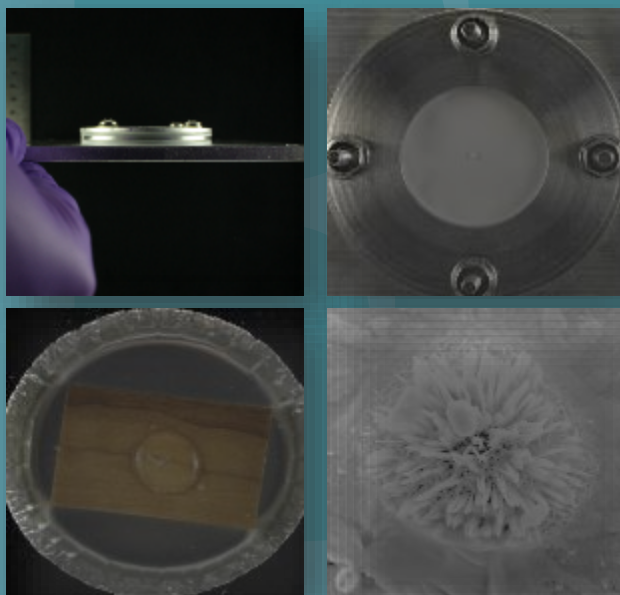


Improving Surface Decontamination Methods for Permeable Materials Contaminated with Chemical Warfare Agent Surrogates Malathion and 2-CEPS



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Improving Surface Decontamination Methods for Permeable Materials Contaminated with Chemical Warfare Agent Surrogates Malathion and 2-CEPS

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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 addresses options to improve on the decontamination of permeable materials that are contaminated with a toxic chemical that has transferred into such material. Here, two surrogates of chemical warfare agents are considered to investigate the degree of transport, material interaction and subsequent efforts to degrade the chemical via *in situ* degradation.

Gregory Sayles, Ph.D., Director

Center for Environmental Solutions and Emergency Response

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Acronyms and Abbreviations

"	inch(es)
2-CEPS	2-chloroethyl phenyl sulfide
AS	acrylic solid surface countertop (material)
ASTM	ASTM International (formerly The American Society for Testing and Materials)
ATH	alumina trihydrate
BMC	bulk material coupon
°C	degree(s) Celsius
CAS	Chemical Abstract Services
CESER	Center for Environmental Solutions and Emergency Response
CGB	concentrated germicidal bleach
cm ²	square centimeter(s)
cm ³	cubic centimeter(s)
CS	control spike
CSL	chemical safety level
COTS	commercial off-the-shelf
CT	contact time (chemical)
CWA	chemical warfare agent
DE	decontamination efficacy
DI	deionized (-water)
DQI	data quality indicator
DT	dwell time (decontaminant)
DUP	duplicate(s)
ED	EasyDECON DF200
EIDC	environmental indoor dissipation chamber
EPA	U.S. Environmental Protection Agency
FAC	free available chlorine
FESEM	field emission scanning electron microscopy
FSP	free standing paint
FSS	free standing sealant
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
h	hour(s)
HD	sulfur mustard
HPL	high-pressure decorative laminate (material)
HPLC	high-performance liquid chromatography
HSMMD	Homeland Security and Materials Management Division
HSRP	Homeland Security Research Program
g	gram(s)
ICAL	instrument calibration

ID	Identification
IPA	2-propanol (isopropanol, isopropyl alcohol)
IS	internal standard
ISO	International Organization for Standardization
L	liter(s)
LB	laboratory blank(s)
LOQ	limit of quantification
LVAP	low volatility agent permeation (apparatus)
μL	microliter(s)
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
MPC	(chemical-) mass positive control
MTC	(chemical-) mass test coupon
NA	not applicable
ng	nanogram(s)
NIST	National Institute of Standards and Technology
NT	not tested
ORD	Office of Research and Development (EPA)
OSL	Organic Support Laboratory (EPA)
PB	procedural blank(s)
PC	positive control
PMMA	polymethyl methacrylate
PTFE	polytetrafluoroethylene
ppm	part(s) per million
PSS	painted stainless steel
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
PI	principal investigator
R ²	coefficient of determination
RH	relative humidity
RSD	relative standard deviation
RTP	Research Triangle Park
SD	standard deviation
SEM	scanning electron microscope/microscopy
SLB	Splash-Less Bleach
S/N	signal-to-noise
SPE	solid-phase extraction

SS	stainless steel
SSS	sealed stainless steel
TC	test coupon
TIC	toxic industrial chemical
UBA	universal blade applicator
VCP	vinyl composition plank (material)
VOC	volatile organic compound
VX	S-{2-[di(propan-2-yl)amino]ethyl} O-ethyl methylphosphonothioate

Acknowledgments

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

This effort was directed by the principal investigator (PI) from the Office of Research and Development's (ORD's) Center for Environmental Solutions and Emergency Response (CESER), with support from project team members. The contributions of the following individuals have been a valued asset throughout this effort.

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Executive Summary

The U.S. Environmental Protection Agency's (EPA's) Homeland Security Research Program (HSRP) conducts research necessary for the identification of methods and technologies that can be used during hazardous materials remediation and cleanup efforts. The available processes to recover buildings and structures that have been contaminated with chemical warfare agents (CWAs) or other toxic chemicals of concern have primarily focused on the remediation of nonporous materials. Most *in situ* chemical decontamination technologies use aqueous oxidizers (e.g., bleach, liquid hydrogen peroxide), which typically yield high degradation efficacies for nonporous materials. Many surfaces in the built environment are, however, (semi)porous or permeable to the contaminants. Aqueous decontamination procedures generally have limited efficacy if the contaminant (partially) migrates into a permeable surface or farther into an underlying porous sublayer. This work determined the degree of transport/permeation of two CWA surrogates, the organophosphate pesticide 2-[dimethoxyphosphorothioyl)sulfanyl]butanedioate (malathion) and 2-chloroethyl phenyl sulfide (2-CEPS), into painted or sealed materials and into three permeable building materials that are representative of common indoor flooring, walls, and other surfaces. This determination was followed by decontamination approaches using commercially available off-the-shelf bleach formulations (Clorox Concentrated Germicidal Bleach, and Clorox Splash-Less Bleach with surfactants) and an activated hydrogen peroxide-based commercial decontaminant (EasyDECON DF200). Selected material-chemical-decontaminant test conditions were evaluated for structural changes and material-compatibility effects using field emission scanning electron microscopy (FESEM).

Transport of Malathion and 2-CEPS into Paint and Sealant Layers

Results of the permeation studies showed that the permeation rates were chemical- and surface-material-specific, with lower permeation rates observed for malathion compared to 2-CEPS. After 72 hours, permeation was somewhat higher into an acrylic latex paint layer (30% and 95% for malathion and 2-CEPS, respectively) than for the polyurethane sealant layer (10% and 95% for malathion and 2-CEPS, respectively). Microdroplets of malathion remained visible on paint and sealant surfaces at the end of the permeation period (72 h). The higher permeation of malathion through paint layers in comparison to the sealant layer was attributed to evidence of some blistering of the paint layer observed during a visual inspection of malathion exposed paint layer. The malathion-induced structural changes of the paint layers were confirmed by microscopy analyses of the coatings. Additional FESEM analyses of coatings that were not exposed to a chemical indicated higher overall surface pore morphology of the paint layers, which suggest higher general pore morphology of acrylic-latex paint when compared to the tested polyurethane sealant.

The lower recovery of 2-CEPS on the surface of the layers corresponded to findings of visual assessment of 2-CEPS exposed layers, with no chemical contamination droplet noticeable on tested paint or sealant surfaces at 72 h after spiking onto the surface. In addition to different permeation rates, 2-CEPS had a lower overall recovery with less than 25% of the initial chemical surface loading detected in the combined surface and paint/sealant layer after 72 h. This lower recovery of 2-CEPS can be attributed to the higher volatility of 2-CEPS versus malathion leading to significant evaporation. The corresponding average recovery of malathion was higher than 90% for both types of coatings.

Transport of Malathion and 2-CEPS into Bulk Materials

All three bulk materials tested (acrylic countertop, high-pressure laminate, and vinyl composition floor plank) were permeable to the targeted chemicals with different permeation rates for 2-CEPS versus malathion. At 72 h after spiking, 2-CEPS was detected primarily in the sublayer extractable fractions (via extraction of the material post surface swiping), with below level-of-quantitation (<LOQ) detection on the surface. Evaporation losses of 2-CEPS over a 72-h period resulted in less than 1% detected on the surface and in sublayers. Additional tests showed higher detection of 2-CEPS on the surface at a shorter contact time, with up to 99% of the total chemical mass detected present on the surface of bulk materials at 24 h after spiking. For corresponding malathion tests, approximately 76 to 85% of the total chemical mass detected was still present on the surface of these three materials after a 72-h contact time.

Decontamination of 2-CEPS and Malathion on Paint and Sealant Layers

Initial decontamination experiments performed using a single application of undiluted Clorox concentrated germicidal bleach (6.5% measured free available chlorine (FAC)) showed very good efficacy against 2-CEPS on both a paint and a sealant layer but only for malathion on the sealant layer. A single application of concentrated germicidal bleach formulation resulted in < LOQ concentrations of 2-CEPS in extractable sublayers and nondetectable levels on the surface, with an average cumulative decontamination efficacy (DE) of 96% and 97% for free-standing paint (FSP) layer and free-standing sealant (FSS) layer experiments, respectively. Corresponding average DEs for malathion were 54% and 99%. The results from these initial, baseline, and decontamination experiments suggested modifications to decontamination procedure were needed for improved degradation of malathion. Among different modified approaches tested, the procedure using two applications of concentrated germicidal bleach improved the malathion degradation on the FSP to approximately average 70% DE. Other decontaminants tested such as the Clorox Splash-Less Bleach (3.5% free available chlorine (FAC)) yielded lower efficacies in comparison to the single or double application of concentrated germicidal bleach (16% DE for single application; 45% DE for double application). An activated hydrogen peroxide solution (EasyDECON DF200) yielded lower efficacy: 10% versus 37% for a single or double application. Further, within the limits of this study, there is no clear evidence that any of the tested decontaminants (germicidal concentrated bleach, Splash-Less Bleach, and EasyDECON DF200) and decontamination approaches (single versus double application) degrades malathion that permeated into the FSP and farther into a porous material (represented here by a solid phase extraction (SPE) disk. All measured degradation of malathion is limited to malathion remaining on the surface. One-step concentrated germicidal bleach procedure was proven very effective for degradation of malathion from real-life building materials with average DE $\geq$ 97% reported for all bulk materials tested. No further decontamination optimization was conducted for these malathion-contaminated bulk materials.

The performance of all decontamination product-decontamination procedure combinations tested on the nonporous control material (stainless steel) was comparable for all methodologies tested, with average DEs ranging from 91% to $\geq$ 99% for malathion and average DE $\geq$ 99.9% for 2-CEPS. The comparison of degradation efficacies achieved for test materials and reference material suggests that the surface characteristics and type of chemical to be decontaminated should be considered important factors in the selection of oxidant-based decontamination strategies of toxic industrial chemicals and chemical warfare agents.

Impact

The research described in this report addresses many practical aspects of decontamination of toxic industrial chemicals absorbed into various permeable environmental matrices. The results contribute to a better understanding of how to remediate challenging types of permeable building materials. However, additional research is needed to determine the effects of the environmental factors (e.g., temperature, humidity, ventilation rates), material properties (e.g., porosity, chemical resistance), and physicochemical properties of target chemical and decontaminants (e.g., volatility, corrosivity, concentration) on the sublayer transport of both chemicals and decontaminants. Further, the adherence of a paint or sealant to a porous subsurface may change the amount of chemical that permeates when compared to the separate layers used in this study.

Analyses of possible post-decontamination chemical degradation products, including oxidation byproducts, were not performed in the current study, and should be considered in future work to ensure that procedures recommended for remediation do not result in the formation of toxic byproducts.

1.0 Introduction

Cleanup and remediation activities following a release of a toxic persistent chemical are likely to involve the *in situ* degradation of the chemical via oxidation or nucleophilic substitution. This situation especially holds true for more persistent chemicals that remain present on surfaces for days or longer. Most, if not all, of the efficacious decontamination technologies are water-based and can yield high efficacy if the contaminant is found on the surface. Finding the contaminant on the surface would be the case for a nonporous material [1-5]. As has been observed in the case of the decontamination of chemical warfare agents (CWAs) and other toxic industrial chemicals (TICs), including pesticides, the efficacy of a liquid decontaminant is material-dependent, which can be partially attributed to the permeability or porosity of the material [4,5]. The transport of a chemical into a permeable material makes it more challenging to decontaminate as a water-based decontaminant would likely not be able to reach the permeated chemical. This issue can be compounded if the chemical is transferred even farther into a porous material under a painted or coated surface film such in the case of a painted wall or sealed wooden floor. If chemical migration into this more porous sublayer occurs, the chemical of concern may remain present and eventually resurface after the decontamination has taken place, recreating the contaminated surface hazard. A recent study confirmed that the CWAs bis(2-chloroethyl) sulfide (sulfur mustard; HD) and to a lesser degree S-[2(di(propan-2-yl)amino)ethyl] O-ethyl methylphosphonothiolate (VX) can transport into a paint or sealant layer and even transfer farther into a porous substrate below the paint or sealant layer [6].

The physical and chemical parameters that determine the rate of permeation of a chemical into a permeable material are not well defined. The chemical nature (molecular vs ionic) is expected to be important as well as parameters such as polarity, viscosity, zeta potential, solubility in water or solvents, temperature, etc. Similarly, there is a wide variety in paints (oil, enamel, latex, or water-based) and sealants (polyurethane, water, and solvent-based). The identification of potential CWA surrogates would allow for research to be conducted outside surety agent facilities/programs which will increase the ability to study permeation processes in more detail. Very little is known about the partitioning of chemicals that are considered surrogates of CWAs into building materials and even less is known about the efficiency of standard decontamination techniques for permeated chemicals.

This research focused on the development and modification of decontamination approaches for the degradation of chemicals that have partially absorbed into permeable building materials. Information gathered from this research will aid in the development of the most appropriate field cleanup and decontamination procedures.

1.1 Project Objectives

The main objective of this research was to determine the performance of commercially available decontamination solutions for degradation of more persistent and/or stable chemicals present in a permeable material or in a porous sublayer of selected building materials. In general, it is nearly impossible to separate surface layer(s) - e.g., paint or sealant – from a porous material such as drywall, wood, or concrete without the use of solvents, reactive chemicals or by physical removal/separation methods that would alter the residual chemical amounts. Therefore, in this project, a compartmentalized structure of material layers (or permeation cell) was constructed to understand the transport of the target chemical as

deposited on the permeable surface, into the surface, and potentially into the underlying porous material. The subsequent phase of the research was the decontamination of the partially absorbed chemical.

The objectives of this project were:

- Develop testing equipment and analytical methods to study the transport of selected chemicals into the subsurface layers of permeable building materials at conditions mimicking indoor environmental conditions. Permeation cell tests were performed beside testing of associated control samples (coated and noncoated nonporous reference material, stainless steel).
- Determine the efficacy of decontamination technologies and procedures for degradation of chemicals that have (partially) absorbed into permeable building materials. This was to identify whether oxidation-based decontamination techniques, previously established for nonporous materials, were efficacious for degradation of the chemical compounds in this study without any procedural modifications. This process also established a so-called decontamination baseline.
- Evaluate possible modifications of decontamination solution/solutions to address potential limitations of traditional techniques/unmodified decontaminants; this evaluation was only performed if unmodified decontamination (as described above) did not provide the desired cleanup efficacy.

2.0 Experimental Approach

This study was performed in three consecutive phases. The first phase was a determination of the fate and transport of selected chemicals across a permeable layer into a porous subsurface. During this initial research, custom-made low volatility agent permeation (LVAP) cells (Section 3.4) were utilized to achieve controlled compartmentalization of a permeable surface layer consisting of free-standing paint (FSP) or free-standing sealant (FSS) (Section 3.2.3) and a porous subsurface represented by a solid phase extraction disk (SPE disk; Section 3.2.4). The use of this compartmentalized system permitted a distinct sampling of the top surface layer, extraction of the layer, and extraction of the porous media underneath leading to a full evaluation of the surface-specific permeation of chemicals. The transport of chemicals into selected (bulk) building materials was also investigated (Section 3.7). The second phase was testing of commercially available liquid decontaminants for (baseline) decontamination of permeated chemicals, followed in the third phase by testing of a modified decontaminant and/or modified approaches for improved degradation (Section 3.8). The general experimental scheme of testing is shown in Figure 2-1.

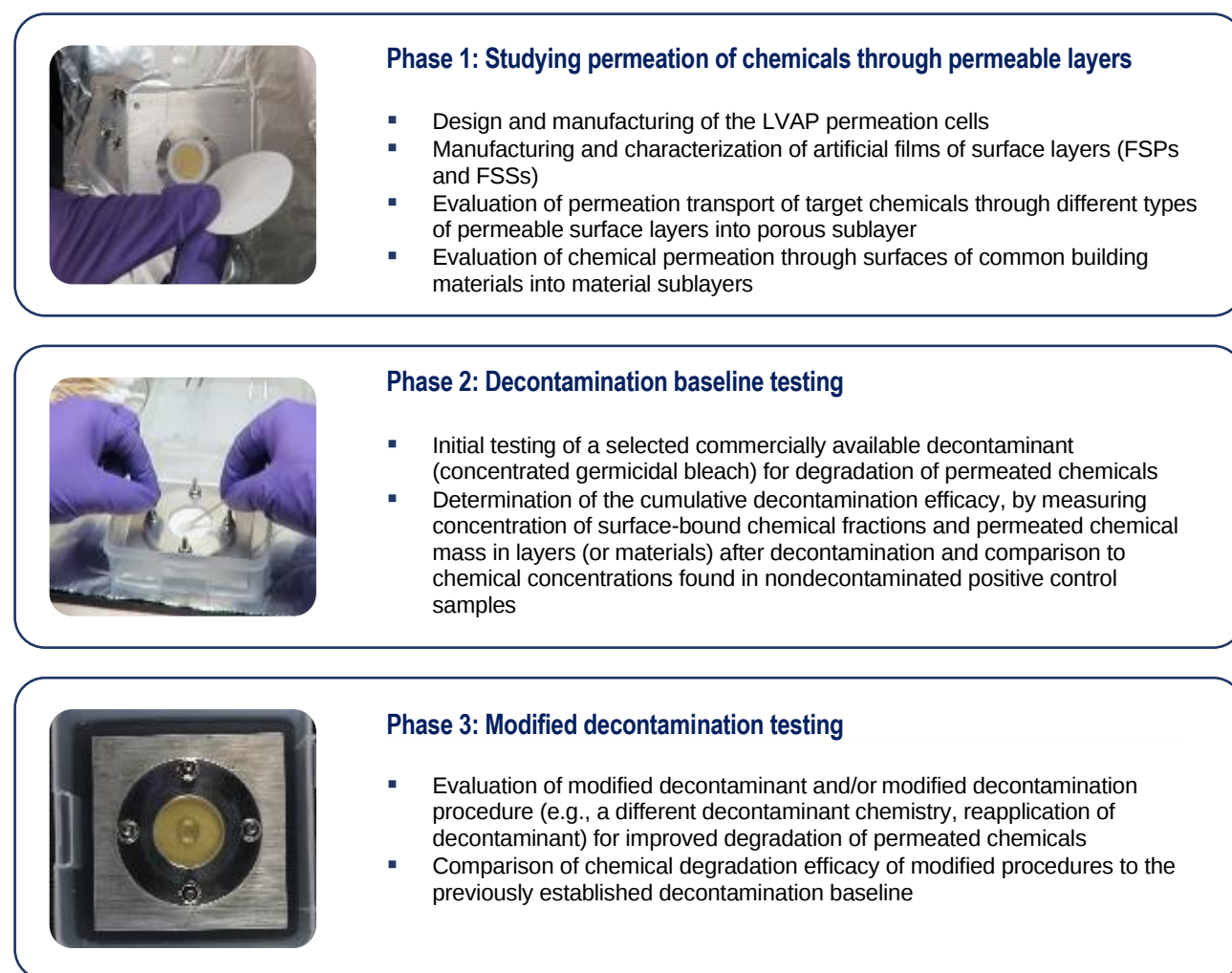


Figure 2-1. General experimental scheme of permeation transport and decontamination testing

3.0 Materials and Methods

3.1 Testing facilities

All experimental work was performed in U.S. EPA Office of Research and Development (ORD) Chemical Safety Level 4 (CSL-4) laboratories in Research Triangle Park (RTP), North Carolina (NC). The contamination and decontamination of coupon procedures, LVAP apparatus assembly/disassembly, sampling, extractions, and preparation of samples for analysis were performed within a chemical safety hood.

Curing of coupons and chemical weathering were performed in an environmental indoor dissipation chamber (EIDC) located in the chemical safety hood. The EIDC was a commercially available enclosure, (24 inches (") x 24" x 12" Indoor/Outdoor Steel Enclosures NEMA 1; Hammond Manufacturing, Guelph, ONT, Canada) made of powder-coated 16-gauge steel, with stainless-steel cover and a 1/4-turn coin-slot latch and concealed stainless-steel hinges. The enclosure was modified to include shelving constructed from perforated stainless-steel sheeting. The relative humidity (RH), temperature, and air exchange rate within the EIDC chamber were controlled and recorded, with target RH and temperature in the chamber set to 50% and 24°C, respectively, at one air exchange per hour. Compressed air was metered through mass flow controllers (Tylan Model FC260 Mass Flow Controller, Allen, TX, USA and Sierra Model 840 Mass Flow Controller, Sierra Instruments, Monterey, CA, USA) and routed via ¼" tubing in one of two ways to the chamber: If the RH sensor (HMD-53, Vaisala, Helsinki, Finland) indicated an RH increase above the setpoint, dry air was flowing directly to the chamber. If the RH dropped below the setpoint, the air was routed through an impinger containing deionized water, and humidified air was carried to the chamber.

All gas chromatography-mass spectrometry (GC/MS) analyses were performed by the U.S. EPA Organic Support Laboratory (OSL) located at the U.S. EPA facilities in RTP, NC. Microscopy analyses were performed using a Tescan Mira 3 Field Emission Scanning Electron Microscope (FESEM; Tescan Orsay Holding, A.S., Brno, Czech Republic).

3.2 Test materials

Several types of building materials and two types of coatings with expected different permeabilities were selected for the evaluation of permeation and decontamination procedures in this study. A zero-volatile organic compound (VOC), 100% acrylic latex paint interior flat paint (Table 3-1) was used to make the FSP coupons (Section 3.2.3 with manufacturing details in Appendix A-3.2). A water-based polyurethane sealant (Table 3-1) recommended by the manufacturer for the protection of wood and concrete floors was used to construct FSS coupons (Section 3.2.3 with manufacturing details in Appendix A-3.2). In addition, multipurpose stainless steel, a relatively smooth and nonpermeable material, was used as a reference and control material for sampling and recovery of target chemicals. The general specifications of all test materials are provided in Table 3-1. Procedures for preparation of test coupons are given in Sections 3.2.1 through 3.2.5.

Table 3-1. Specifications of building materials

Material (material ID)	Description	Manufacturer/ Supplier Name/Location/Country	Coupon Type and Dimensions, Length x Width x Thickness (mm)	Coupon Preparation
Stainless steel (SS)	Multipurpose stainless steel (1.2 x 1.2 m), type 304, #2B mill (unpolished), 0.091 cm thick	McMaster-Carr Douglasville, GA, USA	SS: 40 × 25 × 9.1	Section 3.2.1
Acrylic Paint (FSP or PSS) ^a	Behr Ultra-Pure White, interior flat paint, 100% acrylic latex paint, P/N 105001	Behr Companies Santa Ana, CA, USA	FSP: 50 × 0.076 PSS: 40 × 25 × 0.076	Section 3.2.3 Section 3.2.2
Polyurethane Sealant (FSS or SSS) ^a	Rust-oleum 6711 System Water-Based Polyurethane P/N 4MG61,	Grainger Chicago, IL, USA	FSS: 50 × 0.152 SSS: 40 × 25 × 0.152	Section 3.2.3 Section 3.2.2
Solid Phase Extraction Disk (SPE)	3M Empore SDB-XC SPE disk, 47 mm diameter, P/N 14-386-4	VWR Radnor, PA, USA	SPE: 36 (diameter) × 0.152	Section 3.2.4
Acrylic Solid Surface Countertop (AS)	Everform Solid Surface Countertop, River Rock Mosaic, P/N 656	Formica Cincinnati, OH, USA	40 × 25	Section 3.2.5
High-Pressure Decorative Laminate (HPL)	Amber Maple Matte Finish P/N 7012-58	Formica Cincinnati, OH, USA	40 × 25	Section 3.2.5
Vinyl Composition Plank (VCP)	Polyvinyl chloride (PVC) floor plank P/N 50SLV501	US Floors Dalton, GA, USA	40 × 25	Section 3.2.5
^a FSP and FSS are free layers of paint and sealant, respectively (Section 3.2.3), PSS and SSS are paint and sealant coatings on the stainless-steel substrate				

3.2.1 Stainless-steel Coupons

Stainless-steel (Table 3-1) coupons were cut from larger pieces of material by hydraulic shears to obtain a uniform length (4.0 centimeters (cm)) and width (2.5 cm). Stainless-steel coupons were cleaned with a laboratory-grade detergent solution to remove any lubricant/grease from shearing, then wiped clean with water and wiped dry using a Kimwipe (Kimberley-Clark, Inc., Irving, TX, USA; P/N 34133) to remove dust before use in the tests. A stainless-steel coupon ready for testing is shown in Figure 3-1a.

3.2.2 Painted or Sealed Stainless-steel Coupons

A zero-VOC 100% acrylic latex paint interior flat paint (Table 3-1) purchased from a national retailer (Home Depot, Reynoldsburg, OH, USA) was used for the preparation of painted stainless-steel (PSS) coupons. A polyurethane coating (Table 3-1) was used for the preparation of sealed stainless-steel (SSS) coupons. Paint or sealant was applied onto the 14" x 14" stainless-steel surface using a modified method derived from ASTM D823 "Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels" [7].

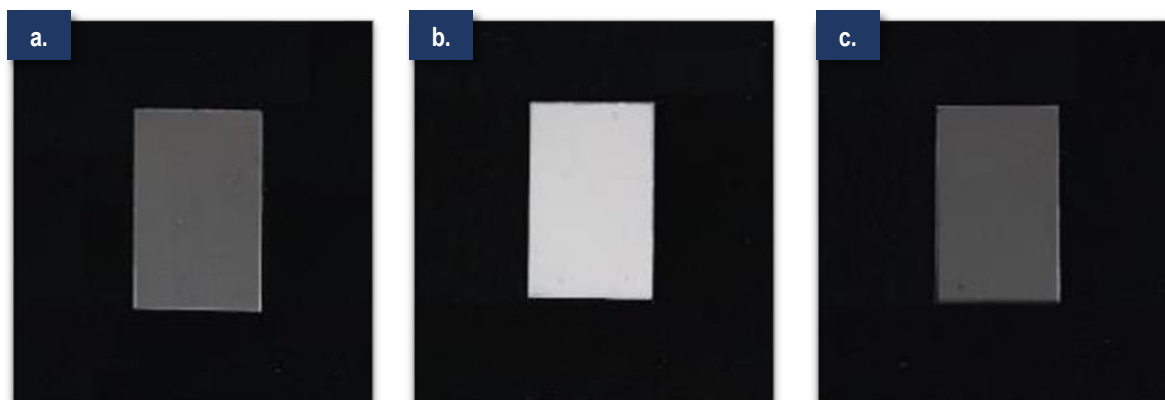


Figure 3-1. Stainless-steel (a), Painted-Stainless steel (b), and Sealed Stainless-steel (c) Coupons

In this study, the Universal Blade Applicator (UBA, AP-G08, Paul N. Gardner Company, Pompano Beach, FL, USA; Figure 3-2) was used for paint and sealant application.

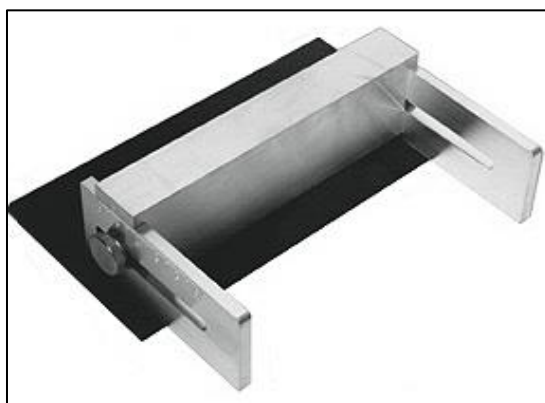


Figure 3-2. Universal Blade Applicator

The white paint was applied from the original container after mixing for 10 min (minutes) on a twin arm paint shaker. The transparent sealant was applied after gentle mixing with a paint stirrer. The target paint wet application thickness was 5 mils (0.127 mm), resulting in the dry paint film thickness of 3 mils (0.076 mm). The target sealant wet application thickness was 7 mils (0.178 mm), resulting in the dry sealant film thickness of 6 mils (0.152 mm). These thicknesses are representative of what can be found in the built environment. The procedure for the manufacture of uniformly coated stainless-steel coupons is summarized in Appendix A-1. The painted or sealed stainless-steel coupons were allowed to dry/cure for a minimum of 24 h (hours) at ambient environmental conditions prior to testing [8]. The fully cured painted or sealed stainless-steel sheets were cut with hydraulic shears into 4.0 cm × 2.5 cm coupons. The thickness of the film was measured with the Eddy current gauge (PosiTector 6000, DeFelsko Corporation, Ogdensburg, NY, USA) per ASTM E376 [9], on the center, bottom, and top of each coupon, with acceptance criteria of 70 to 130% of target thickness, and relative standard deviation (RSD) of <30% between triplicate measurements of each coupon. All coupon edges were cleaned with a laboratory-grade detergent solution to remove any

lubricant/grease from shearing, then wiped clean with water and wiped dry using a Kimwipe to remove dust before use in the tests.

