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EFFECT OF CHEMICAL PURITY ON MEASUREMENT OF AGENT RESISTANCE AND DECONTAMINATION PERFORMANCE FOR MATERIALS

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There is a need to understand and predict how decontamination technologies will work on real assets in the field upon contamination with actual chemical weapons (i.e., not refined laboratory-grade agents). Current methodologies primarily focus on the testing of clean, ideal materials, such as flat, horizontal surfaces in a laboratory environment, using highly purified agents. The magnitude of the effects of the dominant mechanisms responsible for interactions between agents and materials in the limits of complex features, dirty surfaces, and agent impurities is not known. Toward this end, this work was focused on determining whether the use of high-purity agent over- or underestimates decontamination performance results as compared with agent and material configurations that may be observed in operational environments. Results are presented on the characterization of how impurities in agent solutions influence decontamination performance and potential exposure to personnel as compared with high-purity agent, especially for materials susceptible to contaminant absorption.

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PREFACE

The work described in this report was authorized under project no. CB10409. The work was started in December 2016 and completed in March 2018.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

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EFFECT OF CHEMICAL PURITY ON MEASUREMENT OF AGENT RESISTANCE AND DECONTAMINATION PERFORMANCE FOR MATERIALS

1. PROJECT BACKGROUND AND OBJECTIVE

1.1 Introduction

The need exists to understand and predict how decontamination technologies will work on real assets in the field that have been contaminated with actual chemical weapons (rather than refined laboratory-grade agents). Current methodologies primarily focus on the testing of clean, ideal materials, such as flat, horizontal surfaces in a laboratory environment, using highly purified agents, including chemical agent standard analytical reference materials (CASARM). One aspect of this challenge is to evaluate whether the use of high-purity agent over- or underestimates decontamination performance results as compared with the agent–material configurations that may be observed in operational environments. Generally speaking, the magnitude of the effects of the dominant mechanisms responsible for interactions between agents and materials in the limits of complex features, dirty surfaces, and agent impurities is not known. Figure 1 broadly illustrates the scope of the challenge in connecting ideal laboratory conditions to operational systems, including delineation of the factors under consideration with respect to influence on decontamination performance. In this report, results are presented that characterize how impurities in agent solutions influence decontamination performance and potential exposure to personnel as compared with high-purity agents, especially for materials susceptible to contaminant absorption.

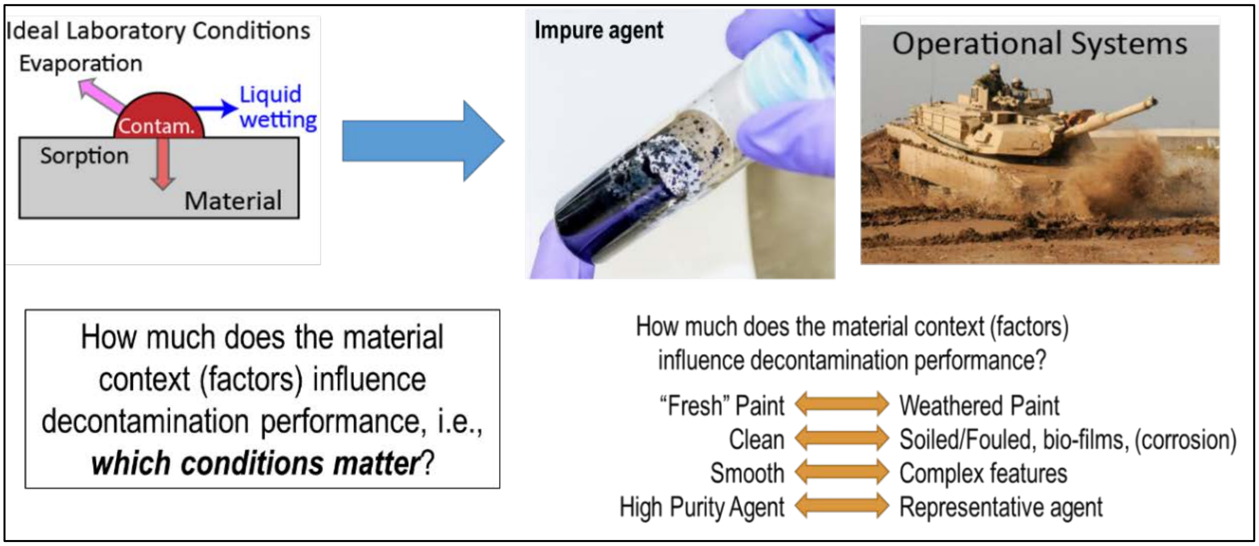


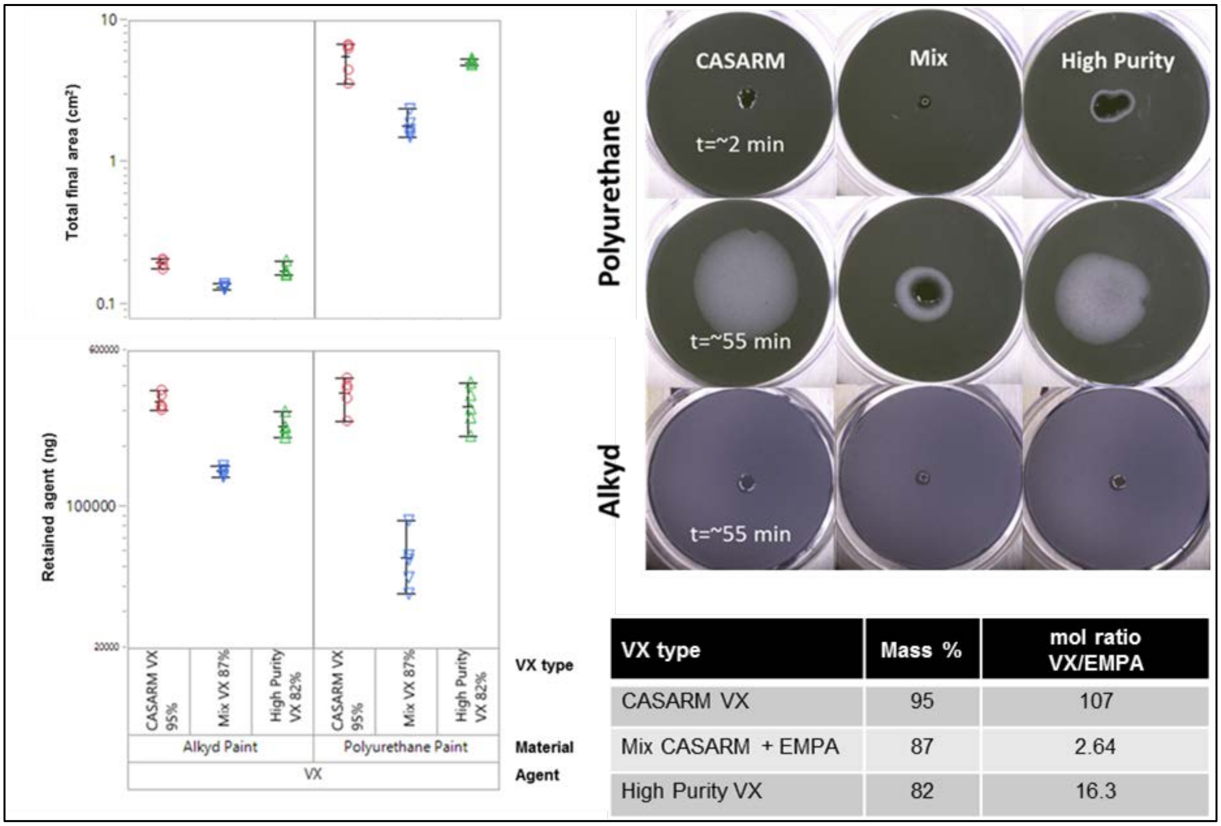
Figure 1. Factors to be considered when evaluating the applicability and relevancy of results produced from ideal laboratory conditions to operational systems.

1.2 Background

Numerous chemical interactions and physical properties are responsible for agent transport and reaction networks in the limits of contamination and decontamination processes for materials. When multiple chemical species such as contaminant-specific byproducts and impurities are involved in a contamination event, it is possible that the degree of contamination and the subsequent decontamination burden will be influenced. For example, liquid spreading on surfaces can be altered significantly as a function of solution composition, due to changes in liquid surface tension and viscosity. Changes in spreading can influence the likelihood that specific routes of ingress into different materials will occur. An example of composition dependence on liquid spreading has been documented for 2-(diisopropylamino)ethyl-*O*-ethyl methylphosphonothioate (VX) on impermeable surfaces, where the degradation of the agent results in very different spreading behavior.[1]

Similarly, a change in liquid adhesion due to solution composition is likely to affect the residence time and the interaction area between a contaminant solution and the material surface, which would have a significant impact on the spread or drip of droplets on vertical surfaces.[2] Examples of the influence of VX solution composition on liquid spreading on absorptive materials and also on amounts of retained chemical are shown in Figure 2. The presence of ethyl methylphosphonic acid (EMPA), a common VX byproduct, can significantly alter the wetting behavior and the subsequent chemical mass absorption, depending on the material. Additionally, boundary conditions for evaporation and absorption can be driven by the mole fraction of agent in the contaminant liquid.[3–5] In the case of liquid-phase decontamination, a reaction network can change because of the presence of other chemicals, such as impurities. These chemicals may exhibit a broad range of effects, from only serving as spectator species to scavenging active ingredients, shifting and buffering pH, and modifying the solubility and rate of dissolution of specific chemical species. In the material phase, the presence of chemical species can affect reaction pathways and the availability of active sites within the solid state and can especially influence extraction efficiency in the limit of multispecies transport.[6,7]

The overall objective of this work was to determine which factors have the most significant effects on decontaminant performance and how these considerations should influence methodology protocols. The determination of the degree of influence that each of the effects has on contamination and decontamination, or *how these factors matter*, will be used to identify how and when these effects should be included in decontamination evaluations and to enable the development of methodologies to test these systems. This report focuses on the impact of impurities in agents (e.g., weapons-grade, nonpurified synthetic systems) with respect to evaluations of decontamination performance and potential exposure to personnel as compared with work performed with CASARM-grade (i.e., high-purity) agent.



VX type	Mass %	mol ratio VX/EMPA
CASARM VX	95	107
Mix CASARM + EMPA	87	2.64
High Purity VX	82	16.3

Figure 2. Example of influence of EMPA in a VX solution on liquid spreading on polyurethane- and alkyd-based coatings as well as retained agent (RA).

