

Persistence of Toxic Industrial Chemicals and Chemical Warfare Agents on Building Materials Under Conventional Environmental Conditions: Investigation Report



Persistence of Toxic Industrial Chemicals and Chemical Warfare Agents on Building Materials Under Conventional Environmental Conditions

INVESTIGATION REPORT

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Disclaimer

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's 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, the EPA's Office of Research and Development (ORD) provides data and science support that can be used to solve environmental problems and 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 National Homeland Security Research Center (NHSRC). NHSRC is part of the ORD; it manages, coordinates, supports, and conducts 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 decontaminate 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 and drinking water supplies and infrastructure, and for decontaminating structures and the outdoor environment. In addition, environmental persistence information is also important for containment and decontamination decisions.

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

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Abbreviations/Acronyms

APCI MS/MS	atmospheric pressure chemical ionization tandem mass spectrometry
BBRC	Battelle Biomedical Research Center
C	Celsius
cm	centimeter
CWA(s)	chemical warfare agent(s)
DMMP	dimethyl methylphosphonate
ft min ⁻¹	feet per minute
EPA	U.S. Environmental Protection Agency
FPD	flame photometric detection
g	gram
GB	Sarin
GC	gas chromatography
GD	Soman
g m ⁻²	gram per square meter
h	hour(s)
h ⁻¹	per hour
Hg	Mercury
IS	internal standard(s)
L	liter
M	meter(s)
m/z	mass-to-charge ratio (dimensionless)
mm	millimeter(s)
MDL(s)	method detection limit(s)
MFC(s)	mass flow controller(s)
min	minute(s)
min ⁻¹	per minute
mL	milliliter(s)
mg	milligram(s)
MS	mass spectrometry
NA	not applicable
NC	not calculated
ND	not detected
NT	not tested
NHSRC	National Homeland Security Research Center
ORD	Office of Research and Development
ppb	parts per billion
ppm	parts per million
PE	performance evaluation
QA	quality assurance
QC	quality control

QMP	quality management plan
RH	relative humidity
RT	retention time
SARM	Standard Analytical Reference Material
SRS(s)	surrogate recovery standard(s)
SD	standard deviation
TBP	tributyl phosphate
Temp	temperature
TGD	thickened soman
TIC(s)	toxic industrial chemical(s)
TNT	2,4,6-trinitrotoluene
TSA	technical systems audit
TTEP	Technology Testing and Evaluation Program
μg	microgram(s)
μL	microliter(s)
VX	VX nerve agent

Executive Summary

The U.S. Environmental Protection Agency's (EPA's) NHSRC Technology Testing and Evaluation Program (TTEP) is helping to protect human health and the environment from adverse impacts resulting from acts of terror by carrying out performance tests on homeland security technologies. The persistence of three different toxic industrial chemicals (TICs) and three different chemical warfare agents (CWAs), each on various types of building materials, was investigated at environmental conditions typical of an office building. In this work, persistence is a relative term describing a compound's ability to remain over time on the building material.

This report presents the results of a screening investigation to determine whether TICs and CWAs of interest persist sufficiently on selected indoor building materials to allow further investigation of decontamination technologies that might be used to remove the chemicals from contaminated surfaces. (A subsequent report will present the results of the investigation of decontamination technologies.)

The primary objective of this work was to determine the persistence of TICs and CWAs at conditions that would provide a baseline for decontamination technology investigations. While this also provides data on natural attenuation of TICs and CWAs from building materials, investigation of causes of persistence or manipulation of environmental factors to impact persistence (except for the increased air flow over TICs) was beyond the scope of this task order. Because fumigation technologies may include air movement across the coupons, the impact of high air flow was evaluated for the TICs. In addressing this objective, this research investigates the following questions:

- Do TICs and CWAs persist on indoor building materials?
- Does air flow over the contaminated building materials change persistence?
- Do TICs and CWAs persist to such an extent on various indoor materials to permit testing of decontamination technologies?

Differences in physicochemical properties of various TICs and CWAs, as well as the properties of the building materials, may result in differences in persistence of the chemicals on the materials. Properties that would be expected to have a significant impact on persistence include, for example, vapor pressures and hydrolysis rates. In addition, the physical properties of the building materials, such as surface area, sorption capacity, and their relative affinity for water, also have a significant impact on persistence of TICs and CWAs. This investigation analyzed the persistence of TICs and CWAs on a variety of building materials.

Three TICs were selected for this effort, including the organophosphate insecticide malathion, the sarin surrogate dimethyl methylphosphonate (DMMP), and the explosive 2,4,6-trinitrotoluene (TNT). Three CWAs were also selected, including sarin (GB), thickened soman (TGD), and VX. The wide range of vapor pressures and hydrolysis rates for these six

compounds ensured that persistence on building materials would vary significantly. The building materials were test coupons (3.5–10 square centimeters [cm^2]) of nylon carpet (absorptive), decorative melamine laminate (nonporous), galvanized metal ductwork (nonporous), and concrete (porous). Decorative laminate, carpet, and concrete were used with the TICs. Because of apparent interaction between malathion and concrete, galvanized metal rather than concrete was used for the CWA testing. The persistence tests were performed under conventional building environmental conditions of 22 °C–24 °C and 40% (TICs) or 17% (CWAs) relative humidity (RH). The duration of the testing was up to seven days. Persistence tests with the TICs and CWAs were carried out under conditions simulating an indoor office building or residential environment, that being one air exchange rate per hour (h^{-1}) and no overt air flow over the surfaces. Additional persistence tests were carried out with the TICs under these same conditions with the addition of a continuous rapid air flow at 400 feet per minute (ft min^{-1}) over the building materials in order to represent the use of industrial fans for mixing.

Methods for extraction and analysis were developed and validated for TICs and CWAs on building material test coupons selected for use in this investigation. The analytical work also included the development of techniques for measuring these chemicals in the gas phase over test coupons. For the TICs, the measurement of gas-phase levels involved a real-time mass spectrometry (MS) technique; for the CWAs this involved time-integrated air sampling onto Carboxen™ sorbent. The CWA was extracted from the sorbent with chloroform. Sample extracts were analyzed using gas chromatography with flame photometric detection. Air sampling analysis was needed to ascertain the extent to which persistence was tempered by volatilization into air and removal at normal ventilation rates. The analytical methods were sensitive, selective, and reproducible — allowing detection of levels as low as 0.05% of the initial spike amount made to each type of test coupon.

The test chambers designed and fabricated for this investigation incorporated controls for temperature, humidity, air exchange, and additional air flow over the test surfaces.

The persistence tests were conducted by spiking 400–500 micrograms (μg) of TICs onto the surface of 3.5–5 cm^2 test coupons, or spiking 1000 μg of CWAs onto 10 cm^2 test coupons, to achieve an initial surface loading of approximately 1 gram per square meter (g m^{-2}). A loading of 1 g m^{-2} is representative of a potential worst-case indoor contamination scenario. The three different types of test coupons were each spiked sequentially and expeditiously with the chosen TIC or CWA, and then all coupons were loaded into the test chamber at the same time. Sufficient coupons were spiked to allow five replicate test coupons of each building material to be removed for analysis at each of the chosen time intervals comprising a persistence test. Additional test coupons were spiked and not placed into the test chamber, but extracted immediately to establish a baseline against which

persistence could be measured. For the TICs, coupons were removed from the test chamber at Day 1, Day 3, and Day 7 after spiking. The test coupons spiked with CWAs were removed at 1 h, 4 h, Day 1, Day 3, and Day 7 after spiking. To assess redistribution inside the test chamber for the CWAs, procedural blank coupons were placed in the chamber and removed for analysis along with the previously spiked test coupons.

The persistence of the chemicals on test coupons in relatively still air (one air exchange rate per hour) in the test chamber is summarized in Table ES-1 below. The percent persistence is the mean mass of TIC or CWA recovered from the coupons at a given time divided by the mean mass of TIC or CWA recovered from coupons at Time 0 x 100%. The persistence of malathion and TNT on industrial carpet and concrete was approximately equal with either the fans on or the fans off (still air); however, on laminate, the persistence was approximately half with the fans on. The persistence of the CWAs was not tested under conditions with fans directing air over the surfaces of the building materials.

The persistence on industrial carpet and laminate coupons was apparently related to the vapor pressure of the TIC or CWA, with the most volatile ones exhibiting lowest persistence. A similar trend was observed for the persistence of the CWAs on the metal ductwork coupons. The persistence of the TICs on concrete may be a function of several factors. The malathion may be lost due to a heterogeneous hydrolysis reaction, as the CWA VX, which has a chemical structure similar to malathion, has been shown

to hydrolyze on concrete.^[1, 2] Given the structural similarities between VX and malathion, a similar hydrolysis reaction may occur between malathion and concrete. DMMP was essentially retained on the concrete; the lower persistence of less-volatile TNT cannot be fully explained at this time, unless basic sites on the concrete facilitated hydrolysis or degradation.

Measurement of the gas-phase concentration of the TICs and the CWAs in the test chamber air showed that there were quantifiable levels of these compounds present. However, levels in the air accounted for less than 5% of the total mass of TIC or CWA originally placed into the chamber. The procedural blank coupons placed in the chamber during the CWA persistence tests showed that gas phase material was redistributed to sorptive surfaces, as levels on the carpet procedural blanks were much higher than those on laminate or ductwork procedural blank coupons. At the end of the seven-day test period, as much as 76% of the DMMP, 58% of the malathion, and 50% of the TNT were not accounted for by residual levels remaining on test coupons and the volatile chemicals measured in the air of the test chamber. These results suggested that in real-world decontamination scenarios it would be essential to take into account that certain TICs and CWAs do volatilize and that certain building materials may have a greater affinity or capacity than others to retain one or more chemicals. Furthermore, the volatilized compounds may adsorb onto or absorb into other materials.