The detailed procedure for manufacturing paint and sealant layers on stainless steel is summarized in Appendix A-1.1. Specifications of PSS and SSS layers are summarized in Table 3-2. Painted and sealed stainless-steel coupons ready for testing are shown in Figure 3-1b and c, respectively.

Table 3-2. Specifications of PSS and SSS layers

Type of layer	Material	Dimensions	Target thickness	Measured thickness ^{a,b}
PSS	Acrylic latex paint	25 mm x 40 mm	0.076 ± 0.023 mm	0.086 ± 0.0097 mm (n=49)
SSS	Water-based polyurethane sealant	25 mm x 40 mm	0.051 ± 0.015 mm	0.048 ± 0.0066 mm (n=37)

^a cured (dry) layer; ^b average for the stainless-steel layer coupons used in testing

3.2.3 Free Standing Paint or Sealant Film Coupons

The same type of paint and sealant as used for the preparation of painted and sealed steel (Section 3.2.2) was used to make FSP and FSS sheets. FSP and FSS sheets were prepared using a modified method derived from ASTM D823 [7]. Here, polytetrafluoroethylene (PTFE) sheets (American Sealing & Packaging, Santa Ana, CA, USA) were used as the panel substrate instead of stainless steel for FSP production. Multipurpose unpolished stainless steel (type 304, #2B mill, McMaster-Carr, Douglasville, GA, USA) was used as the substrate for FSS production. The paint does not bond with PTFE, so following curing, paint layers were removed from the substrate, creating free-standing layers. The sealant only mildly bonds with the stainless-steel substrate so that the sealant layer can be physically peeled off following curing. The FSP and FSS coupons were die-cut with an arch punch to a diameter of 50 mm and cleaned using dry compressed air. The thickness of the coupons was then measured using ASTM D1005 “Standard Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers” [10], on the center, bottom, top, left and right of each free-standing layer coupon, with acceptance criteria of 70 to 130% of target thickness, and RSD of <30% between quintuplicate measurements of each coupon. The procedure for manufacturing FSP and FSS layer sheets is detailed in Appendix A-1.2. Specifications of FSP and FSS layers are summarized in Table 3-3. FSP and FSS coupons ready for testing are shown in Figure 3-3a and b, respectively.

Table 3-3. Specifications of FSP and FSS layers

Type of layer	Material	Diameter	Target thickness	Measured thickness ^{a,b}
FSP layer	Acrylic latex paint	12 or 50 mm ^c	0.076 ± 0.023 mm	0.079 ± 0.0093 mm (n=56)
FSS layer	Water-based polyurethane sealant	12 or 50 mm	0.051 ± 0.015 mm	0.049 ± 0.0083 mm (n=68)

^a cured (dry) layer; ^b average for free-standing layer coupons used in testing; ^c millimeters

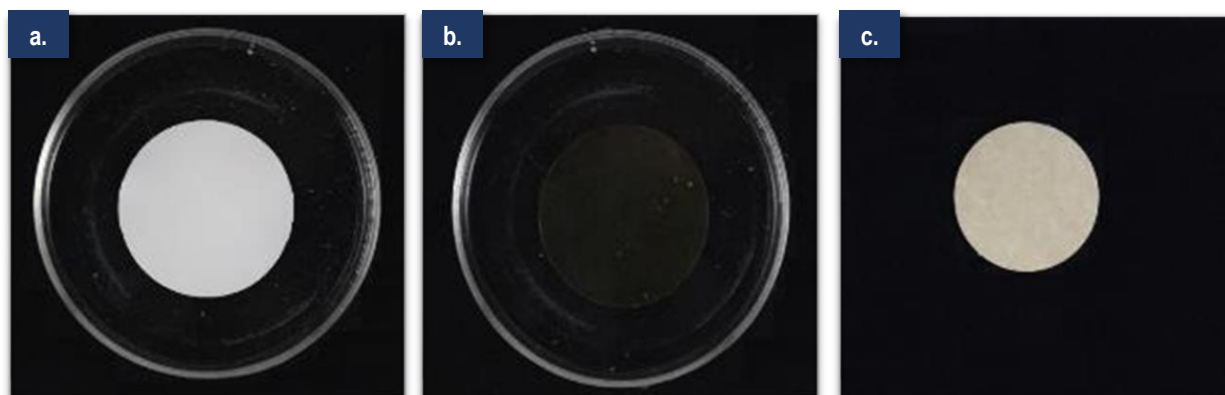


Figure 3-3. FSP (a) and FSS (b) layers and SPE (c) coupon.

For FESEM analyses, smaller FSP and FSS coupons (approximately 12 mm in diameter) were punched out from 50-mm material coupons that were characterized to confirm that they meet the average target thickness criteria from an average of five measurements across each layer (Table 3-3). The small FSS and FSP coupons were mounted to 12.7 mm scanning electron microscope (SEM) pin stubs (each engraved in a unique stub identification (ID) on the underside of the stub) using adhesive black carbon tape. Figure 3-4 shows stubs with FSP and FSS layers ready for testing.

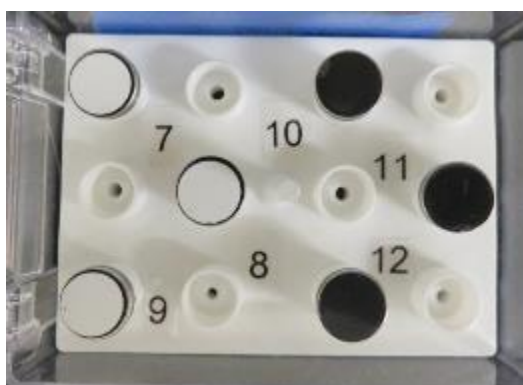


Figure 3-4. FSP and FSS layers assembled onto SEM stubs.

3.2.4 Solid Phase Extraction Disks

The 47-mm in diameter 3M Empore SDB-XC solid-phase extraction (SPE) disk (Table 3-1) made of poly(styrene-divinylbenzene) copolymer was used as a porous material surrogate for this project. The 47 mm diameter SPE disks (0.15 mm thickness) were die-cut with an arch punch to a diameter of 36 mm to provide a 10 square centimeter (cm²) contact area. An SPE coupon ready for testing is shown in Figure 3-3c.

3.2.5 Bulk Materials

Bulk materials used in this study were representative of common polymer-based indoor surfaces, were tested for chemical transfer to sublayers, and are listed below:

- Solid Acrylic Surface Countertop (Table 3-1). A solid, nonporous, homogeneous surfacing material, composed of acrylic resin (butyl acrylate-methyl methacrylate polymers, >30%), and natural minerals (alumina trihydrate (ATH) derived from bauxite, and extracted aluminum; 40-70%). A similar material (mix of polymethyl methacrylate (PMMA) and ATH) is also manufactured by DuPont (Wilmington, DE, USA) and sold under the trademark of Corian
- High-Pressure (Decorative) Laminate (HPL), also known as 'Formica' (Table 3-1). This common indoor material is made of resins (30-50%) and paper/fiber (40-70%).
- Vinyl Composition Tile (Plank) (Table 3-1) is made of polyvinyl chloride (PVC). Some manufacturers may utilize an additional sealant for high traffic areas. Such treatment was not included in this study.

Bulk material coupons were cut from larger pieces of material using hydraulic shears to obtain a uniform length (4.0 cm) and width (2.5 cm). Bulk material coupons were cleaned with acetone and hexane, sequentially. Finally, isopropanol was used to remove any lubricant/grease from shearing, the coupon was then wiped clean with water and wiped dry using a Kimwipe to remove dust before use in the tests.

Coupons of bulk materials readied for testing are shown in Figure 3-5, below.

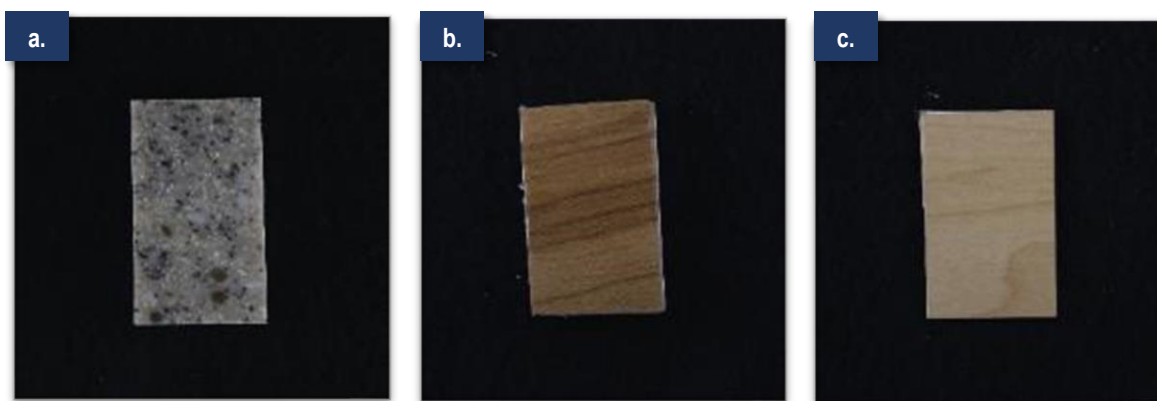


Figure 3-5. Coupons of bulk materials: acrylic surface (a), vinyl composite plank (b), and high-pressure laminate (c).

3.3 Chemicals and Reagents

The target chemicals used in this study, 2-[dimethoxyphosphorothioyl)sulfanyl]butanedioate (malathion) and 2-chloroethyl phenyl sulfide (2-CEPS), are commonly used surrogates of CWAs. Malathion is an organophosphate insecticide widely used in agriculture, pest control, and in residential landscaping, and is a known surrogate for the VX nerve agent for decontamination studies [3]. Based on chemical similarity, 2-CEPS is considered a valid surrogate for the sulfur mustard (HD) for decontamination studies

[2,4]. It should be noted that differences in functional groups between a CWA and an identified surrogate may also impact the permeation rate into a permeable material.

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%). The relevant physical and chemical properties of these chemicals are listed in Table 3-4. Chemical application procedures are described in Section 3.3.1.

Table 3-4. Physicochemical properties of target chemicals

Property	2-CEPS	Malathion
CAS ^a Registry Number	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 ^b) 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 ^c	0.084 g/L
Log K _{ow}	2.36-2.89	3.58
^a Chemical Abstracts Service, ^b cubic centimeters, ^c grams/liter		

Information on internal standard and surrogate compound analytical standards used in this study are given in Section 4.4. Other chemical reagents are listed in Table 3-5.

Table 3-5. Chemical reagents

Chemical Reagent	Purity/Grade	Product No.	Manufacturer
Hexane ^a	ACS/HPLC	H303-4	Fisher Scientific, Fair Lawn, NJ, USA
Acetone	ACS/HPLC	A949-1	Fisher Scientific, Fair Lawn, NJ, USA
Isopropyl alcohol	ACS Plus	A416-4	Fisher Scientific, Fair Lawn, NJ, USA
^a Mixture, as purchased, of <i>n</i> -hexane (45-60%), hexane (<i>-isomers</i>) (15-40%), and cyclohexane (3%). ^b HPLC - High-performance liquid chromatography.			

3.3.1. Contamination of Coupons

Neat chemical solutions were applied to test coupons (TCs) using a discrete droplet (micro) application method via a liquid spike. Prior to chemical microdroplet application, each clean coupon was placed in an aluminum weighing boat for labeling and transport. The FSP and FSS coupons were secured in LVAP cells and placed in prelabeled secondary containment boxes prior to spiking. Section 3.4 describes the LVAP assembly.

Vials with analytical standards were removed from refrigeration and placed in the chemical hood for at least two hours before use. Additionally, the vial of malathion analytical standard was placed in a 1-L beaker filled with approximately 200 milliliters (mL) of warm water to reduce the viscosity of the neat

chemical for spiking. The water temperature was tracked with a temperature probe, and the water was replaced when the temperature of the bath decreased below 30 degrees Celsius (°C).

To spike coupons, a 2-microliter (μL) droplet of neat 2-CEPS or malathion analytical standard (Table 3-4) was applied to the center of each coupon using a 2- μL microsyringe (Microliter Microsyringe, 2.0 microliter [μL], 25 gauge; Hamilton, Reno, NV, USA; P/N 88400), resulting in surface concentration of 2.34 milligrams [mg] and 2.46 mg per test coupon, respectively. Before and after spiking, the syringe was cleaned with a 50:50 acetone:hexane mixture. The accuracy and precision of spiking the neat solution preparation was tested along with each experimental batch by analysis of control spike (CS) samples (see Table 4-2 for results of the analysis of CSs).

Chemical solutions for gasket permeation testing (see Section 3.4 for definition of gasket and Section 3.7.1 for test matrix) were applied to the coupons under room temperature conditions within a chemical safety hood using a separate tip-programmable, electronic, repeater pipette (Eppendorf Repeater Plus Single Channel Repeater Pipette, Eppendorf AG, Hamburg, Germany; P/N 22260201). After chemical application, the test coupons were moved to the EIDC for simulated weathering or contact time (CT).

Figure 3-6 shows examples of the chemical droplet contamination on test surfaces immediately after spiking.

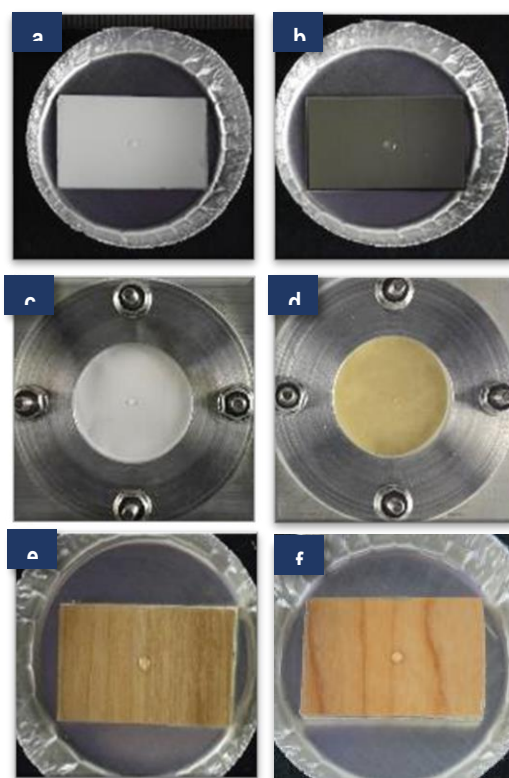


Figure 3-6. Discrete microdroplet application of chemicals onto the test surfaces; examples shown are malathion droplets immediately after spiking onto (a) painted stainless steel; (b) sealed stainless steel; (c) FSP layer in the LVAP; (d) FSS layer in the LVAP; (e) high-pressure laminate, and (f) vinyl plank flooring.

FSP and FSS layers for microscopy analyses were contaminated using the microdroplet application described above but were not processed in the EIDC. The chemical weathering was performed in the chemical hood with SEM stubs assembled in a plastic holder plate, placed in an acrylic box with lid for safe transport to the FESEM laboratory. Figure 3-7 shows paint and sealant layers immediately after spiking with malathion. Note that the sealant layer is highly transparent, and the black appearance is caused by the (black) carbon tape.



Figure 3-7. Malathion microdroplets after application onto FSP (left) and FSS (right) layers assembled onto SEM stubs.

3.4 LVAP Apparatus

A series of custom-built LVAP devices was used to evaluate the transport of chemicals through FSP and FSS layers into a porous subsurface surrogate material (SPE disk). The LVAP cells were also used to study the decontamination of chemicals. The FSP/FSS-SPE assembly was supported by custom-made full face and O-ring PTFE gaskets and held in close contact using steel bolts. The initial design of the LVAP apparatus is shown in Figure 3-8 with the top and side view of the constructed LVAP system shown in

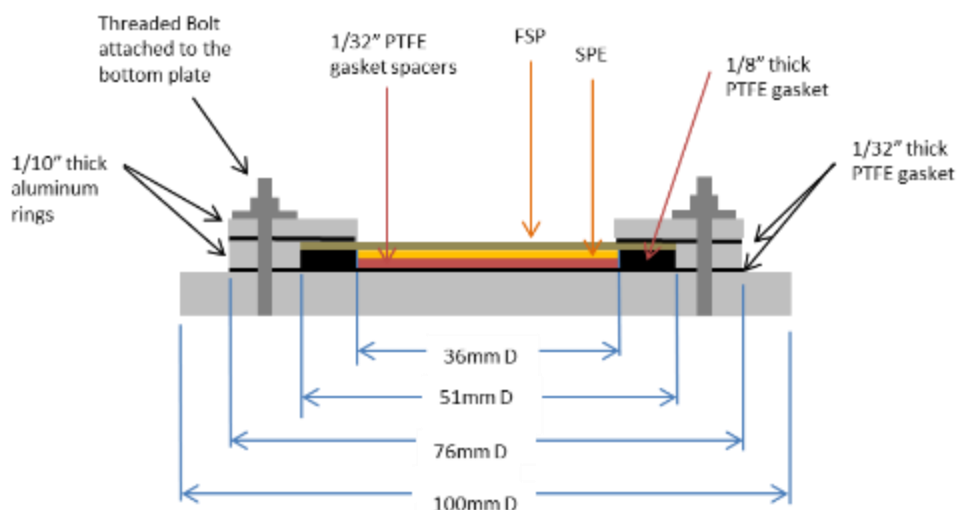


Figure 3-8. The prototype design of the LVAP apparatus.

Figure 3-9. Note that threaded bolts were replaced by machine screws as shown in Figure 3-9A. The procedure for assembly of the LVAP cell is detailed in Appendix A-2.

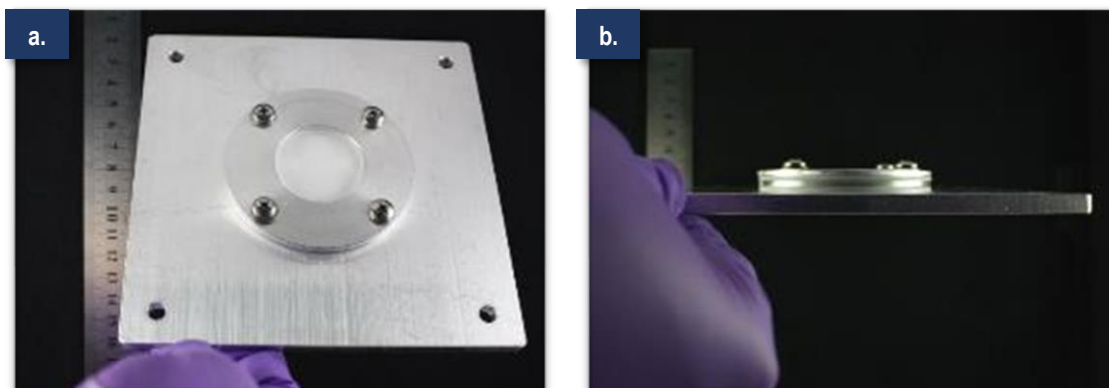


Figure 3-9. Top (a) and side view (b) of the LVAP system.

Before testing, the PTFE gaskets, aluminum spacers, and steels nuts/bolts for the LVAP apparatuses were cleaned with a 50:50 (volume:volume) acetone:hexane mixture and sonicated for 15 min. The large aluminum LVAP bottom plate was cleaned with acetone then hexane and wiped dry with Kimwipes. The assembled LVAP cells were placed inside a clean, labeled secondary containment (small modular supply case; clear polypropylene; 5" x 5¼" width x 2" height size; IRIS USA Inc., Surprise, AZ, USA; P/N 585170) for spiking with a chemical (Section 3.3.1), and then the secondary containment was closed to ensure safe transfer to the EIDC for weathering. After transfer to EIDC, the containers were opened and remained open until weathering was completed. The polypropylene secondary containers were precleaned using a laboratory-grade detergent solution in tap water, wiped with acetone and deionized (DI) water, and wiped dry.

3.5 Decontamination Solutions and Application of Liquid Decontaminants

Decontamination solutions used in this study were selected based on their reported acceptable efficacy for malathion and 2-CEPS shown under previous EPA Homeland Security Research Program (HSRP) research efforts or reported in the literature [3,4]. General information and properties of decontamination solutions are given in Table 3-6.

Table 3-6. Decontamination solutions

Decontamination Solution	Manufacturer/Supplier	Active Ingredient(s) ^a	Other functional ingredients ^b	pH range
Clorox Concentrated Germicidal Bleach	The Clorox Company Oakland, CA, USA	8.3% sodium hypochlorite	- Sodium hydroxide (pH adjuster stabilizer) - Sodium chloride (thickener and stabilizer) - Sodium carbonate (alkalinity builder and water softener) - Sodium chlorate (breakdown product of sodium hypochlorite)	11–12
Clorox Splash-Less Bleach	The Clorox Company Oakland, CA, USA	1-5% sodium hypochlorite	- Sodium hydroxide (pH adjuster stabilizer) - Sodium chloride (thickener and stabilizer) - Sodium carbonate (alkalinity builder and water softener) - Sodium chlorate (breakdown product of sodium hypochlorite) - Sodium polyacrylate (detergent and water locking ingredient) - Cetyl betaine, sodium xylene sulfonate (surfactants and wetting agents)	~12.5
EasyDECON DF200	Envirofoam Technologies, Pooler, GA, USA Intelagard, Lafayette, CO, USA	~ 8%hydrogen peroxide (Part A); < 4% in the finished blend	- Quaternary ammonium compounds, dimethyl benzyl alkyl, diacetin (surfactants and activators of hydrogen peroxide)	9.6–9.7

^a Per Safety Data Sheet (SDS), all concentrations are in the finished blend; ^b Data from <https://www.thecloroxcompany.com/responsibility/healthy-lives/product-stewardship/sds/https://www.thecloroxcompany.com/en-us/what-were-made-of/ingredients-inside/clorox/clorox-splash-less-regular-bleach-44600307848/> and <https://intelagard.com/wp-content/uploads/2015/06/EasyDECON-Part-1-SDS-2015.pdf>, <https://intelagard.com/wp-content/uploads/2015/06/EasyDECON-Part-2-SDS-2015.pdf>, and <https://intelagard.com/wp-content/uploads/2015/06/EasyDECON-Part-3-SDS-2015.pdf>

All products were purchased from local suppliers or authorized distributors. Fresh batches of EasyDECON DF200 solution were prepared daily through proportional mixing as per the manufacturer's instructions. Before use, the manufacturer-recommended EasyDECON Fortifier Test Kit was used to test the EasyDECON DF200 finished blend. This test (a "Go/No Go" test) measures the percentage of the 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 measurements of the finished blend (target pH range: 9.6-9.9). Bleach products were used as is (no additional preparation steps); pretest evaluations of the bleach solutions included free available chlorine (FAC), pH and temperature measurements as well.

3.6 Method Development Tests

3.6.1 Chemical Recovery Tests

3.6.1.1. Bulk Extraction of Coupons

Methods were optimized if needed to maintain a consistent level of analytical quality assurance (QA) among the different types of samples. The bulk material extraction efficacy tests were designed to determine the ability to recover target chemicals from the different types of test materials. These tests also provided initial information on the stability and/or volatilization of target chemical spikes on permeable layers

of building surfaces, as compared to the reference material (stainless steel). The extraction method for stainless steel was used for the extraction of bulk materials. The long-term (up to several days) surface stability of chemicals was determined during permeation testing (Section 3.7.2).

All bulk material extraction efficacy tests were performed at a 30-min CT. The coupons were spiked with 2 μ L of neat 2-CEPS or malathion analytical standard using techniques described in Section 3.3.1. Tests were performed in triplicate ($n = 3$) for each chemical–test material combination. One procedural blank (PB) of each uncontaminated material was extracted as well, to monitor for possible cross-contamination or quantitative interferences that might result from the extraction procedure. Three CS samples, generated by directly spiking of the chemical into the extraction solvent at concentrations corresponding to 100% of the chemical amount applied to test materials, were prepared for each test day to verify precision and accuracy of the chemical application. The recovery acceptance criteria were 80-120% from the theoretical recovery value with a coefficient of variance between triplicates of less than 30% (Section 5.2).

Material extraction procedures are detailed in Section 4.2.2. Recoveries of target chemicals for each material and chemical combination are provided in Section 6.1.2.

3.6.1.2. Surface Sampling of Coupons

The wipe sampling method demonstration tests were conducted to evaluate the wipe (swab) sample technique and wipe extraction efficiency from the surface swab. Like the bulk coupon extraction tests described in Section 3.6.1.1, surface sampling optimization tests were performed at a 30-min CT and chemical surface loadings of approximately 2.3 to 2.5 mg per coupon, resulting from a single 2- μ L liquid spike of neat 2-CEPS or malathion, respectively. Surface samples were collected using four cotton swabs (Puritan 3" Large Cotton Swab w/Wooden Handle; Puritan Medical Products Company LLC, Guilford, MA, USA; P/N 803-WCL) per coupon using sampling procedure described in Section 4.1. Swabs were preferred over gauze wipes considering the small surface area and limited access to the surface in the LVAP device. The type of swab used for sampling has an extra-absorbent large tip that is approximately 6 mm (0.234") in diameter and 17.5 mm (0.687") long and is made of medical-grade quality lint-free cotton. The wood handle is approximately 74 mm (2.906") long and can fit inside the tubes used for extraction. Four swabs from the sampling of each coupon were pooled together in the 50-mL polypropylene extraction tube (DigiTUBE, SCP Science, Quebec, Canada; P/N 010-500-263) and extracted in 30 mL of hexane as one composite sample.

All surface sampling and extraction tests were performed in triplicate ($n = 3$) for each chemical and coated stainless steel and free layer LVAP layer test combination, as well as for reference material. The surface sampling method developed for stainless steel was used for swab sampling of bulk materials. One PB of each uncontaminated material was swab-sampled as well. Three CS samples were prepared per test event. The recovery acceptance criteria were 80-120% from the theoretical recovery value, with a coefficient of variance between triplicates of less than 30% (Section 5.2).

The swab extraction procedure is described in detail in Section 4.2.1. Recoveries of target chemicals from surface swab samples are presented in Section 6.1.1.

3.7 Permeation Tests

3.7.1 Gasket Contamination and Nonpermeation Transport Tests

Prior to the chemical permeation testing (Section 6.3), the LVAP setup was used to assess the retention of the target chemicals in the SPE disks and to assess the potential for possible propagation of the chemicals out of the SPE disks into the PTFE gaskets of the LVAP system. This gasket contamination test was designed to demonstrate that gaskets do not serve as a sink for chemicals introduced to the LVAP system. The SPE retention and gasket contamination tests were performed at the maximum contact time (CT = 72 h) for each chemical–SPE–free layer (FSP or FSS) combination (Table 3-7). Briefly, the bottom (flat face) gasket and SPE disk coupons were assembled in three clean LVAPs and spiked with a target chemical solution of the chemical in ethanol at 50 mg/mL. A 10- μ L spike was delivered onto the center of each SPE disk using an electronic pipette (Section 3.3.1). The resulting concentration was at approximately 20% of the chemical amount that was spiked onto the coupons as derived from an assumed 20% permeation-related transfer through the paint layer into a (surrogate) porous material. After spiking of the SPE, the LVAP assembly was completed for each cell by placing a clean O-ring gasket and unspiked FSP coupon on the top of each contaminated SPE disk. After 72 hours, the SPE disks were extracted and prepared for analysis using procedures described in Sections 4.2.2 and 4.3. In addition to the spiked SPE disks, gaskets and unspiked FSP coupons were also extracted and analyzed to evaluate the potential propagation of the target compound from the SPE disks to gaskets and to the paint layer; each gasket type was extracted as a composite sample (n=3; Table 3-7).

Additionally, three blank LVAP cells were assembled to look for any nonpermeation related transport of chemicals to LVAP components placed in the EIDC (nonpermeation transfer test, Table 3-7) and followed the identical test setup and extraction scheme described above for test samples with contaminated SPE discs.

Table 3-7. Experimental parameters for gasket contamination and nonpermeation transport tests

Test type	Chemical	LVAP component spiked	Spiked chemical amount [mg] ^a	Contact time [h]	Extraction solvent type ^b	Extraction solvent volume [mL]	LVAP components extracted
Gasket contamination	2-CEPS	SPE	0.50	72	Hexane	30	SPE, FSP, gaskets ^c
		SPE	0.50	72	Hexane	30	SPE, FSS
	Malathion	SPE	0.50	72	Hexane	30	SPE, FSP, gaskets ^c
		SPE	0.50	72	Hexane	30	SPE, FSS
Nonpermeation transfer	2-CEPS	None	No spike	72	Hexane	30	SPE, FSP, gaskets ^c
	Malathion	None	No spike	72	Hexane	30	SPE, FSP, gaskets ^c

^a 10- μ L spike of chemical solution at 50 mg/mL; ^b detailed specifications of extraction solvent used in this study are in Table 3-4; ^c composite extraction of three O-ring and three full-face gaskets below SPE disks

The acceptance criterion for the total recovery of each target compound from the gasket material from the gas contamination test was set to be less than 1% of the amount spiked onto the SPE disk (or less than 0.005 mg) detected in the gasket materials.

The criterion for the total recovery of the target chemical from an uncontaminated SPE in the nonpermeation transfer test was less than 1% of the (coupon) surface concentration (or less than 0.023 to 0.025 mg) detected in the SPE from the uncontaminated LVAP assembly. The results from gasket contamination and nonpermeation transfer tests are summarized in Section 6-2.

3.7.2 Baseline Permeation Tests

Baseline permeation tests were designed to allow for the measurement of 2-CEPS and malathion permeation through surface layers of FSP, FSS or into bulk materials at the longest CT of 72 h and occasional shorter CTs (down to 3 h) following the deposition of a chemical on the surface, as compared to the stainless-steel reference material, and other control samples including painted or sealed stainless steel as warranted. After a discrete single 2- μ L droplet of neat chemical was deposited onto each test coupon (Section 3.3.1), a 3 to 72 hours-long pesticide-surface interaction test was conducted in the EIDC. The remaining amounts of target chemicals were determined through a combination of surface wiping followed by extraction of the coupon types and quantities (Table 3-8). Tests were performed in triplicate ($n = 3$) for each test configuration and time point. One PB of each uncontaminated material was extracted as well at CT = 72 h. Three CSs were generated per each spiking event.

Table 3-8 summarizes the entire test matrix and key operational parameters for the test procedure (sample types and number and sampling approaches used for each type of coupon/test material). Sampling and analysis methods are described in detail in Section 4.0. Results are given in Section 6.3.

