with STS. All extracts were then spiked with chemical solutions corresponding to 10% of the target chemical concentration on the coupon surface, or the equivalent of 10% transfer to liquid waste (Figure 3-18). After spiking, all samples were sonicated for 5 minutes and allowed to stand for 15 minutes, then prepared for analysis as per Section 3.6.3.

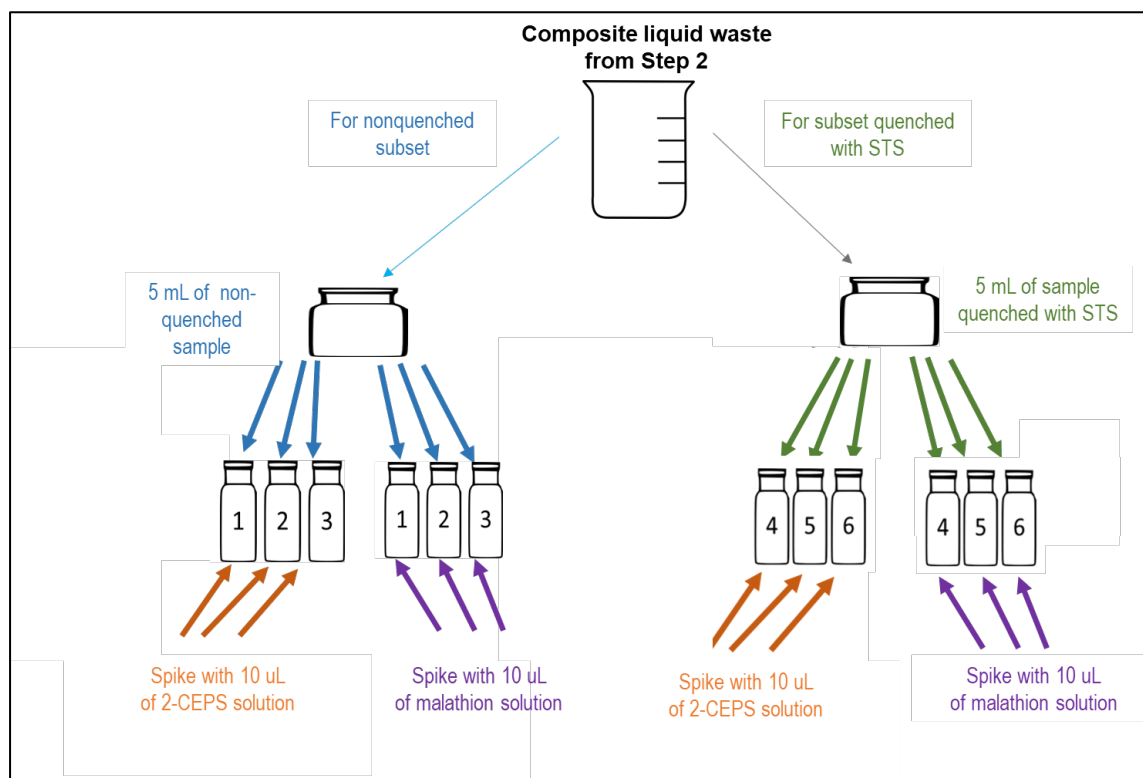


Figure 3-18. Effect of decontamination solution in liquid waste tests.

In addition, CS samples were prepared by direct spiking of chemical solution into hexane. Results from these experiments of the liquid waste are shown in Figure 3-19.

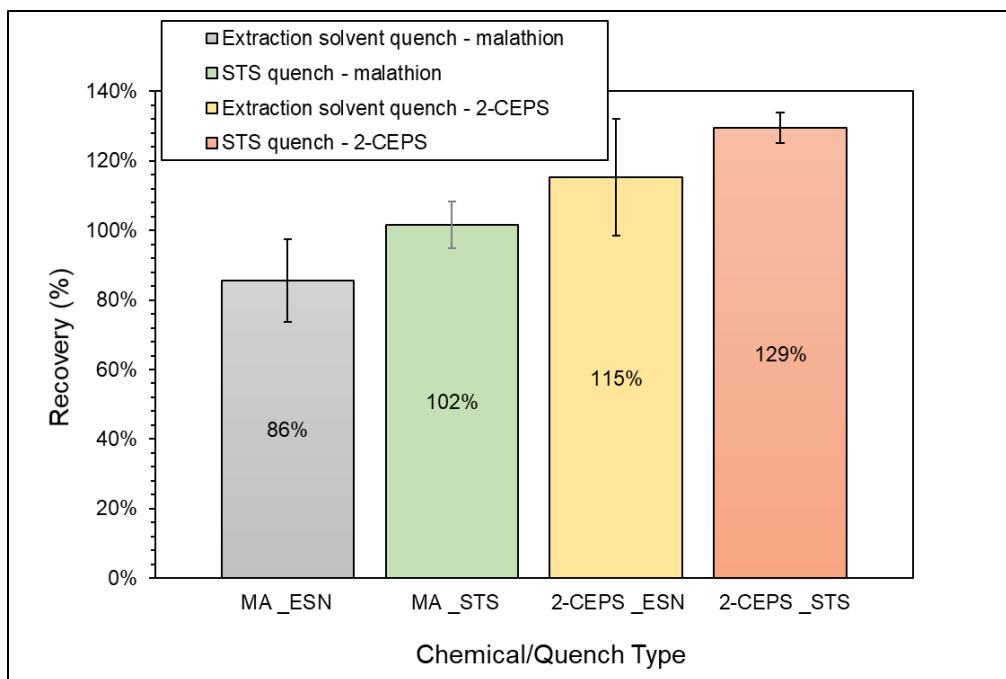


Figure 3-19. Recovery of malathion and 2-CEPS from DF200 runoff using extraction solvent only (ESN) and extraction solvent with sodium thiosulfate (STS).

Recoveries of malathion and 2-CEPS in the Step 2 liquid waste (or DF200 runoff) without STS (i.e., extraction solvent only) were $86 \pm 12\%$ (RSD = 14%) and $115 \pm 17\%$ (RSD = 15%), respectively. The relative % difference between the two types of sample preparation processes was less than 20% and met the quality assurance (QA) criteria of at least 80% of the amount of chemical (with RSD less than 30%) recovered in solvent-only extracted liquid waste samples, versus the same liquid waste samples that underwent quenching with the STS addition step. The addition of STS did improve the recoveries somewhat. However, the objective to recover at least 80% of the spiked solution was met without the use of STS as an additional quenching agent. Therefore, the STS quenching agent was not included in the final procedure of the waste extraction. All waste samples were immediately extracted, followed by sonication and separation of organic extracts from post-extraction aqueous layer of the final sample.

3.6.2. Decontamination process design for horizontal and vertical coupon testing

After completion of the method development tests, a multiple group material- and orientation-specific decontamination process/experimental design was used for each test. This process for horizontal and vertical surface decontamination testing is shown in Figures 3-20 and 3-21, respectively. Each decontamination test was accompanied by the collection of reference (nondecontaminated) positive controls. The process design that was used for testing of PC coupons is shown in Figure 3-22. The implemented sampling and extraction methods for surface wipes and liquid waste are summarized in Section 3.6.2.1 and 3.6.2.2.

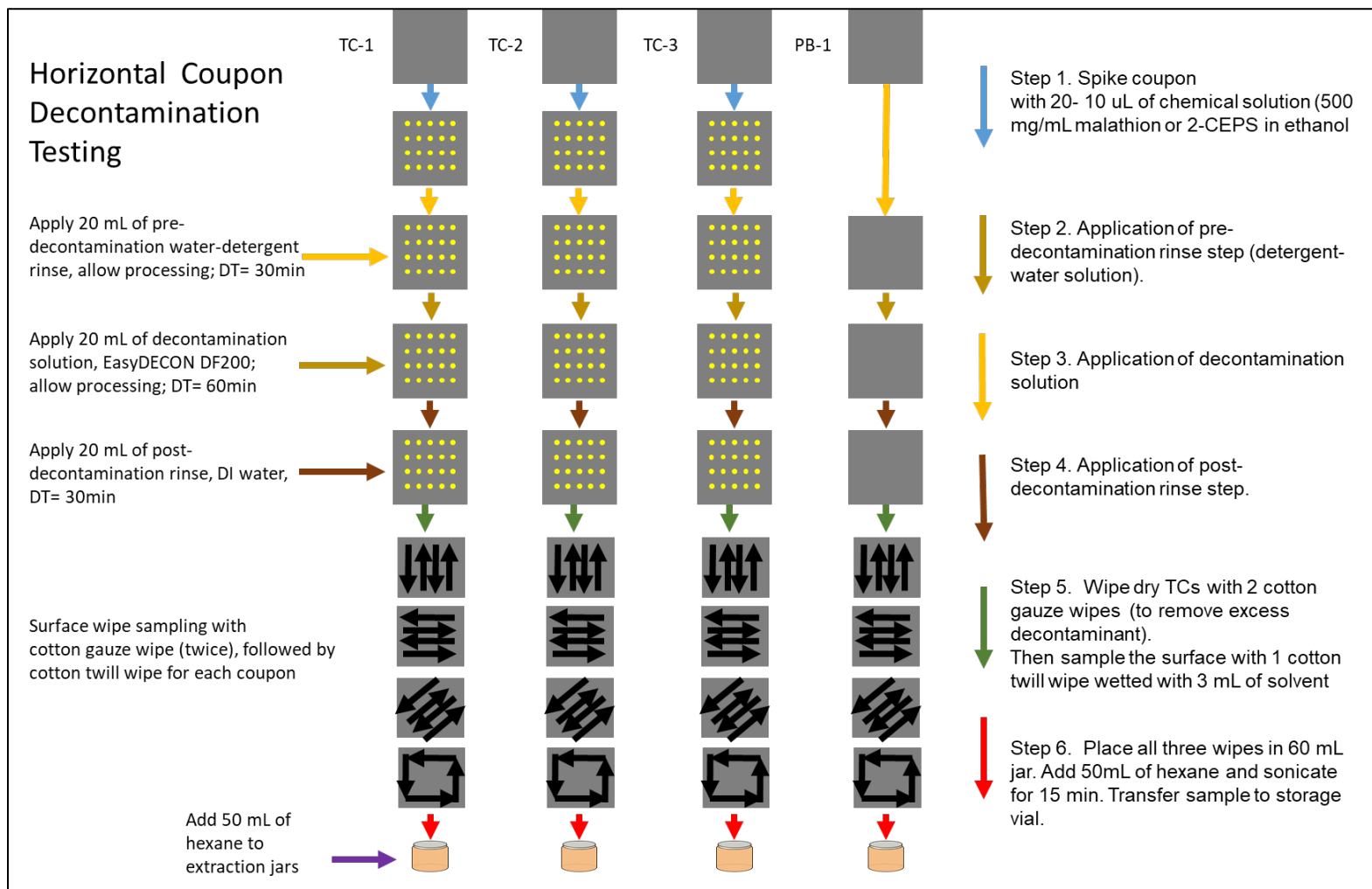


Figure 3-20. Sample process design for horizontal coupon decontamination testing.

