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Decontamination of Toxic Industrial Chemicals and Chemical Warfare Agents on Building Materials Using Chlorine Dioxide Fumigant and Liquid Oxidant Technologies

TECHNOLOGY INVESTIGATION REPORT

Office of Research and Development
National Homeland Security Research Center

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Decontamination of Toxic Industrial Chemicals and Chemical Warfare Agents On Building Materials Using Chlorine Dioxide Fumigant and Liquid Oxidant Technologies

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ERRATA Sheet

For the document: Decontamination of Toxic Industrial Chemicals and Chemical Warfare Agents On Building Materials Using Chlorine Dioxide Fumigant and Liquid Oxidant Technologies (EPA/600/R-09/012) February 2009

Updated 07/2009 with the following modifications:

- Table 4-13 (Page 27): The numbers in the rightmost column were made bold to correspond with footnote c [Decontamination efficacy shown in bold indicates a statistically significant difference in recovery with and without decontamination ($p \leq 0.05$)].

- Table 4-19 (Page 34): The numbers in the rightmost column were made bold to correspond with footnote a [Calculated using Eq (8); values given in bold are statistically significant].

- Page 31(Left Column, 2nd paragraph): 100% bleach (6% hypochlorite) was modified to read 10% bleach (0.6% hypochlorite).

Notice

Foreword

The EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, ORD provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

In September 2002, EPA announced the formation of the NHSRC. The NHSRC is part of the ORD; it manages, coordinates, and supports a variety of research and technical assistance efforts. These efforts are designed to provide appropriate, affordable, effective, and validated technologies and methods for addressing risks posed by chemical, biological, and radiological terrorist attacks. Research focuses on enhancing our ability to detect, contain, and clean up in the event of such attacks.

NHSRC's team of world renowned scientists and engineers is dedicated to understanding the terrorist threat, communicating the risks, and mitigating the results of attacks. Guided by the roadmap set forth in EPA's Strategic Plan for Homeland Security, NHSRC ensures rapid production and distribution of security-related products.

The NHSRC has created the Technology Testing and Evaluation Program (TTEP) in an effort to provide reliable information regarding the performance of homeland security related technologies. TTEP provides independent, quality assured performance information that is useful to decision makers in purchasing or applying the tested technologies. It provides potential users with unbiased, third-party information that can supplement vendor-provided information. Stakeholder involvement ensures that user needs and perspectives are incorporated into the test design so that useful performance information is produced for each of the tested technologies. The technology categories of interest include detection and monitoring, water treatment, air purification, decontamination, and computer modeling tools for use by those responsible for protecting buildings, drinking water supplies and infrastructure, and for decontaminating structures and the outdoor environment.

The investigation reported herein was conducted by Battelle, under the direction of NHSRC, as part of TTEP. Information on NHSRC and TTEP can be found at http://www.epa.gov/nhsrc.

Acknowledgments

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Abbreviations/Acronyms

ANOVA	analysis of variance		N	normal
BBRC	Battelle Biomedical Research Center		ND	not detected
ClO$^-$	hypochlorite ion		NT	not tested
ClO$_2$	chlorine dioxide		NHSRC	National Homeland Security Research Center
cm	centimeter(s)		NIST	National Institute of Standards and Technology
CWA(s)	chemical warfare agent(s)		ORD	Office of Research and Development
CT	concentration x contact time		PE	performance evaluation
DEEP	diethyl ethylphosphonate		ppm	parts per million
DIMP	diisopropyl methylphosphonate		QA	quality assurance
DMMP	dimethyl methylphosphonate		QC	quality control
EPA	U.S. Environmental Protection Agency		QMP	quality management plan
Eq	equation		RH	relative humidity
FPD	flame photometric detection		SD	standard deviation
ft	feet		sec	second(s)
g	gram(s)		SRS(s)	surrogate recovery standard(s)
GB	sarin		STS	sodium thiosulfate
GC	gas chromatograph; gas chromatography		TBP	tributyl phosphate
GC/FPD	gas chromatography/flame photometric detection		TGD	thickened soman
GC/MS	gas chromatography/mass spectrometry		TIC(s)	toxic industrial chemical(s)
GD	soman		TD	thermal desorption
h	hour(s)		TSA	technical systems audit
IS	internal standard		TTEP	Technology Testing and Evaluation Program
KD	Kuderna-Danish			
HVAC	heating, ventilation, and air conditioning			
L	liter(s)			
m	meter(s)			
M	molarity; moles/liter			
MDL	method detection limit			
MFC	mass flow controller			
μg	microgram(s)			
μL	microliter(s)			
μm	micrometer(s)			
m	meter(s)			
mg	milligram(s)			
min	minute(s)			
mL	milliliter(s)			
mm	millimeter(s)			
MS	mass spectrometer			
m/z	mass-to-charge ratio (unitless)			
n	number of samples			

Executive Summary

The purpose of this effort was to determine the effectiveness of several decontamination technologies against both toxic industrial chemicals (TICs) and chemical warfare agents (CWAs) on standard building materials was recently completed. Prior to the test design for this effort, an assessment of the state of the knowledge for TIC and CWA decontamination on complex building materials was performed. Following this assessment, combinations of TICs, CWAs, building materials, decontamination technologies and conditions were selected for the study. The first phase of the testing included a study of the persistence of the TICs and CWAs on the materials at typical ambient conditions[1]. Decontamination studies were only performed with combinations of agents and materials in which persistence was determined sufficient in order to observe an impact of the decontamination treatment. The TICs that were used in this testing included malathion and dimethyl methylphosphonate (DMMP). These TICs were chosen for a combination of two reason: (1) for their properties as TICs, and (2) their potential as simulants for VX and sarin (GB), respectively, due to the similarities in key structural elements. The CWAs that were tested included sarin, thickened soman (TGD), and VX. The technologies investigated included fumigation with chlorine dioxide (ClO_2) and soaking in liquid oxidants.

Fumigation at 80% relative humidity (RH) and 3000 parts per million (ppm) ClO_2 used a commercially available system manufactured by Sabre, Inc. This Sabre technology was tested against:

- Malathion on carpet and laminate materials
- DMMP on carpet and ceiling tile
- GB on carpet
- TGD on carpet, laminate, and metal ductwork
- VX on carpet, laminate, and metal ductwork.

The liquid oxidants included diluted commercial bleach (diluted 1:10 with water; 5000 ppm hypochlorite ion [ClO^-]) and an aqueous solution of 3000 ppm ClO_2. Aqueous bleach was tested against:

- GB on carpet
- TGD on carpet, laminate, and metal ductwork
- VX on carpet, laminate, and metal ductwork.

The aqueous ClO_2 solution was tested against VX on carpet, laminate, and metal ductwork.

This decontamination research addressed the following questions:

- What is the percent recovery of TICs and CWAs exposed to the specified treatments?
- What is the relative recovery (decontamination efficacy) of TICs and CWAs in the presence of the decontamination technology compared to a similarly matched control?
- Is there visible surface damage to building materials as a result of the decontamination technology?

The above matrix of test agent and building material coupons reflects the results of the persistence study that preceded this decontamination study. In that prior testing, persistence was found to vary widely, from as low as 0% GB recovered from laminate after five minutes (min) up to 85% malathion recovered from carpet after seven days.[1] While there was evidence for complex interactions between test compound and substrate, persistence could mostly be predicted and explained on the basis of vapor pressure and hydrolysis rate of the compounds, and the type of the building material. Hence, only combinations of chemicals and materials in which the agent was persistent enough to determine the effect of the decontamination were used, and some substitutions in materials were made in some cases to provide longer persistence (e.g., for DMMP, ceiling tile was used rather than laminate).

Very similar bench-scale testing approaches were used for these technology investigations as were utilized for the persistence testing. This included liquid spiking of a known amount of an individual TIC or CWA onto replicate coupons of the building material (five identical coupons each either 5 square centimeters [cm^2] for TICs or 10 cm^2 for CWAs were utilized). These coupons were allowed to contact the decontamination technology for a fixed amount of time up to 7 hours (h) in a sealed chamber under controlled conditions of temperature, RH, and air movement. Each coupon was then extracted to measure the amount of TIC or CWA that remained on the coupons. These tests used spikes of 500 micrograms (µg) of TICs onto 5 cm^2 coupons, or 1000 µg of CWAs onto 10 cm^2 coupons, so as to approximate a surface loading of 1 g m^{-2}, which is assumed to be a worst-case contamination scenario.

The persistence of these chemicals under conventional environmental conditions is highly variable, and in some cases the chemicals have limited persistence. For these reasons, the fumigant decontamination tests were matched with positive control tests of the chemical on the same type of building material coupon for the same duration and at the same temperature as the decontamination test, so that the effectiveness of the decontamination technology could be accurately differentiated from other loss mechanisms such as volatilization and decomposition unrelated to the fumigation.

Fumigation with ClO_2 resulted in statistically significant efficacy against malathion on both carpet and laminate at 1, 3, and 7 h exposures; a small, but statistically significant efficacy (7.5%) was observed against DMMP only on ceiling tile at 7 h. Fumigation with ClO_2 resulted in statistically significant efficacy >99% against VX on carpet, laminate, and ductwork after a 1h exposure; a smaller statistically significant efficacy (34% – 62%) was observed against GB and TGD on carpet after a 1 h exposure. No statistically

significant efficacy of ClO_2 fumigation was observed against TGB on laminate or ductwork.

As shown in Tables ES-1 and ES-2, VX was reduced to non-detectable levels on all materials with all three of the decontamination technologies tested. When VX was exposed to high RH only (as a control for the fumigant ClO_2 decontamination test), the mean recovery was high, indicating that the vapor phase ClO_2 itself was effective at decontaminating the VX.

Liquid technologies were screened for efficacy in preliminary testing in which the CWA was placed into decontamination technology and neutralized decontamination technology. The CWA was extracted from the solution and analyzed to determine the mass of CWA in the extract. The results of the tests, shown in Table ES-2, demonstrated that, except for GD in bleach, the difference in mean recovery between the decontamination technology and neutralized decontamination technology was negligible. VX, which is persistent on building materials exposed to air, was not recovered from neutralized bleach or neutralized ClO_2 solutions when extracted within 15 seconds (sec); causes were not determined but could include hydrolysis of the VX or an ineffective recovery method. In bleach, none of the three CWAs were recovered. Only small amounts of GB (1%) were recovered after 15 sec in neutralized bleach. There was little or no difference between the mean recovery of any CWA after 15 sec in neutralized ClO_2 or after 1 h exposed to ClO_2 decontamination; a large percentage (58%) of GD was recovered from the ClO_2 solution.

Table ES-3 summarizes the mean percent recovery of the TICs and CWAs on different building materials following liquid decontamination treatments. The bleach decontamination tests were matched with positive controls exposed to air. The positive controls used with liquid bleach were placed in empty vials. The results in Table ES-3 show that in all cases, when compared to untreated coupons, the CWA recovered from coupons soaked in bleach were significantly lower and in most cases not detected, after

Table ES-1. Mean Percent Recovery of TICs and CWAs on Building Materials With and Without ClO_2 Fumigation (Normalized to Recovery at Time 0)

TIC/CWA	Material	Time (n)	Mean Recovery, % of T0 ± SD	
			Without Decontamination	With ClO_2 Fumigation
DMMP	Carpet	7 h (n = 5)	16 ± 3	23 ± 4
	Ceiling tile	7 h (n = 5)	12 ± 1	8.7 ± 0.3
Malathion	Carpet	7 h (n = 5)	87 ± 1	24 ± 2
	Laminate	7 h (n = 5)	94 ± 10	0.4 ± 0.2
GB	Carpet	4 h (n = 5)	5.7 ± 0.2	3.3 ± 1.0
TGD	Carpet	2 h (n = 5)	57 ± 6	36 ± 17
	Laminate	2 h (n = 5)	1.3 ± 1.6	0.10 ± 0.11
	Ductwork	2 h (n = 5)	5.9 ± 2.6	7.4 ± 9.0
VX	Carpet	1 h (n = 5)	105 ± 31	ND, <0.7[a]
	Laminate	1 h (n = 5)	86 ± 8	ND, <0.7
	Ductwork	1 h (n = 5)	101± 3	ND, <0.7

a) ND = not detected; method detection limit converted to equivalent recovery value

Table ES-2. Mean Percent Recovery of CWAs Spiked Directly into Decontamination Solutions With and Without Neutralization

Solution – Hold Time Before SRS Addition and Hexane Extraction	CWA Mean Recovery, % of Spike ± SD (n = 3)		
	GB	GD	VX
Bleach - 1 h	ND, <0.1	ND, <0.1	ND, <0.7
Neutralized bleach - 15 sec	1 ± 0	41 ± 10	ND, <0.7
ClO_2 - 1 h	8 ± 2	58 ± 5	ND, <0.7
Neutralized ClO_2 - 15 sec	8 ± 1	56 ± 10	ND, <0.7

ND = not detected

exposures of 10 to 30 min. The positive controls used with liquid bleach were placed in empty vials, so that apparent decontamination with this solution could not be distinguished from other potential loss processes such as aqueous hydrolysis. The results shown in Tables ES-2 and ES-3 suggest that bleach is effective for decontamination of GD/TGD. However, the low recoveries of GB and no recovery of VX from the neutralized bleach require caution in interpreting these results; based on these data, apparent effectiveness cannot be distinguished from other explanations of low recoveries such as aqueous hydrolysis or ineffective recovery methods. Further research is needed to isolate the cause.

The tests with liquid ClO_2 decontamination of VX (which is unstable in alkaline solutions) were matched with positive controls in acidified water to attempt to reduce the hydrolysis effects of water for comparison with the decontamination effects of ClO_2. For VX on carpet and laminate, a statistically significant reduction of 86% and 63% was achieved after 10 min exposure to liquid ClO_2; efficacy against VX on ductwork was indeterminate.

The ClO_2 fumigation was shown to be highly effective against VX. In some but not all cases, dependent on the type of coupon, ClO_2 resulted in statistically significant reductions in GB and TGD.

The TGD levels on the three materials were reduced to very low levels (<1% of the initial mass applied to the coupon) using liquid bleach; fumigant ClO_2 was not as effective as liquid bleach in attacking TGD on carpet and ductwork. Liquid bleach was effective in removing TGD from the surfaces of the building materials. There was no attempt to measure TGD in the bleach solution. TGD may have been hydrolyzed by the aqueous bleach or effectively solubilized by it.

Similarly, GB was effectively removed from the carpet by liquid bleach; however, the investigation did not clarify whether this removal was due to volatilization, hydrolysis, solubilization, or a combination of these processes. No decontamination efficacy was observed for liquid ClO_2 against GB or GD in the solution testing; efficacy against VX was indeterminate.

No damage or visible change to any of the materials was observed comparing extracted laboratory blank coupons (not exposed to decontamination) to extracted procedural blank coupons (exposed to decontamination) directly after decontamination treatment. Materials exposed to the liquid decontaminants were not evaluated at subsequent time post-decontamination. For ClO_2 fumigation, the coupons were relatively unchanged after three months, and the carpet showed some very minor "bleaching" after six months.

This work demonstrated that there are very simple and effective methods for removing toxic chemicals from the surfaces of building materials. In some cases the results from this investigation could not be used to establish the mechanisms and processes involved in removal of the chemicals from the surfaces because measurement of the residual chemical on the building material surface did not indicate whether the chemical was transferred intact to the aqueous decontamination solution or whether it was degraded or hydrolyzed to another chemical. These types of questions may best be answered by direct analyses (e.g., no solvent extraction) of the decontamination solutions to verify whether intact toxic chemicals or degradation products are present. Insofar as this program was designed to evaluate residuals on surfaces after decontamination treatments, the goals were achieved, and reliable technologies for decontamination were identified.

Table ES-3. Mean Percent Recovery of CWAs from Building Materials Following Various Treatments

CWA	Material	Time	Mean Recovery, % of Mass Recovered at Time 0 ± SD	
			Without Decontamination (in air in a sealed vial)	With Bleach Decontamination
GB	Carpet	10 min	93 ± 7	ND, <0.1[a]
TGD	Carpet	10 min	121 ± 33	ND, <0.1
	Laminate	10 min	90 ± 10	3.7 ± 1.9
	Ductwork	10 min	130 ± 39	3.2 ± 1.9
VX	Carpet	30 min	107 ± 7	ND, <0.7
	Laminate	30 min	102 ± 6	ND, <0.7
	Ductwork	30 min	95 ± 11	ND, <0.7
			Without Decontamination (in acidified water)[b]	With ClO_2 (Liquid) Decontamination
VX	Carpet	10 min	5.0	ND, <0.7
	Laminate	10 min	1.9	ND, <0.7
	Ductwork	10 min	ND, <0.7	ND, <0.7

a) ND = not detected
b) Results from ANOVA modeling of recovery data

The EPA's NHSRC is helping to protect human health and the environment from adverse impacts resulting from intentional acts of terror. With an emphasis on decontamination and consequence management, water infrastructure protection, and threat and consequence assessment, NHRSC is working to develop tools and information that will help detect the intentional introduction of chemical, biological or radiological contaminants in buildings or water systems, contain these contaminants, decontaminate buildings and/or water systems, and facilitate the disposal of material resulting from cleanups.

NHSRC's TTEP works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the voluntary participation of individual technology developers in carrying out performance tests on homeland security technologies. The program evaluates the performance of innovative homeland security technologies by developing test plans that are responsive to the needs of stakeholders, conducting tests, collecting and analyzing data, and preparing peer-reviewed reports. All investigations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and high quality are generated and that the results are defensible. TTEP provides high-quality information that is useful to decision makers in purchasing or applying the tested technologies. It provides potential users with unbiased, third-party information that can supplement vendor-provided information. Stakeholder involvement ensures that user needs and perspectives are incorporated into the test design so that useful performance information is produced for each of the tested technologies.

1.1 Objectives

This testing was conducted to measure the effectiveness of different decontamination technologies against two representative TICs and three representative CWAs on a range of indoor building materials. The recovery (extractable mass) of the chemicals with and without the decontamination agent was ascertained initially. The effectiveness of the decontamination technology was assessed as the statistically significant relative recovery of TIC or CWA from building

material coupons after a specified time period with or without contact with the decontamination technology. This approach controls for losses due to normal environmental processes such as volatilization.

This decontamination research addressed the following questions:

- What is the relative recovery of TICs and CWAs in the presence of the decontamination technology compared to a similarly matched control?

- What is the percent reduction of TICs and CWAs exposed to various treatments?

- What is the decontamination efficacy of the decontamination technology for removal of TICs and CWAs?

- Is there visible surface damage to building materials as a result of the decontamination technology?

1.2 Approach

The general approach developed and utilized for decontamination testing was to apply a known amount of each TIC or CWA to each of several test coupons of the same building material (replicate coupons, identical in size and shape) and allow these spiked test coupons to age under controlled environmental conditions of temperature and RH, either with the decontamination agent or without this agent. At specified intervals, replicate test coupons were extracted and the extracts were analyzed to determine the amount of the TIC or CWA that remained on the test coupon at that specific time.

The overall approach developed and applied for decontamination testing of fumigant and liquid decontamination technologies was generally the same; however, the fumigant technology testing was conducted in a sealed chamber whereas the liquid decontamination was conducted in individual sealed vials. The fumigant technology was applied to both TICs and CWAs; the liquid decontamination was applied to only the CWAs. The specific details for the methodologies used for decontamination testing of TICs and CWAs are described in detail in Section 2.0.

1.3 Experimental Design

The chemicals that were selected for use in this investigation include:

TICs

- Malathion
- DMMP

CWAs

- GB
- TGD
- VX.

Table 1-1 specifies the building materials used in this decontamination investigation which included industrial grade carpet, decorative laminate, galvanized metal ductwork, and ceiling tile. Building materials were cut into coupons of small, defined size and the TICs and CWAs were applied at a rate equivalent to 1 g m^{-2}, which is representative of a potential indoor contamination scenario. The coupons to which TICs were applied were approximately 5 cm^2 and the coupons to which CWAs were applied were approximately 10 cm^2. The sizes were chosen so as to take advantage of the available area in the test chambers and to optimize the spiking volume of chemical being applied to the coupons.

All decontamination testing with TICs was carried out in standard chemical laboratories at Battelle. Due to the stringent controls needed for working with CWAs, decontamination tests for CWAs were carried out at one of Battelle's certified chemical surety facilities (Battelle Biomedical Research Center [BBRC]) near West Jefferson, Ohio. Special test chamber equipment and protocols were prepared and utilized for conducting this investigation. For fumigant decontamination and its associated controls, tests were conducted with coupons inside specially fabricated test chambers which allowed for controls on temperature, RH, air flow over the coupons, and air exchange rate in the chamber.