Table 3-8. Test parameters for permeation testing and types of samples collected

Test material	Chemical	Nominal spiked chemical amount [mg]	CT(s) tested [h]	Components analyzed ^b		Control samples	
				Sample type	Sampling method(s)	Sample type	Sampling method(s)
LVAP tests							
FSP over SPE	2-CEPS	2.3	72	FSP	SW + E	SS, PSS, PB, LB, CS	SW + E or E
				SPE	E		
	Malathion	2.5	3, 6, 24, 72	FSP	SW + E	SS, PSS, PB, LB, CS	SW + E or E
				SPE	E		
FSS over SPE	2-CEPS	2.3	72	FSS	SW + E	SS, SSS, PB, LB, CS	SW + E or E
				SPE	E		
	Malathion	2.5	72	FSS	SW + E	SS, SSS, PB, LB, CS	SW + E or E
				SPE	E		
Bulk material tests							
AS	2-CEPS	2.3	24, 72	BMC	SW + E	SS, PB, LB, CS	SW + E or E
	Malathion	2.5	72	BMC	SW + E	SS, PB, LB, CS	SW + E or E
HPL	2-CEPS	2.3	24, 72	BMC	SW + E	SS, PB, LB, CS	SW + E or E
	Malathion	2.5	72	BMC	SW + E	SS, PB, LB, CS	SW + E or E
VCP	2-CEPS	2.3	24, 72	BMC	SW + E	SS, PB, LB, CS	SW + E or E
	Malathion	2.5	72	BMC	SW + E	SS, PB, LB, CS	SW + E or E
FSP – Free standing paint layer coupon (wiped and extracted); FSP – Free standing paint layer coupon (wiped and extracted); SPE – SPE disk coupon (extracted); AS – acrylic countertop surface (wiped and extracted); HPL – high-pressure laminate countertop surface (wiped and extracted); VCP – vinyl composition plank flooring (wiped and extracted); BMC – bulk material coupon (wiped and extracted) SW + E – surface wipe sampled, then extracted; E – bulk material extraction only; PB – Procedural blank; LB – Laboratory blank; CS – control spike							

3.8 Decontamination Tests

3.8.1 Decontamination Baseline

In the initial phase of the efficacy testing a decontamination procedure using a commercial off-the-shelf (COTS) product (concentrated germicidal bleach) was deployed via surface application to investigate its efficacy for degradation of the chemicals. The decontamination procedure consisted of a single application of 200 μ L of decontaminant over the central portion of the coupon contaminated with the chemical. The application was performed at 72 hours after spiking (CT=72 h). This procedure did not include any mechanical scrubbing or rinsing after application of the decontaminant. The procedure was based solely on the chemical oxidation reaction, or degradation of target chemical by high concentration sodium hypochlorite and potentially other minor ingredients of decontaminant (e.g., pH stabilizer sodium hydroxide). After a prescribed dwell time (DT) of 18 hours (indicative of an overnight drying), the postdecontamination chemical mass on the surface and in subsurface layers was determined by wipe sampling and extraction techniques, or a combination thereof. Due to the high natural attenuation rate of 2-CEPS observed for bulk building material permeation testing (results in Section 5.3), the decontamination baseline for bulk materials was tested only for more persistent malathion using one application of germicidal bleach. The test matrix for baseline decontaminant testing is given in Table 3-9, below. Results are given in Section 6.4.1.

Table 3-9. Test parameters for baseline decontamination testing: Single application of concentrated germicidal bleach with a dwell time of 18 h.

Test material	Chemical	Nominal spiked chemical amount [mg] ^a	CT [h]	Decontaminant/ decontaminant volume [μL]	DT [h]	Components analyzed ^b		Control samples	
						Sample type	Sampling method(s)	Sample type	Sampling method(s)
LVAP tests									
LVAP-FSP	2-CEPS	2.3	72 ^a	Concentrated germicidal bleach/200	18	FSP	SW + E	SS, PSS, PB, LB, CS	SW + E or E
						SPE	E		
	Malathion	2.5	72	Concentrated germicidal bleach/200	18	FSP	SW + E	SS, PSS, PB, LB, CS	SW + E or E
						SPE	E		
LVAP-FSS	2-CEPS	2.3	72 ^a	Concentrated germicidal bleach/200	18	FSS	SW + E	SS, SSS, PB, LB, CS	SW + E or E
						SPE	E		
	Malathion	2.5	72	Concentrated germicidal bleach/200	18	FSS	SW + E	SS, SSS, PB, LB, CS	SW + E or E
						SPE	E		
Bulk material tests									
AS	Malathion	2.5	72 ^b	Concentrated germicidal bleach/200	18	BMC	SW + E	SS, PB, LB, CS	SW + E
HPL	Malathion	2.5	72 ^b	Concentrated germicidal bleach/200	18	BMC	SW + E	SS, PB, LB, CS	SW + E
VCP	Malathion	2.5	72 ^b	Concentrated germicidal bleach/200	18	BMC	SW + E	SS, PB, LB, CS	SW + E
^a tested in the 'open' and 'closed' LVAP configuration; FSP – Free standing paint layer coupon (wiped and extracted); FSP – Free standing paint layer coupon (wiped and extracted); SPE – SPE disk coupon (extracted); AS – acrylic surface countertop (wiped and extracted); HPL – high-pressure laminate (wiped and extracted); VCP – vinyl composite plank flooring (wiped and extracted); BMC – bulk material coupon (wiped and extracted) SW + E – surface wipe sampled, then extracted; E – bulk material extraction only; PB – Procedural blank; LB – Laboratory blank; CS – control spike									

3.8.2 Modified Decontamination Testing

The modified decontamination approaches tested were developed for degradation of chemicals that were identified to be remaining on the surface or within the subsurface layers after the baseline decontamination using a single application of concentrated germicidal bleach (Section 3.8.1). The research focused on targeted changes that may result in improvements in the decontamination procedure. The changes tested were a combination of functional and operational modifications listed below:

- use of different commercial decontaminant (i.e., different decontamination chemistry, e.g., activated hydrogen peroxide)
- use of modified decontaminant (e.g., bleach with additives)
- use of modified multistep application of various decontaminants

The overall effectiveness of the modified decontamination approaches used an adaptive experimental design. Namely, each subsequent decontamination procedure modification considered the results from preceding procedures that did not offer a cumulative decontamination efficacy of surface-bound or permeated chemical fraction. The executed test matrix for the modified decontamination testing is shown in Table 3-10. The results are given in Section 6.4.2.

Table 3-10. Test parameters for modified decontamination testing

Test material	Chemical	Spiked chemical amount [mg] ^a	CT(s) tested [h]	Decontaminant/decontaminant volume [μL]	DT [h]	Components analyzed ^b		Control samples	
						Sample type	Sampling method(s)	Sample type	Sampling method(s)
Modified Decontamination Procedure 1 (MDT-1)									
Description: Two applications of concentrated germicidal bleach; application 1 at CT=72 h, application 2 at DT = 2 h; total DT = 2 + 18 h									
LVAP-FSP	Malathion	2.5	72	Concentrated germicidal bleach/ 2 x 200	2 +18	FSP	SW + E	SS, PB, LB, CS	SW + E or E
						SPE	E		
Modified Decontamination Procedure 2 (MDT-2) and 2a (MDT-2a)									
Description: One or two applications of Splash-Less bleach; application 1 at CT=72 h, 2 nd application 2 at DT = 2 h; total DT = 2 + 18 h									
LVAP-FSP	Malathion	2.5	72	Splash-Less Bleach / 200	18	FSP	SW + E	SS, PB, LB, CS	SW + E or E
						SPE	E		
				Splash-Less Bleach / 2 x 200	2 +18	FSP	SW + E	SS, PB, LB, CS	SW + E or E
						SPE	E		
Modified Decontamination Procedure 3 (MDT-3) and 3 a (MDT-3a)									
Description: One or two applications of EasyDECON DF200; application 1 at CT=72 h, 2nd application 2 at DT = 2 h; total DT = 2 + 18 h									
LVAP-FSP	Malathion	2.5	72	EasyDECON DF200/ 200	18	FSP	SW + E	SS, PB, LB, CS	SW + E or E
						SPE	E		
				EasyDECON DF200/ 2 x 200	2 +18	FSP	SW + E	SS, PB, LB, CS	SW + E or E
						SPE	E		
FSP – free standing paint layer coupon (wiped and extracted); FSP – free standing paint layer coupon (wiped and extracted); SPE – SPE disk coupon (extracted); SW + E – surface wipe sampled, then extracted; E – bulk material extraction only; PB – procedural blank; LB – laboratory blank; CS – control spike.									

3.9 Microscopy Analyses

FESEM was used to characterize general material properties and morphology like porosity, thickness, and structural integrity of paint and sealant layers after exposure to a decontaminant, and after malathion-only and bleach-only exposures. Microscopy images of malathion, malathion-decontaminant, and decontaminant exposure areas were compared to those of the nonexposed areas of laboratory blank coupons to determine if the malathion or bleach had an impact on the paint and sealant material properties and morphology. After the exposure(s) at prescribed CTs and DTs, the coupons were coated with a thin layer of carbon using a Cressington 208C carbon coater (CREST Gateway Technologies, Dublin, Ireland) before microscopy analysis to mitigate the impacts of sample charging. The test matrix for microscopy analyses is given in Table 3-11. Qualitative results are incorporated throughout Section 6.0 to support experimental findings from permeation and decontamination studies.

Table 3-11. Test matrix for microscopy analyses

Test Material	Sample type	Material exposure(s) and contact times (CT)
Condition 1		
FSP	SPC	Malathion (CT = 72 h)
FSS	SPC	Malathion (CT = 72 h)
Condition 2		
FSP	STC	Malathion (CT = 72 h) + Clorox germicidal bleach ^a (DT = 18 h)
FSS	STC	Malathion (CT = 72 h) + Clorox germicidal bleach ^a (DT = 18 h)
Condition 3		
FSP	SDC	Clorox germicidal bleach ^a (DT = 18 h)
FSS	SDC	Clorox germicidal bleach ^a (DT = 18 h)
Negative controls		
FSP	SLB	Laboratory blank (no exposures)
FSS	SLB	Laboratory blank (no exposures)
^a regular (i.e., nonconcentrated) version of germicidal bleach was used in FESEM experiments due to limited market availability of the concentrated product; per label, sodium hypochlorite concentration in the regular version is ~6.25% compared to ~8.25% of the concentrated germicidal bleach (Table 3-6). SPC – contaminated positive control (on SEM stub); TC – Contaminated and decontaminated test sample (on SEM stub); SPB – Decontaminated-only control sample (on SEM stub); LB – Laboratory blank (on SEM stub); CT – contact time; DT – dwell time		

4.0 Sampling and Analysis

4.1 Surface Sampling Methods

Each rectangular (SS, SSS, PS or bulk material) and circular (FSP or FSS) coupon was wipe-sampled using four cotton swabs (FisherBrand Cotton-Tipped Applicators, Fisher Scientific, Thermo Fisher Scientific, Waltham, MA, USA; P/N 23-400-101) prewetted with pesticide-grade isopropanol wetting solvent (Table 3-5). All cotton-tipped applicators were precut to a total length of less than 4" before sampling to allow the cotton swabs to fit inside the extraction vessels. The cotton swabs were used to sample the coupon in separate sampling motions: the first swab sampled the "hot zone" with a rotating motion of the wood handle; the second swab used overlapping horizontal strokes; the third swab used vertical overlapping strokes; and the last swab sampled the perimeter. Given the small surface area of the coupons, strokes were short (coupon length/width) and overlapped each other. The multistep wipe sampling procedure is summarized in detail in Appendix A-3. Figure 4-1 shows examples of surface sampling using the swab-based method.

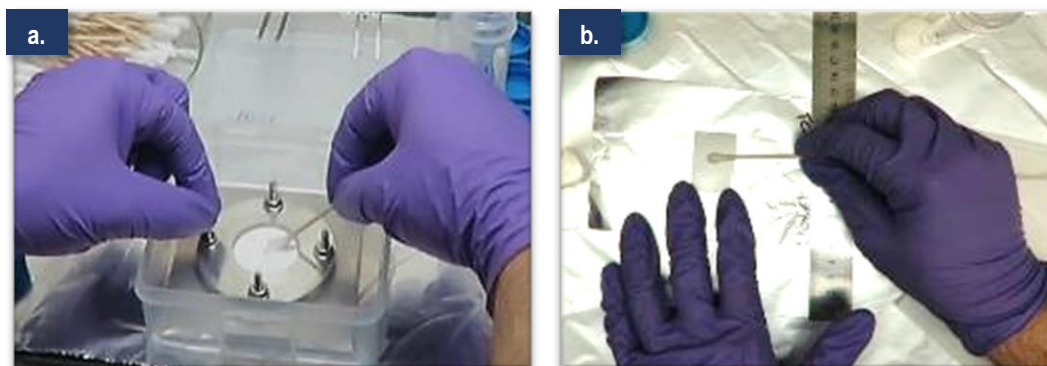


Figure 4-1. Surface sampling of test coupons using prewetted cotton swab; examples shown are LVAP-FSP (a) and SS (b).

Swab samples were collected directly to extraction vials (four swabs per extraction tube) and immediately extracted using procedures described in Section 4.2.1. After the disassembly of LVAPs was completed, the wipe-sampled FSS and FSP coupons were transferred to the prelabeled 50-mL extraction vials (solvent- and acid-resistant digestion/extraction vial; DigiTube Non RackLock with caps; SCP Science, Quebec, Canada, P/N 010-500-263). SPE disks were not wipe-sampled and underwent direct extraction – as described in Section 4.2.2 – immediately after the disassembly of the LVAP was completed.

4.2 Extraction Methods

This section summarizes the extraction procedures used for all types of surface samples, coupons, and bulk materials. All extraction methods were verified before persistence and decontamination testing.

4.2.1 Extraction of Surface Wipes

After completion of wipe sampling using swabs (Section 4.1.3), four swab wipes used for surface sampling of coupons (Section 4.1) were placed in a new prelabeled 50-mL vial (solvent- and acid-resistant digestion/extraction vial; DigiTube Non RackLock with caps) for composite extraction. Each extraction vial was filled with 30 mL of hexane (Table 3-5) and capped. Lids were not tightened completely to avoid the pressure buildup during extraction. Extraction vials were then placed in an extraction rack and transferred to the sonicator (Branson 8510, Branson, Danbury, CT, USA) containing room-temperature water. Extraction vials containing the swabs were sonicated for 15 minutes. After extraction, samples were refrigerated at 4 ± 2 °C until further processing. Sample extract preparation for instrumental analysis is described in Section 4.3.

4.2.2 Extraction of Coupons and Bulk Materials

After completion of permeation or decontamination testing, each coupon was placed in a new prelabeled 50-mL vial (solvent- and acid-resistant digestion/extraction vial; DigiTube Non RackLock with caps). Each tube was then filled with 30 mL of hexane (Table 3-5) and capped. Lids were not tightened completely to avoid pressure buildup during extraction. Extraction vials were then placed in an extraction rack and transferred to the sonicator (Branson 8510, Branson, Danbury, CT, USA) containing room-temperature water. Extraction vials containing the coupons were sonicated for 15 minutes. Figure 4-2 shows FSP and SPE coupons immediately after extraction.

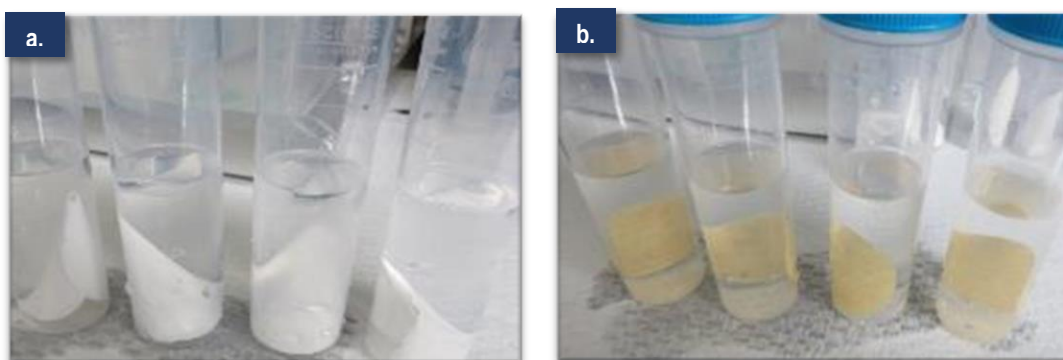


Figure 4-2. FSP (a) and SPE (b) coupons immediately after the conclusion of hexane extraction.

After extraction, samples were refrigerated at 4 ± 2 °C until further processing. Procedures for the preparation of extracts for instrumental analysis are described in Section 4.3.

4.3 Preparation of Samples for Analysis

Extracts resulting from surface sampling (Section 4.2.1) and coupon extractions (Section 4.2.2) were prepared for analysis in 1.8-mL amber glass gas chromatography (GC) vials (Sigma Aldrich, St. Louis, MO, USA). Due to the lack of the cleanup step in the analytical procedure, all sample extracts were diluted 10-fold in hexane, including procedural blanks, laboratory blanks, and gasket contamination samples. The

CS samples were also diluted up to 25-fold. If prepared samples were outside the upper limit of the calibration range, the dilutions were adjusted using preliminary results, and samples were prepared from archived extracts and reanalyzed. All samples were spiked at 1000 nanograms [ng]/mL level with isotopically labeled internal standard (ISs) and surrogate standard: phenanthrene-d10 from EPA Method 8270 standard mix (ERS-020-1.2ML; Sigma Aldrich) and malathion-d10 (DLM-4476-1.2, Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA), respectively. After the preparation of the sample for analysis was completed, the sample level (solvent level) was marked on the vial. Samples were refrigerated at 4 ± 2 °C or below before analysis. The remaining raw extracts were archived at 4 ± 2 °C or below. All analytical batches were accompanied by a chain of custody form and inspected at the analytical laboratory upon receipt.

4.4 Instrumental Analyses

Instrumental analyses were performed by the EPA OSL using GC/MS. The exact conditions for the GC/MS were optimized prior to sample analysis and are given below in Table 4-1.

Table 4-1. GC/MS parameters for analysis of 2-CEPS and malathion.

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)
Column	DB-5, 20 m × 0.25 mm ID, 0.25 µm df (Agilent, Santa Clara, CA, USA)
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
Injection volume/type	1.0 µL/splitless
Inlet temperature	250 °C
MS source temperature	250 °C
MS transfer line	250 °C
<i>df: film thickness</i>	

The calibration range was 100-10,000 ng/ml, with quantitation performed using two 5-point curves that were dependent on the sample concentration. The high-concentration curve (1,000-2,500-5,000-7,500-10,000 ng/mL) was used for the analysis of sample materials that had high sampling efficacy and CSs at a 100% target concentration. The low-concentration curve (100-250-500-750-1,000 ng/mL) was used for the 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-*d*₈ (from EPA 8270 semivolatile internal standard mix [CRM46955, MilliporeSigma, St. Louis, MO]); IS was also present in all test and CS samples at the same concentration level (Section 4.6.2). Prior to sample analysis, a minimum 5-point instrument calibration (ICAL) was performed, and the coefficient of determination (R^2) was determined (target $R^2 \geq 0.995$). The continuous calibration was performed using a middle 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 quality control (QC) criteria were not met, the instrument was recalibrated, and any affected samples were reanalyzed. Additional QC samples

included duplicates (DUPs) of test samples (one DUP per analytical run; acceptance criteria: relative percent difference [RPD] <20%) and analysis of blanks (PBs and laboratory blank [LBs]).

Prior to testing, an initial laboratory proficiency evaluation was performed. Accuracy and precision were determined by analysis of multiple measurements of the CS solutions (n = 5 for two concentration levels; single analytical run). CS samples were generated by spiking the target chemical or target chemical solution used during testing directly into the injection solvent (hexane). All CSs were sonicated for 10 minutes and then diluted as needed per Section 4.4. Each CS set was accompanied by one LB sample (1 mL of solvent used for the preparation of samples for analysis). These CS experiments were used as independent verifications of the results obtained from the analytical laboratory. The initial and continuing laboratory proficiency results are listed in Table 4-2.

Table 4-2. Initial and continuing laboratory proficiency results

Target Chemical	Control Spike Sample Analysis results		Solvent Blank
	Accuracy and Precision	Number of samples analyzed	
	(% of true value $\pm$ 1 SD ^c ; RSD [%])	(n)	
Malathion, 10% target (initial ^a)	86% $\pm$ 6% SD; RSD = 7%	5	<LOQ
Malathion, 100% target (initial ^a)	102% $\pm$ 7% SD; RSD = 7%	5	<LOQ
Malathion (continuing ^b)	88% $\pm$ 15% SD; RSD = 17%	34	<LOQ
2-CEPS, 10% target (initial ^a)	94% $\pm$ 3% SD; RSD = 4%	5	<LOQ
2-CEPS, 100% target (initial ^a)	112% $\pm$ 7% SD; RSD = 7%	5	<LOQ
2-CEPS (continuing ^b)	96.7% $\pm$ 7% SD; RSD = 7%	15	<LOQ
^a Direct spike into solvent; QC samples prepared for initial laboratory proficiency testing. ^b Direct spike into solvent; QC samples prepared for each analytical batch resulting from tests performed. ^c Standard deviation (SD)			

The acceptance criteria for the initial laboratory proficiency tests were 80–120% for accuracy (as recovery compared to theoretical concentration [true value]) and <30% RSD precision for each concentration level for replicate analysis for each concentration target. The results from the initial analyses of CS samples – calculated as average ($\pm$ 1 standard deviation [SD], %RSD) from results of multiple injections of the initial proficiency evaluation CSs, (Table 4-2) – were within the acceptance criteria described above. The results from ongoing evaluations performed by single injections of multiple analytical batch-specific CSs were 88.3% $\pm$ 15.3% SD (RSD=17%) and 96.7% $\pm$ 6.6% SD (RSD=6.9%) for malathion and 2-CEPS, respectively (Table 4-2). All solvent blanks were below LOQ.

4.5 Data Reduction Procedures

4.5.1 Chemical Concentration Calculations

The following data reduction procedures were performed to summarize chemical concentration analytical results:

1. The total amount of chemical recovered from the surface of each replicate coupon:

- The average concentration in mg per replicate coupon group;
- SD and %RSD for each group of replicate coupons.

2. For control samples associated with a test condition:

- Sampling and extraction controls (replicates, average, SD, %RSD);
- Procedural blank coupons results (if detected above LOQ);
- Laboratory blanks (if detected above LOQ);
- Control spikes (replicates, average, SD, %RSD).

The GC/MS concentration results (ng/mL) were converted to the total mass of chemical per sample (mg per sample) by multiplying by the extraction solvent volume and dilution factor, if applicable (Eq. 1):

$$M_S = C_S \times V_E \times D_F / 1.0E6 \quad (\text{Eq.1})$$

where:

M_S : mass of chemical in the sample (mg)

C_S : concentration (ng/mL) from an individual replicate sample

V_E : extraction solvent volume (mL)

D_F : sample dilution factor (if any)

The percent recovery of chemical from samples was calculated against the chemical amount spiked onto the surface (Eq. 2):

$$\%R = M_S / M_{CS} \times 100 \quad (\text{Eq.2})$$

where:

M_S : mass of chemical (mg) in a test sample

M_{CS} : mass of chemical (mg) in the control spike, corresponding to the chemical level spiked onto the surface

The chemical mass (M_S) results used for decontamination efficacy (Section 4.5.2) calculations were not adjusted for QC sample recovery (%R).

4.5.2 Decontamination Efficacy Calculations

The decontamination cleanup efficacy was calculated using the average of chemical mass recovered from the replicate test coupons (TCs) and the average chemical mass recovered from the associated set of positive control (PC) coupons (Eq. 3).

$$\bar{x} \text{ DE} = (1 - M_{TCn} / M_{PCn}) \times 100 \quad (\text{Eq.3})$$

where:

$\bar{x}$ DE: average decontamination efficacy (%)

M_{TCn} : average of the chemical amount remaining on a replicate TC (decontaminated) coupon or LVAP set (mg)

M_{PCn} : average of the chemical amount remaining on replicate PC (nondecontaminated) coupons or LVAP sets (mg)

The average decontamination efficacy, along with the SD, was a cumulative decontamination efficacy (or resulting from the application of all procedural steps for each test). If the mass of remaining agent on all subcomponents of one sample was found to be below the LOQ, the efficacy was calculated using the LOQ value and reported as “greater than” the calculated value.

If the sample concentration was found to be below the lowest point of the calibration curve, but the signal-to-noise (S/N) ratio was greater than 10, the results were reported as estimated and flagged as estimated. All other results that were nondetect and detections at $3 < S/N < 10$ were reported as below LOQ ($< LOQ$). Student's *t*-tests (two-tailed with unequal variance) were used to check if the observed differences in decontamination efficacies of various methods tested were statistically significant. The *p*-values are reported at a significance level of 95% ($\alpha=0.05$).

5.0 Quality Assurance and Quality Control

5.1 Test Equipment Calibration

All equipment was verified as calibrated at the time of use. Instruments were calibrated at the frequency shown in Table 5-1. In case of any deficiencies, instruments were adjusted to meet calibration tolerances or recalibrated before testing. In the case of the GC/MS instrument, any initial calibration deficiencies were noted. The GC/MS instrument was recalibrated before the analysis. If the tolerances for continuous calibration were not met, the GC/MS instrument was recalibrated, and affected samples were reanalyzed.

Table 5-1. Instrument calibration frequency

Equipment	Calibration/Certification	Expected Tolerance	Results
Thermometer	Compare to independent NIST thermometer (a thermometer that is recertified annually by either NIST or an ISO-17025 facility) value once per quarter.	$\pm 1^{\circ}\text{C}$	100%
Stopwatch	Compare to official U.S. time at time.gov every 30 days.	± 1 min/30 days	100%
Micropipettes	Certified as calibrated at time of use; recalibrated by gravimetric evaluation of performance to manufacturer's specifications every year.	$\pm 5\%$	100%
Microsyringes	Certified as calibrated at time of use	$\pm 5\%$	100%
Relative humidity	Vaisala probe (RH) certified as calibrated at time of use. Calibration verified yearly by the EPA Metrology Laboratory.	$\pm 3\%$ RH	100%
Temperature	Vaisala probe (T)	$\pm 0.35^{\circ}\text{C}$	100%
Paint or sealant layer thickness and uniformity	Eddy current certified by manufacturer; calibration was checked and zeroed using standards prior to each use.	$\pm 1\text{ }\mu\text{m}$ (0-50 μm) $\pm 2\text{ }\mu\text{m}$ (>50 μm)	100%
	Micrometer certified by manufacturer	$\pm 2\text{ }\mu\text{m}$ (at 20°C)	100%
	Universal blade applicator certified as calibrated at time of use. Thickness of layer verified using Eddy current gauge or micrometers after each paint layer application	± 0.5 mil (0-10 mil) ± 1 mil (0-50 mil)	100%
Solvent Volume	Solvent dispenser certified by manufacturer; checks performed with graduated cylinder prior to use.	$\pm 1\text{ mL}$	100%
Scale	Certified as calibrated at time of use; calibration verified yearly by the EPA Metrology Laboratory.	$\pm 1\text{ g}$	100%
Graduated cylinder	Certified by manufacturer at the time of use. Certified as calibrated at time of use. Calibration verified yearly by the EPA Metrology Laboratory.	$\pm 1\text{ mL}$	100%
Solvent dispenser	Certified by manufacturer at the time of use; rechecked volume delivered using graduated cylinder prior to use.	$\pm 1\text{ mL}$	100%
Gas chromatograph/mass spectrometer	5-point calibration prior to analysis; continuous calibration prior to each analytical run; recalibrate when continuous calibration fails acceptance criteria and/or after system maintenance; details in Section 4.4.	$\pm 20\%$ at mid-point	100%
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 project objectives:

- Surface concentration of target chemicals as determined by instrumental analysis
- Chemical concentration in coupons, including SPE disk
- Chemical concentration in extracts
- Contact and dwell times
- Environmental conditions during weathering
- Thickness and uniformity of all paint and sealant layers.

The data quality indicators (DQIs) for 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-specific quality assurance project plan) were not indicative of any systematic error introduced into the experimental results and do not change the general findings of this study.

Table 5-2. Acceptance criteria for critical measurements and corresponding test results

Critical Measurement	Target Value and Acceptance Criteria	Results
Contact/weathering time	3-72 h $\pm$ 5 min	3 h CT: 3:00:00 h $\pm$ 00:00 min 6 h CT: 6:00:00 h $\pm$ 00:00 min 24 h CT: 24:00:00 h $\pm$ 00:00 min 72 h CT: 72:00:00 h $\pm$ 00:00 min
Dwell time	18 to 20 h $\pm$ 5 min	18 h DT: 18:00:04 h $\pm$ 00:13 min 20 h DT: 19:58:44 h $\pm$ 04:14 min
Environmental conditions ^a	Temperature: 24 $\pm$ 3 °C Relative humidity: 50 $\pm$ 5% RH	Temperature: 22.9 $\pm$ 1.0 °C Relative humidity: 47.6 $\pm$ 6.0 % RH
Delivery of target surface concentration of chemical ^b	80–120% of target chemical mass	Malathion: 88% $\pm$ 15% SD (RSD =17%) 2-CEPS: 97% $\pm$ 6.6% SD (RSD =6.9%)
Thickness and uniformity of pain layers	70-130% of target thickness (3 mils for FSP layers; 2 mils for FSS layers)	FSP: 3.1 $\pm$ 0.37 (RSD = 12%) FSS: 1.9 $\pm$ 0.33 (RSD = 17%)
Recovery of chemical from surface samples ^c	<30% coefficient of variation for identical test set ^d	Malathion: bulk material extraction RSD: 3.2 – 21%; surface sampling RSD: 1.8 – 8.4% 2-CEPS: bulk material extraction RSD: 2.5 – 6.8%; surface sampling RSD: 1.1 – 10.1%
Procedural blank	<5% of the analyte amount recovered from the positive control.	All procedural blank samples within acceptance criteria; all reported <LOQ; test-specific results are in Tables 6-1 through 6-12.
Solvent blank	<LOQ	All solvent blanks reported <LOQ

^a target conditions in EIDC at one air exchange per hour; temperature and RH measurements were taken at 1 min intervals; ^b determined by analysis of control spikes; criteria for recovery of chemical from the surface; ^c for optimized analytical procedures used during permeation and decontamination operational-scale testing; ^d between replicate samples of the identical test set (n=3)

6.0 Results and Discussion

6.1 Verification of Surface Sampling and Material Extraction Methods

6.1.2 Efficacy of Surface Sampling Using Swabs

Average percent recoveries – calculated as chemical mass recovered in comparison to control spike results – were 63 to 87% for 2-CEPS and 66 to 89% for malathion across the various surfaces (CT of 30 min). The recovery of 2-CEPS from the surface of stainless steel was $87 \pm 7\%$; RSD = 8%, hence within project-specific acceptance criteria of 80-120% for reference material, with a coefficient of variance between triplicates of less than 30%. The average recovery of malathion was $78 \pm 3\%$; RSD = 3% or only minimally lower than the 2-CEPS results above. The detailed results of the surface sampling method development tests for different types of test materials are shown in Appendix B Tables B1 and B2, for 2-CEPS and malathion, respectively. The sampling method efficiencies were deemed satisfactory to study the 2-CEPS and malathion permeation and measure decontamination efficacies and were not further optimized. This surface sampling method was also used for sampling of bulk materials without prior evaluation for these materials.