Table ES-1. Persistence of TICs and CWAs^a in Still Air Conditions

Duration	Malathion	DMMP	TNT	GB	TGD	VX
Persistence on Carpet, % remaining of initial mass ± SD (n=5)						
1 h	-	-	-	18 ± 4	84 ± 47	103 ± 8
4 h	-	-	-	9 ± 4	43 ± 3	101 ± 18
Day 1	103 ± 3	16 ± 3	80 ± 7	3.3 ± 2.6	12 ± 1	88 ± 6
Day 3	94 ± 3	11 ± 2	84 ± 8	2.0 ± 1.2	12 ± 7	36 ± 3
Day 7	85 ± 3	7 ± 2	61 ± 8	0.4 ± 0.5	4 ± 0	18 ± 1
Persistence on Laminate, % remaining of initial mass ± SD (n=5)						
1 h	-	-	-	Not Detected at 5 min	17 ± 4	99 ± 7
4 h	-	-	-		0.28 ± 0.01	105 ± 28
Day 1	97 ± 3	0.5 ± 0.4	69 ± 11		0.11 ± 0.04	52 ± 4
Day 3	87 ± 6	0.5 ± 0.1	68 ± 17		ND, <0.1	8 ± 4
Day 7	72 ± 3	0.2 ± 0.3	45 ± 13		ND, <0.1	4 ± 3
Persistence on Concrete, % remaining of initial mass ± SD (n=5)						
Day 1	46 ± 10	106 ± 7	81 ± 19	-	-	-
Day 3	17 ± 11	87 ± 4	85 ± 21	-	-	-
Day 7	7 ± 4	99 ± 5	57 ± 9	-	-	-
Persistence on Metal Ductwork, % remaining of initial mass ± SD (n=5)						
1 h	-	-	-	Not Detected at 15 min	41 ± 12	97 ± 5
4 h	-	-	-		1.39 ± 0.23	117 ± 24
Day 1	-	-	-		0.91 ± 0.13	89 ± 5
Day 3	-	-	-		0.91 ± 0.33	55 ± 20
Day 7	-	-	-		0.51 ± 0.04	24 ± 8

^a TICs and CWAs on various materials were exposed to conditions simulating an indoor environment, that being one air exchange h⁻¹ and no overt air flow over the surface.

- Not tested

1.0

Introduction

The EPA's NHRSC 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, radiological, or biological contaminants into buildings, subways, water systems, or outdoor environments; contain these contaminants; decontaminate these environments; and facilitate the disposal of material resulting from cleanups.

NHRSC's TTEP works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permittees; and with the full 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 evaluations 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.

Inherent characteristics of chemicals, such as volatility or the ability to react with surface materials, may result in the low persistence of chemicals on given surfaces. If chemicals do not persist on a given surface, investigations of decontamination technologies against such chemical-surface combinations would not generate useful information. Therefore, screening tests were needed prior to performing the systematic decontamination investigations in order to ensure that only useful combinations of chemicals and building materials were included in the decontamination investigation. This report presents the results of a screening investigation to determine whether TICs and CWAs of interest persist sufficiently on selected indoor building materials to allow further investigation of decontamination technologies that might be used to remove the chemicals from contaminated surfaces.

1.1 Objectives for Persistence Testing

This testing was conducted to measure the persistence, under conventional indoor building conditions, of three representative TICs and three representative CWAs on a range of indoor building materials. The primary objective of this work was to determine the persistence of TICs and CWAs at conditions that would provide a baseline for decontamination technology investigations. Investigation of causes of persistence or manipulation of environmental factors to impact persistence (except for the increased air flow over TICs) was beyond the scope of this task order. Because fumigation technologies may include air movement across the coupons, the impact of high air flow was evaluated for the TICs. Persistence in this investigation was assessed by quantifying the amount of TIC or CWA extracted at different times from test coupons of the selected building materials, which had been initially spiked with known quantities of a TIC or CWA. In other words, persistence is a relative term describing a compound's ability to remain, or persist, over time on the test coupons.

To address the objective, this research investigates the following questions:

- Do TICs and CWAs persist on indoor building materials?
- Does air flow over the contaminated building materials change persistence?
- Do TICs and CWAs persist to such an extent on various indoor materials to permit testing of decontamination technologies?

Differences in physicochemical properties of various TICs and CWAs, as well as the properties of the building materials, may result in differences in persistence of the chemicals on building materials. Properties that would be expected to have a significant impact on persistence include, for example, vapor pressures and hydrolysis rates. In addition, the physical properties of the building materials, such as surface area, sorption capacity, and their relative affinity for water, also have a significant impact on the persistence of TICs and CWAs. This investigation analyzed the persistence of TICs and CWAs on a variety of building materials. Physicochemical properties of representative TICs and CWAs are listed in Table 1-1.

Table 1-1. Physicochemical Properties of Representative TICs and CWAs

Property	TICs			CWAs		
	Malathion	DMMP ^a	TNT ^b	GB ^c	TGD ^d	VX
Molecular weight, g/mole	330.3	124.8	227.1	140.0	182.2	267.4
Melting point, °C	2.8	-50	80.9	-56	-42	-39
Boiling point, °C	157	181	240	158	198	300
Vapor pressure, millimeter (mm) Hg at 25 °C	3.38e-06	1.2	8.0e-06	2.9	0.4	6.3e-04
Hydrolysis rate, half-life, days	21	NA ^e	730	1.6	1.9	42
Octanol:water partition; Log K _{ow}	2.36	0.5	1.6	0.3	1.78	2.09

^a DMMP = dimethyl methylphosphonate

^b TNT= 2,4,6-trinitrotoluene

^c GB= sarin

^d TGD = GD thickened with polymethyl methacrylate; thickened soman

^e NA= not available

1.2 Approach

The general approach developed and used for persistence testing was to apply a known amount of each TIC or CWA to each of several test coupons of the same building material and allow these spiked test coupons' surfaces to age under controlled environmental conditions. 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 approach developed and applied for testing the persistence of TICs and CWAs was generally the same, and therefore this section gives information that is applicable to persistence testing that was performed for both TICs and CWAs. The specific details for the methodologies used to test the persistence of TICs and CWAs are described in Section 2.0.

The scope of the study was to screen TICs and CWAs to ensure that the chemicals exhibited adequate persistence on the selected materials to support decontamination testing. The results also served as a baseline for comparison with the application of decontamination technologies in later investigations. A systematic investigation of other factors that are likely to affect persistence (e.g., ambient temperature effect or changing RH) was not performed because it was beyond the scope of this screening study.

1.3 Study Design

Table 1-2 includes the TICs and CWAs that were selected for this study. It also includes important elements of the analytical methods used for each compound, including the surrogate recovery standard (SRS) used to track extraction efficiency and analytical recovery, and the internal standard (IS) used for quantification (see Section 2.0). As described further in Sections 2.0 and 4.0, the SRS for each TIC or CWA is an important element of the analytical plan used here. Each SRS was chosen for its structural similarity to a given analyte; its recovery was

used to correct for variation in extraction efficiency and recovery through the analytical method. Table 1-2 also includes the general analysis method employed for extracts of building materials, as well as the sampling and analysis methods employed in measuring the chemicals in the air over the building materials during persistence testing.

The building materials used in this persistence investigation included industrial grade carpet, laminate countertop material, unpainted concrete, and galvanized metal ductwork. The objective was to find a combination of building materials and chemicals on which the chemicals were persistent and from which the chemicals could be efficiently recovered. As will be discussed, preliminary work with TICs showed that malathion (a surrogate for VX) appeared to react with concrete. Given these results, an alternate building material (galvanized metal ductwork) was evaluated for use with the CWAs.

Building materials were cut into coupons of small, defined size, and the toxic chemicals were applied at a rate equivalent to 1 g m⁻², which is representative of a potential worst-case indoor contamination scenario. The coupons to which TICs were applied were approximately 5 cm², and the coupons to which CWAs were applied were approximately 10 cm². The sizes were chosen so as to take advantage of the available area in the test chambers and to optimize the spiking volume of chemicals being applied to the coupons.

All testing with TICs was carried out in standard chemical laboratories at Battelle. Due to the stringent controls needed for working with CWAs, persistence tests for CWAs were carried out at Battelle's certified chemical surety facility (Battelle Biomedical Research Center [BBRC]) in West Jefferson, Ohio). The persistence tests were conducted with coupons inside specially fabricated test chambers with controls for air exchange rate (see Section 2.1). The persistence of each chemical (TIC or CWA) was investigated separately; however, the behavior of a given chemical was investigated on all building material coupon types simultaneously.

Table 1-2. Selected TICs and CWAs with Analytical Measurement Parameters

Parameter	TICs			CWAs		
	Malathion	DMMP	TNT	GB	TGD	VX
SRS	Fenclorophos	DEEP ^a	TNB ^b	TBP ^c	TBP	TBP
IS	DBB ^d	DIMP ^e	3-NBP ^f	DIMP	DIMP	DIMP
Extraction	Sonication	Sonication	Sonication	Shake/stand	Shake/stand	Shake/stand
Analysis	GC/MS ^g	GC/MS	GC/MS	GC/FPD ^h	GC/FPD	GC/FPD
Air sample collection	Real-time head space ⁱ	Real-time head space	Real-time head space	Carboxen TM sorbent	Carboxen TM sorbent	Carboxen TM sorbent
Air sample analysis	APCI MS/MS ^j	APCI MS/MS	APCI MS/MS	GC/FPD	GC/FPD	GC/FPD

^a DEEP = diethyl ethylphosphonate

^b TNB = 1,3,5-trinitrobenzene

^c TBP = tributyl phosphate

^d DBB = dibromobiphenyl

^e DIMP = diisopropyl methylphosphonate

^f 3-NBP = 3-nitrobiphenyl

^g GC/MS = gas chromatography/mass spectrometry in the multiple ion detection mode

^h GC/FPD = gas chromatography/flame photometric detection

ⁱ Real time = monitoring of headspace (air) in the chamber in real time

^j APCI MS/MS = atmospheric pressure chemical ionization tandem mass spectrometry

Table 1-3 presents a summary of the matrix of building materials and chemicals, together with the test chamber conditions that were used in the persistence testing. For TICs, persistence of each TIC was tested under two sets of conditions—with and without air flow over the coupons.

Preliminary tests carried out to assess recovery of CWAs from ceiling tile provided some insights into persistence on this building material (see Section 4.2.1). The temperature and humidity in the chamber, the air exchange rate in the chamber, and the times at which test coupons were removed for analysis were physical factors manipulated in the investigation of the persistence of TICs and CWAs. For the persistence testing of TICs, two fans were placed inside the test chamber such that, when activated, air passed over the coupons at approximately 400 ft min⁻¹. This additional air flow over the coupons served to simulate the use of fans during decontamination, for example to distribute or cycle fumigant. The increased rate of volatilization of chemicals from various materials due to the increased air speed

might decrease their persistence and confound decontamination testing. The results from the TICs testing were considered sufficient to understand the impact of air speed on persistence of volatile and relatively nonvolatile chemicals on various types of materials. Therefore, no CWA persistence tests were conducted with high air flow over the coupons.

The temperature and RH inside the test chambers and air velocity over the coupons (for TICs) were monitored and recorded. The air flow into the chambers, and therefore, the air exchange rate, was constantly controlled. Five replicate coupons of each building material type were analyzed at each time point, for each chemical.

Throughout each trial, the amount of TIC or CWA in the gas phase in the test chamber was measured using either atmospheric pressure chemical ionization tandem mass spectrometry (APCI-MS/MS) or collection of a known quantity of air on a Carboxen™ sorbent tube. In the latter case, the sorbent was extracted and the resultant extract was analyzed for the CWA.

