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Normalization of Contamination Conditions for Measurement of Agent Retention and Decontamination Performance on Materials

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PREFACE

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EXECUTIVE SUMMARY

The fundamental intent of laboratory-based testing for chemical warfare agent hazard mitigation technologies is to characterize how discrete drops of liquid agents interact with materials to determine whether the technology reduces the quantity of agent retained by the material. It is expected that results from laboratory testing indicate how a technology would perform in an operational environment on actual military assets, such as vehicles and other tactical support equipment. As a result, test parameters are configured to directly represent certain aspects of operational conditions. One of these parameters is contamination density (i.e., starting challenge), which indicates the mass of agent per unit of material area (in grams per square meter) based on deposition of liquid drops on test substrates. However, results presented here show that specifying starting challenge alone as a test parameter is insufficient for an accurate and conclusive measurement of performance for hazard mitigation technologies. This report presents a new data analysis approach that accounts for variable liquid drop volume and count and provides more capability and resolution toward the translation of laboratory results to performance for variable contamination conditions, including operational contexts. Normalization of the retained agent mass per drop as a function of the drop volume using an empirical least-squares regression reveals prevailing trends in the assessment of decontamination efficacy that are otherwise not resolvable. This normalization approach captures the effect of drop volume and variable contamination density and enables simple calculations to translate from laboratory to operational context.

There are significant advantages to the new normalization approach. First, this analysis enables the calculation of operationally relevant hazard mitigation performance independent of starting challenge. Rather than performing isolated evaluations for explicit contamination density conditions using discrete drop application with multiple replicates per condition (e.g., $1 \times 2 \mu\text{L}$ drop on a 2 in. diameter panel, 5 replicates), testing would consider a range of drop volumes and counts. The resulting fit of per-drop normalized retained agent to drop volume would include the degrees of freedom (i.e., pooled replication) of all tested configurations (requiring fewer sample replicates), and the results would be more extensible to variable operational contamination densities.

Second, the new analysis is more flexible and can capture potential variance in decontamination efficacy with drop volume. Decontamination burden and efficacy is strongly influenced by the manner in which liquid agents distribute on test substrate materials upon contamination, and this behavior depends on pairwise interactions between contaminant and material. This work illustrates the relationship between contamination condition (i.e., how many drops of specific volumes are deposited) and decontamination performance. If the drop volume used in laboratory testing does not correspond to the volume range that may occur operationally, there may be significant bias in the actual efficacy when the technology is implemented in the field.

Third, the change in test parameter from starting challenge to drop volume relieves some previous material area constraints and allows for a wider range of panel configurations to be considered for laboratory testing. Panel size was previously selected as 2 in. diameter disks to facilitate generation of specified starting challenges (e.g., 1 g/m^2). The use of

per-drop normalization enables the use of smaller panels that can result in significant increases in test throughput. Further, this approach can be employed for multiple panel types, including flat horizontal panels and recently developed shim panels since the assessments depend on per-drop effects on test substrate features rather than assuming uniform contamination distributions.

Lastly, this empirical analysis enables the calculation of variable contamination levels on operational scale assets. A wide range of operational conditions can be represented using laboratory test data by identifying the number of drops of agent that would be present on specific materials of an asset. This is based on quantification of asset-level efficacy for any contamination density and drop volume distribution. The normalization approach enables a simple equation to accomplish these calculations compared to current analysis methods that depend on variable material area estimates and data derived in the context of fixed starting challenge levels.

This per-drop normalization analysis could have a broad impact on decontamination technology evaluations since starting challenge has traditionally dictated test conditions for a variety of agent testing methods for materials. The data presented here establish the foundation for this per-drop normalization capability; however, more testing is needed to validate this approach.

CONTENTS

	PREFACE	iii
	EXECUTIVE SUMMARY	v
1.	INTRODUCTION	1
2.	BACKGROUND	2
2.1	Agent Distributions and Hazard Mitigation Performance	2
2.2	Laboratory Testing Conditions	4
2.3	Limiting Reagent	6
2.4	Translation of Laboratory Results to Operational Context.....	6
3.	MATERIALS, PROCESSES, AND METHODS.....	8
3.1	Contamination.....	8
3.2	Materials	10
3.3	Decontamination Treatments	11
3.4	Panel Extraction	12
4.	RA RESULTS AS A FUNCTION OF CONTAMINATION CONDITIONS	12
4.1	Contamination Imaging	12
4.2	RA for Variable Contamination Configurations with SWI Treatment.....	16
4.3	Log Reduction Relative to SWI.....	20
5.	PER-DROP NORMALIZATION OF RA RESULTS.....	24
5.1	Contamination Parameter Correlations.....	24
5.2	Developing a Normalization Approach	26
5.3	Per-Drop Normalization for Different Treatment Processes	29
5.4	Per-Drop Normalization Summary	39
5.5	Future Considerations Using Modeling and Simulation.....	41
6.	CONCEPTS FOR TRANSLATING LABORATORY TESTING TO OPERATIONAL CONTEXT	42
7.	CONCLUSIONS.....	46
	LITERATURE CITED	49
	ACRONYMS AND ABBREVIATIONS	53
	APPENDIXES	
	A: SPHERICAL CAP DROP RELATIONSHIPS	55

B: DOSE CONFIRMATION SAMPLES	59
C: COMPARISON OF RETAINED AGENT FOR 10 g/m ² STARTING CHALLENGE USING DIFFERENT DROP VOLUMES	61
D: RETAINED AGENT CORRELATION PLOTS.....	63
E: DETAILED PER-DROP REGRESSIONS	67
F: CONSIDERATIONS TOWARD TRANSLATING LABORATORY DATA TO OPERATIONAL CONTEXT	71

FIGURES

1.	Schematic of side or cross-sectional view for contamination distributions and various mechanisms that may influence agent distribution through contamination, decontamination, and post-decontamination periods.....	3
2.	Liquid–air surface area and liquid–material wetted surface area trends as a function of drop volume, assuming spherical cap geometry for different equilibrium contact angles (θ)	5
3.	Treatment process for measurement of RA mass	8
4.	Arrangement of agent drops for each target starting challenge	9
5.	Representative images of HD spreading behavior for each contaminant delivery variation on PU coating (left), silicone elastomer (center), and alkyd coating (right) after 120 min.....	13
6.	M8 chemical agent detector paper responses for the $4 \times 2 \mu\text{L}$, $4 \times 4 \mu\text{L}$, and $16 \times 1 \mu\text{L}$ contaminant delivery variations of HD on PU coating, showing that some quantity of HD flowed off of the panel surface during the contamination duration with $>8 \mu\text{L}$ of dispensed liquid.....	13
7.	Representative images of the spreading behavior for each contaminant delivery variation on PU coating (left) and silicone elastomer (right) after a 1440 min contaminant–material interaction period for HD.....	14
8.	Representative images of the spreading behavior for each contaminant delivery variation for VX on PU coating (left) and silicone elastomer (right).....	15
9.	M8 chemical agent detector paper responses for the $5 \times 4 \mu\text{L}$ and $20 \times 1 \mu\text{L}$ contaminant delivery variations of VX on PU coating, showing that some quantity of VX flowed off of the panel surface during the contamination duration, as indicated by the green color on the M8 paper.....	16
10.	RA for the SWI treatment across three materials, each exhibiting different trends for the contaminant delivery	16
11.	RA for PU coating using the rinse and SWI treatment process for different agents and contamination durations	17
12.	RA of HD and VX on alkyd coating using the rinse and SWI treatment process	18
13.	RA of HD and VX on silicone using the rinse and SWI treatment process	19
14.	Relative performance (LD) for each treatment relative to the SWI treatment process for HD at 120 min. Error bars represent the 95% CI on the difference.....	21
15.	Relative performance (LD) for each treatment relative to the SWI process for HD at 1440 min	22
16.	Relative performance (LD) for each treatment relative to the SWI process for VX at 120 min	23
17.	RA linear correlations for HD on three materials for the SWI treatment process for 120 min contamination duration	25
18.	Example regressions of RA/drop versus drop volume for HD on PU and on alkyd coatings for the SWI treatment	27
19.	Accuracy of the fit to predict the original experimental results for HD on PU coating (left) and alkyd coating (right) using the SWI treatment process	28

20.	Linear correlation plots for HD on PU coating, alkyd coating, and silicone elastomer for 120 min contamination duration with a bleach treatment process	30
21.	RA/drop results for HD on PU coatings for 120 min (left) and 1440 min (right) contamination durations.....	31
22.	Comparison of fit versus measured RA values for HD on PU coating for a 120 min (left) and 1440 min (right) contamination period for different decontamination treatments	33
23.	Log reduction of RA per-drop trends for HD on PU coating for 120 min (left) and 1440 min (right) contamination durations	34
24.	(Left) RA per-drop results for HD on alkyd coating for a 120 min contamination duration	35
25.	Comparison of fit versus measured RA values for HD on alkyd coating for a 120 min contamination period as a function of decontamination treatment.....	35
26.	RA per-drop results for HD on silicone elastomer for 120 and 1440 min contamination durations.....	36
27.	Log reduction of RA per-drop trends for HD on silicone elastomer	36
28.	Comparison of fit versus measured RA values for HD on silicone elastomer for 120 min (left) and 1440 min (right) contamination periods	37
29.	RA per-drop results for VX on PU coating (left) and silicone elastomer (right) for 120 min contamination duration	38
30.	Log reduction of RA per-drop trends for VX on PU coating (left) and silicone elastomer (right).....	38

TABLES

1.	Potential Rate-Limiting Processes for Decontamination	4
2.	Contaminant Liquid Density and Purity	9
3.	Comparison of Starting Challenge Levels to Actual Contamination Density Values	10
4.	Test Material Information	11
5.	Decontamination Treatment Information	11
6.	Per-Drop Regression Fit Parameters for HD on PU Coating	32
7.	Material Composition for an Example Full-Scale Asset and Number of Drops of Specified Drop Volume Required to Produce 1 g/m ² HD on Each Material Area.....	43
8.	Regression Coefficients for HD at 120 min Contamination Duration for PU and Alkyd Coatings	43
9.	Total Mass Remaining per Material or Asset	44
10.	Log Reduction per Material and Total Asset after HD Treatment Process (120 min Contamination Duration).....	45

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NORMALIZATION OF CONTAMINATION CONDITIONS FOR MEASUREMENT OF AGENT RETENTION AND DECONTAMINATION PERFORMANCE ON MATERIALS

1. INTRODUCTION

Hazard mitigation technology studies associated with materials contaminated by liquid chemical warfare agents (CWAs), including assessments of decontamination processes or materials with enhanced chemical resistance, investigate a decontaminant's ability to remove agent or to reduce the decontamination burden. The fundamental intents of this work were to characterize the way in which agents interact with materials as a result of deposition of discrete liquid agent drops on materials and determine whether the hazard mitigation technology reduced the quantity of agent retained by the material. It is commonly expected that results from laboratory testing indicate how a technology would perform in an operational environment on actual military assets, such as vehicles and other tactical support equipment. Because of these expectations, laboratory testing parameters are often defined to directly reflect key elements of operational conditions. The description of the amount of contamination that may be present in an operational environment for a hazard mitigation technology to address is often referred to as the contamination density or *starting challenge*,* typically specified as the mass of liquid contaminant per unit area of material (typically in units of grams per square meter).¹ Contamination density is an operational context that has previously been used as a constraint applied to laboratory test designs (i.e., test materials are contaminated to a specified contamination density).

Historically, hazard mitigation technology performance has been characterized in the limit of specific, individually evaluated contamination densities (e.g., 1 and 10 g/m²). Panels are contaminated by applying a specific number of agent drops of specific volumes to the materials to generate the desired contamination density. For example, one 2.0 μ L drop of *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX) may be applied to a 2 in. diameter panel (i.e., 0.00202 m² surface area) to generate a 1 g/m² contamination density. The results are then typically presented for each tested contamination density, and these data cannot be used to interpolate or extrapolate to results for other contamination conditions.

This report explores how liquid contamination conditions that include different drop counts and volumes of agent may influence agent retention and decontaminant performance. A new approach to normalizing laboratory data collected across different contamination conditions and specifying contamination for laboratory testing is presented. This approach provides more capability and resolution toward the translation of laboratory results to indicate performance at other contamination conditions, including operational contexts. For example, the analysis presented here shows that a specific data normalization (i.e., per-drop) can be used to describe the results from multiple drop configurations across different contamination

* Contamination density tends to be in relation to the dispersion of agent in an environment; starting challenge is usually in the context of the quantity of agent that must be addressed by a hazard mitigation technology. The terms contamination density and starting challenge both represent the mass of agent per unit area and are used interchangeably throughout the report.

densities. This approach enables the calculation of operationally relevant hazard mitigation performance without testing each explicit contamination density of interest.

The investigation of drop volume and count makes it possible to evaluate how a per-drop-based analysis relates to parameters like contamination density. The use of a per-drop characterization of contamination enables greater flexibility in representing operational conditions. For example, there is often an interest in evaluating the contamination of an asset to different extents, such as with a few drops deposited onto a limited area (localized contamination) or with multiple drops over the full surface area of the asset (uniform contamination). This per-drop approach allows for better translation of laboratory test conditions to the variable contamination calculations for full-scale assets. Furthermore, the use of a per-drop context in the test methodology enables the use of different test designs and material size constraints that can significantly increase test throughput. Recent work in characterizing liquid entrainment in small gaps has identified the benefit of quantifying contamination on a per-drop basis.² This work extends per-drop normalization to flat panel testing.

In this study, several contamination densities (1, 5, and 10 g/m²) were generated using different drop volumes (1–4 µL). The agent was applied to several materials, including a polyurethane (PU) coating, an alkyd coating, and a silicone elastomer. Different agent distributions were generated on and in the materials by allowing agent to interact with the materials for 2 and 24 h after deposition. A variety of material treatment processes were conducted to evaluate the efficacy of agent removal or neutralization by different decontamination chemistries for variable contamination conditions, including soapy water immersion (SWI) as well as bleach and alcohol-based solution treatments. The key experimental data collected was retained agent (RA) mass, which is the mass of chemical agent that remains on and within a material after a decontamination process. These RA measurements as a function of contamination and decontamination parameters were used to calculate decontaminant effectiveness (e.g., log reduction). The results suggest that the combination of a judicious choice of test conditions paired with a per-drop normalization analysis provides an increased capability to translate laboratory results to operational context.

2. BACKGROUND

Sections 2.1–2.4 provide an overview of factors and considerations regarding the contamination process, the ways in which those factors may influence hazard mitigation technology evaluation execution, and the translation of laboratory results to operational context.

2.1 Agent Distributions and Hazard Mitigation Performance

When a material is contaminated with agent, various agent–material interactions and mass transfer processes determine the redistribution of the agent in and on the material. These include liquid spreading on the material surface, liquid absorption into the material, liquid evaporation and subsequent vapor sorption, and adsorption onto the material surface (Figure 1).^{3–8} The quantity of agent that strongly interacts with a material is dependent on the physical and chemical properties of the agent and the material. Typical materials of interest include polymers or paint systems for which absorption occurs via molecular diffusion.^{4,9–12}

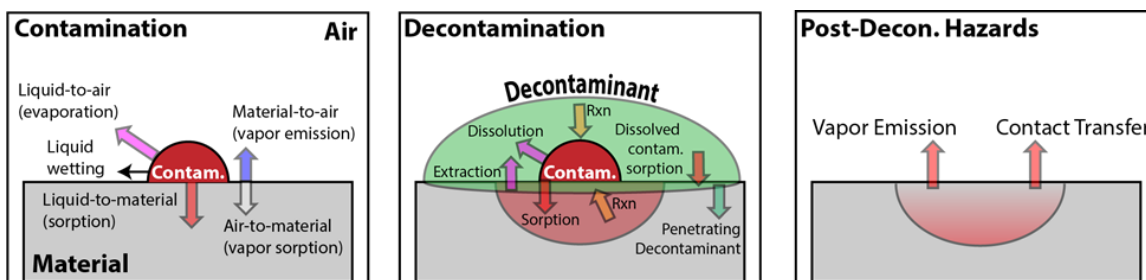


Figure 1. Schematic of side or cross-sectional view of contamination distributions and various mechanisms that may influence agent distribution through contamination, decontamination, and post-decontamination periods.

For a decontaminant to remove agent from a material, the decontaminant must access the agent from these different distributions. A given decontaminant may have variable apparent performance as a function of the agent distribution in or on the material due to different rate limiting mechanisms (Table 1). In general, anything that alters or influences the agent distribution will likely influence decontamination performance or post-decontamination hazards. As a result, the way in which contamination is applied may influence the agent distribution on and in a material. In these decontamination technology evaluations, many influential factors exist that are not trivial to disentangle.

The aim of this study was to specifically resolve the influence of contamination conditions on end-state experimental data such as RA and provide an outlook on how to use the collected data as effectively as possible for subsequent analysis. The contaminants, materials, decontaminants, and test conditions were chosen to inform the resolved trends but not necessarily to provide a comprehensive and quantitative accounting of all of the factors that determine RA.

Table 1. Potential Rate-Limiting Processes for Decontamination

Decontamination Related Processes	Description and Notes on Type or Degree of Influence on Decontamination Measurement
Evaporation	Determined by quantity of liquid surface area of the agent
Desorption (vapor emission from the material)	Determined by transport rate of the agent in the material ¹³
Reaction	Kinetics and thermodynamics of chemical reaction of the agent with the decontaminant will vary as a function of contaminant–decontaminant combination
Dissolution	Dissolution rate for liquid agent into the decontaminant solution can be rate limiting to allow for reaction to occur; ¹⁴ rate of dissolution is potentially sensitive to shear flow effects during decontaminant application (e.g., spraying) and liquid surface area of the drop as well as thickener or other agent impurities
Decontaminant penetration	Ability or rate of components of the decontaminant to penetrate the material to access absorbed agent ^{15,16} depends on chemical interactions between decontaminant and material
Extraction	Ability of a decontaminant to extract agent from the material into the decontaminant solution phase, either for removal or to facilitate reaction, is determined by affinity of the contaminant for the decontaminant solution

2.2 Laboratory Testing Conditions

Although contamination density values are often provided as laboratory test parameters, the drop volumes used to generate the contamination density are not specified; many small drops or a few larger drops can be used to generate a contamination density. However, many factors that are not constant across different drop volumes can strongly influence contamination for a liquid deposited on a material surface. Drop volume and the equilibrium liquid–material contact angle (θ) determine the surface area to volume ratio of the drop (Figure 2), specifically with regard to liquid–air and liquid–material interfaces for drops on surfaces. The degree to which contaminant liquid is in contact with different media, whether surrounding air or substrate material, ultimately influences absorption into and evaporation from the surface as a function of contaminant–material pair. The associated equations for these relationships are provided in Appendix A. The data in Figure 2 are general relationships for any agent–material relationship. Over time, as a drop evaporates, absorbs, and possibly spreads, the volume, contact angle, and wetted area may evolve. This evolution generally manifests as three characteristic behaviors:¹⁷ (1) pinned contact lines, where the liquid wetted area is constant as the drop evaporates (common); (2) shrinking drop area, where the drop wetted area contracts as the liquid volume decreases (less common with CWA on relevant materials); and (3) liquid spreading, where the drop wets the material surface (θ goes to zero) over the course of seconds to hours (e.g., observed on PU coatings).

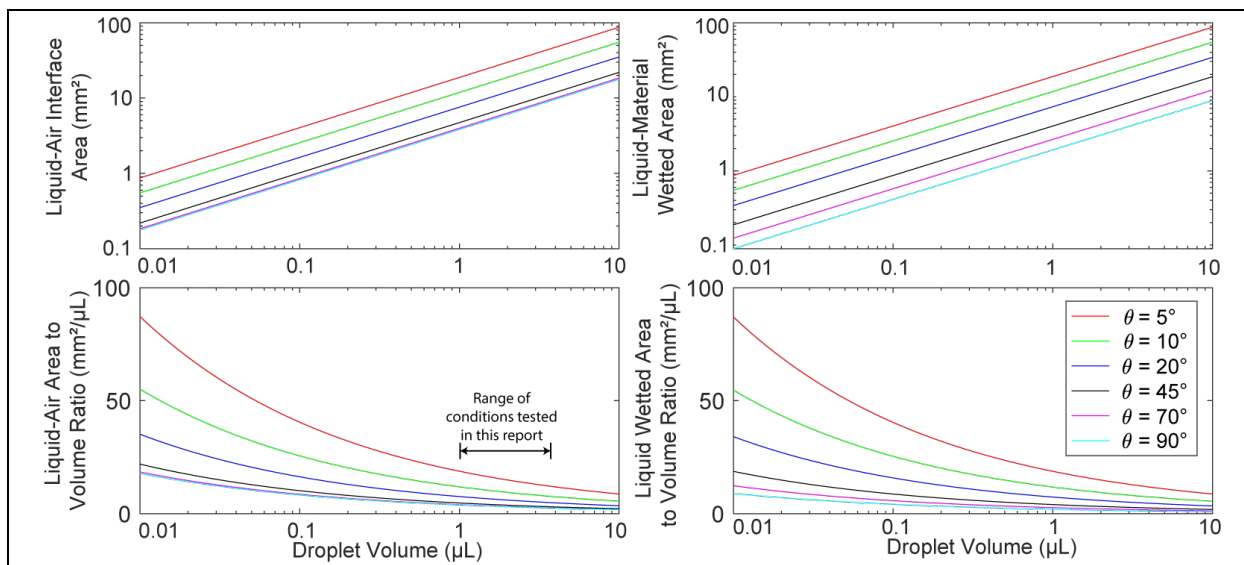


Figure 2. Liquid–air surface area and liquid–material wetted surface area trends as a function of drop volume, assuming spherical cap geometry for different equilibrium contact angles (θ). Constitutive relationships are presented in Appendix A.

This variation in liquid–material interactions can then affect the mass of agent absorbed by the material and, therefore, the subsequent decontaminant performance. The effect of drop volume on surface area to volume ratios is more significant for more wetting conditions (i.e., lower θ values). For example, if a larger-volume drop does not spread on a surface, bulk liquid may remain on the surface longer due to the lower exposed liquid surface area to volume ratio, resulting in potentially longer evaporation time per drop. Furthermore, depending on the spreading behavior on the surface, there may be less interfacial liquid–material surface area to facilitate absorption. In contrast, the relative quantity of agent mass that evaporates or absorbs may increase for many smaller drops of the same total mass due to increased liquid surface area to volume ratios. The degree of impact depends on which mass transfer mechanisms are more influential or rate limiting as a function of agent and material. For example, evaporation may be highly influential for high-volatility agents and non-influential for low-volatility agents, and the evaporation rate will also depend on how the agent is distributed on and in the material. The relative rates of evaporation and absorption for a given agent–material (temperature) combination will determine whether more mass is lost from the material or absorbed for a given drop volume. As a result, the drop volume and number of drops applied in laboratory testing could alter the relative agent distributions and thereby alter the apparent performance of a hazard mitigation technology.

In an operational context, two drop-size regimes are relevant to consider: larger-volume drops (on the order of microliters) that fall on a ballistic trajectory from an agent dissemination device, and smaller-volume drops that may flow in wind currents (i.e., aerosol-size drops) and settle on materials over time. In practice, any dissemination device will produce a wide range of drop volumes, often following a log-normal distribution. In this report, various ballistic-scale drops on the order of 1–4 μL were used to generate the starting challenge to assess whether drop volume for similar starting challenges influences hazard mitigation performance

measurements. Smaller-volume drops (i.e., $<1\ \mu\text{L}$) were not considered because they have not typically been used in testing due to the limitations associated with conventional laboratory-scale dispensing devices used for liquid agents. Traditional laboratory repeater pipettes (e.g., Repeater M4 [Eppendorf; Hamburg, Germany]) can reproducibly deliver down to $1\ \mu\text{L}$ drops. Although other technologies exist that could be considered for small-drop dispensing, there are limitations on the types of liquids that can be used as well as possible safety and logistical constraints in an agent delivery context. For example, commercial air-piston pipettes can deliver smaller drops, but these are for delivery from aqueous solutions only. Furthermore, air-piston pipettes are not appropriate for accurate dispensing of the higher-volatility and higher-viscosity agents. Syringes with mechanical repeaters may be an option to generate small drop contamination, assuming sufficient throughput and accuracy could be achieved. Alternately, newer inkjet-like nanodrop dispensing devices may be considered, but these devices are often expensive, may not work with higher viscosity liquids like agents, and would likely require tuning and validation to work with agents. Additionally, enhanced safety precautions may need to be considered for smaller volumes to ensure the drops do not become aerosolized as part of the contamination process and escape engineering controls.

The lower limit on drop volume dispensation dictates the panel dimensions for the materials used for this report and in traditional testing. A circular panel with a diameter of about 5.08 cm (2 in.) to produce a $20.2\ \text{cm}^2$ ($0.00202\ \text{m}^2$) surface area is required to achieve the contamination density of $1\ \text{g}/\text{m}^2$. The lower volume limit on ability to deliver agent determines the size of the panels to produce a $1\ \text{g}/\text{m}^2$ contamination density. On a related note, the size of the panel has a significant influence on the throughput capabilities of a laboratory, and the ability to miniaturize panels is limited by the ability to deliver the desired contamination density.

2.3 Limiting Reagent

It is generally assumed that hazard mitigation technologies can address up to the maximum tested contamination density. Typically, the quantity of decontaminant applied to a material is in significant excess relative to the quantity of agent; limiting reagent effects are not expected to occur for most cases. Therefore, hazard mitigation technology evaluations have typically applied the same quantity of decontaminant to the material regardless of the contamination density (i.e., 1 or $10\ \text{g}/\text{m}^2$).¹ This assumption of excess is predicated on liquid phase reactivity, where there are no mass transport limitations associated with interaction between decontaminant species and agent. In this study, multiple contamination densities were evaluated to determine whether the decontaminant was truly in sufficient excess; that is, whether the relative quantity of agent present did or did not influence performance. The quantity of decontaminant applied was constant, and the quantity of agent varied, which thereby altered the decontaminant to contaminant ratio. If this ratio influenced the observed performance, it would likely result in improved efficacy for lower contamination densities.

2.4 Translation of Laboratory Results to Operational Context

The process to represent a full-scale asset in an operational context uses a bottom-up construct. Materials that compose an asset are identified and tested separately, and the hazard mitigation technology evaluation for the composite asset in an operational context is treated as a weighted, linear combination of non-interacting responses from the individual materials. This

may seem facile; however, this calculation for translation of laboratory-based analyses to evaluations that consider the full suite of operational contributions can become complicated in many ways. Issues related to hazard mitigation technology test designs, how experimental data is collected, and then how the data are ultimately used for a translation from laboratory to field context are listed below.