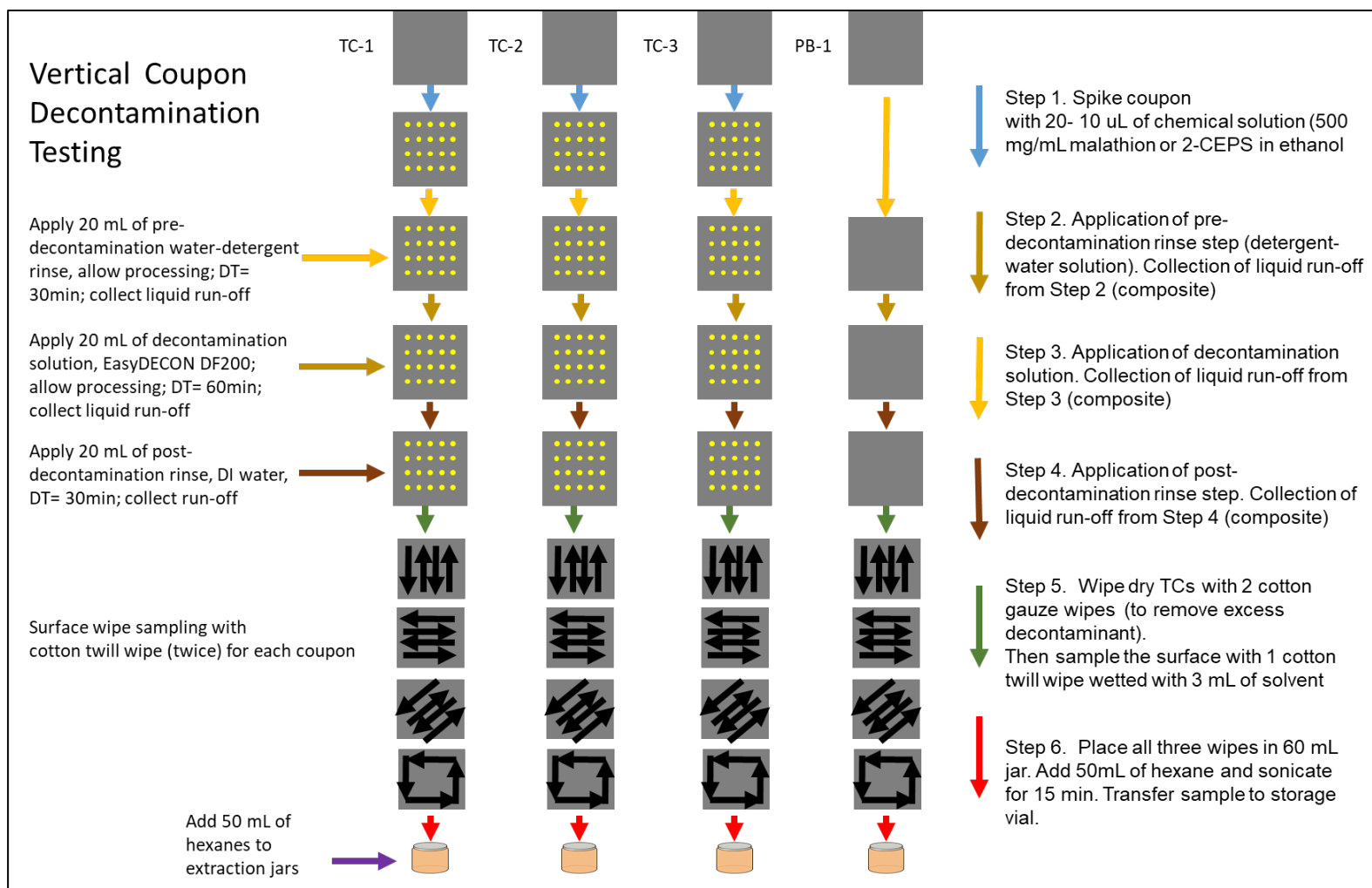


Figure 3-21. Sample process design for vertical coupon decontamination testing.

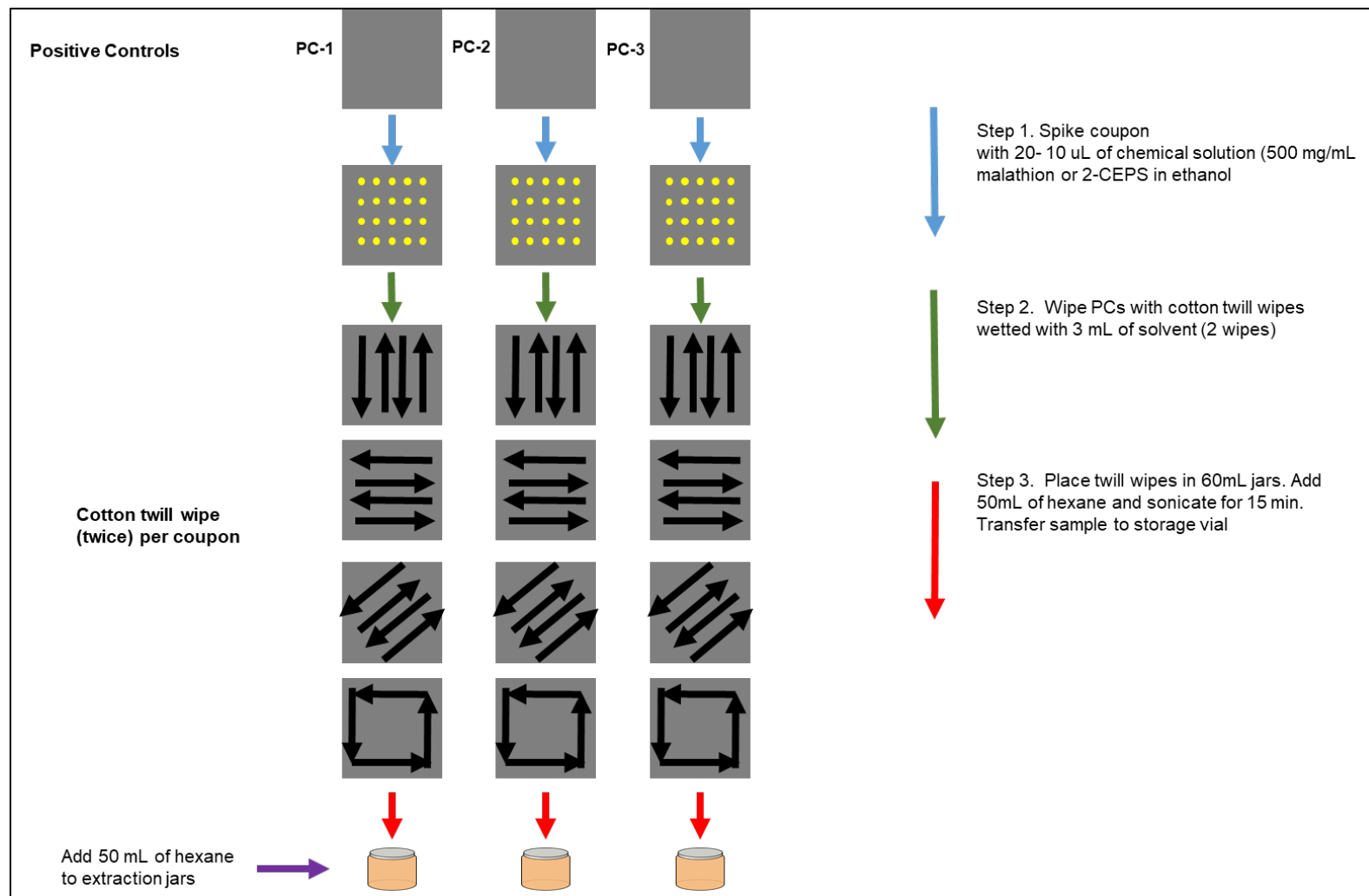


Figure 3-22. Sample process design for positive control testing.

3.6.2.1. Surface sampling and extraction methods

Table 3-8 summarizes test parameters for wipe sampling and extraction methods for all material-test-orientation combinations. Test parameters were identical for tests with malathion- or 2-CEPS-contaminated materials. Table 3-8 includes types of wiping media, wetting solvents, and amount of wetting solvents for all material-orientation combinations that were used for collection of pre- and post-decontamination surface wipe samples. Wipe sampling methods were optimized prior to testing as described in Section 3.6.1.1. The surface wipe sampling of each coupon was a multistep process involving two to three wipes per coupon:

- for horizontal-test-orientation materials, two cotton gauze wipes were used first to remove excess liquid decontaminant that did not run off or dry out. After collection of two cotton gauze samples, a final cotton twill wipe was deployed across the same material;
- for vertical materials and all positive controls, two twill wipes were deployed on each coupon.

Table 3-8. Surface Sampling Parameters for Malathion and 2-CEPS

Material	Wipe	Number of wipes per coupon	Wetting Solvent	Wetting Solvent Volume per Wipe	Extraction Solvent
Galvanized metal [horizontal, decontaminated]	Cotton gauze/Cotton twill wipe	2/1	None/Acetone	0/3 mL	Hexane
Galvanized metal [horizontal, nondecontaminated]	Cotton twill wipe	2	Acetone	3 mL	Hexane
Galvanized metal [vertical, decontaminated]	Cotton twill wipe	2	Acetone	3 mL	Hexane
Painted [sealed] concrete flooring [horizontal, decontaminated]	Cotton gauze/Cotton twill wipe	2/1	None/Acetone	0/3 mL	Hexane
Painted [sealed] concrete flooring [horizontal, nondecontaminated]	Cotton twill wipe	2	Acetone	3 mL	Hexane
Painted [sealed] concrete block [vertical, contaminated and nondecontaminated]	Cotton twill wipe	2	Acetone	3 mL	Hexane
Vinyl [horizontal, decontaminated]	Cotton gauze/Cotton twill wipe	2/1	None/Acetone	0/3 mL	Hexane
Vinyl [horizontal, nondecontaminated]	Cotton twill wipe	2	Acetone	3 mL	Hexane

Each surface wipe sampling used a four-step process consisting of a series of horizontal, vertical, diagonal and perimeter wiping strokes, in which the wipe was folded over after each step (with contaminated side always inward). A detailed procedure is shown in Appendix C. Figures 3-23 and 3-24 show examples of the wipe sampling of horizontal and vertical materials, respectively.

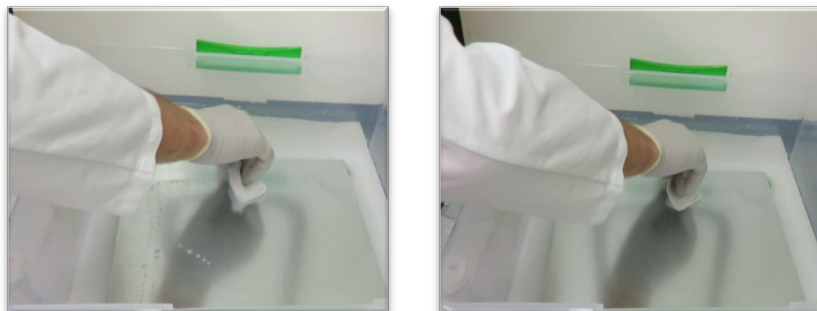


Figure 3-23. Example of surface wipe sampling in horizontal orientation (left – cotton gauze sampling of galvanized metal; right – the follow-on cotton twill wipe sampling of galvanized metal)



Figure 3-24. Example of surface wipe sampling in vertical orientation (left – cotton twill wipe sampling of galvanized metal; right – cotton twill wipe sampling of painted concrete block)

After completion of sampling, wipes resulting from each coupon were placed in pre-cleaned 60- or 120-mL wide-mouth extraction jars with polytetrafluoroethylene (PTFE)-lined lids (Thermo Fisher Scientific Inc., Waltham, MA; P/N 240-0060 and P/N 240-0120, respectively). Each jar received 50 mL of *n*-hexane, capped, and transferred to a sonicator. Wipe samples were extracted via sonication for 15 minutes. After extraction was completed, a 15-mL aliquot of extract was transferred to a 20-mL glass vial and refrigerated at $4 \pm 2^\circ\text{C}$ for further processing. The remainder of the sample extracts was discarded. Sample preparation for instrumental analysis is described in Section 3.6.3.

3.6.2.2. Liquid waste sampling and extraction procedures

Liquid waste (runoff) extraction, preservation, and quenching methods for dealing with residual oxidant were optimized prior to testing as described in Section 3.6.1.2. Malathion and 2-CEPS were extracted from liquid waste samples using a simplified liquid-liquid extraction procedure that did not include preservation or quenching of the decontaminant active ingredient (hydrogen peroxide), as solvent extraction (with no preservation of sample) was proven efficacious during method development tests. After the determination of the waste volume for each type of collected runoff, liquid waste samples were transferred to clean extraction vials and an equal volume of hexane was added to each sample (1:1 v/v liquid waste:hexane). Additionally, 25 grams of sodium chloride was added to the detergent-water runoff samples from Step 1 to salt-out the soap from the solution. Each sample was manually shaken for one minute. After

the aqueous and hexane layer separated, the entire hexane layer was carefully collected using a Pasteur pipette (KIMBLE® Disposable Borosilicate Pasteur Pipet Unplugged, 9 in; DWK Life Sciences, LLC, Rockwood, TN; P/N 63B92) into a 15-mL graduated test tube, and the total extract volume was recorded. One (1) mL of hexane extract was then transferred into a 1.8-mL amber glass screw top GC vial (Thermo Scientific™ GC vial, PTFE/Silicone/PTFE septum, Thermo Fisher Scientific Inc., Waltham, MA; P/N C5000188W). Samples were then refrigerated prior to shipment to the subcontracting laboratory or transfer to onsite analytical laboratory for analysis. In addition, a 10-mL aliquot of the remaining extract was transferred to a 12-mL vial and archived at $4 \pm 2^\circ\text{C}$. Sample preparation for instrumental analysis is described in Section 3.6.3.