Table 1-3. Parameters for Persistence Testing

Chemical	Building Materials	Temperature, RH Maintained	Air Exchange Rate	Air Flow over Coupons	Sampling Points in Time
TIC					
Malathion	Carpet Laminate Concrete	24 °C, 40% RH	1 h ⁻¹	0 ft min ⁻¹ 400 ft min ⁻¹	0 h, Day 1, 3, 7
DMMP	Carpet Laminate Concrete	24 °C, 40% RH	1 h ⁻¹	0 ft min ⁻¹ 400 ft min ⁻¹	0 h, Day 1, 3, 7
TNT	Carpet Laminate Concrete	24 °C, 40% RH	1 h ⁻¹	0 ft min ⁻¹ 400 ft min ⁻¹	0 h, Day 1, 3, 7
CWA					
GB	Carpet	22 °C, 17% RH	1 h ⁻¹	0 ft min ⁻¹	0 h, 1 h, 4 h, Day 1, 3, 7
TGD	Carpet Laminate Ductwork	22 °C, 17% RH	1 h ⁻¹	0 ft min ⁻¹	0 h, 1 h, 4 h, Day 1, 3, 7
VX	Carpet Laminate Ductwork	22 °C, 17% RH	1 h ⁻¹	0 ft min ⁻¹	0 h, 1 h, 4 h, Day 1, 3, 7

2.0 Methods

All testing was performed in accordance with the peer-reviewed and EPA-approved *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*^[3] as amended to include Appendices 1 and 2.

2.1 TICs

2.1.1 Test Chamber

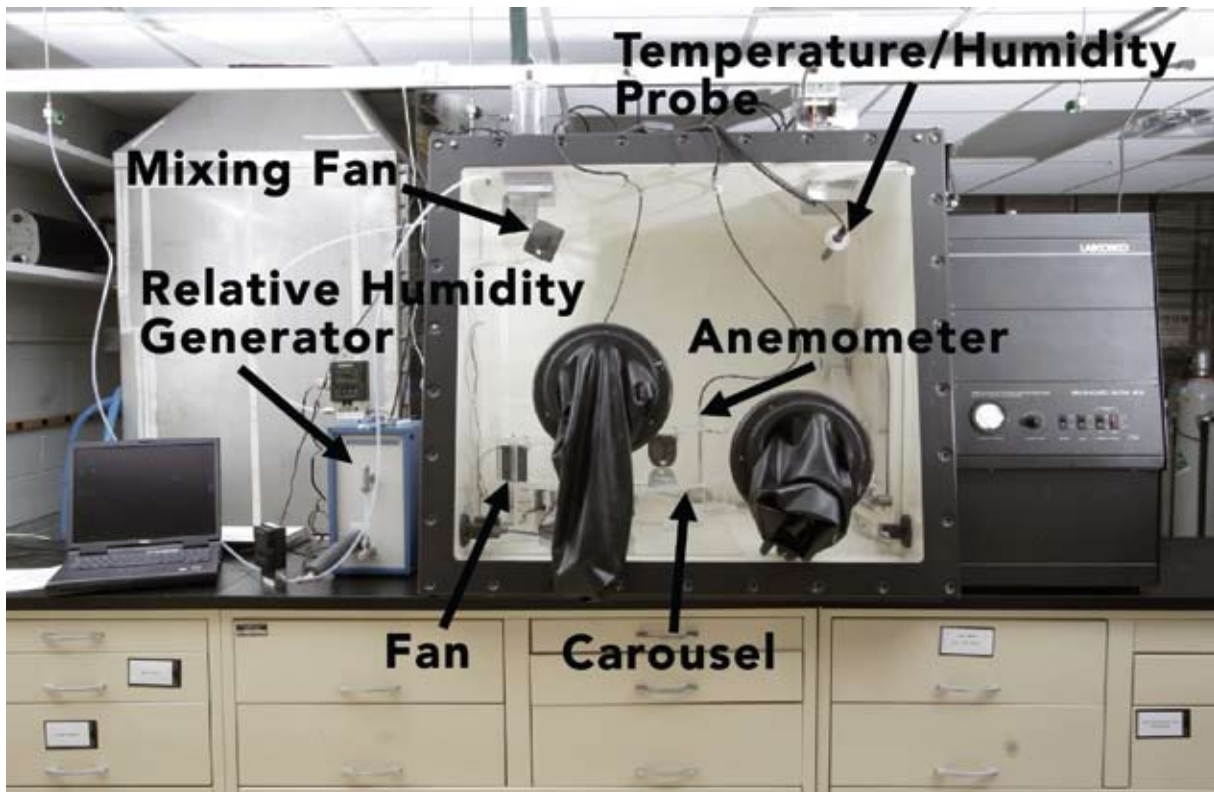
A customized test chamber consisting of fabricated and off-the-shelf equipment and components was assembled and used to carry out all experiments for persistence of TICs. The 448-liter (L) test chamber (Labconco) is shown in Figure 2-1. The temperature in the chamber was maintained between 24 °C and 25 °C. Zero air (nominally hydrocarbon-free air with approximately <0.1 ppm hydrocarbons) was supplied to the test chamber by a zero air generator (AADCO). To achieve an air exchange rate of one h⁻¹, the total air flow into the test chamber was set to 7.5 L min⁻¹, using two separate 0–10 L min⁻¹ mass flow controllers (MFC; Sierra Instruments). One MFC admitted moisture-free air to the test chamber at a rate of 4.25 L min⁻¹. Dry air was metered through the second MFC, passed through a humidity generator (10 L min⁻¹ model, Fuel Cell Technologies), and admitted into the test chamber at 3.25 L min⁻¹. At these two flow rates, the RH was maintained at 40%. A small 8-cm

fan (Papst Model 8412), mounted in the upper left side of the chamber, was used to circulate and mix the gas phase components of the test chamber atmosphere. Temperature and RH in the test chamber were monitored in real time, using a National Institute of Standards and Technology-traceable thermohygrometer (Traceable Hygrometer, Model 4185, Control Company). During testing, approximately 4 L min⁻¹ of the test chamber air was withdrawn into the APCI MS/MS instrument for monitoring the gas phase TIC concentration. The remainder of the test chamber effluent (3.5 L min⁻¹) was directed to vent.

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 directly above the carousel 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 (min). 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 seven-day test. Each of the two fans produced an air velocity of 400 ft min⁻¹ as measured by anemometers (TSI model 8455) 1 to 2 mm above the carousel (very nearly at or just below the surface of the coupons) placed downstream of each of the two carousel fans.

The test chamber included an air lock through which coupons could be removed at the end of a given time interval while minimizing disturbance to the test chamber atmosphere.^[4]

Figure 2-1. Frontal (top) and Overhead (bottom) Views of Test Chamber Used for Persistence Test of TICs



2.1.2 Building Materials

The test coupons used (see Table 2-1) included both porous (concrete and industrial grade carpet) and nonporous (decorative laminate) surfaces representing a variety of building materials. Test coupons were cut (to the sizes indicated in Table 2-1) from larger pieces of stock material. Each coupon was visually inspected prior to being used in any experiment or test. Coupons with anomalies on the application surface were discarded.

2.1.3 TICs, SRSs, and IS

The source, lot number, and purity of each TIC used for the recovery experiments and persistence tests are listed in the upper

section of Table 2-2; these parameters are also listed in the lower section of Table 2-2 for the secondary source material used in the QA performance evaluation (PE) audit.

The surrogate recovery standards (SRSs; see Table 1-2) were obtained from multiple sources: fenchlorphos and DEEP from ChemService and TNB from Aldrich. The IS for quantification (see Table 1-2) were also obtained from multiple sources: DBB and 3-NBP from Aldrich and DIMP from Cerilliant.

2.1.4 Application of TICs to Test Coupons

For both analytical method recovery testing and persistence testing, the test coupons were each spiked with individual TICs to achieve a loading of $\sim 1 \text{ g m}^{-2}$. These levels are listed in Table 2-3.

Table 2-1. Building Material Test Coupon Characteristics for TIC Persistence Tests

Material	Lot, Batch, or Observation	Manufacturer/ Supplier Name	Approximate Coupon Surface Size, L x W, in cm
Decorative Laminate	Laminate/ Formica/ White Matte Finish	Solid Surface Design	3.5 x 1.5 (5.25 cm ²)
Industrial-grade Carpet	ShawTek, EcoTek 6	Shaw Industries, Inc	3.5 x 1.5 (5.25 cm ²)
Concrete, Retaining Wall	Five parts sand: two parts cement	Wysong Concrete	3.5 x 1.0 (3.5 cm ²)

Table 2-2. Source of TICs

Chemical	Manufacturer/ Supplier Name	Lot Number	Purity or Concentration	Concentration as Applied
Materials used for recovery experiments and persistence tests				
Malathion	ChemService	343-110B	99.2%	10 mg mL ⁻¹ in acetone
DMMP	Aldrich	10110EA	97%	10 mg mL ⁻¹ in acetone
TNT	Battelle magazine	Unknown	Unknown	10 mg mL ⁻¹ in acetone
Materials used for QA performance audit				
Malathion	ChemService	332-16B	98%	NA ^a
DMMP	ChemService	08113TC	97%	NA
TNT	Restek	A033065	1000 µg/mL (in acetonitrile)	NA

^a NA= Not applicable

Table 2-3. Spike Amounts of TICs Applied to Building Material Coupons

Coupon Type	Coupon Size, cm ²	Spike Volume	Spike Amount, µg
Carpet	5.3	50 µL of 10 mg mL ⁻¹	500
Laminate	5.3	50 µL of 10 mg mL ⁻¹	500
Concrete	3.5	40 µL of 10 mg mL ⁻¹	400

The addition of 500 µg of a TIC to carpet or laminate coupons is equivalent to 0.5 mg per 5.3 cm², or about 1 mg per 10 cm² or 1 g m⁻². Similarly, the addition of 400 µg to a concrete coupon is equivalent to 0.4 mg per 3.5 cm², or about 1 mg per 10 cm² 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. Laboratory blank coupons were not exposed to TICs or to the laboratory atmosphere in which the test chamber resides. Instead, when the coupons were retrieved from storage, one coupon of each type was placed immediately into an airtight vial for subsequent extraction as a method laboratory blank coupon. All other coupons retrieved from storage were placed in the fume hood where the test coupons and positive controls were spiked. The procedural blank coupons were not spiked but were in the hood during the spiking and handling of the test coupons.