To use laboratory-derived data to inform an operational context, an assessment should be made of what field-inspired factors are the most influential in producing hazards. Rather than replicate the field contamination conditions in the laboratory, the methodology should identify and evaluate the intrinsic characteristics of contamination and the actions of hazard mitigation so that laboratory measurements can be confidently translated to operational context. Laboratory replication of operational contamination density may not be the optimal constraint to enable this translation.

Next, the influence of testing constraints on measured decontamination efficacy must be accounted for so that the laboratory-scale data can be used appropriately. This includes capturing the effects of contamination conditions on measuring hazard mitigation technology performance for individual materials. For this type of testing, measurements are performed for RA, or a relative log reduction is compared to a reference condition for a given treatment process on a specific agent–material–contamination condition. As stated earlier, *the foundation of the approach to translate laboratory results to operational context is accounting for the abundance of materials in the operational environment and the way in which they were contaminated.* However, in the laboratory, the direct measurements are specific to the test materials and, as noted, the choice of contamination condition can matter a great deal. A procedure should be in place to permit collection of experimental data in the laboratory that is prioritized for prediction of the behavior in the operational context. *The test parameters must be informed by the most critical variables from the operational context that influence contamination and decontamination, and these must be defined sufficiently to allow for the desired output.* This report addresses these needs by considering the material area of an asset and accounting for the abundance of drops of agent on the various materials.

Lastly, and intimately related to the issue of measurement constraints, the fundamental issue of how to scale contamination needs to be considered. In previously published methods, such as the vapor composite system calculation (VCSC),¹ material area is used as a scaling factor to enable small panels to represent the total surface area of a material found on a full-scale asset and then allow for aggregation of the results across the multiple materials found on the asset. In the case of VCSC, the test panels were typically tested at a specified contamination density, and it was assumed that the full-scale asset was also contaminated to the same contamination density. However, material area scaling only works if the materials of the full-scale asset are assumed to be uniformly contaminated to the laboratory-tested contamination density. As part of recent efforts to assess the factors that influence the decontamination of small gaps between materials (i.e., constrained geometry features²), it was determined that single drop interactions rather than uniform contamination densities would provide the construct necessary for considering variable levels of contamination on an operational asset. The methodology focuses on single drop interactions with the features of interest. The approach to represent the asset was to multiply the single drop result by the number of drops on the full-scale asset. This enables a simple calculation for variable levels of contamination on the operational asset. This

single drop interaction characterization could be applied to flat panel assessments as well. The concept of a per-drop normalization and translation to a full-scale asset is demonstrated in Section 6.

3. MATERIALS, PROCESSES, AND METHODS

Laboratory test procedures were in accordance with the chemical contaminant and decontaminant source document for the RA test.¹ Materials were contaminated using different combinations of drop volume and number of drops of bis(2-chloroethyl) sulfide (HD) and VX to achieve varying contamination densities. Materials were then decontaminated using treatment procedures detailed in in Section 3.3. The decontaminated material was extracted in agent-specific solvent for 60 min, and the extraction solution was analyzed to determine the mass of contaminant retained by the panel after the treatment process. The panels were stored in a 20 °C and 50% relative humidity environment during the treatment steps. Each contaminant–starting challenge–material–decontaminant combination was tested in triplicate at minimum. Figure 3 illustrates the test process.

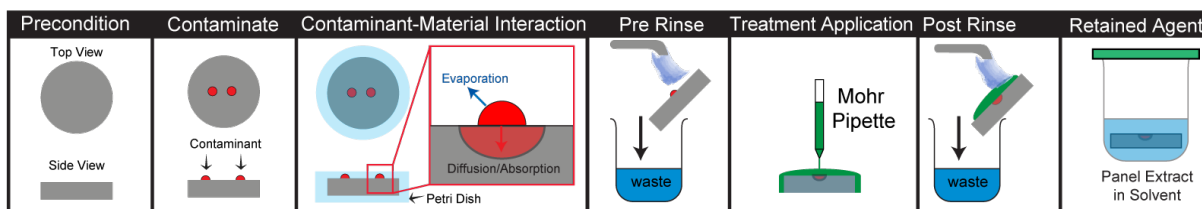


Figure 3. Treatment process for measurement of RA mass.

3.1 Contamination

The contaminants HD and VX were used as part of this study to evaluate moderate and low-volatility agents (Table 2), and the agent sources used were chemical agent standard analytical reference material (CASARM) high-purity grade. The contaminant was applied to the test materials using four different starting challenge presentations. In theory, the number of drops to achieve the specified liquid starting challenge on the material area is determined by

$$n_{\text{drops}} = \frac{SC A_{\text{material}}}{\rho V_{\text{drop}}} \quad (1)$$

where

n_{drops} is the number of drops of agent on material (unitless integer),
 SC is the starting challenge (g/m^2),
 A_{material} is the material surface area (m^2),
 ρ is the liquid density (g/mL), and
 V_{drop} is the drop volume (mL).

Although eq 1 relates the number of drops to the starting challenge as a function of the liquid agent density, drop volume, and material surface area, there are rounding steps for either number of drops or drop volume that ultimately have to take place. Starting challenges of 1, 5, or 10 g/m² are considered to be nominal contamination densities and are integer values. Liquid agent density and material surface area are not integers, but drop number is an integer value and, due to the constraints on the means of liquid delivery, volume per drop is also an integer value. For example, a 2 µL drop was chosen to represent the 1 g/m² challenge for HD, but a drop volume of roughly 1.58 µL would have been more accurate. Pipettes used to deliver the agent to the test panels were limited to 1 µL volume increments. Furthermore, it should be noted that the starting challenge and the actual agent contamination density can differ significantly as the agent purity decreases.

Table 2. Contaminant Liquid Density and Purity

Agent	Liquid Density (g/mL)*	Purity (%)
HD	1.268	99.8
VX	1.008	96.9

*At room temperature.

The number of drops used to achieve a nominal starting challenge varies with agent for the same drop volume due to variation in liquid agent density. For example, because the density of HD is roughly 25% greater than that of VX, fewer drops of HD were used to achieve the same contamination density as compared to VX. Figure 4 illustrates the starting challenges and contamination patterns for each contaminant, as suggested by the methodology documentation.¹ The starting challenge generated from these contamination schemes for HD and VX is provided in Table 3.

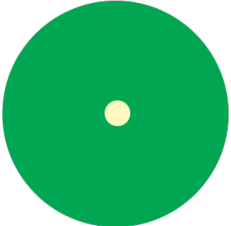
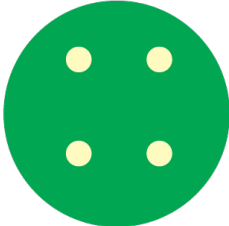
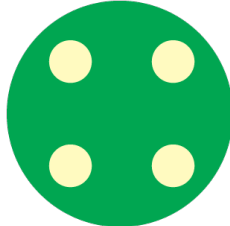
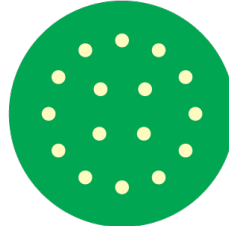
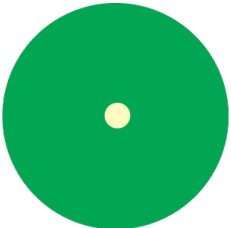
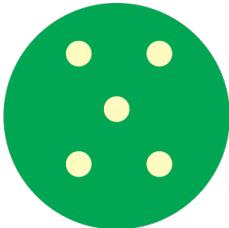
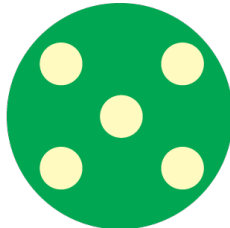
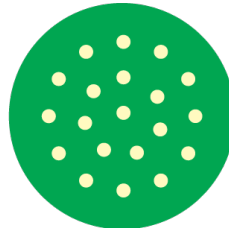
Target Starting Challenge (g/m ²)	1 g/m ²	5 g/m ²	10 g/m ²	10 g/m ²
HD				
	1- 2 µL Droplet	4- 2 µL Droplets	4- 4 µL Droplets	16- 1 µL Droplets
VX				
	1- 2 µL Droplet	5- 2 µL Droplets	5- 4 µL Droplets	20- 1 µL Droplets

Figure 4. Arrangement of agent drops for each target starting challenge.

Table 3. Comparison of Starting Challenge Levels to Actual Contamination Density Values

Agent	Starting Challenge (g/m ²)	Drop Count	Drop Volume (μL)	Mass (mg)		Actual Contamination Density (g/m ²)	
				Liquid	Agent	Liquid	Agent
HD	1	1	2	2.536	2.531	1.255	1.253
	5	4	2	10.144	10.124	5.022	5.012
	10	4	4	20.288	20.247	10.044	10.023
	10	16	1	20.288	20.247	10.044	10.023
VX	1	1	2	2.016	1.954	0.998	0.967
	5	5	2	10.08	9.768	4.990	4.835
	10	5	4	20.16	19.535	9.980	9.671
	10	20	1	20.16	19.535	9.980	9.671

Note: Values generated from the contamination schemes shown in Figure 4, using a 2 in. diameter panel for the material area. Liquid mass calculated from drop volume and CASARM liquid density, and agent mass subsequently determined from liquid purity (see Table 2).

Dose confirmation samples (DCS) quantify how much analyte mass is delivered to the panels. DCS were prepared by dispensing a drop of the contaminant into a known amount of solvent in the same manner that it would be applied to a test panel. The DCS represent five replicates for each contamination condition (i.e., number of drops and volume per drop) and are summarized in Appendix B.

The contaminant–material interaction periods were 120 min for VX samples and 120 and 1440 min for HD samples. The variable contamination duration time used for HD allowed for an investigation into the effect of contaminant–material interaction time on RA and decontamination efficacy as well as an accounting of time-dependent effects such as evaporation of bulk liquid agent, absorption of agent into the material, and vapor emission of agent from the contaminated material.

3.2 Materials

Three different materials were used during the study, including silicone as an absorptive elastomer and two paints: a green PU coating on which liquid agents tend to spread and a gray alkyd coating on which liquid agents tend to not spread (i.e., remain sessile). Using the silicone elastomer also supplied a contrast between bulk materials (>1 mm thick) and thin polymer composite coatings (<100 μm thick). These materials were chosen because (1) they are commonly used in decontamination evaluations, (2) previous work has shown that these materials absorb agent, and (3) the spreading behavior of the agents was known to be different across these materials.¹⁸ Table 4 provides information regarding the test materials used in the form of 2 in. (5.08 cm) circular panels.

Table 4. Test Material Information

Material	Description	Thickness
PU coating	Green PU coating on grade 304 stainless steel, 2B mill finish substrate	~100 μm (topcoat and primer)
Alkyd coating	Gray alkyd coating on grade 304 stainless steel, 2B mill finish substrate	~100 μm (topcoat and primer)
Silicone	Silicone elastomer MQ/VMQ/PMQ/PVMQ, part number SI303300, GoodFellow (Pittsburgh, PA)	3.2 mm

3.3 Decontamination Treatments

Three different decontamination treatments were evaluated when applied to each contaminated material (Table 5). Each material was immersed in 8 mL of approximately 6% bleach, 50/50 v/v methanol/water (M/W) mixture, or soapy water. The bleach and M/W resided on the panel for 30 min, and the soapy water resided on the panel for 3 s prior to rinsing and extraction. The SWI treatment process was designed to remove the liquid agent from the surface, leaving the mass of absorbed agent and any agent strongly bound to the material surface.^{14,19,20} Through the course of performing the experiments, there were select cases where the pre-rinse was not performed, as indicated and discussed in the results. In all cases, the post-rinse was performed to remove the decontaminant solutions to ensure no interference would be observed in the extraction process and chromatography analysis.

Table 5. Decontamination Treatment Information

Decontaminant	Pre-Rinse Conditions	Volume Applied (mL)	Decontaminant Residence Time (min)	Post-Rinse Conditions
Bleach	3 $\times$ 20 mL applications of deionized water*	8	30	3 $\times$ 20 mL applications of deionized water
M/W			30	
SWI			0.05	

*For the bleach and M/W conditions, a pre-rinse was only applied to 1440 min contaminant–material interaction period panels.

The decontaminant selection included a reactive solution (bleach), an alcohol-based solution (M/W), and a treatment that removes the bulk liquid from the material surface (SWI).^{18,21} The SWI treatment served as a reference condition for evaluating how much better the M/W or bleach treatments performed as compared to the mild SWI treatment process.

3.4 Panel Extraction

All extractions were performed for 1 h in either chloroform for HD or isopropyl alcohol for VX. Extraction solution samples were diluted, and the analytes were quantified using gas chromatography (GC) for HD (Agilent 6890/7890 GC equipped with a 5975 mass selective detector [Agilent Technologies; Santa Clara, CA]) or liquid chromatography (LC) with a mass spectrometer for VX (Agilent 1200/1290 series LC and Applied Biosystems [Carlsbad, CA] API5000/5500 triple-quadrupole mass spectrometer equipped with a TurboV ion source). Details on use of the chromatography platforms have been published elsewhere.²²

4. RA RESULTS AS A FUNCTION OF CONTAMINATION CONDITIONS

This section presents results to describe how RA varies as a function of configuration and quantity of agent delivery, liquid agent spreading behavior, and agent–material interactions. Decontamination performance is subsequently mapped to these trends.

4.1 Contamination Imaging

Images were recorded of liquid agent spreading behavior on the materials for each agent and contamination duration investigated. Results were quantified at the end of the contamination duration (i.e., 120 or 1440 min) to provide the total liquid-wetted area for each panel. The wetted area was used in later analysis to identify correlations with the RA. The images for HD contamination after 120 min are presented in Figure 5. HD spread on the PU coating but remained sessile on the silicone elastomer and on the alkyd coating. The 10 g/m² starting challenge conditions resulted in agent flow off of the panel as detected by M8 paper placed under the panels during contamination of the PU coating (Figure 6). No attempt was made to limit the flow of agent off of the panel; the quantity of agent applied seemed to saturate the surface and flow off, which would occur in a laboratory or operational context. The images for HD contamination after 1440 min are presented in Figure 7. In this case, most of the HD liquid was no longer visible, indicating the agent had either absorbed into the material or evaporated before the treatment process was conducted.

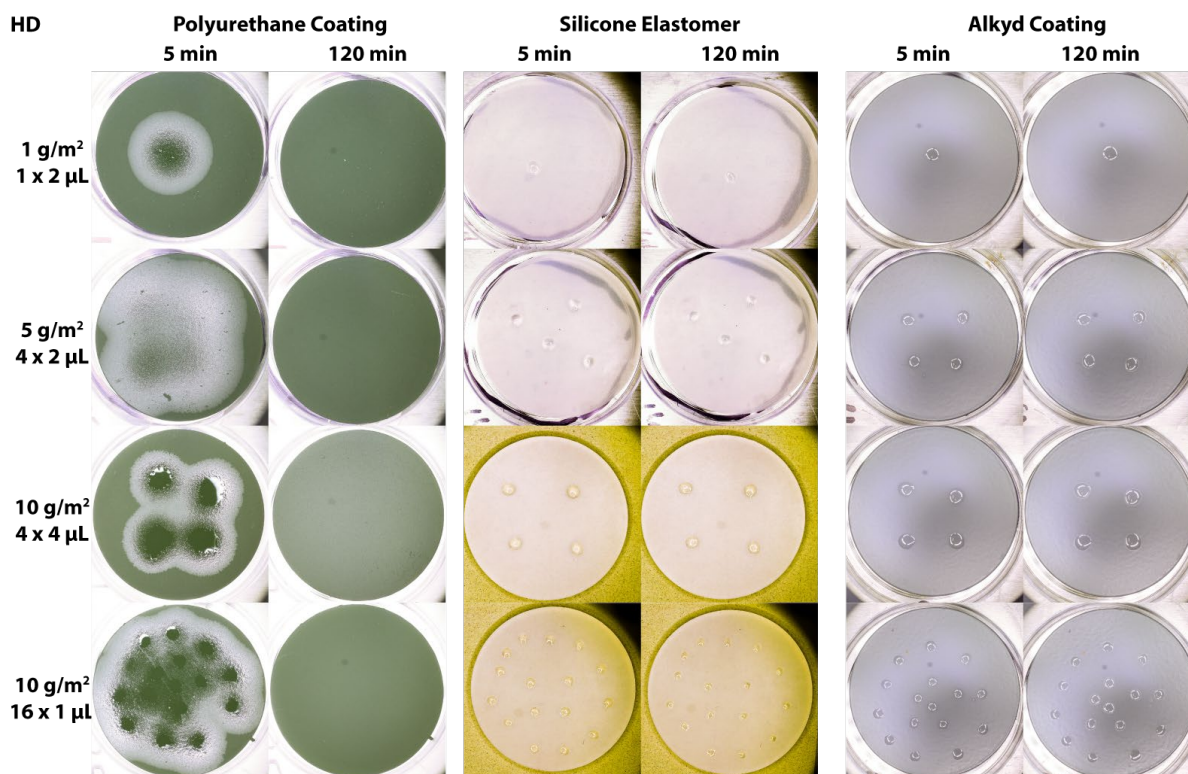


Figure 5. Representative images of HD spreading behavior for each contaminant delivery variation on PU coating (left), silicone elastomer (center), and alkyd coating (right) after 120 min.

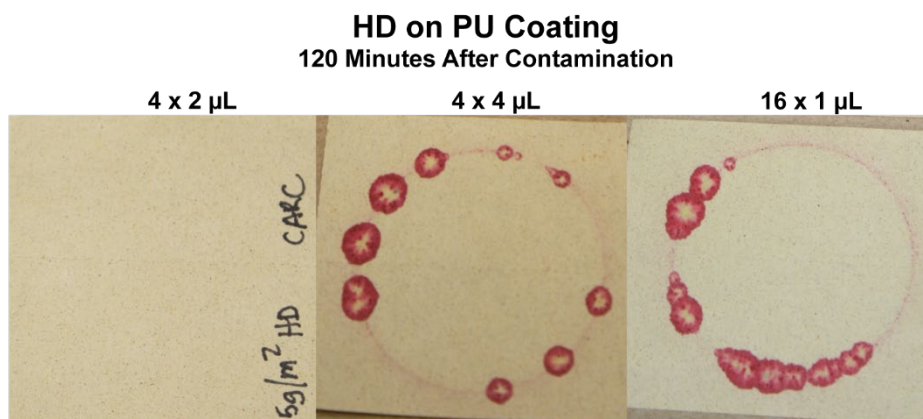


Figure 6. M8 chemical agent detector paper responses for the 4 × 2 μL, 4 × 4 μL, and 16 × 1 μL contaminant delivery variations of HD on PU coating, showing that some quantity of HD flowed off of the panel surface during the contamination duration with >8 μL of dispensed liquid. M8 paper for other materials did not indicate agent transfer off of the panel.

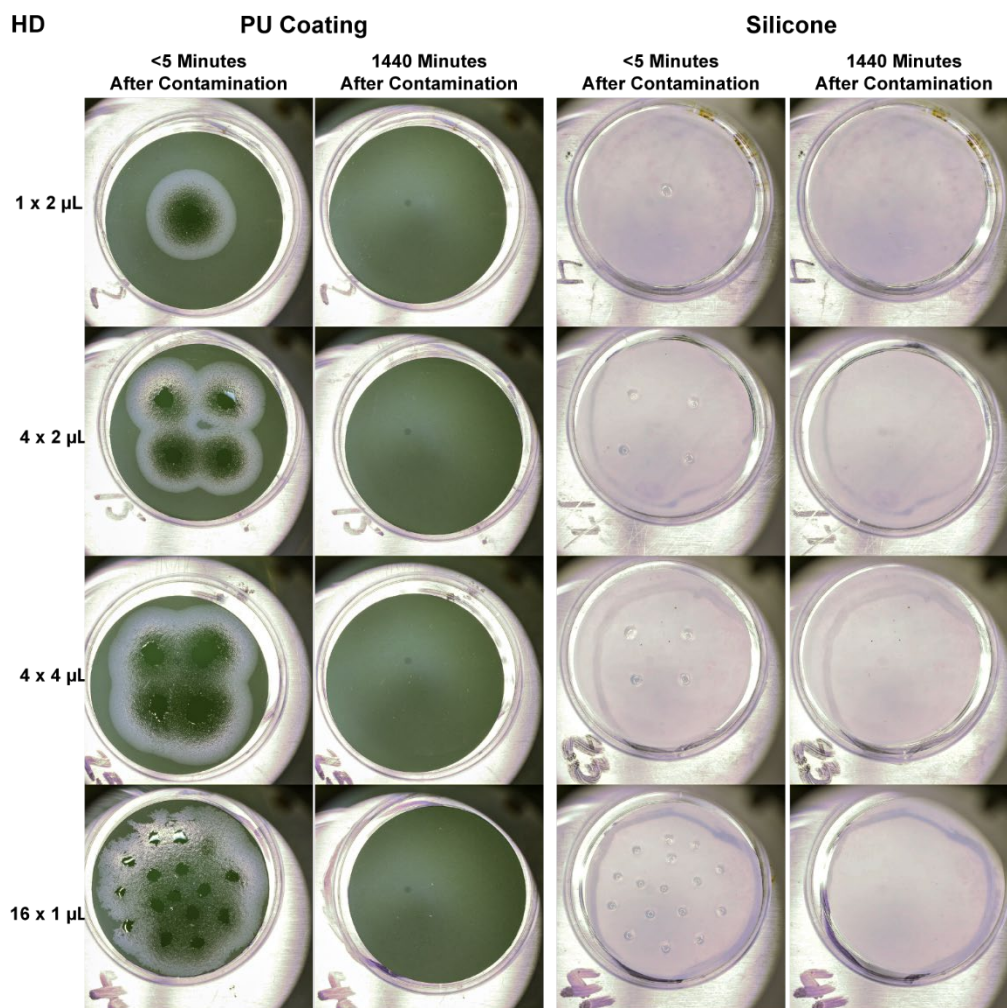


Figure 7. Representative images of the spreading behavior for each contaminant delivery variation on PU coating (left) and silicone elastomer (right) after a 1440 min contaminant–material interaction period for HD.

For VX on the PU coating at 120 min (Figure 8), the agent rapidly spread to a thin film, and for the high starting challenges, some of the agent flowed off of the panel surface, as shown by the green color on the M8 paper in Figure 9 for the $20 \times 1 \mu\text{L}$ drop (10 g/m^2 starting challenge). Flow off of the panel was not observed for the silicone elastomer.

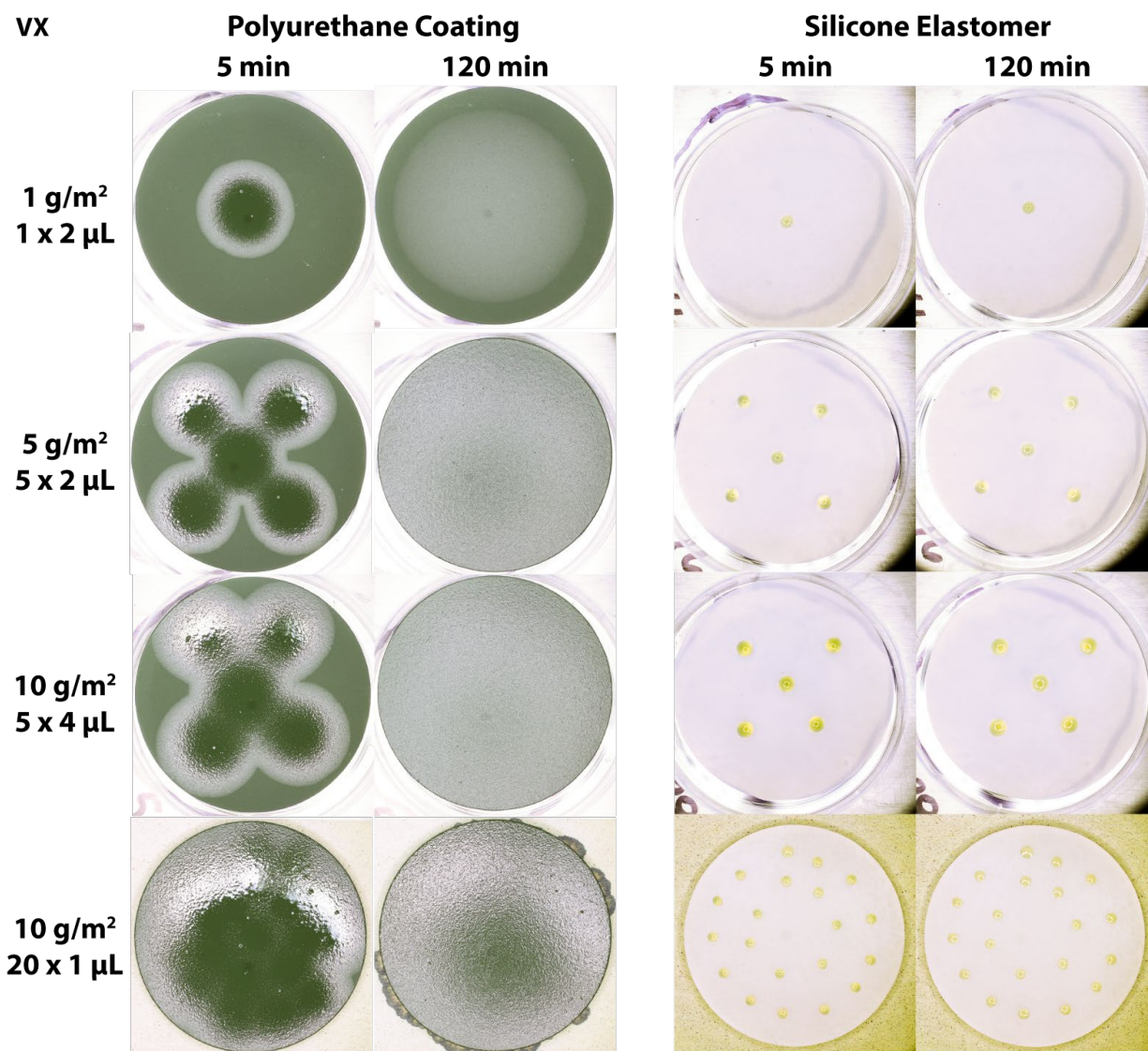


Figure 8. Representative images of the spreading behavior for each contaminant delivery variation for VX on PU coating (left) and silicone elastomer (right). The slight yellow color of the VX drops on silicone was enhanced (with post-processing) to provide better visual contrast.