As expected, the recovery from surface wipe samples of stainless-steel reference coupons generally exceeded the recovery from wipe (swab) samples collected from other more permeable test materials, indicating that both the surface layers and free-standing layers of paint and sealant had a noticeable amount of permeation and/or adherence of malathion and 2-CEPS into the paint layers even during the relatively short CT of 30 min that was used for surface sampling method development. The contaminant retention by the paint and sealant layer was further evaluated during the fate and transport studies (Section 6.3).

6.1.3 Coupon Extraction Efficacy

Recoveries of 2-CEPS and malathion, average $95 \pm 3\%$; RSD = 3% and $95 \pm 6\%$; RSD = 6%, respectively, were observed for reference nonpainted SS coupons during extraction testing. These values were within the acceptance criteria for SS, namely, 80-120% of chemical amount spiked onto the surface with less than 30% RSD between replicates. Detailed results for the extraction method development tests for different types of test materials are shown in Appendix B, Tables B3 and B4 for 2-CEPS and malathion, respectively. The high percent recoveries indicate the high effectiveness and reproducibility of the analytical method for the extraction of target chemicals present on the surface of the reference material. Similar or better recoveries were observed for other test materials (Tables B3 and B4). The extraction method validated for stainless steel was deployed during bulk materials testing without further prior evaluation.

6.1.4 Comparison of Coupon Extraction Versus Surface Sampling

A comparison of relative recoveries for surface wipe sampling versus coupon extraction for 2-CEPS and malathion is shown in Figure 6-1, with lower and upper limit QA acceptance criteria for reference material shown as red dashed lines.

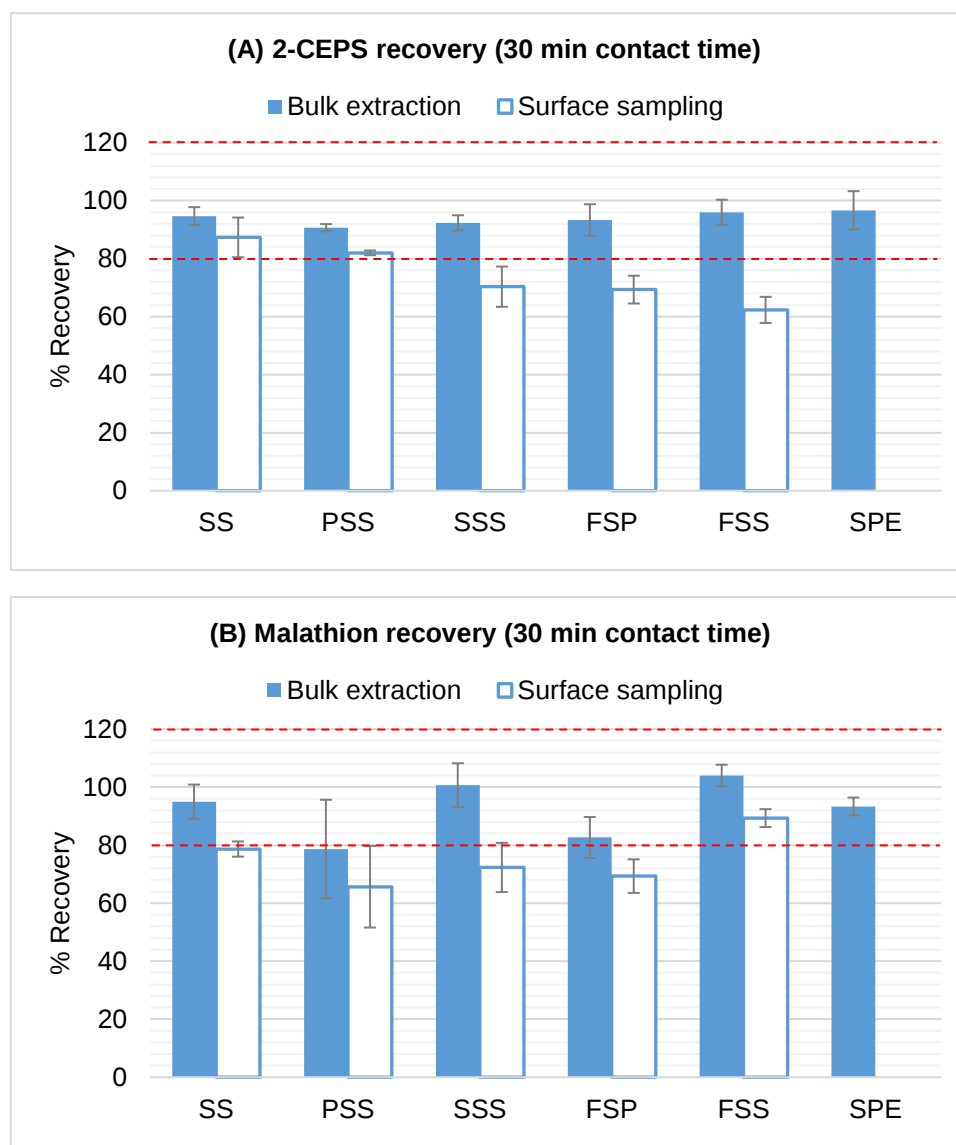


Figure 6-1. Recovery of 2-CEPS (A) and malathion (B) from reference and test materials; SS: stainless steel; PSS: painted stainless steel; SSS: sealed stainless steel; FSP: free-standing paint layer; FSS: free-standing sealant layer; SPE: solid-phase extraction disk; dashed lines are representing the lower (80%) and upper (120%) limit of recovery acceptance criteria set for reference material (SS).

The implemented sampling protocols were reproducible, with coefficients of variance ranging from 1.1 to 21% RSD among triplicates (Figure 6-1 and Appendix B, Table B3 and B4). For four out of five materials - 2-CEPS and three out of five material-malathion combinations tested, average percent recoveries (relative to the control spikes) were statistically significantly ($p < 0.05$) higher for the direct extractions than the average percent recoveries for wipe sampling, with an average 8 to 17% reduction in the absolute percent recovery of 2-CEPS and malathion from extraction and wiping, respectively (Figure 6-1 and Appendix B, Table B3 and B4). Only recoveries of 2-CEPS from stainless steel by extraction versus wipe sampling were not significantly different ($p = 0.27$). This is not too surprising considering the relative

ease of sampling a smooth, nonporous and nonpermeable material. The two materials for which no significant difference was observed between extraction and surface wipe sampling for malathion were painted stainless steel ($p=0.45$) and free-standing paint ($p=0.11$). A statistically significant difference in recovery between extraction and surface wipe sampling of malathion from stainless steel ($p=0.04$) was observed, which is the opposite from what was observed for 2-CEPS and could be attributed to a generally poorer surface wipe sampling efficiency for malathion.

Chemical recoveries from the extraction of painted and sealed stainless-steel surfaces and their free-standing layer counterparts were not statistically different for 2-CEPS ($p>0.05$ for all 10 intramaterial comparisons) and similarly not statistically different for malathion in 9 out of the 10 intramaterial comparisons. The only significant difference was found in the comparison of the extracted malathion amount from FSP versus FSS ($p=0.03$).

Chemical recoveries from the surface sampling using swabs of painted and sealed surfaces and free layers were mostly (7 out of 10 intramaterial comparisons for 2-CEPS and 8 out of 10 intramaterial combinations for malathion) not statistically different with recoveries from extraction of the material consistently higher than the recoveries from extraction of surface wipe sampling. Statistically significant differences for the 2-CEPS recovery were found between the SS and FSP ($p=0.04$), SS and FSS ($p=0.02$), and PSS and FSS ($p=0.02$) while differences in recovery for malathion were different between SS and FSS ($p=0.02$) as well as FSP and FSS ($p=0.02$).

6.2. Gasket Contamination and Nonpermeation Transport

The results from the LVAP gasket contamination and nonpermeation transport evaluation for 2-CEPS and malathion are shown in detail in Appendix B, Tables B5 through B7. No target chemical was recovered from any gasket samples above the $<1\%$ mass recovery criterion established as target QA criterion prior to testing (Table B5). No malathion detections were observed for the top gasket, which was located between the FSP and the aluminum top plate from the LVAP apparatus. Trace amounts of malathion –below LOQ – were observed in the PTFE O-ring (gasket around the SPE disk) data set and all three-spacer gaskets (PTFE gasket directly below the SPE disk). All gaskets had ultra trace-level concentrations of 2-CEPS ($<<LOQ$ at an estimated 1 to 4 μg per composite sample). These minor detections in the O-ring and spacer gaskets means that only a very small amount ($<1\%$) of each target chemical may migrate through the SPE disk into the PTFE gaskets, but without introducing any significant bias into studying permeability of chemicals using LVAP devices.

The 2-CEPS and malathion recoveries from the SPE, FSP, and FSS used in the gasket contamination tests are shown in Appendix B Tables B6 and B7 for 2-CEPS and Tables B8 and B9 for malathion. In these tests, the SPE was spiked at 20% of the target test matrix concentration and an FSP or FSS was placed immediately on top of the SPE. During the 72-hour long CT, approximately 93 to 99% of 2-CEPS contamination migrated back from the spiked SPE disk into the free layers of paint or sealant, with the LVAP mass balance showing an average chemical recovery of approximately 41% (Σ FSP+SPE recoveries) to 42% (Σ FSS+SPE recoveries) (Tables B6 and B7). The mass balance of malathion was an average of 101% (Σ FSP+SPE recoveries) to 108% (Σ FSS+SPE recoveries), with only an average of 12 to 25% retained by previously uncontaminated FSS and FSP layers. Figure 6-2 shows average recoveries and

partitioning of target chemicals from contaminated SPE to previously uncontaminated surface layers of LVAP systems.

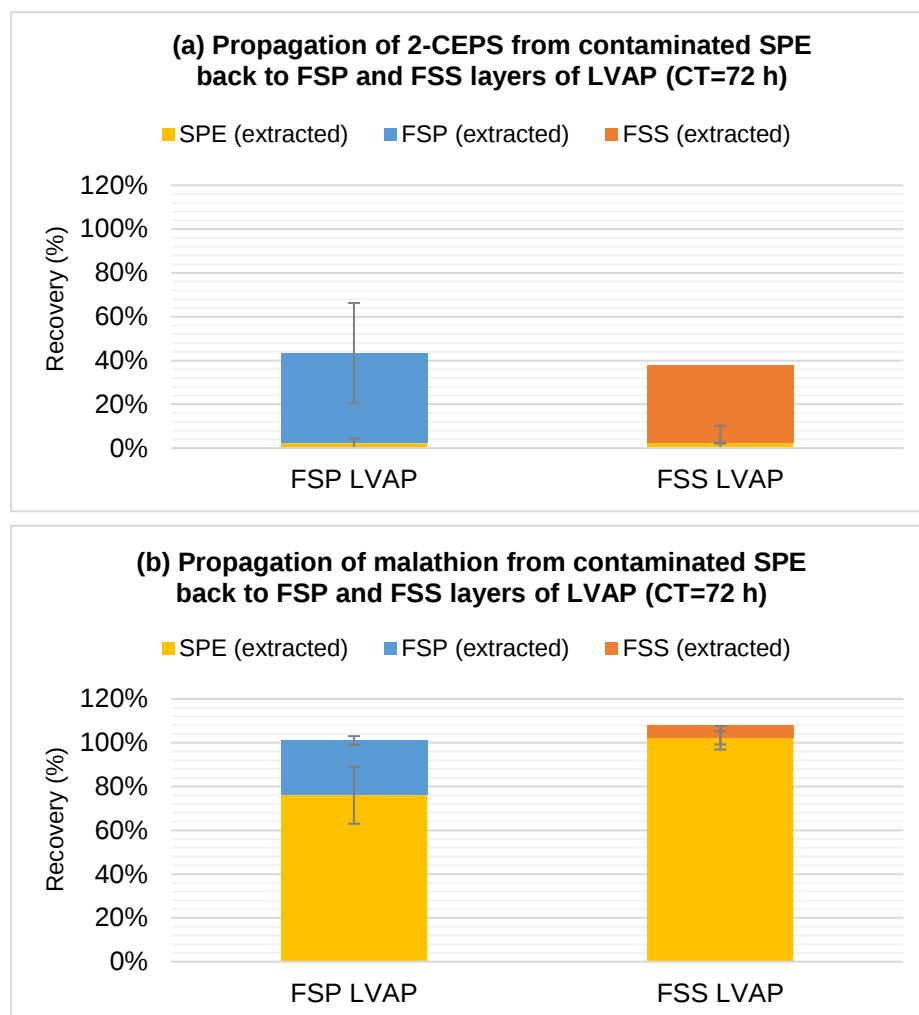


Figure 6-2. Average recoveries and migration of 2-CEPS (a) and malathion (b) for LVAP-FSP and LVAP-FSS system components; recoveries were calculated against theoretical amount of chemical spiked determined by analysis of associated CS samples. Chemical mass results for each layer are averages ($n=3$) $\pm$ 1 SD.

The lower total mass recovery of 2-CEPS can be attributed to the more volatile characteristics (in comparison to malathion) leading to higher evaporation-related losses (physicochemical properties of target chemicals are given in Table 3-4). 2-CEPS also has a much higher reverse migrated amount from the contaminated porous sublayer (SPE disk) to the paint/sealant material, which may make it more susceptible to surface-based decontamination. The less volatile malathion is more persistent in contaminated sublayers, with no natural attenuation observed during controlled 72 hour-long weathering. Malathion had a limited and surface layer type-dependent potential for reverse migration to the paint/sealant surface layer. Polyurethane sealant seems to be particularly resistant to malathion, which is in line with the follow-on permeation studies, as described in Section 6.3.

6.3 Permeation Testing

Test specific summaries of the permeation test results for different types of test and control materials are provided in the following sections for 2-CEPS and malathion separately.

6.3.1 Permeation of 2-CEPS

At 72 hours after application of 2-CEPS onto LVAP top surface layers, approximately 1 to 2% of the recovered chemical mass was detected in the SPE disk, with 95% detected in the extracted FSP or FSS layers, and approximately 4% on the surface, as determined by wipe sampling (Table 6-1 and 6-2). This study did not use a wipe to recover agent from the SS coupon (direct extraction only; amount recovered below the LOQ) while the painted or sealed SS (PSS and SSS) coupons were not tested. The overall chemical recovery for 2-CEPS was below 25% (compared to spike controls) of the initial surface concentration which can be attributed to noticeable volatilization of this chemical from the paint or sealant surface over the 72-h CT. This volatilization occurs as a process competing with the observed transportation of 2-CEPS into and through paint and sealant layers.

Table 6-1. Permeation of 2-CEPS through FSP layers - chemical mass recovery results in LVAP components and associated control samples at CT = 72 h

CT [h]		SS		PSS		FSP		SPE
		Chemical mass recovery [mg]						
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction
72 h	Average (n=3)	NT	<0.03	NT	NT	0.020 (J)	0.44	0.0052
	SD	NT	NA	NT	NT	0.001 (J)	0.019	0.0025
	PB	NT	<0.03	NT	NT	<0.03	<0.03	<0.03
Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10).; NT – not tested; NA – not applicable SS: Stainless Steel; PSS: Painted Stainless Steel; FSP: Free Standing Paint [layer]; SPE: Solid Phase Extraction [-disk; below FSP]								

Table 6-2. Permeation of 2-CEPS through FSS layers - chemical mass recovery results in LVAP components and associated control samples at CT = 72 h

CT [h]		SS		SSS		FSS		SPE
		Chemical mass recovery [mg]						
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction
72 h	Average (n=3)	See Table 6-1 (shared SS coupons)		NT	NT	0.019 (J)	0.50	0.010 (J)
	SD			NT	NT	0.0030 (J)	0.064	0.0019 (J)
	PB			NT	NT	<0.03	<0.03	<0.03
Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10); NT – not tested; NA – not applicable SS: Stainless Steel; SSS: Sealed Stainless Steel; FSS: Free Standing Sealant [layer]; SPE: Solid Phase Extraction [-disk; below FSS]								

The low detections of 2-CEPS in the surface (wipe) fractions of the LVAP paint and sealant (Tables 6-1 and 6-2) corresponded to noticeable visual changes on the FSP and FSS layers, with no chemical contamination droplet visually present after 72 hours after spiking as visible in Figure 6-3.

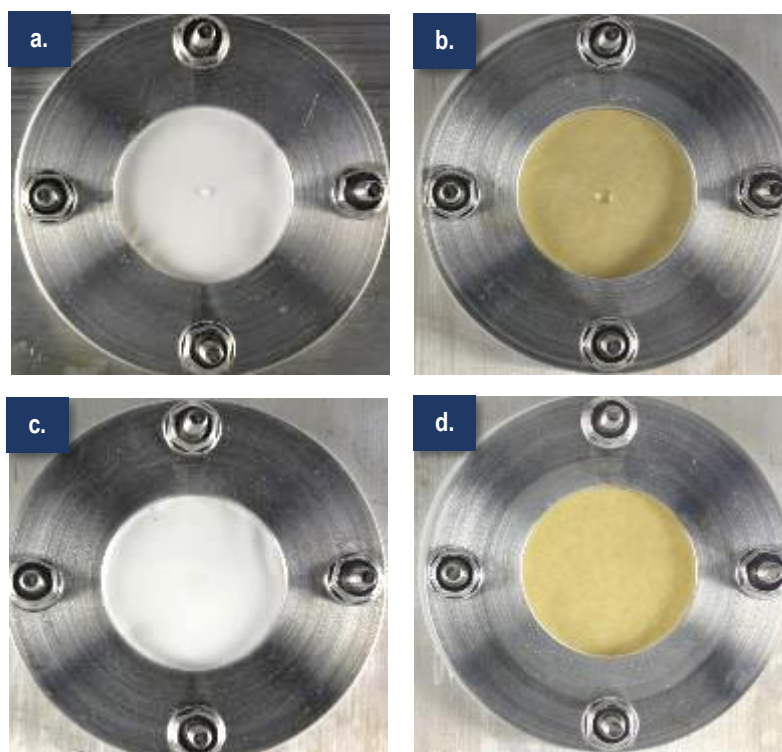


Figure 6-3. 2-CEPS droplet on the surface of LVAP-FSP and LVAP-FSS layers immediately after spiking (a and b, respectively) and after completion of the 72-h chemical weathering period, with no visible chemical contamination present on the surface (c and d, respectively).

Most notably, at CT=72 h, no 2-CEPS was detected in the associated extracted stainless-steel control samples (Tables 6-1 and 6-2), indicating that over 99% reduction could be attributed to volatilization of the chemical at normal indoor environmental conditions and one air exchange per hour.

The 2-CEPS permeation results for the three bulk materials and stainless steel as a nonporous reference material are summarized in Table 6-3. Considering the negligible detection of 2-CEPS on SS after 72 h as part of the paint and sealant permeation test, the bulk material permeation tests were also performed at shorter contact times (CT = 24 h); see Table 6-3 for results.

Table 6-3. Permeation of 2-CEPS through building material surfaces-chemical mass recovery results in bulk material and associated control samples at CT= 24 h and 72 h.

CT [h]		SS		AS		HPL		VCP	
		Chemical mass recovery [mg]							
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Wipe	Extraction
24 h	Average	NT	1.47	0.64	0.16	1.1	0.0079 (J)	0.63	0.26
	SD	NT	0.10	0.23	0.06	0.53	0.0028 (J)	0.24	0.041
	PB	NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
72 h	Average	NT	<0.03	0.0003 (J)	0.0069(J)	0.022 (J)	0.0013 (J)	0.0008 (J)	0.12
	SD	NT	NA	NA	0.0019 (J)	NA	0.0010 (J)	0.0003 (J)	0.02
	PB	NT	<0.03	<0.03	0.0002 (J)	<0.03	0.000010(J)	<0.03	0.003 (J)
Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N>10); NT – not tested; NA – not applicable AS: acrylic solid surface countertop; HPL: high-pressure decorative laminate; VCP: vinyl composition plank									

After 24 hours, as calculated by Eq. 2 in section 4.5.1, recoveries of 2-CEPS (sum of wipe + extraction recoveries) ranged from average 32 to 45%, with 71 to 99% of the recovered chemical detected on the surface (Table 6-3). The high-pressure laminate surface was least permeable to 2-CEPS, with the sublayer chemical fraction accounting for less than 1% of the total amount detected. Vinyl flooring had the highest permeability to 2-CEPS, with approximately 29% of a chemical mass detected in the subsurface layer, as determined by direct extraction (Table 6-3).

After 72 hours, the recoveries of 2-CEPS (sum of wipe + extraction recoveries) dropped to 0.3 to 5%, with nearly all the 2-CEPS remaining on the surface for HPL (95%) while nearly all 2-CEPS ($\geq 96\%$) was found within the bulk material for the AS and VCP materials (Table 6-3). These results are consistent with what was observed after 24 h. Most of the 2-CEPS dissipates from the surface, predominantly by evaporation.

Figure 6-4 shows surfaces of bulk materials after spiking and after simulated weathering under normal environmental conditions. Figure 6-5 summarizes average recoveries and partitioning of target chemicals from permeation tests for both LVAP systems (CT = 72 h) and three bulk materials (CT = 72 h and 24 h).

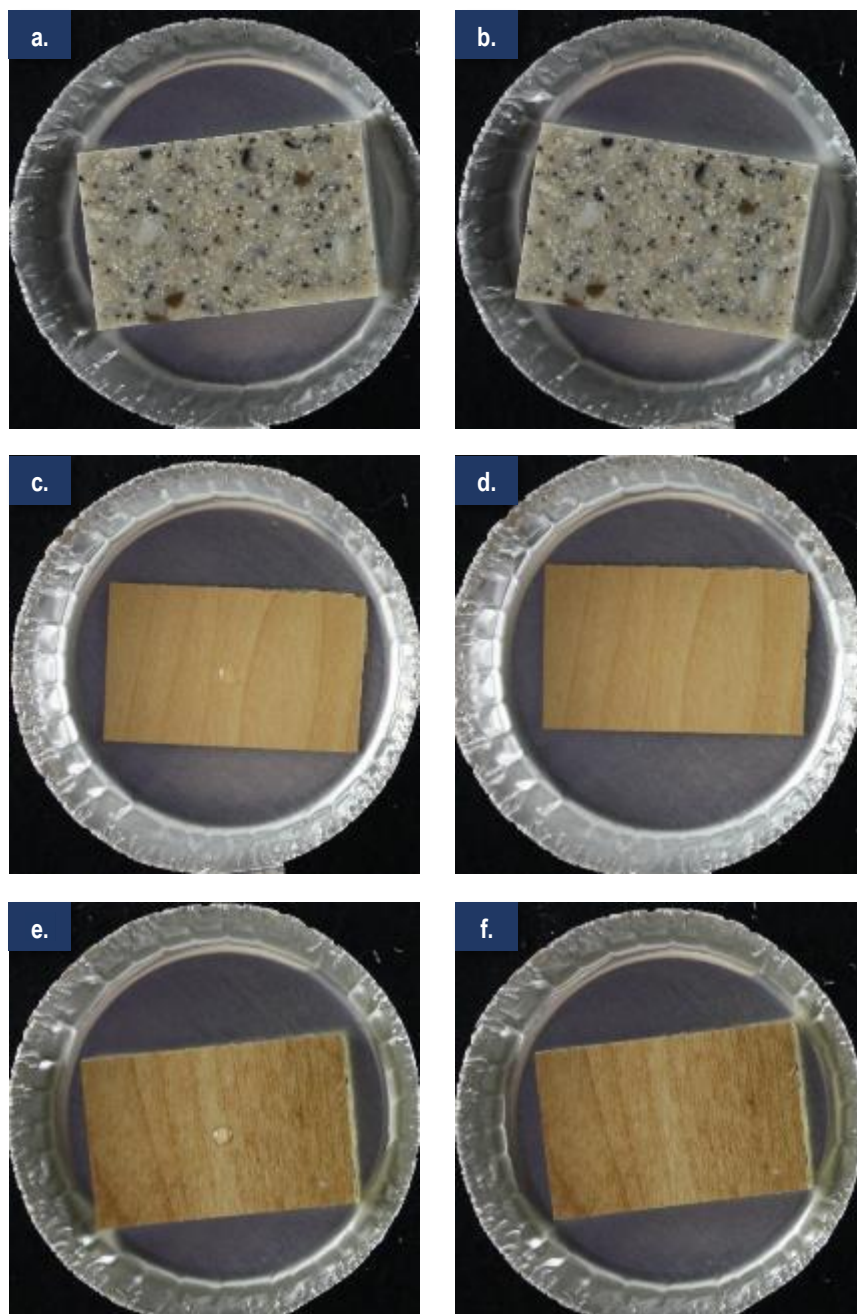


Figure 6-4. 2-CEPS droplet visible on the surface of the acrylic high-pressure laminate and vinyl composite plank immediately after spiking (a, c, and e, respectively) and test materials 72 hours after spiking, with no visible chemical contamination present on the surface (b, d, and f).

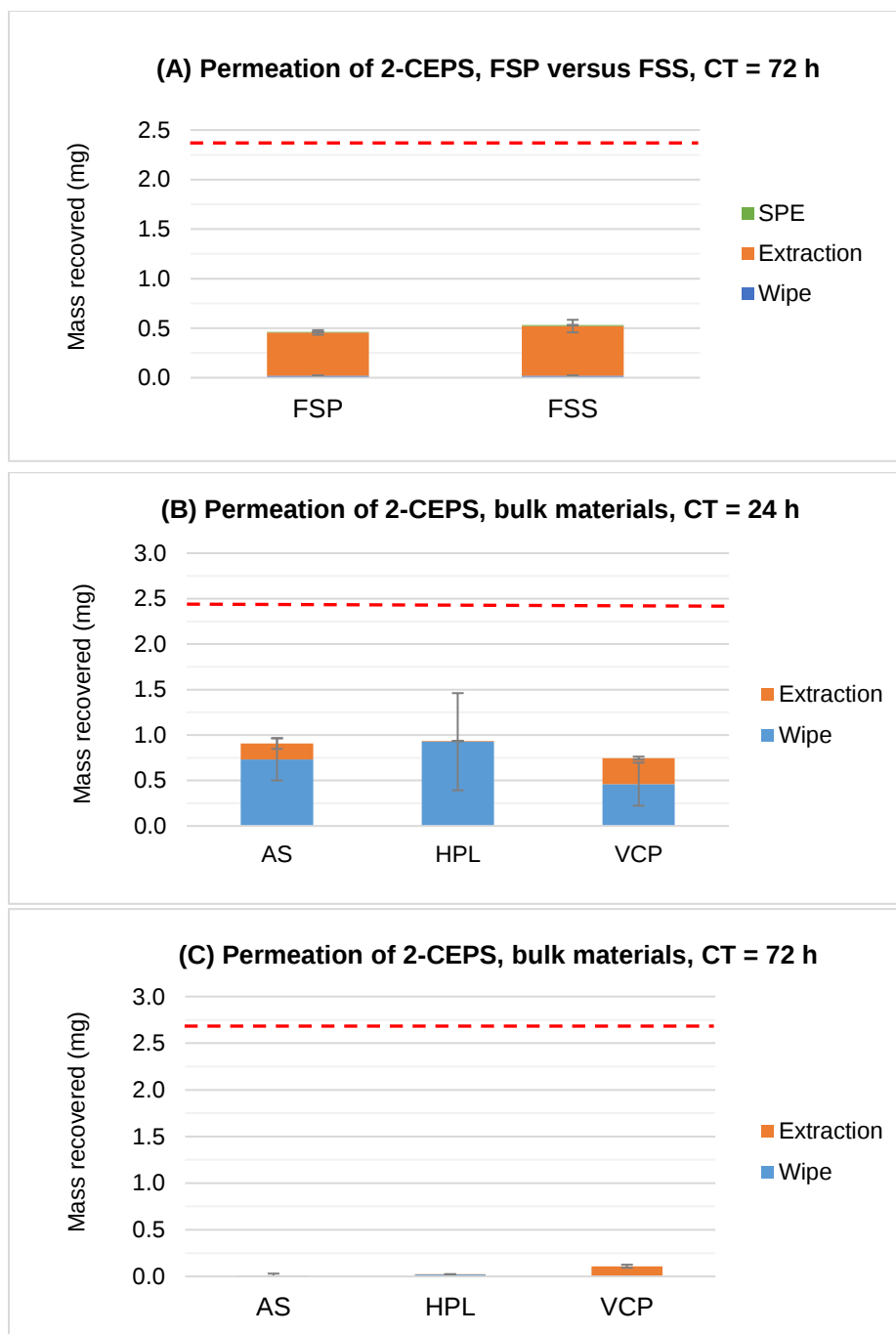


Figure 6-5. 2-CEPS permeation in LVAP-FSP and LVAP-FSS and bulk materials at CT = 72 h (A and C) and CT = 24 h (B); FSP and FSS: free-standing paint and sealant layers from LVAP permeation tests (wipe- sampled, then extracted); SPE: solid-phase extraction disk from LVAP permeation tests (extracted only); bulk materials were wipe sampled, then extracted. Dashed red lines represent recovered mass from control spike. Chemical mass results for each layer are averages ($n=3$) $\pm$ 1 SD.