2. MATERIALS, PROCESSES, AND METHODS

Pinacolyl methyl phosphonofluoridate (GD), bis(2-chloroethyl) sulfide (HD), and VX of varying types and purities, including CASARM-grade, diluted agent solutions as well as munitions-grade agents (recovered from a ton container, as is) were used as part of this study. These agents are listed in Table 1 and illustrated in Figures 3 and 4. Distinct color differences were evident despite relatively small variations in purity. All agents (both CASARM and munitions grade) were used as received without further processing. Gas chromatography–flame ionization detector (GC–FID) analysis was used to verify purity and to qualitatively assess the relative abundance of other chemical species. Figure 5 shows chromatograms for the different vials of agent that were used as part of this study. Note the increase in the number of peaks and therefore the number of chemical species present between CASARM-grade and non-CASARM-grade agents. The spectra were offset such that the purity level was highest for the bottom trace (blue) and lowest for the top trace (gray).

Table 1. Purity and Grade for Different Agents Used in This Study*

Agent	Vial No.	Purity (%)	Grade
GD	2323	99.2	CASARM
	5134	97.7	Munitions
	0167	96.7	Munitions
HD	5223	99.9	CASARM
	7025	95.3	Munitions
	6343	87.3	Munitions
VX	U-7165	96.9	CASARM
	U-5244	93.7	Munitions
	U-1122	88.7	Munitions

*Matching labels are shown in Figure 4.

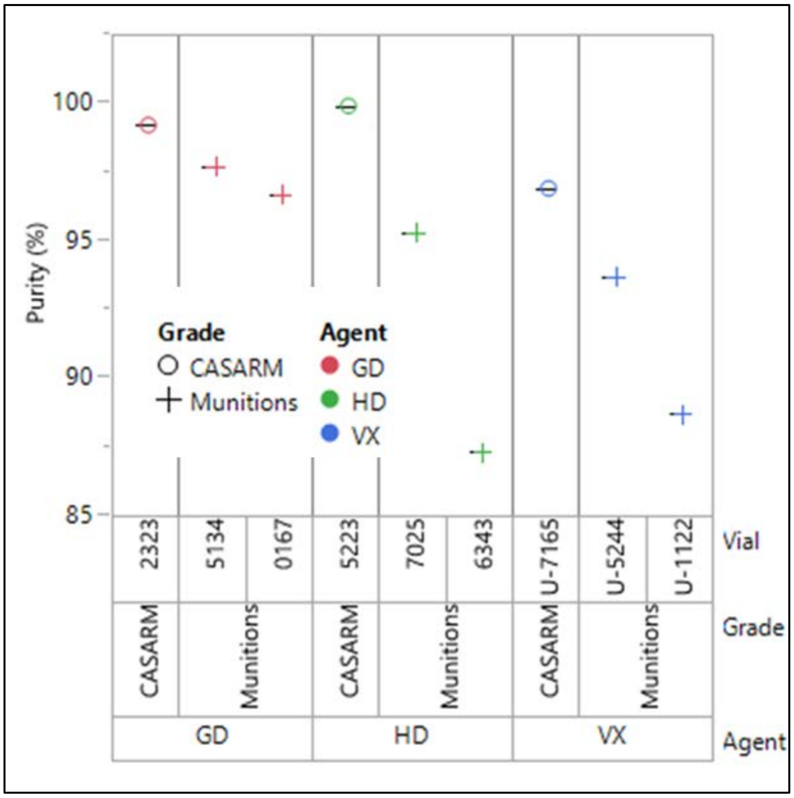


Figure 3. Comparison of purity for each vial of agent. Variability gauge chart representation of Table 1.

Figure 4. Agent solutions with variable agent purity. Both CASARM- and munitions-grade agents are shown.

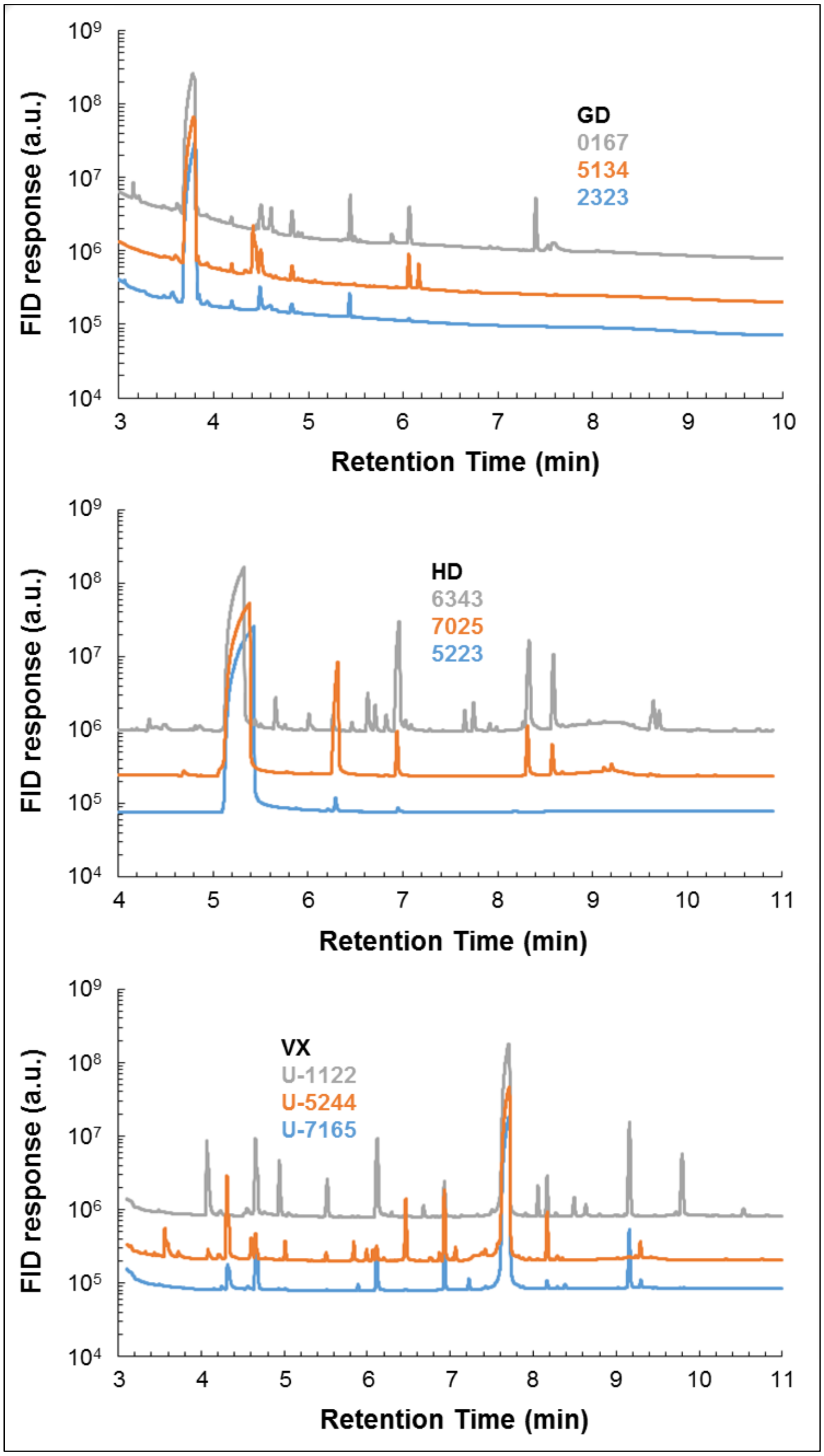


Figure 5. FID results (i.e., chromatograms) for agent solutions of GD, HD, and VX, illustrating variation in number of chemical species per vial. Blue traces represent CASARM-grade agents and orange and gray represent munitions-grade agents of decreasing purity: blue > orange > gray. Chromatograms were offset by 2.5× and 10× for orange and gray traces, respectively; a.u. stands for arbitrary units.

Three different materials were considered. Impermeable materials (bare metals) were used as controls, and the focus was on permeable polymers (polyurethane paint and silicone). Contamination of materials involved the delivery of a 2 µL droplet of agent (~1 g/m^2 contamination density) that was deposited at 20 °C. The agent was permitted to interact with the material for 60 min (droplet residence time). Additional details regarding the handling of materials as well as the methods used for evaluation of retained agent (RA) in the materials are published elsewhere.[8]

Two different representative decontamination processes were performed, namely, soapy water immersion or ~6% bleach, for evaluation of agent retention in polymeric materials as a function of agent type and purity. The soapy water immersion treatment served as a baseline condition for removal of surface-bound agent with minimal extraction of absorbed agent. The bleach condition represented a typical reactive decontaminant. All extractions were performed for 1 h in analyte-specific solvent solutions (acetonitrile for GD, chloroform for HD, and isopropyl alcohol for VX) and analyzed by GC or liquid chromatography (LC) as a function of analyte for evaluation of RA. Contact transfer (CT) tests were performed as a three-touch sequence with natural latex samplers. Tables 2 and 3 list the details of the test setup, and technical report ECBC-TR-980 provides other CT method descriptions.[8]

Table 2. Overall Test Settings for Evaluation of Agent Purity

Setting	Values	Rationale
Contaminants	GD, HD, and VX (both CASARM and variable-purity munitions grade)	Select contaminants spanning range of properties
Contamination	1 × 2 µL droplet	Reproducible quantity of agent delivered to each sample
Materials	Polyurethane paint, silicone elastomer, and impermeable metal (either aluminum or steel)	Range of materials for evaluation of wetting and absorption of agent
Age time (min)	60	Typical intermediate contamination duration to provide sufficient time to observe absorption
Treatment	Deionized water pre-rinse, then either soapy water immersion (3 s) or bleach immersion (15 min), followed by deionized water post-rinse	Evaluation of decontamination performance of a single decontaminant (bleach) against a baseline treatment
Replicates	3 replicates/condition for RA and CT	Sufficient replication for statistics
Environment	20 °C, 50% relative humidity	Ambient conditions
Measurement	a. RA and three-time-stamp photography b. CT-3 touch sequence (see Table 3)	Established metrics for decontaminant performance

Table 3. CT Test Settings for Evaluation of Agent Purity

Touch	Touch Start Time (min)	Touch Duration (min)	Rationale
1	15	5	Match typical start time, make duration work for testing logistics
2	45	5	Capture an intermediate time point within first hour
3	300	5	Indicate a longer-term presence of agent