3.6.3. Preparation of extracts for analysis

Extracts generated from the extraction of wipes and liquid waste were prepared for analysis in 1.8-mL amber glass autosampler vials. The concentration of chemicals in the raw extract was expected to be approximately 2,000 $\mu\text{g/mL}$. The detection limit for GC/MS analysis of these two compounds was expected to be 1 $\mu\text{g/mL}$ with a dynamic calibration range of 1 – 100 $\mu\text{g/mL}$. Based on surface sampling recovery established in method development tests, PC extracts from galvanized metal tests underwent a 20-fold dilution - a 50- μL aliquot of raw extract was drawn using an appropriate size micropipette (Eppendorf AG, Hamburg, Germany) and added to a GC vial filled with 950 μL of hexane. The control spike samples were also diluted 20-fold. Other extracts (PCs from nonreference material, all decontaminated TCs, blanks, and liquid waste extracts) were submitted to the subcontracting laboratory as is - a 1000- μL aliquot of sample was drawn from each extract using an electronic pipette and added to the GC vial. If analytical results were outside the calibration range, the laboratory performed necessary dilutions and reported dilution factors along with QC data packages. The samples were refrigerated at $4 \pm 2^\circ\text{C}$ or below prior to shipment. All shipments were accompanied by the chain of custody (COC) form and were inspected by the analytical laboratory upon receipt.

3.6.4. Instrumental analysis

Instrumental analyses were performed by the subcontracted analytical laboratory (EMSL Analytical, Inc.; Cinnaminson, NJ, USA) using modified National Institute for Occupational Safety and Health (NIOSH) Method 5600 [17] or by the EPA Organic Support Laboratory (OSL). EMSL analyzed samples that were generated with nongrimed coupons while OSL analyzed samples related to the grimed surface studies. These tests were completed in chronological order with no overlap in analyses by both laboratories on the same extract.

Sample extracts were analyzed by means of GC/MS. Malathion was detected with ions 93, 125 and 173 (quantitation with ion m/z 173). 2-CEPS was detected with ions m/z 123 and m/z 172 (quantitation with ion m/z 123). The instrumental parameters and conditions for GC/MS analyses for both analytes are given in Tables 3-9 through 3-12.

Table 3-9. Instrumental Parameters and Conditions for GC/MS Analyses of Malathion by EMSL Analytical, Inc.

Parameter	Description/Conditions
Instrument	Agilent 6890 Gas Chromatograph equipped with Agilent 5973 Mass Selective Detector (Agilent Technologies, Santa Clara, CA, USA)
Autosampler	Agilent 7683 Automatic Sampler (Agilent Technologies, Santa Clara, CA, USA)
Column	Rtx®-5Sil MS w/5 m Integra-Guard® column, 30 m × 0.25 mm I.D., 0.25 µm df; part no. 13623-124 (Restek Corporation, Bellefonte, PA, USA)
GC column program	100°C initial temperature, hold 0 min, 15°C/min to 250°C, hold 5 min
Carrier gas flow rate	1.0 mL/min (helium)
Injection volume/type	1.0 µL/splitless
Inlet temperature	250°C
MS quad temperature	150°C
MS source temperature	230°C
MS transfer line	270°C
Solvent delay	4 min

df: film thickness

Table 3-10. Instrumental Parameters and Conditions for GC/MS Analyses of 2-CEPS by EMSL Analytical, Inc.

Parameter	Description/Conditions
Instrument	Agilent 6890 Gas Chromatograph equipped with Agilent 5973 Mass Selective Detector (Agilent Technologies, Santa Clara, CA, USA)
Autosampler	Agilent 7683 Automatic Sampler (Agilent Technologies, Santa Clara, CA, USA)
Column	Rtx®-MS5 column, 30 m × 0.32 mm I.D., 0.50 µm df; part no. 13439 (Restek Corporation, Bellefonte, PA, USA)
GC column program	100°C initial temperature, hold 0 min, 15°C/min to 25 °C, hold 5 min
Carrier gas flow rate	1.0 mL/min (helium)
Injection volume/type	1.0 µL/splitless
Inlet temperature	225°C
MS quad temperature	150°C
MS source temperature	230°C
MS transfer line	270°C
Solvent delay	4 min

df: film thickness

Table 3-11. GC/MS Parameters for Analysis of Malathion by OSL

Parameter	Description/Conditions
Instrument	Thermo Trace 1300 Gas Chromatograph GC ISQ™ Mass Spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA)
Autosampler	AS/AI 1310 Autosampler (Thermo Fisher Scientific, Inc., Waltham, MA)
Column	DB-5, 20 m × 0.25 mm ID, 0.25 µm df (Agilent, Santa Clara, CA)
GC column program	60 °C initial temperature, hold 0 min, 8 °C/min to 260 °C, hold 8 min
Carrier gas flow rate	1.3 mL/min (helium)
Injection volume/type	1.0 µL/splitless
Inlet temperature	250 °C
MS source temperature	250 °C
MS transfer line	250 °C

df: film thickness

Table 3-12. GC/MS Parameters for Analysis of 2-CEPS by OSL

Parameter	Description/Conditions
Instrument	Thermo Trace 1300 Gas Chromatograph GC ISQ™ Mass Spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA)
Autosampler	AS/AI 1310 Autosampler (Thermo Fisher Scientific, Inc., Waltham, MA)
Column	DB-5, 20 m × 0.25 mm ID, 0.25 µm df (Agilent, Santa Clara, CA)
GC column program	60 °C initial temperature, hold 0 min, 8 °C/min to 260 °C, hold 8 min
Carrier gas flow rate	1.3 mL/min (helium)
Injection volume/type	1.0 µL/splitless
Inlet temperature	250 °C
MS source temperature	250 °C
MS transfer line	250 °C

df: film thickness

The calibration range for EMSL was 1 - 100 µg/mL for both analytes; a 7-point nonlinear (no weighting) calibration curve (1-10-20-40-60-80-100 µg/mL) was used for initial calibration, with reporting limit verification (RLV) and initial calibration verification (ICV) analyses performed at lowest and mid-calibration level, respectively, prior to each analytical run. EMSL restricted the concentration range of the calibration curve to less than 7 points, when applicable, to obtain a linear response. Additionally, analysis of laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) was performed prior to each analytical run. A continuous calibration standard at mid-concentration level was analyzed every ten samples, with calibration end check performed at the end of each analytical run. Additional QC samples included duplicate injections of test samples and analysis of laboratory blanks. Samples with results below the lowest calibration point (i.e., 1 µg/mL) were reported as less than the quantitation limit (<LOQ). Acceptance criteria for quality control (QC) checks are listed in Table 3-13, below.

Table 3-13. QC Checks for Instrumental Analyses

QC check	Acceptance limits
Initial Calibration (ICAL)	7-point initial calibration prior to analysis*
Reporting Limit Verification at lowest point concentration (RLV)	60 - 140%
Initial calibration verification at midpoint concentration (ICV mid)	80 - 120%
Laboratory Control Sample at midpoint concentration (LCS)	70 - 130%
Laboratory Control Sample Duplicate at midpoint concentration (LCSD)	<25% RPD
Continuous calibration (CC) at midpoint concentration	80 - 120%
End check of calibration (EC) at midpoint concentration	80 - 120%
Duplicate injections (DUP)	<25% RPD
Laboratory (solvent) blank (LSB)	<LOQ

***re-calibrate when continuous calibration fails acceptance criteria and/or after system maintenance; RPD – relative percent difference**

The calibration range for EPA OSL was 100–10,000 ng/mL, with quantitation performed using two 5-point curves that were dependent on the sample concentration. The high-concentration calibration curve (1,000-2,500-5,000-7,500-10,000 ng/mL) was used for analysis of sample materials that had high sampling efficacy and CSs at a 100% target concentration. The low concentration calibration curve (100-250-500-750-1,000 ng/mL) was used for analysis of sample materials that had low sampling efficacy, CSs at a 10% target concentration, and blanks. Each calibration standard included 1,000 ng/mL of the internal standard (IS), naphthalene-d8 (from EPA 8270 semivolatile internal standard mix [CRM46955, Millipore Sigma, St. Louis, MO]); IS was also present in all test and CS samples at the same concentration level. Prior to sample analysis, a minimum 5-point initial calibration (ICAL) was performed, and the coefficient of determination (R^2) was calculated (target $R^2 \geq 0.995$). The continuous calibration verification was performed using a mid-concentration calibration standard, that is, approximately every 10 test samples and at the end of the analytical run, with an acceptance control limit of 80–120% of the ICAL concentration. If QC criteria were not met, the instrument was recalibrated, and any affected samples were reanalyzed. Additional QC samples included duplicates of test samples (one duplicate per analytical run; acceptance criteria: relative percent difference (RPD) <20%) and analysis of blanks (PB, laboratory blank [LB], and laboratory solvent blank [LSB]).

Prior to testing, an initial laboratory proficiency evaluation was performed by both analytical laboratories. Accuracy and precision were determined by analysis of multiple measurements of control spike solutions at concentrations corresponding to 100% and 10% of chemical amount applied to test materials (n = 3 to 5 for each concentration level; single analytical run).

Two sets of control spike samples were generated by spiking the same amount of chemical solution (200 µL) as used during the decontamination testing directly into the extraction solvent. All control spikes were sonicated for 10 minutes and then diluted as needed per Section 3.6.3 for one set and with an additional ten-fold dilution to create a 10% level control spike as the second set. Each control spike set was accompanied by one solvent blank sample (1 mL of *n*-hexane used for extraction and preparation of samples for analysis). These control spike experiments were used as independent verifications of the results obtained from the outside chemical analysis laboratory. The laboratory proficiency results are listed in Table 3-14.

Table 3-14. Laboratory Proficiency Results

Target Chemical	Laboratory	Spike Control A	Spike Control B	Solvent Blank
		100% Target Concentration, No Coupon [*] ; n=3 to 5	10% Target Concentration, No Coupon [*] ; n=3 to 5	
		Accuracy and precision		
Malathion (initial)	EMSL	95 ± 2.5%; RSD = 3%	80 ± 3.1% SD; RSD = 4%	<LOQ
Malathion (ongoing ^{**})	EMSL	88 ± 12%; RSD = 13%	Not prepared	<LOQ
2-CEPS (initial)	EMSL	72 ± 2.9%; RSD = 4%	63% ± 1.4% SD; RSD = 4%	<LOQ
2-CEPS (ongoing ^{**})	EMSL	95 ± 25%; RSD = 26%	Not prepared	<LOQ
Malathion (initial)	OSL	102 ± 8.3% SD; RSD = 8.1 %	86 ± 6.2%; RSD = 7.2 %	<LOQ
Malathion (ongoing ^{**})	OSL	103 ± 11%; RSD = 10 %	Not prepared	<LOQ
2-CEPS (initial)	OSL	112% ± 8.2% SD; RSD = 7.3%	94 ± 3.7%; RSD = 4.0 %	<LOQ
2-CEPS (ongoing ^{**})	OSL	116 ± 10%; RSD = 8.4%	Not prepared	<LOQ

* direct spike into hexane; ** results for QC samples prepared for core-matrix decontamination tests

The acceptance criteria for laboratory proficiency tests were 80 – 120% for accuracy (as recovery) and < 30% RSD precision for each concentration level. Malathion analytical results were within QC criteria (both at 100% and 10% target concentration) for the initial performance evaluation for both laboratories and above lower acceptance criteria for continuing QC checks during decontamination tests (both laboratories). These results are in line with EPA method 8270D multilaboratory performance for analysis of semivolatile organic compounds by GC/MS at a test concentration similar to 100% target concentration tested, i.e., 100 µg/mL (Method 8270D Table 6 Multilaboratory Performance Data [18]).

Although the 2-CEPS results (Table 3-14) from the initial evaluation (EMSL) did not meet the accuracy target, the laboratory performance was considered satisfactory based on high repeatability of the

analytical measurement and good results of analysis of control samples prepared by the subcontracting laboratory (accuracy for LCS/LCSD at mid-point concentration was 95% and 96% of true value, respectively; RSD <1%; data not shown); the follow-on analyses of continuing QC checks of CS samples prepared along with 2-CEPS decontamination samples from this study have shown both high accuracy and precision of analytical measurement by both laboratories.

3.7. Data Reduction Procedures

3.7.1. Chemical concentration in extract calculations

The GC/MS concentration results ($\mu\text{g/mL}$) were converted to total mass of chemical per sample (mg per sample) by multiplying by the extraction solvent volume and dilution factor (if applicable):

$$M_s = C_s \times V_E \times D_F \times 1000$$

where:

M_s : mass of chemical in sample (mg)

C_s : concentration ($\mu\text{g/mL}$) from an individual replicate sample

V_E : extraction solvent volume (mL)

D_F : sample dilution factor prior to analysis (if any)

The percent recovery of chemical from QC samples (e.g., control spikes) was calculated against theoretical chemical amount spiked into solution:

$$\%R_{QC} = C_{QC} / (V_{SP} \times S_C / V_T / D_F) \times 100\%$$

where:

$\%R_{QC}$: percent recovery for an individual QC sample (versus theoretical)

C_{QC} : concentration ($\mu\text{g/mL}$) from an individual replicate QC sample

V_{SP} : volume of spike (mL)

S_C : concentration of chemical in spiking solution (500 mg/mL or 50 mg/mL)

V_T : total sample volume (mL)

D_F : sample dilution factor prior to analysis (if any)

The sample concentration (M_s) results used for decontamination efficacy calculations (as described in Section 3.5.2.) were not adjusted for QC sample recovery ($\%R_{QC}$).