For the analytical method recovery tests, the TIC and SRS solutions were spiked onto the coupons just prior to extraction. In this way, the recovery of each shows the extent to which the combined extraction efficiency and analytical recovery of the SRS agrees with that of its matched TIC. A short drying time was used to allow the solvent to evaporate before extraction. Similarly, for persistence tests, the coupons were placed in the laboratory fume hood and spiked with the TIC solution. The solvent was allowed to evaporate before the coupons were placed in the test chamber. The solvent evaporation times, listed in Table 2-4, were selected on the basis of the TIC and coupon type. Evaporation time was selected based on the relative volatility of the chemical and the porosity of the substrate. Longer drying time (and soak-in time) was provided for less volatile chemicals

(TNT and malathion) on porous materials (carpet and concrete). A short drying time was used for volatile DMMP on all materials. The test chamber was already equilibrated at the appropriate temperature, RH, and air flow when the coupons were added. For the persistence tests, the SRS was not spiked onto each coupon until after coupons were removed from the test chamber, just before analytical extraction. For the analytical method recovery tests, the TIC solution was spiked onto the coupons and the solvent allowed to evaporate as indicated in Table 2-4. As with all other coupons, SRS was not spiked onto these coupons until just prior to extraction.

2.1.5 Extraction Method for TICs

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). A 20-mL aliquot of acetone was added to each vial; the vial was sealed with a screw-cap lid and sonicated for 30 min in an ultrasonic bath (Branson 5510). The extract was decanted through a quartz fiber filter (Pallflex QAT-UP) to either a 200-mL TurboVap tube or a 25-mL Kuderna-Danish tube with attached 125-mL reservoir. Carpet and concrete samples were extracted with three replicate aliquots of acetone; extracts were combined before concentration. Laminate coupons required only one extraction cycle. The number of extraction cycles and the concentration technique used for each TIC and building material combination are listed in Table 2-5. 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 (see Table 1.2) to give a 50-µg mL⁻¹ concentration. The extract was then filtered through a disposable syringe filter (GD/X; Whatman) prior to the GC/MS analysis.

Table 2-4. Solvent Evaporation Times for TIC Spikes in the Analytical Method Recovery Tests

TIC	Material	Evaporation Time, min
TNT, Malathion	Industrial Grade Carpet Concrete Retaining Wall	30
TNT, Malathion	Decorative Laminate	3
DMMP	Decorative Laminate, Industrial Grade Carpet, Concrete Retaining Wall	1

Table 2-5. Extraction and Concentration Techniques Used for TICs

Coupon Type	TIC	Extraction Technique	Extraction	Concentration Technique
Carpet, Concrete	TNT, Malathion	Sonication	Acetone; 3 x 20 mL	TurboVap
Carpet, Concrete	DMMP	Sonication	Acetone; 3 x 20 mL	Kuderna-Danish
Laminate	TNT, Malathion	Sonication	Acetone; 1 x 20 mL	TurboVap
Laminate	DMMP	Sonication	Acetone; 1 x 20 mL	Kuderna-Danish

2.1.6 Analysis Method for TICs

Sample extracts were analyzed using GC/MS in selected 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 three different TICs are listed in Table 2-6.

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 (RT) ± 0.02 min chromatographically co-maximized primary and secondary ions and the correct ratio of the intensity 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.^[5] The IS was present at the same concentration in all samples and standards. The 11-point calibration curve spanned the concentration range of 0.1–150 $\mu\text{g mL}^{-1}$. This concentration

range is equivalent to 0.1% to 150% recovery of the spike amount used in recovery tests and persistence tests. R^2 values for all regression curves were greater than 0.990.

The full calibration curve was generated at the start of each analysis set. Then samples were analyzed with the 20- $\mu\text{g mL}^{-1}$ standard run after every five samples as a continuing check on the calibration. If the calculated concentration of the continuing calibration standard was more than 20% different compared to 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. TNT data was fitted with two 6-point calibration curves, one covering 0.1 to 5 $\mu\text{g mL}^{-1}$ and the other covering 5 to 150 $\mu\text{g mL}^{-1}$.

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

Parameter	Condition
GC column ^a	DB-1701; 30 m x 0.25 mm ID 0.15 μm film thickness; J&W Scientific
Inlet liner	Siltek double goose neck
Temp program for malathion	100 °C (2 min); 100 °C–180 °C @ 10 °C/min; 180 °C–220 °C @ 5 °C/min; 220 °C–260 °C @ 20 °C/min (20 min run time)
Temp program for DMMP	50 °C (2 min); 50 °C–95 °C @ 3 °C/min; 95 °C–250 °C @ 20 °C/min; hold 2.25 min (27 min run time)
Temp program for TNT	100 °C (2 min); 100 °C–180 °C @ 10 °C/min; 180 °C–210 °C @ 5 °C/min; 210 °C–260 °C @ 15 °C/min; hold 3 min (22.3 min run time)
GC injection	1 μL splitless at 280 °C
Transfer line temp	280 °C
MS source temp	230 °C
Quadrupole temp	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 and TNT.

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

Chemical	GC RT, 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
TNT	14.8	210	89
SRS	15.5	213	75
IS	14.6	199	152

2.1.7 Measurement of TICs in Test Chamber Air

Throughout each test, approximately 4 L min⁻¹ of air from the test chamber was continuously withdrawn and introduced to the Perkin Elmer Sciex APCI MS/MS for quantification of the TIC air concentration in real time. Multipoint calibration curves, consisting of a minimum of six points, were generated at the beginning and end of each seven-day test period for each TIC. The responses comprising the two curves were averaged and the resultant mean response factor was used to quantify the TIC. For calibration, known amounts of a specific TIC were admitted to the APCI MS/MS at a known rate; the delivery method depended on the volatility of the TIC. For malathion and TNT, dilute aqueous solutions of varying concentration (typically from 0.1 to 10 µg mL⁻¹) were prepared and directed into the MS source through a custom-built vaporizer at a known flow rate (typically 5 to 15 mL h⁻¹) using a syringe pump. As the air flow into the APCI MS/MS was constant, variation of the aqueous concentration and liquid delivery rate allowed for different gas-phase concentrations to be delivered to the MS/MS. For the higher volatility DMMP, the effluent from a diffusion tube containing DMMP maintained at a constant temperature in a permeation oven was introduced to the MS/MS source in varying amounts through a heated transfer line. That is, in order to generate a multipoint calibration curve, the amount of DMMP delivered to the APCI inlet was adjusted by varying the fraction of the oven air stream that was vented away from the transfer line and replaced with DMMP-free makeup air.

The TIC concentration was calculated using the measured MS/MS response and the mean response ratio from the appropriate calibration curves. Further discussion of this analysis method is presented in Appendix A.

2.1.8 Calculation of Analytical Recovery and Persistence

The analytical method performance recovery was determined initially for both the TIC and its matched SRS according to the following formula:

$$\text{Analytical Method (Raw) Recovery, \%} = \frac{\text{Concentration of extract, } \mu\text{g / mL} \times \text{Extract volume, mL}}{\text{Mass applied, } \mu\text{g}} \times 100\% \quad (1)$$

In many analytical methods, an isotopically labeled chemical version of an analyte (e.g., labeled with deuterium- or carbon-13) is used as the SRS; in that case the analyte and SRS are generally recovered through an analytical method to the same extent because among the population of native and labeled molecules, there is no discernible difference in losses between the native and labeled versions with respect to the types of analytical procedures. In this case, the SRS recovery in each particular sample is used to correct for extraction efficiency and analytical method losses. Where an isotopically labeled version of the 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 between the two compounds. When the SRS and the analyte are not a perfect match to one another, the correction addressed by the SRS recovery needs to be modified by the relative ratio of SRS to analyte recovery. This ratio of SRS to TIC recovery was taken from the recovery measurements of these compounds in the method performance tests.

The analytical method recovery, calculated as shown in Equation 1, for the TIC and its matched SRS was determined, and the ratio of the means of those recoveries were used in Equation 2 to determine the ratio of the SRS recovery to the TIC recovery.

$$\text{SRS / TIC Recovery Ratio} = \frac{\text{Mean analytical method SRS recovery, \%}}{\text{Mean analytical method TIC recovery, \%}} \quad (2)$$

The (raw) recovery of the individual TIC or SRS (calculated using Equation 1) from a building material coupon during a persistence test was corrected by its corresponding SRS (raw) recovery (calculated using Equation 1) and the SRS/TIC recovery ratio (calculated in Equation 2). This resulted in the TIC corrected recovery calculated according to the following equation:

$$\text{TIC Corrected Recovery, \%} = \frac{\text{TIC (raw) recovery, \%}}{\text{SRS (raw) recovery, \%}} \times \text{SRS / TIC recovery ratio} \times 100\% \quad (3)$$

The TIC corrected recovery at each sampling interval, calculated using Equation 3, was then used to calculate percent persistence as shown in Equation 4. The percent persistence at each time point, calculated as shown in Equation 4, represent the primary outcome of this investigation. These results are presented graphically as percent persistence versus time.

$$\text{Persistence, \%} = \frac{\text{TIC corrected recovery at time}_x}{\text{TIC corrected recovery at time}_0} \times 100\% \quad (4)$$

The calculation of the level of a TIC in a blank coupon was calculated according to the following formula:

$$\text{Blank Level, \% of Spike} = \frac{\text{TIC concentration in blank extract, } \mu\text{g / mL} \times \text{Extract volume, mL}}{\text{Mass of TIC applied to test coupons, } \mu\text{g} \times \text{SRS recovery, \%}} \times \frac{\text{Average SRS recovered}}{\text{Average TIC recovered}} \times 100\% \quad (5)$$

To convert a gas-phase TIC concentration from parts per billion (ppb) to a mass concentration at one atmosphere of pressure and 25 °C, the following equation^[6] was used:

$$\text{Concentration in air, } \mu\text{g m}^{-3} = \frac{\text{Concentration, ppb}}{0.0409 \times \text{Molecular Weight}} \quad (6)$$

For the TICs, a calculation of mass balance was carried out to determine the extent to which measurements of the TICs on the coupons and in the chamber air (and in the air that was vented to maintain the air exchange rate) could account for the known amount of the TICs initially spiked onto the coupons.

This mass balance assessment required calculation of the total amount of TIC applied to coupons that were in the chamber at each test interval and the total amount of TIC remaining on those coupons at the end of each test interval. The total mass of spiked TIC was the sum of the spiked mass on the carpet, laminate and concrete coupons, according to the following equation:

$$\text{Mass of spiked TIC, mg} = \sum_{x=1}^3 \text{spiked mass on coupon type}_x \quad (7)$$

The mass on each coupon type was:

$$\text{Spiked mass on coupon type}_x = \# \text{coupons of type}_x \text{ at time}_y \times \text{spike amount per coupon, mg} \quad (8)$$

For example, 0.5 mg was spiked onto each carpet and laminate coupon and 0.4 mg was spiked onto each concrete coupon. There were five replicate coupons of each type for each of the three time intervals (Day 1, Day 2–3, and Day 4–7). On Day 1, with 45 coupons in the chamber, there was a total of 21 mg of a given TIC on all coupon types in the chamber. After removal of 15 coupons at the end of Day 1, there was a maximum of 14 mg of that TIC on coupons during the test interval of Day 2–3. Then, after removal of another 15 coupons at the end of Day 3, there was a maximum of 7 mg of that TIC on coupons during the test interval of Day 4–7.