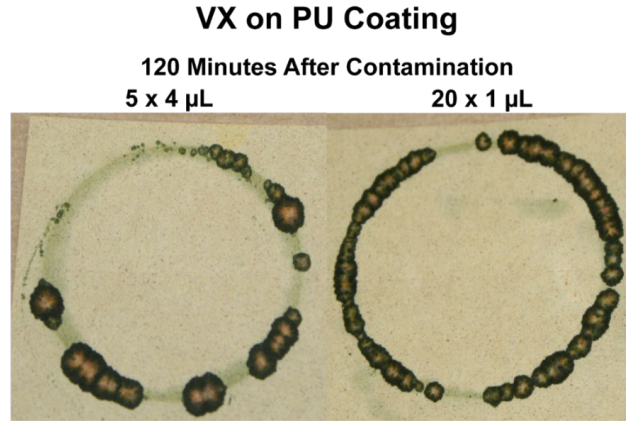
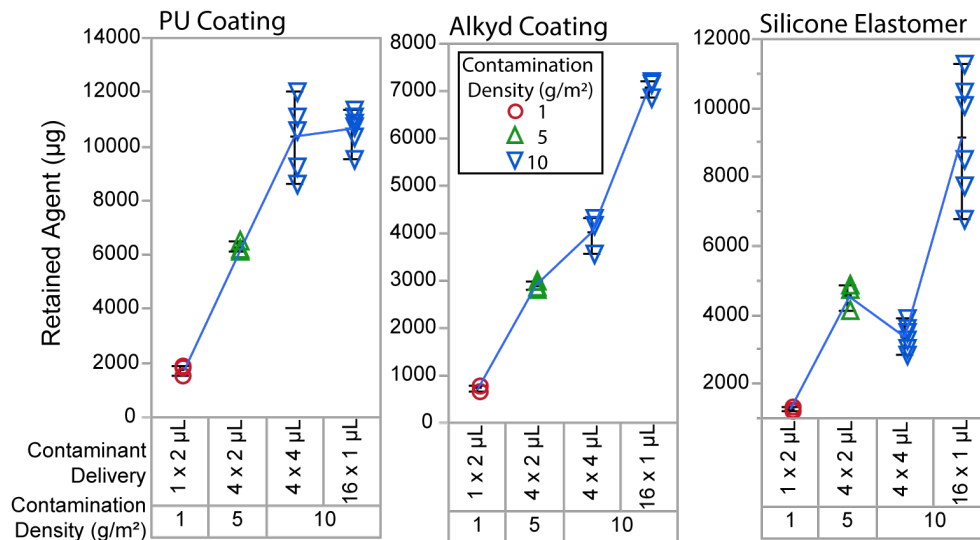


Figure 9. M8 chemical agent detector paper responses for the $5 \times 4 \mu\text{L}$ and $20 \times 1 \mu\text{L}$ contaminant delivery variations of VX on PU coating, showing that some quantity of VX flowed off of the panel surface during the contamination duration, as indicated by the green color on the M8 paper.

4.2 RA for Variable Contamination Configurations with SWI Treatment

The RA exhibited different trends across the contamination configurations for the three materials tested, as shown in Figure 10. For the same treatment process of SWI with HD, PU coating showed an increase in RA with contamination density and similar values for both 10 g/m^2 configurations. For the alkyd coating, RA increased with contamination density, but the $1 \mu\text{L}$ drops produced significantly more retention than $4 \mu\text{L}$ drops for the same 10 g/m^2 contamination density. The trend for silicone elastomer was unexpected and showed one case where the $4 \mu\text{L}$ drops at 10 g/m^2 retained less agent than the 5 g/m^2 condition. *This led to the observation that contamination density is not a unique specification describing the contamination of materials; the drop volume used to generate the contamination density influences the observed RA.*



HD, contamination duration 120 min, Soapy Water Immersion Treatment

Figure 10. RA for the SWI treatment across three materials, each exhibiting different trends for the contaminant delivery.

For the next grouping of data, the responses for one material with different contamination durations and agents are considered. The RA measurements for all of the contamination configurations indicated in Table 3 are shown for PU coating (Figure 11) after an SWI treatment. The observed RA did not scale proportionally with the contamination density; that is, the 10 g/m² RA results were not 10 times the 1 g/m² RA results. This may be a result of flow off of the panel, as occurred on the M8 detector paper at higher contamination densities. For HD contamination after 1440 min, the RA values were slightly lower than those for the 120 min duration (comparing Figure 11, A and B). No liquid was visible in the image recorded at 1440 min (Figure 7), which indicates that evaporation may have been responsible for the lower RA values. It is not clear why the 16 × 1 μL contamination condition produced an RA so much lower than that for the 4 × 4 μL contamination condition at 1440 min (Figure 11B). However, the images recorded at 120 min (Figure 5) provide a clue. The surface treated with 4 × 4 μL drops appeared shiny or wet after 120 min, whereas the surface treated with 16 × 1 μL drops looked normal or dry. This potentially indicates faster evaporation in the case of the 16 × 1 μL contamination condition due to the way the liquid was distributed on the surface at the time of delivery (i.e., more uncontaminated surface area was initially present for the larger 4 μL drops).

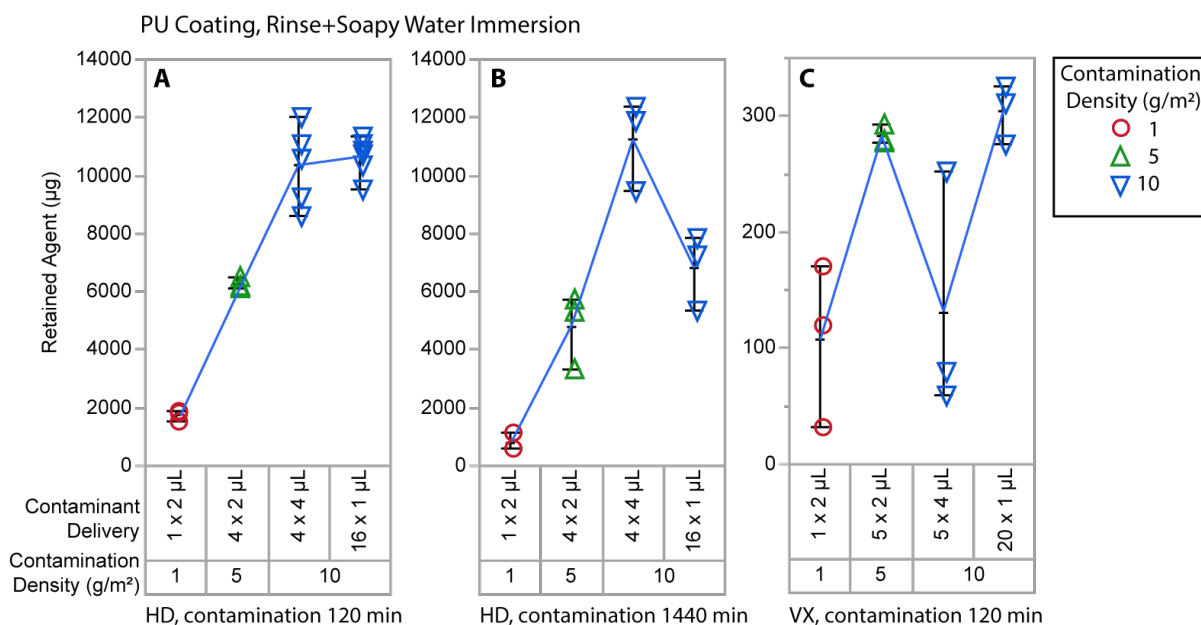


Figure 11. RA for PU coating using the rinse and SWI treatment process for different agents and contamination durations.

The results of VX contamination on PU coating (Figure 11C) indicate that the material had minimal agent retention (i.e., hundreds of micrograms rather than thousands); results were similar across the contaminant configurations. Based on the images (Figure 8), the agent spread over the full material area, and it is likely that the agent remained as a liquid on the surface and did not significantly sorb. As a result, once the material surface was overwhelmed (i.e., fully wetted) by VX, the addition of more liquid did not facilitate more retention. Once excess liquid was present, additional liquid did not alter the results. And, in this case, the SWI treatment removed the majority of the liquid agent. Therefore, there was no significant trend

between RA and contamination density. This may indicate that PU coating is somewhat resistant to VX, and that no matter how much agent is applied, only a small quantity is retained on the material surface. Furthermore, because the agent spread significantly on the surface, the liquid-wetted area did not change as more liquid was added. Other impermeable materials may respond similarly.

For the alkyd coating and silicone elastomer, the contaminant remained as a sessile drop and did not run off of the material during the contamination duration. The retention of the alkyd coating (Figure 12) was different for each contamination configuration. In this case, HD data were only collected for a 120 min contamination duration. For silicone (Figure 13), the RA scaled with contamination density in the limit of longer contamination duration (Figure 13B). However, it was most unexpected that less agent was retained with a 10 g/m^2 contamination density applied as $4 \times 4 \text{ }\mu\text{L}$ drops than with a 5 g/m^2 contamination density (Figure 13A). The similarity in the 5 and 10 g/m^2 conditions was also observed for VX (Figure 13C).

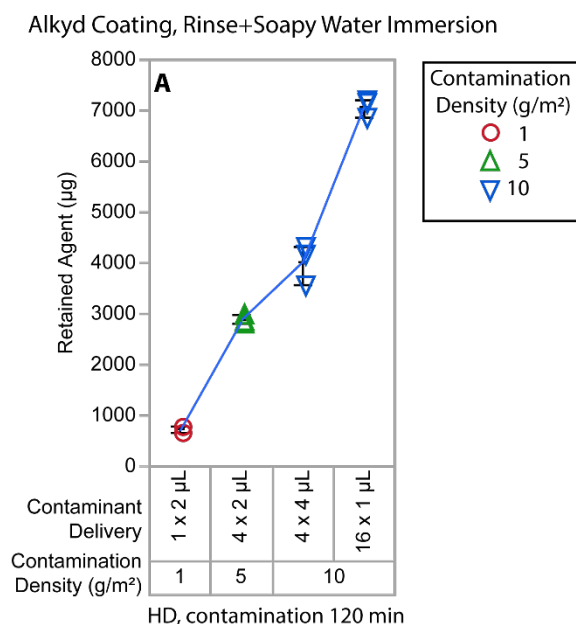


Figure 12. RA of HD and VX on alkyd coating using the rinse and SWI treatment process.

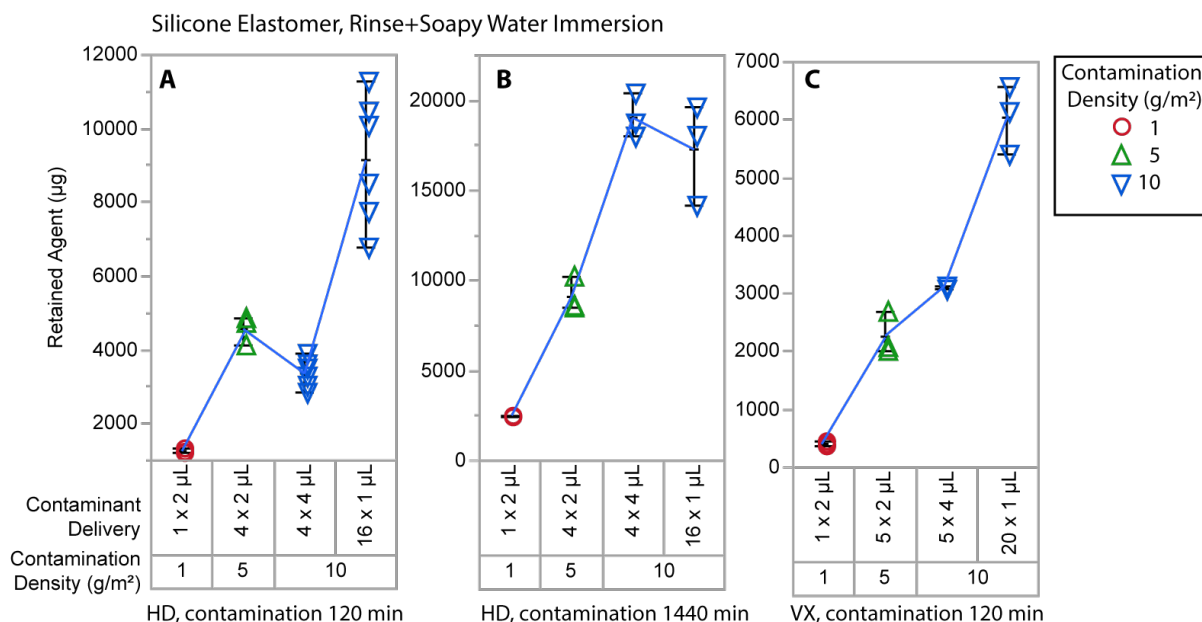


Figure 13. RA of HD and VX on silicone using the rinse and SWI treatment process.

The difference in HD RA for the different contamination durations on silicone elastomer resulted from the treatment process halting absorption at 120 min, whereas the 1440 min condition allowed absorption and evaporation to occur until no liquid remained on the surface. This contrasts with the PU results; on that surface, a lower RA was observed at the 1440 min duration. This was likely because HD spread on the PU coating surface, which resulted in increased sorption and evaporation such that all liquid HD was gone near the 120 min duration, as evidenced by the images (Figure 5). Further evaporation of absorbed HD from the PU coating decreased the RA. The images of the silicone surface in Figure 5 show that the drops were still present and continuing to absorb after 120 min, thereby increasing the RA.

It is hypothesized that the differences in RA across contamination conditions are related to variations in the agent distribution when the decontaminant treatment was conducted. Three cases were observed in these data:

1. The agent spread on the material, in most cases fully wetting the material area with potential flow off of the material. The liquid may or may not have been visually observable when the treatment process was conducted, depending on contamination duration and extent of absorption and evaporation. This was often the case for HD on PU coating at both short and long contamination durations (Figures 5 and 7).
2. The agent remained as a sessile drop (i.e., did not spread), and was still visually present when the decontamination treatment was performed. This was often the case for HD on the alkyd coating and silicone elastomer at short contamination durations (Figure 5). In this case, the decontaminant is addressing bulk liquid agent on the surface in addition to absorbed agent, and various rate limiting processes (Table 1) may influence the RA results.
3. The agent remained sessile but could no longer be visually observed as a drop on the surface when the decontamination treatment was performed due to evaporation and

absorption. This was often the case for silicone at 1440 min contamination duration (Figure 7). As a result, the bulk liquid rate limiting processes are not likely to influence the RA results.

One of several factors to consider in these data is that the solubility and rate of dissolution of the agent into the decontaminant solution may be significantly different across the agent–decontaminant combinations used here. HD tends to be hydrophobic with lower solubility and dissolution rates into aqueous solutions, whereas VX may be slightly hydrophilic with higher solubility and faster dissolution in aqueous solutions. Some of the trends seen here may be influenced by the solubility and dissolution rates of the SWI treatment.

In general, the 4 μL drop volume RA results seem to be similar to or less than results observed for 1 μL drop volumes for the same starting challenge (except for HD on PU coating at 1440 min). The larger-volume drops have lower surface area to volume ratios (Figure 2) and smaller wetted areas per drop that may influence the relative quantity of mass that is evaporated and absorbed. *These results indicate the need to normalize the results to more than just contamination density.*

4.3 Log Reduction Relative to SWI

Decontamination efficacy is calculated here as the difference in RA response for a contaminant–material pair between a decontamination technology and an SWI treatment. The SWI treatment is assumed to only remove the weakly bound liquid agent from the material and allows for a measurement of RA mass by the material due to bulk absorption or liquid adhesion at the surface. The RA measured after the SWI treatment serves as a reference to enable the quantitative assessment of how well other decontamination technologies remove the absorbed and adhered agent. Different liquid-based decontamination treatments, as a function of their composition, will be more or less sensitive to the contamination present in and on the material as a function of the contamination conditions. Therefore, it is important to determine how sensitive decontamination efficacy is to contamination density for the select set of model decontamination treatments discussed in Section 3.3. To evaluate the efficacy between a reference condition (*ref*) and comparison point (*B*), a log difference (LD) calculation for RA was used as defined by:

$$\begin{aligned} \text{LD} &= \log_{10} \frac{\text{RA}_{\text{Ref}}}{\text{RA}_B} \\ &= \overline{\log_{10}(\text{RA}_{\text{Ref}})} - \overline{\log_{10}(\text{RA}_B)} \end{aligned} \quad (2)$$

The details of the LD calculations are provided as Procedure 5 of the *Test Methodology Source Document*,¹ and the error bars calculated from these results provide the 95% confidence interval (CI) on the difference. The LD is calculated for each treatment relative to the SWI treatment process for the identical drop deposition pattern. Results are provided in Figures 14–16. For each figure, the RA data are provided in the bottom chart, and the LDs are provided in the corresponding top chart.

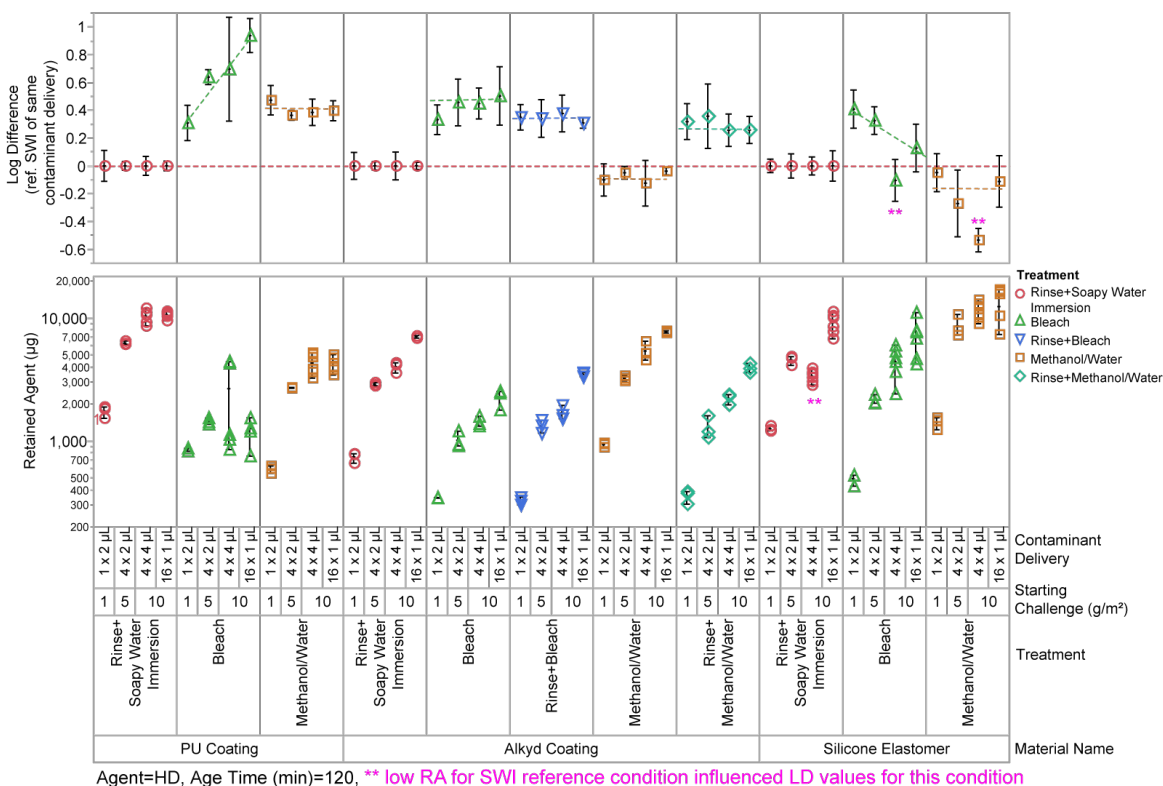


Figure 14. Performance (LD) for each treatment relative to the SWI treatment process for HD at 120 min. Error bars represent the 95% CI on the difference. The LD is calculated for matching contaminant delivery conditions (e.g., $1 \times 2 \mu\text{L}$ for SWI is compared to the $1 \times 2 \mu\text{L}$ condition for other treatments).

In general, a similar LD (relative reduction) was observed for all contaminant depositions for the alcohol-based M/W treatments; the same relative reduction in RA was observed across the tested contamination densities. Some variations in LD were observed for silicone for the $4 \mu\text{L}$ drop condition, indicating that drop volume may affect decontaminant performance. In the initial test design, a pre-rinse was not included in the treatment process. For the M/W treatment (30 min immersion) on the alkyd coating and silicone, it was observed that higher RA values were observed compared with the SWI condition (a 3 s immersion), resulting in a negative LD. The lack of a pre-rinse allowed HD to continue sorbing into the material during the decontamination treatment period. Subsequent testing included a pre-rinse step to remove the bulk liquid HD, which resulted in the M/W treatment reducing the RA and providing a positive LD (only demonstrated on the alkyd coating here).

For bleach treatment, the LD varies with contamination density for the PU coating and silicone, but not for the alkyd coating. Further, the relative performance shows opposing trends for the PU coating and silicone as a function of contamination density. The relative agent distributions for these materials are quite different as a result of the spreading behavior, and the material properties may result in different dominant rate limiting processes toward agent removal from the materials (i.e., decontamination).

The LD calculation was also performed on the long contamination duration results (Figure 15). The longer contamination duration typically results in more absorption into the material, the potential for more evaporation, and less liquid agent present on the material surface, as shown in Figure 7. As a result of this change in agent distribution, the LD compared to the SWI treatment is much lower than that observed at the 120 min contamination duration.²³ These differences may indicate that the majority of decontaminant performance at 120 min is related to removing agent liquid from the material surface rather than removing agent that is absorbed in the material. In most cases of long duration contamination, the LD is either similar across the contamination density or may decrease with increasing starting challenge; however, the error bars for the LD values indicate that these trends may not be statistically significant. The decontaminants are much less effective for long contamination durations compared to short duration contaminations; the LD may change at most by 0.5.

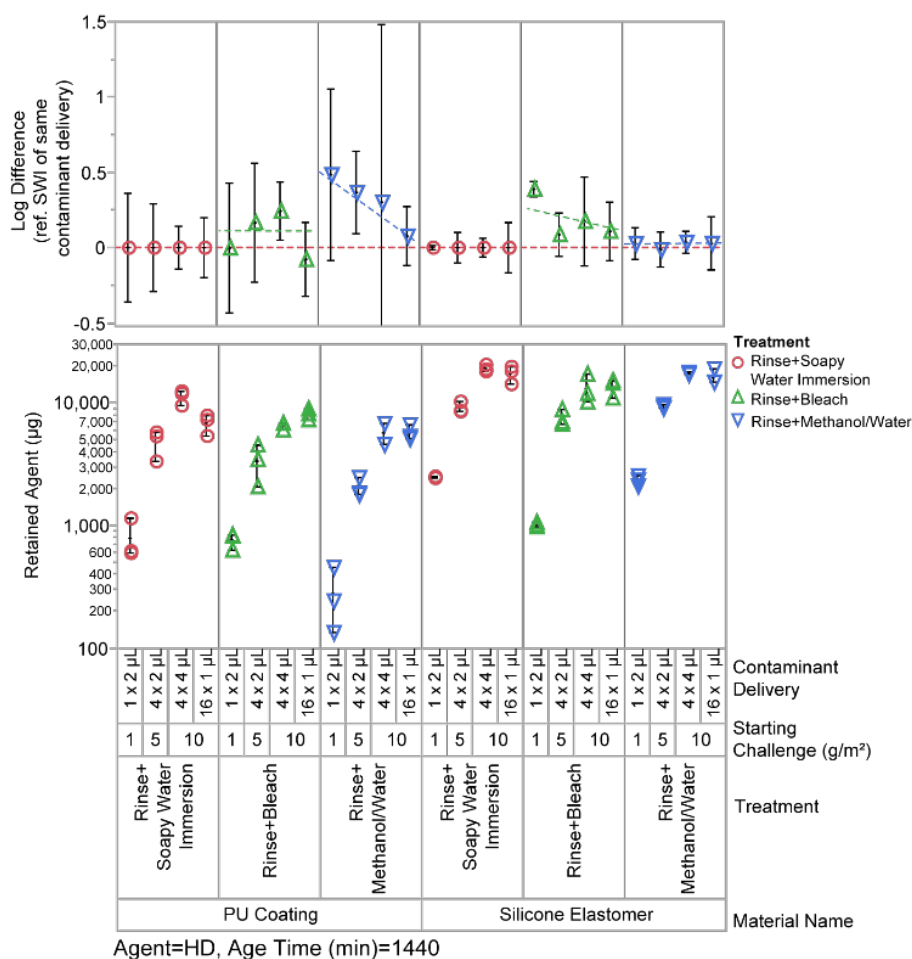
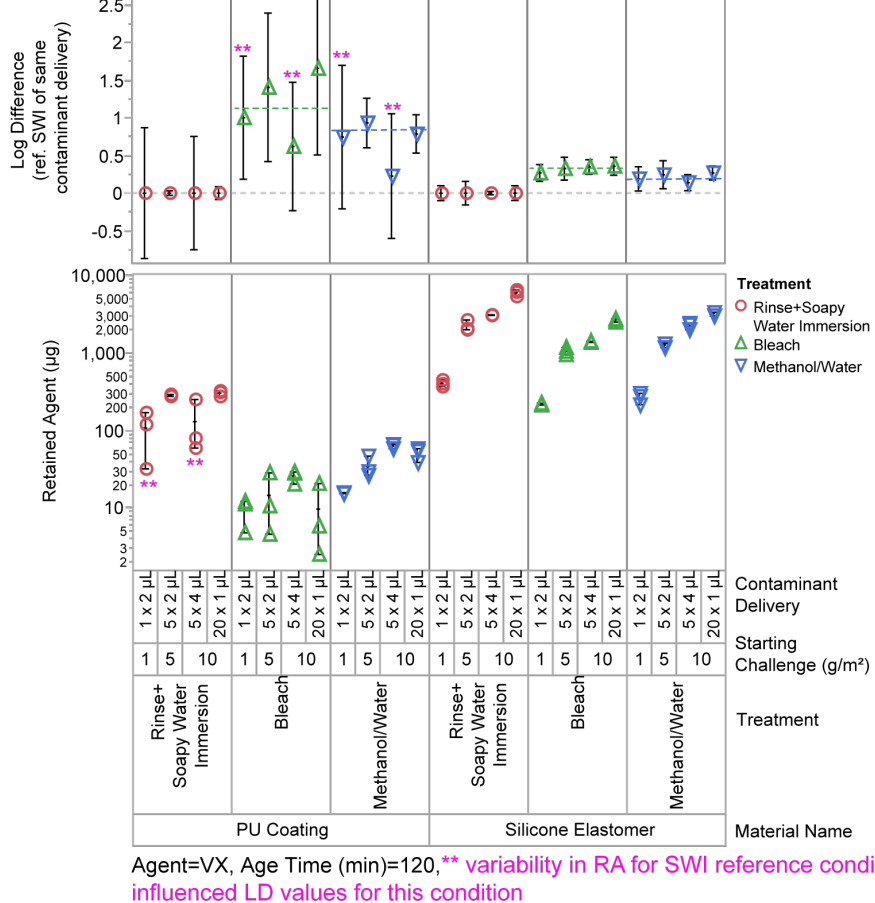


Figure 15. Performance (LD) for each treatment relative to the SWI process for HD at 1440 min. Error bars represent the 95% CI on the difference.