In these tests, the decontamination of each chemical (TIC or CWA) was investigated separately; however, the behavior of a given chemical was investigated on all building material types simultaneously. For decontamination tests using liquids, the test coupons and associated controls were placed in sealed vials containing the decontamination liquid.

Table 1-2 (on page 3) presents a summary of the matrix of building materials and chemicals, together with the target test chamber conditions and fumigant and liquid decontamination technologies. The materials and chemicals selected for testing were based on the previous persistence study and preliminary solution testing of liquid decontamination technologies. Only the material/chemical combinations with chemical persistence sufficient to determine the decontamination effects were included in the matrix. For DMMP, ceiling tile was used rather than laminate because the persistence study showed less than 1% of the spiked DMMP was recovered from laminate after one day. Similarly, decontamination of GB was evaluated only on carpet because GB was not detected on laminate and ductwork in as little as 15 min after spiking. GB and TGD were not evaluated with liquid ClO$_2$ because preliminary solution testing showed no efficacy compared to the control solution. Therefore, only VX on coupons was investigated with the liquid ClO$_2$; spiked coupons were placed in water, acidified with acetic acid to reduce hydrolysis, as a control.

The temperature and RH inside the test chambers were monitored and recorded. There were five replicate coupons of each building material type analyzed at each time point, for each TIC or CWA. For TICs testing only, air velocity over the coupons was measured. To ensure that air was passed uniformly across the TIC coupons, two fans were used that produced an air velocity of 400 ft min^{-1} over the coupons. A smaller test chamber was used in the investigation of fumigation of CWAs. Uniform gas distribution was not anticipated to be a problem, so fans were not used in this test chamber.

Table 1-1. Building Materials Used in Decontamination Investigation

Material	Lot, Batch, or Observation	Manufacturer/ Supplier Name
Decorative laminate	Laminate/Formica/White Matte Finish	Solid Surface Design
Industrial grade carpet	EcoTek 6; Style #M7978, color #910; Carpet Corp of America	Shaw Industries, Inc
Galvanized metal ductwork	Industry HVAC standard 24 gauge galvanized steel; Adept Products Inc	Accurate Fabrication
Ceiling tile	Armstrong 954, Classic Fine Textured	Armstrong

1.4 Definitions of Coupon Treatments

The types of test and control coupons used in this investigation are described in Table 1-3. Test coupons and positive control coupons are spiked with TICs or CWAs. Laboratory, handling, and procedural blank coupons are not spiked with TICs or CWAs. Test and procedural blank coupons are exposed to the decontamination treatment. Positive control coupons and laboratory and handling blanks are not exposed to the decontamination treatment.

Table 1-4 (on page 4) shows surrogate recovery standard (SRS) and internal standard (IS) compounds that were utilized in the quantitative chemical analyses (See Section 2.0). This table summarizes the analysis method for extracts of building materials and the sampling and analysis methods employed in measuring the chemicals in the air over the building materials during decontamination.

Table 1-2. Target Parameters for Decontamination Testing

Chemical	Building Materials	Temperature and RH[a]	Decontamination Agent	Air Flow Over Coupons	Sampling Points in Time
TIC					
Malathion	Carpet Laminate	24°C, 80% RH	Fumigant ClO_2 at 3000 ppm	400 ft min^{-1}	0, 1, 3, 7 h
DMMP	Carpet Ceiling Tile	24°C, 80% RH	Fumigant ClO_2 at 3000 ppm	400 ft min^{-1}	0, 1, 3, 7 h
CWA					
GB	Carpet	22°C, 80% RH	Fumigant ClO_2 at 3000 ppm	0 ft min^{-1}	0, 1, 4 h
GB	Carpet	22°C, NA	Liquid bleach[b] at 5000 ppm ClO^-	0 ft min^{-1}	0, 10, 20, 30 min
TGD	Carpet Laminate Ductwork	22°C, 80% RH	Fumigant ClO_2 at 3000 ppm	0 ft min^{-1}	0, 1, 2 h
TGD	Carpet Laminate Ductwork	22°C, NA	Liquid bleach at 5000 ppm ClO^-	0 ft min^{-1}	0, 10, 20, 30 min
VX	Carpet Laminate Ductwork	22°C, 80% RH	Fumigant ClO_2 at 3000 ppm	0 ft min^{-1}	0, 1, 4 h
VX	Carpet Laminate Ductwork	22°C, NA	Liquid bleach at 5000 ppm ClO^-	0 ft min^{-1}	0, 10, 20, 30 min
VX	Carpet Laminate Ductwork	22°C, NA	Liquid ClO_2 at 3000 ppm	0 ft min^{-1}	0, 10, 20, 30 min

a) RH is not applicable (NA) to testing in which liquid decontamination technologies is used

b) Commercial bleach diluted 1:10 with water

Table 1-3. Coupon Treatments

Coupon	Treatment
Positive control coupon	Building material coupon spiked with TIC or CWA that is not exposed to the decontamination treatment; analyzed together with test coupons at the designated time interval
Test coupon	Building material coupon spiked with TIC or CWA and exposed to the decontamination treatment for the designated time interval
Laboratory blank	Building material coupon that is loaded into an extraction vial before all other test activities
Handling blank	Building material coupon that is exposed to the fume hood atmosphere during sample spiking, and then loaded into an extraction vial
Procedural blank	Building material coupon, with no TIC or CWA spike, that is exposed to the decontamination or control treatment for the designated time interval

Table 1-4. Selected TICs and CWAs with Analytical Measurement Parameters

Parameter	TICs		CWAs		
	Malathion	**DMMP**	**GB**	**TGD**	**VX**
SRS	Fenchlorphos	DEEP[a]	TBP[b]	TBP	TBP
IS	DBB[c]	DIMP[d]	DIMP	DIMP	DIMP
Extraction	Sonication	Sonication	Shake/stand	Shake/stand	Shake/stand
Analysis	GC/MS[e]	GC/MS	GC/FPD[f]	GC/FPD	GC/FPD
Air sample collection	Tenax® sorbent	Tenax® sorbent	Not collected	Not collected	Not collected
Air sample analysis	Extract & C/MS	TD-GC/MS[g]	Not applicable	Not applicable	Not applicable

a) DEEP - diethyl ethylphosphonate

b) TBP - tributyl phosphate

c) DBB - dibromobiphenyl

d) DIMP - diisopropyl methylphosphonate

e) GC/MS - gas chromatography/mass spectrometry in the multiple ion detection mode

f) GC/FPD - gas chromatography/flame photometric detection

g) TD-GC/MS - thermal desorption GC/MS of analytes from Tenax®

2.1 ClO$_2$ Fumigant Decontamination Technology Used with TICs and CWAs

2.1.1 Sabre Technical Services ClO2 Generator

The Sabre ClO$_2$ generator consisted of a 20.3 cm x 20.3 cm base onto which a 15.2 cm x 15.2 cm, 91.4 cm high sparging column was mounted. A 19 L container with 15 L of the ClO$_2$ decontamination solution was placed at the base of the sparging column. The ClO$_2$ decontamination solution (an aqueous solution consisting of 3 g L^{-1} of ClO$_2$ plus 1000 ppm of sodium chlorite) was prepared just prior to use in each test. Using a peristaltic pump, the ClO$_2$ decontamination solution was pumped into the sparging column. Air from the test chamber was also pumped into and through this column and this air was used to sparge the ClO$_2$ solution so as to form a fine mist; this air stream re-entered the test chamber with ClO$_2$ at the desired concentration. Variation in the flow rate of liquid and air into the sparging chamber was used to establish the desired ClO$_2$ concentration in the test chamber. Liquid from the reservoir of ClO$_2$ decontamination solution was initially introduced into the sparging column at 60 mL min^{-1}. When the desired ClO$_2$ concentration in the test chamber was achieved, the liquid introduction into the sparging column was decreased to 0 mL min^{-1} until the concentration dropped; at that time the system was restarted at brief intervals to maintain the desired concentration. The spent liquid exiting the sparging column was collected in a reservoir. The air from the chamber was recirculated into and out of the sparging column. At the end of the decontamination test the ClO$_2$ in the system was destroyed by pumping the exhaust air through a scrubber containing a sodium thiosulfate (STS) trap. The test chambers are described in greater detail in Sections 2.3.1 and 2.4.1.

2.1.2 Measurement in the Test Chamber Atmosphere

The concentration of ClO$_2$ in the test chamber was monitored before beginning a test and periodically during the test using a titration method. Use of this method assumes, as has previously been demonstrated using the Sabre generation method, that ClO$_2$ is the only chlorine species in the gas being sampled. For this titration method, air in the chamber was sampled using an impinger (at a rate of 1 L min^{-1} for 2 min) containing 15 mL of 5% potassium iodide in phosphate buffer (pH 7.0). Under these conditions ClO$_2$ oxidizes iodide in the phosphate buffer solution to iodine and ClO$_2$ gas is reduced to the chlorite ion (ClO$_2^-$) which dissolves in solution. The molecular iodine that is produced appears yellow-brown in aqueous solution. After sampling the chamber atmosphere, the impinger solution is acidified and the chlorite is allowed to react further with the iodide ion, forming additional iodine and reducing the chlorite to

chloride. The total resulting iodine is then reduced to iodide by titrating with standard 0.1 M (molarity, moles per liter) STS. The titration endpoint is determined when the color of the solution changes from yellow-brown to colorless. The volume (mL) of STS needed to achieve the color change (brown to colorless) is proportional to the amount of iodine generated, which is proportional to the gas-phase ClO$_2$ concentration in the air that passed through the impinger. Using the formula below, the concentration of ClO$_2$ (in parts per million [ppm] volume in air) is calculated as

$$ClO_2, ppm = \frac{V, mL \ x \ M, moles \ L^{-1}}{SR, L \ min^{-1} \ x \ Time, min} \times \frac{1}{5} \times 24.45, L \ mol^{-1} \times 1000, L \ m^{-3}$$

(1)

where V is the volume of STS titrant (mL, which is 10^{-3} L); M is the molarity of STS titrant (g divided by formula weight) which for STS is equal to its normality, N); SR is the sampling rate through the impinger (L min^{-1}); Time is the sampling time (min); 1/5 is the stoichiometric ratio of 1 mole (mol) ClO$_2$ reacting with 5 mol STS; 24.45 is the ideal gas constant, L mol^{-1}, at 25°C, 1 atm; and 1000 is the conversion factor (L m^{-3}). The formula weight of an ion species is equal to its concentration in ppm at 10^{-3} M; therefore the results from this equation are equivalent to ppm. The calculation of concentration of ClO$_2$ is limited to two significant figures (e.g., 3100 ppm). The allowable variation in the ClO$_2$ concentration (±10%) encompasses the <2% variation introduced by differences in test barometric pressure and temperature conditions from ideal gas constant conditions (1 atm and 25°C).

2.2 Liquid Decontamination Technologies Used with CWAs

Two aqueous solutions of oxidants were selected for testing. One oxidant solution was diluted liquid bleach (sodium hypochlorite) and the other was aqueous ClO$_2$.

2.2.1 Liquid Decontamination Solutions Tested

The diluted bleach was prepared fresh daily using Clorox® brand bleach that was less than 3 months old (based on the code on the bottle). Clorox® bleach, 5%–6% sodium hypochlorite, was diluted ten fold with deionized water to give a nominal concentration of 5000 ppm ClO$^-$ oxidant. (The concentration of ClO$^-$ in the bleach was not measured.)

The ClO$_2$ was prepared fresh daily at a nominal concentration of 3000–3500 ppm. This was prepared by adding 36 mL of 6 N hydrochloric acid, 105 mL of Clorox® bleach, 100 mL of 25% aqueous sodium chlorite to 3000 mL of deionized water. The aqueous ClO$_2$ solution was stored in a dark bottle. The pH was checked to ascertain that it was between 4.5 and 7.5 units.

An STS titration method was used to measure the concentration of the ClO_2 in the liquid decontamination solutions. For this titration method, 5.0 mL of phosphate buffer (pH 7.0) and a 5.0 mL sample of the ClO_2 solution was added to potassium iodide solution (150 mL water into which 1.0 g of potassium iodide was dissolved). Under these conditions ClO_2 oxidizes iodide in the phosphate buffer solution to iodine and ClO_2 gas is reduced to the chlorite ion which dissolves in solution. The molecular iodine that is produced appears yellow-brown in aqueous solution. The total resulting iodine is then reduced to iodide by titrating with standard 0.1 M STS. The titration endpoint is determined when the color of the solution changes from yellow-brown to colorless and is recorded as "A". To the solution, 5.0 mL of 6 N hydrochloric acid is added and the titration is repeated; the result is recorded as "B".

The concentrations (mg/L) of ClO_2 and chlorite in the solution are calculated using Equations 2 and 3.

$$ClO_2, mg\ L^{-1} = \frac{A, mL\ x\ N, moles\ L^{-1}\ x\ 67,450\ mg\ mole^{-1}}{V, mL} \quad (2)$$

A = mL of titrant to endpoint before acidification

N = normality of STS titrant (moles = equivalents)

V = mL of sample

67,450 = equivalent weigh (g mole^{-1}) of ClO_2 x 1000 mg g^{-1}

$$\textbf{\textit{Chlorite}}, mg\ L^{-1} = \frac{(B, mL - 4A, mL)\ x\ N, moles\ L^{-1}\ x\ 16,860\ mg\ mole^{-1}}{V, mL} \quad (3)$$

B = mL of titrant to endpoint after acidification

4A = proportion of chlorite measurement due to ClO_2

16,860 = equivalent weight (g mole^{-1}) of chlorite x 1000 mg g^{-1}

2.2.2 Liquid Decontamination Test System

The liquid decontamination tests were carried out in 40 mL glass vials. A coupon of specified building material was spiked with the indicated CWA and placed into the vial which contained 10 mL of decontamination solution. The cap was placed securely on each vial, and the vial was laid horizontally so that the decontamination solution fully covered the test coupon. The liquid decontamination investigation is described further in Section 2.4.2.

2.3 TICs

2.3.1 Test Chamber for Fumigant Decontamination Tests

A customized test chamber consisting of fabricated and off-the-shelf equipment and components was assembled and used to carry out the investigation of the decontamination of TICs. The 448 L test chamber (Labconco) is shown in

Figure 2-1 (on page 6). The temperature in the chamber was maintained between 23°C and 25°C. Hydrocarbon-free zero air was supplied to the test chamber by a zero air generator (AADCO). To achieve the desired RH in the chamber at the start of a test, mass flow controllers (MFC; Sierra Instruments) admitted both dry air and humid air in known proportions. One MFC admitted moisture-free air to the test chamber at a rate of 4.25 L min^{-1}. The second MFC admitted 3.25 L min^{-1} of dry air through a 10 L min^{-1} RH generator (Fuel Cell Technologies). The relative amounts of the two air streams were adjusted to reach 80% ± 5% RH inside the test chamber. A small 8-cm fan (Papst Model 8412), mounted in the upper left side of the chamber, ensured that the test chamber atmosphere remained well-mixed.

Temperature and RH were either recorded in real-time every minute (for six of eight tests with TICs) with a National Institute of Standards and Technology (NIST)-traceable thermo-hygrometers (Control Company Model 4185), or in near real-time roughly every 15 to 20 min (for two of the eight tests) with a hygrometer (Control Company model number 15551-126).

The building material coupons were placed on a custom-fabricated polycarbonate carousel that was mounted inside the test chamber, as shown in Figure 2-1. Two 8-cm fans were positioned in a straight line along the carousel diameter so as to pass air directly above the coupon surfaces. The carousel completed one full rotation each minute. The operation of the carousel was controlled to ensure that air was passed across all coupons as uniformly as possible for the duration of each 7 h test. Each of the two fans produced an air velocity of 400 ft min^{-1} over the coupons as measured by anemometers (TSI model 8455) placed downstream of each of the two carousel fans.

To maintain one air exchange h^{-1} in the test chamber during the without decontamination test with malathion, 7.5 L min^{-1} of hydrocarbon-free air (containing less than approximately 0.1 ppm total hydrocarbons) was admitted to the chamber. For all other tests, no air was admitted to the chamber during testing; maintaining essentially static conditions inside the test chamber allowed for better stability in the ClO_2 concentration. The flow rate of the air sampling performed using Tenax® adsorbent cartridges to determine the gas-phase TIC concentrations resulted in small air exchange rates—only 0.03 to 0.05 air exchanges h^{-1} during 1 or 3 h of sampling. Additional description of the air sampling is provided in Section 2.3.7. Because the control tests without fumigant ClO_2 were conducted at a higher air exchange rate (1 air exchange h^{-1}), the control test for the volatile DMMP was repeated with the minimal air exchange rate. As there was no loss of malathion from the control coupons at the high air exchange rate, this control was not repeated at a lower air exchange rate.

2.3.2 Building Materials

The test coupons included both porous (ceiling tile and industrial grade carpet) and non-porous (decorative laminate) surfaces. Test coupons were cut to 3.5 cm length x 1.5 cm width (5.25 cm^2) from larger pieces of stock material. Test coupons were each visually inspected prior to being used in any test. Coupons with anomalies on the application surface were not used.

2.3.3 Sequence of Testing

The test sequence for each TIC and type of building material was (1) the control condition (without ClO_2 decontamination) followed by (2) decontamination at 3000 ppm ClO_2. Each test included 25 coupons described in Table 2-1. At each time point (1, 3, and 7 h), five test coupons, and one each of the procedural blank, handling blank, and positive control coupon were extracted and analyzed to determine the mass of

the TIC in the extract. At each time point during the control condition tests (1, 3, and 7 h), five positive control coupons, and one each of the procedural blank, handling blank, and handling positive control coupon were extracted and analyzed to determine the mass of the TIC in the extract. The laboratory blank coupon was analyzed with the 1 h samples. The same regimen was used for the tests done both with and without decontamination. The test chamber was thoroughly ventilated after a test with ClO_2 before starting a control test where there was no ClO_2 being admitted to the chamber.