The percentage distribution on the coupons at the end of a test interval was the amount recovered from the coupons at that time interval divided by the amount originally spiked onto the coupons present in that test interval. The percentage distribution in the air was the amount of the TIC in the vented air divided by the amount originally spiked onto the coupons present in that test interval. The sum of these two percentages was subtracted from 100% to obtain the percentage of the mass that was not accounted for in these two known compartments (coupons and air). The unaccounted for mass may have been distributed between compartments such as the chamber walls and degradation products.

2.1.9 Statistical Analysis of Persistence and Impact of Fans

The TIC persistence data calculated using Equation 4 were used in a statistical analysis to determine whether there was a statistically significant difference between persistence at the start of the experiment (Time 0) and at the end of the test interval (after seven days) (i.e., was there a reduction in persistence over the course of the evaluation?) and whether there was a statistically significant difference in persistence after seven days with fans on and with fans off for each combination of TIC and building material.

The first objective was evaluated with a one-sample t-test, with the p-value reported. The p-value is the probability of finding, by chance, a result as extreme or more extreme than that observed if the preliminary assumption of no loss of persistence is true. P-values less than 0.05 mean that there was at least 95% confidence that the persistence after seven days was lower than persistence at Time 0.

The second objective was evaluated with a two-sample t-test, with the p-value reported. The p-value is the probability of finding, by chance, a result as extreme or more extreme than that observed if the preliminary assumption of no difference in persistence between the fans on and fans off conditions is true. P-values less than 0.05 mean that there was at least 95% confidence that the persistence was different between the two tested conditions. For the two-sample t-test, a preliminary test was conducted to determine whether there was a statistically significant difference in the variability of the data for the two conditions (fan on and fan off). If no significant difference was found, the t-test was performed with a variance estimate formed by pooling the data for the two conditions. If a significant difference was found, the t-test was performed using a Satterthwaite approximation for the variance.

The t-tests were performed in SAS® v 9.2, using the PROC TEST procedure.

2.2 CWAs

Persistence testing for CWAs was used to establish an environmental baseline condition for subsequent liquid and fumigant decontamination investigations. Based on the results

from the TICs persistence investigation, the impact of varying air velocity by use of fans blowing over the coupons for CWAs was not investigated here.

2.2.1 Test Chamber

The test chamber consisted of a specially fabricated polycarbonate (Lexan®) chamber inside a stainless steel cage [with double security locks. The coupons were placed on removable custom built shelves made of 26 gauge cold rolled steel inside the chamber. The inner chamber had dimensions of 26 x 29 x 27 cm, or 20.4 L. A new polycarbonate chamber and shelves were used for each CWA tested. An MFC (Sierra Instruments) was used to adjust and maintain an air exchange rate of one change h^{-1} in the chamber with laboratory air. Air removed from the test chamber was vented through a carbon scrubber column before being discharged into the laboratory fume hood where the chamber was housed.

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

At the conclusion of tests, the chambers were decontaminated and decommissioned according to U.S. Army regulation (AR50-6) and BBRC standard operating procedures.^[4, 7-11]

2.2.2 Building Materials

The building materials that were spiked with CWAs to assess analytical recovery and persistence are listed in Table 2-8; these materials included porous, adsorptive, and nonporous surface types. Test coupons were cut to the sizes indicated in Table 2-8 from larger pieces of stock material.

2.2.3 CWAs and SRSs

The source, lot number, and purity of the CWAs and SRS used for the recovery experiments and persistence tests 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 thickened GD was prepared in a batch.

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

Material	Lot or Batch	Manufacturer/ Supplier Name	Approximate Coupon Surface Size, L x W, cm (Surface area)	Material Preparation
Decorative laminate	Grade 10, nominal thickness 1.2 mm, matte white finish	Solid Surface Design	6.5 x 1.5 (9.75 cm ²)	None
Industrial-grade carpet	Style #M7978, color #910; Carpet Corp of America, Rome, GA	Shaw Industries, Incorporated	6.5 x 1.5 (9.75 cm ²)	None
Galvanized metal ductwork	Industry HVAC standard 24 gauge galvanized steel; Adept Products Inc, West Jefferson, OH	Accurate Fabrication	6.5 x 1.5 (9.75 cm ²)	Clean with acetone
Ceiling tile ^a	Armstrong 954, Classic Fine Textured	Armstrong	6.5 x 1.5(9.75 cm ²)	None

^a Limited analytical method recovery tests conducted with ceiling tile and GB; no persistence tests conducted due to significant losses

Table 2-9. Source of CWAs and SRSs

Chemical	Manufacturer/Supplier	Purity or Concentration	Concentration as Applied
Materials used for analytical methods tests and persistence tests			
GB	U.S. Army	96	Neat
GD	U.S. Army	94	95% neat
VX	U.S. Army	70	Neat
TBP (SRS)	Aldrich	99	Neat
Standard Analytical Reference Material (SARM) used to confirm CWA purity			
GB	US Army Medical Research Institute of Chemical Defense	1 mg/mL	Not Applicable
GD	US Army Medical Research Institute of Chemical Defense	1 mg/mL	
VX	US Army Medical Research Institute of Chemical Defense	1 mg/mL	

2.2.4 Application of CWAs to Test Coupons

For both analytical method recovery testing and persistence testing, the coupons were spiked with the individual CWA to achieve a loading of approximately 1 g m^{-2} . All building materials were spiked with $1 \text{ }\mu\text{L}$ of neat agent to deliver approximately 1 mg . A $50\text{-}\mu\text{L}$ repeating dispenser pipette (Hamilton) that delivers 50 equal volumes per syringe load was used to apply the CWA to the test coupons. Because the syringe volume and dispensed volume are not adjustable, it was not possible, for example, to apply $1.4 \text{ }\mu\text{L}$ of VX so as to offset the 70% purity. Concurrently with the spikes to the test coupons, a $1\text{-}\mu\text{L}$ spike of each agent was made directly into 10 mL of the extraction solvent and this solution was analyzed to assess the amount of CWA applied to the building materials. The amounts of CWAs applied to test coupons are listed in Table 2-10.

Table 2-10. Spike Amounts of CWAs Applied to Building Material Coupons

Chemical	Amount of CWA Applied
GB	$840 \text{ }\mu\text{g}$
TGD	$840 \text{ }\mu\text{g}$
VX	$580 \text{ }\mu\text{g}$

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

2.2.5 Extraction Method for CWAs

For extraction of building material coupons, the SRS was first applied directly to the coupon as neat material; $1 \text{ }\mu\text{L}$ of the SRS delivered 1 mg . The coupon was then loaded into a 40-mL sample extraction vial and a 10-mL aliquot of hexane containing the IS at $100 \text{ }\mu\text{g mL}^{-1}$ was added. The vial was shaken briefly and then the building material was allowed to stand in the solvent overnight ($\sim 14\text{--}16 \text{ h}$) for passive extraction. Several times after addition of the solvent, the vials were shaken to facilitate extraction and dispersion.

2.2.6 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 included the correct GC retention time $\pm 0.02 \text{ min}$. The GC retention times are listed in Table 2-12. The quantification was performed using the IS method. The IS was present at the same concentration in all samples and standards. The 9-point calibration curve spanned the range of $0.24\text{--}190 \text{ }\mu\text{g mL}^{-1}$. This concentration range is equivalent to 0.24 to 190% recovery of the spike amount used in recovery tests and persistence tests.

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

Parameter	Condition
GC column for GB ^a	DB-5; 25 meter x 0.32 mm ID x 0.52 μm film thickness; Agilent
Temp program for GB	$55 \text{ }^{\circ}\text{C}$ (1 min); $55 \text{ }^{\circ}\text{C}\text{--}100 \text{ }^{\circ}\text{C}$ @ $10 \text{ }^{\circ}\text{C/min}$; $100 \text{ }^{\circ}\text{C}\text{--}250 \text{ }^{\circ}\text{C}$ @ $25 \text{ }^{\circ}\text{C/min}$ (11.5 min run time)
GC column for TGD ^a	Rtx-5; 30 meter x 0.32 mm ID x 0.50 μm film thickness; Restek
Temp program for TGD	$40 \text{ }^{\circ}\text{C}$ (1 min); $40 \text{ }^{\circ}\text{C}\text{--}100 \text{ }^{\circ}\text{C}$ @ $10 \text{ }^{\circ}\text{C/min}$; $100 \text{ }^{\circ}\text{C}\text{--}250 \text{ }^{\circ}\text{C}$ @ $30 \text{ }^{\circ}\text{C/min}$ (12 min run time)
GC column for VX ^a	DB-5; 25 meter x 0.32 mm ID x 0.52 μm film thickness; Agilent
Temp program for VX	$55 \text{ }^{\circ}\text{C}$ (1 min); $55 \text{ }^{\circ}\text{C}\text{--}100 \text{ }^{\circ}\text{C}$ @ $10 \text{ }^{\circ}\text{C/min}$; $100 \text{ }^{\circ}\text{C}\text{--}300 \text{ }^{\circ}\text{C}$ @ $25 \text{ }^{\circ}\text{C/min}$ (13.5 min run time)
GC injection	$1 \text{ }\mu\text{L}$ splitless at $250 \text{ }^{\circ}\text{C}$
Detector temp	$250 \text{ }^{\circ}\text{C}$
Hydrogen flow	70 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

2.2.7 Measurement of CWAs in Test Chamber Air

Measurement of the CWA concentration in the test chamber air was performed by collection of an air sample onto a Carboxen sorbent tube at defined intervals during the seven-day test period. A portion (100 mL min^{-1}) of the vented chamber air (340 mL min^{-1}), vented to maintain an air exchange rate of one exchange h^{-1} , was collected on the Carboxen sorbent tube. Sample collection was 1 h in duration, with three sampling periods during Day 1, four sampling periods during Days 2–3, and four sampling periods during Days 4–7. Following collection of the gas-phase CWA, the Carboxen was removed from the sorbent tube and

placed in a 2-mL sample vial. A 1-mL aliquot of chloroform containing the IS for quantification was added to the vial. The sorbent and solvent were mixed vigorously on a vortex mixer for 30 seconds; the sorbent was allowed to settle and a portion of the extract was removed for analysis. The sorbent extract was analyzed as described above for the coupon extracts.

2.2.8 Calculation of Percent Recovery and Persistence

The calculations of percent recovery in analytical method test experiments and calculations of persistence were carried out using the same equations listed and described in Section 2.1.8 for the TICs.