3.7.2. Decontamination cleanup efficacy calculations

The decontamination cleanup efficacy was calculated using the mean of chemical mass recovered from the replicate test coupons (TCs) and the mean chemical mass recovered from the associated set of positive control (PC) coupons.

$$DE = (1 - \bar{x}TC_n / \bar{x}PC_n) * 100$$

where:

DE – mean decontamination efficacy (%)

$\bar{x}TC_n$ – mean of chemical amount remaining on replicate TC (decontaminated) coupons (mg)

$\bar{x}PC_n$ – mean of chemical amount remaining on replicate PC (nondecontaminated) coupons (mg)

The mean decontamination efficacy along with the standard deviation was a cumulative decontamination efficacy (or resulting from application of all three procedural steps for each test). The standard deviation of the efficacy was calculated by propagation of error using the standard deviation of the average mass of agent remaining on the test coupons and on the positive control coupons. If the average mass of remaining agent on the test coupon was found to be below the LOQ, the efficacy was calculated using the LOQ value and reported as “greater than” this calculated value.

4. Results

4.1. Surface Decontamination Tests

4.1.1. Nongrimed coupons

Residual malathion and 2-CEPS surface contamination on different materials before and after treatment with the multi-step decontamination procedure is shown in Figure 4-1 for nongrimed surfaces. Test-specific results including overall decontamination efficacy (DE) are given in Table 4-1.

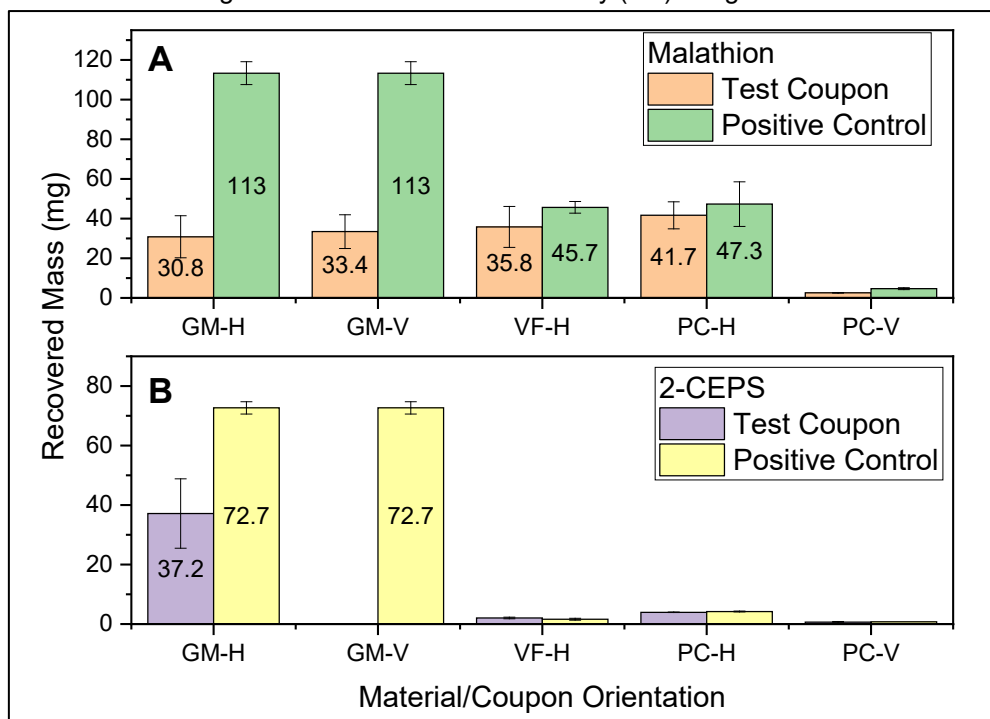


Figure 4-1. Recovered mass of (A) malathion and (B) 2-CEPS from test coupons and positive controls on nongrimed surfaces: GM-H, VF-H, PC-H: galvanized metal, vinyl tile, and painted concrete paver (tested in horizontal orientation); GM-V, PC-V: galvanized metal, and painted concrete block (tested in vertical orientation).

For malathion, the theoretical mass spiked was 100 mg per coupon (Section 3.4). Recoveries for positive controls (not decontaminated coupons) exceeded the minimum requirement of 70% recovery for galvanized metal only. After a 120-min contact time between malathion and vinyl and painted concrete, a significant amount of malathion appears to permeate into the vinyl/paint layer. This permeation may have been enhanced using ethanol in the application of malathion. The surface wipe sampling does not efficiently collect malathion that has permeated into these sublayers, leading to lower recoveries. The same observation can be made for 2-CEPS, namely, only the surface wipe sampling of galvanized metal resulted in high (>70%) recoveries. As for malathion, the theoretical 2-CEPS mass spiked was 100 mg per coupon (Section 3.4). Recoveries for positive controls from vinyl and painted concrete are even lower than observed for malathion.

Table 4-1. Material- and -Orientation-Specific Decontamination Test Results of Nongrimed Materials for Malathion and 2-CEPS

Material-Type	Material Orientation	ID	Decontaminated Coupons			Positive Controls			Procedural Blank	Decontamination Efficacy, DE	
			Mean	±SD	RSD	Mean	±SD	RSD			
			mg/coupon			mg/coupon			mg/coupon	%	SD
Malathion											
Galvanized metal	Horizontal	1M	31	11	34%	113	5.8	5.1%	<0.05	73	25
Galvanized metal	Vertical	2M	33	8.5	25%	113	5.8	5.1%	<0.05	70	18
Vinyl flooring	Horizontal	3M	36	10	29%	46	2.9	6.4%	<0.05	22	6.4
Sealed concrete [paver]	Horizontal	4M	42	6.8	16%	47	11	24%	<0.05	12	3.4
Sealed concrete [cinder block]	Vertical	5M	2.6	0.18	7%	4.7	0.46	10%	<0.05	45	5.4
2-CEPS											
Galvanized metal	Horizontal	1C	37	12	31%	73	2.1	2.9%	<0.05	49	15
Galvanized metal	Vertical	2C	<0.05 (UJ-)	NA	NA	73	2.1	2.9%	<0.05	>99.9 (J+)*	2.9
Vinyl flooring	Horizontal	3C	2.1	0.25	12%	1.6	0.33	20%	<0.05	no decon	NA
Sealed concrete [paver]	Horizontal	4C	4.0	0.07	2%	4.2	0.13	3%	<0.05	6.3	0.2
Sealed concrete [concrete block]	Horizontal	5C	0.63	0.21	33%	0.75	0.0	0%	<0.05	16	5.2

(UJ-) samples were reported at <LOQ

(J+) results likely overestimated problems during weathering of chemical prior to decontamination; runoff of chemical solution droplets observed on vertical TC coupons

Legend:

Statistically significant reduction of chemical surface loading for decontaminated versus nondecontaminated coupons ($p < 0.05$; Student's *t*-test)

The most effective decontamination for both chemicals was observed on the nonporous galvanized metal surfaces (Table 4-1). Figure 4-2 shows an example of a galvanized metal coupon contaminated with 2-CEPS after application of the Step 1 water-detergent rinse, with a distinct (oily droplet) contamination pattern of 2-CEPS still visible.

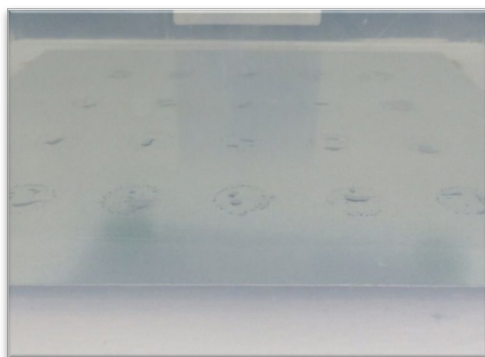


Figure 4-2. Galvanized metal coupon contaminated with 2-CEPS after application of the Step 1 water-detergent rinse.

The material orientation was not a statistically significant factor in the decontamination (at confidence level of 95%; Student's t-test) of malathion-contaminated galvanized metal (no grime present). For painted concrete, efficacy values for the vertical orientation were higher than for the horizontally positioned painted concrete. However, recoveries from painted surfaces were poor (both for horizontal and vertical orientation painted concrete), leading to some ambiguity of the efficacy value.

For 2-CEPS, the vertically positioned galvanized metal had surface DE >99.9% compared to an average of 49% DE for galvanized metal tested in horizontal position, possibly due to the characteristic of 2-CEPS post-weathering that appears as oily small droplets on galvanized metal material surface (Figure 4-3), as opposed to completely dried-out malathion (Figure 3-3 in Section 3.2). After turning the coupon to the vertical orientation, a partial runoff of spiking solution/chemical contamination was observed (Figure 4-3), leading to a larger localized contaminated area at lower localized surface concentrations.

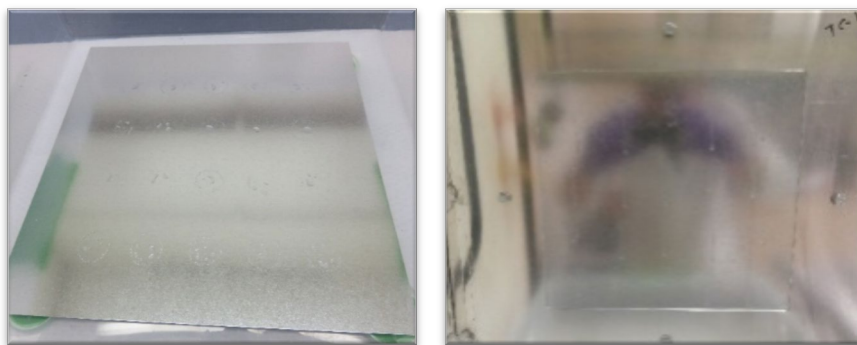


Figure 4-3. 2-CEPS droplets on horizontal coupons and runoff of chemical contamination after turning galvanized metal in vertical orientation (30 minutes post-spiking).

The distribution of discrete droplets into a chemical film could have been more prone to chemical reaction during decontamination. Analytical data and decontamination efficacy results for tests in which the residual agent was below the limit of quantification are flagged as appropriate in Table 4-1.

For semi-porous and porous materials, the maximum DE was $45 \pm 5.4\%$, observed for the malathion test on the painted concrete block (Table 4-1). For tests using materials other than nongalvanized metal, the computed DE was $<16\%$, and differences between the chemical loading before- and post-decontamination were not statistically significant (at the 95% confidence level; Student's t-test), most likely due to inherent permeability of vinyl and painted concrete materials causing migration of chemicals [spiked as ethanol solutions] into deeper layers of those materials. Such a migration could deter both decontamination and surface (wipe-based) sampling effectiveness. A recent study [9] suggests that CWAs permeate into painted/sealed porous materials at significant rates, e.g., sulfur mustard (HD) can quickly migrate through latex semigloss paints, with less than 20% of initial concentration detected by wipe-based surface sampling within 3 hours after spiking, and 70% confirmed to be retained in the paint layer and another 10% retained in the underlying porous material simulant, SPE disk. Authors have also suggested that different types of paint layer and/or underlying porous material can serve as a potential chemical reservoir, creating potential for diffusive transport of chemicals back to the surface. This observation is in line with the lower surface recovery of target chemicals observed in this study for positive controls of vinyl and painted concrete materials (as compared to galvanized metal). A similar study was recently performed for malathion [19], with surface concentration of neat chemical reduced by approximately 20% after 3 hours (post spiking), due to transfer to paint and underlying porous material simulant. It is then plausible that a small fraction of chemicals, especially 2-CEPS, was potentially inaccessible to decontamination on vinyl and painted/sealed concrete coupons, due to into-the-material transfer (“in-transfer”).

4.1.2. Grimed coupons

Decontamination testing of grimed materials was limited to galvanized metal only. Figure 4.4 shows the recovered amounts of malathion (A) and 2-CEPS (B) after the three-step decontamination process.