2.3.4 Source of TICs

The source, lot number and purity of the TICs used for the decontamination tests are listed in Table 2-2 (on page 8) (upper section of table); these parameters are also listed in Table 2-2 (lower section) for the secondary source material used in the QA performance evaluation (PE) audit.
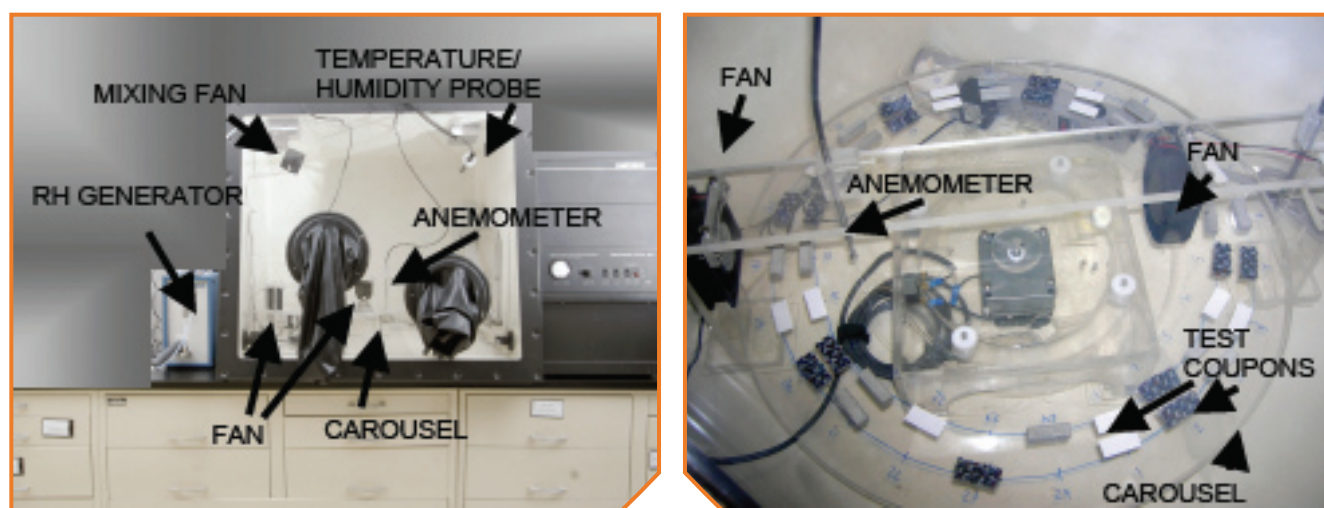
Figure 2-1. Frontal (left) and Overhead (right) Views of Test Chamber Used for Decontamination Test of TICs

Table 2-1. Types of Coupons Used in the TIC Fumigation Investigation

Coupon (n)	Treatment	Coupons per Time
Test coupon (n = 15)	Spiked with TIC and exposed to chamber conditions (with or without ClO_2)	Five removed from chamber after each of 1, 3, and 7 h exposure times
Procedural blank (n = 3)	Not spiked with TIC, and exposed to chamber conditions (with or without ClO_2)	One removed from chamber after each of 1, 3, and 7 h exposure times
Handling blank (n = 3)	Not spiked with TIC, exposed in the fume hood during the spiking process, then placed into sealed vials	One removed from vial and analyzed along with test coupons at each time point (1, 3, and 7 h)
Handling positive control (n = 3)	Spiked with TIC and sealed in vials outside of test chamber	One removed from vial and analyzed along with test coupons at each time point (1, 3, and 7 h)
Laboratory blank (n = 1)	Not spiked with TIC and sealed in vial outside of test chamber	One removed from vial and analyzed at 1 h time point

n = number of samples

Table 2-2. Source of TICs and PE Audit Standards

Chemical	Manufacturer/ Supplier Name	Lot Number	Purity or Concentration	Concentration as Applied
Materials used for recovery and efficacy tests				
Malathion	Chem Service, Inc.	343-110B	99.2%	10 mg mL^{-1} in acetone
DMMP	Sigma-Aldrich	10110EA	97%	10 mg mL^{-1} in acetone
Materials used for QA performance evaluation audit				
Malathion	Chem Service, Inc.	332-16B	98%	10 mg mL^{-1} in acetone
DMMP	Chem Service, Inc	08113TC	97%	10 mg mL^{-1} in acetone

2.3.5 Application of TICs to Test Coupons

For both analytical method recovery testing and decontamination testing, the test and positive control coupons were spiked with 50 µL of 10 mg per mL (mg mL^{-1}) of individual TICs to achieve a loading of 500 µg (~1 g m^{-2}). The addition of 500 µg of a TIC to carpet, laminate, or ceiling tile coupon is equivalent to 0.5 mg per 5.3 cm^2, or about 1 mg per 10 cm^2 or 1 g m^{-2}. The spike of each TIC was delivered from a variable volume pipettor (Eppendorf) onto each test coupon in a laboratory fume hood separate from the test chamber.

One laboratory blank coupon per test was not exposed to TICs or to the laboratory atmosphere in which the test chamber resides. Instead, when the coupons were retrieved from storage, these blank coupons were placed immediately into an airtight vial for subsequent extraction. Additional laboratory blank coupons that were designated as handling laboratory blanks for the different sampling intervals were exposed to the laboratory air during the spiking of samples. These blanks were loaded into vials when other coupons were loaded into the chamber. Then, when coupons were retrieved from the chamber for analysis, a handling blank coupon was also retrieved for analysis. All other coupons retrieved from storage were placed in the fume hood where the test coupons and positive controls were spiked. The process handling blank coupons were not spiked with TICs, but were in the hood during the spiking and handling of the test coupons. Subsequently, the process blank coupons were in the chamber during the decontamination test.

For the analytical method recovery tests, the TIC and SRS solutions were spiked onto the coupons just prior to extraction. A short drying time was used to allow the solvent to evaporate before extraction (Table 2-3). Similarly, for decontamination tests, the coupons were placed in the laboratory fume hood and spiked with the appropriate TIC solution. The solvent was allowed to evaporate before the coupons were placed in the test chamber. The solvent evaporation times, listed in Table 2-3, were selected on the basis of the TIC and coupon type. The test chamber was already equilibrated at the appropriate temperature and RH when the coupons were added. For the decontamination tests, the SRS was not spiked onto each coupon until just before analytical extraction.

Table 2-3. Solvent Evaporation Times for TICs Spiked on Various Building Materials

TIC	Material	Evaporation Time (min)
Malathion	Carpet	30
Malathion	Laminate	3
DMMP	Carpet, ceiling tile	1

2.3.6 Extraction Method for TICs from Test Coupons

For extraction, each coupon was placed into a 22 mL amber glass vial and then spiked with 25 microliters (µL) of a 10 µg µL^{-1} solution of the appropriate SRS (to deliver 250 µg) for extraction. A 20 mL aliquot of acetone was added to each vial; the vial was sealed with a screw-cap lid and ultrasonicated for 30 min in an ultrasonic bath (Branson 5510). The extract was decanted to either a 200 mL TurboVap tube or a 25 mL Kuderna-Danish (KD) tube with attached 125 mL reservoir. Carpet samples were extracted with three replicate aliquots of acetone; extracts were combined before concentration. Laminate and ceiling tile coupons required only one extraction cycle. The number of extraction cycles and concentration technique used for each TIC and building material combination are listed in Table 2-4. Extracts were concentrated to a final volume of 5 mL and spiked with 25 µL of a 10 µg µL^{-1} solution of the appropriate IS to give a 50 µg

Table 2-4. Extraction and Concentration Techniques Used for TICs

Coupon Type	TIC	Extraction Technique	Extraction	Concentration Technique
Carpet	Malathion	Sonication	3 x 20 mL	TurboVap
Carpet	DMMP	Sonication	3 x 20 mL	KD
Laminate	Malathion	Sonication	1 x 20 mL	TurboVap
Ceiling tile	DMMP	Sonication	1 x 20 mL	KD

mL^{-1} concentration. A 1 mL aliquot was then filtered through a disposable syringe filter (GD/X; Whatman) prior to the gas chromatography/mass spectrometry (GC/MS) analysis.

2.3.7 Air Sampling and Analysis of TICs Using Tenax® Sorbent Air Sampling Tubes

Sampling of the chamber air to assess vapor phase concentrations of the TICs was accomplished using active sampling onto the Tenax® TA™ sorbent. The air sampling cartridges consisted of stainless steel thermal desorption tubes (0.25 inch outside diameter x 3.5 inch length) packed with 200 mg of 60/80 mesh Tenax® TA polymer (Markes International, Ltd). Sampling was performed using calibrated mass flow controllers. For malathion, sampling rates were 500 mL min^{-1} for control conditions and 200 mL min^{-1} for test conditions, both for 3 h. The sampling rates were lowered to reduce the air exchange rate in order to stabilize the ClO$_2$ concentration during decontamination testing. For DMMP, all sampling was performed at 100 mL min^{-1} for 1 h. The longer sampling times and higher sampling rates for malathion were used because it was expected that chamber air concentrations of malathion would be considerably lower than those of DMMP due to vapor pressure differences.

At the conclusion of sampling during malathion tests, the Tenax® air cartridges were spiked with 100 µg of the SRS (fenchlorphos) and extracted with 2 mL of acetone; after addition of the IS, the 2 mL volume was analyzed without further concentration. The GC/MS analysis for the air extracts was performed as described in Section 2.3.8 for coupon extracts.

At the conclusion of sampling during DMMP tests, the Tenax® air cartridges were spiked with diisopropyl methylphosphonate (DIMP) as an IS and analyzed using thermal desorption (TD) GC/MS technique (using a Markes Unity Thermal Desorption unit interfaced to an Agilent 6890/5973 GC/MS). Before desorption, a tube leak check was performed to ensure quantitative sample transfer. After the leak check, the tube was flushed with helium for one min at 40 mL min^{-1}, with the effluent sent to vent. Following the purge, analytes were desorbed from the sorbent tube at 20 mL min^{-1} for 10 min at 300°C; analytes were collected on the focusing trap (Markes General Purpose Graphitized Carbon trap) which was held at 25°C. The analytes were then desorbed from the focusing trap at 300°C for five min using the maximum heating rate (>60°C sec^{-1}) and a flow rate of 40 mL min^{-1}. A portion of this flow was directed to the GC/MS. Minor modification of the tube desorption flow rate was used in various sets of analyses to optimize the percentage of analyte transfer from sorbent tube to GC/MS for analysis. In each set, however, samples and standards were analyzed under identical conditions. The GC/MS conditions for analysis of vapor phase DMMP are given in Table 2-5.

2.3.8 Analysis Method for TICs

Coupon extracts were analyzed using GC/MS in multiple ion monitoring mode on an Agilent 6890/5973 GC/MS. Data collection, reduction, and analysis were performed using Agilent Chemstation software, version B.02.05. The GC and MS conditions used for analyses of the two different TICs are listed in Table 2-6.

Table 2-5. GC and MS Conditions for Analysis of DMMP in Air Samples

Parameter	Condition
GC column	DB-5ms; 60 meters (m) x 0.32 mm inside diameter x 0.25 µm film thickness (Agilent)
Temperature program	50°C (2 min); 50°C–140°C @ 6°C min^{-1}; 140°C–250°C @ 20°C min^{-1}; hold 0.5 min (23 min run time)
Transfer line temperature	280°C
MS source temperature	230°C
Quadruple temperature	150°C
Flow rate	1.5 mL min^{-1} at 50°C
Ions monitored	m/z 94, 79 for DMMP and m/z 97, 123 for DIMP

Table 2-6. GC and MS Conditions for TIC Analyses

Parameter	Condition
GC column[a]	DB-1701; 30 m x 0.25 mm ID x 0.15 µm film thickness; J&W Scientific
Inlet liner	Siltek double gooseneck
Temperature program for malathion	100°C (2 min); 100°C–180°C @ 10°C min^{-1}; 180°C–220°C @ 5°C min^{-1}; 220°C–260 °C @ 20°C min^{-1} (20 min run time)
Temperature program for DMMP	50°C (2 min); 50°C–95°C @ 3°C min^{-1}; 95°C–250°C @ 20°C min^{-1}; hold 2.25 min (27 min run time)
GC injection	1 µL splitless at 280°C
Transfer line temperature	280°C
MS source temperature	230°C
Quadruple temperature	150°C

a) In all cases helium was the carrier gas: 0.8 mL min^{-1} flow for malathion; 1 mL min^{-1} for DMMP

Table 2-7. GC Retention Times and Monitored Ions for TIC Analyses

Chemical	GC Retention Time, min	Ions Monitored, m/z	
		Quantification Ion	Qualifier Ion
Malathion	17.2	173	127
SRS	15.5	285	125
IS	16.5	312	152
DMMP	9.0	94	79
SRS	17.0	111	93
IS	15.6	97	123

Two ions were monitored for each TIC, SRS, and IS. The primary ion was used for quantification and the secondary ion was used for qualitative confirmation of identification. Criteria for identification of an analyte included the correct GC retention time ±0.02 min, chromatographically co-maximized primary and secondary ions and correct ratio between the relative intensities of the primary and secondary ions. The monitored ions and GC retention times are listed in Table 2-7.

The quantification was performed using the IS method.[2] The IS was present at the same concentration in all samples and standards. The 11-point calibration curve spanned the range of 0.1–150 µg mL^{-1}. This concentration range is equivalent to 0.1% to 150% recovery of the mass applied to coupons.

The full calibration curve was analyzed at the start of each analysis set. Samples were then analyzed with the 20 µg mL^{-1} standard run after every five samples as a continuing check on the calibration. If the calculated concentration of the continuing calibration standard showed a variance more than 20% beyond its true concentration, the cause of the problem was investigated and the five samples before and after this standard were reanalyzed. Calibration curves were constructed using a quadratic least-squares regression analysis routine with the weighting scaled by the inverse of the analyte concentration. Typically, the calibration data could be fitted to a single curve for malathion and DMMP. However, due to the wide calibration range, occasionally two separate calibration curves (one with high values and one with low values) were needed to define the malathion calibration data.

2.3.9 Calculation of TIC Recovery Efficiency, Percent Recovery, and Decontamination Efficacy

The analytical method performance recovery efficiency for both a TIC and its matched SRS extracted from a spiked coupon was determined according to the following formula:

$$Analytical\ Method\ Recovery\ Efficiency,\% = \frac{Concentration,\ \mu g/mL \times Extract\ Volume,\ mL}{Mass\ Applied,\ \mu g} \times 100\% \qquad (4)$$

Using results from Equation 4 for SRS and TIC recoveries, the analytical method recovery ratio between the mean analytical method SRS recovery and the mean analytic method TIC recovery was determined using the following equation:

$$SRS/TIC\ Recovery\ Ratio = \frac{Mean\ Analytical\ Method\ SRS\ Recovery,\%}{Mean\ Analytical\ Method\ TIC\ Recovery,\%} \qquad (5)$$

The raw recovery value for the individual TIC or SRS from a building material coupon during a test was calculated by multiplying the mass (µg mL^{-1}) determined in the analytical method by the extract volume (mL). The raw recovery values were adjusted using the SRS/TIC recovery ratio from Equation 5 to generate the normalized TIC recovery values according to the following equation:

$$Normalized\ TIC\ Recovery,\% = \frac{Raw\ TIC\ recovery,\ \mu g}{Raw\ SRS\ recovery,\ \mu g} \times SRS/TIC\ Recovery\ Ratio \times 100\% \qquad (6)$$

The mean normalized TIC recovery from Equation 6, at each sampling interval, was divided by the mean normalized TIC recovery at Time 0 of the test to obtain the percent recovery at a given time reported in the results:

$$Recovery\ at\ Time_x, \% = \frac{Mean\ Normalized\ Recovery\ at\ Time_x, \%}{Mean\ Normalized\ Recovery\ at\ Time_0, \%} \times 100\% \quad (7)$$

The decontamination efficacy of a decontamination technology was calculated as the ratio of the mean recoveries extracted from a coupon at a given time (from Equation 7) for the test (decontaminated) and control using the following equation:

$$Decontamination\ Efficacy\ at\ Time_x, \% = \left(1 - \frac{Recovery\ of\ TIC\ at\ Time_x\ With\ Decontamination, \%}{Recovery\ of\ TIC\ at\ Time_x\ Without\ Decontamination, \%}\right) \times 100\% \quad (8)$$

The SRS recovery in each particular sample was used to correct for potential differences in application of the analytical method to each individual sample. The SRS/TIC recovery ratio, calculated using Equation 5, used data from the recovery measurements of these compounds in the method performance tests. This ratio was used to make an adjustment for the fact that an isotopically-labeled chemical equivalent (e.g., deuterium - or C13-labeled) of each TIC was not available for use as the SRS. In many analytical methods, a labeled version of an analyte is used as the SRS; in that case the analyte and SRS are assumed to be recovered through an analytical method to the same extent. Where an isotopically-labeled version of an analyte is not available, an SRS is chosen to be as similar as possible to a given analyte so as to minimize the potential for differential loss mechanisms. However, there may be differences in recovery between an analyte and SRS, and this difference requires a minor adjustment based on differential recoveries.

To convert a Tenax® sorbent sample extract concentration for malathion to an air concentration of malathion in the test chamber, the following equation was used:

$$Concentration\ in\ Air, \mu g\,m^{-3} = \frac{Concentration\ in\ Extract, \mu g\,mL^{-1} \times Extract\ Vol, mL}{Sampling\ Rate, L\,min^{-1} \times Sampling\ Time, min} \times 10^3\ L\,m^{-3} \quad (9)$$

To convert an amount of DMMP measured on a Tenax® sorbent tube to a DMMP air concentration in the test chamber, the following equation was used:

$$Concentration\ in\ Air, \mu g\,m^{-3} = \frac{Amount\ Desorbed\ from\ Tube, \mu g}{Sampling\ Rate, L\,min^{-1} \times Sampling\ Time, min} \times 10^3\ L\,m^{-3} \quad (10)$$

2.4 CWAs

2.4.1 Test Chamber for Fumigant Decontamination Tests

Two test chambers were constructed for testing of each CWA. One chamber housed the control coupons that were not exposed to ClO_2; the second chamber was interfaced to the Sabre ClO_2 generator, so that the coupons housed in this chamber could be decontaminated. Each chamber consisted of a specially fabricated polycarbonate (Lexan®) housing with removable custom built shelves made of 26 gauge cold rolled steel. The chamber had dimensions of 26 cm x 29 cm x 27 cm, or 20.4 L. A new polycarbonate chamber with shelves was used for each CWA tested. The temperature in the chambers was that of the ambient air in the laboratory. An ultrasonic fog generator was used to establish ~100% RH air in a separate fogging chamber. The humidified air from the fogging chamber was pumped through a water trap and then into the two test chambers until the test chambers reached 80% RH. Each chamber was then sealed for the test. The test chamber was interfaced with the Sabre ClO_2 generator, which was described earlier (Section 2.1.1). At the conclusion of each test, the chambers were decontaminated and decommissioned according to Department of the Army regulations and BBRC standard operating procedures.

The temperature and humidity in the chamber were monitored continuously (at 30 min intervals) by the heating, ventilation, and air conditioning (HVAC) system. The HVAC readings were verified twice daily using a calibrated NIST-traceable thermometer/hygrometer with accuracy of ±1°C for temperature and ±5% for RH. All of the readings taken in the laboratory indicated that the temperature and RH were constant throughout the test periods.

2.4.2 Test Chamber for Liquid Decontamination Tests

As described earlier (Section 2.2.2), the testing for decontamination of building material coupons with liquid solutions was carried out in individual 40 mL vials. Each spiked or blank coupon was placed in a vial and 10 mL of decontamination solution was added. The vial was capped securely laid horizontally so that the coupon was bathed completely in the decontamination solution during the test period. The vials were periodically shaken for the first few hours to extract the CWA from the coupon and the coupons were allowed to stand in the extraction solution overnight. At the completion of the specified decontamination period, the coupon was removed and shaken lightly to remove as much aqueous liquid as possible; the SRS was added to the coupon immediately and placed into a 40 mL vial containing 10 mL of extraction solvent. The vials were again shaken a few times before the coupon was removed.

Neutralization of the decontamination solution was not used in the decontamination efficacy tests because the preliminary solution tests (Section 2.2.2) suggested that loss of CWA recovery occurred in neutralized solution, except possibly for GD. Rapid extraction was preferred to inclusion of a neutralization step. Therefore, the coupons were removed from the decontamination solution, shaken lightly to remove excess liquid, spiked with the SRS, and placed directly into the extraction solution.

2.4.3 Building Materials

The building materials that were utilized in testing for decontamination efficiency for fumigant and liquid decontamination technologies are listed in Table 2-8; these materials included porous, adsorptive and non-porous surface types. Test coupons were cut to the sizes indicated in Table 2-8 from larger pieces of stock material.

Table 2-8. Building Material Test Coupon Characteristics for CWA Decontamination Tests

Material	Approximate Coupon Surface, Length x Width, cm	Material Preparation
Laminate	6.5 x 1.5 (9.75 cm^2)	Clean with acetone
Carpet	6.5 x 1.5 (9.75 cm^2)	None
Ductwork	6.5 x 1.5 (9.75 cm^2)	None

2.4.4 Sequence of Testing

For the fumigant testing with ClO_2 generated by the Sabre system, all building material types were tested concurrently in a given test. However, since the test (i.e., fumigant) and control chambers were both sealed to maintain the RH, only enough coupons were loaded into the identical chambers for a single time increment of decontamination. For example, when testing decontamination of VX, the identical chambers were each loaded with five spiked carpet coupons, five spiked laminate coupons, five spiked ductwork coupons, and one procedural blank of each material type. The chambers were sealed and the decontamination and control tests were then carried out for 1 h. After unloading the chambers and

ventilating them, an identical set of coupons were prepared, loaded into the chambers, and this time the test was conducted for 2 or 4 h, depending on CWA.

To select appropriate conditions for the liquid decontamination tests, several preliminary tests were conducted to determine whether neutralization of the liquid decontamination agent was needed prior to extraction of the CWA with the organic solvent. To carry out this test, each CWA was spiked into both the full strength liquid decontamination (bleach or ClO_2) and the neutralized liquid decontamination solution. The CWA was held in the 10 mL decontamination solution for 1 h prior to addition of the SRS and the 10 mL of hexane for extraction; in contrast, the CWA was held for 15 sec in the neutralized decontamination solution prior to addition of the SRS and the 10 mL of hexane for extraction. The neutralized solution consisted of the decontamination liquid and STS equivalent to 10% more than that required to neutralize the oxidant; this solution was then adjusted to pH 7.0 by the addition of acetic acid before extraction with hexane.