In a manner identical to that described in Section 2.1.8, a calculation of the distribution of the CWA between the known compartments (air and coupons) and the unknown compartments (walls, degradation products) was carried out for the first sampling interval (first h of the persistence test). The CWA recovered from the coupons was divided by the total amount that was known to have been spiked onto the coupons to obtain the analytical method (raw) recovery percentage from the coupons. The CWA measured in the sampled air was divided by the total amount that was known to have been spiked onto the coupons to obtain the percentage in the air. The sum of these two compartments was subtracted from 100% to obtain an estimate of the amount of the originally spiked mass that was not accounted for in the known compartments.

Quality Assurance/Quality Control

QA/quality control (QC) procedures were performed in accordance with the TTEP Quality Management Plan (QMP)^[12] and the test/QA plan^[3] for this investigation. 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 experiments. For the three 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 percent difference less than 25%; results were well within the target tolerance.

3.2 Technical Systems Audit

The Battelle QA Manager conducted a technical systems audit (TSA) to ensure that the tests were being performed in accordance with the test/QA plan^[3] and QMP.^[12] As part of the audit, the Battelle QA Manager 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 that might impact the quality of the evaluation results were noted in this audit. The records concerning the TSA are permanently stored with the Battelle QA Manager.

3.3 Data Quality Audit

At least 10% of the data acquired during the evaluation 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. In compliance with the test/QA plan, all data calculations were checked.

3.4 QA/QC Reporting

Each assessment and audit was documented in accordance with the test/QA plan^[3] and QMP.^[12] For this evaluation, no significant findings were noted in any assessment or audit, and no follow-up correction action was necessary. Copies of the TSA and assessment report were distributed to the EPA QA Manager and Battelle staff.

3.5 Deviations from Test/QA Plan

The persistence tests for the CWAs were conducted at RH values of 12%–22%, rather than the 40% RH listed in the test/QA plan. The RH was that of the laboratory air. To expedite work, it was agreed that this would be acceptable for these tests but that modifications would be made to achieve targeted RH values for the decontamination tests. The persistence may have been slightly lower with higher RH, so these results were taken as an upper bound on persistence in planning for the decontamination tests.

In the persistence tests of TNT with the fans on, the coupons were inadvertently spiked with 10% of the targeted spiked amount: 50 µg on the carpet and laminate coupons, rather than 500 µg, and 40 µg on the concrete, rather than 400 µg. Because of the general agreement in results between the fans on and fans off conditions, it appeared that this error did not compromise the utility of the persistence data in planning for the decontamination tests.

The test/QA plan envisioned use of a 317-L test chamber. 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.

During the DMMP test with fans on, the humid air was inadvertently turned off overnight and RH fell outside of the target range for a total of about 20 h. The humidity level in the test chamber was stabilized within 4 h of reactivating the RH generator.

Appendix 1 (Version 3) specifies that the mass flow controller used to control the air exchange rate in the test chamber will be compared to a second NIST-traceable calibrated flow meter before and after the experiment. The comparison of the mass flow controller to a second NIST-traceable calibrated flow meter was not performed during the CWA persistence investigation. Because the flow meters were within their calibration, the staff inadvertently forgot to obtain a second calibrated meter to compare the values. It is believed that there was no negative impact on the study since the mass flow control meters were within calibration and the calibration can be traced to NIST standards.

Table 3-1. PE Audit Results

TIC	Sample ID	Date of Audit	Standard Concentration	Measured Result	% Difference
Malathion	50866-100-19	01/30/2006	100 µg mL ⁻¹	97.65 µg mL ⁻¹	-2.3
DMMP	50866-100-34	02/05/2006	100 µg mL ⁻¹	84.06 µg mL ⁻¹	-15.9
TNT	50866-38-16	09/29/2005	100 µg mL ⁻¹	101.22 µg mL ⁻¹	1.2

3.6 Data Quality Indicators

Table 3-2 summarizes the data quality indicators that were monitored and evaluated in accordance with the test/QA plan. GB recovery from laminate was below the acceptance level specified in the test/QA plan. However, this was believed to be due to high volatility rather than inefficient extraction methods. Therefore, GB on laminate was included in the persistence testing.

No CWA was recovered from laboratory blank coupons. However, GB, TGD, and VX were all found to redeposit at relatively high levels onto procedural blank coupons in the test chamber. In many instances the recovery of CWA from procedural blank coupons was above the acceptance level of <10% of the mass recovered from test coupons that was specified in the test/QA plan. These surprising results were accepted as experimental findings.

Table 3-2. Measurements and Data Quality Indicators for Persistence Testing

Parameter	Measurement Method	Data Quality Indicators	Corrective Action (None except as specified)
Temperature	NIST-traceable thermometer	Thermometer was compared against a calibrated thermometer before and after experiment and agreed within ± 2 °C.	None.
Relative humidity	NIST-traceable hygrometer	Hygrometer was compared against a calibrated hygrometer before and after experiment, agreed within $\pm 10\%$ except one check with bias of -20%.	Subsequent hygrometer calibration check performed at 40% RH, 22 °C found instrument to read within 5% of the challenge concentration.
Air exchange rate in chamber	Mass flow controller	NIST-traceable flow meter used for the air exchange measurements was within calibration. Before and after each experiment the meter was compared to a second NIST-traceable calibrated flow meter.	During the TICs persistence investigation, the calibrated flow control meter was checked 16 times and all checks passed the acceptance criterion. During the CWAs persistence investigation, a calibrated flow control meter was used, but the flow meters were not compared to a second flow meter before or after the experiment. This deviation is described in Section 3.5.
Agent on positive control	Extraction/GC; IS quantitation	48%–91% recovery of TICs from all materials; within 40% to 120% recovery specified in the test/QA plan. 45%–113% recovery of CWA from all materials, except 23% recovery of GB from laminate, within 40% to 120% recovery specified in the test/QA plan. All analytes and IS within 60%–140% of actual value after correction for percent recovery. Results from all coupons were within three standard deviations of the mean—no outliers were excluded. All IS quantitation within 40%–120% specified.	Extraction of GB on laminate was rerun; extraction efficiency of 23% for GB on laminate was accepted for further investigation because the low recovery was believed to reflect evaporation rather than issues with recovery methods.
Agent on laboratory blank or on procedural blank	Extraction/GC; IS quantitation	For all TICs, non-detect to 0.50% of spike amount detected on blank coupons; lower than limits of 1% and 10%, respectively, in test/QA plan. CWA all non-detects (<0.2%) of spike amount on all laboratory blank coupons. Some procedural blank coupons for GB, TGD, and VX were observed to have more than 10% of the amount of analyte compared to that found on test coupons; this exceeded the level of recovery from procedural blank coupons specified in the test/QA plan.	The redeposition of CWA onto procedural blank coupons was accepted as an unanticipated experimental result; findings are included in Section 4.2.4.

Results and Discussion

4.1 Results for TICs

4.1.1 Analytical Method: Recovery of TICs from Building Materials

Prior to testing the persistence of TICs on test coupons of building materials, the analytical method was tested to ascertain accuracy (recovery) and precision (variability). The recoveries of the individual TICs and their matched SRS compounds from the different building materials are listed in Table 4-1. These are raw recovery data calculated using Equation 1 in Section 2.1.8. Because the TICs were being applied to each test coupon as a spike in a solvent carrier, sufficient time was required to allow the solvent to evaporate completely before testing extraction efficiency. The time allowed for solvent to evaporate, 3–30 min, was found to be excessive for DMMP as this TIC is considerably more volatile than the other two. As a consequence, recoveries of DMMP after 3–30 min evaporation times were less than 50%. This test of analytical method recovery was repeated for DMMP using one min evaporation times.

The SRS was chosen so that its recovery in test coupon samples would be similar to the recovery of the analyte of concern and therefore informative about the method performance and recovery of the analyte from the matrix when its level was not known. As seen in Table 4-1, the recovery ratios of SRS/TIC for malathion and DMMP (with short evaporation times) for the different matrices were within 20% of each other (ratio of 0.80–1.20), which is slightly greater than what can be expected when a labeled analog of an analyte is used as the SRS. The recovery ratios for TNT and its SRS tended to be lower than 0.80, indicating that the method recovers the analyte more efficiently than the SRS. Because of the differences in SRS and TIC analytical method recoveries, the concentrations of analytes in blind samples were corrected by relative recoveries of the SRS and TIC, in addition to the normal correction by SRS recovery.

Table 4-1. Mean Percent Recovery of TICs and Matched SRSs from Building Materials

Recovery from Building Material, % \pm SD				
Material	Evaporation time, min	TIC	SRS	SRS/TIC recovery ratio
		Malathion	Fenchlorphos	
Carpet (n = 9)	30	84 \pm 7	95 \pm 5	1.13
Laminate (n = 10)	3	80 \pm 3	87 \pm 3	1.09
Concrete (n = 10)	30	51 \pm 4	56 \pm 7	1.11
		DMMP	DEEP	
Carpet (n = 10)	30	37 \pm 6	78 \pm 10	2.10 ^a
Laminate (n = 9)	3	29 \pm 6	76 \pm 6	2.62 ^a
Concrete (n = 10)	30	46 \pm 4	40 \pm 4	0.87 ^a
		DMMP	DEEP	
Carpet (n = 10)	1	72 \pm 4	86 \pm 4	1.20
Laminate (n = 10)	1	71 \pm 9	82 \pm 3	1.15
Concrete (n = 10)	1	48 \pm 4	52 \pm 4	1.09
		TNT	TNB	
Carpet (n = 9)	30	91 \pm 6	69 \pm 7	0.76
Laminate (n = 10)	3	76 \pm 16	62 \pm 8	0.81
Concrete (n = 10)	30	48 \pm 9	32 \pm 14	0.68

^a Ratio listed to show effect of evaporation time on relative losses of TIC and SRS; not used in sample analyses.

Recovery of the SRS during method development and during persistence testing followed the same method described for the TICs in Section 2.1. The recoveries of the SRSs in the analytical method tests and the persistence tests were generally in good agreement, with greater agreement for the SRS of malathion and lesser agreement for the SRS of DMMP, presumably due to the high volatility of the DEEP SRS used (compared to the generally lower volatility of the malathion SRS). The similarities of these SRS recoveries indicated that the method of analyte correction based on SRS recovery is reasonable. The comparison of SRS recoveries in the analytical method and persistence tests is given in Table 4-2.

The approximate method detection limits (MDLs) for the TIC are listed in Table 4-3. The MDL was estimated based on the signal of the lowest level calibration standard ($0.1 \mu\text{g mL}^{-1}$), the signal-to-noise ratio for this concentration, and the peak area that can be integrated reliably for any signal.