5. PER-DROP NORMALIZATION OF RA RESULTS

The variable contamination density data enable the possible correlation of contamination parameters with the observed RA data. A per-drop normalization of the RA results for different contamination conditions was found to capture various factors that influence RA. These empirical results indicate better ways to normalize experimental data and to identify what test design factors need to be controlled for translation of laboratory results to operational conditions.

5.1 Contamination Parameter Correlations

The categorical analysis associated with contamination parameters in Section 4 aimed to identify trends for relative retention or LD. In this section, correlations were considered for the HD RA results, for which the data set is most robust, including relative per-drop normalization (RA/drop count) and raw RA compared to multiple experimental parameters using a linear fit (Figure 17). The applied mass parameter was the same as the contamination density associated with the starting challenge, except the parameter was not divided by the material area (0.00202 m^2).

For PU coating, strong correlations were observed between RA and applied mass as well as between RA per drop and drop volume. HD drops on PU coating spread to fully wet (and potentially flow off of) the material area (Figure 5), preventing the use of any correlations involving contaminated area. For the alkyd coating, very strong correlations were identified between RA and contaminated area, RA per drop and contaminated area per drop, and RA per drop and drop volume. The correlation with contaminated area was more influential than the correlation with applied mass, where there was deviation with the different drop volumes. Bear in mind that contaminated area is a sum of per-drop interaction areas with the surface. Lastly, for the silicone elastomer, correlations were observed between RA per drop with both contaminated area and drop volume, similar to the other materials.

These data demonstrate that the correlation between RA or RA per drop and contamination parameter may vary with the material, likely as a result of agent–material interactions and the way liquid agent spreads on the material. For the case where HD liquid spread on the PU surface and the surface showed very little visible bulk liquid after the contamination duration (i.e., all of the liquid absorbed into the material), it is reasonable to expect a correlation between RA and applied mass as well as between RA per drop and drop volume. The total HD mass delivered to the material scales with the total RA or RA per drop for the total applied mass or on a per-drop volume basis (essentially equivalent to mass per drop), respectively. However, for the instances where HD drops remained sessile, normalizing to single drops is necessary. The individual interactions of isolated drops must be summed, and the interaction area between each drop and the surface is important. The total RA will not necessarily correlate with the total applied mass because not all of the applied mass was capable of interacting with the material. These trends are a result of the interactions between HD and these materials, as evidenced by wetting and absorption behavior.

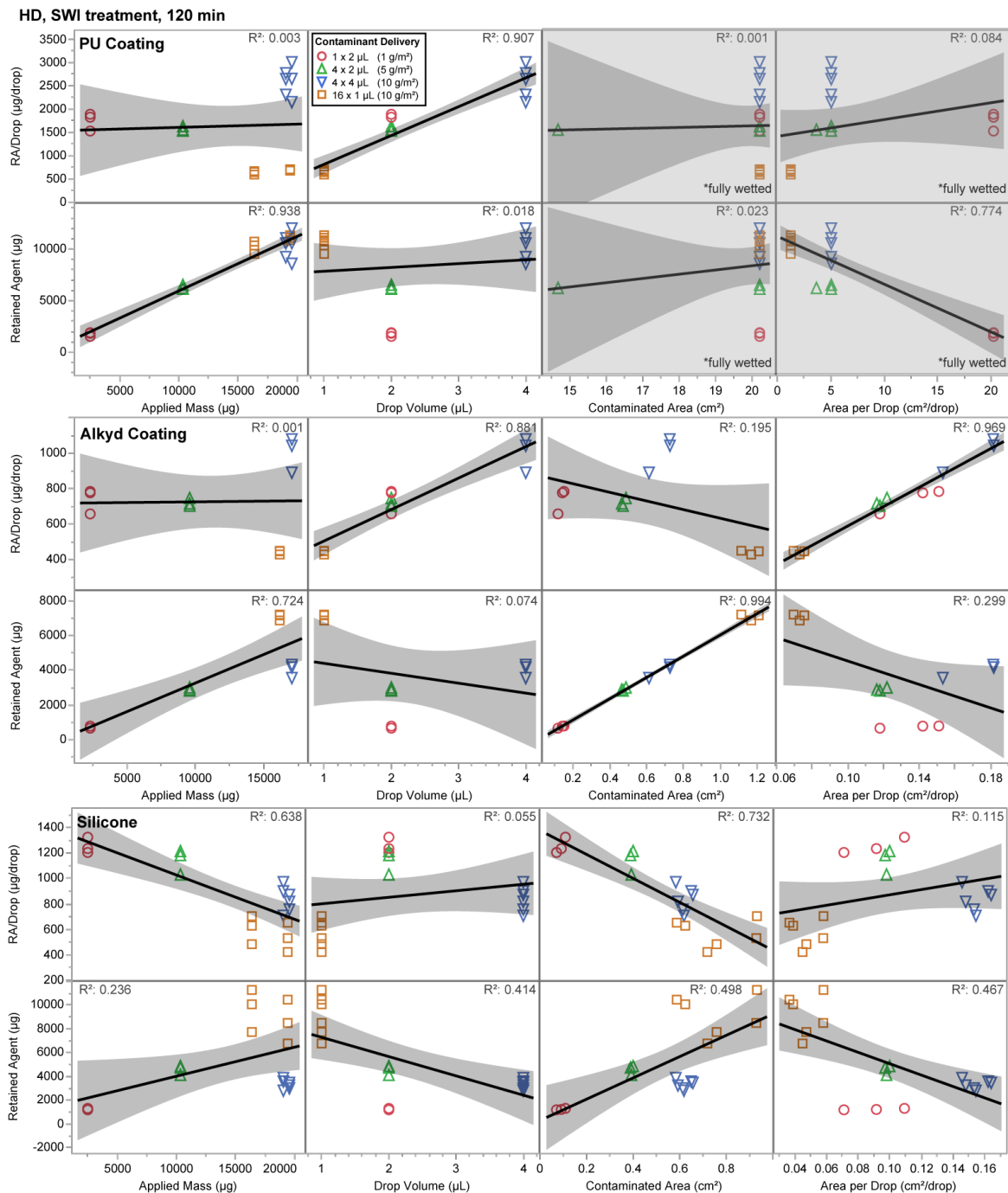


Figure 17. RA linear correlations for HD on three materials for the SWI treatment process for 120 min contamination duration. Light gray boxes over the contaminated area parameters for the PU coating indicate samples that were fully wetted, and correlations with area are not informative. Gray-shaded regions for each plot indicate the 95% CI on the fit.

5.2 Developing a Normalization Approach

Contaminant–material interactions are expected to strongly determine RA signal contributions, which presents a challenge for the development of a universal normalization of RA to particular contamination condition parameters. The data in Figure 17 for HD indicate that the strongest correlations with the RA may be with the applied mass or the contaminated area. Both of these terms can be expressed as a function of the drop volume. The applied mass can be determined by the combination of the number of drops applied, the drop volume, and the agent density (ρ) and purity (Ψ). Therefore, for systems where the RA is correlated with applied mass (likely when the agent significantly spreads), the RA per drop is related to $RA/drop = \rho\Psi V$; RA/drop is directly proportional to drop volume (V).

In cases where drops do not spread, the RA was observed to be related to the contaminated area. The liquid–material wetted area for a sessile drop is a function of the drop volume and the contact angle with the material. The liquid-wetted area, W , of a drop was related to the liquid drop volume by

$$W = \pi \frac{2^{4/3} \left(\frac{3V}{4\pi} \right)^{2/3} \sin^2 \theta}{(1 - \cos \theta)^{4/3} (2 + \cos \theta)^{2/3}} \quad (3)$$

where W is the liquid wetted area of the material (mm^2), and V is the volume of the liquid drop (μL).

The derivation of this equation is provided in Appendix A. Each agent–material pair may have a different equilibrium contact angle (reached over variable time, depending on drop size); however, the equilibrium contact angle should be consistent for an agent–material pair across different drop volumes. Therefore, the contaminated area per drop is proportional to $V^{2/3}$; furthermore, this suggests that RA/drop is also proportional to $V^{2/3}$ for sessile droplets because RA/drop directly depends on contaminated area. Even for cases where the agent liquid spreads over time (e.g., θ approaches zero) and the contaminated area may increase during the contamination duration, the area is still influenced by the volume of liquid applied but not necessarily with the same relationship as for sessile drops.²⁴ For cases where there is minimal absorption into a material and the liquid contaminant spreads, then the material area represents the contaminated area. This is akin to treating the liquid on the surface as one large drop, and any contaminant that is not in contact with the material surface is removed in a treatment process. This seems to be the behavior observed for VX in certain cases (e.g., VX deposited on PU).

Given these relationships between RA/drop and drop volume for fully wetted and sessile drop behavior, the hypothesis is that the RA/drop is proportional to V^m , where the slope m varies depending on whether the contaminated area or applied mass dominates the correlation with the RA/drop (i.e., degree of liquid spreading). This is an empirical power law relationship where the m term can be determined by a regression. If the data are transformed using a natural logarithm, the transformed inputs can be used in a standard linear least-squares regression to determine a slope m and intercept b as

$$\ln\left(\frac{RA}{\text{drop}}\right) = m \ln(V) + b \quad (4)$$

An example of this regression is provided in Figure 18. A linear regression is used to fit the natural logarithm transformed data; the associated adjusted coefficient of determination (R^2) value, fit equation, and fit statistics are provided for each case. The adjusted R^2 value can be considered a description of the proportion of data variance explained by the regression; a value of 0.5 indicates that 50% of the data variation is explained by the regression. The shaded region in each graph corresponds to the 95% CI for the fit. The parameter estimates provide the slope and intercept estimates, standard error (SE), and probability $> |t|$ value, which provides the t test value; values <0.05 have a 95% confidence the estimate is not zero. Note that the use of the natural log transform also enforces the left-censored nature of the measurement, so RA per drop cannot be negative. Because of the log transformation, negative values of b indicate smaller values of RA per drop, rather than the potential for negative mass.

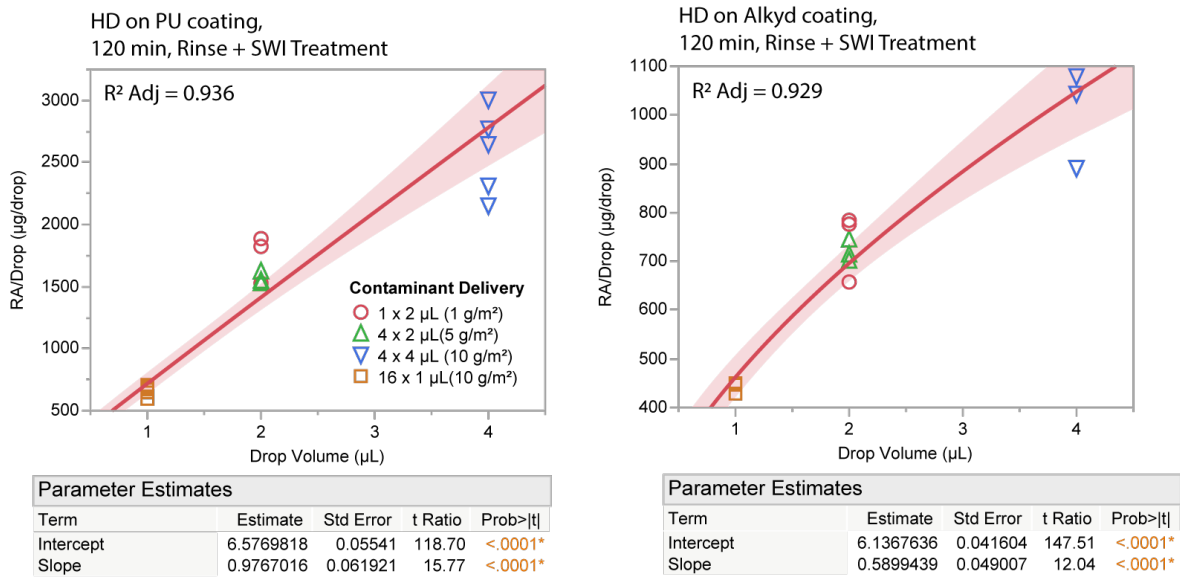


Figure 18. Example regressions of RA/drop versus drop volume for HD on PU and on alkyd coatings for the SWI treatment. Shaded regions correspond to 95% CI on the prediction. Fit is shown using the form of eq 5.

This single relationship provides an impressively good correlation with results that are *independent* of the contamination density used and *does not require measuring of the contaminated area*. Note that the data points in Figure 18 indicated by the red and green markers were both obtained using 2 μL drops but correspond to contamination densities of 1.2 and 5.0 g/m^2 . Equation 4 can be inverse-transformed to provide

$$\frac{RA}{\text{drop}} = \exp(b) V^m \quad (5)$$

This equation can be modified to translate the results back to the RA mass as

$$RA_{Fit} = \exp(b) V^m n_{drops} \quad (6)$$

where RA_{Fit} is the RA mass that would result from the contamination conditions (in micrograms of agent).

Applying eq 6 to the panel test results using drop volume and number of drops across the contamination densities can be compared to the experimentally measured total RA (Figure 19). The accuracy of the fit is determined by the ratio of $RA_{Measured}/RA_{Fit}$; if the prediction is accurate, the ratio should be 1.0. The uncertainty in the ratio was calculated using the 95% CI on the mean and the 95% CI on the fit prediction. If the CI of the ratio overlaps 1, then the prediction is statistically similar to the measured results. For this example, the prediction is statistically similar for all cases except for the $1 \times 2 \mu\text{L}$ and $4 \times 2 \mu\text{L}$ contamination conditions. The prediction for those contamination conditions is at most a factor of 1.2 lower than the measured value. This is a relatively small deviation for RA data. This analysis has produced a good fit and captured differences in RA response for different contamination conditions on materials where the agent spread (PU coating) and where the agent remained sessile (alkyd coating). For the case of PU coating with $1 \times 2 \mu\text{L}$ drops, this deviation may be a result of agent flowing off of the panel in all other 10 g/m^2 conditions; the $1 \times 2 \mu\text{L}$ and likely the $4 \times 2 \mu\text{L}$ contamination conditions are cases where spreading seemed constrained to the material surface and resulted in a slightly higher RA per-drop response.

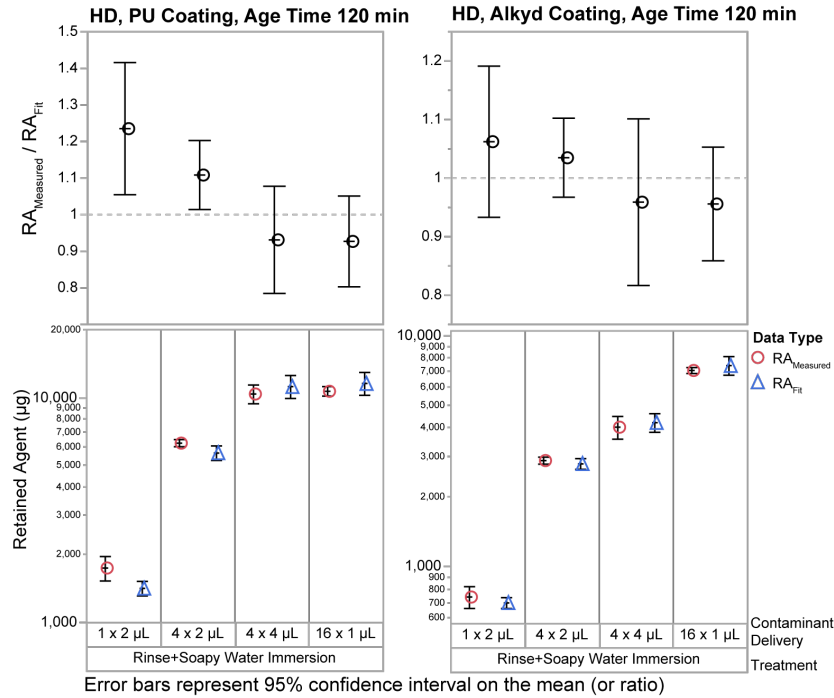


Figure 19. Accuracy of the fit to predict the original experimental results for HD on PU coating (left) and alkyd coating (right) using the SWI treatment process. Top graphs show the $RA_{measured}/RA_{Fit}$ ratio; an ideal prediction would produce a ratio of 1.0. Bottom graphs show the original data.

For the range of contamination parameters, prediction within a factor of 1.2 is a good indication that this empirical normalization approach is capturing the salient variables that influence the RA. *These data represent the range of 1–10 g/m² contamination density conditions; these trends between RA per drop and drop volume suggest that the drop volume and its influence on the resulting agent distribution provide a better measure of the important process variables that the starting challenge misses.* If drop volume is a significant factor in agent retention or decontaminant performance, then *it may be vital for laboratory testing to match the drop volumes that may be observed operationally* or for a relationship like this to enable the prediction of the effect of drop volume. Furthermore, describing RA on a per-drop basis and accounting for the drop volume effects makes it possible to translate laboratory test conditions to a wide range of variable-contamination operational conditions as a function of how many drops of various volumes are involved in the contamination of a given asset. This offers greater flexibility and ability to use laboratory data to represent operational conditions.

5.3 Per-Drop Normalization for Different Treatment Processes

The previous section showed the viability of a per-drop normalization approach for a single treatment condition (i.e., SWI treatment process) that removed the bulk liquid contamination from the surface of the material. Ideally, the empirical regression would work for other treatment processes beyond SWI that incorporate reactive chemistry, solvent chemistry, or other physical processes to remove agent from the material. However, the convolution of different mass transport processes associated with agent and decontaminant species in and on the material may complicate the physical interpretation of the empirical fit parameters. Overall, the RA/drop versus drop volume regression only provides an empirical trend describing the quantity of mass retained by a material after a contamination and SWI treatment process.

As a first step in considering the applicability of analysis to treatment processes other than SWI, the *linear* correlation of RA and RA/drop with various contamination conditions for the bleach treatment are provided in Figure 20. Similar to the SWI treatment, the reactive chemistry and associated reduction of agent from the materials shows strong correlations with applied agent mass, drop volume, and contaminated area. This indicates the proposed regression analysis may still capture how drop volume influences the RA/drop for decontamination treatments. Similar correlation plots for multiple agent–material–treatment conditions are provided in Appendix D; similar correlations were observed for all treatments evaluated.

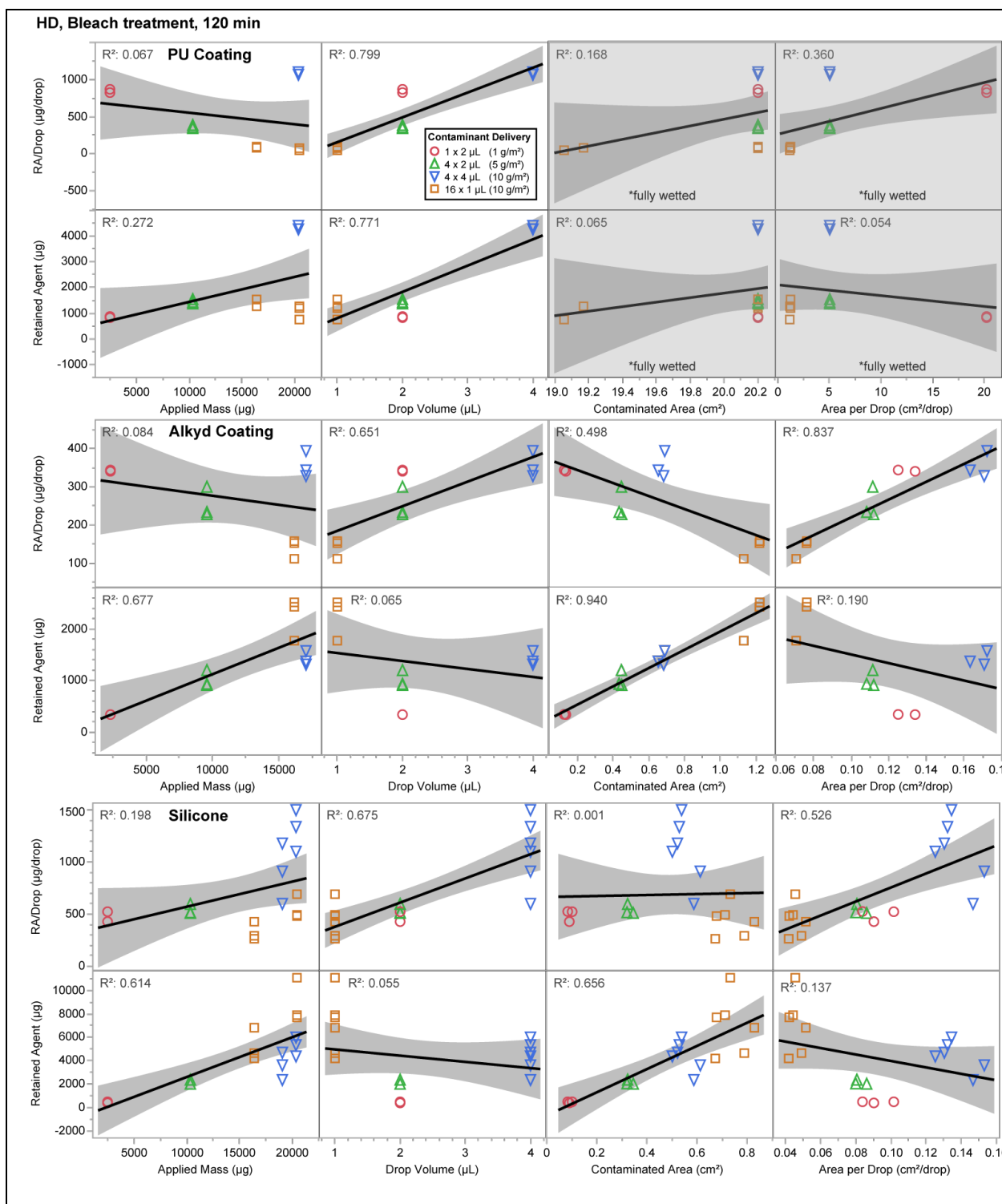


Figure 20. Linear correlation plots for HD on PU coating, alkyd coating, and silicone elastomer for 120 min contamination duration with a bleach treatment process. Light gray boxes over contaminated area parameters for the PU coating indicate samples were fully wetted, and correlations with area are not informative. Gray-shaded region on each plot is the 95% CI on the fit.

The regression analysis from eq 4 was applied to the various treatment conditions for HD on PU coating, as illustrated in Figure 21. Details of each regression are provided in Appendix E. There was good accuracy for the fits for each treatment condition, as indicated by the SE for the parameters and the adjusted R^2 ; fit parameters are provided in Table 6. Some conditions (e.g., bleach for 120 min contamination duration) produced a large m value (2.04). For the range of drop volumes tested, the RA per drop was reduced more significantly for smaller drops for bleach as compared to the other treatments. Association of specific ranges of fit values with experimental results, particularly with respect to physical interpretation and validity, is part of ongoing and future work.

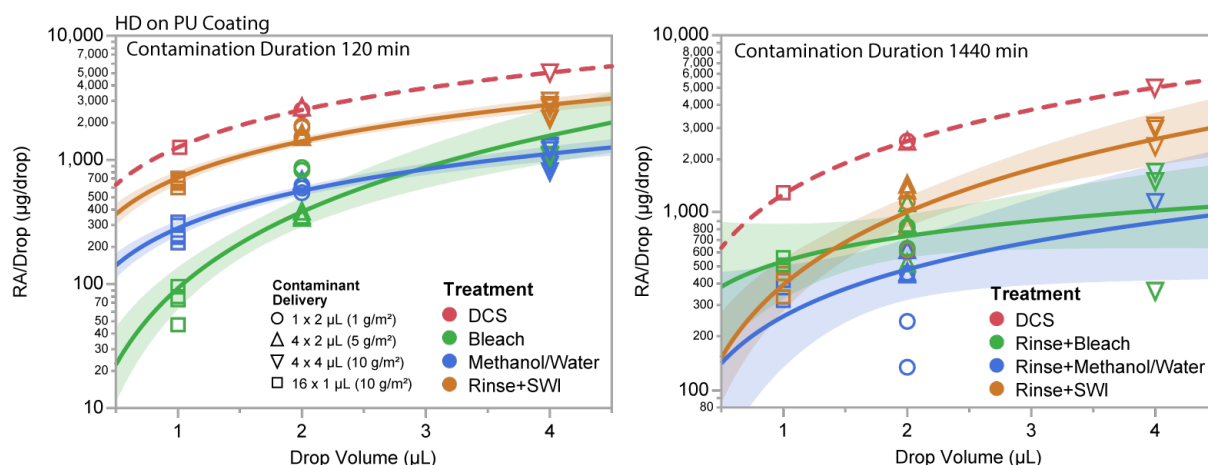


Figure 21. RA/drop results for HD on PU coatings for 120 min (left) and 1440 min (right) contamination durations. Shaded regions indicate the 95% CI on the fit. Red dashed line represents the applied mass per drop from the DCS.

Interestingly and tangentially related to the fitting analysis, for the bleach treatment at 120 min, the $1 \times 2 \mu\text{L}$ (1 g/m^2) condition provided a higher RA per drop than did the $4 \times 2 \mu\text{L}$ (5 g/m^2) condition (both $2 \mu\text{L}$ conditions; see green circles and triangles, respectively, in the left panel of Figure 21). It would be expected that the lower contamination density would produce a lower RA per drop than the other conditions because this represents the highest decontaminant to agent ratio (highest decontaminant excess) tested. The positive deviation of the $1 \times 2 \mu\text{L}$ (1 g/m^2) condition could be related to agent spread on PU coating; in all other cases, sufficient agent was applied that it seemed to flow to the panel edge and off of the panel in some cases, as indicated by the M8 paper. The positive deviation may be a result of all of the applied agent remaining on the material surface for the $1 \times 2 \mu\text{L}$ case. In the $4 \times 2 \mu\text{L}$ case, it is possible that the overlap of the wetting fronts from multiple drops resulted in more residual liquid agent on the surface that the bleach was able to access, whereas more of the liquid in the $1 \times 2 \mu\text{L}$ case absorbed more on a per-drop basis, making it more difficult to access. However, if this was the case, it would be expected that other treatment conditions (SWI or M/W) would also exhibit this trend, but they did not. Comparison of the data measured for the 1×2 and $4 \times 2 \mu\text{L}$ (5 g/m^2) conditions for bleach versus the other treatments shows that the ratio of RA data is suspiciously higher than expected for bleach. To determine whether this was a real effect or an anomalous result would require further testing.