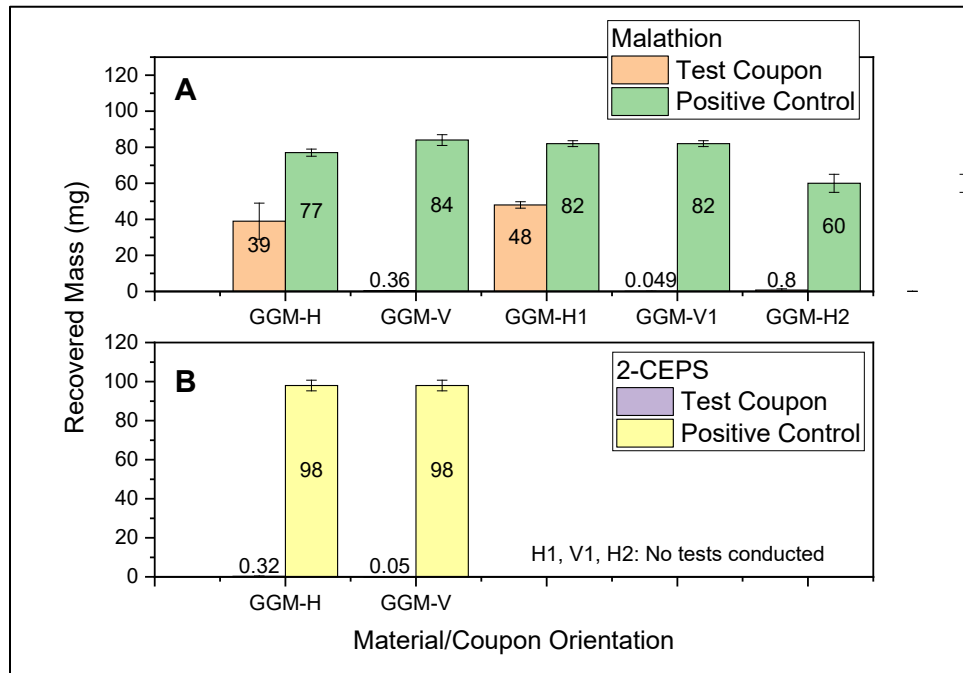


Figure 4-4. Recovered mass of (A) malathion and (B) 2-CEPS from test coupons and positive controls on grimed surfaces: GGM-H, H1, H2: galvanized metal (tested in horizontal orientation); GGM-V: galvanized metal (tested in vertical orientation).

Test-specific results including overall DE are provided in Table 4-2. For malathion, the decontamination tests included two modifications to the decontamination procedure. The first modification was to use the decontaminant solution DF200 as the first “pre-rinse” step instead of the detergent and water solution. The second modification was an approach to collect liquid waste residing on the horizontal surface by skimming of the excessive liquid from the surface as described in Section 3.5.3. Recoveries from grimed positive controls were, in general, high (>70% of the theoretical 100 mg applied) for malathion. Note that one set of positive controls was shared for both horizontal and vertical test conditions for the first modified testing and appears therefore twice in Figure 4-4. Recoveries from positive controls were not expected to have been different based on orientation of the nonporous galvanized metal coupon. The recovery for the positive control associated with the second decontamination procedure modification was only 60%. No evidence was found for any deviation from normal procedures that would explain this lower recovery.

Table 4-2. Material- and Orientation- Specific Decontamination Test Results of Grimed Materials for Malathion and 2-CEPS

Material- Type	Material Orientation	ID	Decon method	Decontaminated Coupons			Positive Controls			Procedural Blank	Decontaminatio n Efficacy, DE	
				Mean	±SD	RSD	Mean	SD	RSD			
				mg/coupon			mg/coupon			mg/coupon	%	SD
Malathion												
Grimed galvanized metal	Horizontal	6M	UM	39	10	26%	77	2.0	2.6%	<0.05	50	13
Grimed galvanized metal	Vertical	7M	UM	0.36 (J)	0.15	36%	84	3.0	3.6%	<0.05	>99.5	0.4
Grimed galvanized metal	Horizontal	8M	Mod1	48	1.8	3.7%	82	1.6	2.0	<0.05	41	1.7
Grimed galvanized metal	Vertical	9M	Mod1	0.049 (J)	0.0012	2.1%				<0.05	>99.94	0.002
Grimed galvanized metal	Horizontal	10M	Mod2	0.80 (J)	0.66	8.3%	60	5.0	8.3	<0.05	>98.7	1.1
Grimed galvanized metal	Horizontal	11M	Mod2A	0.085 (J)	0.074	85%				<0.05	>99.2	0.007
2-CEPS												
Grimed galvanized metal	Horizontal	6C	UM	0.32	0.076	24%	98	2.7	2.7%	<0.05	99.7	0.078
Grimed galvanized metal	Vertical	7C	UM	<0.05	NA	NA				<0.05	>99.94	NA

UM
–

unmodified method, Mod1- modified method 1; Mod2 – modified method 2; Mod2A – modified method 2A

(J) estimated results reported below LOQ

Legend:

Statistically significant reduction of chemical surface loading for decontaminated versus nondecontaminated coupons ($p < 0.05$; Student's t-test)

The calculated DE for malathion from the grimed galvanized metal appeared to be strongly dependent on the orientation of the coupon. Whereas minimal malathion was found on the vertically positioned coupon after the three-step decontamination procedure, a significant amount (39 mg) was found in the wipe of the horizontal surface. One significant difference is that the vertically oriented surface had minimal liquid remaining on the surface when wiped due to the gravitational pull on the liquid. The horizontal coupons still had a significant amount of liquid on the surface, which became part of the wipe sample. Hence, residual malathion that is dissolved in the liquid on the surface is included in the recovered amount of malathion from a horizontal surface. The pre-rinse step of the coupon in the vertical position also reduced the chemical loading somewhat based on the presence of malathion in the liquid waste of this first step (approximately 8% of applied amount; see Section 4.2).

The modification in the three-step procedure to replace the detergent-water solution with the actual decontaminant DF200 did not make a significant difference in overall decontamination efficacy; recoveries in the horizontal orientation remained moderately high leading (39 mg recovered when using a detergent-water pre-rinse vs 48 mg when using a DF2000 pre-rinse). With the galvanized metal in the vertical position, residual malathion on the vertical coupon was significantly less and just slightly above or at the limit of quantification for malathion. The second modification (Tests 10M and 11M) to the three-step decontamination procedure which included a skimming of the liquid from the surface prior to wipe sampling did make a significant change in the amounts recovered from the horizontally oriented test coupons. In these two tests, the residual malathion was significantly lower and similar to the low amounts (less than 1 mg) recovered from vertical coupons. This result can be explained by the introduced physical removal of excessive liquid on the surface prior to the wipe sampling. Indeed, a significant amount of malathion was detected in the liquid waste as discussed in detail in Section 4.2.

DEs for 2-CEPS from the grimed galvanized metal were greater than 99.7% for both horizontal and vertical orientations (Table 4-2), which is noticeably different from what was observed for malathion. Spiking of the 2-CEPS in ethanol solution leaves a visible pattern leading to an enlarged area of actual contamination in comparison to the initial discrete droplets. No runoff of 2-CEPS solution was observed from the grimed PCs, suggesting that the grime coating may act like a sink for the surface-delivered liquid spike (Figure 4-5).

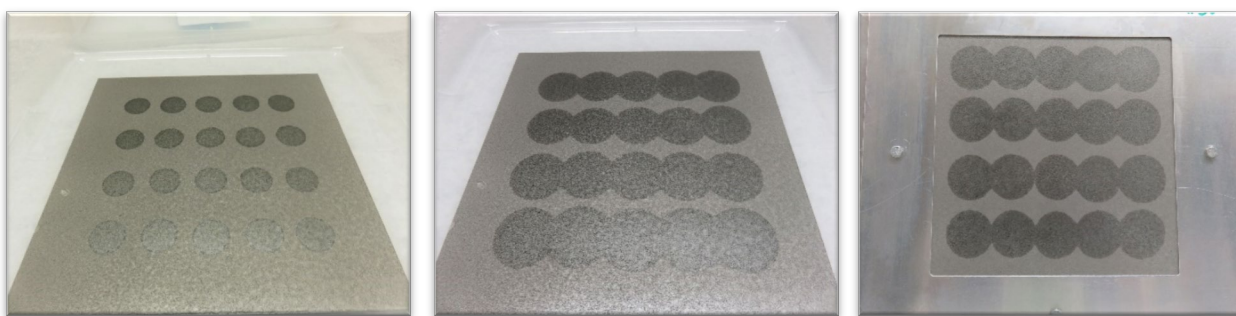


Figure 4-5. 2-CEPS spiking pattern on grimed galvanized coupons immediately after spiking, after weathering and readied for the vertical orientation testing.

4.2. Transfer to Liquid Waste – Vertical Coupons

The overall effectiveness of a decontamination approach is a measure of its ability to remove the target chemical from material surfaces (i.e., represented by coupons in this study; decontamination results are discussed in Section 4.1), while taking into account residual chemical that might be transferred to liquid

and sometimes solid waste fractions. Such waste streams necessitate additional remediation and disposal strategies. Those strategies were not studied in this work. Instead, this study provides initial estimates of the transfer of the contaminant/chemical to liquid waste as collected for materials where runoffs are present due to their orientation.

Composite samples of the liquid waste (or runoff) of the three replicate test coupons were collected during each step of the decontamination procedure. The results expressed as the average (n=3) mass of the contaminant recovered and as in the actual concentration of the liquid waste are shown in Figure 4-6 and Figure 4-7 for malathion and 2-CEPS, respectively, and summarized in Table 4-3.

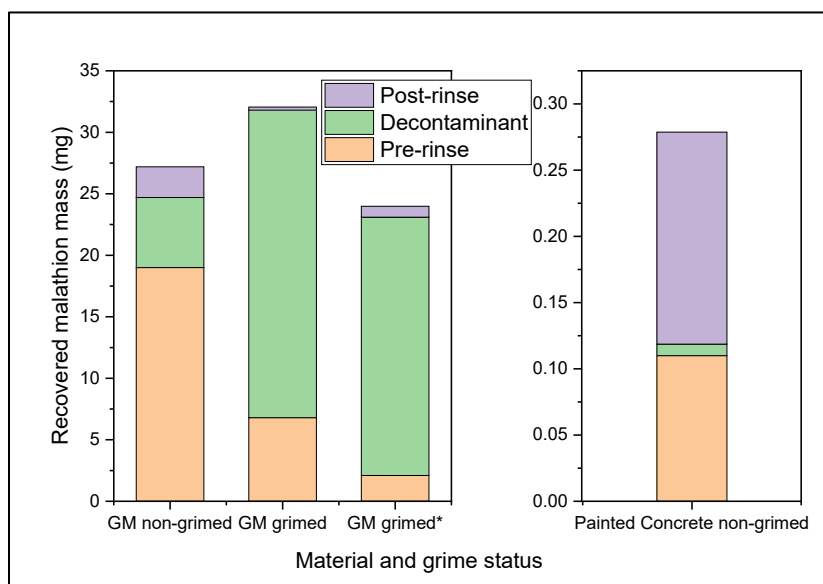


Figure 4-6. Transfer of malathion contamination from galvanized metal (GM) in vertical position to different types of liquid waste from decontamination process. Grime* refers to the use of DF200 in the pre-rinse step.

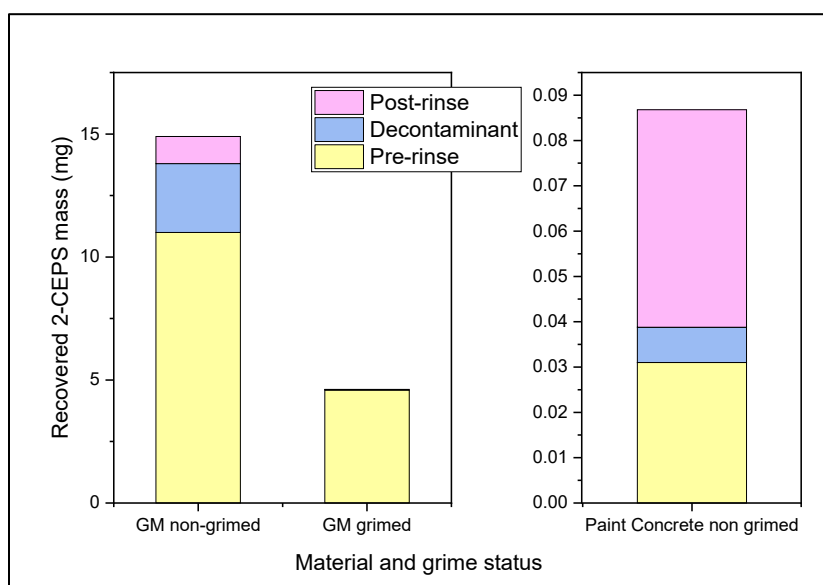


Figure 4-7. Transfer of 2-CEPS contamination from galvanized metal (GM) in vertical position to different types of liquid waste from decontamination process.