6.3.2 Permeation of Malathion

Malathion had limited ability to transfer into and through tested paint and sealant. At three days after spiking onto a paint surface (CT = 72 h), 18% of total malathion mass recovered was detected in SPE, 10% in the FSP layer and 72% remained on the surface (Table 6-4). The corresponding ratios for the sealant were approximately 0.1% in SPE disk, 10% in the extracted FSS, and 90% on the sealant layer surface, as determined by wipe sampling (Table 6-5). The sum of recoveries from SPE, layer, and remaining malathion on the surface was 95% of the amount recovered from the stainless-steel coupon after 72 h. The same number (95%) was calculated for the sealant material.

The transport of malathion through the LVAP-FSP layer was studied at four different time-points: 3, 6, 24 and 72 h (Table 6-4). A consistent trend of decreasing and increasing average recovery of malathion among coupons versus permeable materials was apparent for the first 24 hours after application of malathion onto painted surfaces or FSP layers placed over a SPE disk. After 24 hours, a reverse phenomenon seemed to occur, where the chemical was diffusing back to the surface from the SPE and paint layer deposits, as the relative proportion of surface available chemical (recovered from wipe samples) had increased in the cumulative chemical mass recovered from wipes and extracted materials at 72 hours after application (Table 6-4). The total chemical mass recoveries from permeation cells versus CS results were equal at 95% for the combined components of LVAP-FSP and LVAP-FSS, indicating that malathion was stable on the two test surfaces and – unlike 2-CEPS – was not prone to volatilization-related losses in a simulated indoor environment.

Table 6-4. Permeation of malathion through FSP layers - chemical mass recovery results in LVAP components and associated control samples

CT [h]		SS		PSS		FSP		SPE
		Chemical mass recovery [mg]						
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction
3 h	Average	1.80	0.23	1.40	0.56	1.71	0.15	0.21
	SD	0.12	0.19	0.07	0.01	0.22	0.04	0.10
6 h	Average	1.60	0.12	1.63	0.40	1.50	0.14	0.29
	SD	0.08	0.06	0.08	0.06	0.21	0.08	0.15
24 h	Average	1.62	0.24	1.21	0.58	1.25	0.28	0.65
	SD	0.12	0.12	0.30	0.08	0.20	0.12	0.03
72 h	Average	1.67	0.32	1.55	0.47	1.42	0.20	0.35
	SD	0.48	0.28	0.27	0.071	0.14	0.032	0.13
PB	Average	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03

Results reported at < 0.03 were below LOQ

Results reported at < 0.03 were below LOQ

Table 6-5. Permeation of malathion through FSS layers - chemical mass recovery results in LVAP components and associated control samples

CT [h]		SS		FSS		SPE
		Chemical mass recovery [mg]				
		Wipe	Extraction	Wipe	Extraction	Extraction
72 h	Average	NT	2.1	1.41	0.20	0.0013
	SD	NA	0.02	0.31	0.033	0.0008
PB	Average	<0.03	<0.03	<0.03	<0.03	<0.03
Results reported at < 0.03 were below LOQ; NT – not tested; NA – not applicable						

The average malathion mass transferred into bulk materials is provided in Table 6-6. The bulk material recoveries (sum of wipe and extraction masses) were, on average 63% (VCP) to 97% (HPL) of the CS, which demonstrates minimal natural dissipation from test surfaces at a CT = 72 h. For comparison, 2-CEPS was either nondetected or present at less than 1% of the initial surface loadings spiked onto bulk materials (Table 6-3) and was nondetected on the surface of stainless steel. The highest percentage of malathion that transferred into the material was 24% of the total for acrylic while this percentage was 15% for both the laminate and vinyl.

Table 6-6. Permeation of malathion through building material surfaces-chemical mass recovery results in bulk material layers and associated control samples at CT= 72 h.

CT [h]		SS		AS		HPL		VCP	
		Chemical mass recovery [mg]							
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Wipe	Extraction
72 h	Average	NT	1.86	1.3	0.40	1.50	0.26	0.96	0.18
	SD	NA	0.065	0.26	0.10	0.021	0.091	0.31	0.13
	PB	NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03

Results reported at < 0.03 were below LOQ; NT – not tested; NA – not applicable
AS: acrylic solid surface countertop; HPL: high-pressure decorative laminate; VCP: vinyl composition plank

For both LVAP systems, the chemical analysis results agreed with visual characterizations of test surfaces performed immediately after spiking and at 72-h-long malathion permeation study. Figure 6-6 shows visible malathion contamination present on paint and sealant surfaces assembled in LVAP cells. The visual inspection tests also revealed a blistering of latex paint exposed to malathion (Figure 6-6c).

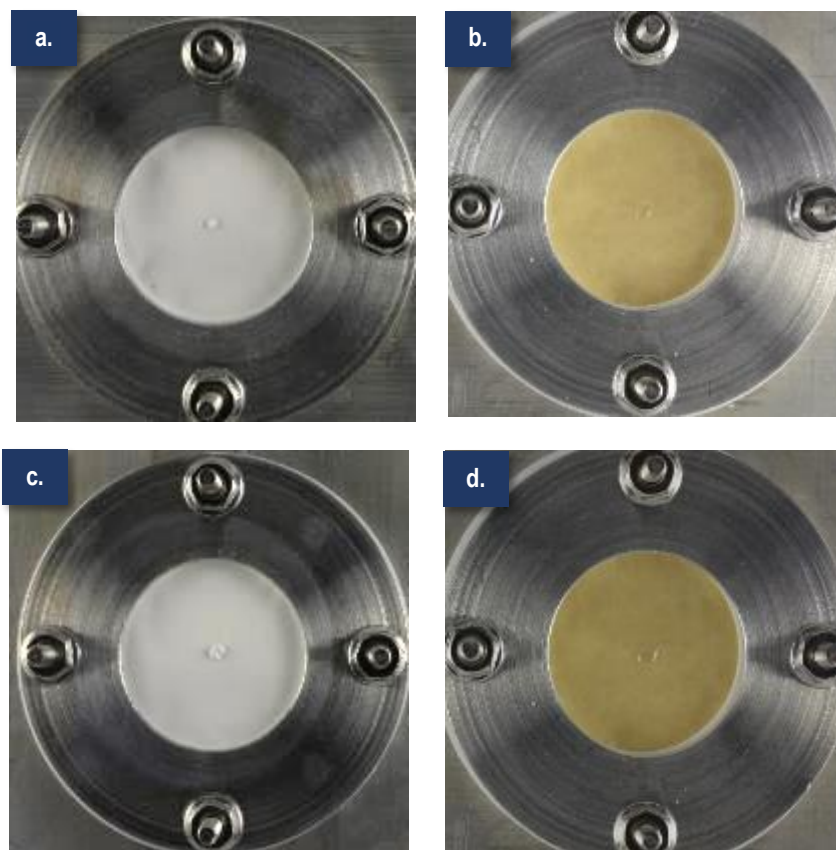


Figure 6-6. Malathion droplet on the surface of FS and FSS layers of LVAP immediately after spiking (a and b, respectively) and 72 hours after spiking (c and d, respectively).

For bulk materials, there was no visible malathion droplet on the surface of the acrylic surface (Figure 6-7b) and high-pressure laminate (Figure 6-7d) at CT=72 h. However, chemical analysis results indicated that chemical was mostly present in the surface-bound fraction collected via wiping, that was performed prior to bulk material extraction of the entire coupon. The observed visual differences could be related to the different surface-chemical interactions between surface materials and malathion, potentially affecting the spread of the droplet.

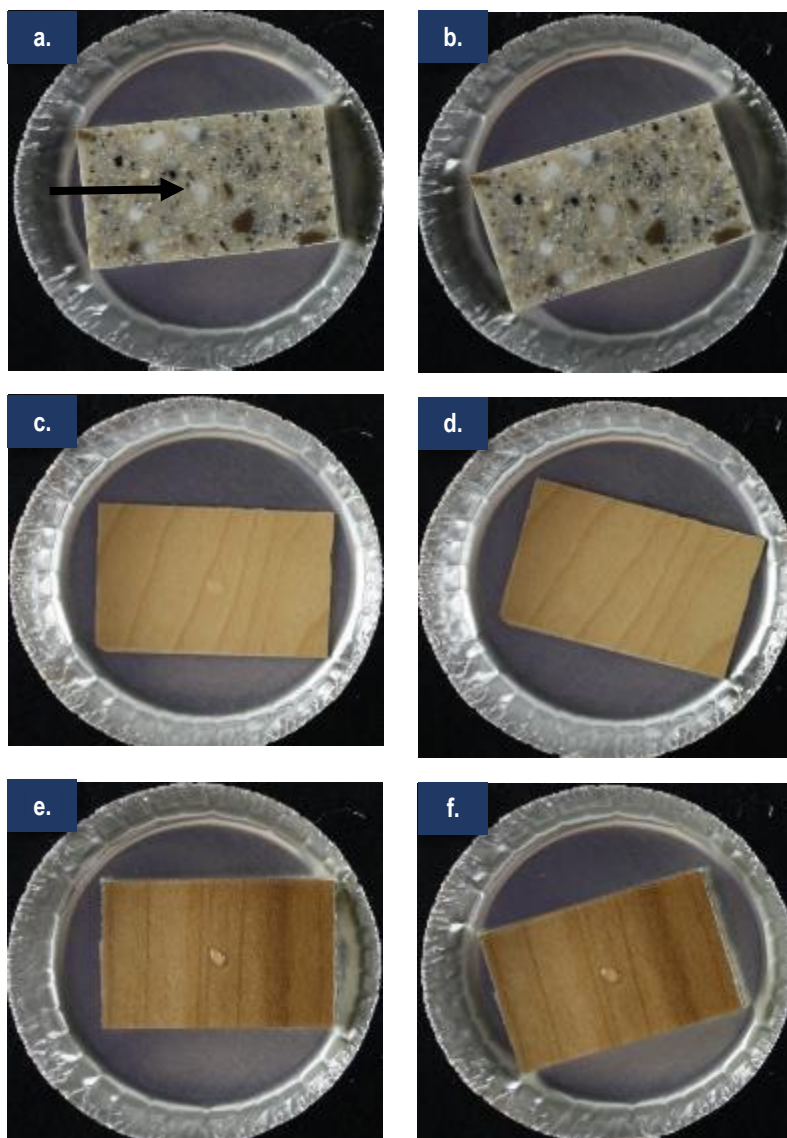


Figure 6-7. Malathion droplet visible on the surface of the acrylic high-pressure laminate and vinyl composite plank immediately after spiking (a, c, and e, respectively) and test materials after 72 hours (b, d, and f, respectively). Location of droplet after spiking identified by black arrow.

Figure 6-8 summarizes average recoveries and partitioning of malathion in permeation tests for both LVAP systems and bulk materials (CT = 72 h).

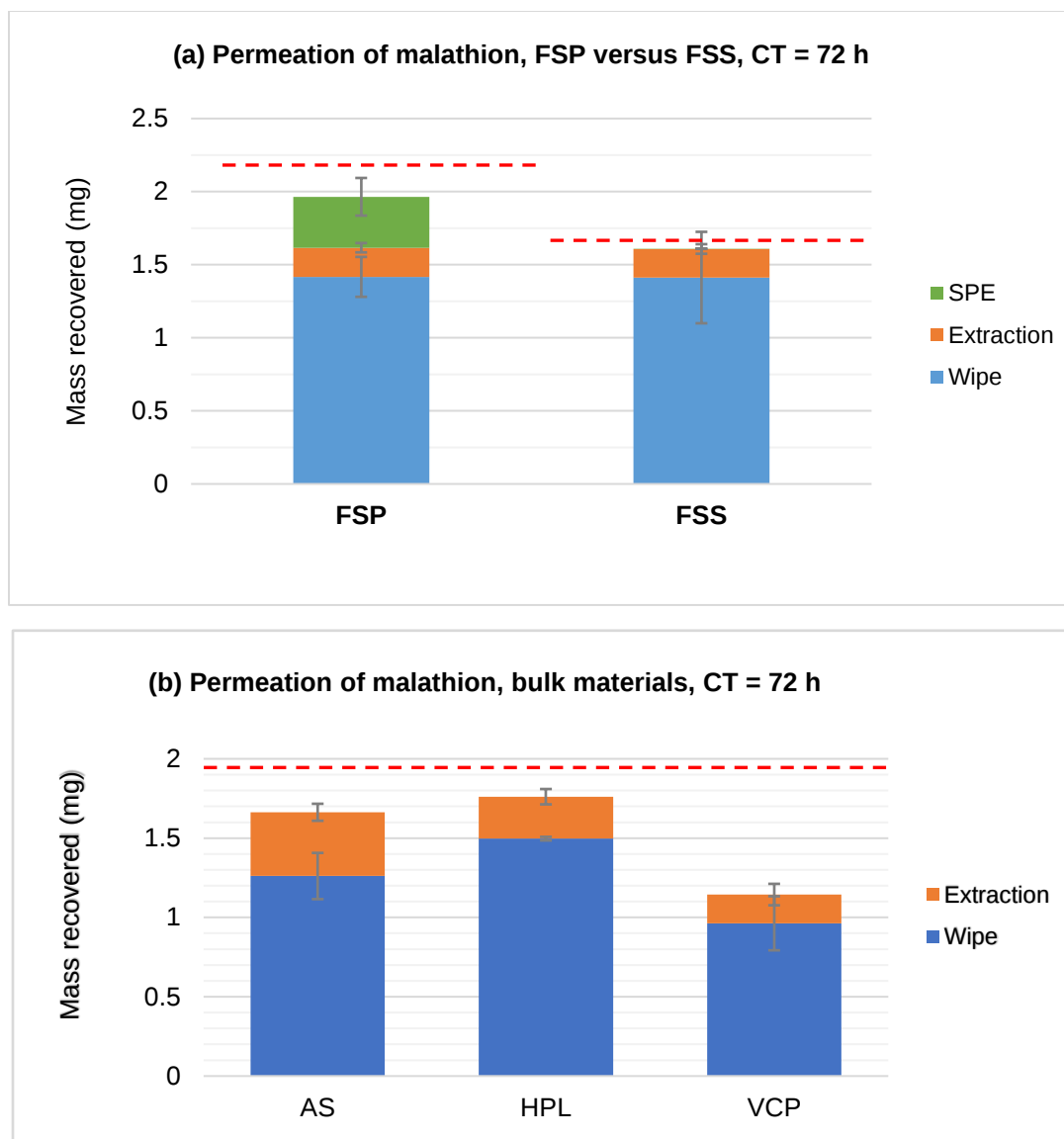


Figure 6-8. Malathion permeation in LVAP-FSP and FSS systems (a) and bulk materials (b) at CT = 72 h; FSP and FSS: free-standing paint and sealant layers from LVAP permeation tests (wipe sampled, then extracted); SPE: solid-phase extraction disk from LVAP permeation tests (extracted only); bulk materials were wipe-sampled, then extracted. Dashed red lines represent mass recovered from control spike. Chemical mass results for each layer are averages ($n=3$) $\pm$ 1 SD.

6.3.3 Permeation Comparisons 2-CEPS Versus Malathion

Overall, the surface permeation patterns of 2-CEPS and malathion were very different. Figure 6-9 shows a summary of the chemical fraction distribution in wiped surface fractions, extracted subsurface layers, and – for LVAP cells – extracted SPE disks representing porous subsurface below the FSP and FSS layers. Except for HPL material, 2-CEPS was detected primarily in the extractable fractions (minimal on the surface), while malathion was detected primarily on the surface.

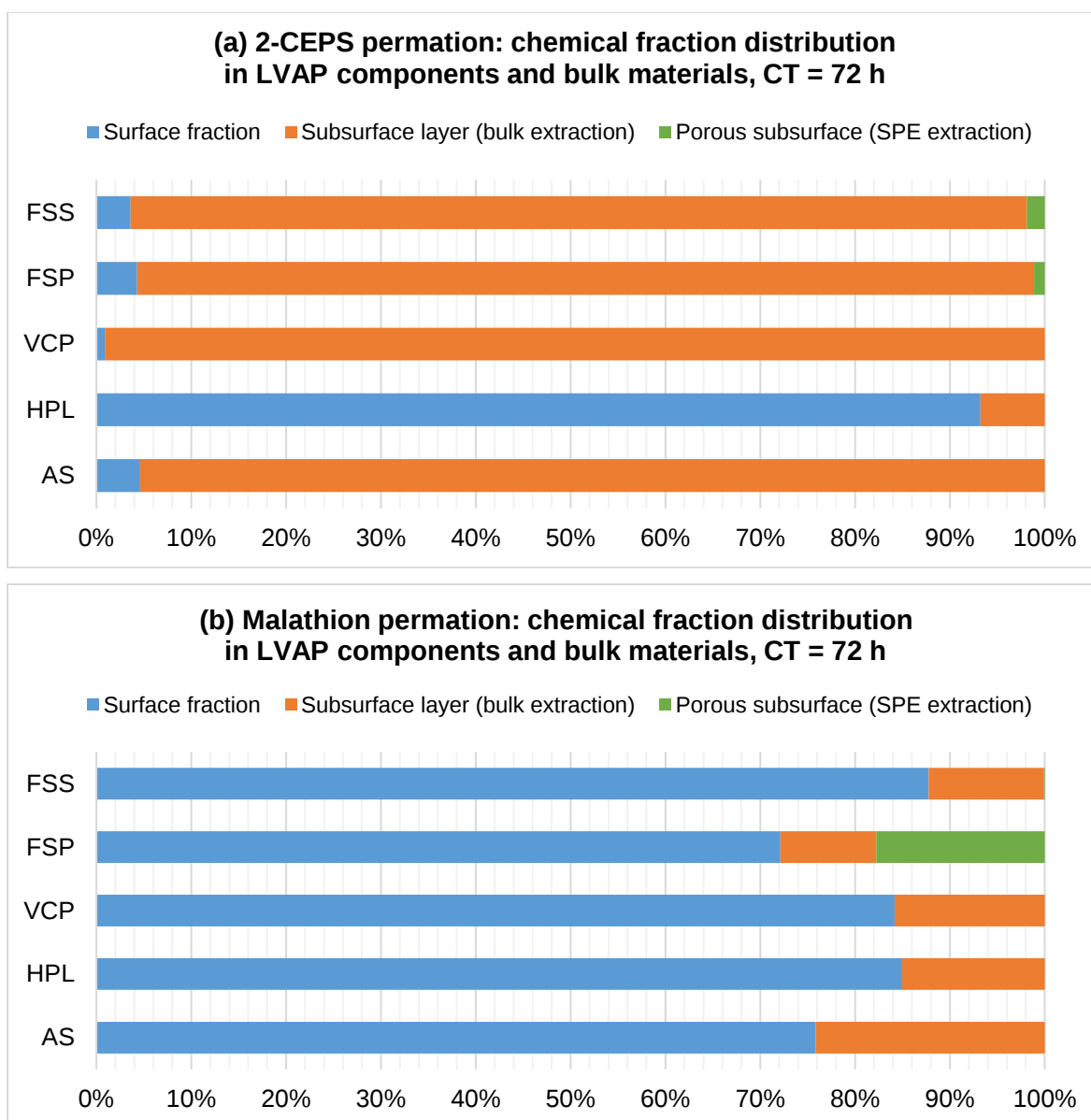


Figure 6-9. Average percent distribution of the total 2-CEPS (a) and malathion (b) mass detected in LVAP components and bulk materials during permeation testing, CT=72 h. FSP and FSS: free-standing paint and sealant layers from LVAP permeation tests (wipe-sampled, then extracted); SPE: solid-phase extraction disk from LVAP permeation tests (extracted only); bulk materials were wipe-sampled, then extracted.

Material impacts of malathion on free-standing layers were further studied using FESEM. Microscopy images of malathion-exposed FSP and FSS layers are shown in Figure 6-10. Bulk material-malathion surface interactions were not included. The higher permeation of malathion through FSP layers was linked to the blistering of paint observed during a visual inspection of surfaces (Figure 6-6c) and confirmed by FESEM analyses (Figure 6-10a). No significant blistering or “bubbling” was observed during a visual inspection of malathion-exposed FSS layers (Figure 6-6d). However, microscopy indicated some structural changes that appeared to be a result of expanding and shrinking, resulting in the uneven, wrinkled appearance of the edge of the malathion-exposed areas (Figure 6-10b).

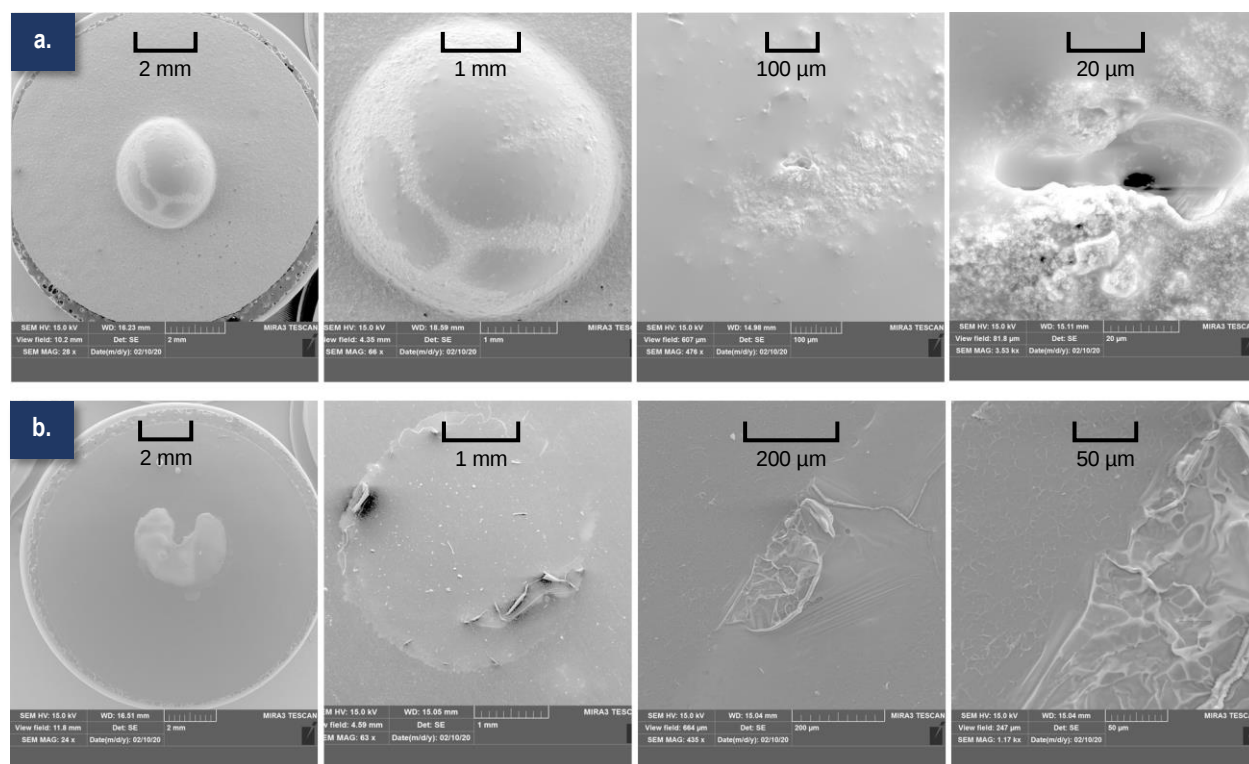


Figure 6-10. FESEM images of malathion-exposed FSP (a) and FSS (b) layers at different magnifications. Contact time of malathion was 72 h for both layers; remaining chemical droplet was removed from surfaces before testing using a cotton swab. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage at magnifications ranging from 24 x to 3.53k x.

Coupons were vacuumed in a desiccator with an attached carbon filter in chemical hood to volatilize any residual malathion on coupons prior to sputter coating and FESEM analysis under vacuum. The “bubble”-like appearance of paint blisters – as shown in Figure 6-10a – was likely due to thinning of the paint at the location of the blister, and due to changes in elasticity of the paint that was then lifted from the SEM stub surfaces during vacuum microscopy analyses. These observed structural changes are in line with findings of post-sampling visual inspection of FSP layers, where surface perforations – hole or multiple smaller holes – were observed after sampling of malathion (the perforations were not visible before wipe sampling). An example malathion-exposed FSP layer with the visible hole after sampling is shown in Figure 6-11.

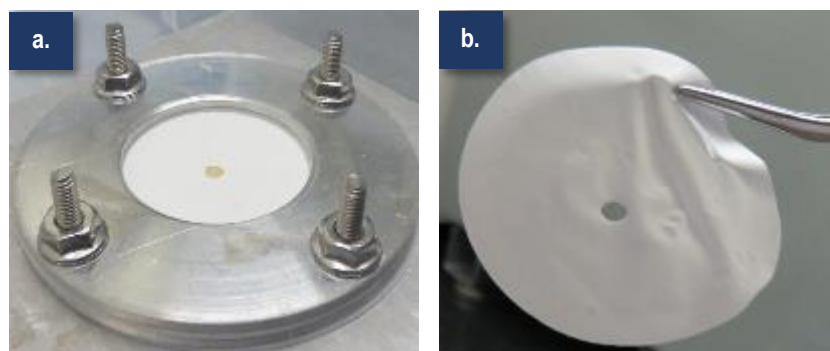


Figure 6-11. Postsampling perforation of malathion-exposed FSP layer; FSP postsampling in the LVAP (a) and prior extraction (b).

Like FSP layers, most of the PSS surfaces showed blistering and damage to the paint layer after sampling (swabbing) of malathion (Figure 6-12), suggesting that exposure to malathion significantly affected the structural integrity of both types of acrylic-latex layers, i.e., free layers placed on the top of porous SPE and painted directly over the nonporous stainless-steel material.

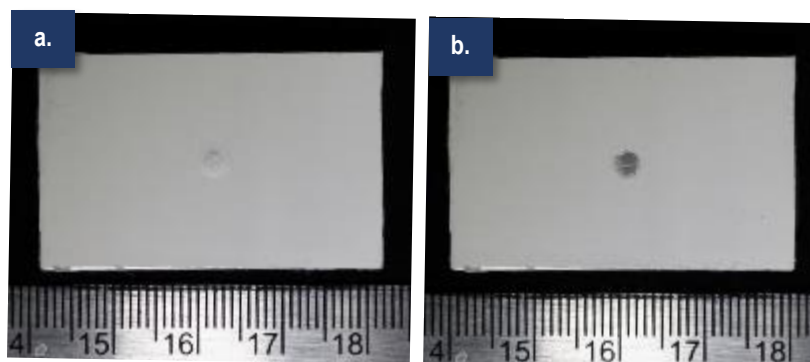


Figure 6-12. Blistering of paint layers observed after 72-h-long exposure of PSS to malathion, with a chemical droplet still present on the surface (a) and PSS surface after surface sampling, with visible stainless steel exposed in the previously blistered area (b).

The visual inspection of PSS surfaces did not indicate any material changes, and no perforations of sealant layers were observed after the surface sampling or extraction of polyurethane coated stainless steel exposed to malathion. Noteworthy is that no damages of paint or sealant layers were observed for 2-CEPS-contaminated coupons (Figure 6-3); consequently, 2-CEPS exposed materials were not analyzed using FESEM.

High-magnification FESEM analyses of procedural blank paint and sealant layers (materials that were not exposed to malathion) suggested a higher surface pore morphology of FSP versus FSS layers (Figure 6-13).

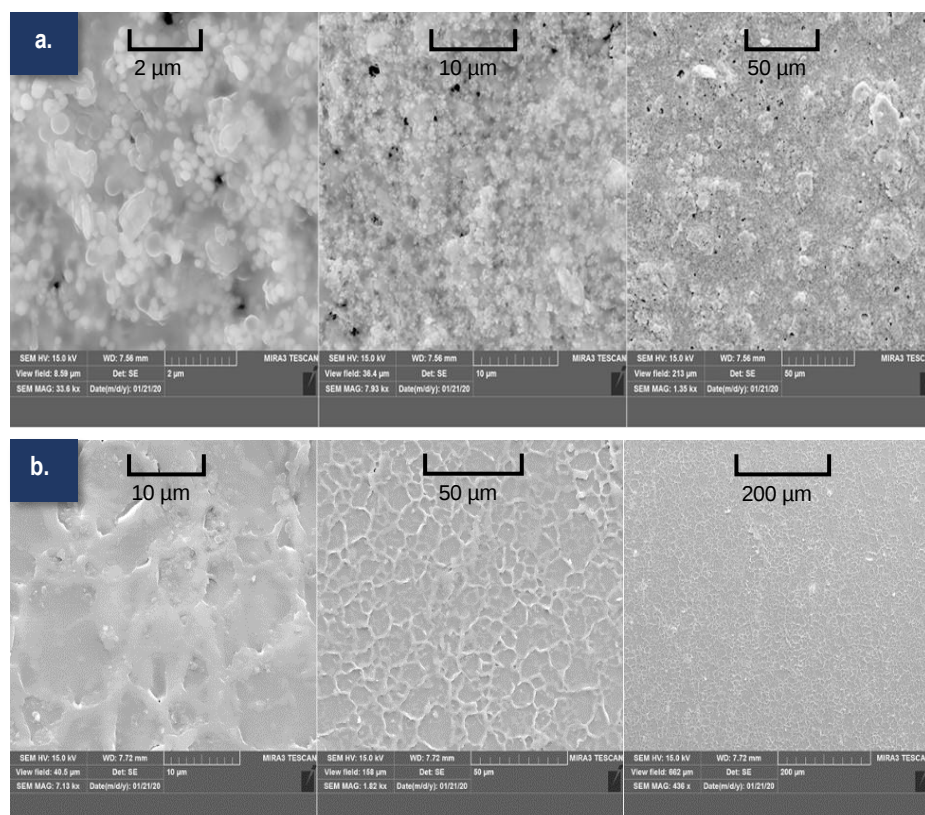


Figure 6-13. FESEM images of nonexposed FSP (a) and FSS (b) layers. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage at magnifications ranging from 436 x to 33,600 x.