The fit to the experimental DCS results is provided in Figure 21 and Table 6. The RA per drop for this condition represents the upper-bound value for a given drop volume, as it represents the applied mass per drop. Reduction from the DCS condition is an indication of mass loss due to the hazard mitigation treatment (i.e., efficacy of the treatment) and other mass loss mechanisms (e.g., agent evaporation). As expected, m was very close to 1.0 for DCS, indicating the RA per drop applied was directly proportional to the drop volume.

Table 6. Per-Drop Regression Fit Parameters for HD on PU Coating

Agent	Material	Age Time (min)	Treatment	$m \pm \text{SE}$	$b \pm \text{SE}$	R ² Adjusted
HD	PU coating	N/A	DCS	1.016 ± 0.016	7.081 ± 0.014	0.982
		120	Bleach	2.044 ± 0.237	4.526 ± 0.180	0.840
			M/W	0.996 ± 0.072	5.641 ± 0.064	0.919
			Rinse and SWI	0.977 ± 0.062	6.577 ± 0.055	0.936
		1440	Rinse and Bleach	0.476 ± 0.257	6.271 ± 0.218	0.181
			Rinse and M/W	0.880 ± 0.374	5.557 ± 0.292	0.313
			Rinse and SWI	1.366 ± 0.179	5.967 ± 0.152	0.838

N/A, not applicable.

The accuracy of the fit, as indicated by the $\text{RA}_{\text{Measured}}/\text{RA}_{\text{Fit}}$ ratio, is shown in Figure 22. For all conditions, the ratio was similar to 1, except for the $1 \times 2 \mu\text{L}$ condition with bleach at 120 min, which underestimated the RA by a factor of 2.2. This positive deviation can also be seen in the green data points in Figure 21. For the SWI and M/W treatments at 120 min, a comparison of 1×2 and $4 \times 2 \mu\text{L}$ drops shows that the application of four times the number of drops generated about four times the RA. This was not the case for the bleach treatment, where the application of four drops resulted in only 1.7 times the RA compared to one drop. Either something was physically different about bleach at this condition, resulting in different RA trends, or some aspect of the test data was somehow different (although all data quality and image inspection showed the data as similar to other conditions). Additional testing would be required to determine whether this deviation is repeatable.

It is worth noting that, even in cases with a low R^2 adjusted value (0.181) for the regression fit (such as the rinse and bleach case at 1440 min; Figure 22, right side), the CI of the $\text{RA}_{\text{Measured}}/\text{RA}_{\text{Fit}}$ ratio includes 1.0, indicating the fit is statistically similar to the data (i.e., still accurate). A low R^2 adjusted value does not indicate an unacceptable fit; rather, it indicates that the empirical fit did not capture all of the observed data variance as a function of drop volume in this case.

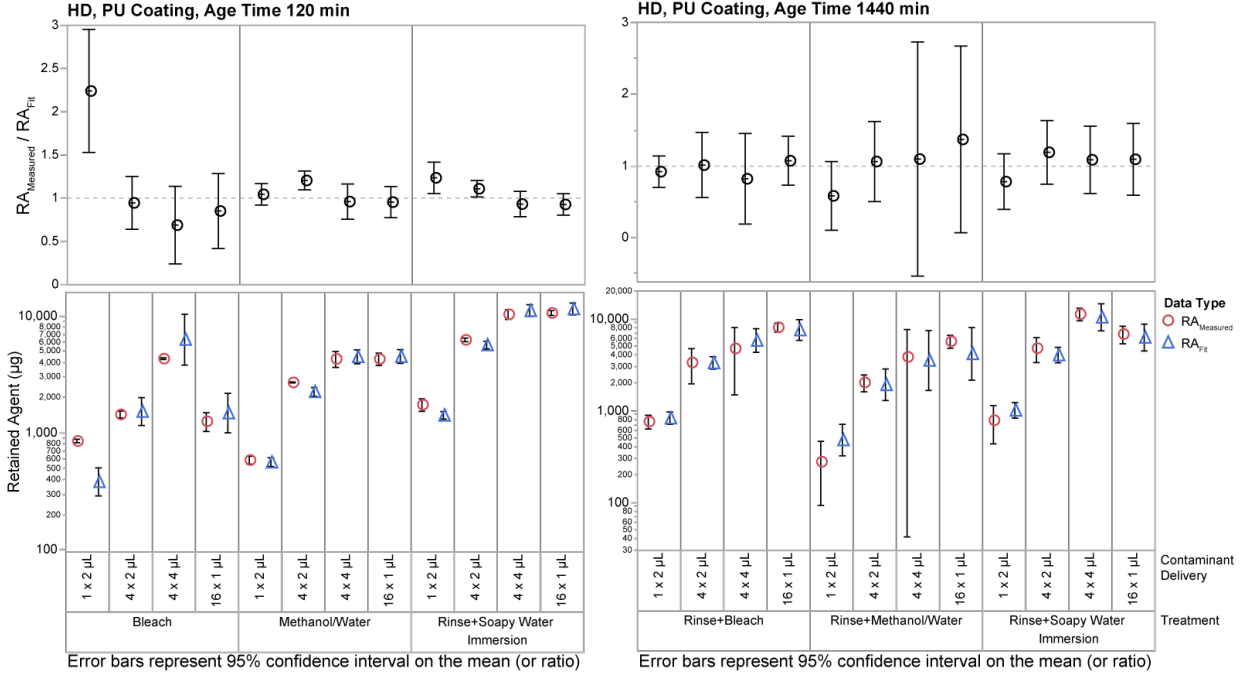


Figure 22. Comparison of fit versus measured RA values for HD on PU coating for a 120 min (left) and 1440 min (right) contamination period for different decontamination treatments.

In Section 4.3, decontamination efficacy was calculated using an LD for discretely tested conditions. The use of a regression to characterize RA per drop makes it possible for the LD of a treatment process to be calculated as a function of drop volume, using eq 4. In this case, the LD calculation becomes

$$LD(V) = \log_{10} \left(RA_{Fit, Treatment\ Ref}(V) \right) - \log_{10} \left(RA_{Fit, Treatment\ A}(V) \right) \quad (7)$$

Figure 23 shows the RA per-drop LD as a function of drop volume when the SWI and bleach are compared to DCS and to each other, including the predicted LD trend lines calculated from eq 7 for the same treatment cases, with an interpolation between values based on the regression equation. The RA_{Fit} values for each treatment condition were determined by eq 6. Essentially, the trend lines serve as fits to the $RA_{Measured}$ values in LD format. The approach used in eq 7 is a comparison calculation between two regressions. The overlay of the explicitly calculated LD values can be used to evaluate how accurately eq 7 may describe the specific differences for each contamination condition. As expected, the differences between the LD trend and specific LD calculations tend to coincide with conditions where the fit was less accurate (e.g., $1 \times 2 \mu L$ drop for bleach at 120 min). Overall, the CI of the data is often similar to the trend line.

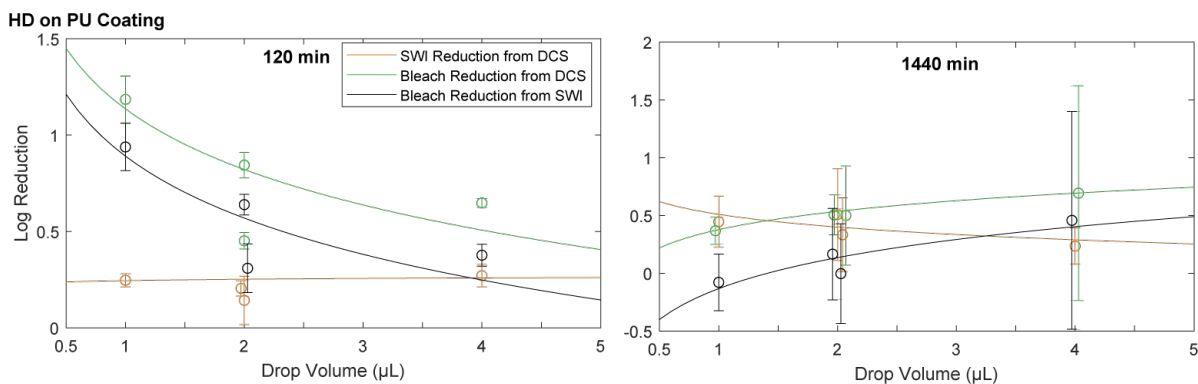


Figure 23. Log reduction of RA per-drop trends for HD on PU coating for 120 min (left) and 1440 min (right) contamination durations. Solid line represents calculation from eq 7; data points and error bars represent LD calculated from data for each contamination configuration. In both panels, for cases of significant overlap, data points were slightly offset for better visualization.

Here, the RA per drop for the DCS condition was included to enable the calculation of a “reduction from starting challenge”. In the case of the SWI treatment compared to the DCS applied mass, the efficacy was observed to be independent of the drop volume. The log reduction of bleach compared to SWI (black line, Figure 23) demonstrates how the reactive moiety contributed to the reduction of agent in the material. For the 120 min duration, the bleach provided a significant reduction as compared to SWI; however, for the 1440 min contamination duration, the bleach was at best a 0.5 LD better, and at small drop volumes, the SWI may provide similar results. Because the agent spread significantly on this material (and in some cases flowed off), it is less apparent why drop volume may influence agent removal.

These data also show the effect of contamination duration; the LD for bleach decreased by a factor of six from 120 to 1440 min (e.g., from an LD of 1.2 to 0.4 for $16 \times 1 \mu\text{L}$ drops). It is hypothesized that the longer contamination duration resulted in the agent becoming dispersed in the coating and thus less accessible to the decontamination treatment, which resulted in a lower LD. This dispersed distribution may be responsible for the lack of significant trends as a function of drop volume.

The results for HD on alkyd coatings are provided in Figure 24, and RA_{Fit} accuracy analysis is shown in Figure 25. The details of each individual regression are provided in Appendix E. Overall, the accuracy of the empirical relationship was excellent, with deviation of a factor of 1.4 observed only for the $1 \times 2 \mu\text{L}$ condition with the bleach treatment. The LD compared to the DCS as a function of drop volume (Figure 24, right) shows that efficacy significantly increased with drop volume. This may be because HD remained sessile on the alkyd coating, potentially resulting in more agent remaining as an accessible liquid on the surface, as compared to the spreading observed for the PU coating (Figure 5). If this trend holds for smaller drops, then the decontamination efficacy may be significantly lower for aerosol-sized drops, and laboratory testing with larger drops could be producing a significant positive bias. However, extrapolation of this empirical trend should not be relied upon; testing with smaller drops would be required to evaluate whether this trend is accurate for smaller drops.

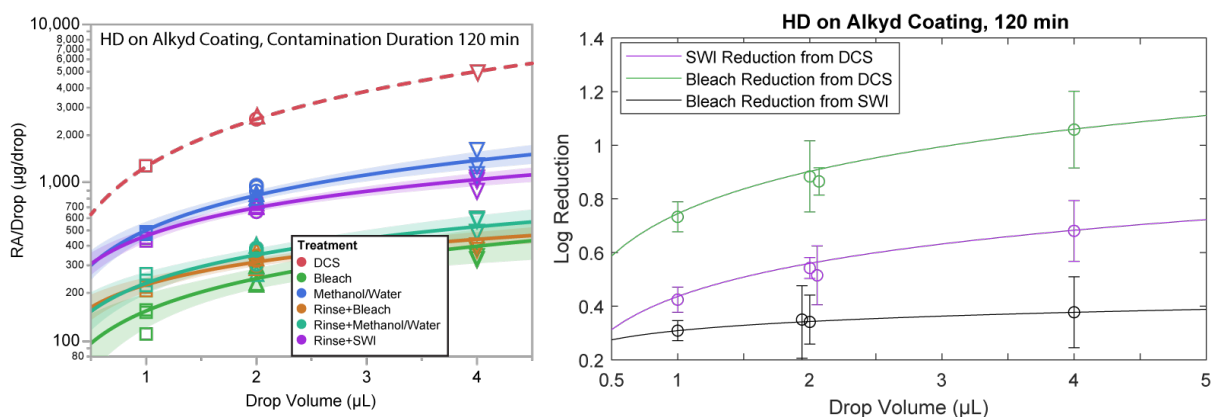


Figure 24. (Left) RA per-drop results for HD on alkyd coating for a 120 min contamination duration. Shaded regions indicate the 95% CI on the fit. DCS treatment corresponds to applied mass per drop. (Right) Log reduction of RA per drop for HD on alkyd coating. Solid line represents the calculation from eq 7; data points and error bars represent the LD calculated from the data for each contamination configuration. Because two conditions with 2 µL drops are shown at right, data points were slightly offset for better visualization.

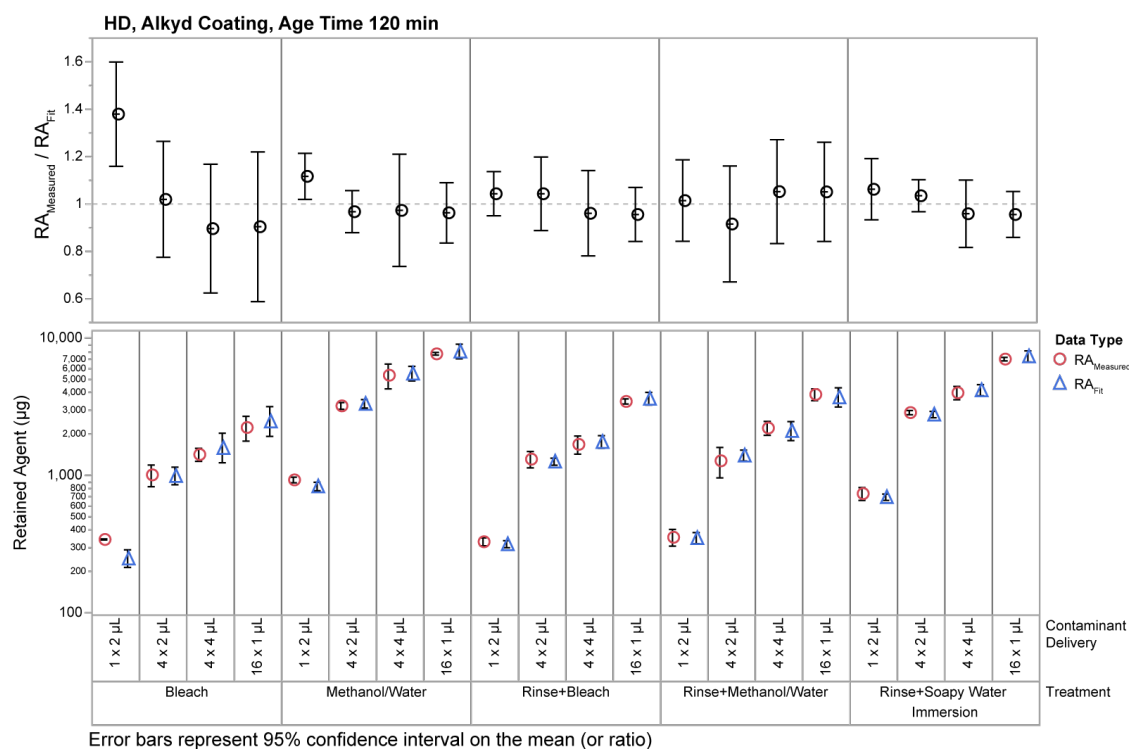


Figure 25. Comparison of fit versus measured RA values for HD on alkyd coating for a 120 min contamination period as a function of decontamination treatment.

The results for HD on silicone elastomer are provided in Figures 26 and 27. The details of the individual regressions are provided in Appendix E. The accuracy of the fit is illustrated in Figure 28. The SWI treatment process condition with 2 μL drops did deviate from the trend to some degree; however, other treatment conditions exhibited good correlation with the 2 μL volume. Similar to the results from the alkyd coating, the various treatment processes provided lower efficacy for smaller drops. The results for the 1440 min contamination duration showed that RA per-drop values were very close to those for the DCS condition, indicating that most of the applied agent remained in the panel after treatment. The exception was the bleach treatment, which did show some reduction in RA per-drop values. The comparison of the log reduction for bleach to SWI shows that the bleach was required to remove agent from the material.

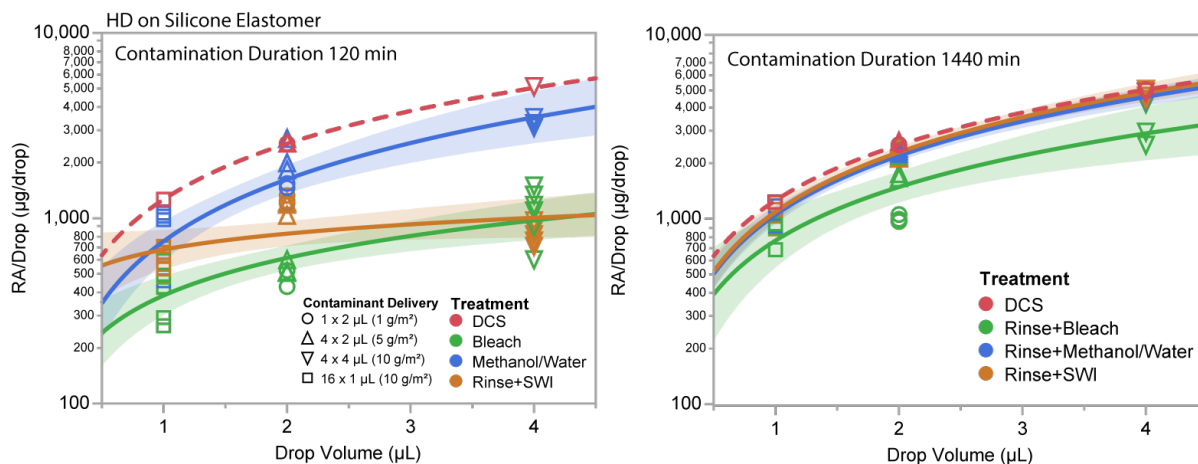


Figure 26. RA per-drop results for HD on silicone elastomer for 120 and 1440 min contamination durations. Shaded regions indicate the 95% CI on the fit. DCS treatment corresponds to the applied mass per drop.

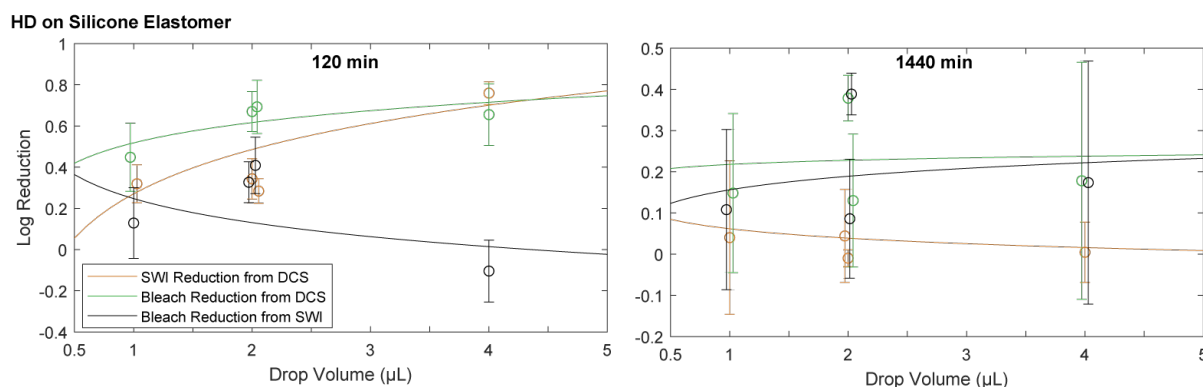


Figure 27. Log reduction of RA per-drop trends for HD on silicone elastomer. Solid line represents the calculation from eq 7; data points and error bars represent LD calculated from data for each contamination configuration. In both panels, for cases of significant overlap, data points were slightly offset for better visualization.

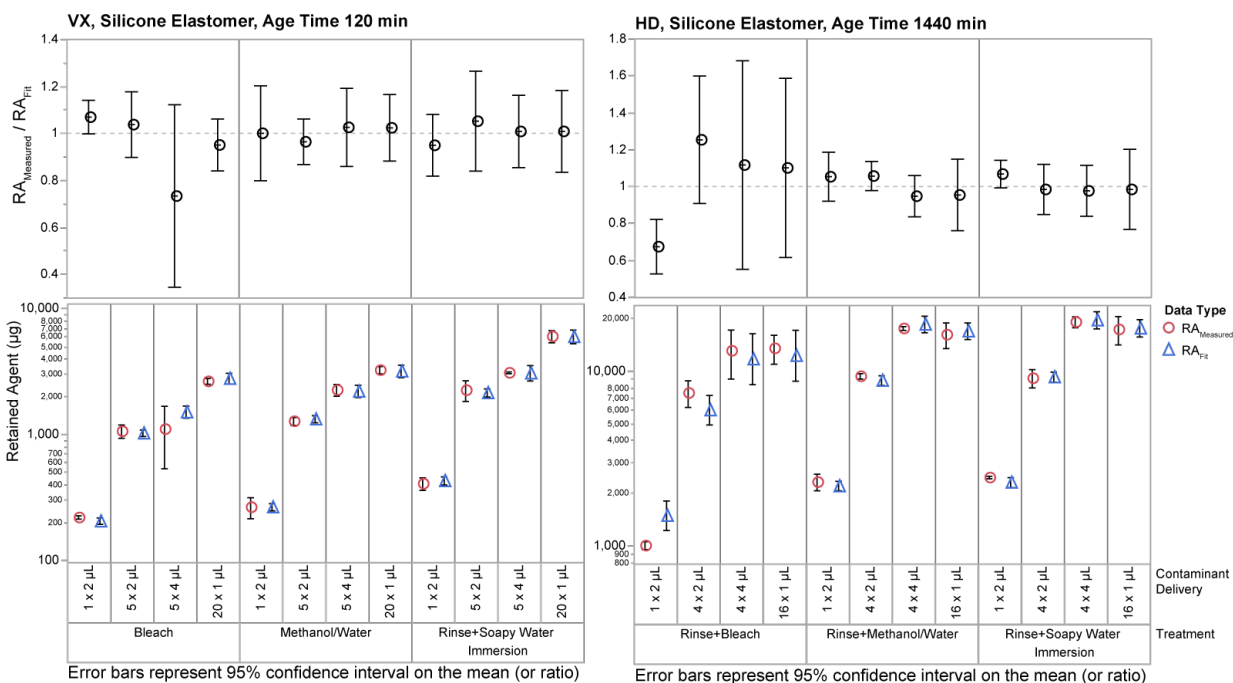


Figure 28. Comparison of fit versus measured RA values for HD on silicone elastomer for 120 min (left) and 1440 min (right) contamination periods.

As discussed in Section 4.3, the M/W treatment was used without a pre-rinse for the HD on silicone elastomer with a 120 min contamination duration. In this case, more agent retention was observed for the M/W treatment as compared to the SWI treatment. As indicated in Section 2.1, if the more polar M/W solution did not have sufficient solubility or rate of dissolution to rapidly remove the nonpolar liquid HD from the surface, absorption into the material continued during the treatment process.

The results for VX on PU coating and on silicone elastomer are provided in Figure 29. The details of the individual regressions are provided in Appendix E. Recall that the PU coating seemed to be somewhat resistant to VX retention for the SWI treatment and provided similar RA values across all contamination densities. Similar to the results for HD on PU coating, decontamination efficacy seemed to improve with smaller drop volumes (Figure 30). This may be a common theme for materials upon which the agent spreads, but more data are necessary to confirm or understand this trend. The silicone data show a trend that is similar to that observed in previous HD results: decontamination efficacy increased with drop volume.

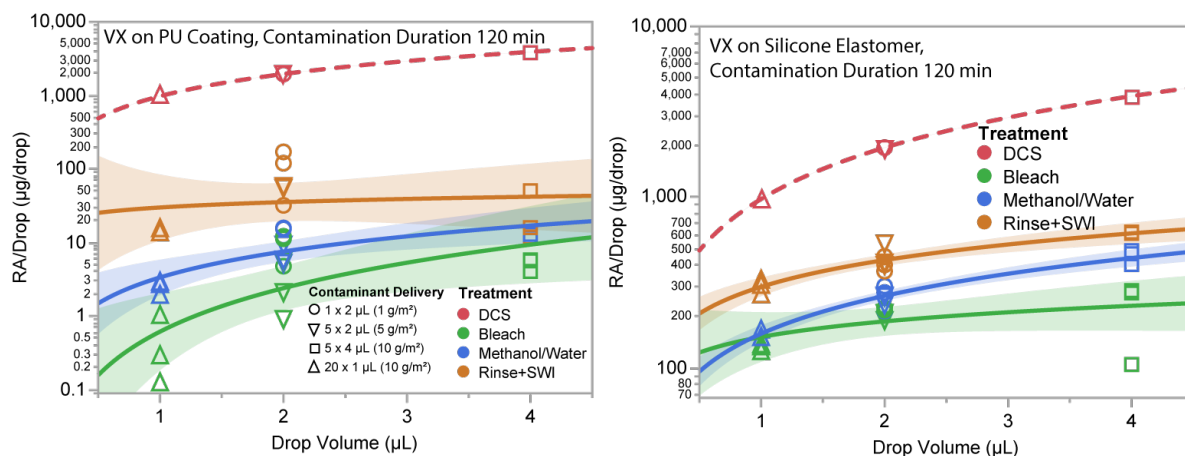


Figure 29. RA per-drop results for VX on PU coating (left) and silicone elastomer (right) for 120 min contamination duration. Shaded regions indicate 95% CI on the fit. DCS treatment corresponds to applied mass per drop.

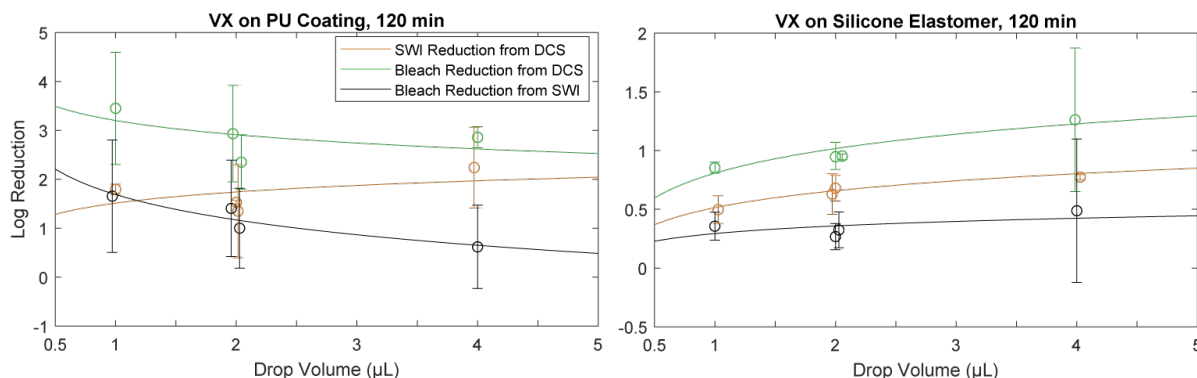


Figure 30. Log reduction of RA per-drop trends for VX on PU coating (left) and silicone elastomer (right). Solid line represents calculation from eq 7; data points and error bars represent LD calculated from data for each contamination configuration. In both panels, for cases of significant overlap, data points were slightly offset for better visualization.