Table 4-3. Recovered Mass and Concentration of Malathion and 2-CEPS in Liquid Waste from Decontamination Procedures

Material	Material orientation	ID	Type of waste	Recovered mass in runoff (mg/coupon)*	Concentration in waste [g/L]*
	Malathion				
Galvanized metal	Vertical	2M	Pre-rinse detergent-water runoff (Step 1)	19	2.1
			Decontaminant runoff (Step 2)	5.7	0.86
			Post-decon water rinse runoff (Step 3)	2.5	0.19
Painted concrete block	Vertical	4M	Pre-rinse detergent-water runoff (Step 1)	0.11	0.016
			Decontaminant runoff (Step 2)	0.0087	0.0013
			Post-decon water rinse runoff (Step 3)	0.16	0.024
Galvanized metal	Vertical and grimed	7M	Pre-rinse detergent-water runoff (Step 1)	6.8	0.59
			Decontaminant runoff (Step 2)	25	2.48
			Post-decon water rinse runoff (Step 3)	0.25	0.023
Galvanized metal	Vertical and grimed	9M	Pre-rinse DF200 runoff (Step 1)	2.1	0.25
			Decontaminant runoff (Step 2)	21	1.9
			Post-decon water rinse runoff (Step 3)	0.89	0.084
	2-CEPS				
Galvanized metal	Vertical	2C	Pre-rinse detergent-water runoff (Step 1)	11	1.1
			Decontaminant runoff (Step 2)	2.8	0.56
			Post-decon water rinse runoff (Step 3)	1.1	0.097
Painted concrete block	Vertical	4C	Pre-rinse detergent-water runoff (Step 1)	0.031	0.0044
			Decontaminant runoff (Step 2)	0.0078	0.0039
			Post-decon water rinse runoff (Step 3)	0.048	0.0063
Galvanized metal	Vertical and grimed	7C	Pre-rinse detergent-water runoff (Step 1)	4.6	0.49
			Decontaminant runoff (Step 2)	0.0055	0.00083
			Post-decon water rinse runoff (Step 3)	0.015	0.0023

*composite sample of waste runoffs collected from three test coupons.

The average amount of malathion and 2-CEPS transferred from nongrimed galvanized metal in a vertical orientation was estimated at 27 and 15 mg per coupon, respectively (Figure 4-6 and 4-7), corresponding to 24% and 21% of the initial chemical loading of the coupon (using the average PC recovered amount of 113 and 73 mg for malathion and 2-CEPS, respectively [Table 1]). For the grimed coupons, a total of 32 mg of malathion was recovered in the liquid waste (38% of applied amount based on

positive control recovery) while for 2-CEPS, 4.6 mg was recovered (5% of applied amount based on positive control recovery). The largest mass transfer of malathion from the galvanized metal material was in the Step 1 detergent-water waste followed by Step 2 decontaminant runoff and Step 3 post-decontamination water rinse, implying that the actual contamination at the start of the decontamination step was noticeably lower. For the grimed coupons contaminated with malathion, the largest amount recovered was for Step 2 followed by Step 1 and Step 3. For the grimed material, it is plausible that the initial detergent and water rinse did not remove an appreciable amount of grime with malathion from the surface while the DF200 runoff (Step 2) contained significant amounts of malathion (25 mg or 30%). Similarly, most of the 2-CEPS was recovered in the Step 1 liquid waste followed by Step 2 and Step 3. For 2-CEPS, this order did not change when assessing the liquid waste from the grimed material with Step 1 holding more 2-CEPS than Step 2 or 3.

The average amount of chemical transferred to liquid waste from the decontamination process for the more permeable painted concrete block tested in the vertical orientation was a fraction ($\leq 1\%$) of the chemical mass that transferred into liquid waste from the nonpermeable galvanized metal as estimated at 0.28 mg (malathion) and 0.087 mg (2-CEPS) per coupon (Figures 4-6 and 4-7), corresponding to 6% and 12% of the recovered chemical loading of the coupon (using the average PC recovered amount of 4.7 mg and 0.75 mg for malathion and 2-CEPS, respectively, as a reference). Considering that the spiked malathion and 2-CEPS amounts were 100 mg per coupon, these liquid waste amounts add up to less than 0.3% of the spiked amount. As discussed previously in Section 4.1.1, both malathion and 2-CEPS are either strongly bound or permeated into the paint layer leading to low recoveries in the pre-rinse liquid waste similar to the low recovery of the positive control wipe samples. The ratio of chemical mass transfer between liquid waste fractions was different when comparing painted concrete (permeable) against galvanized metal (nonpermeable) with the majority of malathion and 2-CEPS found in Step 3 water rinse followed by Step 1 pre-rinse waste. The amount of chemicals corresponding to the decontaminant application step (Step 2) was less than 5% of total chemical mass transferred to liquid waste from each coupon.

The malathion and 2-CEPS concentrations that were detected in the liquid waste fractions in this study (Table 4-3) are up to three orders of magnitude higher than hazardous waste control limits (HWCL) for HD- and VX- containing liquid waste derived from the chemical agent toxicity and exposure values for workers with possible occasional exposure at hazardous waste facilities (0.7 mg/L and 0.08 mg/L, respectively) [20]. If 2-CEPS and malathion were to simulate HD and VX, respectively, the generated liquid wastes in this study would require further treatment. The reaction of chemical agents in the liquid waste was not addressed in this study. See Section 4.3.1 for an assessment of the liquid waste concentration one day after the decontamination when the waste was created.

4.3. Transfer to Liquid Waste – Horizontal Coupons

4.3.1 Direct extraction

Liquid waste from horizontal grimed galvanized material was collected via physical removal using a squeegee (Section 3.5.3) as a composite sample of replicate test coupons and collected for each step of the decontamination procedure. The results expressed as the average ($n=3$) mass of the contaminant recovered per coupon and as in the actual concentration of the liquid waste are shown in Figure 4-8 and summarized in Table 4-4.

Figure 4-8. Transfer of malathion contamination from galvanized metal (GM) in horizontal position to different types of liquid waste by physical removal from decontamination process. Grime* refers to the modified method that uses DF200 in the pre-rinse step.

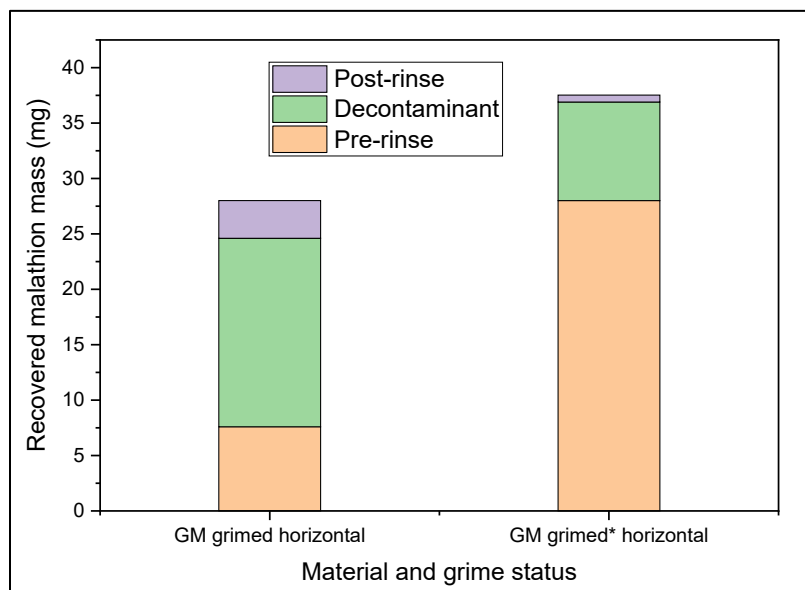


Table 4-4. Recovered Mass and Concentration of Target Chemicals in Liquid Waste from Decontamination Procedures for Horizontal Grimed Galvanized Metal

Material	Material Orientation	ID	Type of waste	Recovered mass in runoff (mg/coupon)*	Concentration in waste [g/L]*
Malathion					
Galvanized metal	Horizontal	10M	Pre-rinse detergent-water runoff (Step 1)	7.6	0.79
			Decontaminant runoff (Step 2)	17	1.5
			Post-decon water rinse runoff (Step 3)	3.4	0.24
Galvanized metal	Horizontal	11M	Pre-rinse DF200 runoff (Step 1)	28	2.6
			Decontaminant runoff (Step 2)	8.9	0.94
			Post-decon water rinse runoff (Step 3)	0.62	0.049

*composite sample of waste runoffs collected from three test coupons.

The average amount of malathion that was physically removed from the horizontal galvanized metal coupon was estimated at 28 mg when Step1 was a detergent and water rinse while 38 mg of malathion was physically removed when Step1 was a DF200 application (Figure 4-8). This result corresponds to 46% and 62% of the initial chemical loading of the coupon (using the average PC recovered amount of 60 mg for malathion [Table 1]). These recovered amounts are like those measured in the runoff from the vertically placed grimed galvanized metal coupons (32 mg for test with detergent and water as pre-rinse and 25 mg for test with DF200 as the first pre-rinse step). The presence of the unreacted malathion in the liquid on the horizontal coupon is also like the amount that was recovered on the coupon via wiping (39 mg, see Table 4-2), suggesting that a large fraction of the residual malathion as collected via wipe sampling of the grimed surface in the presence of the remaining liquids is found in the liquid and would not be an indication of

unreacted malathion remaining on the coupon surface itself. This hypothesis is supported by the minimal amount recovered on the horizontal surface (0.80 mg) when most of the liquid has been physically removed from the surface. Hence, reported efficacy values for horizontal surfaces based on surface wipe samples that contain all remaining pre-rinse, decontaminant, and post-rinse liquids are biased low.

4.3.1. Delayed extraction

A split sample of the generated combined liquid waste was extracted (and hereby the reactivity halted) for Test ID 10M and 11M (Table 4-4) after 24 h. Based on collected volumes for each of the three steps, the malathion concentration in the liquid waste immediately after the decontamination was calculated to be 0.81 and 1.1 g/L for Tests 10M and 11M, respectively. The malathion concentrations recovered after 24 h were reduced to 0.0028 and 0.0013 g/L, respectively, accounting for a more than 99% reduction in malathion concentration due to the presence of residual decontaminant in the combined liquid waste. A further degradation may occur after 24 h but was not investigated. This high reduction shows that the waste stream is reactive and may become less hazardous over time.

5. Quality Assurance/Quality Control

5.1. Test Equipment Calibration

All equipment was verified as calibrated at the time of use. Calibration of instruments was done at the frequency shown in Table 5-1. In case of any deficiencies, instruments were adjusted to meet calibration tolerances and/or were recalibrated prior to testing.

Table 5-1. Instrument Calibration Frequency

Equipment	Calibration/Certification	Expected Tolerance
Thermometer	Compare to independent NIST thermometer (a thermometer that is recertified annually by either NIST or an ISO-17025 facility) value once per quarter.	$\pm 1^{\circ}\text{C}$
Stopwatch	Compare to official U.S. time @ time.gov every 30 days.	± 1 min/30 days
Micropipettes	Certified as calibrated at time of use. Recalibrated by gravimetric evaluation of performance to manufacturer's specifications every year.	$\pm 5\%$
Scale	Compare reading to Class S weights every day.	$\pm 1\%$
pH meter	Two-point calibration using NIST-traceable buffer solutions immediately prior to testing.	± 0.1 pH units
Graduated cylinder	Certified by manufacturer at the time of use (class A cylinder)	± 1 mL

NIST = National Institute of Standards and Technology; ISO = International Organization for Standardization

5.2. Data Quality Results for Critical Measurements

The following measurements were deemed critical to accomplishing a part of or all the project objectives:

- Initial and post-decontamination surface concentrations of malathion and 2-CEPS, both in the surface wipe samples and in liquid waste extracts as determined by GC/MS.
- Contact time and dwell times.
- Hydrogen peroxide concentration and pH of DF200 decontamination solution prior to each test.
- Volume of decontaminant (DF200) and rinse water applied.
- Mass of liquid waste (pre- and post-decontamination water rinse and decontaminant runoffs).
- Volume of extraction solvent.

The data quality indicators (DQIs) for the test measurements are provided in Table 5-2. The limited number of results/tests that were not within acceptance criteria as determined in the project QAPP were not indicative of any systematic error introduced into the experimental results and do not change the general findings of this study. The lower surface delivery rate of DF200 was due to significant foaming but this foaming allowed for complete coverage of test areas. Test coupons were still wet after 60 minutes of contact time. The excess decontaminant was removed with dry wipes prior to surface sampling with solvent (wipe samples were extracted as a composite sample).