4.1.2 Persistence Over Time of TICs on Building Materials

The persistence for each TIC on each of the building materials was conducted simultaneously. The mean temperature and % RH in the test chamber during the persistence testing is included in Table 4-4. Details of the temperature and RH and air velocity

measurements are described in Section 4.1.6. One positive control coupon was spiked and extracted immediately, along with a laboratory blank coupon. A total of 45 test coupons (15 carpet test coupons, 15 laminate test coupons, and 15 concrete test coupons) were spiked with $500 \mu\text{g}$ ($400 \mu\text{g}$ for concrete) of the TIC, as described in Section 2.1.4, and loaded into the test chamber. A total of 5 spiked test coupons of each building material type were removed after 24 h (one day), after an additional 48 h (three days total), and after an additional 96 h (seven days total). These test coupons were analyzed as described in Section 2. Each test was conducted once with fans blowing air over the coupons with a linear velocity of 400 ft min^{-1} (fans on) and once with the fans turned off (fans off). The percent recoveries of the spiked TICs from each building material type at initiation (Day 0) and on subsequent days (Day 1, Day 3, Day 7), with the fans on and fans off, were calculated as described in Section 2.1.8, using Equation 3, and are listed in Table 4-4. The spike recovery assumes spike amounts as listed in Table 2-3. Spiked amounts were not checked against an independent spike check samples as the Day 0 samples were assumed to fulfill that role.

The between-trial variability in Day 0 recoveries (e.g., fans-on and fans-off Day 0 recovery of malathion from carpet) had a mean of 7.8% with a SD of 0.08% and ranged from <1% to 24%. These results exclude Day 0 for TNT on concrete because of the difference in mass spiked onto the coupons on those two days.

Table 4-2. Comparison of Mean Percent SRS Recoveries by Building Material for Analytical Method Recovery Tests and Persistence Tests

SRS (matched TIC)	Material	Mean SRS Recovery, % \pm SD	
		Method test (n=9 or 10)	Persistence test (n=32)
Fenchlorphos (Malathion)	Carpet	95 ± 5	97 ± 9
	Laminate	87 ± 3	85 ± 12
	Concrete	56 ± 7	52 ± 14
DEEP (DMMP)	Carpet	86 ± 4	74 ± 5
	Laminate	82 ± 3	66 ± 6
	Concrete	52 ± 4	56 ± 13
TNB (TNT)	Carpet	69 ± 7	58 ± 16
	Laminate	62 ± 8	71 ± 13
	Concrete	32 ± 14	25 ± 13

Table 4-3. MDLs for TICs

MDL			
	Malathion	DMMP	TNT
In solution	$0.01 \mu\text{g mL}^{-1}$	$0.01 \mu\text{g mL}^{-1}$	$0.025 \mu\text{g mL}^{-1}$
On coupon	$0.05 \mu\text{g}$	$0.05 \mu\text{g}$	$0.125 \mu\text{g}$

Table 4-4. Mean Recovery of TICs from Building Materials Under Environmental Conditions

Mean TIC Remaining on Building Material as Percent of Expected Spike Amount, % \pm SD ^a						
Malathion						
	Carpet		Laminate		Concrete	
Time	Fans on 25 °C, 38% RH	Fans off 24 °C, 41% RH	Fans on 25 °C, 38% RH	Fans off 24 °C, 41% RH	Fans on 25 °C, 38% RH	Fans off 24 °C, 41% RH
Day 0 (n=1)	115	112	101	119	63	103
Day 1 (n=5)	104 \pm 8	115 \pm 3	101 \pm 9	115 \pm 4	24 \pm 8	48 \pm 10
Day 3 (n=5)	102 \pm 2	105 \pm 3	76 \pm 11	103 \pm 7	12 \pm 8	17 \pm 11
Day 7 (n=5)	91 \pm 4	94 \pm 3	33 \pm 8	85 \pm 4	5 \pm 3	7 \pm 4
DMMP						
	Carpet		Laminate		Concrete	
Time	Fans on 25 °C, 36% RH	Fans off 24 °C, 42% RH	Fans on 25 °C, 36% RH	Fans off 24 °C, 42% RH	Fans on 25 °C, 36% RH	Fans off 24 °C, 42% RH
Day 0 (n=1)	110	112	89	71	98	74
Day 1 (n=5)	23 \pm 5	18 \pm 3	0.7 \pm 0.2	0.3 \pm 0.3	102 \pm 22	78 \pm 5
Day 3 (n=5)	12 \pm 2	13 \pm 2	0.6 \pm 0.3	0.4 \pm 0.1	58 \pm 20	65 \pm 3
Day 7 (n=5)	7 \pm 3	8 \pm 2	0.6 \pm 0.3	0.2 \pm 0.2	53 \pm 8	74 \pm 4
TNT						
	Carpet		Laminate		Concrete	
Time	Fans on ^b 25 °C, 37% RH	Fans off 25 °C, 39% RH	Fans on ^b 25 °C, 37% RH	Fans off 25 °C, 39% RH	Fans on ^b 25 °C, 37% RH	Fans off 25 °C, 39% RH
Day 0 (n=1)	129	101	91	100	5	53
Day 1 (n=5)	121 \pm 11	81 \pm 7	40 \pm 5	69 \pm 10	8 \pm 3	43 \pm 10
Day 3 (n=5)	126 \pm 21	85 \pm 8	16 \pm 7	68 \pm 17	12 \pm 4	45 \pm 11
Day 7 (n=5)	114 \pm 16	62 \pm 8	11 \pm 7	45 \pm 13	21 \pm 14	30 \pm 5

^a Mean recovery corrected by sample SRS mean recovery and by ratio of SRS to TIC recovery.

^b TNT inadvertently spiked with 10% of the planned amount.

Graphical representation of the spike recovery trends listed above for malathion, DMMP, and TNT are shown in Figures 4-1, 4-2, and 4-3, respectively. In the figures, fan off corresponds to the condition in which the two fans above the carousel were off during the test. Fan on corresponds to the test in which the two fans were on throughout the duration of the experiment.

To assess persistence, the recovery data for Day 1, 3, and 7 were corrected by the amount measured in the extract of the Day 0 positive control sample. The TIC persistence on individual coupons was calculated using Equation 4 in Section 2.1.8. The mean persistence of the TICs over time is given in Table 4-5, along with notation of whether there was a statistically

Figure 4-1. Recovery of Malathion from Building Materials (Mean conditions fans on: 25 °C and 38% RH; fans off: 24 °C and 41% RH; error bars are 1 SD)

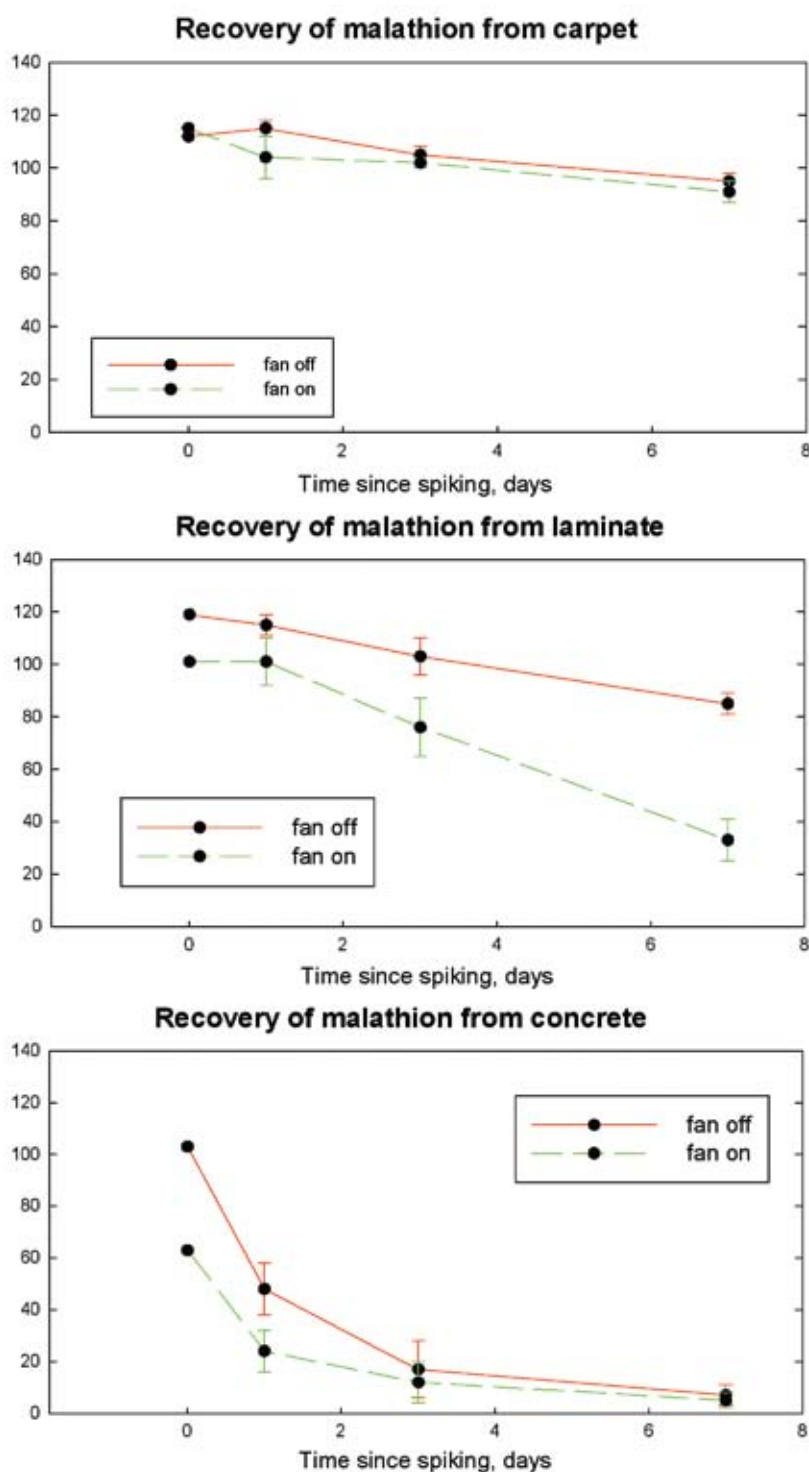


Figure 4-2. Recovery of DMMP from Building Materials
(Mean conditions fans on: 25 °C and 36% RH; fans off:
24 °C and 42% RH; error bars are 1 SD)