The principal data shown in this work are values for mass of agent retained by materials, as measured by the soapy water immersion process (shown in Figure 6), which was quantified by analytical chromatography. Liquid-phase extraction solutions were analyzed to evaluate material retention of chemical species. Extraction solution samples were diluted, and the analytes were quantified using GC for HD and GD (a model 6890/7890 GC system equipped with a model 5975 mass selective detector [Agilent Technologies; Santa Clara, CA]) and using LC with mass spectrometry for VX (an Agilent 1200/1290 series LC system and an Applied Biosystems [Carlsbad, CA] API 5000/5500 triple-quadrupole mass spectrometer equipped with a Turbo V ion source). Details on the use of the chromatography platforms are published elsewhere.[9]

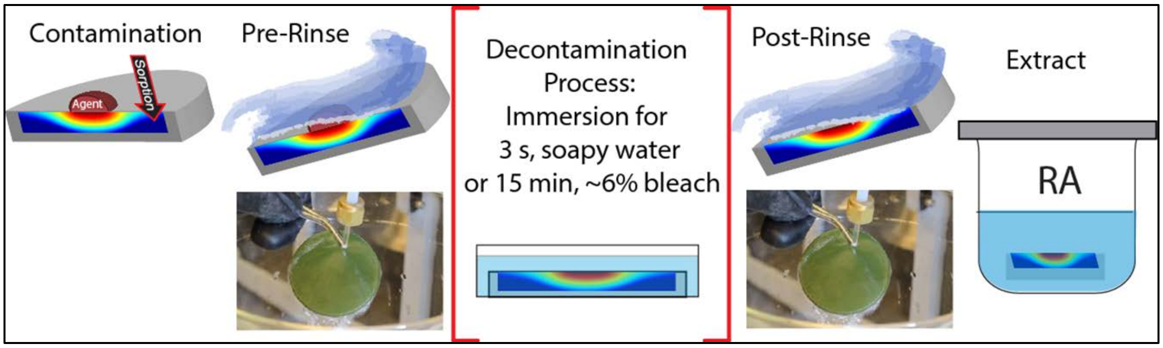


Figure 6. Material treatment process used for measurement of RA.

3. RESULTS

3.1 Dose-Confirmation Samples (DCSs)

The decontamination test methodology stipulates that the metric of the starting challenge is grams of liquid per square meter of material.[8] As such, a constant volume of *liquid* (i.e., 2 µL) is delivered to each sample, and the mass of agent varies with the purity of the contaminant. It is assumed that the density of the liquid is approximately the same, and the delivered mass of liquid is similar across agent purities. The DCSs quantify how much analyte is delivered to the panels; those values are reported in Table 4. The normalized DCS mass values (referenced to the highest-purity agent tested, namely, CASARM) are provided to support comparison of agent composition across the reported agent purities. Overall, the normalized mass indicated that substantially less agent mass may have been delivered to the panels than would have been expected, given the reported purity. The log difference (LD) was used to compare the RA results and was calculated across the agent purities (referenced to the highest-purity agent tested). In Section 3.3 of this report, the LD of RA is compared across the various agent purities, and a correlation is shown between the DCS mean response and the panel RA results to identify relationships between these values.

Table 4. Mass of Agent Delivered to Panels

Agent	Agent Lot (Vial No.)	Reported Purity (%)	DCS Mean (ng)	DCS Standard Deviation (ng)	Normalized DCS Mass to CASARM (unitless)
GD	2323	99.2	1,900,576	177,988	1.000
	5134	97.7	1,892,592	46,614	0.996
	0167	96.7	1,719,966	137,379	0.905
HD	5223	99.9	2,585,965	153,014	1.000
	7025	95.3	2,175,664	180,173	0.841
	6343	87.3	1,020,797	46,136	0.395
VX	7165	96.9	1,878,321	54,388	1.000
	5244	93.7	1,839,430	99,289	0.979
	1122	88.7	1,477,613	78,592	0.787

3.2 Liquid Spreading Results

Photography was used to capture any impurity-specific influences on liquid spreading behavior on the materials studied. In all cases, there was very little variation in spread behavior within an agent type and material as a function of agent purity. Figures 7–9 show the results for impermeable metal substrates, silicone, and a polyurethane coating, respectively.

Although the agent purity did not significantly influence the spreading area, it is still plausible that solutions with greater concentrations of certain impurities could alter the wetting characteristics for different agents on different material surfaces. Of particular note is the case of HD and polyurethane paint, as shown in Figure 9: In contrast with the munitions-grade cases, for the CASARM-grade case, no liquid appeared to remain on the surface at 55 min. This difference in interactions between the two grades of agents and the polyurethane paint may be principally responsible for the observed differences shown in Section 3.3. The case of VX and its impurities presented in Section 1.2 of this report is a particularly salient example of this effect. In the future, more work is warranted with systematic variations in specific impurity mole fractions relative to the agent.[1]

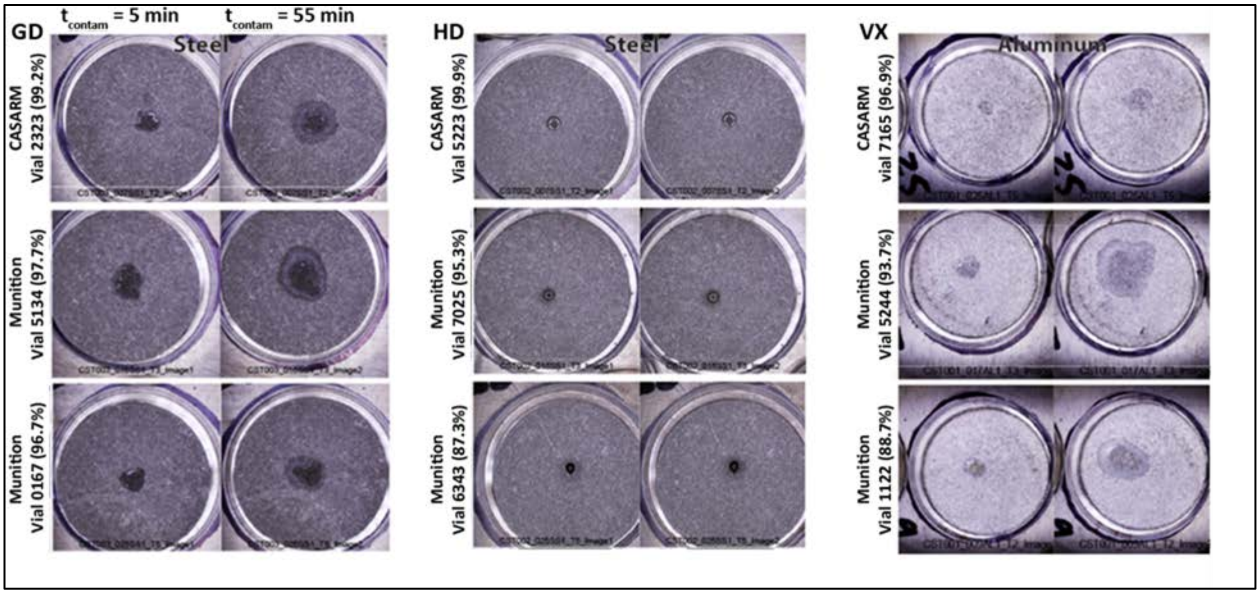


Figure 7. Photography was used to track GD (left), HD (center), and VX (right) droplet spreading on steel or aluminum substrates. Comparison between 5 and 55 min after deposition shows no significant agent purity-specific behavior within a given substrate material.

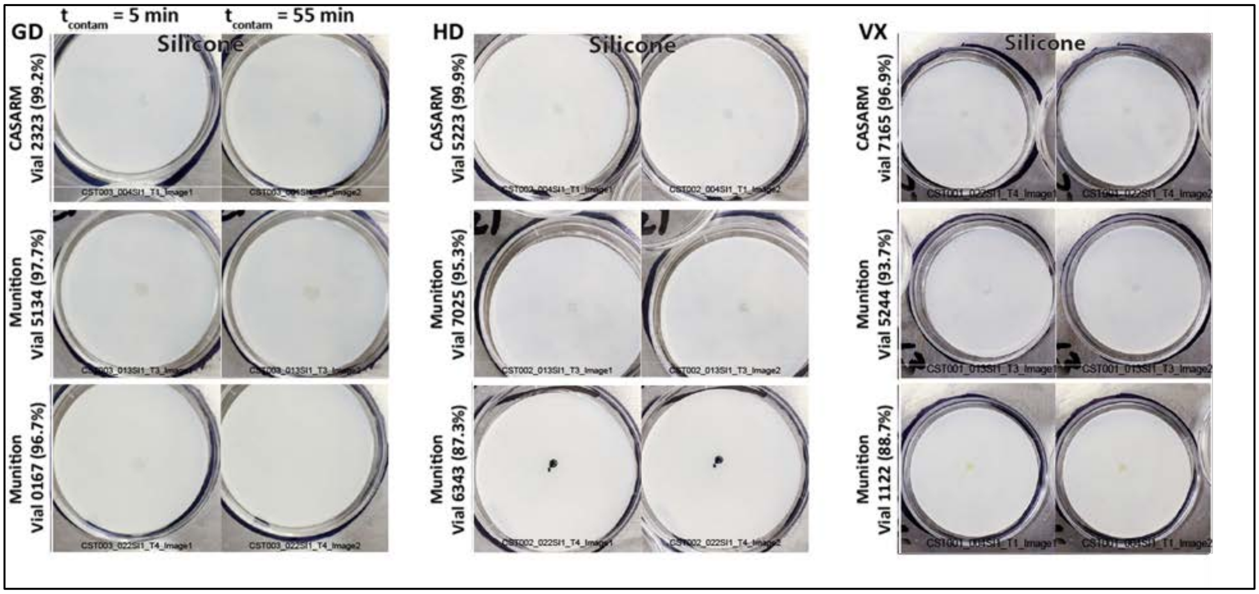


Figure 8. Photography was used to track GD (left), HD (center), and VX (right) droplet spreading on silicone substrates. Comparison between 5 and 55 min after deposition shows no significant agent purity-specific behavior within a given substrate material.