For the tests of decontamination with liquid bleach, testing was done sequentially with individual combinations of CWA and building material because of the very short decontamination times being tested (10–30 min). The sequence of testing included first, the analysis of Time 0 positive controls without decontamination and laboratory blanks of a given building material and CWA for verification of mass applied. This group of samples included five positive control coupons of the building material spiked with 1 mg of the CWA, and one coupon of that material that was a laboratory blank. These coupons were spiked (as needed) and immediately extracted in hexane. Then, that same combination of building material and CWA was tested for different durations with and without decontamination. Each test grouping included, for instance, five carpet coupons spiked with 1 mg of CWA and loaded into vials containing 10 mL of diluted bleach (i.e., with decontamination), five carpet coupons spiked with 1 mg of CWA and placed in empty vials (i.e., without decontamination), and one procedural blank carpet coupon that was placed in a vial with diluted bleach. This sequence was completed for all decontamination test durations with carpet, then laminate and then ductwork first for VX, then repeated again with TGD, and then repeated a third time with GB (here, tested only on carpet coupons because GB was not persistent on laminate or ductwork). The only deviation to the test/QA plan was that positive control coupons (i.e., without decontamination) for VX were not prepared for the 10 and 20 min decontamination durations; these coupons were only prepared for the 30 min test duration due to the very low vapor pressure and expected stability of VX over 10 and 20 min test periods.

In each test combination of CWA and building material, the ten spiked building material coupons were loaded into vials, alternating between a vial containing the decontamination solution and a control vial that was empty, as a control for bleach, or containing acidified water, as a control for ClO_2 decontamination solution. This alteration between test and

control vials was done to minimize the effect of loading time. The same alternating sequence was used in retrieving coupons from vials, spiking them with SRS and loading them into the hexane-containing extraction vials — once again to minimize the effect of time required for spiking SRS and loading the coupon into an extraction vial. This was deemed potentially important for the more volatile CWAs (GB and TGD).

Decontamination tests using ClO_2 decontamination solution were conducted only for VX because the results of the solution tests suggested that decontamination of GB and GD with ClO_2 solution was not effective. Solution testing results with VX were inconclusive, possibly due to hydrolysis in the aqueous solution. For decontamination with ClO_2 solution, the same sequence as described above for bleach was used. This included preparing only one coupon type at a time, and preparing these for only one decontamination duration.

For decontamination of VX with ClO_2 solution, the positive control samples (spiked without decontamination) were handled differently. VX is quite unstable in alkaline solutions and this was a possible explanation for the inability to recover VX from neutralized ClO_2 decontamination solution in the solution tests. Therefore, rather than load the positive control coupons into empty vials for the test duration, they were loaded into vials containing 10 mL of acidified (pH 4.5–<7) water; VX is quite unstable in alkaline solutions. The recovery of VX from acidified water enables the hydrolysis effects of water to be differentiated from the decontamination effects of the ClO_2.

2.4.5 CWAs and Surrogate Recovery Standard

The source, lot number, and purity of the CWAs used in this investigation are listed in Table 2-9.

Polymethyl methacrylate was added, 5% on a weight:volume basis, as a thickening agent for GD. Typically, 5 mL of TGD was prepared in a batch.

2.4.6 Application of CWAs to Test Coupons

For both the control tests (with no ClO_2 admitted to the chamber) and the decontamination tests with ClO_2, the coupons were spiked with the individual CWA to achieve a loading of approximately 1 g m^{-2}. All building materials were spiked with 1 µL of neat CWA to deliver a mass of approximately 1 mg to one 10 cm^2 surface of each coupon. A 50 µL repeating dispenser pipette (Hamilton) that delivers 50 equal volumes per syringe load was used to apply the CWA to the test coupons. Concurrently with spiking the test coupons, 1 µL of each CWA was spiked directly into 10 mL of the extraction solvent and this solution was analyzed to measure the mass of CWA applied to the building materials (i.e., a confirmation spike). The mass of CWA applied to test coupons, as determined from analyses of the confirmation spikes, are listed in Table 2-10.

For these decontamination tests, the coupon spiking was completed within approximately 30 sec, and coupons were loaded directly into the test chambers after spiking. Drying time was not needed since there was no solvent involved.

Table 2-9. Source of CWAs and SRS

Chemical	Manufacturer/Supplier	Purity or Concentration	Concentration as Applied
Materials used in this investigation			
GB	U.S. Army	96	Neat
GD	U.S. Army	94	95% neat
VX	U.S. Army	70	Neat
TBP (SRS)	Sigma-Aldrich	99	Neat
Standard Analytical Reference Material used to confirm CWA purity			
GB	Institute of Chemical Defense	1 mg mL^{-1}	NA
GD	Institute of Chemical Defense	1 mg mL^{-1}	NA
VX	Institute of Chemical Defense	1 mg mL^{-1}	NA

Table 2-10. Mass of CWA Applied to Building Material Coupons

Chemical	Mass of CWA Applied for Decontamination Tests		
	Fumigant ClO_2	Liquid Bleach	Liquid ClO_2
GB	916 µg	830 µg	NT[a]
TGD	880 µg	1530 or 1570 µg, depending on day	NT
VX	833 µg	840 µg	950 µg

a) NT = not tested

2.4.7 Extraction Method for CWAs

For extraction of building material coupons, 1 µL of the SRS (1 µL = 1 mg) was first applied as neat material to the coupon just prior to extraction. The coupon was then loaded into a 40 mL sample extraction vial and a 10 mL aliquot of hexane containing the IS at 100 µg mL^{-1} was added. The vial was shaken briefly and then the building material was allowed to stand in the solvent overnight (~14–16 h) for passive extraction. The vials were shaken again before removal of the analysis aliquot.

2.4.8 Analysis Method for CWAs

Sample extracts were analyzed using gas chromatography with flame photometric detection (GC/FPD) on an Agilent 6890 GC. Data collection, reduction, and analysis were performed using Agilent Chemstation software, Version B.02.05. The GC conditions used for analyses of the three different CWAs are listed in Table 2-11.

The GC retention times were monitored for each CWA, SRS, and IS. Identification of an analyte entailed matching the correct GC retention time ±0.02 min. The GC retention times are listed in Table 2-12. The quantification was performed using the IS method.[2] The 9-point calibration curve spanned the range of 0.24–190 µg mL^{-1}. This concentration range is equivalent to 0.24% to 190% recovery of the mass applied in this investigation. The IS was present at the same concentration in all samples and standards.

2.4.9 Calculation of CWA Recovery Efficiency, Percent Recovery, and Decontamination Efficacy

The calculations of recovery efficiency (Equation 4), percent recovery (Equation 7), and decontamination efficacy (Equation 8) were carried out using the same equations listed and described in Section 2.3.9 for the TICs. The only exception here for the CWAs was that SRS and relative extraction efficiency corrections were not made in calculations for the data from the liquid decontamination tests. In these data, for unknown reasons, the SRS recoveries from the coupons were not stable. The SRS recoveries were measured, but were not useful for comparison.

2.5 Qualitative Evaluation of the Impact of ClO$_2$ Fumigation on Building Materials

A total of eight laboratory blanks (building materials not exposed to ClO$_2$) and 24 procedural blanks (building materials exposed to ClO$_2$) were maintained under controlled ambient temperature and RH conditions for assessment of long-term changes in appearance or structure due to ClO$_2$ fumigation. For this work, two polycarbonate chambers, one 30 L and the other 15 L, were fabricated, and connected via a cylindrical flow-through unit. The front end of the larger chamber was connected to the humidification system described earlier; the back end of the smaller chamber was exhausted to ambient. Ambient air, typically at 24°C and 40% RH, was directed through these chambers with a flow of one air exchange h^{-1}. The laboratory blank coupons were placed in the first chamber and the procedural blank coupons exposed to ClO$_2$ were placed in the second chamber.

Table 2-11. GC/FPD Conditions for CWA Analyses

Parameter	Condition
GC column for GB[a]	DB-5; 25 m x 0.32 mm inside diameter x 0.52 µm film thickness; Agilent
Temperature program for GB	55°C (1 min); 55°C–100°C @ 10°C/min; 100°C–250°C @ 25°C/min (11.5 min run time)
GC column for TGD[a]	Rtx-5; 30 m x 0.32 mm inside diameter x 0.50 µm film thickness; Restek
Temperature program for TGD	40°C (1 min); 40°C–100°C @ 10°C/min; 100°C–250°C @ 30°C/min (12 min run time)
GC column for VX[a]	DB-5; 25 M x 0.32 mm ID x 0.52 µm film thickness; Agilent
Temperature program for VX	55°C (1 min); 55°C–100°C @ 10°C/min; 100°C–300°C @ 25°C/min (13.5 min run time)
GC injection	1 µL splitless at 250°C
Detector temperature	250°C
Hydrogen flow	70 mL min^{-1}
Oxidizer flow	Air at 90 mL min^{-1}
Makeup gas flow	Nitrogen at 15 mL min^{-1}

a) In all cases helium was the carrier gas with a flow rate of 1.7 mL min^{-1}

Table 2-12. GC Retention Times for CWA Analyses

Chemical	GC Retention Time (min)
GB	3.49
SRS	11.6
IS	6.92
TGD isomer 1	6.62
TGD isomer 2	6.67
SRS	11.8
IS	6.92
VX	6.16
SRS	5.74
IS	2.05

QA/quality control (QC) procedures were performed in accordance with the TTEP Quality Management Plan (QMP)[3], the test/QA plan[4], Amendment 2 for ClO_2 decontamination of TICs (March 16, 2006), Amendment 6 for ClO_2 decontamination of CWAs (March 21, 2007), and Amendment 8 for liquid technologies for decontamination of CWAs (July 6, 2007). QA/QC procedures are summarized below.

3.1 PE Audit

A PE audit was conducted to assess the quality of the GC/MS results obtained during these tests. For the two TICs, this PE audit was performed by diluting and analyzing standards obtained from a secondary source. The secondary source standards were diluted to 100 µg mL^{-1} and analyzed using a calibration curve constructed from the primary source standards. The results of this analysis are given in Table 3-1. The target tolerance was a difference less than 25%; results were well within the target tolerance.

A PE audit was conducted to assess the quality of the CWA results obtained during these tests. For the three CWAs, this PE audit was performed by comparing purity of stock solution results against a second source (Standard Analytical Reference Material). In addition, PE audits were performed for the chamber conditions that affected results (time, temperature, RH and flow). The results of

these analyses are given in Table 3-2, except for time. Time comparisons were made four times over the span of 40 min on April 27, 2007 and May 31, 2007. Time was compared to the U.S. government's time provided by both NIST/U.S. Naval Observatory (Military counterpart to NIST) and the Department of Commerce (www.time.gov). Each measurement was exact to the second, resulting in a percent difference of 0.0% for both days. The target tolerance was a difference less than 10%; results were well within the target tolerance.

3.2 Technical Systems Audit

The Battelle QA Manager and his designee conducted a technical systems audit (TSA) to ensure that the tests were being performed in accordance with the QMP, test/QA plan, Amendment 2 for ClO_2 decontamination of TICs (March 16, 2006), Amendment 6 for ClO_2 decontamination of CWAs (March 21, 2007), and Amendment 8 for liquid technologies for decontamination of CWAs (July 6, 2007). As part of the audit, the Battelle QA Manager and his designee reviewed the reference sampling and analysis methods used, compared actual test procedures with those specified in the test/QA plan, and reviewed data acquisition and handling procedures. No significant findings were noted in this audit that might impact the quality of the investigation results. The records concerning the TSA are permanently stored with the Battelle QA Manager.

Table 3-1. TIC PE Audit Results

TIC	Date of Audit	Standard Concentration	Measured Result	% Difference
Malathion	10/27/2006	0.100 mg mL^{-1}	0.087 mg mL^{-1}	-13
DMMP	10/27/2006	0.100 mg mL^{-1}	0.104 mg mL^{-1}	4.0

Table 3-2. CWA PE Audit Results

CWA or Parameter	Date of Audit	Standard	Measured Result	% Difference
GB	6/06/2007	0.110 mg mL^{-1}	0.114 mg mL^{-1} 0.106 mg mL^{-1}	-3.6 3.6
TGD	5/03/2007	0.110 mg mL^{-1}	0.103 mg mL^{-1}	6.4
TGD	5/11/2007	0.110 mg mL^{-1}	0.109 mg mL^{-1} [c] 0.111 mg mL^{-1} [c]	0.9 -0.9
VX	5/02/2007	0.070 mg mL^{-1}	0.073 mg mL^{-1}	-4.3
MFC[a]	5/16–18/2007	1.00 L min^{-1}	1.01 L min^{-1} [b]	-0.6
Temperature	4/27/2007	19.3°C[c]	18.8°C[c]	2.6
RH	4/27/2007	36.3%[c]	37.8%[c]	-4.1
Temperature	5/31/2007	22.1°C[c]	22.4°C[c]	-1.4
RH	5/31/2007	38.8%[c]	41%[c]	-5.8

a) Mass Flow Controller
b) Average of six results, three for 5/16/2007 and three for 5/18/2007
c) Average of four results

3.3 Data Quality Audit

At least 10% of the data acquired during the investigation was audited. Battelle's QA Manager traced the data from the initial acquisition through reduction to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

3.4 QA/QC Reporting

Each assessment and audit was documented in accordance with the test/QA plan and QMP. For this investigation, no significant findings were noted in any assessment or audit, and no follow-up correction action was necessary. Copies of the TSA and assessment reports were distributed to the EPA QA Manager and Battelle staff.

QA/QC procedures were performed in accordance with the Program QMP and the test/QA plan for this investigation.

3.5 Deviations from Test/QA Plan

The test/QA plan envisioned use of a 317 L test chamber for testing decontamination of TICs. When the coupon carousel and equipment would not fit into this sized chamber, a 448 L chamber was substituted. This change did not impact the investigation.

4.0
Results

4.1 Results for Fumigant ClO$_2$ Decontamination of TICs

4.1.1 Analytical Method Development Results

The analytical methods were tested initially to verify the extraction efficiencies of the TICs and their matched SRSs from the building materials that were to be used in the decontamination tests. These recoveries are listed in Table 4-1.

The mean of the extraction efficiencies for the TICs and SRSs were in a range of 73% to 97%. This range of recovery was within the acceptance range specified in Appendix A3 of the test/QA plan (40% to 120%) and all values were within the acceptance level of 3 SD of the mean. The SRS/TIC values (0.91–1.11) show that the SRS recovery correlated well with the respective TIC recovery. These results show that the method development resulted in extraction and analysis methods for the TICs that were sufficient to achieve the data quality objectives of the test/QA plan (inclusive of the requirements in Appendix A3).

The approximate method detection limits (MDLs) for the TICs are listed in Table 4-2. Each MDL was estimated based on the signal of the lowest level calibration standard, the signal to noise ratio for this concentration and the peak area that can be integrated reliably for any signal.

4.1.2 Environmental Conditions during Decontamination Tests

The temperature, RH, ClO$_2$ concentration, and air velocity over the coupons during testing were measured as specified in the test/QA plan.[4] The averages for temperature, RH, ClO$_2$ concentration, and air velocity over the coupons during testing, in control and test chambers, are shown in Table 4-3 (on page 18). Temperature and RH were controlled to 24°C ± 2°C and 80% ± 10% RH. The target ClO$_2$ concentration was 3000 ppm. Differences in air velocities among the tests were observed. The mean of the average velocities for all of the tests was 117 ft min^{-1}; all mean velocities were within 2 SD of the mean of the averages. The differences in velocity within and among tests may be due to small changes in the operation of the fans or positioning of the anemometers.

Originally, one air exchange h^{-1} was planned for the persistence testing and the ClO$_2$ fumigation testing. However, at one exchange h^{-1}, control of the ClO$_2$ concentrations was problematic. Therefore the air exchange rate was reduced to <0.1 air exchange h^{-1} for the ClO$_2$ fumigation testing.

Due to the high volatility of DMMP, there was a concern that the difference in air exchange between the control tests (one air exchange h^{-1}) and the decontamination tests (0.1 air exchange h^{-1}) would present a variable that would interfere with the analysis of data and trends. For this reason, the tests

Table 4-1. Extraction Efficiencies of TICs and Matched SRSs from Building Materials

Material	Recovery from Building Material, % ± SD[a]		SRS/TIC Recovery Ratio[b]
	TIC	SRS	
	Malathion	Fenchlorphos	
Carpet	80 ± 3	73 ± 5	0.90
Laminate	80 ± 19	89 ± 4	1.1
	DMMP	DIMP	
Carpet	87 ± 3	87 ± 7	0.99
Ceiling tile	93 ± 3	97 ± 3	1.1

a) Calculated using Equation (Eq) (4)

b) Calculated using Eq (5); carried out using 3 significant figures on TIC and SRS recoveries

Table 4-2. MDLs for TICs

Matrix	MDL	
	Malathion	DMMP
In solution	0.01 µg mL^{-1}	0.01 µg mL^{-1}
On coupon	0.05 µg	0.05 µg
In air	0.26 µg m^{-3}	0.70 µg m^{-3}

for DMMP (without ClO_2 decontamination) were conducted a second time at the low air exchange rate to determine whether air exchange has any significant effect on recovery. The recovery of DMMP on carpet and ceiling tile with the two different air exchange rates, shown in Table 4-4, demonstrates that there is a small difference after 1 h, but that difference largely dissipates by the conclusion of the 7 h test. Statistical analysis of these data showed that the small differences on the ceiling tile were statistically significant. For DMMP, the recoveries at the low air exchange rate were used as the basis for comparison with the recoveries after decontamination.

There was not a significant loss of malathion from the test coupons over a 7 h at one air exchange h^{-1}. Therefore, the persistence testing was not repeated at the lower air exchange rate. For malathion, the recoveries at one air exchange h^{-1} were used as the basis for comparison with the recoveries after decontamination.

4.1.3 Recovery over Time of TICs on Building Materials With and Without Sabre ClO_2 Fumigant Decontamination

Individual tests, both with and without the Sabre ClO_2 fumigant decontamination technology, were conducted for each building material to assess the recovery of the given TIC on that building material. As noted in Section 1.3 (Experimental Design), the decontamination testing covered a 7 h time span, and five building material coupons were removed from the chamber for testing after 1, 3, and 7 h. In addition, analyses of five spiked building material coupons that were extracted immediately after spiking (Time 0) were used to ascertain the baseline recovery values. The recoveries of the spiked TICs from the coupons at Time 0 (0 h) and at subsequent times (1, 3, and 7 h) with and without application of the Sabre ClO_2 decontamination process are listed in Table 4-5 (on page 19).

Table 4-3. Mean Temperature, RH, ClO_2 Concentration, and Air Velocity during TIC Decontamination Tests

| TIC | Material | Chamber | Mean During the Test | | | |
			Temp, °C ± SD	RH, % ± SD	ClO_2, ppm ± SD (n)	Air Velocity, ft min^{-1} ± SD
DMMP	Carpet	Control	24.3 ± 0.1	80 ± 4	0	102 ± 11
		Test	23.9 ± 0.1	78 ± 3	3300 ± 600 (n = 17)	108 ± 0
	Ceiling tile	Control	24.2 ± 0.2	82 ± 3	0	136 ± 18
		Test	25.1 ± 0.8	83 ± 2	3010 ± 120 (n = 21)	121 ± 3
Malathion	Carpet	Control	23.7 ± 0.1	84 ± 1	0	108 ± 16
		Test	24.4 ± .03	77 ± 2	3050 ± 200 (n = 21)	140 ± 30
	Laminate	Control	22.9 ± 0.2	87 ± 2	0	116 ± 11
		Test	23.0 ± 1.1	79 ± 3	3010 ± 180 (n = 21)	105 ± 13

Table 4-4. Comparison of Mean Percent Recovery of DMMP with Different Chamber Air Exchange Rates

| TIC | Material | Time (n) | Mean Recovery, % ± SD | |
			0.1 Air Exchange h^{-1}	1 Air Exchange h^{-1}
DMMP	Carpet	1 h (n = 5)	33 ± 2	40 ± 5
		3 h (n = 5)	24 ± 3	26 ± 3
		7 h (n = 5)	16 ± 3	18 ± 2
	Ceiling tile	1 h (n = 5)	39 ± 4	32 ± 1
		3 h (n = 5)	28 ± 1	19 ± 2
		7 h (n = 5)	12 ± 1	9.4 ± 0.4

As shown in Table 4-5, the amount of DMMP on carpet and ceiling tile decreased quite substantially both with and without the decontamination treatment. At this point, it is not clear whether the significant decrease over time was due to volatilization of DMMP from the coupons or a combination of degradation and hydrolysis due to the high RH in the chamber. Statistical analysis of the data was used to determine whether there was a statistically significant difference attributable to the ClO_2 decontamination treatment.