Overall, the permeation of target chemicals to the sublayer disk was believed to be due to the combined effects of the chemical volatility that governed the surface stability (persistence) of 2-CEPS and malathion, the surface layer permeability, and the chemical resistance of the surface layer to target chemicals.

6.4 Decontamination Testing

All decontamination experiments were performed against permeated chemicals using either LVAP or standalone bulk material coupons (acrylic, laminate, and vinyl). LVAP allowed for a multilayered measurement of residual chemical contamination in the subsurface porous layer (SPE) and top paint and sealant layer following surface decontamination. For bulk material testing, postdecontamination sampling allowed for the measurement of residual chemical masses on the coupon surface and in the subsurface layer. Figure 6-14 shows an example of different types of materials subjected to a single application of liquid decontaminant, followed by an overnight dwell time. This baseline decontamination procedure using concentrated germicidal bleach as decontaminant was generally highly efficacious for decontamination of 2-CEPS and malathion from the LVAP system, with results described in Section 6.4.1. Malathion decontamination from LVAP-FSP systems was lower (Section 6.4.2), and modifications to the baseline decontamination procedure were evaluated with results given in Section 6.5.

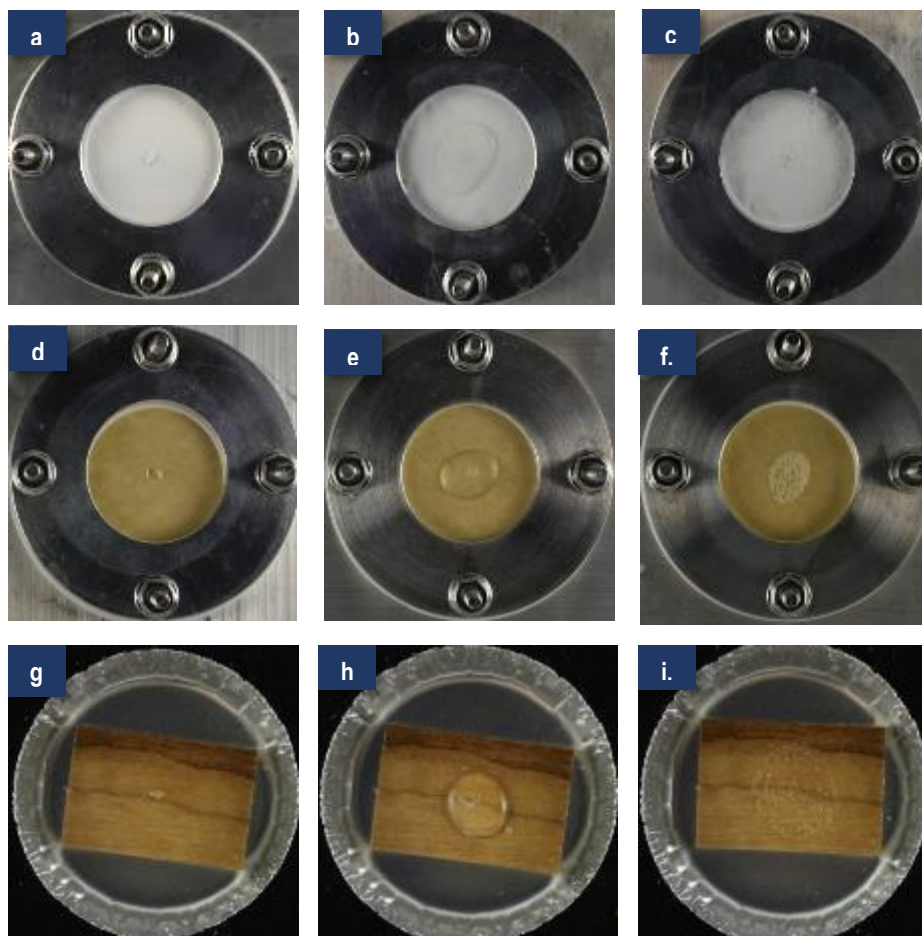


Figure 6-14. Example of baseline decontamination procedure. Shown are decontamination of malathion-contaminated LVAP-FSP, LVAP-FSS, and VLP at CT=72 h (a, d, g, respectively) using concentrated germicidal bleach (b, e, h), followed by overnight dwell of the decontaminant (DT=18 h) (c, f, i).

6.4.1 Baseline Decontamination – 2-CEPS

The efficacy of the baseline decontamination procedure, one application of concentration of concentrated germicidal bleach, followed by an overnight (18-h) DT of the decontaminant, is given in Tables 6-7 through 6-11. Figures 6-15 and 6-16 summarize 2-CEPS and malathion distribution in the chemical fraction associated with different types of LVAP components, before decontamination treatment and after decontamination. Positive controls were wiped and extracted at the same time as the LVAP components.

The baseline decontamination procedure resulted in high (average DE > 95%) reduction of 2-CEPS in decontaminated LVAP-FSP and LVAP-FSS samples (TCs) versus nontreated controls (PCs) (Table 6-7 and 6-8). However, this significant reduction is associated with only a small fraction of 2-CEPS remaining at the start of the baseline decontamination due to the significant volatilization of 2-CEPS from test surfaces, estimated as 75 to 99% depending on the type of material. The volatilization-related attenuation of 2-CEPS from LVAP systems was discussed in more detail in Sections 6-2 and 6-3.

Table 6-7. Decontamination baseline of 2-CEPS from LVAP-FSP components and chemical mass recovery results for associated control samples

Sample type		SS		PSS		FSP		SPE	x̄ DE [% ± 1 SD]	
		Chemical mass recovery [mg]								
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction		
Decontamination Procedure: 1 application of concentrated germicidal bleach, DT = 18 h										
TC	Average	<0.03	NT	<0.03	0.057 (J)	<0.03	0.015	0.003 (J)	95.7 ± 1.0	
	SD	NA	NA	NA	0.006	NA	0.003	0.001		
PC	Average	<0.03	NT	0.020 (J)	0.87	0.003 (J)	0.42	0.0054 (J)		
	SD	NA	NA	0.005	0.08	0.001	0.030	0.002		
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03		
Results reported at < 0.03 were below LOQ: (J) – estimated value, detected at below LOQ (S/N >10); NT – not tested; NA – not applicable										

Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N > 10); NT – not tested; NA – not applicable

Table 6-8. Decontamination baseline of 2-CEPS from LVAP-FSS components and chemical mass recovery results for associated control samples

Sample type		SS		SSS		FSS		SPE	̄ DE [% ± 1 SD]	
		Chemical mass recovery [mg]								
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction		
Decontamination Procedure: 1 application of concentrated germicidal bleach, DT = 18 h										
TC-V	Average	<0.03	NT	<0.03	0.0026 (J)	<0.03	0.014 (J)	<0.03	97.0 ± 3.5	
	SD	NA	NA	NA	0.001	NA	0.01	NA		
PC-V	Average	<0.03	NT	0.0035 (J)	0.61	0.011 (J)	0.41	0.008 (J)		
	SD	NA	NA	0.001	0.05	0.002	0.05	0.009		
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03		
Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10); NT – not tested; NA – not applicable										

Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N > 10); NT – not tested; NA – not applicable

Recoveries from the SPE disk, paint/sealant layer, and surface wipe are shown in Figure 6-15a.

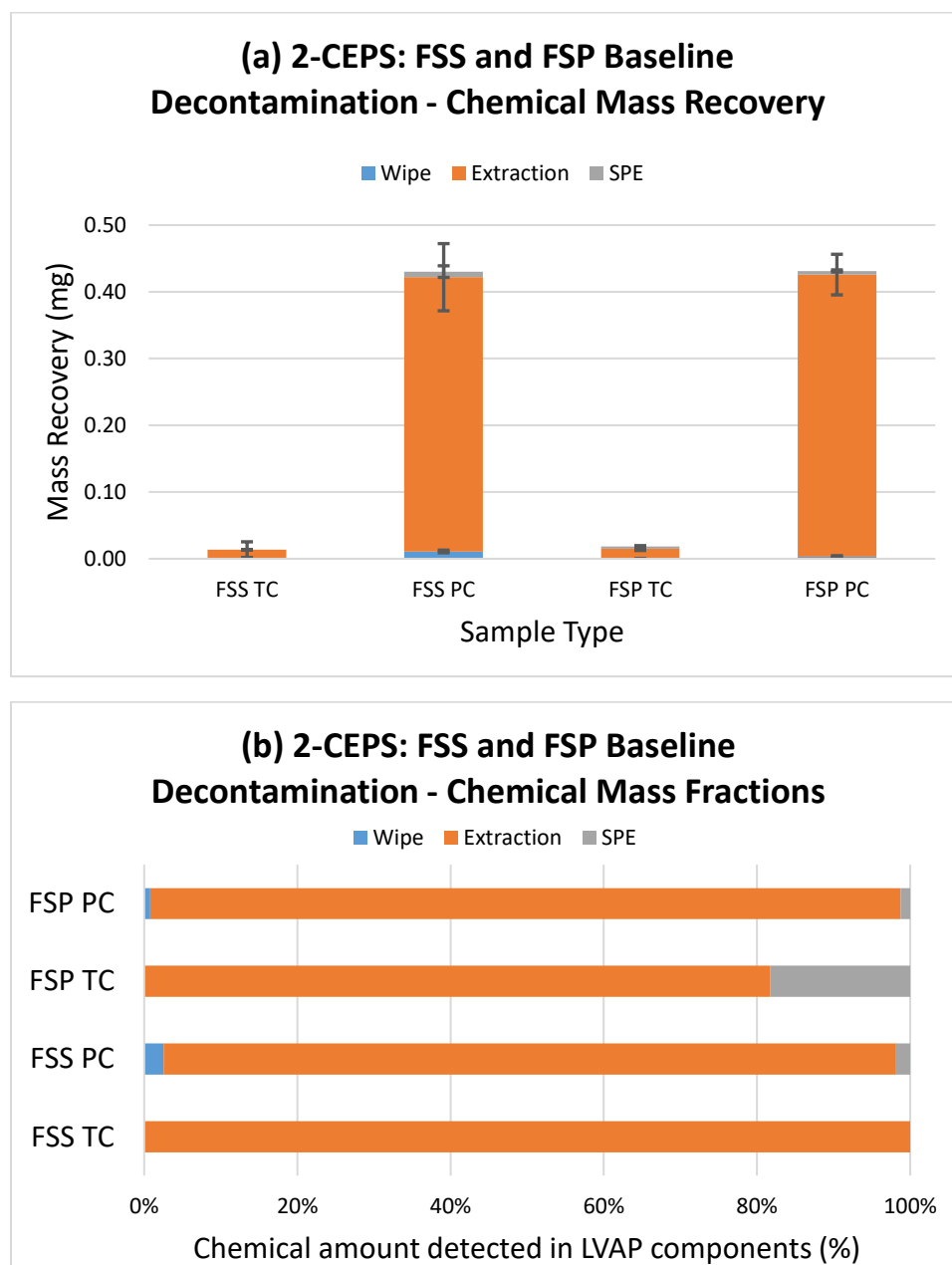


Figure 6-15. Decontamination baseline for 2-CEPS from FSS and FSP layers compared to associated positive control samples; TC – decontaminated test sample; PC – non-decontaminated positive control sample. Chemical mass recovery results (a) for each layer are averages (n=3), and chemical fraction results (b) are relative percent contributions of each fraction to the total chemical mass detected in non-decontaminated and decontaminated samples.

Figure 6-15b shows 2-CEPS chemical mass fraction distribution in decontaminated and non-decontaminated LVAP samples. Analysis of chemical amounts detected in decontaminated TC samples showed no detection of 2-CEPS on the surface or in the top surface layers that were sampled as part of the surface wipe. The extracted FSP layer had a higher relative reduction of extractable chemical mass than FSS, with a 3% and 13% reduction in 2-CEPS concentration in the SPE disk, respectively. However, the relative contribution of the SPE-bound chemical amount to the total chemical detected increased slightly (4.4%) in the decontaminated paint layer, when compared to the nontreated PC. The decontaminated LVAP-FSS had no detection of 2-CEPS in the SPE (Figure 6-15b).

Decontamination tests of bulk materials contaminated with 2-CEPS were not performed, as volatilization-related losses rendered concentrations of this chemical on the surface to below LOQ levels after 72-h-long CT under normal indoor environmental conditions (see Table 6-3, Figure 6-5c; Section 6.3.1).

6.4.2 Baseline Decontamination – Malathion

Decontamination of malathion that transferred through the LVAP-FSP paint layer into SPE was not effective when using one application of concentrated germicidal bleach (DT = 18 h). The average reduction of total chemical mass in the decontaminated LVAP-FSP samples was just above 50% (average DE = 54 ± 8.7 ; Table 6-9). The decontamination occurred mostly on the paint surface, with less than 20% relative reduction of chemical concentration in the SPE (Table 6-9, Figure 6-16b). The average total reduction of malathion in the LVAP-FSS tests – for which no appreciable permeation of malathion to the SPE was observed – was 99% (average DE = $99 \pm 0.77\%$; Table 6-10), with no malathion detections, post decontamination, in the wipe-sampled surface of the sealant. The average reduction in the malathion amount in the extracted sealant fraction of decontaminated TCs was over 0.9 mg – or 90% – when compared to nondecontaminated PCs (Figure 6-16a). The extractable sealant layer chemical fraction was the only component of the LVAP-FSS with trace-level detections of malathion (Table 6-10, Figure 6-16b). The sealant-based test had overall lower recovery of malathion than the paint-based decontamination experiments, with average 1 mg versus 1.4 mg malathion recovered from nonexposed LVAP-FSS and LVAP-FSP samples, respectively (Figure 6-16a), corresponding to an average 47 and 67% chemical recovery, when compared to the associated CS results. Since no analytical problems with spiking, extraction, or instrumental analysis were identified for FSS samples and high decontamination efficacy was reported consistently among replicates, no further optimization of decontamination conditions was deemed necessary.

Table 6-9. Decontamination baseline of malathion from LVAP-FSP components and chemical concentration results for associated control samples

Sample type		SS		PSS		FSP		SPE	̄x DE [% ± 1 SD]	
		Chemical mass recovery [mg]								
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction		
Decontamination Procedure: 1 application of concentrated germicidal bleach, DT = 18 h										
TC	Average	< 0.03	NT	0.24	0.20	0.24	0.19	0.23	54 ± 8.7	
	SD	NA	NA	0.03	0.08	0.07	0.04	0.004		
PC	Average	1.86	NT	0.67	0.51	0.86	0.31	0.27		
	SD	0.10	NA	0.27	0.19	0.13	0.07	0.08		
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03		
Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N>10); NT – not tested; NA – not applicable										

Table 6-10. Decontamination baseline of malathion from LVAP-FSS components and chemical concentration results for associated control samples

Sample type		SS		SSS		FSS		SPE	̄x DE [% ± 1 SD]	
		Chemical mass recovery [mg]								
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction		
Decontamination Procedure: 1 application of concentrated germicidal bleach, DT = 18 h										
TC	Average	See Table 6-9	0.23 (J)	0.02 (J)	<0.03	0.0089 (J)	<0.03	99 ± 0.77		
	SD		NA	0.03	NA	0.0063	NA			
PC	Average		1.51	0.10	0.91	0.090	0.0005 (J)			
	SD		0.29	0.01	0.31	0.015	NA (S)			
PB	Average		<0.03	<0.03	<0.03	<0.03	<0.03			
Results reported at < 0.03 were below LOQ: (J) – estimated value, detected at below LOQ (S/N>10); NT – not tested; NA – not applicable										

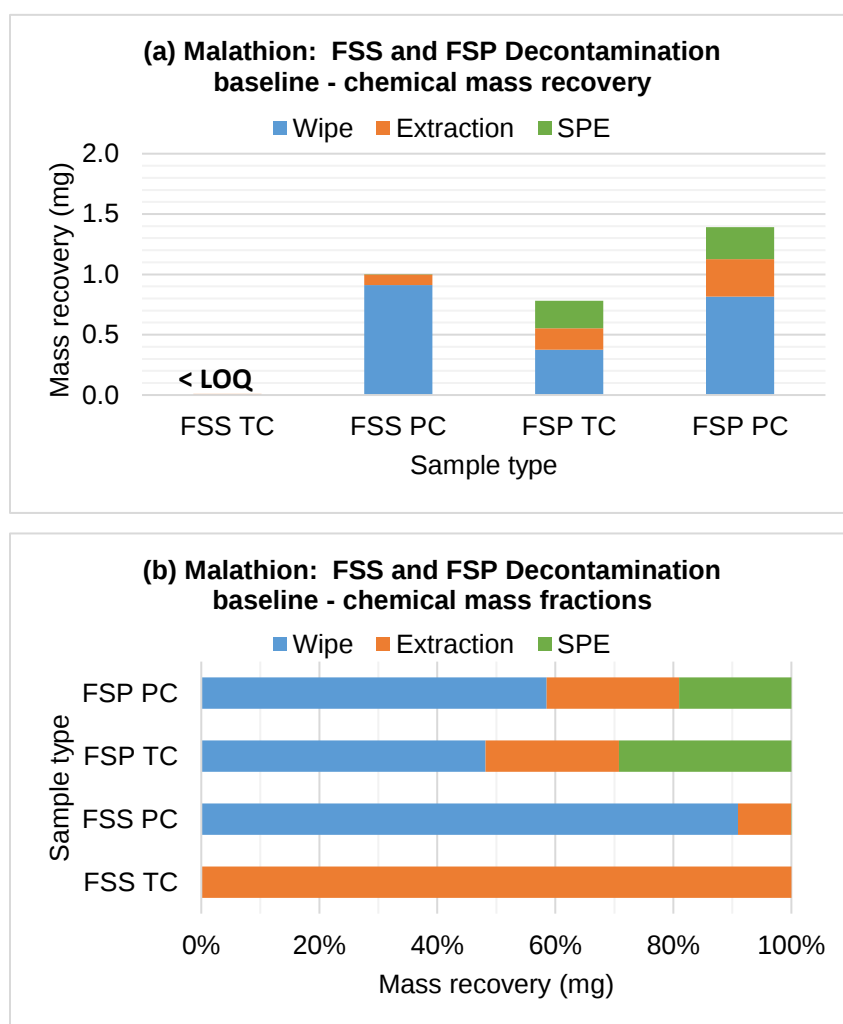


Figure 6-16. Decontamination baseline results for malathion from LVAP-FSS and LVAP-FSP components compared to associated positive control samples; TC – decontaminated test sample; PC – non-decontaminated positive control sample. Chemical mass recovery results for each layer are averages, and chemical fraction results are relative percent contributions of each fraction to the total chemical mass recovered in non-decontaminated and decontaminated samples.

The higher efficacies of decontamination observed for LVAP-FSS are likely related to the lower permeability of the sealant layer to malathion, with a higher relative amount of chemical fraction available for surface decontamination. Additionally, based on the analysis of the FESEM images of bleach exposed paint and sealant layers (Figure 6-17), the FSS appeared to be less permeable to bleach than FSP, with larger and more pronounced salt crystal formations visible on the surface of the sealant after overnight drying corresponding to decontamination DT (18 h) (Figure 6-17b). The higher amount of concentrated hypochlorite solids present on the surface of the sealant was likely one of the surface-dependant experimental variables contributing to higher decontamination efficiency observed for FSS layers.

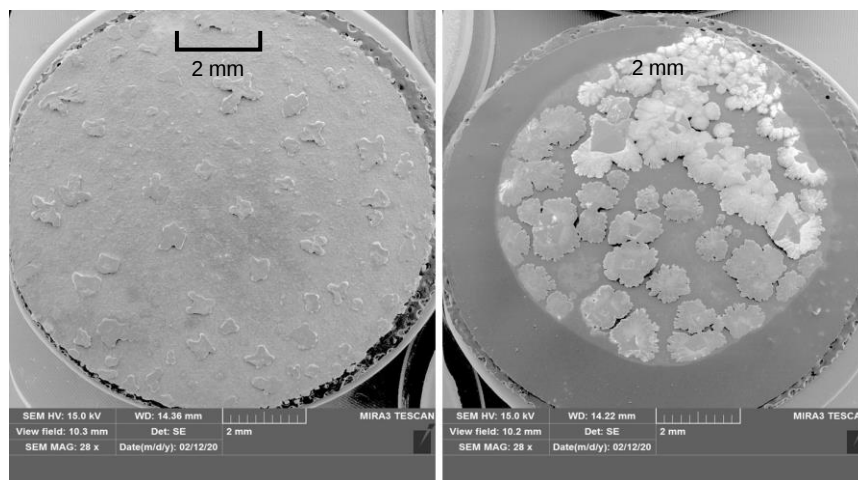


Figure 6-17. Surface of concentrated germicidal bleach-exposed FSP (a) and FSS (b) layers after overnight drying of decontaminant; surfaces were not contaminated before application of bleach. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage; magnification levels are shown in each image.

After completion of the LVAP decontamination experiments, one application of concentrated germicidal bleach with overnight drying – was used for the decontamination of malathion from bulk building materials. The procedure resulted in the degradation of malathion to below detectable levels in both surface and subsurface of the decontaminated test materials, corresponding to average DE $\geq 98\%$. The material-specific results for decontamination of malathion are given in Table 6-11.

Table 6-11. Decontamination baseline of bulk materials with malathion and chemical mass results for associated control samples

Sample type		SS		AS		HPL		VCP	
		Chemical mass recovery [mg]							
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Wipe	Extraction
Decontamination Procedure: 1 application of concentrated germicidal bleach, DT = 18 h									
TC	Average	NT		<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
	SD			NA	NA	NA	NA	NA	NA
PC	Average	2.06	NT	1.04	0.41	1.10	0.63	0.87	0.78
	SD	0.18	NA	0.32	0.13	0.58	0.28	0.41	0.10
PB	Average	NT	NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
x̄ DE (%)		NA		≥ 98		≥ 98		≥ 98	
Results reported at < 0.03 were below LOQ; NT – not tested; NA – not applicable									
AS: acrylic solid surface countertop; HPL: high-pressure decorative laminate; VCP: vinyl composition plank									

Concentrated germicidal bleach was compatible with all bulk materials tested in this study, with no visible damage or discoloration to any test materials after decontamination. Like the LVAP experiments, dried out sodium hypochlorite crystals were visible on test surfaces with overnight drying of bleach (Figure 6-18). FESEM analyses were not performed for bulk material testing.

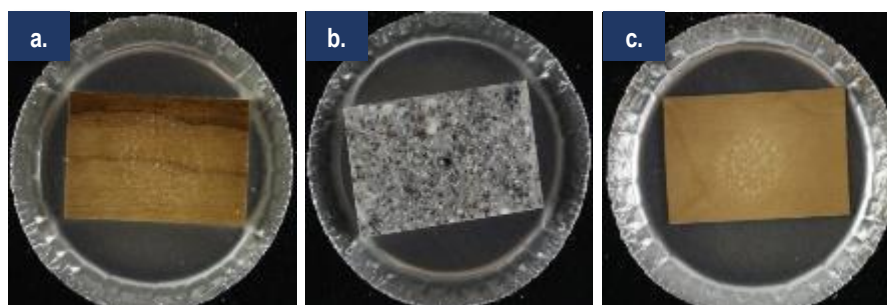


Figure 6-18. Surface of bulk materials after decontamination of malathion using two applications of concentrated germicidal bleach; vinyl plank flooring material, VPL (a); acrylic countertop surface material (b), and high-pressure laminate countertop material, HPL (c).

6.5 Modified Decontamination Processes

Changes to the baseline decontamination approach were considered only for materials that had measurable amounts of the targeted chemical remaining on the surface after the single application of concentrated germicidal bleach with a DT=18 h.

6.5.1 Decontamination Modifications – 2-CEPS

The 2-CEPS mass recoveries following decontamination with bleach (DT = 18 h) from the LVAP-FSP and LVAP-FSS systems yielded amounts near the LOQ (Tables 6-7 and 6-8, respectively, Section 6.4.1), attributed to the high degree of volatilization of this chemical after a 72-hour contact time of 2-CEPS with the FSP and FSS layers (as also observed in the permeation tests described in Section 6.3.1) plus the effective degradation (95.7% decontamination efficacy) of 2-CEPS by bleach (DT=18 h). Further modifications to the decontamination of these materials were not considered so that research could focus on more difficult-to-clean materials that were contaminated with malathion.

6.5.2 Decontamination Modifications – Malathion

Recoveries for malathion from the LVAP sealant wipe and extraction following the decontamination with bleach (DT=18 h) yielded amounts near or below the LOQ (Table 6-10, Section 6.4.1). A single application of bleach resulted in a 99% decontamination efficacy. Therefore, modifications to the baseline decontamination approach using bleach were not considered for this sealant. Instead, the effectiveness of other decontamination procedures was tested for the simulated painted surfaces. The first step was testing of the efficacy of a repeated application of the same concentrated germicidal bleach, followed by testing of different specialized and COTS decontaminants, with single and two-step applications tested in parallel to each other. All decontamination solutions used in this phase of this study were either hypochlorite- or hydrogen peroxide-based oxidizers (Table 3-6).

Both classes of decontaminants were previously reported as chemistries effective for surface degradation of both malathion and structurally similar CWAs such as VX [3,4]. Selected decontaminants (Splash-Less Bleach and EasyDECON DF200) contain surfactants and other active ingredients (Table 3-6) that are intended to improve decontamination efficacy of chemical (and biological) agents. These additives were considered as potentially advantageous for decontamination of malathion that (partially) permeated into and through painted surfaces. Table 6-12 shows results for each decontamination method tested for improved efficacy of malathion degradation from LVAP-FSP components. The corresponding decontamination baseline results established in the initial experiments were provided in Table 6-9 (Section 6.4.1.).

Table 6-12. Modified decontamination methods for LVAP-FSP components contaminated with malathion and chemical concentration results for associated control samples

Sample type		SS		PSS		FSP		SPE	$\bar{x}$ DE [% $\pm$ 1 SD]
		Chemical mass recovery [mg]							
		Wipe	Extraction	Wipe	Extraction	Wipe	Extraction	Extraction	
Modified Decontamination Procedure # 1: 2 applications of concentrated germicidal bleach, DT = 2 h + 18 h									
TC	Average	NT	NT	0.35	0.38	0.23	0.08	0.11	70 $\pm$ 26
	SD	NA	NA	0.17	0.07	0.17	0.06	0.074	
PC	Average	NT	NT	0.86	0.59	0.93	0.18	0.24	
	SD	NA	NA	0.15	0.08	0.10	0.08	0.12	
PB	Average	NT	NT	<0.03	<0.03	<0.03	<0.03	<0.03	
Modified Decontamination Procedure # 2: 1 application of Splash-Less Bleach, DT = 18 h									
TC	Average	0.18	NT	0.64	0.93	0.218	0.67	0.83	16 $\pm$ 7.0
	SD	0.05	NA	0.07	0.02	0.119	0.47	0.50	
PC	Average	1.96	NT	0.57	1.17	0.55	0.48	0.97	
	SD	0.16	NA	0.16	0.14	0.21	0.12	0.28	
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03	
Modified Decontamination Procedure # 3: 2 applications of Splash-Less Bleach, DT = 2 h + 18 h									
TC	Average	0.03 (J)	NT	0.44	0.74	0.23	0.47	0.41	45 $\pm$ 17
	SD	NA (S)	NA	0.24	0.15	0.19	0.27	0.35	
PC	Average	1.96	NT	0.57	1.17	0.55	0.48	0.97	
	SD	0.16	NA	0.16	0.14	0.21	0.12	0.28	
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03	
Modified Decontamination Procedure # 4: 1 applications of EasyDECON DF200, DT = 18 h									
TC	Average	0.005 (J)	NT	0.15	1.44	0.26	0.79	0.38	9.7 $\pm$ 0.63
	SD	0.0032	NA	0.11	0.22	0.03	0.07	0.12	
PC	Average	0.90	NT	0.42	1.33	0.49	0.50	0.63	
	SD	0.23	NA	0.23	0.26	0.31	0.20	0.28	
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03	
Modified Decontamination Procedure # 5: 2 applications of EasyDECON DF200, DT = 2 h + 18 h									
TC	Average	<0.03	NT	0.30	1.12	0.20	0.15	0.76	37 $\pm$ 9.9
	SD	NA	NA	0.20	0.25	0.07	0.19	0.13	
PC	Average	0.90	NT	0.42	1.33	0.49	0.50	0.63	
	SD	0.23	NA	0.23	0.26	0.31	0.20	0.28	
PB	Average	<0.03	NT	<0.03	<0.03	<0.03	<0.03	<0.03	
Results reported at < 0.03 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10); NT – not tested; NA – not applicable									

Only one out of five procedures tested outperformed a single application of concentrated germicidal bleach (Table 6-11; included in Figure 6-19), namely, the procedure using a double application of the same concentrated germicidal bleach (CGB x 2 on Figure 6-19). However, the intra-test variation between the decontaminated subset of LVAP-FSP components was relatively high (RSD = 70%), with two out of three replicate samples showing a DE of approximately 50% and one LVAP-FSP showing DE > 98%, with no detections of malathion in subsurface layer and below LOQ detections in SPE and surface layers. The analytical results were confirmed by the reparation of samples from extracts and reanalysis. No visual differences were observed for replicate LVAP-samples at the end of the decontaminant dwell time or during sampling or extraction. A Student's *t*-test confirmed that a statistically significant difference could not be determined ($p < 0.05$) between the efficacies recorded with a single application of the concentrated germicidal bleach versus the double application of the same product ($p = 0.71$).