Overall, the log difference as a function of drop volume, $LD(V)$, indicated that, although the efficacy was influenced by drop volume in some cases (e.g., many conditions with PU coating), in general, drop volume was not influential; the $LD(V)$ did not change by more than ± 0.2 . Only a small portion of the range of potentially operationally significant drop volumes was tested. Testing with smaller drops that exhibit more drastic differences in surface area to volume ratios (Figure 2) may reveal a more significant influence of agent drop volume on decontaminant performance.

In this section, it was shown that it is appropriate to employ the data analysis methods developed using RA-based data from SWI treatment for other decontamination treatments. The per-drop normalization and drop volume trend was verified to apply to a range of decontamination processes, including applied mass (DCS condition), weathering (1440 min

contamination durations including SWI treatment), physical removal (SWI), reactive chemistries (bleach), and extraction-based chemistries (M/W).

Recall from Section 2.1 that decontamination efficacy is influenced by various rate limiting processes related to agent distribution and relevant interfacial areas. The agent drop volume during the contamination process influences the relative interfacial areas and concentration distributions of agent within the material. The relative rates of transport (e.g., absorption or diffusion of agent or decontaminant) in the material could influence the interfacial regions where agent removal or reaction may occur. The dominant phenomenon for a given agent–material–decontaminant (temperature) combination may drive when and how the performance is influenced by the initial agent drop volume. These factors still remain influential regardless of the decontamination treatment. However, physical interpretation of regression slopes to applied mass or contaminated area may not hold as decontamination processes are evaluated, but the effects of interfacial areas (i.e., those correlated with drop volumes) from contamination do inform correlations with post-decontamination RA.

5.4 Per-Drop Normalization Summary

The previous approach to testing involved conducting evaluations at specific contamination densities and then using the results to represent operational conditions. This work shows that a 10 g/m² contamination density can produce different results if different agent drop volumes are used. Rather than testing to a specified contamination density, it has been found that analyzing the RA per drop as a function of drop volume allows for extrapolation to any contamination density for any drop volume. *The intrinsic characteristic for contamination is drop volume and count rather than contamination density.* Overall, the data fit to RA per drop versus drop volume captures the effect of variable contamination parameters for a range of treatments, from physical removal to reactive or extraction-based decontaminant solutions. The data trend applies for the range of contamination densities (1–10 g/m²) and drop volumes (1–4 µL) analyzed here.

Rather than testing to a contamination density in the test methodology, this analysis indicates that laboratory testing should be conducted for variable drop volumes and counts. The regression could be used to calculate the results for the desired contamination density generated with different drop volume distributions. For the evaluation of decontamination technologies, the results presented here showed that efficacy can vary by a factor of approximately 8–10 for 1–4 µL drop volumes. Operational drop distributions may include drops smaller than 0.1 µL. To accurately estimate operational performance, it may be necessary to test drop volumes spanning operationally relevant drop volumes and use this type of regression.

Current test programs do not specify drop volume for use with multiple starting challenge levels (e.g., 1 and 10 g/m²). The results presented here show that decontaminant efficacy is a function of drop volume rather than starting challenge. Using this regression approach, both drop volume and variable starting challenge results can be obtained and used. With good experimental design, the regression could provide improved accuracy and more operational context, and fewer sample replicates may be required. It should be noted here that all replicates acquired across the various starting challenge levels contributed to the degrees of

freedom in the regression model rather than the per-contamination configurations presented in Section 4.

The results were illustrated for drop volumes down to 0.5 μL , extrapolated from the smallest drop tested at 1 μL . The extent to which extrapolation may be valid is currently unknown. Future studies should consider testing smaller drops if the desire is to include drop distributions such as those found in aerosols. These data were collected with the objective to characterize the effects of starting challenge, and the trends with drop volume were identified through analysis. Future experiments designed specifically to capture drop volume effects and validate the approach are needed.

Panels with a 2 in. diameter were used throughout the testing documented in this report. The results could potentially be scaled up to larger material areas based on the number of drops. Also, these results indicate that, because the relevant variable is drop volume rather than starting challenge, smaller panels could be used in testing, which would result in higher test throughput and less need for resources and expenses such as agent, solvent, material costs, and waste disposal. In future efforts, obtaining data on different panel sizes should be considered, to determine whether the results translate across different material areas.

The current laboratory practice of using starting challenge as a test parameter may not be required. Lifting this constraint could enable significant changes to panel size, test throughput, and overall test costs. The current 2 in. diameter panel size seems to have been selected based on the ability to deliver down to 1 μL and produce a 1 g/m^2 starting challenge. The size of the panel influences the working surface area required in the laboratory and the size of the extraction container (typically an 8 oz jar with an ~ 2.5 in. diameter). The combination of these items quickly consumes the available working area. Recent efforts have explored the use of panels as small as 0.5 in. in diameter that can be extracted in 20 mL scintillation vials. This facilitates almost three times the throughput using the same laboratory resources as the 2 in. panels. Use of this per-drop analysis on the smaller panels could enable significant changes in test throughput (and cost).

Efficacy trends are often a function of the agent distribution when the treatment was performed. Recall that, for HD on alkyd coatings, the agent did not spread, and visible liquid drops were present; in these cases, it seemed as if efficacy increased for larger-volume drops. In comparison, for HD on PU coatings, the agent spread to a thin film and in some cases seemed to dry (Figure 5), and the efficacy seemed to increase (as indicated by LD trends; Figure 23) with smaller drop volumes. The potential deviation from the trend line of the 1 $\times$ 2 μL drop for bleach on the PU coating may be because this was the only case where the agent did not spread to the panel edges. If smaller test panels are implemented, additional consideration of these types of effects may be necessary.

The focus of this study was on variable contamination density. In all cases, the quantity of decontaminant was similar (~ 8 mL). This analysis did not consider how the quantity of decontaminant may influence the results. As long as the decontaminant interacted with the test material, the decontaminant should have overwhelmed the quantity of agent present. For these test conditions, factors such as limiting reagent should not apply because the rate limiting steps are most likely associated with transport of the agent to the decontaminant.²³

The data presented herein represent drop volumes ranging from 1 to 4 μL , whereas aerosol-sized drops could be on the order of 0.1 μL or smaller. Future studies could evaluate smaller drop volumes so the effect of drop volume can be better characterized. The results presented here seem to show that larger-volume drops provide better efficacy results. Future evaluations should be performed to determine whether significantly smaller drops present greater decontamination challenges. This work has focused on RA data; however, future work will need characterize how these trends translate to vapor emission and contact transfer source terms.

Lastly, an additional point to address is the possible wrong conclusion that could be drawn from the results shown earlier (Section 4) that highlight the inadequacy of starting challenge specifications. Changing test parameter requirements by limiting the starting challenge (e.g., only 1 g/m^2) and explicitly specifying the volume and number of drops to be dispensed on surfaces does not address larger capability gaps that exist in measurement of agent retention and decontamination performance on materials. Because the objective of test and evaluation for decontamination technologies is to determine efficacy for field conditions, a flexible approach that permits multiple and alternate material/panel configurations and facilitates a more robust accounting of operational contamination conditions is required. Section 6 addresses the additional benefits that result from per-drop normalized contamination specifications.

5.5 Future Considerations Using Modeling and Simulation

The regression used to characterize the drop volume trend is an empirical fit, with inspiration from the behavior of sessile drops on surfaces as a function of volume, and the reliability of extrapolation beyond the tested conditions is not known. Recent efforts have developed physics-based models that describe contamination and decontamination in two dimensions for drops deposited on flat horizontal materials.^{13,23,25,26} The implementation of physics-based models enables significantly better extrapolation capabilities and an opportunity to perform sensitivity analysis on a much wider range of conditions than may be experimentally feasible. Modeling and simulation (M&S) could enable a characterization of the contamination duration, drop volume, and other factors to identify and refine the focus of the next stages of testing. This could be most advantageous to evaluate factors such as small volume drops that may not be possible to create using current laboratory infrastructure.

The use of M&S in this case could also build a better understanding of the parameters from the empirical fit and what may influence them. For example, M&S could be used to confirm whether the slope of 2 that was observed for HD treated with bleach on the PU coating is physically realistic. Additionally, physics-based models can predict outputs such as vapor emission in addition to RA. This could help researchers relate the per-drop analysis to the source terms needed for exposure assessments.

Empirical analysis and the use of physics-based models are *both* needed. The physics-based modeling enables extrapolation across multiple variables but requires the determination of multiple model parameters using specialized experimental techniques.^{15,16,23} The empirical approach works on most agent–material–decontaminant combinations to indicate the trends at specific tested conditions (i.e., contamination duration, temperature, decontamination duration) and can be determined using standard panel test capabilities. The appropriate technique can be selected based on the needs of the analysis and the available resources.

6. CONCEPTS FOR TRANSLATING LABORATORY TESTING TO OPERATIONAL CONTEXT

Translation of laboratory-based decontamination efficacy results to operational context requires flexible scaling of LD or RA results for individual materials to a composite asset in the field. *Starting challenge levels do not adequately specify the necessary variables to be measured and analyzed in contamination and decontamination processes associated with liquid drops applied to surfaces and ultimately allow for scale-up calculations.* The critical field contamination conditions that must be captured in laboratory test designs and subsequent analysis are the materials exposed to liquid agent, including the exposed surface area, and the distribution of drops (volume and number) impinging on the materials. In contrast to the limitations presented by only specifying starting challenge levels, laboratory results can be translated to a wide range of operational conditions using a per-drop normalization of RA data. For example, an asset could be described as being contaminated by a few drops in specific locations, or the full asset may be covered to a uniform contamination density of 1 g/m². Furthermore, *the total mass present on the asset before and after decontamination could be determined by specifying the volume and count of the drops on the asset. This is a more versatile approach to describing how much agent may be present on an operational asset.*

The following conceptual example presents how laboratory data could be used. The calculation describes a full-scale asset using an abundance-weighted sum of material areas, assuming that the whole is equal to the sum of its parts. For contamination, the number of drops on each material is identified, and scaling is done by drop count. This concept should have further application to variable and larger material areas; however, the experimental effort to demonstrate this was beyond the scope of this study. The data from this work was generated exclusively from 2 in. diameter panels and a narrow range of drop volumes (1–4 µL). In regard to using contamination density to define the operational context, some details regarding agent purity and the specification of material area can be interpreted in different ways that could result in significantly different output. These considerations are presented in Appendix F.

The material areas for a highly simplified (i.e., two-material) conceptual full-scale asset such as a vehicle are provided in Table 7. Using eq 1, the number of 0.5–4 µL HD drops that would result in a 1 g/m² challenge on the indicated material area (abundance) is calculated. In this example, uniform contamination over the full material area was assumed, whereas in other calculations, partial contamination or specific single drop applications to various materials could be used to describe the contamination of the asset for which output is desired. Note that, in this case, the values for the 0.5 µL drops were extrapolated from the regression generated using data for the 1–4 µL drops.

Table 7. Material Composition for an Example Full-Scale Asset and Number of Drops of Specified Drop Volume Required to Produce 1 g/m² HD on Each Material Area

Material	Material Abundance (m ²)	Number of Drops for 1 g/m ² HD per Drop Volume			
		0.5 µL	1 µL	2 µL	4 µL
PU coating	15	23,483	11,719	5,860	2,930
Alkyd coating	22	44,177	22,089	11,045	5,523

To determine the total agent associated with each material, the regression fit parameters (Table 8) are applied to determine the total RA mass per material type in micrograms (RA_{asset material}) as follows:

$$RA_{\text{asset material}} = \exp(b) V^m n_{\text{drops}} \quad (8)$$

The resulting agent mass for each asset material and the total agent mass for the asset are provided in Table 9. The total asset retention (in bold) is the sum of retention from the materials. These results show that the total mass remaining on the asset can vary based on the drop volume used.

Table 8. Regression Coefficients for HD at 120 min Contamination Duration for PU and Alkyd Coatings

Material	Treatment	Fit Parameter	
		<i>b</i>	<i>m</i>
Alkyd coating	DCS	7.141	1.00
	SWI	6.137	0.590
	Bleach	5.044	0.679
PU coating	DCS	7.141	1.000
	SWI	6.577	0.977
	Bleach	4.526	2.044

Table 9. Total Mass Remaining per Material or Asset

Treatment	Material	Mass Retained by Material and by Total Asset, per Drop Volume (g)			
		0.5 μ L	1 μ L	2 μ L	4 μ L
DCS	PU coating	14.800	14.800	14.800	14.800
	Alkyd coating	21.707	21.707	21.707	21.707
	Total asset	36.507	36.507	36.507	36.507
SWI	PU coating	8.555	8.418	8.284	8.151
	Alkyd coating	10.564	7.950	5.983	4.503
	Total asset	19.119	16.369	14.267	12.654
Bleach	PU coating	0.525	1.083	2.233	4.605
	Alkyd coating	3.331	3.906	2.717	1.890
	Total asset	3.855	4.988	4.949	6.494

Note: Results are for HD after 120 min contamination duration if all of agent was applied with a monodisperse drop volume.

Total asset calculations combine the responses from multiple materials that may have different RA per-drop trends with drop volume, different levels of efficacy from a treatment process, or different abundance of material area or contamination. This total asset RA mass is what presents the risk to unprotected personnel interacting with the asset. The data from Table 9 also show which materials contribute the most to potential exposure and should, therefore, be prioritized for testing or optimization efforts. The relative RA contribution of each material would be the total RA from a given material divided by the total asset RA. For example, for 0.5 μ L drops and the bleach condition, the PU coating contributed 0.525 g of the total 3.855 g, or 13.6% of the total RA. The alkyd coating provided the remaining 86.4% of the agent. In this case, the alkyd coating was the most significant contaminant source.

HD on PU at 120 min treated with bleach was another case where strong drop volume effects were observed. As indicated in Table 9, the total asset RA was 6.494 g for 4 μ L drops and 3.855 g for 0.5 μ L drops, or 1.7 times higher for the 4 μ L drop volume. Additionally, for the 4 μ L drop condition, the PU coating contributed 4.605 g of the total 6.494 g RA, or 70.9% of the agent, which is a significant change from the 13.6% contributed by the PU coating when tested with 0.5 μ L drops. This shows that accounting for drop volume effects could alter both the total asset RA and which materials are most significantly contributing to the potential exposure of unprotected personnel. These types of analyses will become more important as all of the materials on actual assets are considered for testing and analysis. Materials with low contribution could be eliminated from an analysis.

Similar to the RA data shown in Table 9, the log reduction from each material and the total asset are provided in Table 10, and DCS was used as the reference condition (similar in concept to a reduction from starting challenge). Although a per-material log reduction calculation indicates how much agent is reduced per material, the reduction from the total asset must be considered to understand what this means operationally. For example, bleach for 0.5 μ L drops on PU coating provided a 1.450 LD compared to the applied mass (DCS) condition and a 0.814 LD for the alkyd coating. When all of the sources are combined to make up the total asset, the net reduction to personnel would be a 0.976 LD as compared to the applied mass. The case of bleach also produces significant variations in LD as a function of drop volume per material and for the total asset.

Table 10. Log Reduction per Material and Total Asset after HD Treatment Process
(120 min Contamination Duration)

Treatment	Material	Log Reduction per Drop Volume			
		0.5 μL	1 μL	2 μL	4 μL
SWI	PU coating	0.238	0.245	0.252	0.259
	Alkyd coating	0.313	0.436	0.560	0.683
	Total asset	0.281	0.348	0.408	0.460
Bleach	PU coating	1.450	1.136	0.821	0.507
	Alkyd coating	0.814	0.745	0.903	1.060
	Total asset	0.976	0.864	0.868	0.750

Based on the results from Section 5, the per-drop normalization enables analysis of laboratory data independent of the starting challenge as a laboratory test condition. The ability to use the per-drop volume analysis indicates that each starting challenge level of interest may not need to be explicitly tested. *More importantly, capturing drop level effects affords the resolution needed for describing operational contexts. This is not possible when only starting challenge, as currently construed, is prescribed.* The starting challenge is an operational context that can be implemented through the determination of the number of drops (n_{drop}), used in eq 8. Therefore, this calculation could be applied to determine how much agent may be present, from single drops applied to the asset up to significant contamination levels, such as 10 g/m². Alternately, calculations could be made for select regions of an asset contaminated to various levels to determine how that contamination may influence operational efficacy or exposures. This drop-focused approach can also be used to characterize contamination in constrained geometry features.²

The data used for the example calculations in this work all represented monodisperse drop distributions. To represent a full-scale asset as accurately as possible, calculations that consider a realistic drop distribution with variable drop counts and volumes in a single contamination event may be required. Typical drop distributions follow a log-normal distribution; therefore, the drop count and drop volume could be adjusted such that the appropriate number of drops for each drop volume are distributed on the asset. The RA per drop would then be calculated for a range of drop volumes and drop counts from the distribution and summed to determine the total mass of agent remaining on the asset.

This work demonstrates that laboratory results can be mapped to operational context by calculating the total mass of agent on an asset; additionally, it shows how a technology reduces (i.e., mitigates) the total potential exposure to personnel. It also demonstrates how to aggregate the results from multiple materials to represent the full-scale asset. From these data, the laboratory-calculated results, such as log reduction from a panel, can be translated to indicate log reduction from a total asset to provide better context on how well a technology is working and whether it is sufficiently effective for a given situation. Additionally, if the total agent mass retained by a given material is exceedingly high as compared to other materials, then optimization of the technology to improve efficacy on that material could be the focus of development efforts.

7. CONCLUSIONS

The fundamental intent of laboratory-based testing for CWA hazard mitigation technologies is to characterize how discrete drops of liquid agents interact with materials to determine whether the technology reduces the quantity of agent retained by the material. Results from laboratory testing are expected to indicate how a technology would perform in an operational environment on actual military assets such as vehicles and other tactical support equipment. Through this work, critical findings were identified to better enable testing and the interpretation of results:

- Contamination density is not a unique specification describing the contamination of materials; the drop volume used to generate the contamination density must be accounted for to describe observed RA trends (Section 4.2).
- The differences in RA across contamination conditions are hypothesized to be related to variations in the agent distribution when the decontaminant treatment is conducted (Sections 2.1 and 4.2).
- Results indicate the need to normalize the results to more than just contamination density (Section 4.2).
- Correlations between RA or RA per drop and applied mass or contaminated area were identified and are hypothesized to be dependent on how the liquid agent spreads on a material (Section 5.1).
- A power law relationship was found between RA mass normalized per drop to drop volume; this single relationship persists independent of the contamination density used and did not require measurement of contaminated area (Section 5.2).
- The trends between RA per drop and drop volume suggest that the drop volume and its influence on the resulting agent distribution provide a better measure of the important process variables than contamination density alone (Section 5.2).
- Results show that the intrinsic characteristics for contamination are the drop volume and count rather than the contamination density; therefore, laboratory testing must be able to match operationally observed drop volumes to enable accurate operational assessments (Section 5.2).
- The per-drop normalization and drop volume trend was demonstrated to apply to various decontamination processes including applied mass, weathering, physical removal, reactive chemistries, and extraction-based chemistries (Section 5.3).
- Starting challenge levels do not adequately specify the necessary variables to measure and analyze in contamination and decontamination processes associated with liquid drops applied to surfaces, and ultimately, allow for scale-up calculations (Section 6).
- In contrast to the limitations presented by only specifying starting challenge levels, laboratory results can be translated to a wide range of operational conditions using a per-drop normalization of RA data (Section 6).

This study evaluated decontaminant performance for different contamination densities by applying differing numbers of drops and drop volumes to materials. RA data were collected at starting challenges ranging from 1 to 10 g/m² using drops from 1 to 4 µL. Different RA results were observed for the same contamination density generated using different agent drop volumes. A subsequent analysis determined that an empirical per-drop normalization capturing the effect of drop volume accounted for the difference in the results.

These trends between RA per drop and drop volume suggest that it is more critical to track the drop volume and its influence on the resulting agent distribution and consequent RA response than to only specify average contamination density levels. This also indicates the necessity of ensuring that the laboratory data can be used to represent the range of drop volumes that may be observed in the operational environment. Furthermore, describing RA on a per-drop basis and accounting for the drop volume effects offer a capability to translate laboratory test conditions to a wide range of variable-contamination operational conditions by specifying how many drops of various volumes are involved in the contamination of a given asset. This offers greater flexibility and the ability to use laboratory data to represent operational conditions.

The approach used here was based on the observation that some materials exhibited RA response correlations with the applied agent mass (e.g., HD on PU coating), whereas other materials exhibited correlations with the total liquid-wetted (i.e., contaminated) area (e.g., HD on alkyd coating and silicone). Both of these terms can be expressed as relationships with drop volume. A regression using natural logarithm transformed RA per drop and drop volume and produced an empirical power law relationship that exhibited good fits for most conditions. The empirical relationship was demonstrated to reproduce the trends observed for materials where the 10 g/m² condition generated similar or different results when generated using 1 versus 4 µL drops.

The influence of drop volume on RA and decontaminant performance can be attributed to the way agent drop volume influences the relative interfacial areas and concentration distributions of agent within the material during the contamination process. The relative rates of transport in the material (e.g., absorption or diffusion of agent or decontaminant) can influence where agent removal or reaction may occur. The phenomenon that is dominant for a given agent–material–decontaminant (temperature) combination may drive when and how the performance is influenced by the drop volume. To better understand these interactions and why larger or smaller drops produce better performance, modeling tools that simulate these processes are required^{15,16,23,27} and may be considered in future efforts.

Previous test parameters described this relationship using a starting challenge specified as a mass of agent per unit area of material. Results obtained at the laboratory-panel scale were assumed to represent operational asset scales if this quantity matched both scales. This work identified that results were influenced by drop volume rather than by the contamination density. Therefore, specification of contamination density alone is insufficient to evaluate decontaminant performance. To estimate accurate operational conditions, the drop size distribution must be specified.

The effects of drop volume on measured RA suggest that in laboratory testing, drop volume distributions similar to what may be *observed operationally* must be considered; this could include large ballistic-sized drops and small aerosol-sized drops. If laboratory data are

intended to directly represent operational conditions, the observed trends with drop volume indicate the risk of bias (up to a factor of 10 for the tested conditions) if the operational drops are significantly smaller than those tested in the laboratory. An example from the data indicated that the bleach treatment with HD on alkyd coatings performed better against larger drops than against smaller drops. Using the drop volume regression approach, these trends could be characterized and applied to more accurately represent operational conditions. However, generating and testing the full range of operationally relevant drop volumes may require additional test infrastructure because generating small (i.e., $<1\ \mu\text{L}$) drop volumes of agent safely and reproducibly may present challenges. Physics-based modeling tools could provide an initial assessment of how smaller drops may behave before laboratory capabilities are developed.

Lastly, an approach to translate laboratory results to operational context was presented that *focuses on describing the abundance of agent that contaminated an asset*. This involves quantifying how many drops of a given volume may interact with all of the materials on the full-scale asset. The quantity of agent applied to the asset can be tuned using either explicit drops or, as demonstrated, using a uniform contamination density to identify the number of drops necessary to contaminate the asset to a specific starting challenge. The use of the RA per drop versus drop volume regression allows the same data set to represent the different contamination densities of interest.

The initial objective of this work was to characterize the effects of starting challenge and identify the RA trends with drop volume. Future experiments designed specifically to capture drop volume effects and validate the approach are needed. Initial test specifications such as the size of the panel seemed to be related to the ability to generate specific starting challenge levels in the laboratory. The material area was not used as part of the analysis in the results presented here. Using regression based on per-drop normalized RA data rather than a starting challenge constraint enables the use of smaller test panels, which could significantly increase test throughput. This is also an important factor in testing materials with complex features (i.e., capillaries), where specific drop-feature interactions are probed on a single-drop basis rather than using a multiple-drop starting challenge. Researchers may consider other factors for future efforts, such as investigating non-sorptive materials. Only a limited drop volume range was investigated, and smaller drop volumes may be relevant for testing. The use of an empirical analysis limits the range of extrapolation. The contamination durations investigated here were at least 120 min, whereas testing often considers shorter time durations. Although it may not be feasible to investigate some of these factors experimentally in the near term, M&S with physics-based models may be able to provide some insight. This work has focused on RA data; however, future work will need to characterize how these trends translate to vapor emission and contact transfer source terms (which could also be initially investigated with M&S tools).

Overall, the approach to using the RA per drop versus drop volume regression can enable the more efficient use of laboratory results to more accurately represent operational conditions with variable contamination densities. In principle, the use of statistical tools (such as those in design of experiments) would require fewer sample replicates to generate the empirical fits. In this work, all replicates acquired across the various contamination density levels contributed to the degrees of freedom in the regression model rather than the categorical per contamination density configurations. All of these factors combined to produce more extensible data with more efficient experimental designs, likely more accurately representing operational conditions using laboratory data.

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ACRONYMS AND ABBREVIATIONS

θ	equilibrium contact angle
CASARM	chemical agent standard analytical reference material
CI	confidence interval
CWA	chemical warfare agent
DCS	dose confirmation samples
GC	gas chromatography
HD	bis(2-chloroethyl) sulfide
LC	liquid chromatography
LD	log difference
M&S	modeling and simulation
M/W	methanol/water
PU	polyurethane
RA	retained agent
SE	standard error
SWI	soapy water immersion
VCSC	vapor composite system calculation
VX	<i>O</i> -ethyl- <i>S</i> -(2-diisopropylaminoethyl) methyl phosphonothiolate

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APPENDIX A SPHERICAL CAP DROP RELATIONSHIPS

The interaction of a drop with a material can produce several conditions of drop spreading on the surface (Figure A-1). Depending on the liquid–material interactions, the contact angle (θ) can range from 180° (fully non-wetting) to 0° (fully wetting). For military-relevant materials, the contact angle for most agents will be less than 90° , and most likely, less than 45° . In this case, a decreasing contact angle will result in a larger wetted area, W , as shown in Figure A-2. For the purposes of this analysis, the relationship between drop volume and wetted area is of interest. As drops increase in volume, the effects of gravity influence the drop shape.¹ If the non-dimensional bond number (B_0), the ratio between hydrostatic forces and surface tension forces, is less than 1, then the spherical cap geometry is valid. For the volume range of interest ($<10\ \mu\text{L}$ drops), it is assumed that the spherical cap geometry is accurate.