For malathion, it was readily evident that the decontamination with fumigant ClO_2 resulted in a significant decrease in the amount of the TIC remaining on the coupons. Without decontamination, most of the malathion remained on the coupon; and with decontamination less than 1% remained on the laminate and approximately 25% remained on the carpet after 7 h.

The recoveries of DMMP and malathion on these coupons, normalized to the recoveries at 0 h, are presented in Appendix A, Table A-1 of this report. These normalized data were used as the input to the statistical analyses described below. The statistical analyses are more informative than the normalized recovery data, in that they provide insight into whether there is a statistical difference between recoveries with and without decontamination. Therefore, to avoid confusion by the presentation of somewhat repetitive, but not identical data here in the body of the report, the normalized recovery data are presented in the appendix.

4.1.4 Statistical Analysis of Recovery Trends and Decontamination Efficacy

Statistical analysis was performed using recovery values (i.e., measured recovery results normalized to the Time 0 recovery) to evaluate whether there were statically significant differences in the TICs recovered from treated coupons compared to controls. For each TIC and material combination, an analysis of variance (ANOVA) model was fit to the data. The form of the model was:

$$Y_{ijt} = \mu + treatment_j + time_t + (treatment_j * time_t) + \varepsilon_{ijt} \quad (11)$$

where Y_{ijt} is the recovery for the ith coupon (i=1 to 5) in treatment group j (with or without decontamination) at time t (1, 3, or 7 h), μ is an overall constant, and ε_{ijt} is the random error left unexplained by the model, assumed to be normally distributed with mean 0 and variance σ^2.

The model included a fixed effect for type of treatment (with or without decontamination) and time (number of hours after application). A treatment by time interaction effect was also included if significant. For the TIC analysis, the interaction term was significant for all TIC and material combinations except for DMMP on carpet. The model above was fit in SAS® v9.1 using PROC GLM. Model diagnostics were evaluated to assure that there were no outliers, that the residuals were approximately normally distributed about the effect means, and that the assumption of consistent variance

Table 4-5. Mean Recovery of TICs from Building Materials over Time With and Without Sabre ClO_2 Fumigant Decontamination

TIC	Material	Time (n)	Mean Recovery, % ± SD[a]	
			Without decontamination	With decontamination
DMMP	Carpet	0 h (n = 3)	97 ± 4	84 ± 9[b]
		1 h (n = 5)	32 ± 2	36 ± 5
		3 h (n = 5)	24 ± 3	24 ± 5
		7 h (n = 5)	15 ± 3	19 ± 3
	Ceiling tile	0 h (n = 3)	102 ± 2	105 ± 1[b]
		1 h (n = 5)	40 ± 4	31 ± 2
		3 h (n = 5)	28 ± 1	16 ± 1
		7 h (n = 5)	13 ± 1	9.1 ± 0.4
Malathion	Carpet	0 h (n = 3)	112 ± 15	95 ± 3[b]
		1 h (n = 5)	100 ± 3	72 ± 3
		3 h (n = 5)	102 ± 3	49 ± 4
		7 h (n = 5)	98 ± 1	23 ± 2
	Laminate	0 h (n = 3)	125 ± 1	105 ± 16[b]
		1 h (n = 5)	126 ± 15	30 ± 20
		3 h (n = 5)	115 ± 7	3.4 ± 1.6
		7 h (n = 5)	118 ± 13	0.4 ± 0.2

a) Calculated using Eq (6)

b) 0 h coupons were positive controls that were not exposed to fumigation

for the groups was appropriate. For DMMP on ceiling tile and malathion on laminate, the variability in recovery from replicate coupon at a given treatment and variability in time means was too large to meet the homogeneous error variance assumption of the model above. Instead, these data were fit to a heterogeneous variance model with the same effects but with separate variance terms for each treatment group and time. This model was fit in PROC MIXED.

From the model output, mean recovery and corresponding confidence intervals were calculated for each treatment and time. The difference (and corresponding confidence interval) in mean recovery between the two treatments (with and without decontamination) was calculated at each time point. The three time point comparisons between the treatment groups were evaluated at joint 95% confidence. Using a Bonferroni approach, this resulted in each separate time point comparison being made at 98.3% confidence. The exception here was for DMMP on carpet, where the lack of a significant interaction term meant that a single estimated comparison (at 95% confidence) of with and without decontamination applied to all three time points.

Table 4-6 shows the statistically-modeled, Eq (11), recovery results and the resulting calculation of decontamination efficacy. For the ANOVA modeling, the recovery data, shown in Table 4-6, were normalized relative to the recovery from the 0 h positive control, i.e., the recovery for 0 h positive controls is assumed to be 100%. The decontamination efficacy values are calculated with reference to the equivalent recovery in the humid air control chamber

tests so as to account for the efficacy due solely to the fumigant ClO_2. Those results where there was a statistically significant difference between decontamination and without decontamination are highlighted in bold.

Recoveries of DMMP from carpet coupons with and without exposure to the Sabre ClO_2 fumigant decontamination steadily declined over the 7 h of testing. There were no statistically significant differences between recoveries of DMMP from carpet coupons without decontamination compared to the recoveries from coupons with decontamination. No decontamination efficacy was observed for ClO_2 fumigation of DMMP on carpet.

Recoveries of DMMP from ceiling tile coupons with and without exposure to the Sabre ClO_2 fumigant decontamination steadily declined over the 7 h of testing. The Sabre decontamination recoveries were slightly lower than the recoveries without decontamination, and the difference was statistically significant at each test point. Although statistically significant, the small differences may not be of practical significance.

For malathion on carpet, the Sabre ClO_2 fumigant decontamination resulted in a steady decline from 76% at 1 h to 24% recovery at 7 h. Coupons without decontamination showed very little reduction in recovery over the 7 h of testing, with recoveries being in excess of 90% over this time period. The Sabre decontamination recovery was therefore statistically significantly less than the recovery without decontamination for all three time periods.

Table 4-6. Statistically Modeled, Eq (11), Percent Recovery of TICs With and Without Sabre ClO_2 Fumigant Decontamination and Decontamination Efficacy

TIC	Material	Time	Recovery, % (Confidence Interval)		Decontamination Efficacy, %[a]
			Without decontamination	With decontamination	
DMMP	Carpet[b]	1 h	35 (33–38)	42 (40–45)	No efficacy[c]
		3 h	23 (20–25)	30 (27–32)	No efficacy
		7 h	15 (13–18)	22 (20–25)	No efficacy
	Ceiling tile[d]	1 h	39 (30–48)	30 (26–34)	**23%** [e]
		3 h	28 (25–30)	15 (14–16)	**46%**
		7 h	12 (10–15)	8.7 (8.1–9.3)	28%
Malathion	Carpet[d]	1 h	89 (86–93)	76 (73–80)	**15%**
		3 h	90 (87–94)	51 (48–55)	**43%**
		7 h	87 (83–91)	24 (20–27)	**72%**
	Laminate[d]	1 h	100 (80–121)	28 (-4.7–61)	**72%**
		3 h	91 (82–101)	3.3 (0.5–6.0)	**96%**
		7 h	94 (76–112)	0.4 (0.1–0.7)	**99.6%**

a) Calculated using Eq (8)

b) Intervals are 95% confidence

c) No decontamination efficacy demonstrated; recovery with decontamination greater than recovery without decontamination

d) Intervals are 98.33% confidence to control error rate at 5% for all three time point comparisons of treatment to control with the TIC and material combination

e) Decontamination efficacy shown in bold indicates a statistically significant difference in recovery with and without decontamination ($p \leq 0.05$)

For malathion on laminate, the Sabre ClO$_2$ fumigant decontamination resulted in a rapid decline from 28% at 1 h to 0.4% recovery at 7 h. Coupons without decontamination showed very little reduction in recovery over the 7 h of testing, with recoveries in excess of 90% over this time period. The Sabre decontamination recovery was therefore statistically significantly less than the recovery without decontamination for all three time periods. These trends are shown graphically in Figures 4-1 and 4-2 for DMMP and malathion, respectively.

The Sabre ClO$_2$ fumigation was shown to be more effective at removing malathion than DMMP. Sabre ClO$_2$ fumigation exhibits a significant and potentially useful level of decontamination efficacy against malathion on both carpet and laminate. There were differences between carpet and laminate in the ClO$_2$ decontamination efficacy against malathion. The results show that Sabre ClO$_2$ exhibits little or no potentially useful decontamination efficacy against DMMP on either carpet or ceiling tile.

S Denotes persistance statistically significantly less with Sabre ClO$_2$ fumigation decontamination

Figure 4-1. Statistically Modeled Percent Recovery Data for DMMP on Coupons With and Without Sabre ClO$_2$ Fumigant Decontamination (Error Bars Show 95% Confidence Interval)

S Denotes recovery statistically significantly less with Sabre ClO$_2$ fumigant decontamination
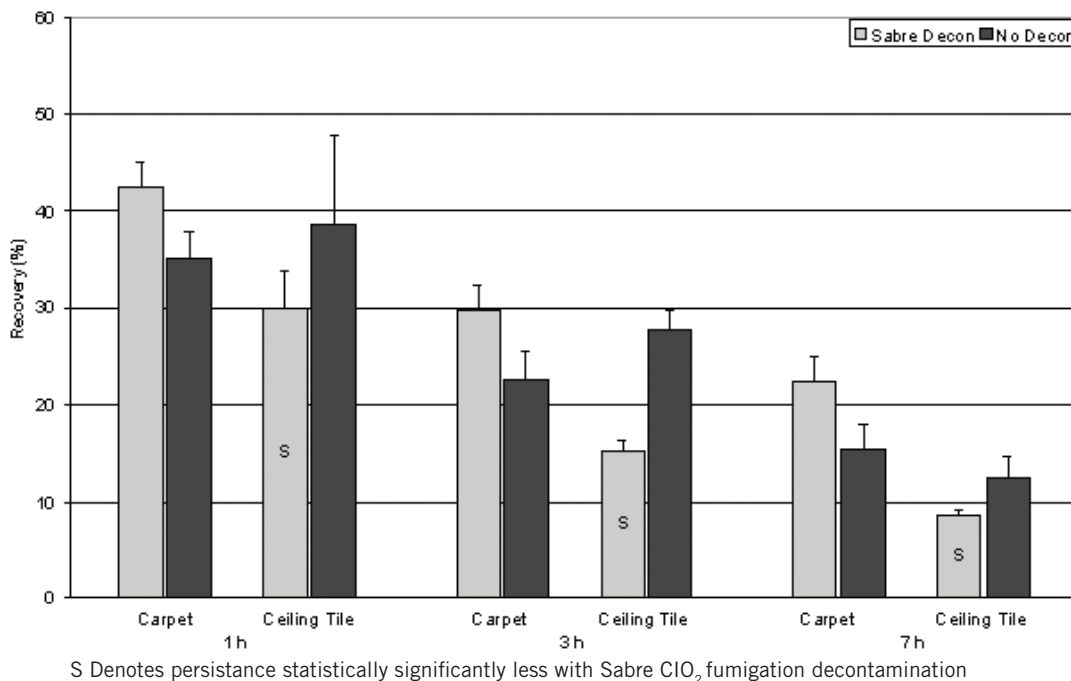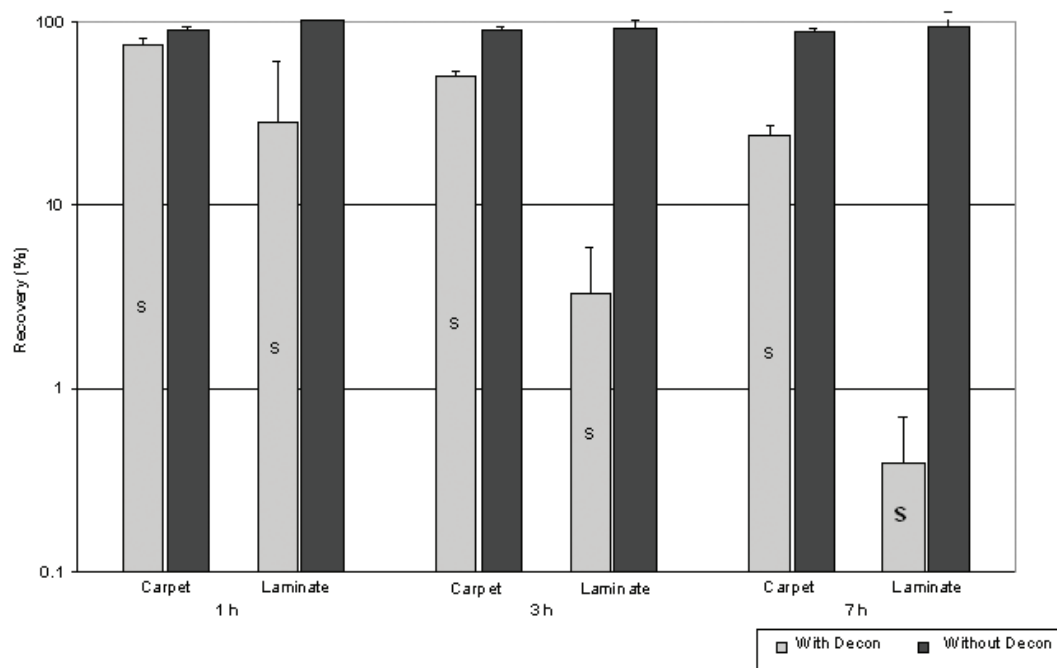
Figure 4-2. Statistically Modeled Percent Recovery Data for Malathion on Coupons With and Without Sabre ClO$_2$ Fumigant Decontamination (Error Bars Show 95% Confidence Interval)

4.1.5 TICs on Laboratory, Handling, and Procedural Blank Coupons

There were three different types of blank coupons employed in the investigation of the Sabre decontamination technology. The laboratory blank coupon of each material was taken from storage directly to an extraction vial and was not exposed to the fume hood where the TICs were spiked. The handling blanks were placed in the fume hood during sample spiking and were then loaded into vials and sealed. At the designated times when coupons were removed from the chamber, one of these handling blanks was also removed from its sealed vial for extraction. The procedural blanks were also placed in the fume hood during sample spiking. These blank coupons were then placed into the test chambers along with the spiked samples, exposed to the fumigation treatment, and removed at the designated times with deliberately spiked coupons.

The levels of the TICs on the laboratory, handling, and procedural blank coupons are listed in Table 4-7. Due to similarity in levels on the laboratory and handling blanks, these data were averaged. Because the procedural blanks show specific trends in the transfer and deposition of material to clean surfaces in the chamber, the procedural blank data are presented individually for the experiments with or without decontamination, and also individually for each sampling time.

As described previously, the laboratory and handling coupons were never in the chamber, while the procedural coupons were blank coupons that were placed in the chamber at the beginning of an experiment. Any level of TIC found on a procedural blank coupon above the handling coupon blank level had to have arisen from redistribution of TICs in the chamber. The levels of DMMP recovered from the procedural blanks were approximately 10 fold higher than the background levels recovered from the laboratory and handling blanks. This appears to arise from volatilization of DMMP from spiked coupons and redeposition onto initially clean surfaces in the test or control chamber. Higher levels of DMMP were recovered from ceiling tile (12.0 µg) than carpet (3.41 µg) after being exposed to the fumigation treatment for 7 h. The recovery of DMMP from procedural blanks did not impact recovery calculations. However, the contamination was recorded and analyzed as an experimental result. No corrective action was deemed necessary.

For malathion, which is considerably less volatile than DMMP, the malathion detected on the procedural blanks was within 2 SD of the mean mass measured on the handling and laboratory blanks (not significantly different).

Because there was only one procedural blank coupon at each sampling interval, it is difficult to determine whether there was a statistical difference in the levels found on these coupons for coupons collected with and without the ClO_2 decontamination — with exception of DMMP on the ceiling tile coupons. The mass of DMMP recovered from procedural blank coupons subjected to decontamination were approximately two to three times lower than the amounts recovered from similar procedural blank coupons that were not subjected to decontamination.

Table 4-7. Mean TIC Levels on Laboratory, Handling, and Procedural Blank Coupons

TIC	Material	Time	Mean Mass on Lab/Handling Blanks, µg	
DMMP	Carpet	0–7 h	0.20 ± 0.34 (n = 8)	
DMMP	Ceiling tile	0–7 h	0.16 ± 0.04 (n = 8)	
Malathion	Carpet	0–7 h	0.65 ± 0.43 (n = 8)	
Malathion	Laminate	0–7 h	0.06 ± 0.06 (n = 8)	
			Mean Mass on Procedural Blanks, µg	
			Without Decontamination	**With Decontamination**
DMMP	Carpet	1 h	2.14	1.81
DMMP	Carpet	3 h	2.79	2.35
DMMP	Carpet	7 h	3.32	3.41
DMMP	Ceiling tile	1 h	17.0	6.22
DMMP	Ceiling tile	3 h	26.7	11.7
DMMP	Ceiling tile	7 h	31.87	12.0
Malathion	Carpet	1 h	1.37	0.97
Malathion	Carpet	3 h	1.24	1.00
Malathion	Carpet	7 h	1.20	0.97
Malathion	Laminate	1 h	ND, <0.05[a]	0.07
Malathion	Laminate	3 h	ND, <0.05	0.22
Malathion	Laminate	7 h	ND, <0.05	0.25

a) ND = not detected; less than stated MDL

4.1.6 TICs in Chamber Air

The concentrations of the TICs in the vapor phase of the test chamber under near-static conditions are listed in Table 4-8. This air concentration is also listed as a percentage of mass applied onto the coupons.

The relatively high air level of DMMP and the relatively low air level of malathion, in the chambers that did not undergo decontamination may be a reflection of the relative vapor pressures of the two TICs. In the decontamination chambers, though, it was evident that the fumigant ClO_2 decreased the amount of both TICs in air. (The higher DMMP concentrations are observed even though the air exchange for malathion was high [one air exchange h^{-1} conditions] compared to the static air conditions for DMMP.) This effect was more pronounced for DMMP since the vapor phase levels were detectable both with and without decontamination. It was interesting to note that with DMMP, fumigant ClO_2 had a greater decontamination effect on vapor phase material than on the residues on the coupons. The recovery of DMMP on the coupons was nearly identical whether exposed to fumigant ClO_2 or not. These air data demonstrated that the fumigant appeared to markedly lower the gas phase levels of DMMP. One caveat applied to the air data collected during decontamination testing is that there were no preliminary recovery tests carried out to determine the stability of the TICs on Tenax® in the presence of vapor phase ClO_2. Thus, these air levels may represent only a portion of the amount present in the chamber.

4.1.7 Detection of Oxidized Malathion Product on Coupons

To evaluate the usefulness of a decontamination procedure against chemical compounds, it is important to determine whether toxic by-products are produced. The extracts of selected carpet and laminate samples were analyzed for the presence of one potential oxidation product of malathion, malathion oxon (or maloxon). In maloxon, the P=S portion of the thiophosphate group on malathion is replaced with P=O, so that the molecule becomes an organophosphate, rather than a thiophosphate. Organophosphates are generally more toxic than the corresponding thiophosphate.

One of each of the three positive controls (spiked with malathion, but not decontaminated) for each coupon type (carpet and laminate) was removed from the chamber after 1, 3, and 7 h and analyzed. Recoveries of maloxon were assumed to be the same as for malathion. Moreover, calibration curves were prepared from maloxon standards and other QC criteria were similar to those applied to the TICs. Maloxon was not detected on any of the positive controls.

In addition, three carpet and three laminate test coupon extracts were similarly analyzed (one each from the 1, 3, and 7 h decontamination tests). For both coupon types, maloxon was detected at levels corresponding to malathion to maloxon conversion percentages that increased in linear proportion to the log of the concentration multiplied by contact time (CT) of ClO_2 to which the coupons were exposed. The results are presented in Table 4-9 and Figure 4-3 (on page 24).