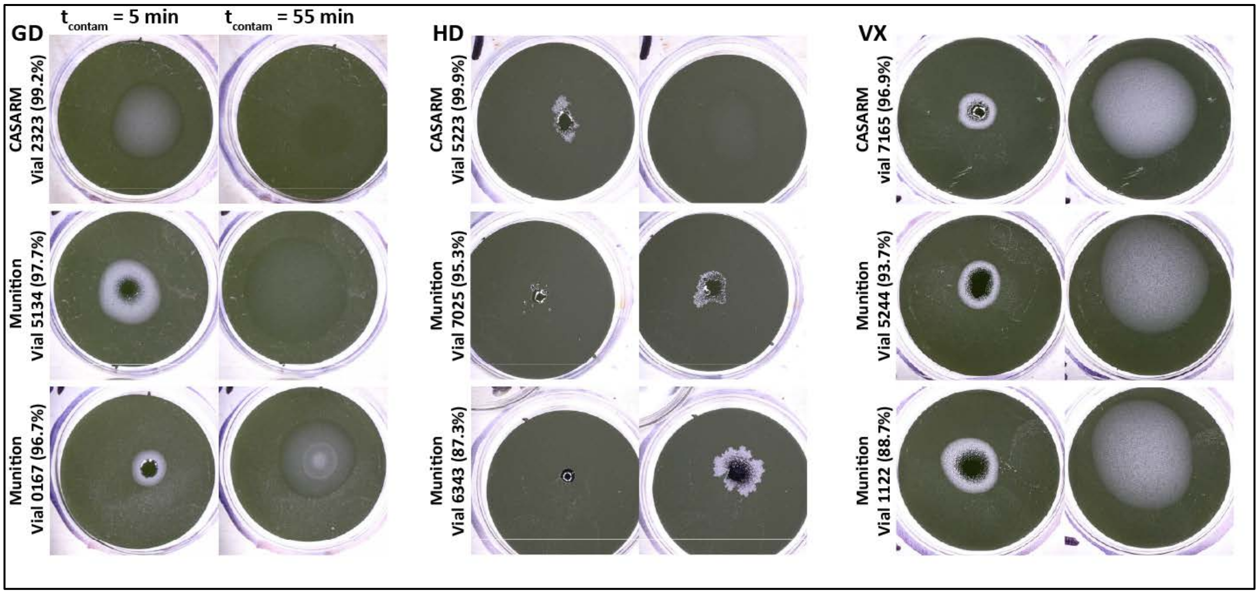


Figure 9. Photography was used to track GD (left), HD (center), and VX (right) droplet spreading on a polyurethane paint coating. Comparison between 5 and 55 min after deposition shows no significant agent purity-specific behavior within a given substrate material.

3.3 RA Measurements

RA measurements are simple, robust indicators of possible vapor and contact source terms presented by contaminated material because those source terms are directly dependent on the mass of chemical retained by the material. If there are impurity-dependent variations in RA, the expectation is that vapor and contact source terms are also likely to be different. LD calculations for this study are a means of comparing the effects of the bleach decontaminant relative to the soapy water reference condition:

$$\mathrm{LD} = \log_{10} \frac{\mathrm{RA}_{\mathrm{bleach}}}{\mathrm{RA}_{\mathrm{soapy\ water}}} = \overline{\log_{10}(\mathrm{RA}_{\mathrm{bleach}})} - \overline{\log_{10}\left(\mathrm{RA}_{\mathrm{soapy\ water}}\right)} \tag{1}$$

The details of the LD calculations are provided as Procedure 5 of the *Test Methodology Source Document*, and the error bars calculated from these results provide the 95% confidence interval on the difference.[8] The LD (i.e., performance) of bleach to soapy water treatments showed similar results in all cases tested (95% confidence interval overlap). The RA masses across conditions were different as a function of agent purity.

For the case of impermeable, metal substrates, the results for RA and LD are shown in Figure 10. There was ostensibly no influence of impurities within an agent type on RA or LD when RA results for bleach and soapy water treatments were compared. This indicates that the impurities did not alter, either to strengthen or weaken, the chemical interactions that dictate the adhesion of the agent to the metal surface. Additionally, the differences in applied mass of each agent (Table 4) did not influence the RA results for impermeable materials. Although there were cases of up to 0.4 LD (for HD) in applied mass, the LDs comparing the soapy water condition to bleach were the same.

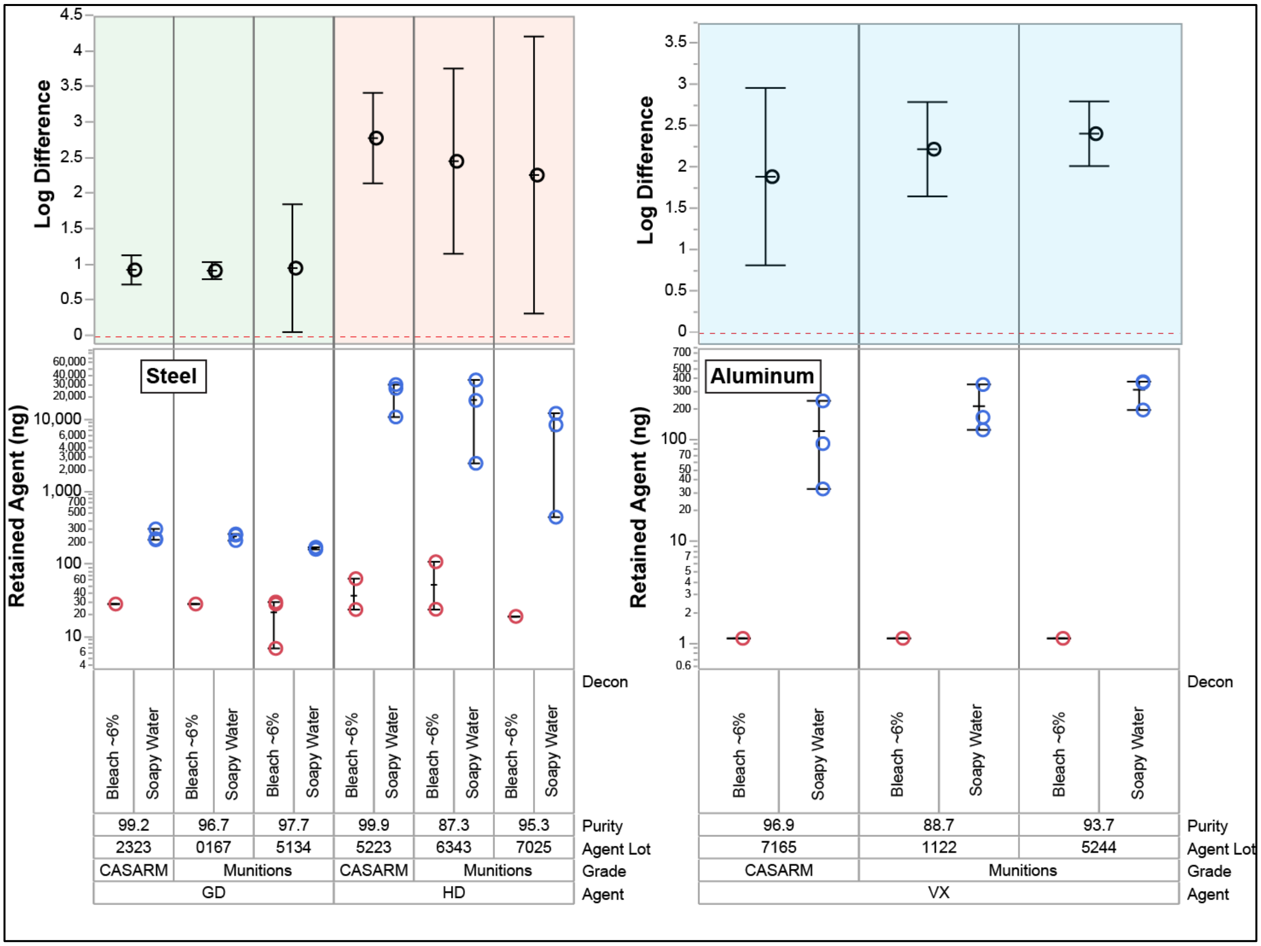


Figure 10. Results for RA on impermeable, metal substrates, including LD calculations to capture differences between bleach and soapy water treatments. Error bars for LD indicate the 95% confidence interval on the difference.

Figure 11 presents the results for absorptive, polymeric materials. The most notable differences occurred for HD and VX; GD showed no correlation across both decontamination processes. For the cases of HD and VX on absorptive materials, the following were observed: (1) VX showed some linear correlation between purity and RA with both soapy water and bleach treatments; (2) HD on silicone showed a linear trend with purity; and (3) HD on polyurethane paint had some potential nonlinear trends with purity (i.e., other chemical species or how they modify liquid properties influence agent retention).

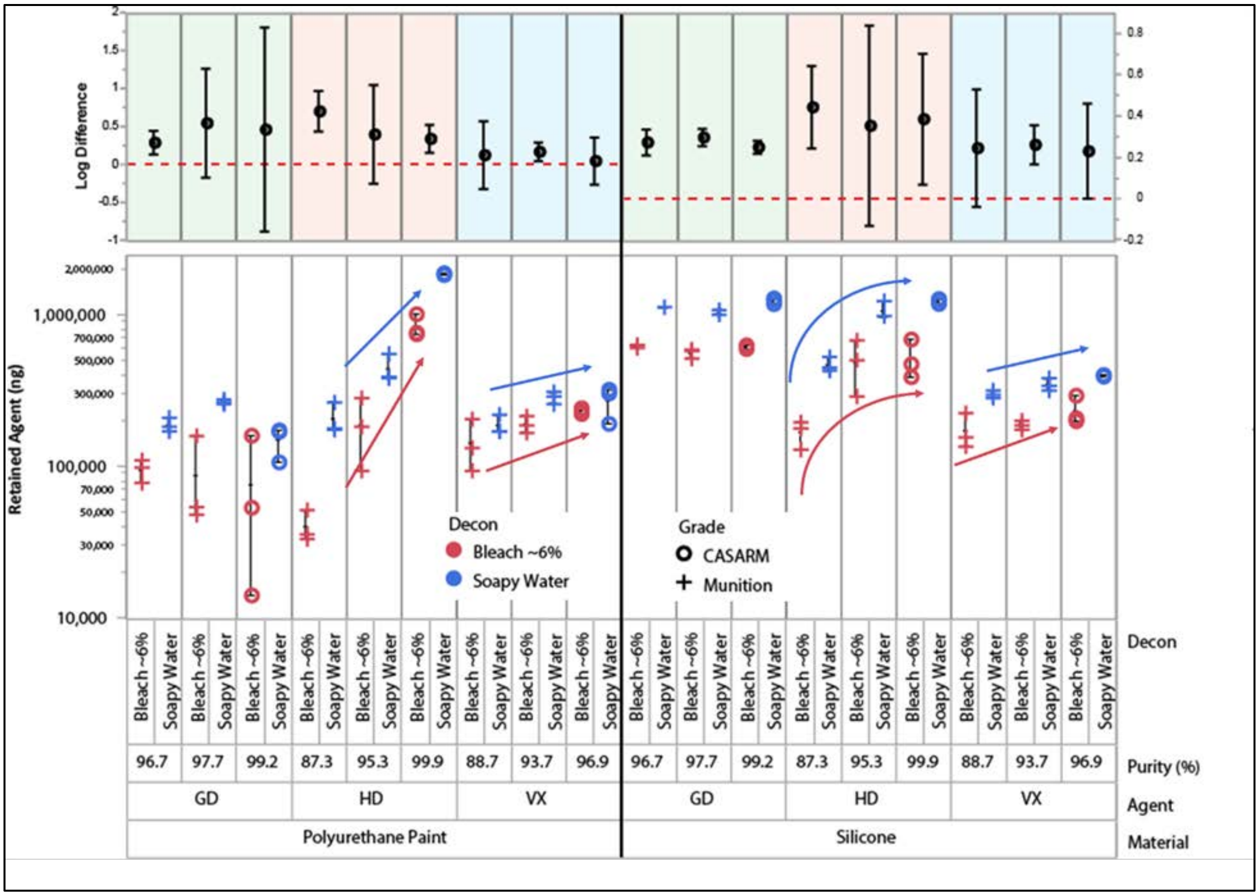


Figure 11. RA results as a function of agent purity, decontaminant, and two different polymeric materials; i.e., polyurethane paint and silicone elastomer. In LD calculations, soapy water was used as the reference condition. Error bars for LD indicate the 95% confidence interval on the difference.