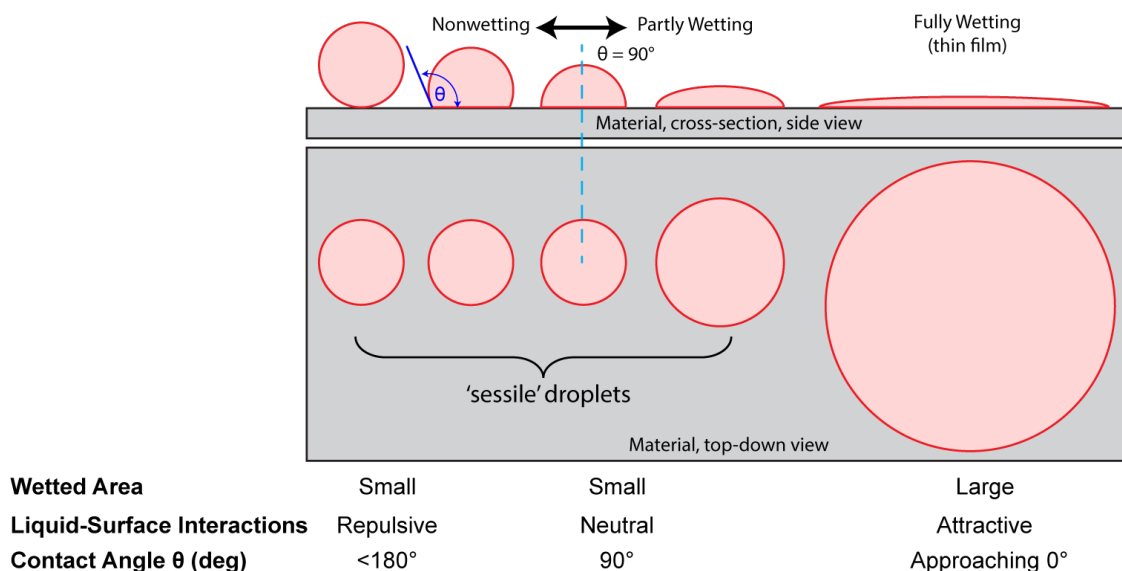


Figure A-1. Illustration of drops interacting with a material for different contact angles.

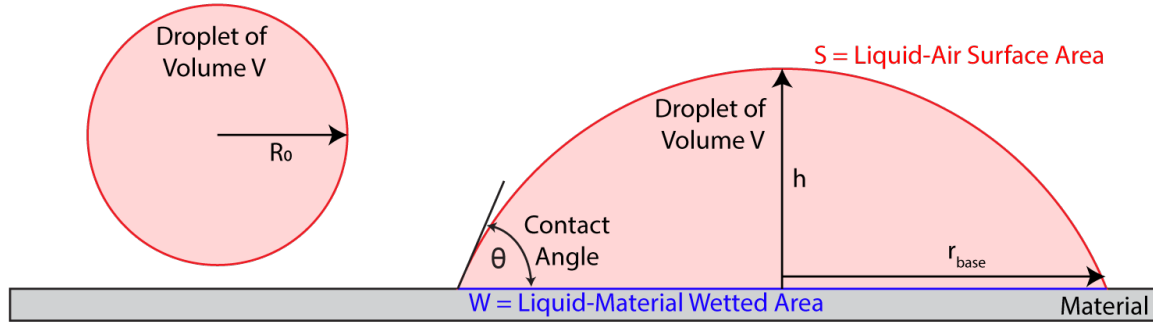


Figure A-2. Spherical cap geometry drop with relevant parameters.

To define the drop wetted area, W , in terms of the drop volume, V , requires a few relationships. First, the radius of the spherical drop before it contacts the surface, R_0 is described by

$$R_0 = \left(\frac{3V}{4\pi} \right)^{1/3} \quad (\text{A-1})$$

For a spherical cap drop on a material, the radius of the drop calculated as²

$$r_{\text{base}} = \frac{2^{2/3} R_0 \sin \theta}{(1 - \cos \theta)^{2/3} (2 + \cos \theta)^{1/3}} \quad (\text{A-2})$$

Substituting eq A-1 into eq A-2,

$$r_{\text{base}} = \frac{2^{2/3} \left(\frac{3V}{4\pi} \right)^{1/3} \sin \theta}{(1 - \cos \theta)^{2/3} (2 + \cos \theta)^{1/3}} \quad (\text{A-3})$$

The drop height, h is calculated as²

$$h = r_{\text{base}} \tan \left(\frac{\theta}{2} \right) \quad (\text{A-4})$$

The liquid–air surface area, S , can be calculated as²

$$S = 2\pi r_{\text{base}}^2 \frac{1}{1 + \cos \theta} \quad (\text{A-5})$$

The liquid–material wetted area, W , can then be shown as

$$W = \pi r_{\text{base}}^2 \quad (\text{A-6})$$

Substituting eq A-3 into eq A-6,

$$W = \pi \frac{2^{4/3} \left(\frac{3V}{4\pi} \right)^{2/3} \sin^2 \theta}{(1 - \cos \theta)^{4/3} (2 + \cos \theta)^{2/3}} \quad (\text{A-7})$$

providing the relationship between the liquid wetted area and the drop volume for a given contact angle. When the drop volume is defined in microliters, the spatial dimensions are in millimeters. The provided relationship assumes a flat horizontal surface with low Bond number ($B_0 \ll 1$). Additionally, drops in laboratory context are applied at a low velocity when ejected from a repeater pipette (i.e., low Weber number). Operationally relevant agent deposition may result in different drop velocities when drops impact surfaces and may result in splashing effects (high Weber number) that could influence the initial liquid wetted area and observed equilibrium contact angle.

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APPENDIX B

DOSE CONFIRMATION SAMPLES

Data for dose confirmation samples (DCS) for the different contamination conditions are reported in Table B-1. Tests were conducted over several test sessions, and the DCS for each test session are reported. These results were used in later analysis to account for the total applied mass. Each panel is associated with the DCS results for a given contamination type and test session. The starting challenge was calculated by dividing the applied agent mass by the area of the 2 in. diameter panel (20.2 cm²).

Table B-1. Dose Confirmation Results for Each Test Session

Agent	Contamination	Test Session	Applied Agent Mass (mg)		Actual Agent Starting Challenge (g/m ²)	
			Mean	SD	Mean	SD
HD	1 × 2 µL	CST019	2.509	0.018	1.242	0.009
		CST023	2.410	0.214	1.193	0.106
		CST024	2.332	0.037	1.154	0.018
	4 × 2 µL	CST019	10.347	0.218	5.122	0.108
		CST023	10.224	0.376	5.062	0.186
		CST024	9.583	0.206	4.744	0.102
	4 × 4 µL	CST019	20.345	1.152	10.072	0.570
		CST021	19.560	0.893	9.683	0.442
		CST022	19.052	0.522	9.432	0.259
		CST023	19.548	0.773	9.677	0.383
		CST024	18.623	0.722	9.219	0.357
	16 × 1 µL	CST019	20.436	0.217	10.117	0.107
		CST021	19.414	0.697	9.611	0.345
		CST022	18.738	0.525	9.276	0.260
		CST023	19.765	0.540	9.785	0.268
		CST024	18.329	0.665	9.074	0.329
VX	1 × 2 µL	CST020	1.943	0.042	0.962	0.021
	5 × 2 µL	CST020	9.540	0.227	4.723	0.112
	5 × 4 µL	CST020	18.437	0.532	9.127	0.264
	20 × 1 µL	CST020	18.940	1.191	9.376	0.589

HD, bis(2-chloroethyl) sulfide; SD, standard deviation;

VX, *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate.

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APPENDIX C

COMPARISON OF RETAINED AGENT FOR 10 g/m² STARTING CHALLENGE USING DIFFERENT DROP VOLUMES

Two test conditions, namely, 1 or 4 μL drops, were used to generate a 10 g/m² contamination density. The data presented in Figures C-1 and C-2 show that, for materials where the agent does not spread, the use of 1 μL drops tends to result in higher retained agent (RA) as compared to challenges generated with 4 μL . There was a case with polyurethane (PU) coating (upon which the agent did spread) in which the opposite trend was observed with bis(2-chloroethyl) sulfide (HD) and, to a lesser extent, *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX). In all cases, the differences between 1 and 4 μL drops were less than 0.5 log difference (LD) (less than $\sim 3\times$), and in many cases, the differences were not statistically significant (the confidence interval included 0.0 LD).

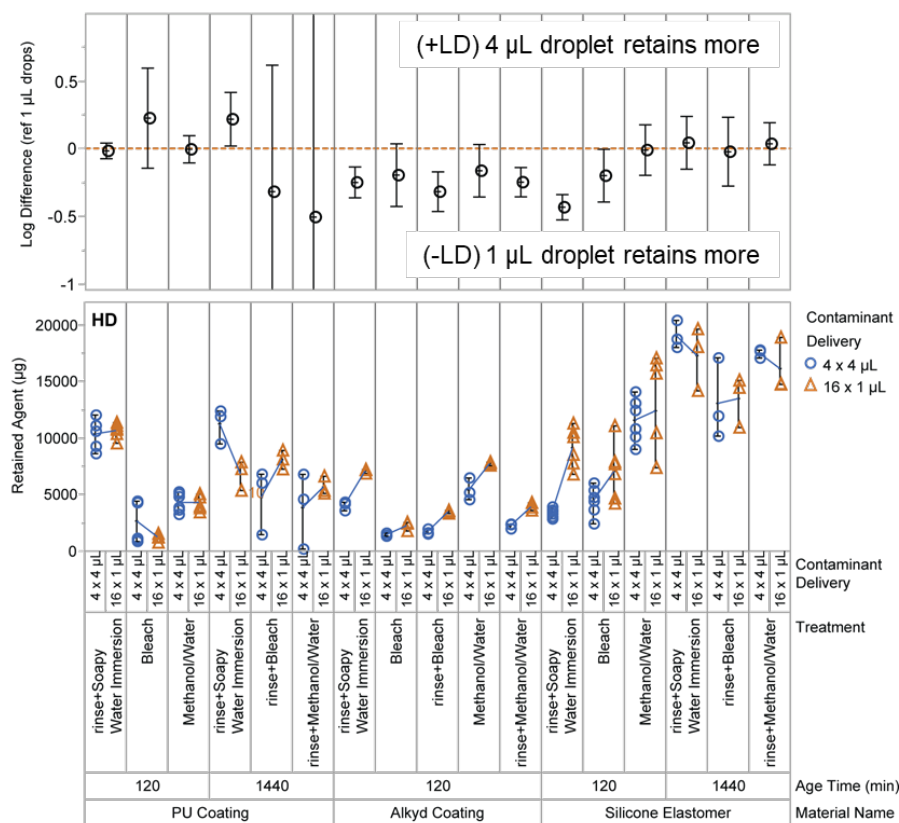


Figure C-1. Comparison of RA for 10 g/m² starting challenge generated with different drop volumes for HD.

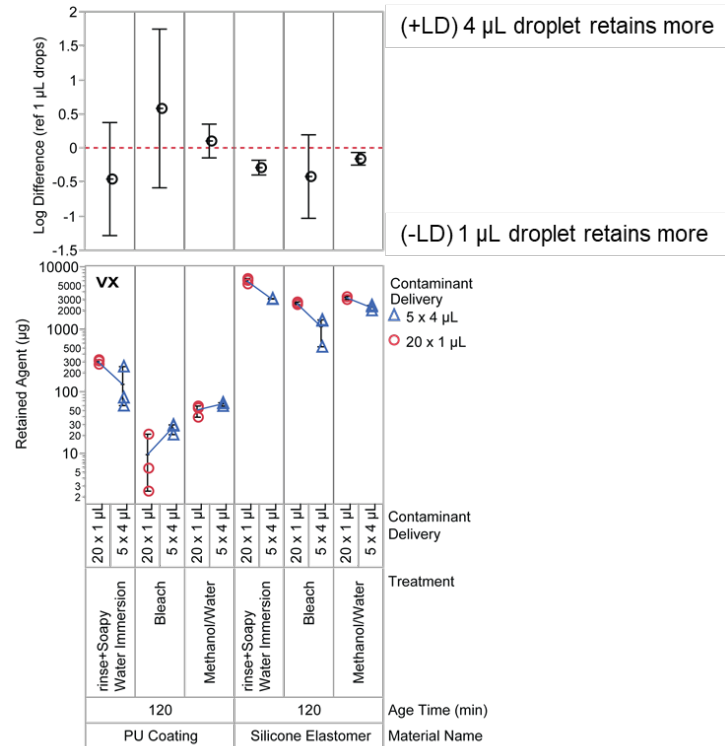


Figure C-2. Comparison of RA for 10 g/m² starting challenge generated with different drop volumes for VX.

This indicates that the current practice of specifying a starting challenge without listing drop distributions may not provide unique or comparable test conditions in all cases. Therefore, both a starting challenge and drop size distribution for testing need to be specified. For example, if the intent is to use laboratory data to indicate what may occur in an operational context, these data may need to be generated using drop volume distributions that represent operational conditions for optimal accuracy. However, this would require (1) knowledge of the operational drop distribution and (2) the ability to generate these distributions in the test environment. In the results provided here, 1 and 4 µL drops were compared; however, operational drop distribution could easily include aerosol-sized drops on the order of 0.1 µL, in which case the differences observed here may (or may not) be magnified. Although the use of different drop sizes for the same starting challenge may result in statistically significant differences in outcomes, there is a need to determine whether this difference must be accounted for in testing. Collecting data at different size distributions or modifying test infrastructure to generate operational drop distributions is not trivial and may provide significant or marginal improvement in the accuracy of laboratory results translated to the operational context. An alternate approach that involves empirically characterizing the effect of drop volume rather than matching operational drop distributions is described in Section 5 of this report.

APPENDIX D

RETAINED AGENT CORRELATION PLOTS

The retained agent (RA) and RA per-drop correlation plots provide a visual representation of the correlation of the measured responses to many of the contamination parameters. The correlation plots for multiple agent–material–treatment conditions are provided here. The data are limited to the 120 min contamination duration because there was no visibly detectable liquid to quantify in the liquid contaminated area after the 1440 min contamination duration. Note that the correlations presented here consider a linear correlation between the variables and not the log-transformed variables used in the regression analysis. This appendix includes RA correlation plots beyond the examples shown in Section 5 of this report for soapy water immersion (SWI) and bleach for bis(2-chloroethyl) sulfide (HD). The results for *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX) for the SWI treatment are provided in Figure D-1. Similar to what was observed for HD, VX on the polyurethane (PU) coating fully wet the surface for most conditions, and as a result, correlations with contaminated area or area per drop are not informative. The PU coating seemed to be somewhat resistant to sorption of VX; across the range of contamination conditions, the RA spanned only 50–300 μg . The small variation in RA resulted in lower apparent correlations. However, the results for silicone showed correlations with applied mass, drop volume, and contaminated area, much like the HD data.

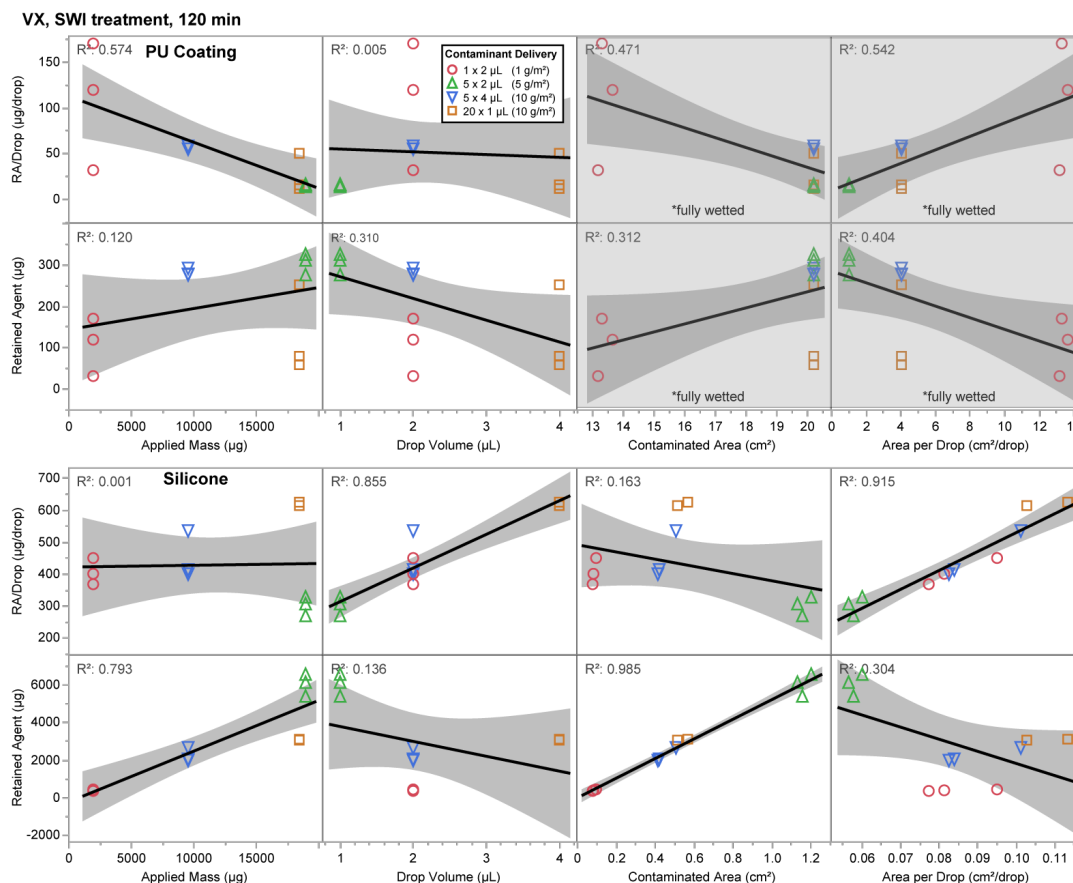


Figure D-1. Linear correlation plot for VX with the SWI treatment for a contamination duration of 120 min. Grey boxes over the contaminated area parameters for the PU coating indicate that these samples were fully wetted, and correlations with area are not informative.

The results for VX with the bleach treatment are provided in Figure D-2. The RA per drop and RA were overall much lower for bleach as compared to SWI for both the PU coating and silicone (approximately 10 times lower for the PU coating and 2 to 3 times lower for silicone). The strongest correlations for VX on the PU coating treated with bleach were either between RA per drop and applied mass or RA and drop volume, which was similar to results observed with the SWI treatment. The similarity between SWI and bleach results may be related to the minimal VX sorption in the PU coating; therefore, the VX was accessible for displacement, dissolution, and reaction. For silicone treated with bleach, RA had a strong correlation with contaminated area, which is consistent with sessile drop behavior. However, the RA per drop did not correlate strongly with drop volume or area per drop, as was the case for SWI.

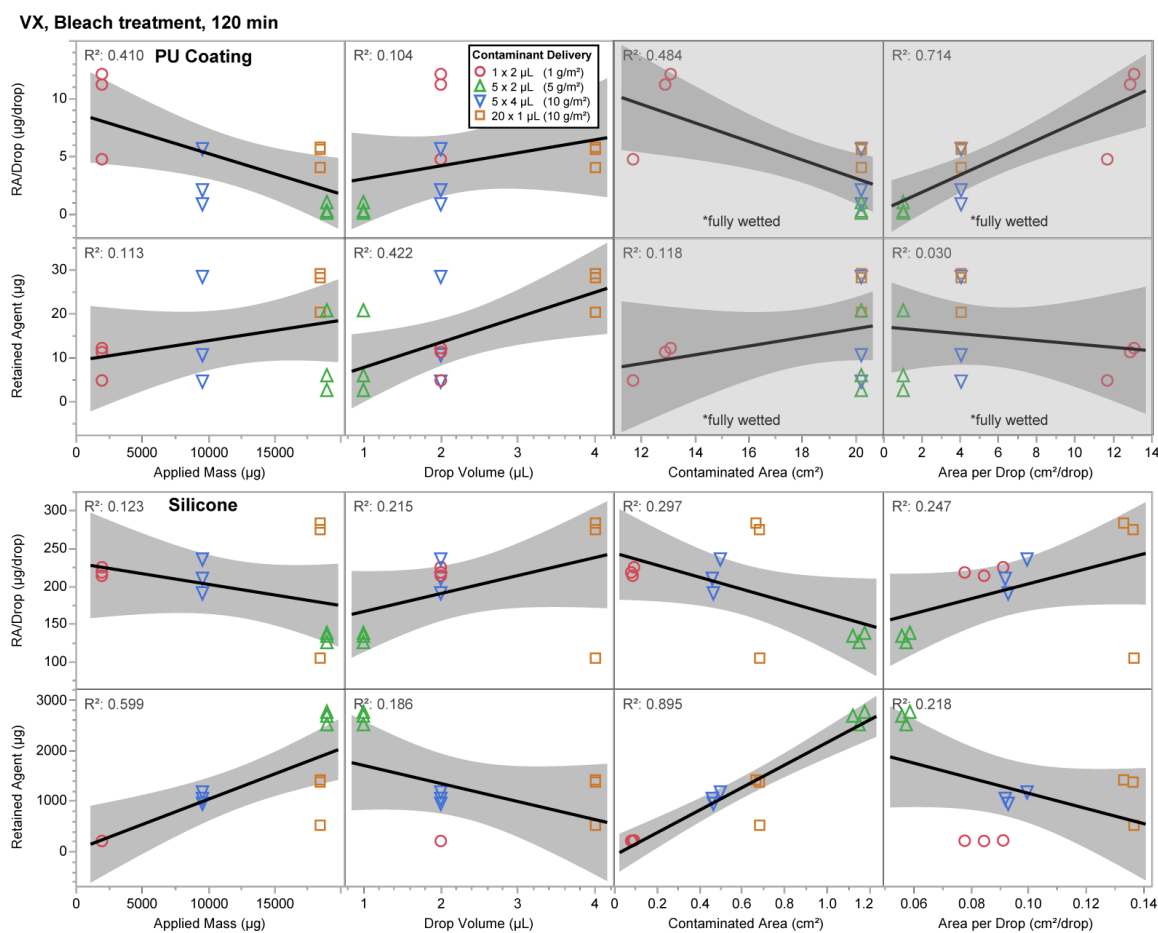


Figure D-2. Linear correlation plot for VX with the bleach treatment for a contamination duration of 120 min. Gray boxes over the contaminated area parameters for the PU coating indicate that these samples were fully wetted, and correlations with area are not informative.

The results for HD and VX with the methanol/water (M/W) treatment are provided in Figures D-3 and D-4, respectively. On average, the M/W solution has a greater penetration into these materials as compared to SWI and bleach. As a result, the decontaminant can access more of the contaminant distribution both at the surface and in the bulk of the

materials. Accordingly, there were strong correlations between RA and applied mass as well as between RA and contaminated area for both HD and VX on all of the materials. This was because the M/W treatment is less sensitive specifically to surface effects (i.e., agent distribution at the surface). This means that, regardless of how the agent spreads on the surface or the degree to which it readily penetrates into the material, there will be stronger per-drop and total RA trends with respect to drop volume and applied mass, respectively.

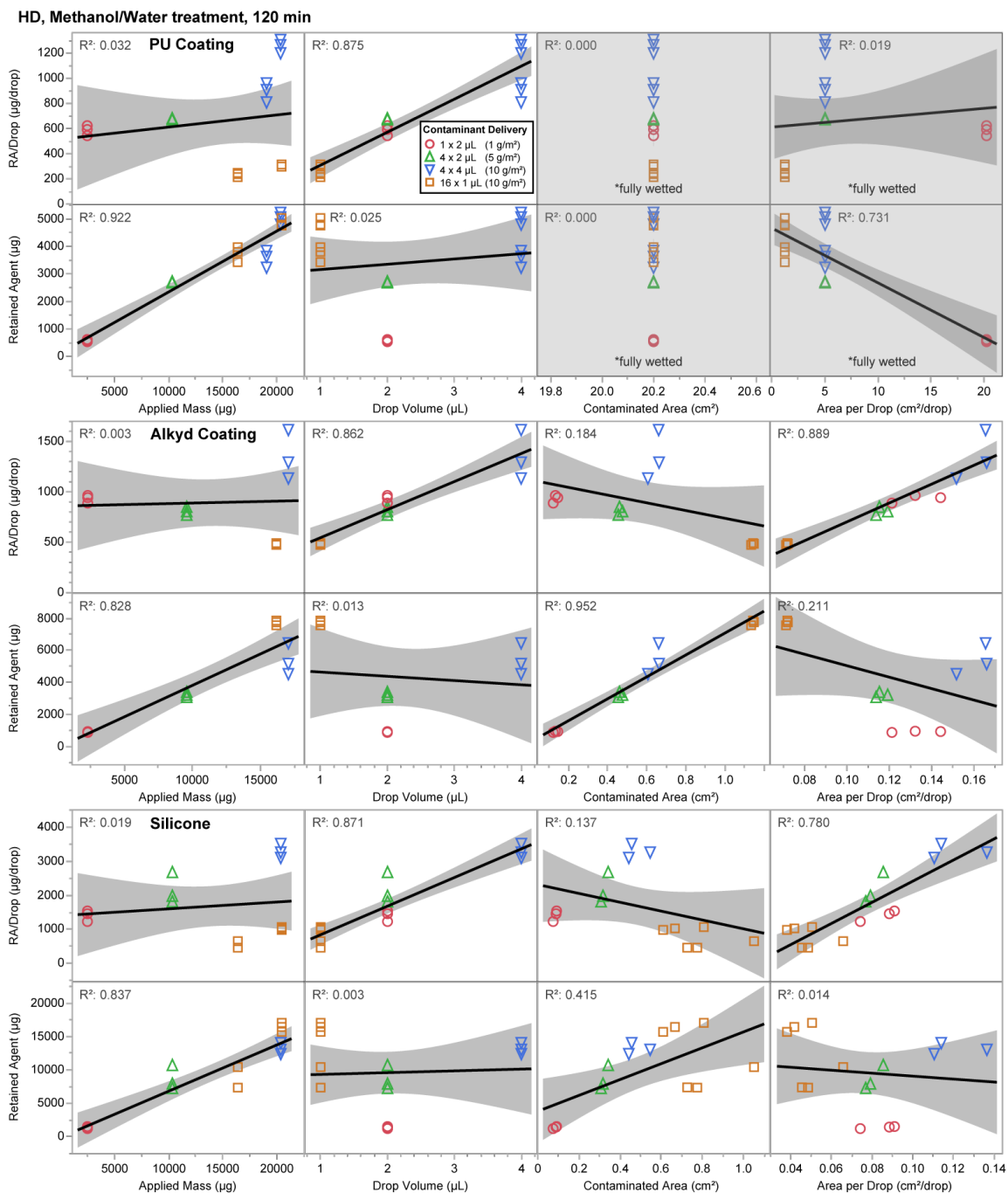


Figure D-3. Linear correlation plot for HD with the M/W treatment for a contamination duration of 120 min. Gray boxes over the contaminated area parameters for the PU coating indicate that these samples were fully wetted, and correlations with area are not informative.