Table 4-8. Mean Concentration of TICs in Test Chamber Air

TIC	Material	Time	Mean Air Concentration, µg m^{-3} (% of Mass Applied)[a, b]	
			Without Decontamination (n = 2)	With Decontamination (n = 2)
DMMP	Carpet	0–1 h	1740 ± 13 (10%)	ND, <3.6 (n = 1) (0.7%)
	Ceiling tile	0–1 h	1430 ± 253 (9%)	484 (n = 1) (2.9%)
Malathion	Carpet	1–3 h	0.42 ± 0.00 (<0.01%)[c]	ND, <0.26 (<0.01%)
	Laminate	1–3 h	0.42 ± 0.00 (<0.01%)[c]	ND, <0.26 (<0.01%)

a) Air concentration expressed as percentage of total amount of TIC in the chamber if there had been no hydrolysis or degradation of the TIC

b) Calculated using Eq (10)

c) This sample was collected from the test chamber under one air exchange h^{-1} conditions; samples were not collected from the test chamber under near-static conditions

Table 4-9. Mean Mass of Malathion Oxidized to Maloxon by Coupon Type and ClO_2 CT

Coupon Type	Decontamination Time, h	ClO_2 CT, ppm-h	Maloxon Recovered, µg	Malathion Converted, µg	% Malathion Oxidized to Maloxon
Carpet	1	3366	78	82	16
	3	9494	143	150	30
	7	21,343	205	215	43
Laminate	1	2926	215	226	45
	3	8941	297	312	62
	7	21,076	338	355	71
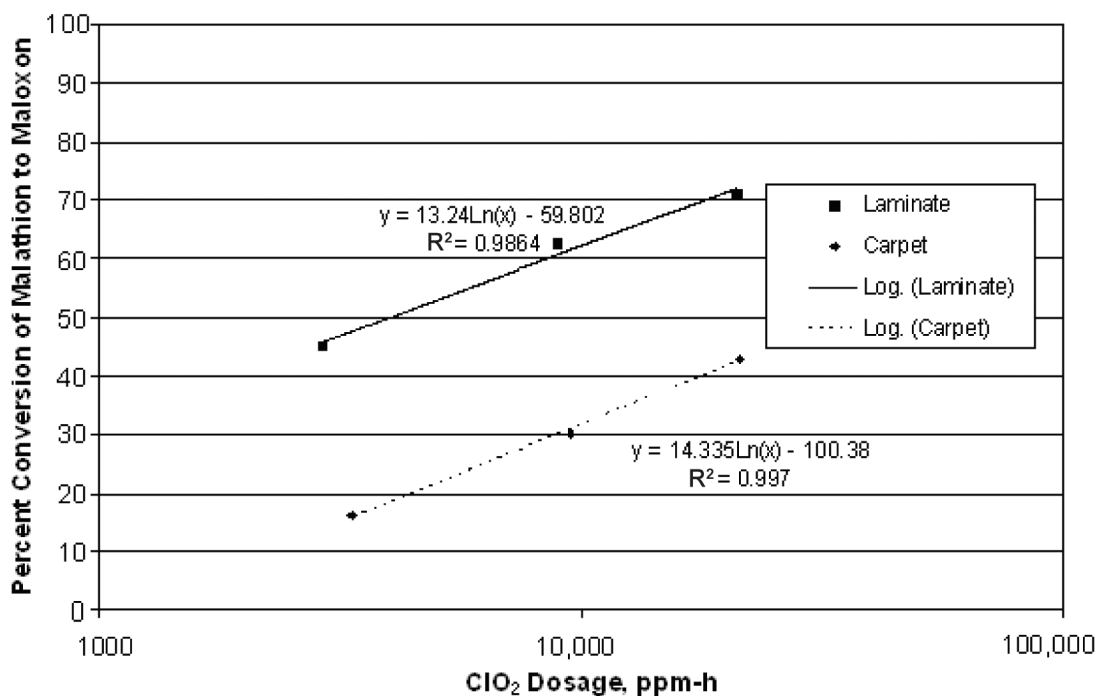
Figure 4-3. Percent Oxidation of Malathion to Maloxon by Coupon Type and ClO_2 Dosage

4.1.8 Condition of ClO_2-Treated Coupons after Six Months

To assess the effect of fumigant ClO_2 on long-term stability and integrity of building materials, eight laboratory blanks (not exposed to ClO_2) and 24 procedural blanks (exposed to ClO_2) were maintained under ambient temperature and RH conditions in open vials for extended periods of time. After three months, and then again after six months, the coupons were inspected to assess any changes in appearance or structural integrity. The coupons were relatively unchanged after three months, and the carpet showed some minor "bleaching" after six months.

4.2 Results for Fumigant ClO_2 Decontamination of CWAs

4.2.1 Analytical Method Results

The recoveries of the CWAs spiked onto the various coupon materials were not replicated after the initial assessment. The analytical method recoveries listed in Table 4-10 (on page 25) are those that were determined prior to decontamination tests, and are presented here as a baseline against which the subsequent decontamination recovery data can be compared.

The approximate MDLs for the CWAs are listed in Table 4-11 (on page 25). Each MDL was estimated based on the peak area of the lowest calibration standard, the signal to noise ratio for this concentration, and the peak area that could be integrated reliably for any peak with the data system.

4.2.2 Recovery over Time of CWAs on Building Materials With and Without Sabre ClO2 Fumigant Decontamination

Side-by-side chambers were installed in the laboratory for these tests, with one chamber (test) having fumigant ClO_2 decontamination and the matching chamber (control) having no ClO_2. The side-by-side design was adopted because of the high volatility of GB and TGD; with this design, any slight variation in laboratory temperature would be eliminated as a variable when assessing decontamination efficacy. A single spiked coupon of each type was analyzed directly after spiking to establish the baseline recovery. The recoveries of the CWAs from coupons at initiation (0 h) and at subsequent times (1 h and 2 or 4 h, depending on CWA) are listed in Table 4-12 (on page 25). The recoveries at initiation (0 h) for TGD from carpet, laminate, and ductwork, and these recoveries of VX from carpet and ductwork do not agree very well with the recoveries shown in Table 4-10 (on page 25) (analytical method recoveries). In theory, these two values should have been very similar. At this time, there is no apparent reason for the difference, and the difference is simply noted here.

In many cases there were measurements made close to the detection limit. When there was at least one detected sample out of the five replicates, the median value of the sample set is reported along with the range, where a non-detectable value is reported as less than the MDL. When all five samples had non-detectable values, the percent recovery was reported as less than the MDL. In addition, the number of non-detected samples in each set of five replicates is also noted in Table 4-12 (on page 25).

Table 4-10. Mean Recovery of CWAs and SRS from Building Materials

Material	Evaporation Time	Mean Recovery from Building Materials, % ± SD[a]		SRS/CWA Recovery Ratio[b]
		CWA	SRS	
		GB	TBP	
Carpet	7 min	91 ± 12	87 ± 14	0.96
		TGD	TBP	
Carpet	5 min	88 ± 18	98 ± 11	1.11
Laminate	5 min	97 ± 8	89 ± 9	0.92
Metal ductwork	5 min	98 ± 11	88 ± 10	0.90
		VX	TBP	
Carpet	5 min	113 ± 9	103 ± 21	0.91
Laminate	5 min	107 ± 6	93 ± 14	0.87
Metal ductwork	5 min	110 ± 6	94 ± 15	0.85

a) Calculated using Eq (4)

b) Calculated using Eq (5)

Table 4-11. MDLs for CWAs

	MDL		
	GB	TGD	VX
In solution	0.1 µg mL^{-1}	0.1 µg mL^{-1}	0.7 µg mL^{-1}
On coupon	1 µg	1 µg	7 µg

Table 4-12. Average Recovery of CWAs from Building Materials over Time With and Without Sabre ClO$_2$ Fumigant Decontamination

CWA	Material	Time, h (n)	Average Recovery, % ± SD[a]	
			Without Decontamination	With Decontamination
GB	Carpet	0 h (n = 1)	87	NA[b]
		1 h (n = 5)	5.1 ± 0.9 (0)[c]	3.6 ± 1.8 (0)[c]
		4 h (n = 5)	4.9 ± 0.2 (0)	2.8 ± 0.9 (0)
TGD	Carpet	0 h (n = 1)	52	NA
		1 h (n = 5)	40 ± 8.7 (0)	15 ± 2.7 (0)
		2 h (n = 5)	30 ± 3.2 (0)	19 ± 8.8 (0)
	Laminate	0 h (n = 1)	89	NA
		1 h (n = 5)	1.3 (<0.1 – 3.6) (1)[e]	5.4 ± 6.1 (0)
		2 h (n = 5)	0.4 (<0.1 – 3.2) (2)[e]	< 0.1 (0.1 – 0.3) (4)[e]
	Ductwork	0 h (n = 1)	73	NA
		1 h (n = 5)	16 ± 5.5 (0)	10 ± 7.9 (0)
		2 h (n = 5)	4.3 ± 1.9 (0)	5.4 ± 6.5 (0)
VX	Carpet	0 h (n = 1)	74	NA
		1 h (n = 5)	77 ± 23 (0)	<0.7 (5)[d]
		4 h (n = 5)	72 ± 7.1 (0)	<0.7 (5)[d]
	Laminate	0 h (n = 1)	94	NA
		1 h (n = 5)	81 ± 7.6 (0)	<0.7 (5)[d]
		4 h (n = 5)	88 ± 5.1 (0)	<0.7 (5)[d]
	Ductwork	0 h (n = 1)	84	NA
		1 h (n = 5)	84 ± 2.6 (0)	<0.7 (5)[d]
		4 h (n = 5)	85 ± 7.6 (0)	<0.7 (5)[d]

a) Calculated using Eq (6) except where non-detects occur, and only the median and range of values is shown

b) NA = not applicable; Time 0 coupons did not have decontamination

c) The number of non-detects is shown in parenthesis

d) All coupons less than stated MDL; value shown is MDL as percentage of mass applied

e) Non-detects occurred – only the median and range of values is shown

Measurable amounts of all CWAs were removed from all building materials with the fumigant ClO_2 treatment. However, for both GB and TGD, there was also a substantial decrease in the amount found on coupons that did not undergo ClO_2 treatment. In these cases, statistical analysis of the data was the only way to accurately assess whether the slight differences could be attributable to the ClO_2 treatment. Other physical processes such as volatilization and redistribution to the chamber and/or aqueous hydrolysis could account for the losses, as both chambers were operated under conditions of 80% RH. The case for VX is much more straight-forward. The VX persisted on the coupons which did not have decontamination treatment, in spite of the high RH of the control chamber; in contrast, VX was not detected on the coupons that were treated with the fumigant ClO_2 process.

The recoveries of GB, TGD, and VX, normalized to the recoveries at 0 h, are presented in Appendix A, Table A-2 of this report. These normalized data were used as the input to the statistical analyses described below. The statistical analyses are more informative than the normalized recovery data, in that they provide insight into whether there is a statistical difference between recoveries with and without decontamination; therefore, to avoid presentation of somewhat repetitive data here in the body of the report, the normalized recovery data are presented in the appendix.

4.2.3 Statistical Analysis of Recovery Trends and Fumigant Decontamination Efficacy

Statistical analysis was performed using recovery values (i.e., measured recovery results normalized to the Time 0 recovery) to evaluate whether there were statically significant differences in the CWA recovered from treated coupons compared to controls. Because the recoveries are normalized to the Time 0 recovery value, it is possible to obtain recovery values that are greater than 100%. Values above 100% were left as calculated, though they should be interpreted in the context they were created, and not truly greater than 100%.

For CWA and material combinations with detectable recoveries on coupons with and without decontamination, an ANOVA model was fit to the data. The model included a fixed effect for type of treatment (with or without decontamination) and time (number of h after application). A treatment by time interaction effect was also included if significant. The model was fit in SAS® v9.1 using PROC MIXED. Model diagnostics were evaluated to assure that there were no outliers, that the residuals were approximately normally distributed about the effect means, and that the assumption of consistent variance for the groups was appropriate.

From the model output, mean recovery and corresponding confidence intervals were calculated for each treatment and time. The difference (and corresponding confidence interval) in mean recovery between the two treatments (with and without decontamination) was calculated at each time point.

The two time point comparisons between the treatment groups were evaluated at joint 95% confidence, so each separate comparison is essentially approximately 97.5% confidence.

For CWA and material combinations with non-detects, e.g., TGD on laminate, the ANOVA approach is not appropriate since the data are censored and may violate the assumptions of normality and constant variance. Instead, a less constrained non-parametric analysis was performed. Consistent with this type of analysis, median (rather than mean) recovery was reported for each treatment and time point. In cases where the median value was a non-detect (i.e., three or more of the five replicate coupons were non-detects), the results are reported as "ND <MDL". To assess the effectiveness of the treatment at each time point, the median recovery with and without the Sabre decontamination were compared using the Wilcoxon-Mann-Whitney test to determine whether the observed median with decontamination is significantly different from the median without decontamination. The Wilcoxon-Mann-Whitney test uses ranks of data to test whether two samples are significantly different. A corresponding estimate of the shift in recovery and accompanying 95% confidence interval were formed with the Hodges-Lehmann procedure which is appropriate for rank order data, such as the medians. These statistical estimates were performed in StatXAct® v7. To perform this analysis, non-detect values were set equal to half the MDL. To estimate the decontamination efficacy when the CWA was not detected, the MDL was used in the calculation.

Table 4-13 (on page 27) shows the recovery results, with the confidence interval, from the statistical analysis. The table also shows the decontamination efficacy for Sabre decontamination as compared with exposure of the CWAs to humidified air (without decontamination). Those results where there was a statistically significant difference between decontamination and no decontamination are highlighted in bold.

For GB and TGD on carpet, and TGD on metal, the results were obtained with the ANOVA approach defined above. The recovery for GB on carpet was low for coupons with and without fumigant ClO_2 decontamination at both 1 and 4 h. However, the recovery with decontamination was statistically less than without decontamination so that it can be concluded the fumigant ClO_2 decontamination was more effective than no decontamination (2.1 percentage points at 1 h and 2.2 percentage points at 4 h).

The recovery of TGD on carpet was statistically significantly less (48 percentage points at 1 h and 21 percentage points at 2 h) in the coupons with fumigant ClO_2 decontamination than without decontamination.

The recovery of TGD on metal decreased over time for both the fumigant ClO_2 decontaminated coupons and the coupons without decontamination. The recovery with ClO_2 decontamination was not statistically significantly different than recovery without decontamination.

Table 4-13. Statistically Modeled, Eq (11), Percent Recovery of CWAs With and Without Sabre ClO_2 Fumigant Decontamination and Decontamination Efficacy

CWA	Material	Time	Recovery, % (Confidence Interval)		Decontamination Efficacy, %[a]
			Without Decontamination	With Decontamination	
GB	Carpet[b]	1 h	6.1 (5.1-7.1)	4.0 (2.9-5.0)	**34%[c]**
		4 h	5.6 (4.5-6.6)	3.4 (2.1-4.8)	**39%**
TGD	Carpet[b]	1 h	77 (63-91)	29 (15-43)	**62%**
		2 h	57 (43-71)	36 (21-50)	**37%**
	Laminate[d]	1 h	1.4	3.2	No efficacy[e]
		2 h	0.5	ND, <0.1[f]	No efficacy[g]
	Ductwork[b]	1 h	21 (13-30)	14 (4.7-23)	No efficacy[g]
		4 h	5.9 (0-15)	7.4 (0-16)	No efficacy[e]
VX	Carpet[d]	1 h	102	ND, <0.7	**>99%**
		4 h	97	ND, <0.7	**>99%**
	Laminate[d]	1 h	89	ND, <0.7	**>99%**
		4 h	91	ND, <0.7	**>99%**
	Ductwork[d]	1 h	99	ND, <0.7	**>99%**
		4 h	105	ND, <0.7	**>99%**

a) Calculated using Eq (6)

b) Reported values are least square means; intervals are joint 95% confidence across time points for the combination of the CWA and the material

c) Decontamination efficacy shown in bold indicates a statistically significant difference in recovery with and without decontamination (p ≤ 0.05)

d) Reported values are medians; ND denotes median value is a non-detect; difference interval is Hodges-Lehmann median shift interval of 95% confidence

e) No decontamination efficacy demonstrated; recovery with decontamination greater than recovery without decontamination

f) ND = not detected; less than coupon MDL converted to percentage of spike amount

g) No statistically significant decontamination demonstrated

For TGD on laminate, and VX on carpet, laminate, and metal, the results were obtained with the nonparametric approach described above.

TGD on laminate exhibited almost complete removal at both time points for coupons with and without fumigant ClO_2 decontamination. No statistically significant difference in recovery was observed for the decontaminated coupons compared to the coupons without ClO_2 decontamination at time 1 h (p=0.15) or at 2 h (p=0.17).

For VX on carpet, metal, and laminate, the coupons without decontamination exhibited very high recovery at each time point, while the fumigant ClO_2 decontaminated coupons showed removal to below the MDL in every case. With p-values of 0.008 for each comparison, the recovery under the fumigant ClO_2 decontamination was statistically significantly less than the recovery without decontamination. The estimated median differences in fumigant ClO_2 decontamination reduction of VX recovery range from 88 percentage points (VX, laminate, 1 h) to 105 percentage points (VX, metal, 4 h).

The recovery of GB, TGD, and VX on the different materials is shown graphically in Figures 4-4, 4-5, and 4-6, respectively (on pages 28 amd 29).

S Denotes recovery statistically significantly less with Sabre ClO$_2$
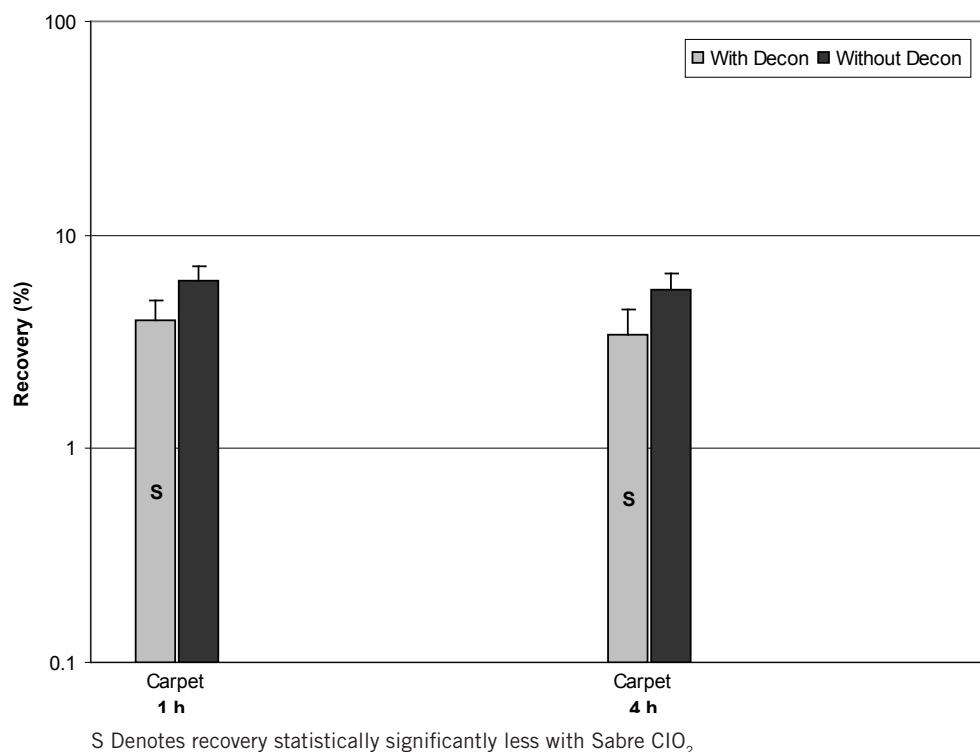
Figure 4-4. GB Recovery (%) on Coupons With and Without Sabre ClO$_2$ Fumigant Decontamination (Error Bars Show 95% Confidence Interval)
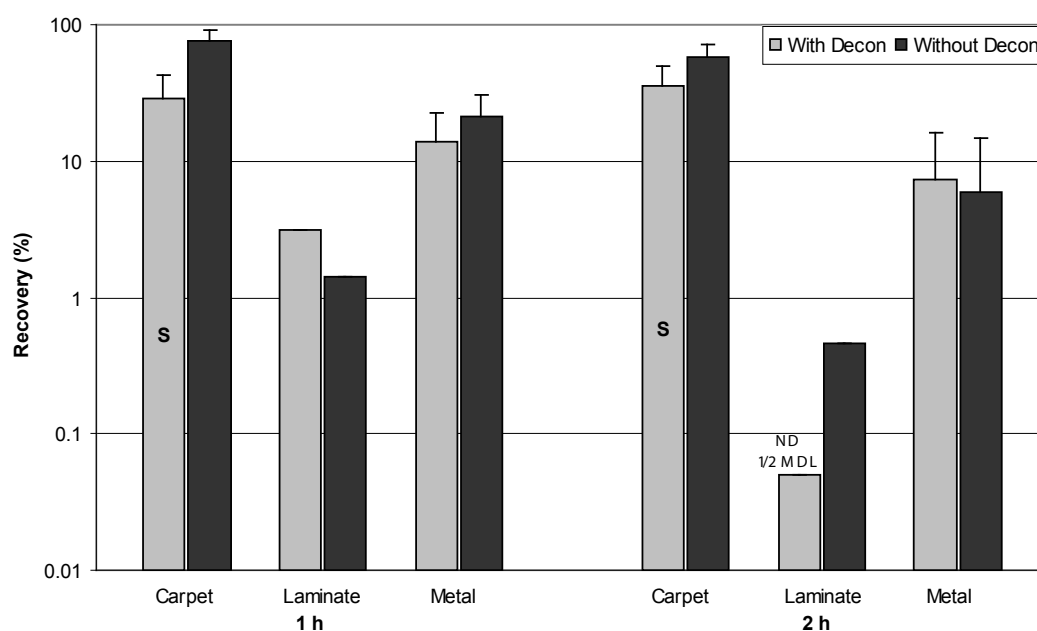
Values shown without errors bars are medians rather than means due to nonparametric statistical model fit to data with non-detects.