The data in Figure 11 compare the RAs of two treatment conditions, to determine whether the active chemistry (i.e., bleach) removed agent better than a soapy water treatment alone. Alternatively, it can be useful to evaluate how well a treatment process removes agent, relative to the starting challenge. In Figure 12, the LDs were calculated relative to the DCSs. For these data, vial 5223 for HD was the CASARM condition, and in the case of both decontaminants for polyurethane paint, this agent purity resulted in the lowest performance (lowest LD relative to DCS) and exhibited the highest RA (in Figure 11, see the HD and polyurethane paint conditions). The other cases did not have significant differences in LD. This shows that although RA was different as a function of purity, the relative reduction measured this way was the same, which is in agreement with the data shown in Figure 11. When the imaging results are compared, the condition using vial 5223 was the only one that had no liquid present during the treatment process (see Figure 9); all of the agent liquid seems to have absorbed or evaporated. This was at least suggestive of the influence of other species in the agent solution on agent absorption.

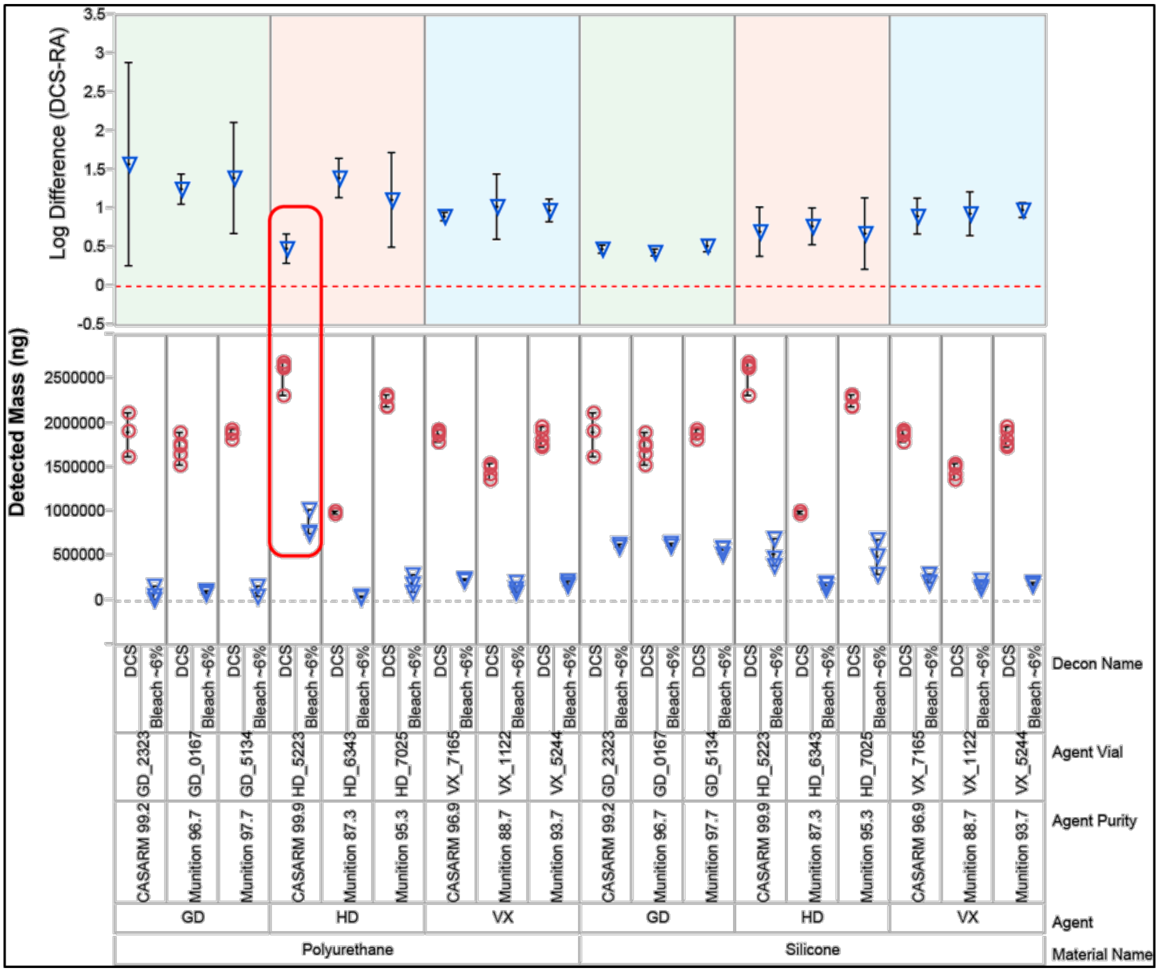


Figure 12. LDs between DCSs and RAs for polyurethane paint and silicone as a function of agent and agent purity, as indicated by vial number (see Table 1 for details on vials). Circled data points correspond to CASARM HD.

Figure 13 shows the RA measured as a function of delivered mass (i.e., DCS mass), which is dependent on agent purity, for each agent–material combination. A linear regression fit and associated confidence bounds on the fit (blue- and red-shaded regions) are included in the figure. To quantify the degree of correlation between variable purity and RA, the Prob < |*t*| for the slope of a fit to RA versus mass delivered indicates the *t*-test *p*-value for the hypothesis that the slope is zero (Figure 14). Values of <0.05 indicate a 95% probability that the reported slope is not zero. These data provide a quantitative relationship showing that across agent–material pairs, the DCS mass may not be influential; or, specifically, *the RA may not be influenced by the mass purity of the agent*.

Clearly, there are combinations where the varied purity did not result in a change in RA, such as what occurred for all of the GD cases. In some circumstances (e.g., HD–silicone and VX–silicone), a linear relationship exists, but in other cases (e.g., HD–polyurethane paint), there was most likely another trend occurring, whereby the presence of other chemical species influenced liquid spreading and transport and absorption into materials. Figure 14 shows that there are only certain conditions for which there was a statistically significant nonzero slope. A statistically significant nonzero slope in Figure 13 would indicate that the mass purity (i.e., the mass delivered to the material) was responsible for the effects on RA. However, if there were differences in RA that did not correlate with the mass delivered, the results could indicate that the presence of other chemicals may influence various transport (e.g., spreading) and absorption processes. Therefore, *variations in RA may or may not be influenced by the impurities in solution*, and further work is needed to address the role of agent-specific impurities in driving or suppressing agent absorption behavior in materials. If the RA is proportional to the mean delivered mass, it is not as significant as may be expected, and in many cases, it does not matter.

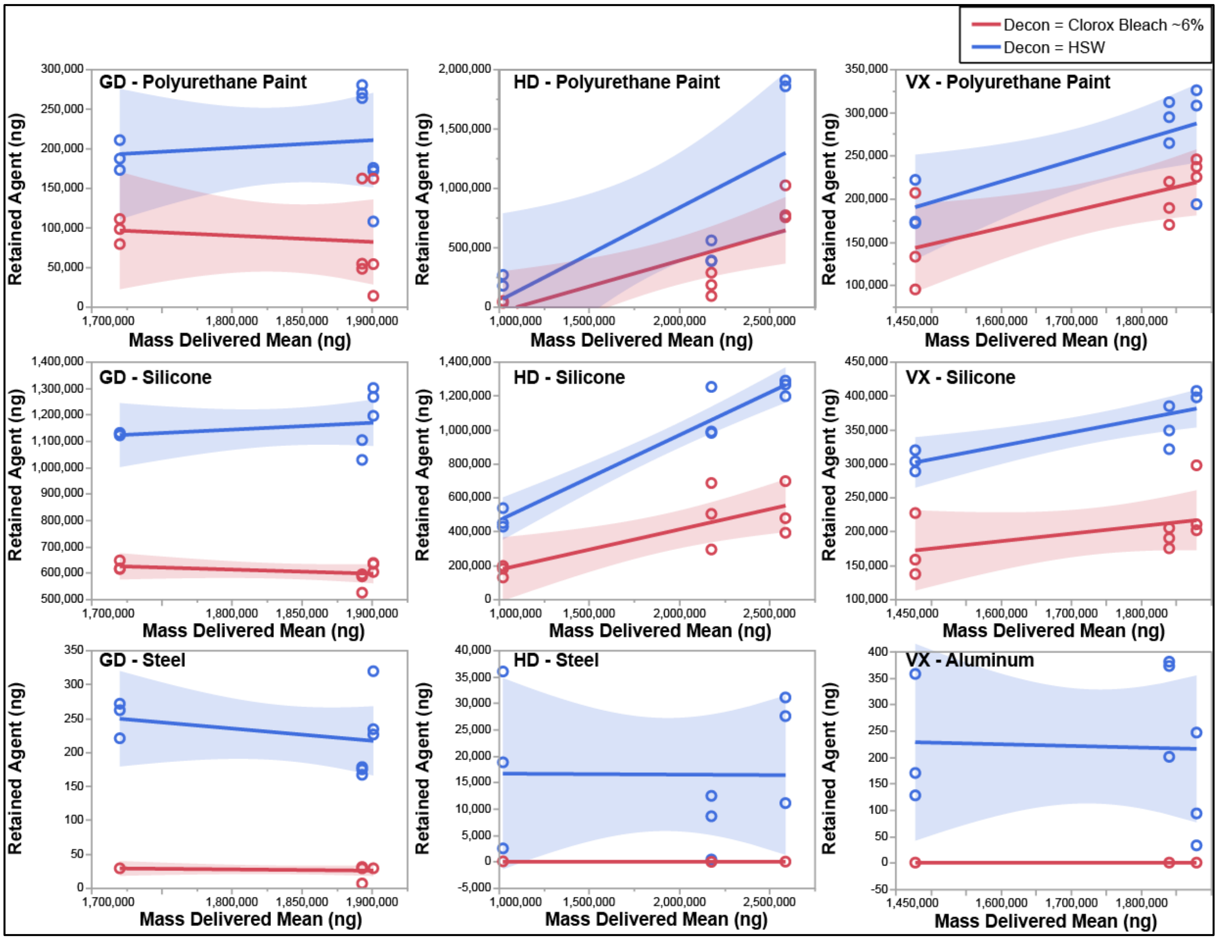


Figure 13. RA as a function of DCS, i.e., mass delivered to the material.