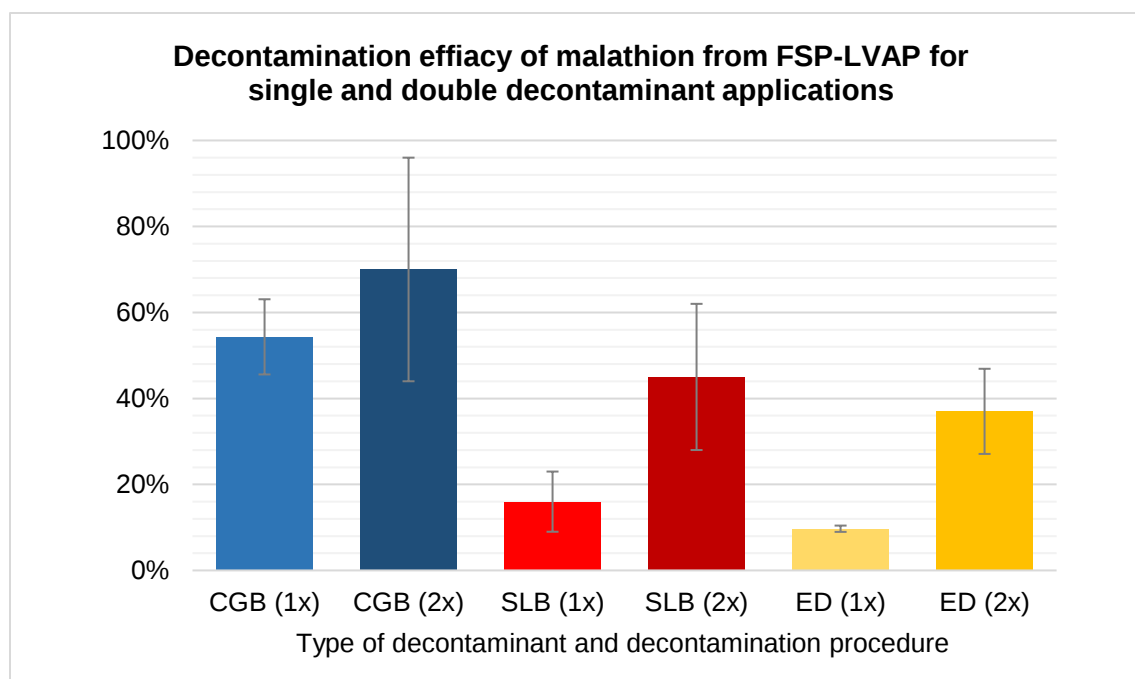


Figure 6-19. Average decontamination efficacy of malathion from FSP-LVAP for all single- and multistep decontamination approaches tested; results are shown as $\bar{x}$ %DE $\pm$ 1 SD; CGB – concentrated germicidal bleach; SLB – Splash-Less Bleach; ED – EasyDECON DF200; 1x and 2 x – procedure using one or two applications of decontaminant, respectively.

A two-step application of Splash-Less Bleach and the procedure using two applications of EasyDECON DF200 resulted in moderate decontamination efficacies (average DEs <50%; Table 6-12, Figure 6-19), which were similar to a single application of concentrated germicidal bleach, suggesting that the presence of surfactants in the Splash-Less Bleach does not improve overall DE in comparison to the germicidal bleach. Further, a change in oxidizer from sodium hypochlorite to activated hydrogen peroxide in EasyDECON DF200 did not improve overall efficacy either. The oxidizer concentration was highest in concentrated germicidal bleach (65,000 parts per million (ppm) free available chlorine (FAC)), followed by Splash-Less Bleach (34,500 ppm FAC), followed by EasyDECON DF200 (hydrogen peroxide concentration in the finished blend approximately 3.6%). A direct comparison of the impact of oxidant chemistries and

concentrations should also consider the reaction mechanism on a molar basis which may be oxidant-dependent.

The reapplication of a decontaminant improved the overall decontamination efficacy with an average increase of 29% and 27% for the Splash-Less Bleach and EasyDECON DF200, respectively (Figure 6-19). A Student's *t*-test indicated that this apparent improvement in efficacy values between a single and double application is insignificant considering calculated *p*-values of 0.09 and 0.16 for the pairwise comparisons of single versus double application of the Splash-Less Bleach and EasyDECON DF200, respectively.

A detailed analysis of the LVAP component-specific chemical mass reductions shows that degradation occurred mainly at the surface-bound non-permeated fraction (Figure 6-20). Two applications of concentrated germicidal bleach resulted in the overall largest decrease in chemical mass that was observed in all chemical components.

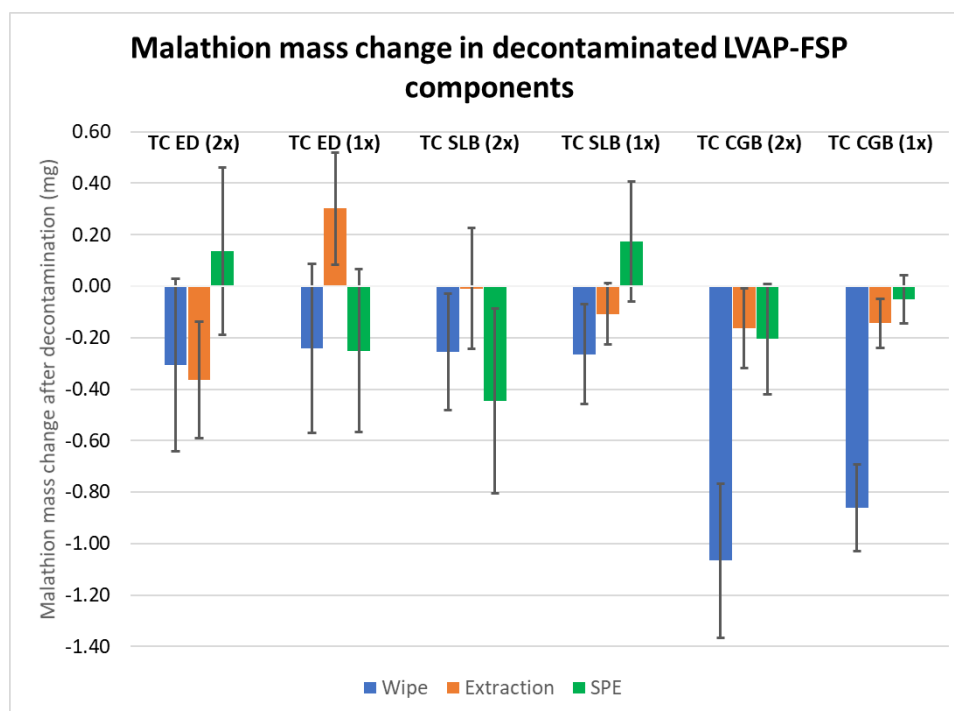


Figure 6-20. Average malathion mass change in the LVAP-FSP test coupon (TC) components relative to the corresponding components of the associated positive control (PC) samples. CGB – concentrated germicidal bleach; SLB – Splash-Less Bleach; ED – EasyDECON DF200; 1x and 2x - procedure using one or two applications of decontaminant.

The three “positive” mass changes in Figure 6-20 indicate that the malathion mass recovery from the test coupons was greater than the malathion mass recovery of the positive control which would be unexpected considering the measured degradation for other components of the LVAP-FSP. These positive mass changes are also associated with near equal or greater SDs than the calculated change in mass. While a positive mass change may be indicative of a transfer of malathion to a different layer in the presence of a decontaminant, it is more likely this is due to the limited number of replicates (*n*=3). Similarly,

the “negative” mass changes for the FSP layer and the SPE disk suggest degradation of malathion but are also associated with high SDs. Hence, within the limits of this study, there is no clear evidence that any of the tested decontaminants (germicidal concentrated bleach, Splash-Less Bleach, and EasyDECON DF200) and decontamination approaches (single versus double application) degrades malathion that permeated into the FSP and farther into the SPE disk. All degradation of malathion is limited to malathion on the surface. A double application of a decontaminant appeared to improve the decontamination of the surface (Table 6-12; Figure 6-20). However, these improvements in comparison to a single application were not statistically significant. Concentrated germicidal bleach was shown to effectively degrade malathion from FSP surfaces without apparent changes in the chemical permeation between surface and sublayers of treated samples (CGB (1x) and (2x) Figure 6-20).

The effect of concentrated germicidal bleach on material properties of paint and sealant layers was studied by FESEM. Figures 6-21 and 6-22 show microscopic images of FSP and FSS layers exposed to germicidal bleach with sodium hypochlorite solid formed on the decontaminated surface after overnight exposure, compared to corresponding laboratory blank coupons. Bleach-exposed FSS and FSP layers have both abundant crystals and amorphous solids. The paint layers seemed to be more structurally affected by bleach (Figure 6-21). However, the topography of the bleach-exposed polyurethane sealant has visually changed as well (Figure 6-22).

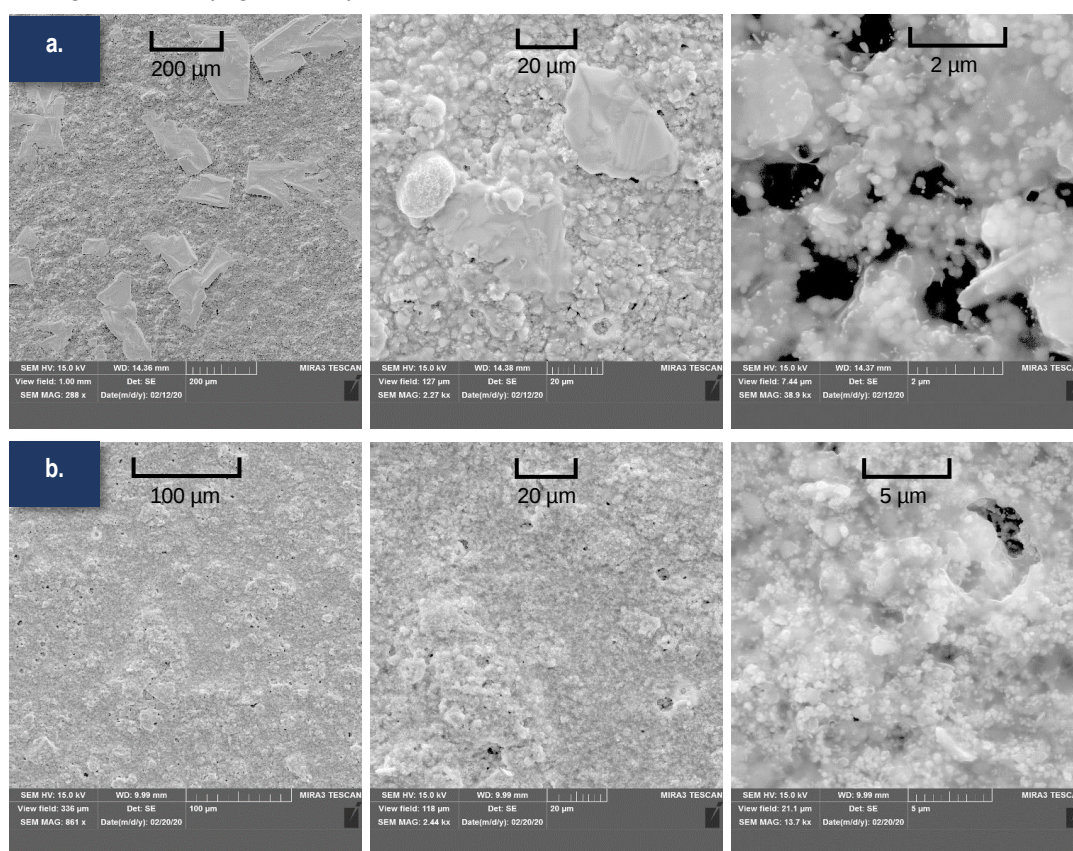


Figure 6-21. Surface of bleach-exposed FSP surfaces (a) and/or nonexposed laboratory blank FSP layers (b) layers after overnight drying of decontaminant; surfaces were not contaminated before application of the regular germicidal bleach. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage; magnifications levels are shown in each image.

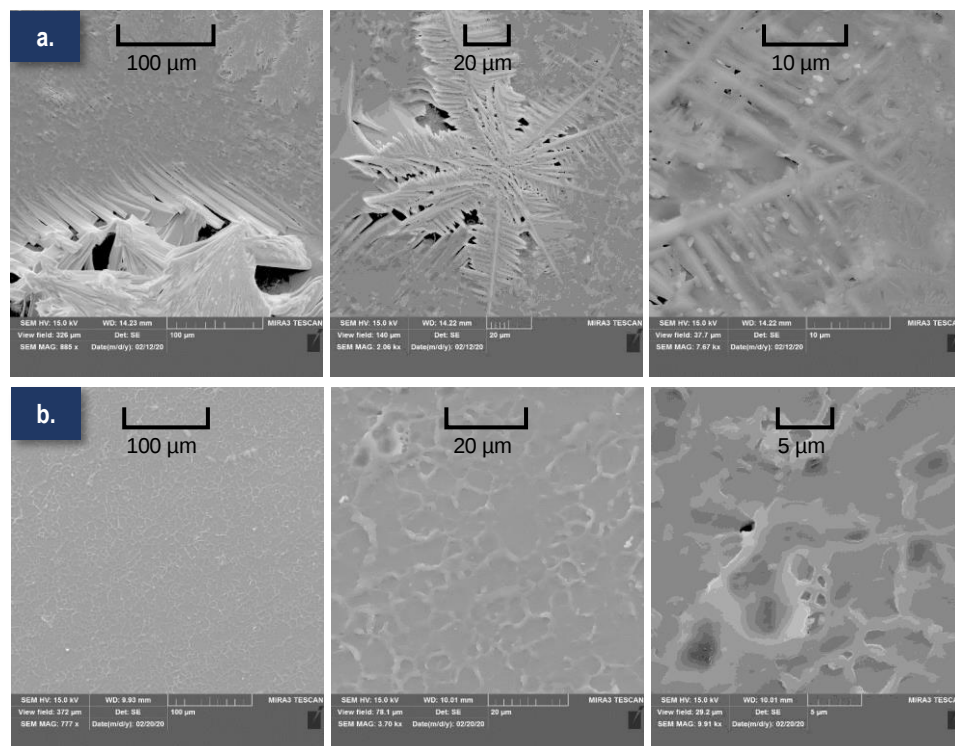


Figure 6-22. Surface of bleach-exposed FSS surfaces (a) and corresponding laboratory blanks, or nonexposed FSS layers (b) layers after overnight drying of decontaminant; surfaces were not contaminated before application of the regular germicidal bleach. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage; magnifications levels are shown in each image.

Bleach treatment of FSP and FSS layers previously contaminated with malathion showed similar salt formations, with visible agglomerations of solids over the contamination hot spots (Figure 6-23). Bands of sodium hypochlorite solids were also visible near the edge of paint blisters that appeared to be compromised by chemical exposure to malathion. That structural damage to the paint was likely allowing easier migration of bleach into the paint layer itself as well as into SPE. However, the interaction of malathion and bleach with paint layers over a porous substrate was not studied during the microscopy portion of this work – all microscopy experiments were performed using FSP and FSS materials assembled onto metal stubs (Section 3.9). Additional experiments, including FESEM analyses of actual building surfaces treated with different types of oxidizers – with and without surfactants – may assist in a better understanding of material-chemical-decontaminant interactions that happen in real life.

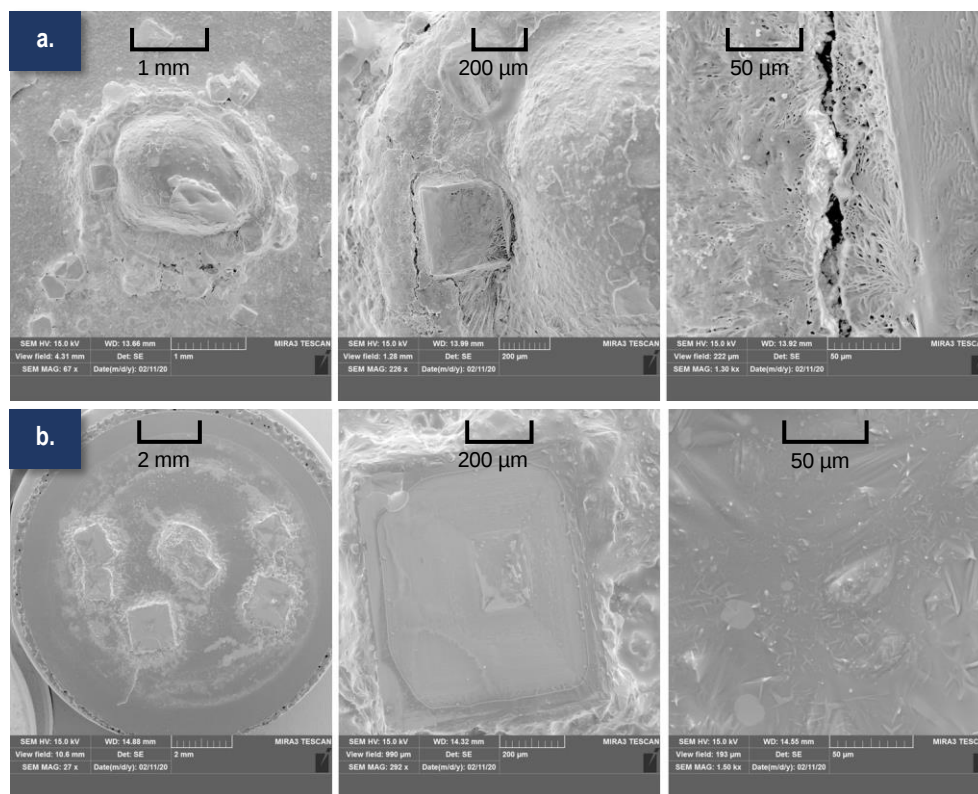


Figure 6-23. Surface of malathion and bleach-exposed FSP (a) and FSS surfaces (b) after 72-h-long exposure to chemical, followed by overnight drying of decontaminant. Images of carbon-coated layers were taken using 15.0 kV accelerating voltage; magnifications levels are shown in each image.

A comparison of results from the malathion decontamination from LVAP-FSP (Figure 6-16) to decontamination efficacy results for the reference material (stainless steel) showed that decontamination efficacies of nonporous stainless steel were significantly higher than the decontamination for LVAP tests for which average DE values ranged from 91% to $\geq 99.4\%$ (Figure 6-24) and did not vary significantly between the type of decontaminant and decontamination procedures tested with calculated Student's p -values always greater than 0.05 except for the single application of Splash-Less Bleach against all other approaches.

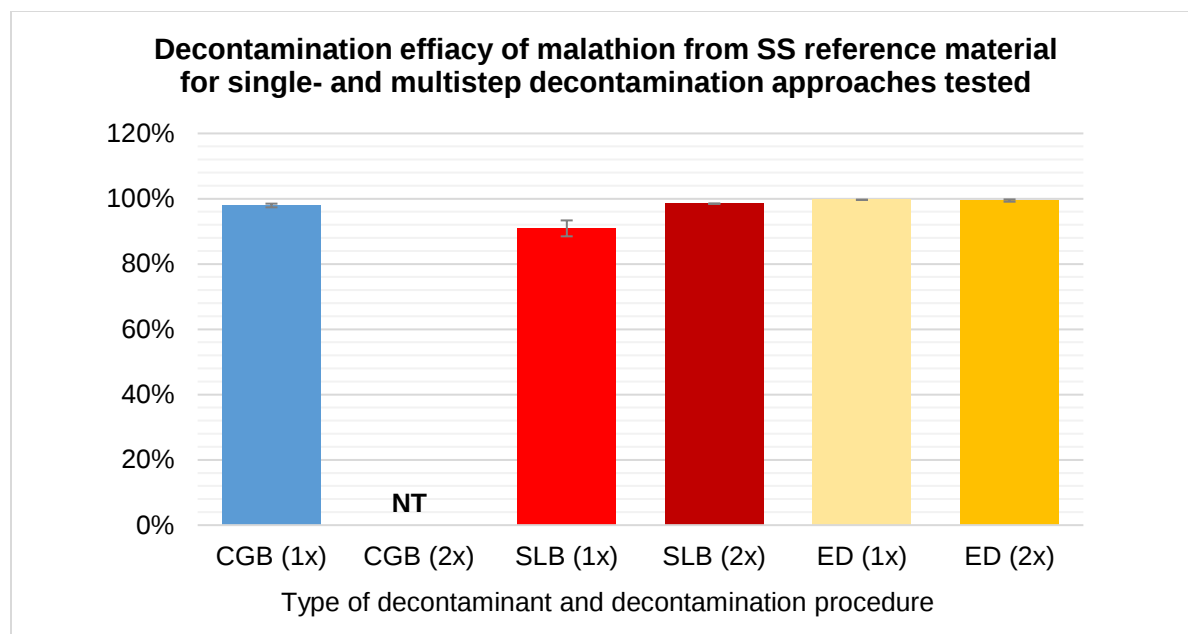


Figure 6-24. Average cumulative decontamination efficacy of malathion from stainless steel for all single- and multistep decontamination approaches tested; results are shown as $\bar{x}$ %DE $\pm$ 1 SD; CGB – concentrated germicidal bleach; SLB – Splash-Less Bleach; ED – EasyDECON DF200; 1x and 2 x - procedure using one or two applications of decontaminant, respectively; NT – not tested.

Summary

The main objectives were to develop testing equipment and analytical methods to study the transport of selected chemicals into the subsurface layers of permeable building materials at conditions mimicking indoor environmental conditions. For that purpose, permeation cells were developed, and tests were performed to determine the efficacy of decontamination technologies and procedures for degradation of chemicals that have (partially) absorbed into permeable building materials. Modifications of decontamination solution/solutions were considered to address potential limitations of traditional techniques/unmodified decontaminants.

The main findings of this study are:

- I. Material properties of building materials – permeability, porosity, chemical resistance, type of the surface coating – and physicochemical properties of chemicals affect the chemical absorption and permeation mechanisms. Polyurethane sealant coating was found to be relatively nonpermeable by tested chemicals when compared to latex-acrylic paint.
- II. Volatilization related losses can be a significant factor contributing to the natural attenuation of chemicals from building materials. In the absence of a chemical decontaminant or other types of degradation, indoor environmental conditions should be considered essential factors contributing to surface dissipation of chemicals.
- III. Chemical oxidation-based degradation occurs mainly on surfaces, with no or very limited decontamination of subsurface layers observed for decontamination procedures tested, with volatile compounds being rendered to nondetectable levels with a one-step application of concentrated germicidal bleach. For noncoated building materials, 2-CEPS dissipated from indoor surfaces due to volatilization (chemical-surface contact time of 72 h). For more surface-persistent malathion, the highest overall degradation from both surface and subsurface layers of building materials was achieved by using two applications of concentrated germicidal bleach, followed by an overnight dwell time. Other decontamination procedures using two different types of oxidation chemistries with the addition of surfactants – had lower degradation efficacies for permeated malathion.
- IV. Current and past research indicates that the use of stronger oxidizers appears to be a better decontamination option for permeated chemicals. However, decontaminant corrosivity – and overall material compatibility with the surface materials and underlying substrate – should be considered during the selection of decontamination procedure. Based on visual assessments of test materials, and confirmed by microscopy analyses, both chemical and decontaminant applications can affect material properties of the surface coatings.

This study provides a detailed understanding of the permeation of chemicals into indoor building materials and building material surrogates covered with custom-made layers of different commercial coatings. This research contributes to the understanding of the material-, chemical- and decontaminant-specific effects on the degradation of permeated chemicals for several oxidation-based methods.

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8. ASTM D3924-16 "Standard Specification for Standard Environment for Conditioning and Testing Paint, Varnish, Lacquer, and Related Materials"
9. ASTM E376 "Standard Practice for Measuring Coating Thickness by Magnetic-Field or Eddy-Current (Electromagnetic) Testing Methods"
10. ASTM D1005 "Standard Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers"

Appendix A: Supporting Information

A-1 Methods for manufacturing paint and sealant layers

The methods below were used to prepare PSS, FSS, FSP and FSS coupon materials for this study. Test materials are listed in Section 3-2. The methods below are intended to be step-by-step instructional material for the analyst

A-1.1 Preparation of Paint Coatings on Stainless-steel Substrates

Painted stainless-steel surface will be produced using a modified method from ASTM D823 “Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels” [7]. In this study, the Universal Blade Applicator (UBA, AP-G08, Paul N. Gardner Company, Pompano Beach, FL, USA) was used for paint application.

The production of PSS coupons is summarized below:

Step 1 Prepare 14"x 14" stainless-steel coupons.

1. Don disposable gloves (double glove). For work with acetone, latex gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used as personal protective equipment; for work with 2-propanol (IPA), nitrile gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used.
1. Wet surface of stainless-steel coupon with acetone and wipe dry using a Kimwipe (Kimberley-Clark, Inc., Irving, TX, USA; P/N 34133; or equivalent) Proceed to wipe sampling immediately.
2. Wet surface of stainless-steel coupon with hexane and wipe dry using a Kimwipe SA or equivalent.

Step 2 Place paint or sealant on paint shaker for 10 minutes.

Step 3 Apply paint or sealant following ASTM D823 Practice E.

1. Place stainless-steel sheet on aluminum foil sheet that is secured to the countertop.
2. Adjust the Universal Blade Applicator (UBA) (AP-G08, Paul N. Gardner Company, Pompano Beach, FL, USA) to the desired wet thickness (5 mils). The wet paint thickness partially can be adjusted by shifting the blade up or down within the two side vertical support plates.
3. Pipette 8 x 2 mL of paint in a line near the edge of the stainless-steel coupon using an Eppendorf Repeater Plus Single Channel Repeater Pipette (EPR-1000R, Eppendorf, Hauppauge, NY, USA; or equivalent).

4. Position the UBA behind the line of paint and uniformly pull the blade (250-300 mm/s) toward the operator, with a constant horizontal and vertical pressure. Make sure to pull the blade past the end of the surface to create a uniform layer.
5. Wipe all excess paint off the UBA with Kimwipes and then clean the UBA with Kimwipes wetted with hexane. Allow to dry before storage.

Step 4 Allow the painted stainless steel to dry at standard atmosphere: 21-25°C and 40-60% RH in accordance with ASTM D3924-16 [8]

1. Allowed to dry for a minimum of 24 hours before measuring and/or cutting. Do not place painted coupons in the fume hood for drying. The increased ventilation rates cause nonuniform drying and cracking to occur during method development testing.

Step 5 Clean all coupons with dry air prior to testing paint film thickness.

Step 6 Measure the paint layer thickness on the stainless-steel coupons using ASTM E376 [9].

1. Check the calibration of the Eddy current gauge (PosiTector 6000, DeFelsko Corporation, Ogdensburg, NY, USA) at the start and routinely throughout the testing event using a reference standard included by manufacturer with instrument (1-20 mils thickness range). If needed perform calibration adjustment following procedures detailed in the user manual. Note calibration results in the laboratory notebook.
2. Follow all procedures outlined in the user manual to obtain multiple readings over the surface. Record measurements in the laboratory notebook or electronic spreadsheet; the target application thickness for these samples is 3 mils ($\pm 20\%$).

Step 6 Grid the zones of the painted stainless steel that pass thickness requirements in the shapes of the target coupon sizes (4 x 2.5 cm)

Step 7 Die cut the painted stainless-steel coupons with assistance from the EPA Mechanical Shop using shears to obtain a uniform length (4.0 cm) and width (2.5 cm). Clean excess grease and oil off the PSS coupons using a Kimwipe wetted with deionized (DI) water.

Step 8 Using the calibrated Eddy current gauge, measure the center, top, and bottom of the cut, cleaned PSS coupons to check uniformity and ensure all coupons meet QA requirements. The target application thickness for these samples is 3 mils ($\pm 20\%$). Ideally, thickness readings within 13 mm (1/2 in) of the edge of the surface shall be avoided, but due to the small coupon size, readings need to be taken within this zone.

Step 8 Record all measurements in an electronic spreadsheet and place PSS coupons into clean prelabeled storage container.

A-1.2 Preparation of Free-standing Paint or Sealant Layers

Free-standing paint and sealant sheets were prepared using modified methods from ASTM D823 “Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels” [7]. PTFE sheets (American Sealing & Packaging, Santa Ana, CA, USA) were used as the panel substrate instead of stainless steel for FSP production. Stainless steel (multipurpose stainless-steel type 304, #2B mil, unpolished, 0.036" thick, McMaster-Carr, Atlanta, GA, USA) were used as the substrate for FSS production. The thickness of the sheets will be measured using ASTM D1005 “Standard Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers” [10]. Coupons were die-cut to a diameter of 50 mm to provide a 10 cm² contact area and cleaned using dry compressed air.

A-1.2.1 Preparation of FSP layers

The procedure for manufacturing FSP layer sheets is as follows:

Step 1 Prepare 10" x 10" PTFE sheets.

2. Don disposable gloves (double glove). For work with acetone, latex gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used as personal protective equipment; for work with 2-propanol (IPA), nitrile gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used.
1. Wet surface of PTFE sheet with acetone and wipe dry using a Kimwipe (Kimberley-Clark, Inc., Irving, TX, USA; P/N 34133; or equivalent) Proceed to wipe sampling immediately.
2. Wet surface of PTFE with hexane and wipe dry using a Kimwipe or equivalent.

Step 2 Mix paint using a paint shaker for 10 minutes.

Step 3 Apply paint following ASTM D823 Practice E:

1. Place PTFE sheets on aluminum foil sheet that is secured to the countertop.
2. Adjust the UBA (AP-G08, Paul N. Gardner Company, Pompano Beach, FL, USA) to the desired wet thickness (7 mils). The wet paint thickness can be partially adjusted by shifting the blade up or down within the two side vertical support plates.
3. Directly before applying paint, spray PTFE sheets with IPA and gently wipe with a Kimwipe. The PTFE sheets can accumulate static charge which can affect the paint application and removal process. Depending on ambient conditions, additional static removal steps might be necessary to produce uniform paint layers.
4. Pipette 5 x 2 mL of paint or sealant in a line near the edge of the PTFE sheet using an Eppendorf Repeater Plus Single Channel Repeater Pipette (EPR-1000R, Eppendorf, Hauppauge, NY, USA; or equivalent).

Step 4 Position the UBA behind the line of paint and uniformly pull the blade (250-300 mm/s) toward the operator, with a constant horizontal and vertical pressure. Make sure to pull the blade past the end of the surface to create a uniform layer.

Step 5 Allow the painted sheets to dry at standard atmosphere: 21-25°C and 40-60% RH in accordance with ASTM D3924-16 [8]. Allowed to dry for a minimum of 24 hours before measuring and/or cutting.

Step 6 After curing is completed, don nitrile gloves and gently peel the FSP sheet from the PTFE surface.

Step 7 Clean all coupons with dry compressed air prior to testing the thickness.