S Denotes recovery statistically significantly less with Sabre ClO$_2$ fumigant decontamination

Figure 4-5. TGD Recovery (%) on Coupons With and Without Sabre ClO$_2$ Fumigant Decontamination (Error Bars Show 95% Confidence Interval)
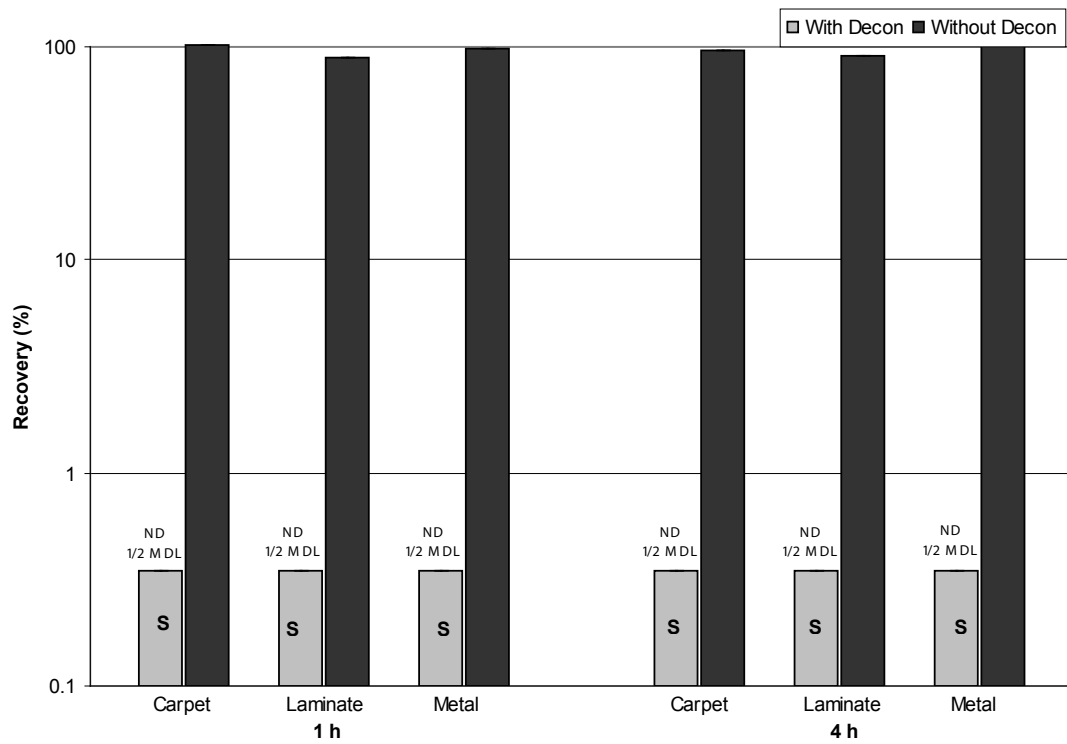
Values shown are medians rather than means due to nonparametric statistical model fit to data with non-detects.

S Denotes recovery statistically significantly less with Sabre CIO$_2$ fumigant decontamination

Figure 4-6. VX Recovery (%) on Coupons With and Without Sabre CIO$_2$ Fumigant Decontamination

4.2.4 CWAs on Laboratory and Procedural Blank Coupons

There were two different types of blank coupons employed in the investigation of the Sabre decontamination technology. The laboratory blank coupon of each material was taken from storage directly to an extraction vial and was not exposed to the fume hood where the TICs were spiked. The procedural blanks were placed in the fume hood during sample spiking. These blank coupons were then placed into the test chambers along with the spiked samples, and removed at the designated times with coupons. These procedural blanks were expected to show the extent to which volatilization and redeposition onto other surfaces may account for some of the losses from coupons. Table 4-14 shows the amounts of the CWAs measured on these different blanks.

As was observed with the TICs, the data in Table 4-14 indicate that GB and TGD, which are more volatile than VX, may migrate from the initially spiked coupons to other surfaces in the chamber, including the procedural blank coupons. For TGD, the carpet coupons absorbed considerably more than the laminate or ductwork coupons.

4.2.5 Concentration of ClO_2 in Test Chambers

The concentrations of ClO_2 measured in the test chambers during decontamination of the three different CWAs are listed in Table 4-15.

Table 4-14. Comparison of Mean CWA Levels on Laboratory and Procedural Blank Coupons

CWA	Material	Time	Mean Mass on Blank, µg		
			Without Decontamination		With Decontamination
			Laboratory Blank	Procedural Blank	Procedural Blank
GB	Carpet	0 h	ND, <1[a]	NT[b]	NT
		1 h	NT	17	5.1
		4 h	NT	31	7.8
TGD	Carpet	0 h	ND, <1	NT	NT
		1 h	NT	66	17
		2 h	NT	179	27
	Laminate	0 h	ND, <1	NT	NT
		1 h	NT	ND, <1	ND, <1
		2 h	NT	ND, <1	ND, <1
	Ductwork	0 h	ND, <1	NT	NT
		1 h	NT	ND, <1	ND, <1
		2 h	NT	ND, <1	ND, <1
VX	Carpet	0 h	ND, <7	NT	NT
		1 h	NT	ND, <7	ND, <7
		4 h	NT	6.6	ND, <7
	Laminate	0 h	ND, <7	NT	NT
		1 h	NT	ND, <7	ND, <7
		4 h	NT	4.7	ND, <7
	Ductwork	0 h	ND, <7	NT	NT
		1 h	NT	ND, <7	ND, <7
		4 h	NT	ND, <7	ND, <7

a) ND = not detected; less than stated MDL

b) NT = not tested at this time

Table 4-15. Mean Concentration of ClO_2 in Test Chamber for CWA Decontamination Tests

CWA	Time	Mean ClO_2 Concentration, ppm
GB	0–1 h	3100 ± 0 (n = 2)
	0–4 h	2960 ± 80 (n = 6)
TGD	0–2 h	3020 ± 140 (n = 8)
VX	0–1 h	3120 ± 100 (n = 4)
	0–4 h	3070 ± 170 (n = 9)

4.3 Results for Liquid Decontamination of CWAs

4.3.1 Recovery of CWAs from Liquid Decontamination Solutions

Initial tests were conducted to determine whether CWAs could be effectively recovered from liquid decontamination solutions or from neutralized liquid decontamination solutions. The purpose of the method development was to determine (1) the maximum percentage of spiked CWA that could be recovered from neutralized decontamination solution and (2) the percentage of spiked CWA recovered after 1 h in the decontamination solution. High recovery from the neutralized decontamination solution would indicate that the neutralization was effective and could be used to end the loss/degradation of the CWA caused by the decontamination solution. A high recovery of CWA from the decontamination solution after 1 h of contact would suggest that the decontamination was ineffective against the CWA.

Recovery of GB, TGD, and VX from 10% bleach (0.6% hypochlorite) and 3000 ppm ClO_2 was tested, as was recovery from neutralized solutions that were created via addition of sodium thiosulfate to the bleach or ClO_2 solutions. CWAs were held in decontamination solutions for 1 h prior to addition of hexane for extraction and the addition of the SRS; the CWAs were held in the neutralized solutions for only 15 sec before addition of the SRS and hexane. The SRS (TBP used as SRS for all three CWAs) was spiked into the liquid decontamination or neutralized decontamination solution just prior to addition of hexane. Contact time for the SRS with any solution was approximately 15 sec. The results of these tests are shown in Table 4-16.

This investigation produced unexpected results. Clearly, the SRS is not completely similar to the CWAs in physico-chemical properties. Either by virtue of slower aqueous hydrolysis or greater solubility in hexane, it is almost fully recovered from the neutralized solutions (neutralized bleach and neutralized ClO_2). In contrast, recovery of GB and VX from neutralized solutions was less than 10%, and in some cases these compounds were not recovered at all; TGD recovery was approximately 50% from the neutralized

solutions. Volatilization from the aqueous solution, rapid hydrolysis and/or poor extraction efficiency into hexane might explain the low recoveries of the CWAs from the neutralized solutions.

When comparing recoveries from neutralized solutions versus oxidant solutions, it appears that bleach is clearly effective in decontamination of TGD. The other cases are somewhat ambiguous because of the potential effect of aqueous hydrolysis or poor extraction efficiency. Because of the possibility that the small, polar CWAs were preferentially retained in the aqueous solution over the hexane, the decision was made to conduct liquid decontamination tests with coupons that would be removed from the liquid before extraction. In addition, the decision was made to collect and record the SRS recovery values (not reported here), but not to correct CWA recovery by the SRS recovery, as they appear to be quite dissimilar in recovery from aqueous media. The data suggest that SRS correction for recovery would not be useful.

4.3.2 Recovery over Time of CWAs on Building Materials With and Without Liquid Decontamination

The recovery of CWAs from building materials immersed in bleach or ClO_2 solutions was evaluated using decontamination times of 10 to 30 min because the results described in Section 4.3.1 suggested that complete decontamination could be expected in less than 1 h. In the preliminary solution tests described in Section 4.3.1, no efficacy of liquid ClO_2 was observed against GB or TGD. Therefore, the decontamination of CWAs by liquid ClO_2 was only tested against VX. In parallel with the VX tests, spiked coupons were placed in vials containing slightly acidic water (pH = 4.5–7). This differed from the liquid bleach decontamination testing where coupons not undergoing decontamination were placed in sealed vials without any liquid solution; initial tests showed that CWAs were largely destroyed by, or not recovered from, aqueous solution. Coupons without liquid ClO_2 decontamination were placed in slightly acidified water (pH comparable to the ClO_2 solution) with the hope that VX, which is known to be especially prone to hydrolysis under basic conditions, might be more stable in an acidic aqueous condition.

Table 4-16. Mean Recovery of CWAs and SRS from Liquid Decontamination Solutions

Solution - Hold Time Before SRS Addition and Hexane Extraction	Mean Recovery, % ± SD (n = 3)					
	CWA			SRS Recovered From CWA Solution		
	GB	TGD	VX	TBP (from GB)	TBP (from TGD)	TBP (from VX)
Bleach - 1 h	ND, <0.1	ND, <0.1	ND, <0.7	96 ± 3	96 ± 2	97 ± 2
Neutralized bleach - 15 sec	1 ± 0	41 ± 10	ND, <0.7	87 ± 1	84 ± 2	86 ± 3
ClO_2 - 1 h	8 ± 2	58 ± 5	ND, <0.7	91 ± 2	93 ± 1	89 ± 3
Neutralized ClO_2 - 15 sec	8 ± 1	56 ± 10	ND, <0.7	75 ± 8	70 ± 23	60 ± 3

ND = not detected

Tables 4-17 and 4-18 show the recoveries of CWA from spiked coupons without decontamination (i.e., stored in sealed vials in air for the duration of the decontamination period), in acidified water, or in decontamination solutions (bleach or ClO_2 solution), showed significant loss of VX; and VX was not recovered from any coupon with liquid ClO_2 decontamination. Table 4-17 reports recoveries as a percentage of the mass of CWA spiked onto the coupons. Table 4-18 (on page 33) reports recoveries as a percentage of the Time 0 recoveries from spiked coupons.

In all cases with 30 min of the decontamination regimen, the CWAs were at non-detectable levels or had recoveries of less than one percent. These are impressive results, especially for the highly sorptive and large surface area carpet material.

While these results show that there are non-detectable levels on the building material, this investigation did not explore the mechanism of this disappearance. The CWA may have undergone aqueous hydrolysis, in which case water might have been an equally effective decontamination agent. Alternatively, the CWAs may have been soluble in the bleach but not degraded. To fully understand the ramifications of this decontamination method, it may be necessary to measure both the CWAs and their degradation products directly (i.e., without extraction into organic solvent) in the decontamination solution.

Because there was no effective control for the CWA solubility and/or aqueous hydrolysis, the decontamination efficacy of the bleach (specifically ClO^-) was not calculated. Similarly,

Table 4-17. Mean Recovery of CWAs from Building Materials after Various Treatments as Percent of Mass Applied

CWA	Material	Time	Mean CWA Recovery, % of Mass Applied[e] ± SD (n = 5)			
			Without Decontamination	Acidified Water	Bleach Decontamination	ClO_2 Decontamination
GB	Carpet	0 min	75 ± 5	Not tested; not included in test/QA plan for baseline bleach testing.	NA[a]	Not tested because no significant efficacy observed in solution testing.
		10 min	70 ± 5		ND, <0.1[b]	
		20 min	66 ± 7		ND, <0.1	
		30 min	63 ± 1		ND, <0.1	
TGD	Carpet	0 min	38 ± 4		NA	
		10 min	46 ± 13		ND, <0.1	
		20 min	53 ± 12		ND, <0.1	
		30 min	51 ± 18		ND, <0.1	
	Laminate	0 min	62 ± 13		NA	
		10 min	56 ± 6		2.3 ± 1.2	
		20 min	48 ± 9		1.1 ± 1.0	
		30 min	47 ± 10		0.1 ± 0.03	
	Ductwork	0 min	38 ± 15		NA	
		10 min	49 ± 15		1.2 ± 0.7	
		20 min	41 ± 17		0.2 ± 0.3	
		30 min	34 ± 11		0.3 ± 0.5	
VX	Carpet	0 min	84 ± 5	77 ± 4 [a]	NA	NA[b]
		10 min	NT[c]	4.5 ± 1.1	ND, <0.7	ND, <0.7[d]
		20 min	NT	1.7 ± 0.4	ND, <0.7	ND, <0.7
		30 min	90 ± 6	2.5 ± 0.5	ND, <0.7	ND, <0.7
	Laminate	0 min	100 ± 5	111 ± 7	NA	NA
		10 min	NT	2.1 ± 0.2	ND, <0.7	ND, <0.7
		20 min	NT	2.8 ± 1.4	ND, <0.7	ND, <0.7
		30 min	102 ± 6	1.9 ± 0.3	ND, <0.7	ND, <0.7
	Ductwork	0 min	101 ± 10	105 ± 8	NA	NA
		10 min	NT	0.5 ± 0.2	ND, <0.7	ND, <0.7
		20 min	NT	ND, <0.07	ND, <0.7	ND, <0.7
		30 min	96 ± 11	ND, <0.07	ND, <0.7	ND, <0.7

a) NA = not applicable; no decontamination done at Time 0

b) ND = not detected; less than MDL converted to equivalent percentage

c) NT = not tested at this time interval

d) n = 4; one outlier

e) Recovery for individual coupons calculated in the same manner as analytical method recovery efficiency, Eq (4) for each individual coupon. The mean and SD of the recoveries for a given condition are reported here.

there was no statistical modeling of the recovery. The raw data do, however, suggest that the decontamination with aqueous bleach was very effective.

Because the initial tests showed that CWAs were largely destroyed by, or not recovered from, aqueous solution, the control samples (without decontamination) were not placed in a liquid solution. Instead, the spiked coupons that did not receive the decontamination technology were allowed to remain in the laboratory fume hood until they were retrieved for extraction. Coupons were withdrawn from the liquid decontamination bath and the fume hood at nearly the same times. The wet coupons were shaken lightly to remove excess liquid, spiked with the SRS and then placed in the extraction vial with hexane for extraction. The recoveries

of the CWAs mirrored the results obtained for the initial 1 h decontamination tests in that the CWAs were not recovered. However, this time, solubility in water cannot be suspected as the cause.

The recoveries of VX on these coupons, normalized to the recoveries at 0 h, are presented in Appendix A, Table A-3 of this report. These normalized data were used as the input to the statistical analyses described below. The statistical analyses are more informative than the normalized recovery data, in that they provide insight into whether there is a statistical difference between recoveries with and without decontamination; therefore, to avoid somewhat repetitive data, the normalized recovery data are presented in the appendix.

Table 4-18. Mean Recovery of CWAs from Building Materials After Various Treatments as Percent of T0 Recovery

CWA	Material	Time	Normalized CWA Recovery, % of Mass Recovered at Time 0[d] ± SD (n = 5)			
			Without Decontamination	Acidified Water	Bleach Decontamination	ClO_2 Decontamination
GB	Carpet	10 min	93 ± 7		ND, <0.1[a]	
		20 min	88 ± 9		ND, <0.1	
		30 min	84 ± 2		ND, <0.1	
TGD	Carpet	10 min	121 ± 33	Not tested; not included in test/QA plan for baseline testing.	ND, <0.1	Not tested because no significant efficacy observed in solution testing.
		20 min	139 ± 31		ND, <0.1	
		30 min	135 ± 47		0.1 ± 0.03	
	Laminate	10 min	90 ± 10		3.7 ± 1.9	
		20 min	77 ± 14		1.7 ± 1.7	
		30 min	77 ± 16		0.2 ± 0.1	
	Ductwork	10 min	130 ± 39		3.2 ± 1.9	
		20 min	109 ± 44		0.5 ± 0.7	
		30 min	91 ± 28		0.8 ± 1.2	
VX	Carpet	10 min	NT[b]	5.0	ND, <0.7	ND, <0.7[c]
		20 min	NT	2.2	ND, <0.7	ND, <0.7
		30 min	107 ± 7	3.3	ND, <0.7	ND, <0.7
	Laminate	10 min	NT	1.9	ND, <0.7	ND, <0.7
		20 min	NT	1.9	ND, <0.7	ND, <0.7
		30 min	102 ± 6	1.7	ND, <0.7	ND, <0.7
	Ductwork	10 min	NT	ND, <0.7	ND, <0.7	ND, <0.7
		20 min	NT	ND, <0.7	ND, <0.7	ND, <0.7
		30 min	95 ± 11	ND, <0.7	ND, <0.7	ND, <0.7

a) ND = not detected, less than MDL converted to equivalent percentage

4.3.3 Statistical Analysis of Recovery Trends and Liquid Decontamination Efficacy

Statistical analysis was performed on the recovery results. For this investigation, liquid ClO_2 decontamination was compared to coupons in acidified water. The residual VX on the surfaces was below the MDL for some samples without decontamination. For coupons with decontamination, VX was below the detection limit for every material (carpet, laminate, and ductwork). For this type of data, it is not appropriate to fit an ANOVA statistical model, since the data are censored and may violate the assumptions of normality and constant variance in an ANOVA. Instead, a less constrained non-parametric analysis was performed. Consistent with this type of analysis, median (rather than mean) recovery was reported for each treatment, material, and time point. In cases where the median value was a non-detect (i.e., three or more of the five replicate coupons were non-detects), the results are reported as "ND <MDL". To assess the effectiveness of the treatment at each time point within each material, the median recovery with the ClO_2 liquid decontamination and in acidified water were compared using the Wilcoxon-Mann-Whitney test. A corresponding estimate of the shift in recovery and accompanying 95% confidence interval were formed with the Hodges-Lehmann procedure. These statistical estimates were performed in StatXAct® v7. To perform this analysis, non-detect values were set equal to half the MDL.

Table 4-19 shows the recovery results from the statistical analysis. To calculate the decontamination efficacy, the MDL was used in the calculation.