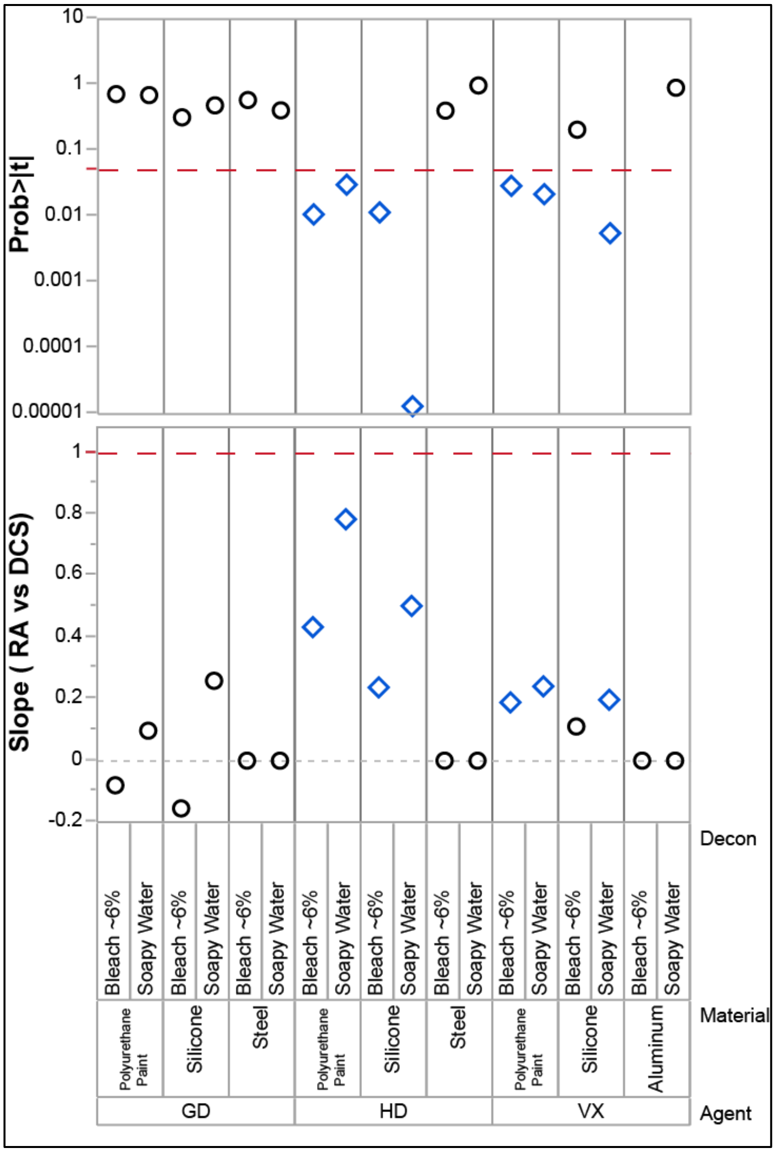


Figure 14. Correlation between purity and RA as a function of agent, material, and purity as determined by slope of linear regression, assuming a linear fit to the RA as a function of delivered agent mass. Only HD and VX (blue diamonds) showed a correlation for polyurethane paint and silicone. Prob < |*t*| for the slope of a fit to RA vs mass delivered indicates the *t*-test *p*-value for the hypothesis that the slope is zero. Red dashed line in top plot corresponds to the threshold below which there is >95% probability that the reported slope is not zero.

One of the primary objectives of this analysis was to determine whether CASARM agent may be over- or underestimating exposure risk or decontaminant performance as compared with more operational configurations of agent. The results shown in Figures 11 and 12 demonstrate that the absolute value of the RA may vary with agent purity, but that *the relative performance (i.e., LD) for two treatment processes are similar across the tested agent purity*. In Figure 15, the LDs for the panel RAs where CASARM agent was the reference condition are shown to illustrate how using agents of different purities or configurations would influence the results. This analysis indicates how different the RA results would be if munitions-grade (rather than CASARM-grade) agent was used. In most cases, the error bars overlapped the LD of zero, which indicates that CASARM- and munitions-grade agents were statistically similar. However, for select cases (e.g., HD–polyurethane) the munitions RA results could be up to 1.3 LD (or $10^{1.3}$, which is 20×) less than if CASARM agent was used. This could be interpreted from two perspectives. First, the use of CASARM-grade agent seems to present the greatest challenge (i.e., the highest RA); as such, it would provide results that are "safe sided" in that the RA value is greatest. Conversely, it is unlikely that CASARM-grade agent would be observed in the field; therefore, the use of CASARM-grade agent could result in cases of overprotection. *Overall, the use of CASARM- versus munitions-grade agents did not produce drastically different RA results for most of the examples tested*. Also note that the differences in RA observed here were not proportional to the agent mass purity. This further supports the idea that the presence of other chemical species in the liquid agent (e.g., surface tension of the liquid) influences the transport, absorption, and decontaminant performance.

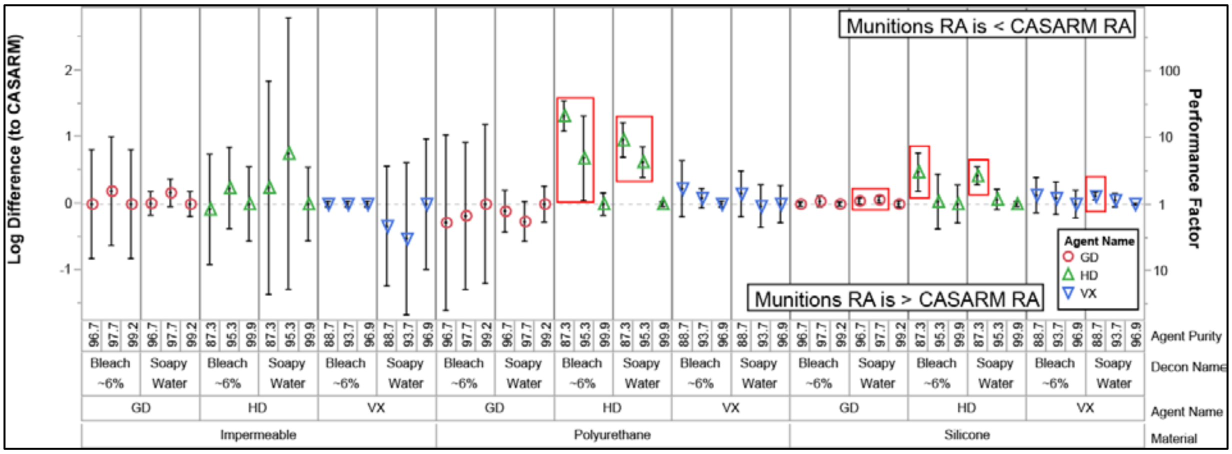


Figure 15. LDs of panel RAs obtained using CASARM-grade agent as the reference condition for each agent–material–decontaminant combination by agent purity. Error bars represent the 95% confidence interval to the difference. Data highlighted with red boxes indicate cases of statistically significant differences.

3.4 Comparing CT to RA Results

Multi-touch CT experiments were conducted for HD and VX for each agent purity and decontamination treatment.[8] The contact test included three touches over the timing presented in Table 3 using a new contact sampler for each touch. Each contact sampler was individually extracted and analyzed, and the sum of all CT masses were used for analysis here. Materials extracted after the CT sequence for residual mass (RES) and total mass, including contact samplers, were compared against an RA measurement. The CT+RES notation indicates the sum of the CT masses from all three touch samples and the RES. The CT data for HD and VX show that in most cases, there was close agreement between RA and CT+RES with respect to the mass tracking profile.

The strongest influence of agent purity on decontamination performance was evident in the HD–polyurethane paint case and was followed by HD–silicone, regardless of decontamination type, as shown in Figure 16. For the case of HD–polyurethane paint, within a decontamination type, the RA values were larger than the CT+RES, which may be due to variations in applied mass or evaporative loss of mass in between touches (Figure 17). Note that panels were left uncovered between touches over a 300 min duration after decontamination. Consistent with the RA results, the trends in CT mass fraction were more dependent upon material and decontaminant process, as illustrated in Figure 18.

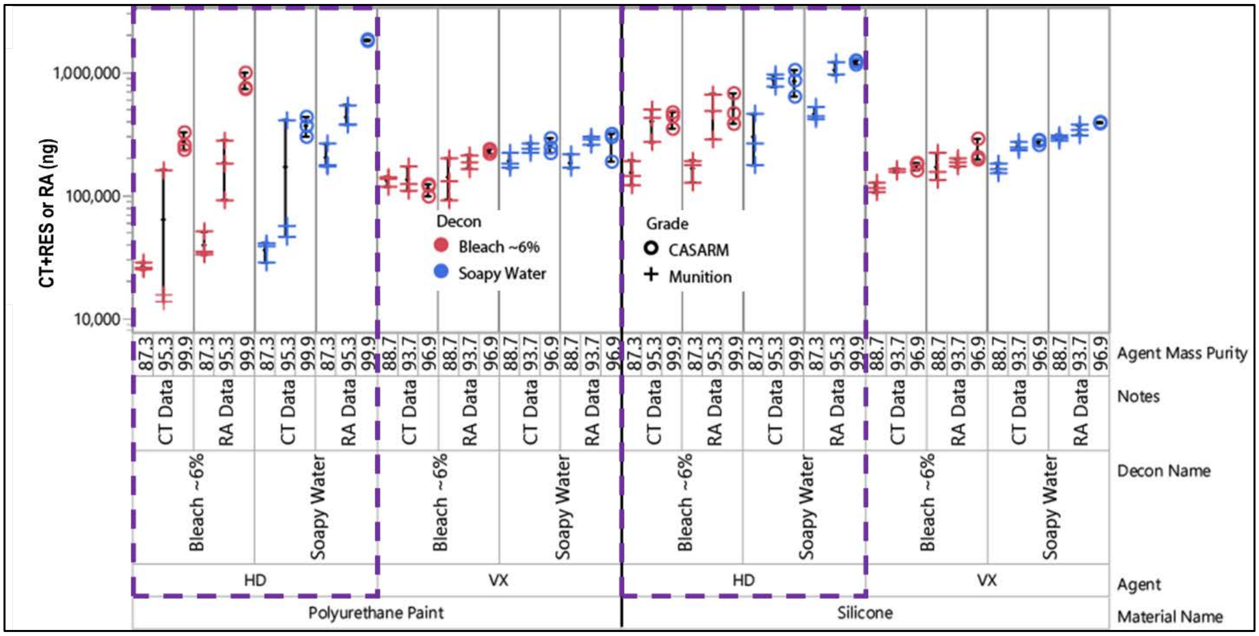


Figure 16. CT results compared to RAs. RES corresponds to the agent extracted from the materials after the touch sequence was completed. Highlighted are the cases for HD where there was greater dependency of either CT+RES or RA mass with agent purity.