Step 8 Measure the FSP layer thickness per ASTM D1005 “Standard Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers” [10]:

1. Using a micrometer (Mitutoyo Digital Micrometer, Mitutoyo America Corporation, Melville, NY, USA, P/N H-2780), separate the anvils to at least twice the distance of the film and place the film, perpendicular to the micrometer, between the anvils. A diagram of the micrometer, including nomenclature for parts can found in ASTM D1005 [10].
2. Bring the anvils into contact with the film without compressing the film.
3. Record film thickness to 0.1 mil (2.5 μm).

Step 9 Place 2 layers of aluminum foil on a cutting board and then place the FSP film on the foil.

1. Die-cut to a diameter of 50 mm using a 50 mm die and arc-punch and rubber mallet.

Step 10 Using the micrometer, measure the center, top, bottom, left and right of the cut FSP coupons to check uniformity and ensure all coupons meet QA requirements. Record all measurements in a spreadsheet and place FSP coupons into clean prelabeled storage container.

A-1.2.2 Preparation of FSS layers

The procedure for manufacturing FSS layer sheets is as follows:

Step 1 Prepare 14" x 14" stainless-steel sheets:

3. Don disposable gloves (double glove). For work with acetone, latex gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used as personal protective equipment; for work with 2-propanol (IPA), nitrile gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used.
1. Wet surface of stainless steel with acetone and wipe dry using a Kimwipe or equivalent. Proceed to wipe sampling immediately.
2. Wet surface of stainless steel with hexane and wipe dry using a Kimwipe or equivalent.

Step 2 Stir sealant gently with a paint stirrer for 5 minutes. Be careful not to force air into the sealant liquid.

Step 3 Apply sealant following ASTM D823 Practice E [7]:

1. Place a stainless-steel sheet on aluminum foil sheet that is placed in the fume hood.
2. Adjust the UBA (AP-G08, Paul N. Gardner Company, Pompano Beach, FL, USA) to the desired wet thickness (9 mil). The wet sealant thickness can be partially adjusted by shifting the blade up or down within the two side vertical support plates.
3. Pipette 14 x 1 mL of sealant in a line near the edge of the stainless-steel sheet using an Eppendorf Repeater Plus Single Channel Repeater Pipette (EPR-1000R, Eppendorf, Hauppauge, NY, USA; or equivalent).

Step 4 Position the UBA behind the line of sealant and uniformly pull the blade (250-300 mm/s) toward the operator, with a constant horizontal and vertical pressure. Make sure to pull the blade past the end of the surface to create a uniform layer.

Step 5 Allow the sealed sheets to dry at standard atmosphere: 21-25°C and 40-60% RH in accordance with ASTM D3924-16 [8]. Allow to dry for a minimum of 96 hours before measuring and/or cutting.

Step 6 After curing is completed, don nitrile gloves and clean all coupons with dry compressed air prior to testing the thickness.

Step 7 Measure the FSS layer thickness per ASTM D1005 "Standard Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers" [10]:

1. Using a micrometer (Mitutoyo Digital Micrometer, Mitutoyo America Corporation, Melville, NY, USA, P/N H-2780), separate the anvils to at least twice the distance of the film and

place the film, perpendicular to the micrometer, between the anvils. A diagram of the micrometer, including nomenclature for parts can found in ASTM D1005 [10].

2. Bring the anvils into contact with the film without compressing the film.
3. Record film thickness to 0.1 mil (2.5 μm).

Step 8 Place 2 layers of aluminum foil on a cutting board and then place the FSS film on the foil.

Step 9 Die-cut to a diameter of 50 mm using a 50 mm die and arc-punch and rubber mallet.

Step 10 Using the micrometer, measure the center, top, bottom, left and right of the cut FSS coupons to check uniformity and ensure all coupons meet QA requirements. Record all measurements in a spreadsheet and place FSP coupons into clean prelabeled storage container.

A-2 LVAP Assembly Procedure

This procedure describes the assembly of LVAP cells using the FSP or FSS, SPE, and custom-made gaskets. It is intended to be step-by-step instructional material for the analyst assembling the LVAP.

A-2.1 Preparation of the LVAP Parts

Prior to testing, clean the PTFE gaskets, aluminum spacers, and steel nuts/bolts for the LVAP apparatuses with a 50:50 (volume:volume) mixture of acetone and hexane. Place all parts in a clean beaker prefilled with the solvent mixture and sonicate for 15 minutes. Place parts on a clean, lint-free laboratory paper for drying. Clean the large aluminum LVAP bottom plate with a laboratory wipe (e.g., Kimwipe or equivalent) prewetted with acetone, then with a second wipe prewetted with hexane and wiped dry with a third wipe.

A-2.2 Assembly of the LVAP

Prior to assembly, don a fresh pair of nitrile gloves (Thermo Fisher Scientific, Waltham, MA, USA, or equivalent)

Step 1 Place clean aluminum foil in the fume hood in H-224 and set the bottom aluminum plate on the foil (Figure A-1).



Figure A-1. Step 1: Place bottom plate on clean surface

Step 2 Place the bottom, full PTFE gasket with bolt holes on the bottom stainless-steel plate, (Figure A-2).

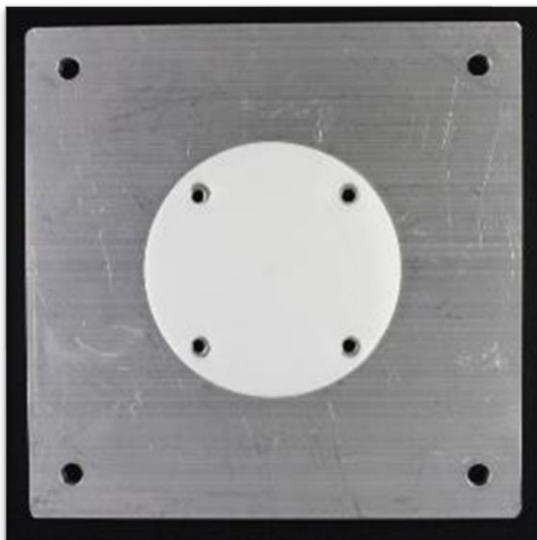


Figure A-2. Step 2: LVAP apparatus with bottom PTFE gasket

Step 3 Place aluminum support ring on top of bottom PTFE gasket (Figure A-3).

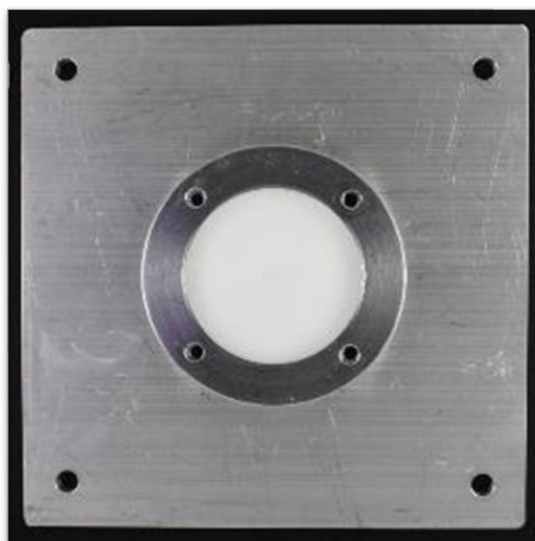


Figure A-3. Step 3: LVAP apparatus with aluminum support ring

Step 4 Place PTFE support ring inside of aluminum spacer ring (Figure A-4).

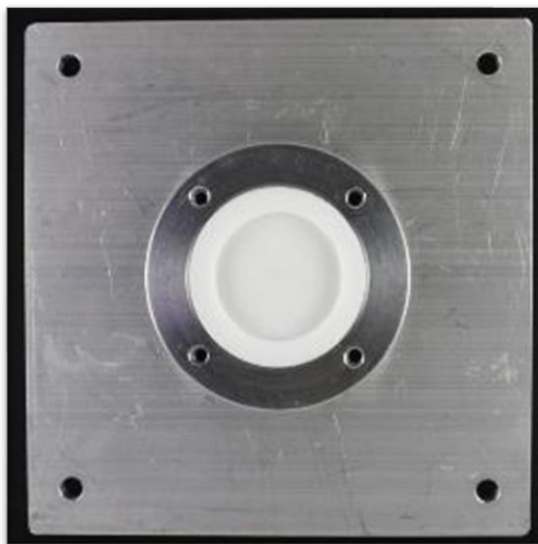


Figure A-4. Step 4: LVAP apparatus with PTFE support ring.

Step 5 Place the first 36 mm diameter PTFE spacer disk inside of PTFE support ring (Figure A-5).

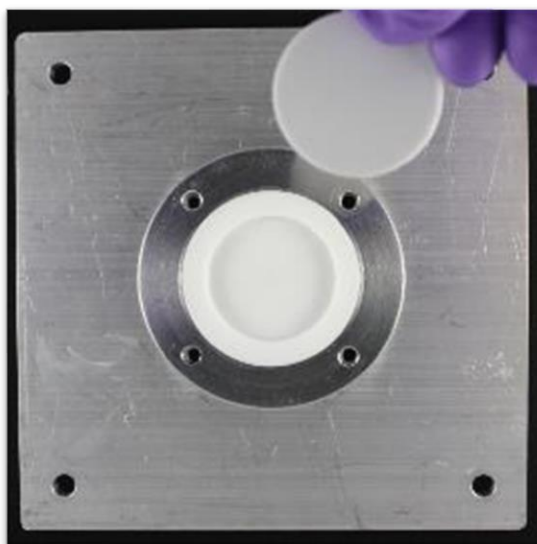


Figure A-5. Step 5: Placement of the first 36-mm PTFE spacer disk in LVAP

Step 6 Place the second 36 mm diameter PTFE spacer disk inside PTFE support ring and on top of first 36-mm diameter PTFE spacer disk (Figure A-6).

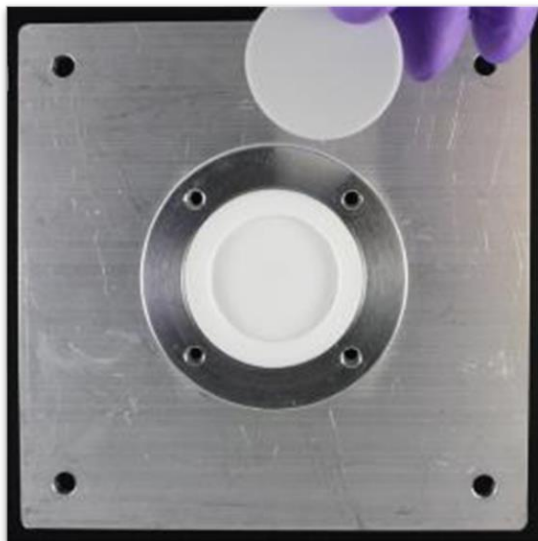


Figure A-6. Step 6: Placement of the second 36-mm PTFE spacer disk in LVAP

Step 7 Place SPE disk on top of 36 mm diameter PTFE spacer disk and inside of PTFE support ring (Figure A-7).

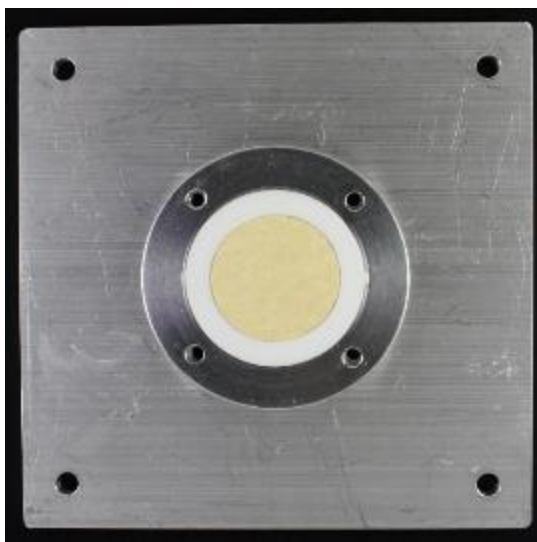


Figure A-7. Step 7: LVAP apparatus with SPE disk centered

Step 8 Center free standing layer – FSP or FSS - on top of SPE disk (Figure A-8).

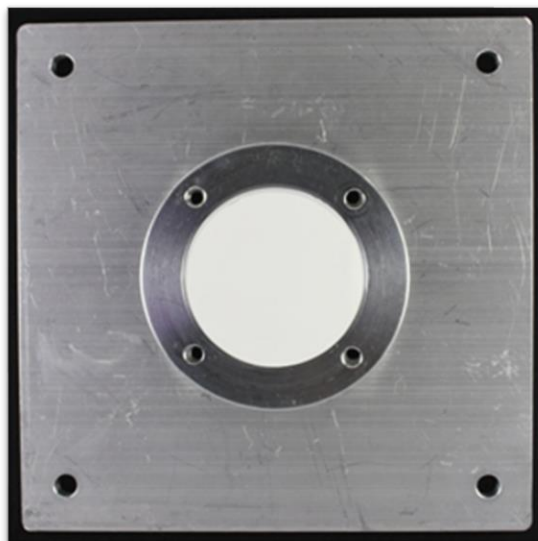


Figure A-8. Step 8: LVAP apparatus with free standing layer; example shown is FSP

Step 9 Place top PTFE gasket on the FSP layer and line up edges with aluminum support ring (Figure A-9)

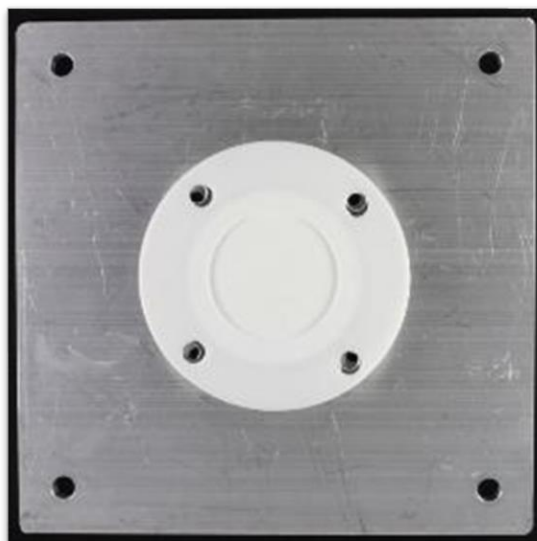


Figure A-9. Step 9: LVAP apparatus with top PTFE gasket centered

Step 10 Place top aluminum plate on the PTFE gasket and line up edges with the rest of the column (Figure A-10).

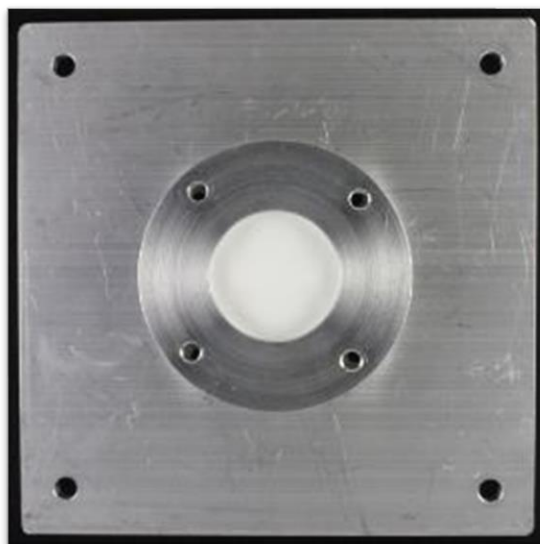


Figure A-10. Step 10: LVAP apparatus with top aluminum ring

Step 11 Place washers on bolts and finger tighten into the predrilled holes in the bottom aluminum plate (Figure A-11).

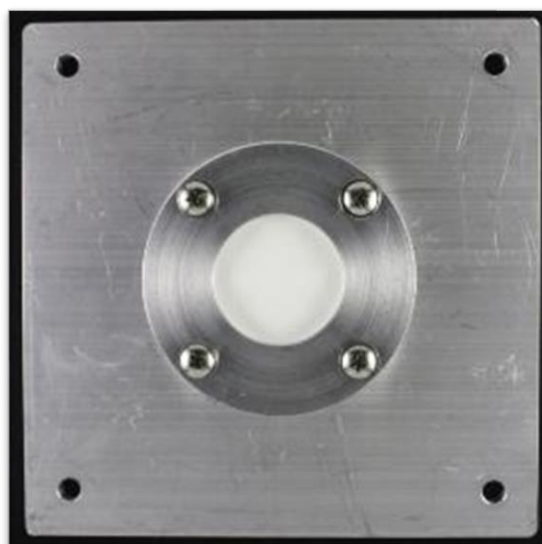


Figure A-11. Step 11: LVAP apparatus with steel bolts finger tight

Step 12 Tighten the bolts to 20 ft-lb using a ¼" torque wrench with Philips drive. The torque wrench will make a clicking noise when it reaches 20 ft-lb of torque. The assembled LVAP is shown on Figure A-12; NOTE: Do not overtighten the bolts. This could strip the threads, pit the top plate, and/or cut the FSS or FSP layer.



Figure A-12. Step 12: Completed LVAP

A-3 Surface Sampling Procedure

The method below was used to collect surface samples in this study. List of materials is listed in Section 3-2. The method below is intended to be step-by-step instructional material for the analyst.

The procedural steps are as follows:

- Step 1** Prepare cotton swabs for sampling
4. Don disposable gloves (double glove). For work with acetone, latex gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used as personal protective equipment; for work with 2-propanol (IPA), nitrile gloves (Thermo Fisher Scientific, Waltham, MA, USA; or equivalent) shall be used.
 5. Dip cotton swab in 2-propanol container (15-mL glass vial) and tap to remove excess solvent by gentle tapping on the edge of the solvent tube.

6. Proceed to wipe sampling (Step 2) immediately.

Step 2 Perform 'hot spot' sampling

1. Don a fresh pair of latex or nitrile gloves.
2. Open the transportation box and move the coupon to the sampling location. Start sampling by rotating the first cotton swab on the location where the malathion droplet is placed on the coupon (hot zone) (Figure A-13). Place the cotton swab in the labeled digitube (50 mL disposable digestion/extraction vial; DigiTube 50 mL Non RackLock with caps; SCP Science, Quebec, Canada, P/N 010-500-263 or equivalent) and prepare the next swab.

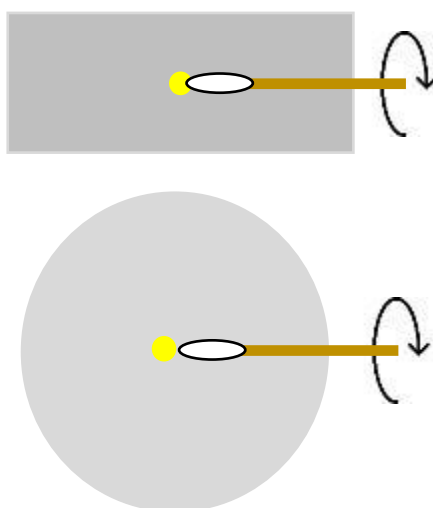


Figure A-13. Hot zone sampling for rectangular and round coupons

Step 3 Perform the horizontal sampling of the entire coupon area

1. Start sampling in the top right corner of the coupon. Wipe the surface horizontally, working from the right to left, to completely cover the coupon surface. (Figure A-14) Add the cotton swab to the labeled digitube and prepare the next swab.

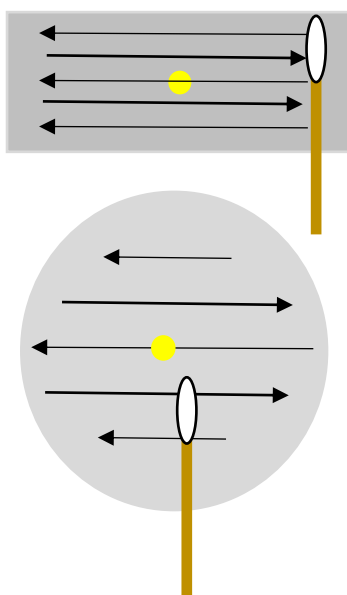


Figure A-14. Horizontal wiping pathway for rectangular and round coupons

Step 4 Perform the vertical sampling of the entire coupon area

1. Starting in the top left corner, wipe the surface vertically, working toward the right, to completely cover the surface. The vertical wipe sampling pathway is shown in Figure A-15. Add the cotton swab to the extraction tube and prepare the next swab.

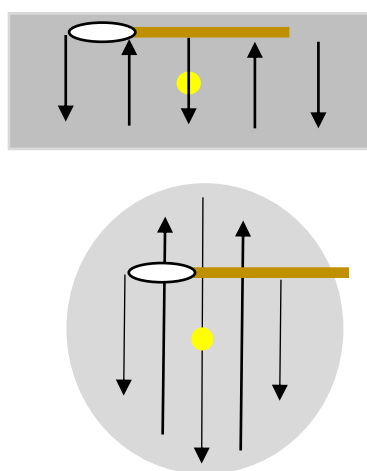


Figure A-15. Vertical wiping pathway for rectangular and round coupons.

Step 5 Perform the perimeter sampling.

1. Starting in any corner, wipe the perimeter of the coupon. The perimeter wipe sampling pathway is shown in Figure A-16. Add the cotton swab to the labeled extraction tube.

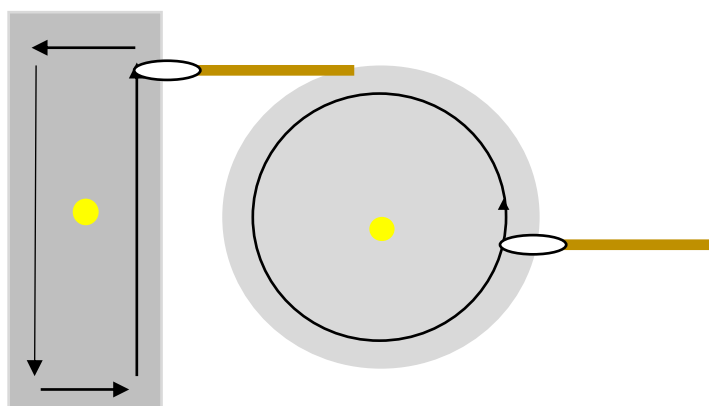


Figure A-16. Perimeter wiping pathway for rectangular and round coupons

Step 6 Prepare for extraction

1. After completion of sampling, all swabs are extracted as a composite-sample. Place all four (4) swabs resulting from one material coupon into a prelabeled extraction tube.
2. Then, place each wipe-sampled material coupon into a separate prelabeled extraction tube.
3. SPE disks do not undergo wipe sampling and are placed in another set of prelabeled extraction tubes.
4. Extraction procedures are described in Section 4.2 of this report.

Appendix B: Method Development Supporting Information

Table B1. Recoveries from surface sampling method development for 2-CEPS

	CS		SS		PSS		SSS		FSP		FSS	
	[mg]	(%) ¹	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²
PB-1	<0.02		<0.02		<0.02		<0.02		<0.02		<0.02	
TC-1	2.29		1.93		1.89		1.57		1.79		1.56	
TC-2	2.38		1.94		1.92		1.88		1.58		1.53	
TC-3	2.38		2.27		1.94		1.50		1.54		1.32	
Average	2.35	100	2.05	87	1.92	82	1.65	70	1.64	70	1.47	63
SD	0.04	1.8	0.16	6.7	0.02	0.9	0.17	7.1	0.11	4.8	0.10	4.5
RSD	1.8%		7.7%		1.1%		10%		6.9%		7.1%	

¹ Percentage with respect to theoretical mass applied
² Percentage with respect to control spike recovery
Results reported at < 0.02 were below LOQ: SD – Standard Deviation; RSD – Relative Standard Deviation

Table B2. Recoveries from surface sampling method development for malathion

	CS1		SS		PSS		FSP		CS2		SSS		FSS	
	[mg]	(%) ¹	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ¹	[mg]	(%) ³	[mg]	(%) ³
PB-1	<0.02		<0.02		<0.02		<0.02		<0.0		<0.0		<0.02	
TC-1	2.25		1.69		1.18		1.42		2.00		1.70		1.86	
TC-2	2.30		1.81		1.36		1.53		1.65		1.40		1.84	
TC-3	2.20		1.80		1.92		1.74		2.42		1.30		1.72	
Average	2.25	92	1.77	78	1.48	66	1.56	69	2.02	82	1.47	72	1.81	89
SD	0.04	1.7	0.06	2.5	0.32	14	0.13	5.8	0.32	13	0.17	8.6	0.06	3.0
RSD	2%		3.2%		21%		8.4%		16%		12%		3.4%	

¹ Percentage with respect to theoretical mass applied
² Percentage with respect to control spike 1 (CS1) recovery
³ Percentage with respect to control spike 2 (CS2) recovery
Results reported at < 0.02 were below LOQ: SD – Standard Deviation; RSD – Relative Standard Deviation

Table B3. Extraction method development for 2-CEPS

	CS		SS		PSS		SSS		FSP		FSS		SPE	
	[mg]	(%) ¹	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²
2-CEPS														
PB-1	<0.02		<0.02		<0.02		<0.02		<0.02		<0.02		<0.02	
TC-1	2.13		2.31		2.15		2.11		2.11		2.34		2.06	
TC-2	2.41		2.16		2.09		2.13		2.07		2.11		2.43	
TC-3	2.47		2.18		2.12		2.23		2.35		2.29		2.30	
Average	2.34	100	2.22	95	2.12	91	2.16	92%	2.18	93	2.25	96	2.26	97
SD	0.15	6.4	0.07	3.0	0.02	1.1%	0.05	2.3%	0.12	5.3	0.099	4.2	0.15	6.6
%RSD	6.5%		3.1%		1.2%		2.5%		5.7%		4.4%		6.8%	

¹ Percentage with respect to theoretical mass applied
² Percentage with respect to control spike recovery
Results reported at < 0.02 were below LOQ: SD – Standard Deviation; RSD – Relative Standard Deviation

Table B4. Extraction method development for malathion

	CS		SS		PSS		SSS		FSP		FSS		SPE	
	[mg]	(%) ¹	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²	[mg]	(%) ²
	Malathion													
PB-1	<0.0		<0.02		<0.02		<0.02		<0.02		<0.02		<0.02	
TC-1	2.08		2.04		1.18		2.40		1.42		1.87			
TC-2	2.09		2.27		1.36		2.12		1.53		1.98			
TC-3	2.34		2.36		1.92		2.02		1.74		2.04			
Average	2.17	88	2.22	95	1.48	79	2.18	100	1.56	83	2.0	104	1.77	94
SD	0.12	4.9	0.14	5.8	0.32	17	0.16	7.5	0.13	6.9	0.07	3.8	0.06	3.7
%RSD	5.5%		6.1%		21%		7.5%		8.4%		3.7%		3.2%	
¹ Percentage with respect to theoretical mass applied														
² Percentage with respect to control spike recovery														
Results reported at < 0.02 were below LOQ; SD – Standard Deviation; RSD – Relative Standard Deviation														

Table B5. Results of gasket contamination test for 2-CEPS and malathion

Sample Type	Top Gasket		O-ring Gasket		Gasket Below SPE Disk	
	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)
2-CEPS						
PB-1	<0.02	<1%	<0.02	<1%	<0.02	<1%
TC-1/2/3	<0.02 (D)	<1% (D)	<0.02 (D)	<1% (D)	<0.02 (D)	<1% (D)
Malathion						
PB-1	<0.02	<1%	<0.02	<1%	<0.02	<1%
TC-1/2/3	<0.02	<1%	<0.02 (D)	<1% (D)	<0.02 (D)	<1% (D)
Results reported at < 0.02 were below LOQ; (D) – below LOQ trace-level detections (S/N < 10) were present						

Table B6. Results for SPE to FSP nonpermeation transport test for 2-CEPS

Sample Type	SPE		FSP		FSP+SPE Mass Balance	
	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)
2-CEPS						
PB-1	<0.02	<1%	<0.02	<1%	<0.02	<1%
TC-1	0.0027 (J)	0.59%	0.080	18%	0.083	18%
TC-2	0.014 (J)	3.2%	0.29	63%	0.30	63%
TC-3	0.013 (J)	2.9%	0.19	42%	0.21	43%
Average	0.010(J)	2.2%	0.19	41%	0.20	41%
SD	0.0006	0.32%	0.10	23%	0.10	23%
RSD	64%		56%		55%	
Results reported at < 0.02 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10)						

Table B7. Results for SPE to FSS nonpermeation transport test for 2-CEPS

Sample Type	SPE		FSS		FSP+SPE Mass Balance	
	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)
2-CEPS						
PB-1	<0.02	<1%	<0.02	<1%	<0.02	<1%
TC-1	0.0013 (J)	0.3%	0.12	18%	0.082	18%
TC-2	0.0071 (J)	1.6%	0.18	63%	0.30	65%
TC-3	0.0070 (J)	1.5%	0.18	42%	0.20	44%
Average	0.0051	0.51%	0.19	41%	0.19	42%
SD	0.0032	0.32%	0.10	23%	0.12	26%
RSD	64%		56%		61%	
Results reported at < 0.02 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10)						

Table B8. Results for SPE to FSP nonpermeation transport test for malathion

Sample Type	SPE		FSP		FSP+SPE Mass Balance	
	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)
Malathion						
PB-1	<0.02	<1%	<0.02	<1%	<0.02	<1%
TC-1	0.34	91%	0.10 (J)	27%	0.45	119%
TC-2	0.29	77%	0.09 (J)	24%	0.38	102%
TC-3	0.22	59%	0.08 (J)	22%	0.31	82%
Average	0.29	76%	0.09 (J)	25%	0.38	101%
SD	0.05	13%	0.01	2%	0.06	15%
RSD	17%		8.4%		15%	
Results reported at < 0.02 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10)						

Table B9. Results for SPE to FSS nonpermeation transport test for malathion

Sample Type	SPE		FSS		FSP+SPE Mass Balance	
	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)	Recovered [mg]	Recovered (%)
Malathion						
PB-1	<0.02	<1%	<0.02	<1%	<0.02	<1%
TC-1	0.49	100%	0.012 (J)	2%	0.50	103%
TC-2	0.49	100%	0.012 (J)	2%	0.50	103%
TC-3	0.52	106%	0.057	12%	0.57	118%
Average	0.50	102%	0.027	5.5%	0.52	108%
SD	0.02	3.3%	0.026	5.4%	0.042	8.7%
RSD	3%		98%		8%	
Results reported at < 0.02 were below LOQ; (J) – estimated value, detected at below LOQ (S/N >10)						



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