Table 5-2. Acceptance Criteria for Critical Measurements

Critical Measurement	Target Value and Acceptance criteria	Results
Contact/weathering time	30 ± 1 min	All contact times (CTs) within 30 ± 1 min from spiking
Dwell/rinse and decontamination interaction time	30 – 60 min ± 5 min	All dwell times (DTs) within 30 - 60 min ± 5 min from application of rinse/decontaminant
Delivery of target surface concentration of chemical*	80 -120% of target	The mean spike controls for decontamination tests were 88 ± 12 % for malathion and 95 ± 25% for 2-CEPS
Recovery of chemical from positive control coupon	60 to 140% with less than a 30 % coefficient of variation for identical test set	Recovery of malathion and 2-CEPS from ungrimed galvanized metal PC was 78 ± 2% and 71 ± 2%. For grimed galvanized metal PC was 81 ± 3.1% and 98 ± 2.7%. Coefficients of variation were ≤5% between replicates (both chemicals)**
Recovery of chemical from positive test coupon	30 % coefficient of variation for identical test set	5 out of 18 tests had >30 % coefficient of variation for TCs resulting from identical test set** <i>Test specific results in Tables 4-1 and 4-2.</i>
Procedural blank	< 5 % of the analyte amount recovered from the positive control.	All PB samples within acceptance criteria
Solvent blank	<LOQ	All solvent blanks reported <LOQ
Decontaminant volume applied	20 mL ± 20 % of target	Average volumes*** for Step 1: 15.7 - 19.2 mL Step 2: 8.2 - 14.3 mL Step 3: 19.2 - 21.9 mL Volumes listed are for unmodified method <i>Test specific results in Tables B-2 through B-4 in Appendix B</i>
H ₂ O ₂ concentration of DF200****	Pass (Go)	All finished blend batches passed Go/No Go test prior to testing <i>Test specific results in Table B-1 in Appendix B</i>
pH of DF200****	9.6 – 9.9	All finished blend batches were within target pH range prior to testing <i>Test specific results in Table B-1 in Appendix B</i>

* As determined by analysis of control spikes; criteria for recovery of chemical from surface.

** Optimized method used for decontamination testing.

*** Volumes that were delivered on the surface as determined by gravimetric measurements of test boxes before and after application; lower delivery rates for DF200 were due to foaming but allowed complete coverage of test areas.

**** For finished blend/product.

6. Summary

After comparing the decontamination efficiencies of the multistep decontamination procedure method deployed onto several building materials, the data indicate the following:

(a) The tested pre-rinse - decontaminant - post-rinse three step procedure has shown potential for decontamination of nonporous materials tested in horizontal and vertical orientation and in the presence of grime; decontamination efficacy against malathion (organophosphate pesticide and simulant for VX nerve agent) and 2-CEPS (simulant for sulfur mustard (HD) CWA) varied from $49 \pm 14\%$ to more than 99.9% depending on the chemical, orientation, and presence of grime. Lower efficacy values for materials in a horizontal position can be partially attributed to the potential presence of a significant amount of nonreacted chemical that can be readily skimmed/physically removed from the surface (and collected as liquid waste) prior to the surface wipe sample to determine the full cleanup efficacy.

(b) A reduced surface decontamination efficiency was observed for semi-porous and porous building materials, with maximum DE of $32 \pm 14\%$, for which a fast (within 120 min) chemical permeation into test material was observed. A possible degradation reaction mechanism of the chemical with the paint layer cannot be excluded. However previous efforts with HD [9], even though with a different coating, has indicated a more complete mass balance that suggest that permeation is more prevalent mechanism for forming a reservoir that resists decontamination.

(c) Added surface grime reduced the average DEs for malathion from galvanized metal tested in horizontal orientation to approximately 50%. However, an addition of mechanical removal of the processed rinse or decontamination liquid rendered the final surface concentration of malathion to below LOQ.

(c) The procedure generated liquid wastes that were significantly contaminated with the applied chemicals [g/L range]. The combined liquid waste contains enough decontaminant runoff to expect a further degradation of the chemical in the waste.

The main finding of this study is that spray-based decontamination methods with no mechanical removal of residual liquid from the surface step combined with a relatively short processing time of decontaminant (dwell times of one hour) shows minimal potential for decontamination of permeable materials contaminated with CWA [simulants]. However, when combined with a mechanical removal technique, the overall efficacy shows promise for some surface materials.

These results indicate that further studies are needed for optimization of decontamination procedures for decontamination of chemical agents absorbed into permeable building materials, including modification of decontamination solution, longer processing times, and/or addition of various mechanical treatment/cleaning steps (e.g. wiping or scrubbing). In addition to relatively poor surface decontamination efficacy, especially for porous materials, the tested methods yielded highly contaminated (liquid) waste materials. The treatment methods for contaminated wastes were not addressed in the present study.

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Appendices

Appendix A: Grime Application Procedure

The multistep grime application procedure that was used in this study is detailed below. The procedure was optimized for grime application onto a 10 in × 10 in coupon.

Step 1 – Set up the sprayer

- ☐ Verify the house air supply is off.
- ☐ Connect the air hose to the screw fitting on the sprayer handle and hand-tighten. Turn on house air and check the air pressure and the hose connection for leaks. The air pressure is read on the regulator gauge and should be 20 psi. If the pressure is not 20 psi, use the black knob on the regulator to adjust the pressure to 20 psi. If the hose connection is leaking, turn the house air off, retighten the connection hose connection and recheck.
- ☐ When there are no leaks and the air pressure is set, turn the house air off and bleed the air pressure by pulling spray trigger. Verify the line pressure is zero on the regulator gauge.

Step 2 – Prepare the grime and ethanol solution

- ☐ Weigh out four grams of standard grime and add to a 400-mL beaker.
- ☐ Add 84 mL of ethanol to the 400-mL beaker. Add a magnetic stir bar, cover the beaker with aluminum foil and slowly stir the grime solution on a stir plate until the grime is in suspension.

Step 3 – Prepare three test coupons for spray application of grime suspension

- ☐ Cover hood floor with clean white paper. Tape the paper down to avoid movement during the application process.
- ☐ Pre-weigh three clean test coupons using the designated laboratory balance (Sartorius BL1500 Basic Lite Portable Balance [P/N # BL1500 Sartorius AG, Göttingen, Germany]).
- ☐ Place three pre-weighed test coupons touching side by side in the bottom of the chemical fume hood.

Step 4 – Spray application of grime to test coupons

- ☐ Add 84 mL grime/ethanol suspension to reservoir of the spray gun. Remove the gray reservoir cap and pour in the standard grime/ethanol solution. Replace cap when finished with the grime/ethanol addition.
- ☐ Turn the house air on, prime the sprayer by spraying a few test sprays into a waste beaker.
- ☐ Set a timer for 45 seconds.
- ☐ Start time and then begin spraying the coupons in an “S” pattern. Start at the top left and move to the right covering all three coupons. When the end of the third coupon is reached, move the sprayer down the coupon surface and go from right to left slightly overlapping the previous pass. Continue this pattern until the bottom edges of the three coupons are reached. Then, work from the bottom to top using the same pattern. Continue until 45 seconds has elapsed and stop spraying. Turn the house air off and pour remaining grime/ethanol back into the 400-mL beaker from step 2. Re-cover beaker with aluminum foil and stir until needed for the next application.
- ☐ Allow the ethanol to evaporate off the coupon surface (about 10 minutes).

- After the ethanol evaporates from the coupon surfaces, rotate the coupons 90 degrees and repeat the complete sequence of Step 4 until all test coupons are covered with standard grime.
- After the ethanol evaporates, weigh each coupon and calculate mass of grime delivered onto each coupon. Each test coupon should contain $1 \pm 0.2\text{g}$ of grime applied.

Appendix B: Experimental parameters

Table B-1. Characterization of DF200 Decontamination Solution

Preparation Date	Decontamination Test	Go/No Go Test Results [Pass or Fail]	pH of Solution [pH units]	Temperature of Solution [°C]
3/1/2017	Malathion on galvanized metal horizontal/vertical	pass	9.78	21.6
3/6/2017	Malathion on vinyl flooring	pass	9.79	24.9
3/8/2017	Malathion on sealed concrete [paver and block]	pass	9.87	23.7
3/2/2017	2-CEPS on galvanized metal horizontal/vertical	pass	9.77	22.3
3/6/2017	2-CEPS on vinyl flooring	pass	9.79	24.9
3/9/2017	2-CEPS on sealed concrete [paver and block]	pass	9.75	22.7
8/20/2018	Malathion and 2-CEPS on grimed galvanized metal horizontal	pass	9.67	22.9
8/23/2018	Malathion on grimed galvanized metal vertical	pass	9.68	22.8
8/28/2018	2-CEPS grimed galvanized metal vertical	pass	9.68	23.3
9/26/2018	Malathion on grimed galvanized metal horizontal	pass	9.76	22.7
9/26/2018	Malathion on grimed galvanized metal vertical	pass	9.65	23.2
12/6/2018	Malathion on grimed galvanized metal horizontal	pass	9.73	22.8
12/6/2018	Malathion on grimed galvanized metal horizontal	pass	9.77	23.1

Table B-2. Characterization of Pre-decontamination Detergent-water Rinse Solution Application

Test Date	Decontamination Test	Detergent-water Spray Mass* [g ± SD]	Detergent-water Spray Volume [mL ± SD]
3/1/2017	Malathion on galvanized metal horizontal	18.7±2.4	18.7±2.4
3/1/2017	Malathion on galvanized metal vertical	15.8±1.9	15.7±1.9
3/6/2017	Malathion on vinyl flooring	16.3±0.8	16.3±0.8
3/8/2017	Malathion on sealed concrete [paver] horizontal	18.3±0.8	18.3±0.8
3/8/2017	Malathion on sealed concrete block vertical	16.4±0.9	16.4±0.9
8/20/2018	Malathion on grimed galvanized metal horizontal	20.7±1.0	20.7±1.0
8/23/2018	Malathion on grimed galvanized metal vertical	19.9±0.3	19.9±0.3
12/6/2018	Malathion on grimed galvanized metal horizontal squeegee	18.7±0.6	18.7±0.6
3/2/2017	2-CEPS on galvanized metal horizontal	19.2±0.5	19.2±0.5
3/2/2017	2-CEPS on galvanized metal vertical	19.0±2.1	18.9±2.0
3/6/2017	2-CEPS on vinyl flooring	18.2±0.1	18.2±0.1
3/9/2017	2-CEPS on sealed concrete [paver] horizontal	16.2±0.3	16.2±0.3
3/9/2017	2-CEPS on sealed concrete block vertical	17.9±0.8	17.9±0.8
8/20/2018	2-CEPS on grimed galvanized metal horizontal	19.8±0.2	19.8±0.2
8/24/2018	2-CEPS on grimed galvanized metal vertical	20.0±0.3	20.0±0.3

*calculated based on cumulative specific gravity $d=1.0006$ g/mL

Table B-3. Characterization of DF200 Decontamination Solution Application

Test Date	Decontamination Test	DF200 Spray Mass* [g] Average $\pm$ SD (n=3)	DF200 Spray Volume [mL] (n=3)
3/1/2017	Malathion on galvanized metal horizontal	14.9 $\pm$ 1.8	12.6 $\pm$ 1.5
3/1/2017	Malathion on galvanized metal vertical	14.1 $\pm$ 0.1	11.9 $\pm$ 0.1
3/6/2017	Malathion on vinyl flooring	16.8 $\pm$ 1.4	14.3 $\pm$ 1.2
3/8/2017	Malathion on sealed concrete [paver] horizontal	13.7 $\pm$ 2.3	11.6 $\pm$ 2.0
3/8/2017	Malathion on sealed concrete block vertical	14.4 $\pm$ 0.5	12.2 $\pm$ 0.4
8/20/2018	Malathion on grimed galvanized metal horizontal	20.2 $\pm$ 0.6	17.1 $\pm$ 0.5
8/23/2018	Malathion on grimed galvanized metal vertical	20.3 $\pm$ 0.2	17.2 $\pm$ 0.2
9/26/2018	Malathion on grimed galvanized metal horizontal 1 st application	19.1 $\pm$ 2.1	16.2 $\pm$ 1.8
9/26/2018	Malathion on grimed galvanized metal horizontal 2 nd application	19.5 $\pm$ 0.7	16.5 $\pm$ 0.6
9/26/2018	Malathion on grimed galvanized metal vertical 1 st application	20.4 $\pm$ 0.7	17.3 $\pm$ 0.6
9/26/2018	Malathion on grimed galvanized metal vertical 2 nd application	20.0 $\pm$ 1.0	16.9 $\pm$ 0.9
12/6/2018	Malathion on grimed galvanized metal squeegee	18.7 $\pm$ 1.1	16.7 $\pm$ 0.9
12/6/2018	Malathion on grimed galvanized metal horizontal 1 st application squeegee	19.7 $\pm$ 1.2	16.7 $\pm$ 1.0
12/6/2018	Malathion on grimed galvanized metal horizontal 2 nd application squeegee	19.5 $\pm$ 0.6	16.5 $\pm$ 0.5
3/2/2017	2-CEPS on galvanized metal horizontal	11.3 $\pm$ 3.8	9.5 $\pm$ 3.2
3/2/2017	2-CEPS on galvanized metal vertical	13.1 $\pm$ 1.1	11.0 $\pm$ 0.9
3/6/2017	2-CEPS on vinyl flooring	9.7 $\pm$ 0.70	8.2 $\pm$ 0.60
3/9/2017	2-CEPS on sealed concrete [paver] horizontal	15.2 $\pm$ 1.4	12.9 $\pm$ 1.2
3/9/2017	2-CEPS on sealed concrete block vertical	11.5 $\pm$ 1.8	9.8 $\pm$ 1.5
8/20/2018	2-CEPS on grimed galvanized metal horizontal	21.0 $\pm$ 0.8	17.8 $\pm$ 0.7
8/24/2018	2-CEPS on grimed galvanized metal vertical	20.0 $\pm$ 0.5	16.9 $\pm$ 0.4