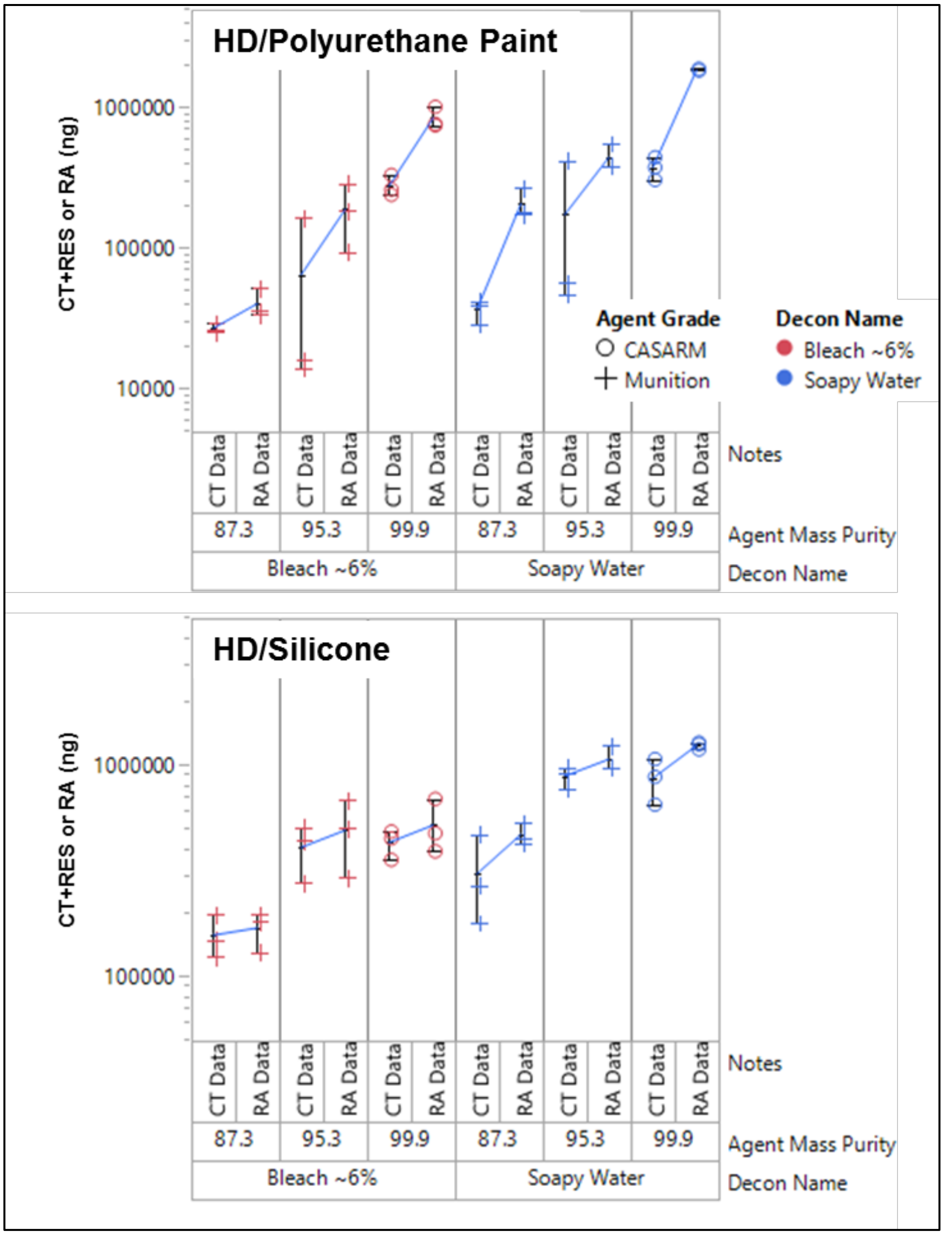


Figure 17. CT results for HD on polyurethane paint and silicone to highlight the differences in CT+RES and RA as a function of agent mass purity. Error bars represent the data range.

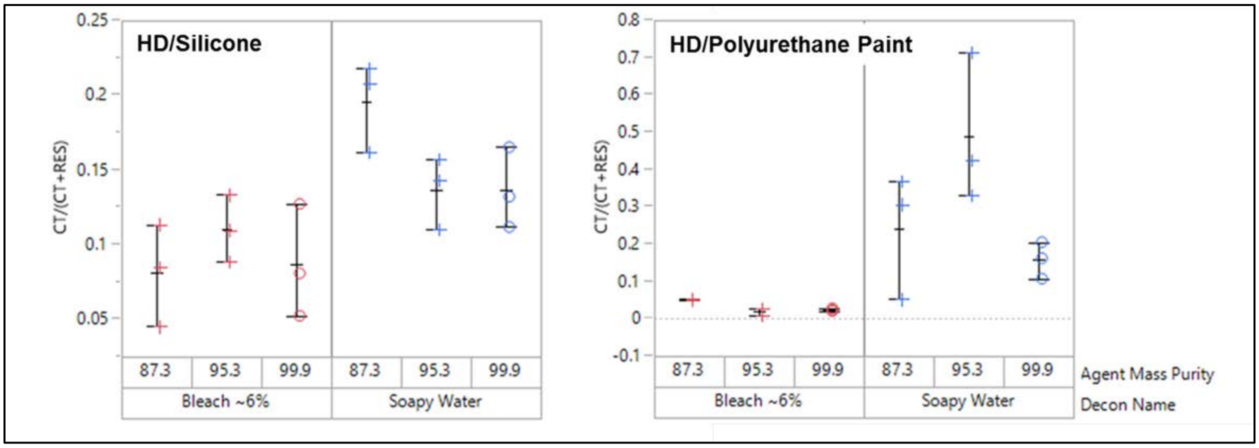


Figure 18. CT fraction of CT+RES for HD on polyurethane paint and silicone as a function of agent purity and decontamination treatment. Error bars represent the data range.

Part of the objective for this effort was toward developing a predictable correlation between RA and CT mass. There appear to be linear trends for both silicone and polyurethane paint between the CT mass (i.e., sum of all three CT samples) and the average RA for the same contamination and decontamination conditions, as illustrated in Figure 19. The material-dependent trends are most likely due to differences in HD transport rates between silicone and polyurethane paint and the role played by chemical distribution in the material in influencing CT mass. From previous work, the room temperature diffusivity for HD in silicone,[4] which is a polymer in a rubbery state at room temperature, was determined to be 5×10^{-10} m^2/s; whereas for polyurethane paint, which is in a glassy state at room temperature, the diffusivity is expected to be 10^3–10^4 times lower (unpublished data from fits to vapor emission profiles). As a result of the different diffusivities, the CT rate is much faster for silicone than for polyurethane.

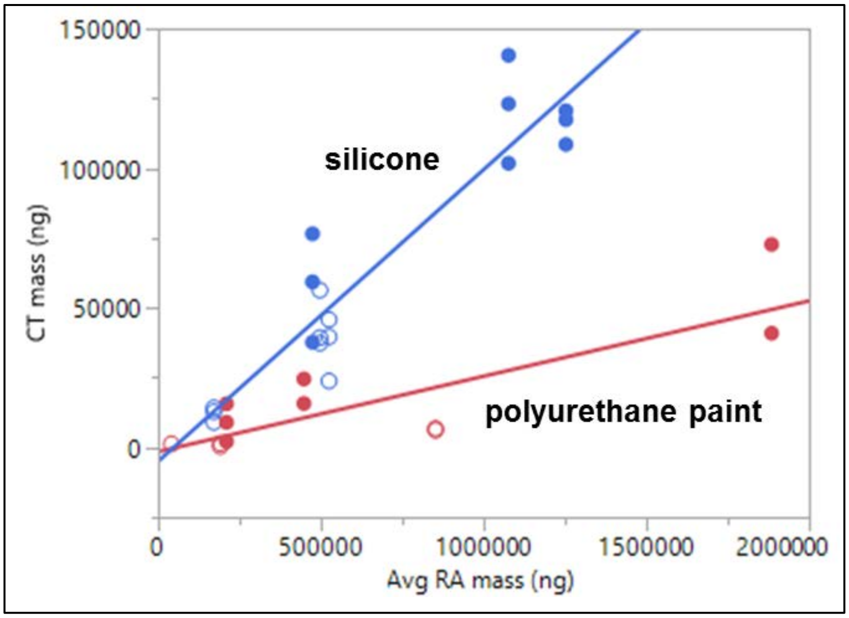


Figure 19. CT mass (not including RES) vs average RA mass results for HD on polyurethane paint and silicone for all of the agent purities tested. Solid circles correspond to soapy water treatment, and open circles correspond to bleach decontamination. Linear fits are included for each material type.

Furthermore, Figure 20 shows that there were decontaminant treatment-specific trends within a material. Although this is a limited data set, the slope for CT as a function of RA was the same for both bleach and soapy water decontamination for HD–silicone. However, for the case of HD–polyurethane paint, the slope for the bleach condition was 4× lower than for soapy water. The change in agent distribution within the polyurethane paint was most likely affected more significantly than for the case of soapy water, especially near the surface region of the material. This in turn has an impact on the CT mass.