VX, Methanol/Water treatment, 120 min

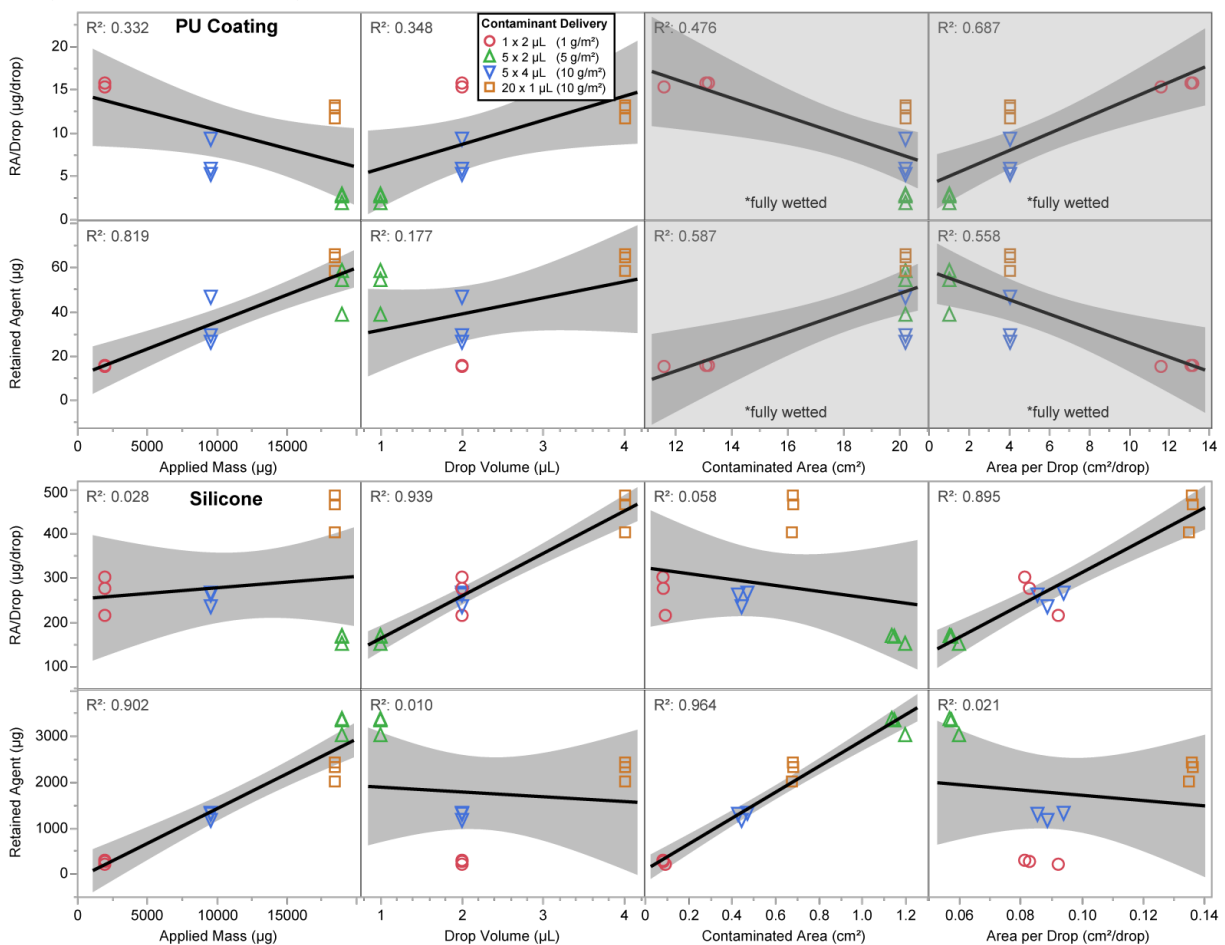


Figure D-4. Linear correlation plot for VX with the M/W treatment for a contamination duration of 120 min. Gray boxes over the contaminated area parameters for the PU coating indicate that these samples were fully wetted, and correlations with area are not informative.

APPENDIX E DETAILED PER-DROP REGRESSIONS

Figures E-1 through E-7 provide the detailed per-drop regression output for each agent–material–contamination–duration–treatment combination. The shaded regions represent the 95% confidence intervals (CIs) on the fits. Across these fits for HD, the $1 \times 2 \mu\text{L}$ condition occasionally deviated from the regression trend. This occurred for the bleach treatment on the polyurethane (PU) and alkyd coatings. For the PU coating, this $1 \times 2 \mu\text{L}$ condition seems to be the only case where the material surface was not overwhelmed by agent. However, the positive deviation was only observed for the bleach treatment. In some cases, similar deviations for the $1 \times 2 \mu\text{L}$ condition were also observed for *O*-ethyl-*S*-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX).

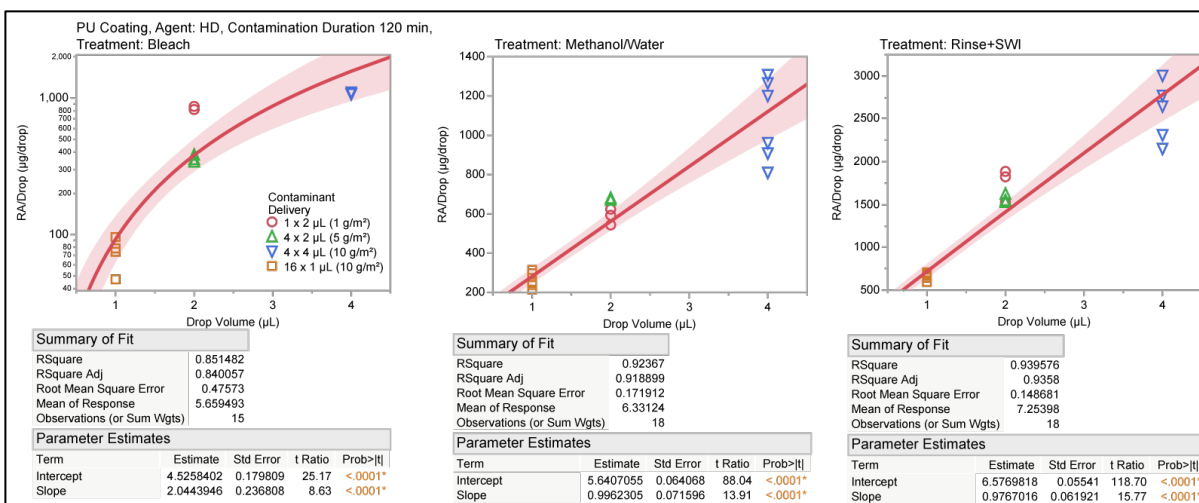


Figure E-1. Per-drop regression for bis(2-chloroethyl) sulfide (HD) on PU coating for 120 min contamination duration.

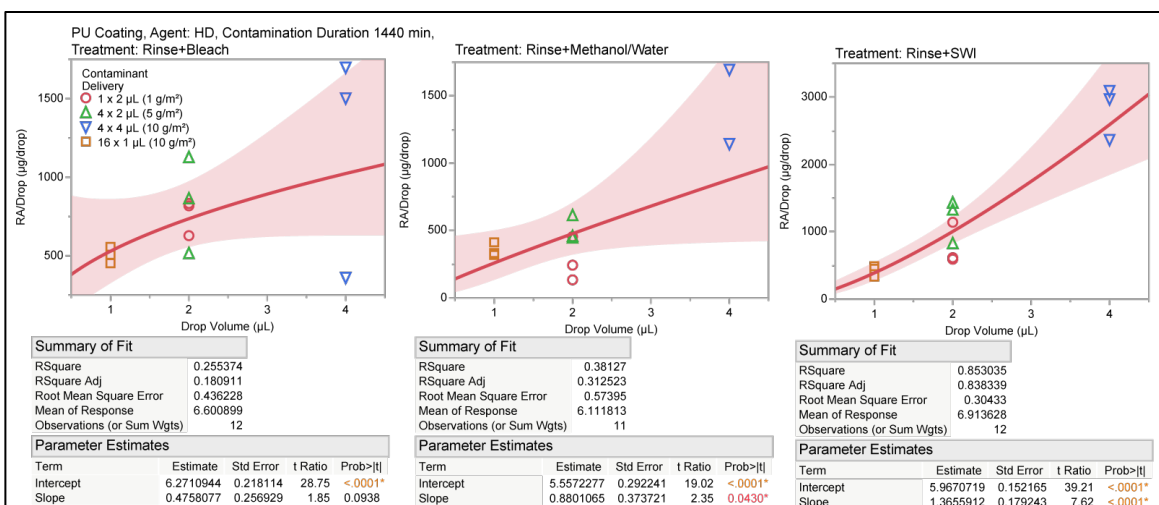


Figure E-2. Per-drop regression for HD on PU coating for 1440 min contamination duration.

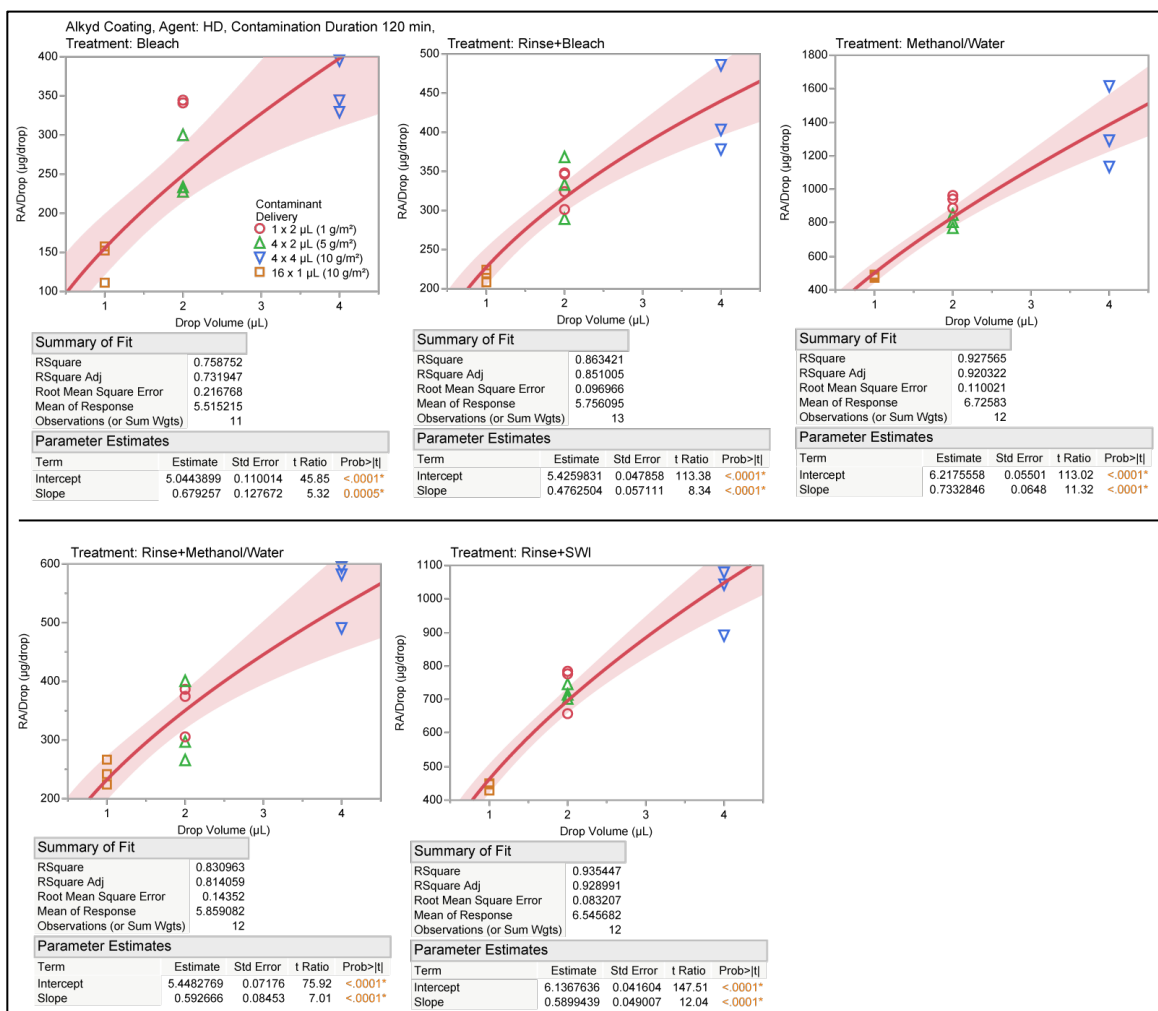


Figure E-3. Per-drop regression for HD on alkyd coating for 120 min contamination duration.

The HD on silicone elastomer with soapy water immersion (SWI) treatment did show some deviations from the trend (Figure E-4). This held for both conditions in which 2 μL drops were used. It is not clear why this occurred for the SWI treatment and not the other two treatment cases. For the PU coating, VX was not significantly retained, which resulted in regressions with wide CIs (Figure E-6). Similar to previous data, the $1 \times 2 \mu\text{L}$ data were greater than the fitted trend line.

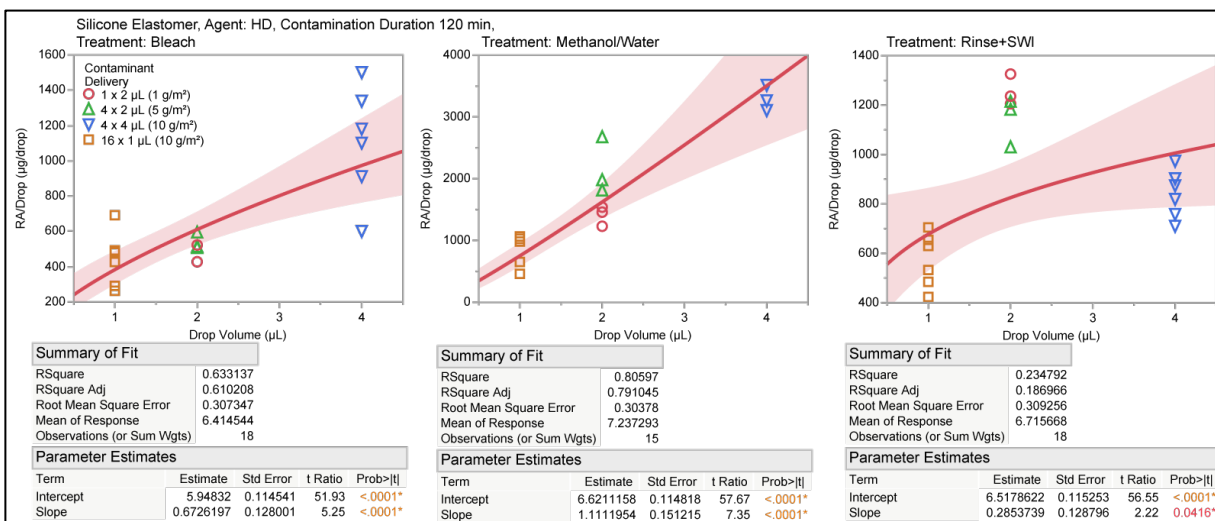


Figure E-4. Per-drop regression for HD on silicone elastomer for 120 min contamination duration.

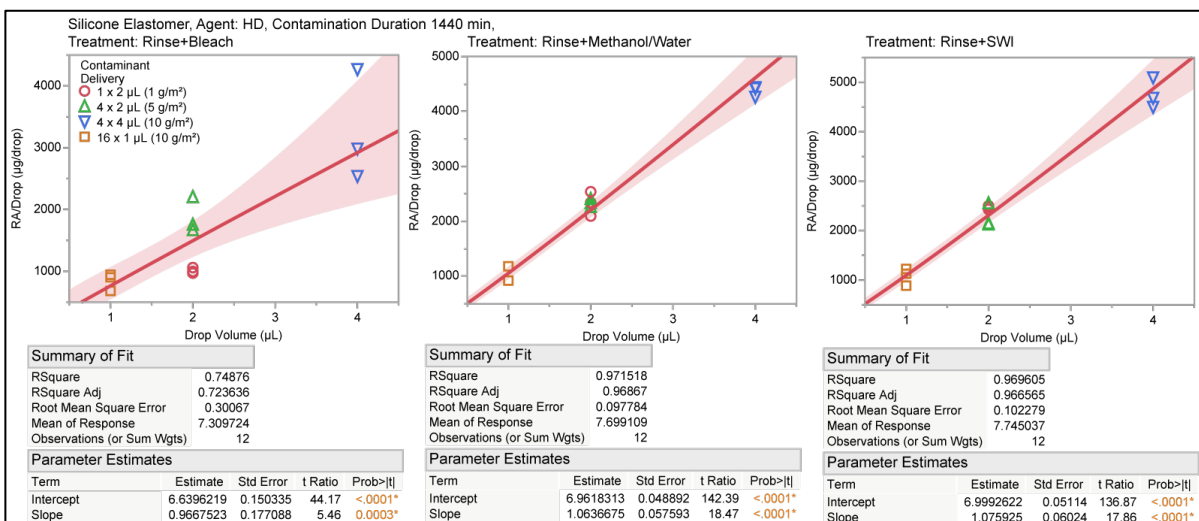


Figure E-5. Per-drop regression for HD on silicone elastomer for 1440 min contamination duration.

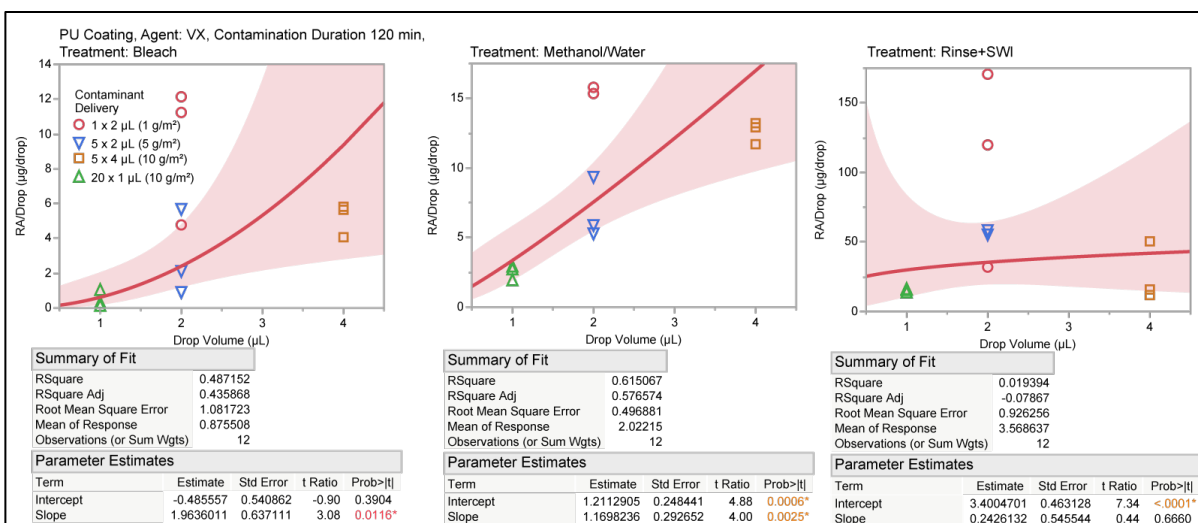


Figure E-6. Per-drop regression for VX on PU coating for 120 min contamination duration.

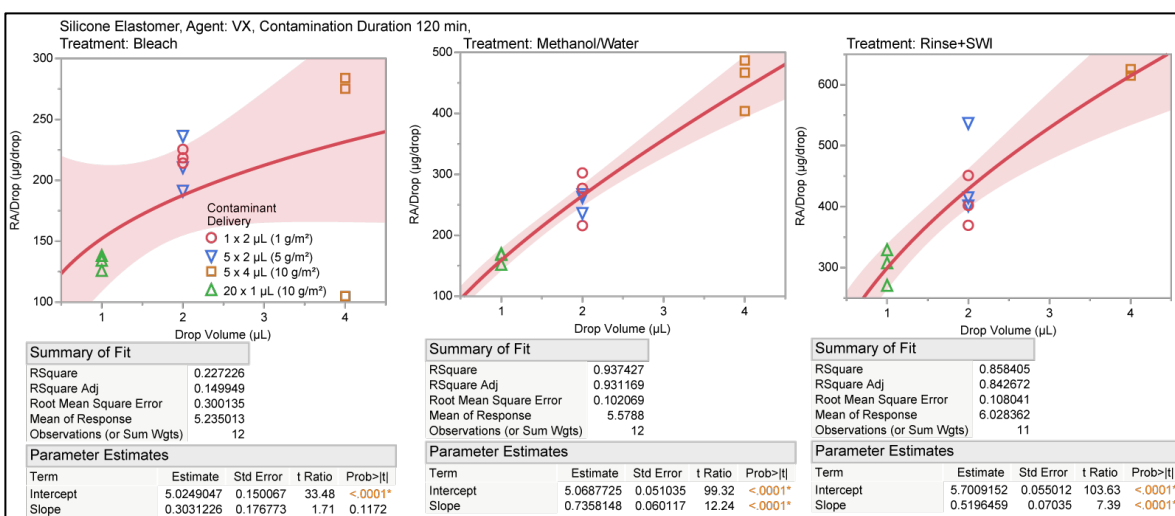


Figure E-7. Per-drop regression for VX on silicone elastomer for 120 min contamination duration.

APPENDIX F

CONSIDERATIONS TOWARD TRANSLATING LABORATORY DATA TO OPERATIONAL CONTEXT

F.1 Defining Area Associated with Contamination Density

Many studies consider a munition detonation to identify the resulting agent distribution on the environmental terrain (i.e., ground) to determine the contamination density. The projection of which agent drops may interact with the surface of an asset may produce a different contamination density. Thus, the area term used for the contamination density may be interpreted in two ways. It may be the environmental surface area (the mass of agent per unit area of terrain where the dissemination occurred) or the full-scale asset material area. For hazard mitigation laboratory testing, the area associated with contamination density is often interpreted as the material area. However, these interpretations lead to different concepts for how the agent may be distributed on the asset.

For example, consider a scenario where the contamination density was defined with regard to the terrain, and a 1 g/m^2 starting challenge was disseminated directly down on a vehicle. If this vehicle was approximately 7 m long and 2.75 m wide, it would have a footprint (top-down area) of 19.25 m^2 . However, the vehicle could present approximately 52 m^2 of material surface area if vertical surfaces and other material textures were considered. Should the top-down area of the vehicle multiplied by the contamination density be used to determine the total quantity of mass that contaminated the vehicle ($19.25 \text{ m}^2 \times 1 \text{ g/m}^2 = 19.25 \text{ g}$ of contaminant)? Should this mass of contaminant then be evenly distributed across all material surfaces (e.g., 19.25 g of contaminant distributed across all 52 m^2 of material area, producing a 0.37 g/m^2 (grams of agent per square meter of total material area) contamination density, or should only the top-down surfaces be considered for contamination in the subsequent calculations? If the desire is to provide an accurate operational prediction, then the details of how the agent is distributed on the asset must be provided. The accuracy of the end result is dependent upon the input conditions accurately representing the actual operational conditions.

If, on the other hand, the output calculation considered all 52 m^2 of asset materials to be evenly contaminated to 1 g/m^2 , this would correspond to 2.7 times more agent on the asset than would be calculated using the environmental area. Further, this would not be physically realistic when compared to the actual environmental contamination; 2.7 times more agent would be on the vehicle than the local environment. This may represent a worst-case approximation, but compounding many worst-case considerations in an analysis may produce unrealistic performance requirements.

When using a contamination density specification for laboratory testing, considerations such as selecting test conditions or defining the contamination levels for an operational context calculation can become nontrivial. However, the use of the per-drop normalization enables either contamination perspective to be addressed in the output calculation.

F.2 Defining Agent Mass for Contamination Density

In addition to the potential ambiguity regarding the referenced area in a starting challenge specification, the definition of contaminant mass introduces another potential complication. Many of the studies that describe munition detonations describe the mass of *liquid* disseminated per unit surface area without accounting for variable agent liquid density and purity. Depending on the density of the contaminant liquid and the contaminant purity, the mass of applied liquid and the mass of contaminant applied to the material may not be equal. For example, chemical agent standard analytical reference material (CASARM) high-purity grade VX can have a mass purity (Ψ) ranging from, for example, 89–97% and a density (ρ) of 1.0083 g/mL. The mass of analyte for an applied volume is calculated as

$$m_{\text{analyte}} = \frac{\rho V \Psi}{100\%} \quad (\text{F-1})$$

where m_{analyte} is the mass of analyte applied to material (g),
 ρ is the density of pure contaminant liquid (g/mL),
 V is the total volume applied (mL), and
 Ψ is the contaminant purity (%).

A 0.002 mL (2.0 μL) liquid drop with 89% purity VX has 1,805,000 ng of VX. Alternatively, the mass of liquid applied to the material is

$$m_{\text{liquid}} = \rho V \quad (\text{F-2})$$

where m_{liquid} is the mass of liquid applied to material (g).

Therefore, a 0.002 mL (2.0 μL) liquid drop of high-purity VX has a mass of 2017 μg (i.e., VX plus any impurities). Delivering this to a 2 in. diameter disk (0.00202 m^2) produces a starting challenge of 0.9985 g/m^2 (grams of liquid per square meter of material). Accounting for the purity (89–97%) produces analyte contamination densities that could range from 0.888 to 0.967 g/m^2 (grams of VX per square meter of material). Previous studies have considered the effect of different agent purity or the presence of thickeners that could also influence how the agent is distributed on materials.^{1,2} Overall, mass purity effects were *not* found to be as influential in post-decontamination results when compared to how other agent constituents influenced the results. However, in terms of agent purity and operational relevance, it is not likely that munitions will contain the same purity and composition as the laboratory grade, high-purity agent often used in testing. It is not practical to expect that the operational agent composition will be known for all situations to test to these compositions. Rather, the use of high-purity agent may enable more reproducible test results.

APPENDIX F: LITERATURE CITED

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