For VX on carpet and laminate, at each of 10, 20, and 30 min, the median recovery was below the MDL with the ClO_2 liquid decontamination, while the median recovery without decontamination was between one and five percent. In each case, the recovery from a given material and at a given time point was statistically significantly lower (p=0.036) for the ClO_2 liquid decontamination compared to recoveries from acidified water. Confidence intervals for these differences exhibited no quantifiable lower bound (i.e., negative infinity). For VX on metal, the ClO_2 liquid decontamination coupon recovery values were all below the MDL at every time point. The same was true for every coupon except one at 10 min for coupons without decontamination. With the median recovery values below the MDL with and without liquid ClO_2 decontamination on metal ductwork at all time points, the statistical tests were unable to conclude any difference in recovery between the treatments. These results are shown graphically in Figure 4-7 (on page 35).

Table 4-19. Statistically Modeled, Eq (11), Percent Recovery of VX With and Without Liquid ClO_2 Decontamination and Decontamination Efficacy (Compared to Recovery from Acidified Water)

CWA	Material	Time	Recovery as % of Time 0		Decontamination Efficacy, %
			Acidified Water	With Decontamination	
VX	Carpet	10 min	5.0	ND, <0.7	**>86%[a]**
		20 min	2.2	ND, <0.7	**>68%**
		30 min	3.3	ND, <0.7	**>79%**
	Laminate	10 min	1.9	ND, <0.7	**>63**
		20 min	1.9	ND, <0.7	**>63**
		30 min	1.7	ND, <0.7	**>59**
	Ductwork	10 min	ND, <0.7	ND, <0.7	Indeterminate[b]
		20 min	ND, <0.7	ND, <0.7	Indeterminate
		30 min	ND, <0.7	ND, <0.7	Indeterminate

a) Calculated using Eq (8); values given in bold are statistically significant

b) Efficacy cannot be determined due to non-detects both with and without decontamination
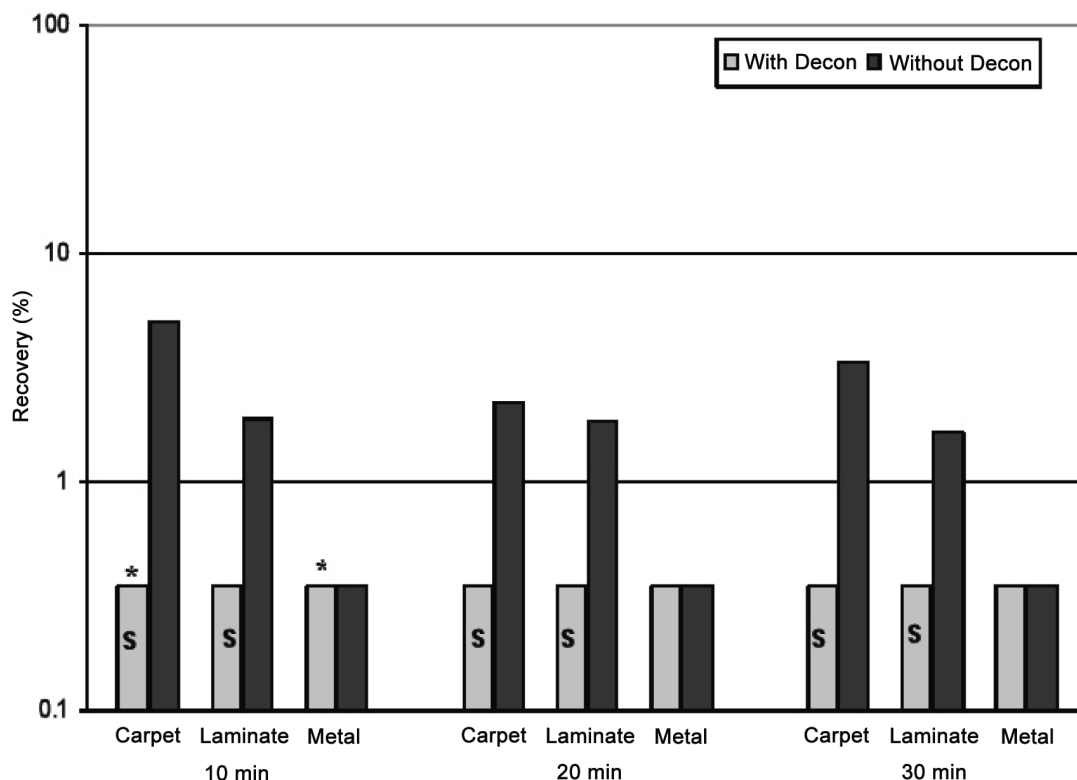
Values shown are medians rather than means due to nonparametric statistical model fit to data with non-detects

S Denotes recovery statistically significantly less with Sabre ClO_2 fumigant decontamination

*Denotes non-detect, ½ MDL used in place of 0 in the analysis

Figure 4-7. Statistical Analysis Results of VX Decontamination with Liquid ClO_2

Table 4-20. CWA Levels on Laboratory and Procedural Blank Coupons with Bleach Decontamination

CWA	Material	Blank Type	Time	Mass, µg
GB	Carpet	Laboratory	0 min	ND, <1[a]
		Procedural	10, 20, 30 min	ND, <1
TGD	Carpet, Ductwork	Laboratory	0 min	ND, <1
		Procedural	10, 20, 30 min	ND, <1
	Laminate	Laboratory	0 min	ND, <1
		Procedural	10, 30 min	ND, <1
		Procedural	20 min	0.9
VX	Carpet, Laminate, Ductwork	Laboratory	0 min	ND, <7
		Procedural	10, 20, 30 min	ND, <7

a) ND = not detected, less than stated MDL

b) NS = not spiked

4.3.4 CWAs on Laboratory and Procedural Blank Coupons During Liquid Decontamination Tests

There were two different types of blank samples collected during the liquid decontamination tests. The laboratory coupon blank of each material was taken from storage directly to an extraction vial and was not exposed to the fume hood where the spiking occurred. The procedural blank coupons were unspiked coupons present in the fume hood when the spiking was done; these blank coupons were then loaded into vials containing the decontamination solution.

The blank coupons were retrieved for extraction and analysis at the same time as the spiked coupons.

The amounts of CWAs measured in the extracts of these blank coupons for bleach decontamination tests are listed in Table 4-20. With exception of one TGD detection at a very insignificant level, the CWAs were not detected on the laboratory or procedural blanks.

For the decontamination tests with liquid ClO_2, there were no laboratory blanks analyzed, as these tests followed closely

after the liquid bleach decontamination tests. The levels of CWAs on the procedural blank coupons acquired during the liquid ClO_2 decontamination tests are listed in Table 4-21. VX was not detected on any of the procedural blanks.

After liquid decontamination of the test coupons, the decontaminated coupons were visually inspected; and any obvious changes in the coupon surfaces were recorded. When testing decontamination with liquid bleach, the control condition consisted of exposure to room air; when testing decontamination with liquid ClO_2, the control condition consisted of exposure of coupons to slightly acidic water. No damage or visible change to any of the carpet, laminate or ductwork test coupons was observed comparing extracted laboratory blank coupons (not exposed to decontamination) to extracted procedural blank coupons (exposed to decontamination) directly after decontamination treatment. Coupons were not re-examined after 3 and 6 months for this part of the effort.

Table 4-21. VX Levels on Procedural Blank Coupons with Liquid ClO_2 Decontamination

CWA	Material	Blank Type	Time	Mass, µg
VX	Carpet, Laminate, Ductwork	Procedural	10, 20, 30 min	ND, <7[a]

a) ND = not detected, less than stated MDL

The effectiveness of fumigant ClO_2, liquid ClO_2, and liquid bleach decontamination technologies for selected TICs and/or CWAs was evaluated on building materials, specifically, carpet, ceiling tile, laminate, and ductwork. Table 5-1 is a summary of the recovery and decontamination efficacy results at the longest time interval tested for each combination of decontamination technology, TIC, or CWA, and building material. The recovery of each chemical is listed in this table for samples with decontamination or under positive control conditions (without decontamination or in acidified water). For instance, fumigant ClO_2 decontamination was operated at about 80% RH; therefore the control conditions without decontamination

consisted of coupons exposed to 80% RH air. Liquid ClO_2 decontamination was in aqueous solution; therefore the control conditions without decontamination consisted of coupons in acidified water. With this design, comparing the recovery of a given chemical under the two conditions allowed assessment of the effectiveness of the ClO_2 itself, rather than the combined effects of ClO_2 and water (liquid or vapor), as many of these chemicals are susceptible to aqueous hydrolysis.

For the fumigant ClO_2 decontamination, it appears that this technology was most effective against malathion and VX. Because these chemicals persisted to a large extent in the presence of high RH under control conditions, it was clear

Table 5-1. Summarization of Percent Recovery With and Without Decontamination Technologies, and Decontamination Efficacy for TICs and CWAs

Technology	Chemical	Material	Duration	Recovery, % Without Decon	Recovery, % With Decon	Decontamination Efficacy %[a]
Fumigant ClO_2 3000 ppm	Malathion	Carpet	7 h	87[g]	24[g]	72
	Malathion	Laminate	7 h	94[g]	0.4[g]	99.6
	DMMP	Carpet	7 h	19[g]	22[g]	No efficacy[b]
	DMMP	Ceiling tile	7 h	9.4[g]	8.7[g]	8
	GB	Carpet	4 h	5.6[g]	3.4[g]	39
	TGD	Carpet	2 h	57[g]	36[g]	37
	TGD	Laminate	2 h	0.5[g]	<0.1[c]	No efficacy[f]
	TGD	Ductwork	2 h	5.9[g]	7.4[g]	No efficacy[b]
	VX	Carpet	4 h	97[g]	<0.7[c]	>99
	VX	Laminate	4 h	91[g]	<0.7[c]	>99
	VX	Ductwork	4 h	105[g]	<0.7[c]	>99
Liquid Bleach	GB	Carpet	30 min	84[h]	<0.1[c]	Complete or nearly complete loss of recoverable CWA from treated compared with untreated coupons[d]
	TGD	Carpet	30 min	135[h]	0.1	
	TGD	Laminate	30 min	77[h]	0.2	
	TGD	Ductwork	30 min	91[h]	0.8	
	VX	Carpet	30 min	107[h]	<0.7[c]	
	VX	Laminate	30 min	102[h]	<0.7[c]	
	VX	Ductwork	30 min	95[h]	<0.7[c]	
Liquid ClO_2	VX	Carpet	30 min	3.3[g]	<0.7[c]	>86
	VX	Laminate	30 min	1.7[g]	<0.7[c]	>59
	VX	Ductwork	30 min	<0.7[c]	<0.7[c]	NA[e]

a) Statistically significant decontamination efficacy between recovery with and without decontamination test conditions

b) No efficacy; recovery with decontamination is greater than recovery without decontamination

c) Not detected; MDL expressed as wpercentage of mass applied to the coupon

d) While decontamination efficwacy may be high, efficacy due to the bleach effect cannot be distinguished from the effect of the water hydrolysis or dissolution because the control coupons were stored in room air

e) NA= not applicable; cannot calculate decontamination efficacy when the analyte is not detected under either the control or test conditions

f) No efficacy; no statistically significant differences in recovery with and without decontamination

g) Statistically modeled data using Eq (11)

h) Calculated using Eq (7)

that the ClO_2, and not water, was responsible for degradation of these two compounds. The high volatilities of DMMP, GB, and TGD make it difficult to assess the effectiveness of fumigant ClO_2 decontamination against these compounds. However, for DMMP where air levels were measured in both the test and control chambers, the considerable difference in these air levels suggested that fumigant ClO_2 was responsible for decontamination of gas-phase DMMP; the loss of DMMP from surfaces may still be due to some extent to either volatilization or aqueous hydrolysis. However, the gas-phase decontamination may be a powerful technique for highly volatile compounds.

When testing with liquid bleach, the positive controls were not placed in any liquid solution. Based on findings from the bleach testing, the approach was revised for testing with liquid ClO_2. For liquid ClO_2 the control condition consisted of exposure of coupons to slightly acidic water. The test coupons and associated controls of the liquid decontamination tests were placed in sealed vials. The temperature and RH of the laboratory hood in which these vials were placed was typically about 24°C and 40% RH.

Shown in Table 5-2, recovery of GB, GD, and VX from 100% bleach (6% ClO^-) and 3000 ppm ClO_2 was tested, as was recovery from neutralized solutions that were created via addition of STS to the bleach or ClO_2 solutions. No CWAs spiked directly into bleach were recovered after 1 h. Likewise, little GB (1%) and no VX were recovered from neutralized bleach after 15 sec. This testing was inconclusive as to whether chemical degradation or inefficient recoveries account for the loss of recoverable CWA. In contrast, a relatively high recovery of GD from neutralized bleach solution with no detectable recovery of GD after 1 h in bleach indicates that bleach was effective against GD.

GB (8% of spike) and GD (58% of spike) were recovered 1 h after being spiked directly into 3000 ppm ClO_2 solution. Within the margin of error, the same amounts of GB (8%) and GD (56%) were recovered from neutralized ClO_2

solution. This testing indicated that the ClO_2 solution was not efficacious against GB or GD. VX was not recovered from neutralized ClO_2 solution at 15 sec or from ClO_2 solution after 1 h. The efficacy of ClO_2 solution against VX could not be determined from these results.

For testing the two liquid decontamination technologies against CWAs on coupons, a slightly different control approach was used for each. When testing with liquid bleach, the positive control coupons (without decontamination) were not placed in any liquid solution — they were maintained in a vial exposed to air. When testing with liquid ClO_2, the control condition (without decontamination) consisted of immersion of coupons in slightly acidic water. The test coupons and associated controls of the liquid decontamination tests were placed in sealed vials. The temperature and RH of the laboratory hood in which these vials were placed was typically about 24°C and 40% RH.

The results of the testing, shown in Table 5-1, suggest that liquid bleach may be a very effective decontamination agent, as none of the CWAs were detected on the coupons after a 20 min soak in the bleach. However, the test was not without confounding parameters. The solution tests, shown in Table 5-2 in which the CWA was directly spiked into bleach and neutralized bleach showed that both GB and VX were not detected in extracts of neutralized bleach, either because of rapid hydrolysis or poor extraction efficiency from aqueous solution into hexane. Thus the low measured recovery of these CWAs from the decontaminated coupons may be due in part to hydrolysis, volatilization, and/or partition of the CWA into the aqueous bleach and poor extraction efficiency into hexane. The low recovery of GD in bleach, combined with the fact that nearly 50% was extracted from a neutralized bleach solution, suggested that the bleach itself was effective in decontaminating GD on the materials tested.

The long-term stability and integrity of building materials after exposure to fumigant ClO_2 indicated that the coupons were relatively unchanged after three months, and the carpet showed some minor "bleaching" after six months.

Table 5-2. Mean Recovery of CWAs Directly Spiked into Liquid Decontamination Solutions

Solution - Hold Time Before SRS Addition and Hexane Extraction	Mean CWA Recovery, % ± SD (n = 3)		
	GB	GD	VX
Bleach - 1 h	ND, <0.1	ND, <0.1	ND, <0.7
Neutralized bleach - 15 sec	1 ± 0	41 ± 10	ND, <0.7
ClO_2 - 1 h	8 ± 2	58 ± 5	ND, <0.7
Neutralized ClO_2 - 15 sec	8 ± 1	56 ± 10	ND, <0.7

Recoveries calculated using Eq (1); mean and SD of recoveries shown here

ND = not detected

6.0
References

1. Persistence of Toxic Industrial Chemicals and Chemical Warfare Agents on Building Materials Under Conventional Environmental Conditions; (EPA/600/R-08/075); July 2008.
   http://www.epa.gov/nhsrc/pubs/600r08075.pdf

2. *Method 8000 "Determinative Chromatographic Separations" as part of SW-846 Third edition.*

3. Battelle, *Quality Management Plan (QMP) for the Technology Testing and Evaluation Program (TTEP); Version 2*. January 2006.

4. Battelle, *Test/QA Plan for the Systematic Evaluation of Technologies for Decontaminating Surfaces Inoculated with Highly Hazardous Chemicals (Chemical Warfare Agents and TICs), Manipulation of Environmental Conditions to Alter Persistence, Version 1*. June 2005.

The recoveries of DMMP and malathion on carpet, ceiling tile, and laminate, normalized to recoveries at Time 0 (0 h), both with and without fumigant ClO_2 decontamination, are listed in Table A-1. Note that the statistical model that uses these data incorporates all data from an experiment into one model; in modeling that data, the averages at each time point change slightly to fit the single model. Thus averages listed in this table do not match precisely the averages listed in Table 4-4.

The recoveries of GB, TGD, and VX on carpet, laminate and ductwork, normalized to recoveries at Time 0 (0 h), both with and without fumigant ClO_2 decontamination, are listed in Table A-2 (on page 42).

Note that the statistical model that uses these data incorporates all data from an experiment; in modeling that data, the averages at each time point change slightly to fit one model. Thus averages listed in this table do not match precisely the averages listed in Table 4-12.

The recoveries of VX on carpet, laminate and ductwork, normalized to recoveries at Time 0 (0 h), with liquid ClO_2 decontamination, are listed in Table A-2 (on page 42).

Note that the statistical model that uses these data incorporates all data from an experiment; in modeling that data, the averages at each time point change slightly to fit one model. Thus averages listed in this table do not match precisely the averages listed in Table 4-19.

Table A-1. Normalized Mean Recovery of TICs on Building Materials over Time With and Without Sabre ClO_2 Fumigant Decontamination

TIC	Material	Time (n)	Normalized Mean Recovery, % ± SD[a]	
			Without Decon	**With Decon**
DMMP	Carpet	1 h (n = 5)	33 ± 2	43 ± 6
		3 h (n = 5)	24 ± 3	28 ± 6
		7 h (n = 5)	16 ± 3	23 ± 4
	Ceiling tile	1 h (n = 5)	39 ± 4	30 ± 2
		3 h (n = 5)	28 ± 1	15 ± 1
		7 h (n = 5)	12 ± 1	8.7 ± 0.3
Malathion	Carpet	1 h (n = 5)	89 ± 2	76 ± 3
		3 h (n = 5)	90 ± 3	51 ± 5
		7 h (n = 5)	87 ± 1	24 ± 2
	Laminate	1 h (n = 5)	100 ± 12	28 ± 19
		3 h (n = 5)	91 ± 5	3.3 ± 1.6
		7 h (n = 5)	94 ± 10	0.4 ± 0.2

a) Calculated using Eq (7)

Table A-2. Normalized Mean Recovery of CWAs on Building Materials over Time With and Without Sabre ClO_2 Fumigant Decontamination

CWA	Material	Time	Normalized Mean Recovery, % ± SD[b]	
			Without Decon	With Decon
GB	Carpet	1 h	5.9 ± 1.1	4.1 ± 2.1
		4 h	5.7 ± 0.2	3.3 ± 1.0
TGD	Carpet	1 h	77 ± 17	29 ± 5.2
		2 h	57 ± 6.1	36 ± 17
	Laminate	1 h	1.5 ± 1.6	6.1 ± 6.9
		2 h	1.3 ± 1.6	0.10 ± 0.11
	Ductwork	1 h	21 ± 7.5	14 ± 11
		2 h	5.9 ± 2.6	7.4 ± 9.0
VX	Carpet	1 h	105 ± 31	0.35 ± 0.00[a]
		4 h	97 ± 10	0.35 ± 0.00
	Laminate	1 h	86 ± 8.0	0.35 ± 0.00
		4 h	94 ± 5.5	0.35 ± 0.00
	Ductwork	1 h	101 ± 3.1	0.35 ± 0.00
		4 h	101 ± 9	0.35 ± 0.00

a)   VX not detected in sample; value reported here is half the MDL

b)   Calculated using Eq (7)

Table A-3. Normalized Mean Recovery of VX on Building Materials With and Without Liquid ClO_2 Decontamination

CWA	Material	Time	Normalized Mean Recovery, % ± SD[a]	
			Without Decon	With Decon
VX	Carpet	10 min	5.8 ± 1.5	ND, <0.7
		20 min	2.2 ± 0.5	ND, <0.7
		30 min	3.2 ± 0.6	ND, <0.7
	Laminate	10 min	1.9 ± 0.2	ND, <0.7
		20 min	2.5 ± 1.2	ND, <0.7
		30 min	1.8 ± 0.3	ND, <0.7
	Ductwork	10 min	0.4 ± 0.2	ND, <0.7
		20 min	ND, <0.07	ND, <0.7
		30 min	ND, <0.07	ND, <0.7

a)   Calculated using Eq (7)

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