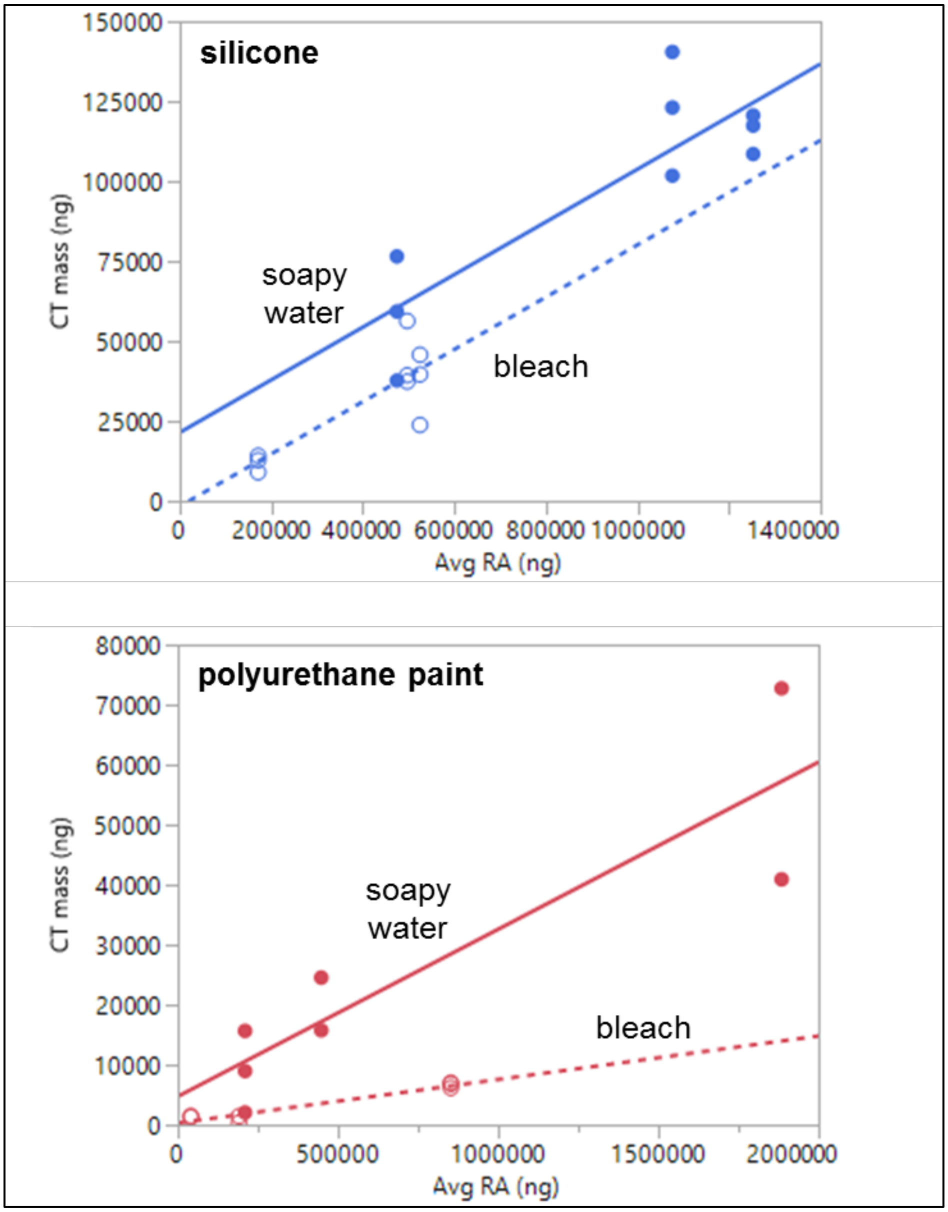


Figure 20. Linear fits for CT mass (not including RES) vs average RA mass results for HD on polyurethane paint and silicone as a function of decontamination treatment for all of the agent purities tested. Solid circles correspond to soapy water treatment, and open circles correspond to bleach decontamination.

Lastly, Figure 21 presents the comparison of CT mass to RA, to highlight the uniformity of the differences between CT and RA within a material type, with some variances within a decontamination process. The CT mass will always be less than or equal to the RA, based on the sampling schedule chosen. The expectation is that this would be true regardless of agent purity.

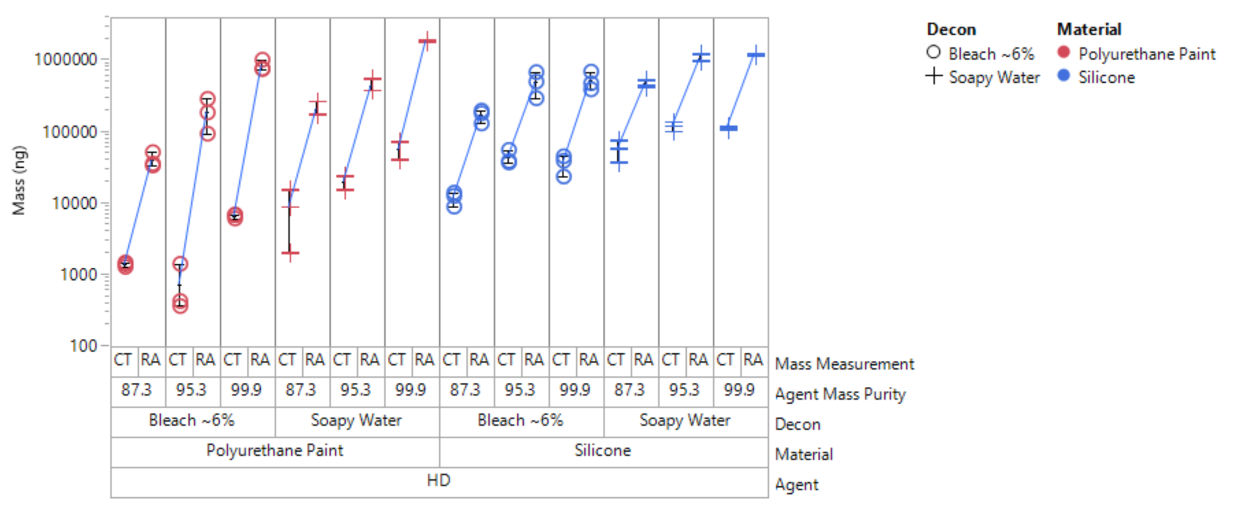


Figure 21. Comparison between CT (not including RES) and RA mass for each decontaminant–material pair as a function of agent mass purity.

4. CONCLUSIONS

This report presented results on the importance of accounting for agent purity and degradation in decontamination efficacy evaluations, especially for absorptive materials. Different vials of CASARM-grade and as-received munitions-grade GD, HD, and VX agents were used to contaminate the surfaces of aluminum and stainless steel, a polyurethane-based coating, and a silicone elastomeric material. A decontamination treatment using bleach was then applied to survey the impact of the agent purity on the measured decontamination performance relative to a soapy water immersion as a reference condition. Measurements of RA as a function of agent purity, material, and decontaminant treatment, as well as multi-touch CT assessments, were used to evaluate agent purity influences in assessing decontaminant performance. The main conclusions of this study are as follows:

1. For impermeable metals, across all agents, there was no influence of impurities within an agent type on RA or LD when comparing RA results for bleach to soapy water treatments.

2. The greatest impact of agent purity occurred for HD and VX exposed to absorptive materials. The trends and correlations varied as a function of agent–material pair, but there was clearly an influence of other chemical species on RA mass. *An increase in the delivered mass with a higher purity source did not result in a proportional increase in RA mass*.

3. In CT measurements, which focused exclusively on HD and VX interactions with absorptive materials, the strongest influence of agent purity on the decontamination performance was evident in the HD–polyurethane paint case, followed by HD–silicone, regardless of decontamination type. The explanation for the effects may be rooted in variations in applied mass or in

evaporative loss between touches. Also, material- and decontaminant-specific correlations between CT and RA mass were elucidated as a function of agent purity that can be understood in terms of diffusivity and chemical distribution profiles of agent in different materials.

4. Although it has been observed that chemical species in an agent solution can alter the wetting properties of the liquid on different surfaces, *for the sources tested* across all agents and materials, there were no significant variations in spreading or wetting characteristics.

5. If differences in RA were observed, they were not proportional to the agent mass purity. This supports the concept that the presence of other chemical species in the liquid agent influence the transport, absorption, and decontaminant performance.

6. Based on conclusions 1–5, testing with CASARM-grade agent may provide a safe-sided estimate to indicate maximum RA and CT values. However, because the variations in chemical composition (rather than the mass purity) may be more responsible for differences in RA, it is not guaranteed that CASARM-grade agent will always be the safe-sided measurement. There are cases where impurities in the munitions-grade agent could result in higher RA values.

These results characterized how impurities in specific agent solutions can influence decontamination performance and potential exposure to personnel as compared with high-purity agent, especially for materials susceptible to contaminant absorption.

5. FUTURE WORK

Multiple factors are under consideration for informing science and technology (S&T) and test and evaluation (T&E) work related to evaluations of chemical resistance of materials as well as decontamination processes. Many key implications and questions result from this work for operational interpretation within T&E. For example, for $\Sigma(\text{Touches}_n)$, does the potential exposure change with agent purity, and how did this correlate with the RA results? Does testing with CASARM-grade agent over- or underestimate different challenges? These data indicate that testing with CASARM-grade agent provides a safe-sided, upper-bound estimate for operational CT exposure and most likely vapor emission as well. This is in line with changes in RA as a function of purity. To understand many of the observed effects, it is necessary to identify specific impurities and related chemical and physical interactions in the limits of contamination and decontamination processes for materials. Future work can also capture the effects of nonpristine material surfaces, complex geometries, and decontamination applications as they relate to the evaluation of decontamination processes. The lack of correlation observed between performance and RA with DCSs illustrates that mass purity of the agent may not be the significant factor to consider in the selection of an agent for S&T or T&E work. Rather, as presented earlier, the presence of various impurities may change other chemical properties that could influence agent transport (e.g., sorption or spreading).

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ACRONYMS AND ABBREVIATIONS

CASARM	chemical agent standard analytical reference materials
CT	contact transfer
DCS	dose-confirmation sample
EMPA	ethyl methylphosphonic acid
FID	flame ionization detector
GC	gas chromatography
GD	pinacolyl methyl phosphonofluoridate, soman, nonpersistent agent
HD	bis(2-chloroethyl) sulfide, distilled mustard agent
LC	liquid chromatography
LD	log difference
RA	retained agent
RES	residual mass
S&T	science and technology
T&E	test and evaluation
VX	2-(diisopropylamino)ethyl-*O*-ethyl methylphosphonothioate

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