*based on cumulative specific gravity $d=1.18$ g/mL

Table B-4. Characterization of Post-decontamination Water Rinse Application

Test Date	Decontamination test	Detergent-water spray mass* [g] (n=3)	Detergent-water spray volume [mL] (n=3)
3/1/2017	Malathion on galvanized metal horizontal	19.2±1.1	19.2±1.1
3/1/2017	Malathion on galvanized metal vertical	20.6±0.20	20.6±0.20
3/6/2017	Malathion on vinyl flooring	21.1±0.11	21.1±0.11
3/8/2017	Malathion on sealed concrete [paver] horizontal	21.4±0.10	21.4±0.10
3/8/2017	Malathion on sealed concrete block vertical	20.9±0.10	20.9±0.10
8/20/2018	Malathion on grimed galvanized metal horizontal	20.4±0.2	20.5±0.2
8/23/2018	Malathion on grimed galvanized metal vertical	20.5±0.5	20.6±0.5
9/26/2018	Malathion on grimed galvanized metal horizontal	20.1±0.9	20.2±0.9
9/26/2018	Malathion on grimed galvanized metal vertical	20.8±0.9	20.8±0.9
12/26/2018	Malathion on grimed galvanized metal horizontal squeegee	19.5±0.5	19.5±0.5
12/26/2018	Malathion on grimed galvanized metal horizontal squeegee	19.3±0.7	19.4±0.7
3/2/2017	2-CEPS on galvanized metal horizontal	20.3±0.40	20.3±0.40
3/2/2017	2-CEPS on galvanized metal vertical	21.1±0.10	21.1±0.10
3/6/2017	2-CEPS on vinyl flooring	21.9±1.5	21.9±1.5
3/9/2017	2-CEPS on sealed concrete [paver] horizontal	20.3±1.2	20.3±1.2
3/9/2017	2-CEPS on sealed concrete block vertical	20.8±0.70	20.9±0.70
8/20/2018	2-CEPS on grimed galvanized metal horizontal	19.9±0.6	20.0±0.6
8/24/2018	2-ECPS on grimed galvanized metal vertical	20.4±0.2	20.4±0.2

*calculated based on specific gravity at 22°C d=0.998 g/mL

Appendix C: Wipe sampling procedure

The details on the wipe sampling procedure below are for a 10 in × 10 in material coupon. This multistep sampling procedure is summarized below:

1. Prepare sampling wipes:
 - Don disposable nitrile gloves.
 - Using forceps, remove one clean wipe from the storage container and place it on a clean Petri dish.
 - Pipette 3 mL of wetting solvent (IPA, hexane, acetone etc.) onto the center of the wipe, cover the dish, and allow the solvent to disperse into the wipe material.
 - Proceed to wipe sampling immediately.
2. Don a fresh pair of nitrile gloves.
3. Grasp the wetted decontamination wipe with one hand and use the other hand to gently fold the wipe (Figure C-1). Do not squeeze the wipe to avoid loss of the wetting solvent.

Note: Photographs show hexane-based wipe sampling; for acetone sampling used in the optimized method in this study, latex gloves were worn over nitrile gloves.

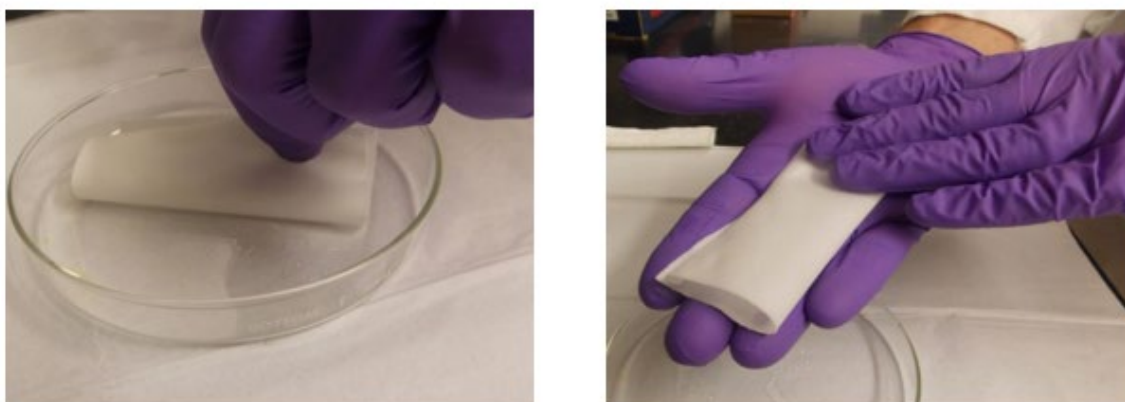


Figure C-1. Folding wipe for sampling the first wiping pathway (horizontal).

4. Starting in the top left corner, wipe the surface horizontally, working downward, to completely cover the surface. The horizontal wipe sampling pathway is shown in Figure C-2.

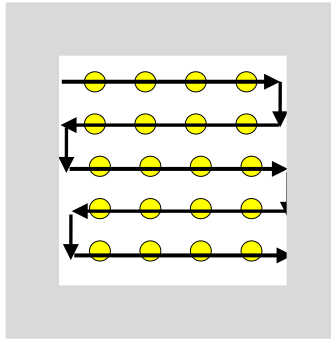


Figure C-2. Horizontal wiping pathway.

5. Using both hands, gently refold the wipe so that that the surface used for the horizontal wipe sampling is now on the inside (Figure C-3).

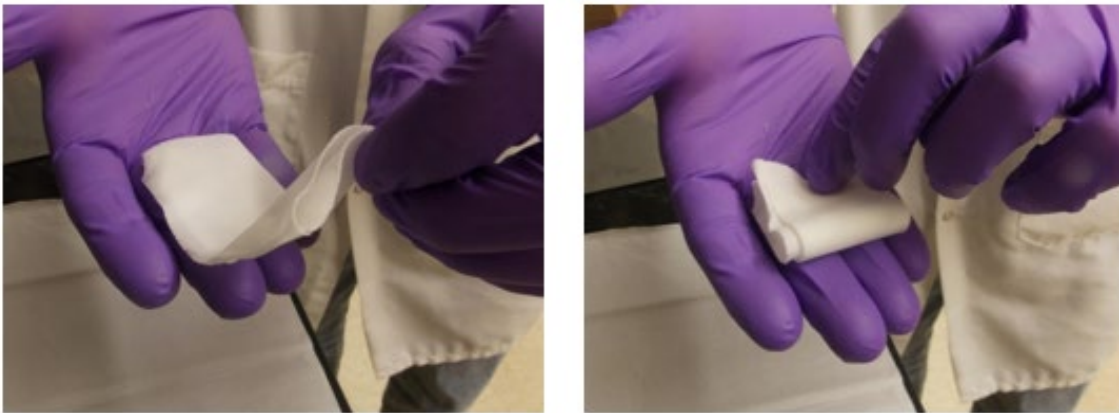


Figure C-3. Folding wipe for sampling the second wiping pathway (vertical).

6. Starting in the bottom left corner, wipe the surface vertically, working toward the right, to completely cover the surface. The vertical wipe sampling pathway is shown in Figure C-4.

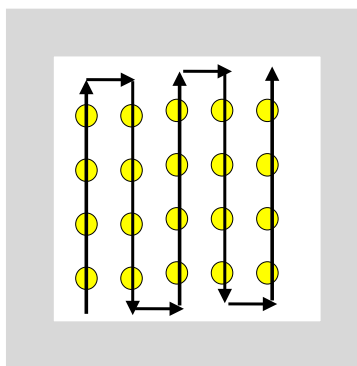


Figure C-4. Vertical wiping pathway.

7. Using both hands, gently refold the wipe diagonally, so that that surface used for the vertical wipe sampling is now on the inside (Figure C-5).

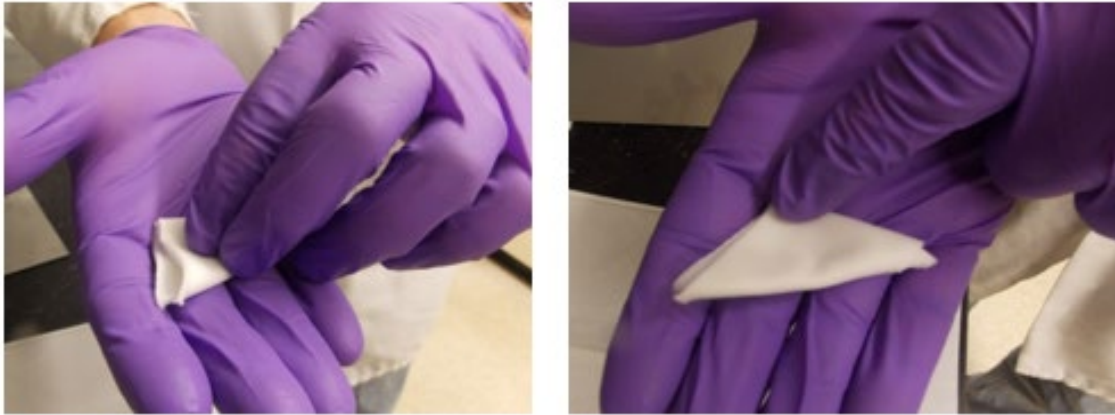


Figure C-5. Folding wipe for sampling the third wiping pathway (diagonal).

8. Starting in the top left corner, wipe the surface diagonally, working toward the bottom right corner, to completely cover the surface. The diagonal wipe sampling pathway is shown in Figure C-6.

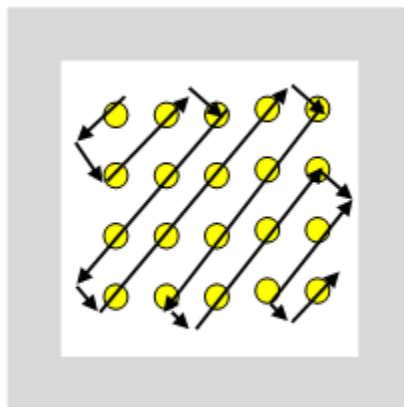


Figure C-6. Diagonal wiping pathway.

9. Using both hands, gently refold the wipe so that that surface used for the diagonal wipe sampling is now on the inside (Figure C-7).

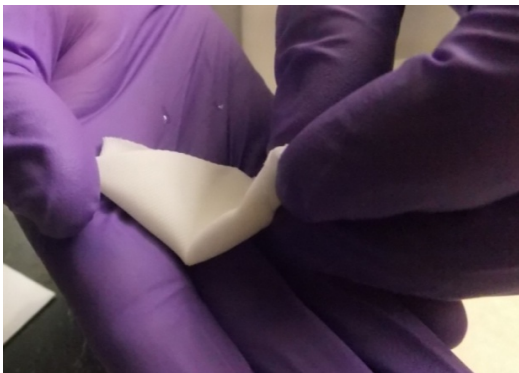


Figure C-7. Folding wipe for sampling the fourth pathway (perimeter).

10. Starting in any corner, wipe the perimeter of the coupon. The perimeter wipe sampling pathway is shown in Figure C-8.

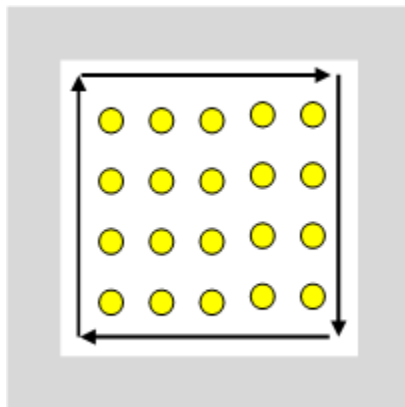


Figure C-8. Perimeter wiping pathway.



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