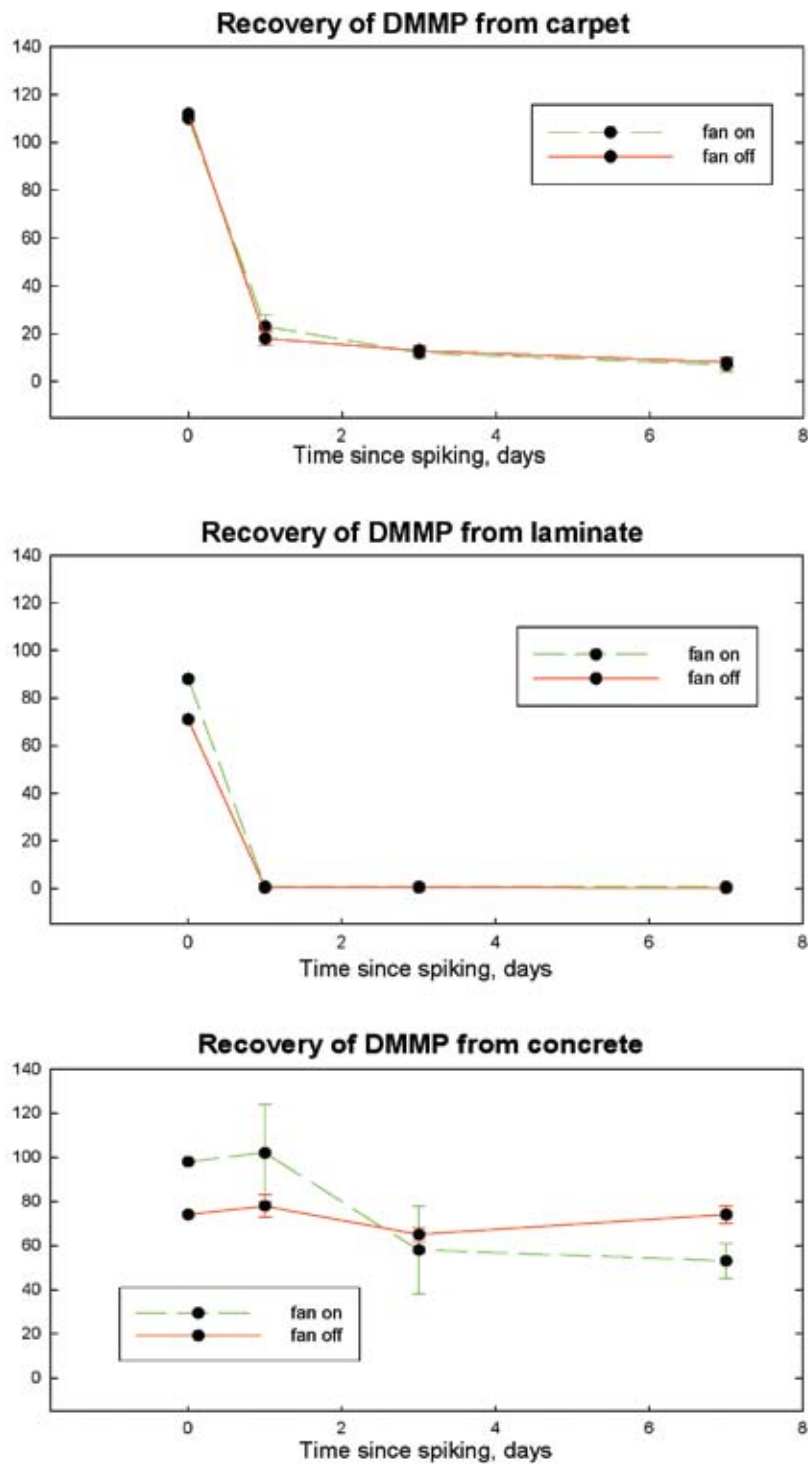
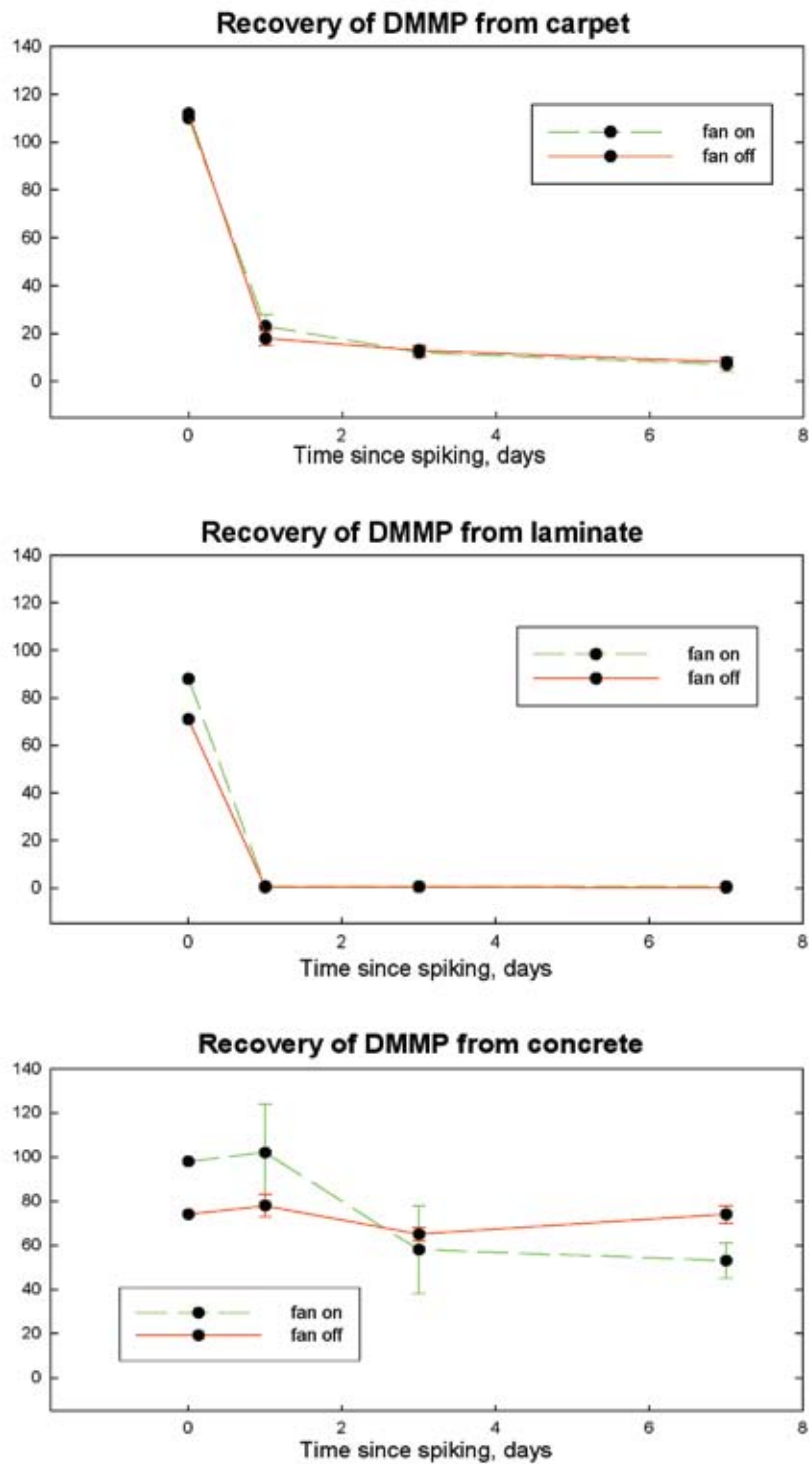


Figure 4-3. Recovery of TNT from Building Materials
(Mean conditions fans on: 25 °C and 37% RH; fans off: 25 °C and 39% RH; error bars are 1 SD)



significant reduction in persistence after seven days compared to the persistence at Day 0 (Time 0); the t-test p-value for this evaluation is listed. Table 4-5 also lists whether there was a statistically significant difference between the persistence at Day 7 for the conditions of “fans on” and “fans off” for each combination of TIC and building material. Similarly, the p-value for the t-test for this evaluation is listed.

As shown in Table 4-5, the fans-on condition had little or no impact on the persistence of malathion on carpet and concrete. However, in the case of malathion on laminate, the fans-on condition resulted in significant and substantial decrease in persistence compared to the fans-off condition.

As indicated in the analytical method recovery tests, recovery of malathion from concrete is about 50% even under relatively short contact times with the matrix. This low recovery of malathion from concrete is probably not due to volatilization losses, but rather to hydrolysis or irreversible binding to the substrate. Concrete is a highly basic substrate and also contains hydrated inorganic complexes. Malathion is readily hydrolyzed under aqueous neutral, basic, and acidic conditions, so the water and/or the basic sites in concrete could lead to degradation of malathion over time. In addition, given malathion’s low vapor pressure, volatilization from concrete may be only a minor contribution to analyte loss. In correcting each TIC recovery by the sample-specific SRS recovery, we have assumed that the losses are

due only to analytical issues, e.g., extraction or concentration. This may lead to an over-estimate of the amount of malathion remaining on the concrete, since the SRS does not account for possible malathion degradation.

In contrast, highly volatile DMMP does not persist on laminate test coupons. This lack of persistence may be attributable to the high vapor pressure and nonporosity of the coupon substrate and low octanol:water partition coefficient of DMMP. On carpet the DMMP is gradually lost from the coupons (down to 11% by Day 3 and 7% by Day 7 with or without the fan on). Since DMMP is not readily hydrolyzed, it appears that its persistence on concrete is governed largely by vapor pressure; with air flow over the surface to disperse vaporized material, the volatilization rate increases. For laminate and carpet, air flow does not reduce persistence. The DMMP is largely retained by the concrete; persistence is reduced by air flow.

TNT is intermediate between malathion and DMMP in vapor pressure and octanol:water partition coefficient, though more similar to malathion than to DMMP. Indeed, TNT clearly persists on carpet, but less on laminate surface. The greater persistence of TNT on carpet with the fans on, compared with the fans off, is difficult to explain or understand on the basis of these data. Given the resistance of TNT to hydrolysis, it appears that its persistence on concrete is governed by its low volatility rather than hydrolysis to alternative products.

Table 4-5. Mean Persistence of TICs on Building Materials over Time as Percent of Day 0 Recovery

	Mean TIC Persistence on Building Material, % of Day 0 Recovery \pm SD					
	Malathion					
	Carpet		Laminate		Concrete	
Duration	Fans on	Fans off	Fans on	Fans off	Fans on	Fans off
Day 1	90 \pm 7	103 \pm 3	100 \pm 9	97 \pm 3	38 \pm 13	46 \pm 10
Day 3	88 \pm 1	94 \pm 2	75 \pm 10	87 \pm 6	19 \pm 13	17 \pm 11
Day 7	79 \pm 4	85 \pm 3	32 \pm 8	72 \pm 4	7 \pm 5	7 \pm 3
Reduction over time?	Yes	Yes	Yes	Yes	Yes	Yes
p-value	p=0.0002	p=0.0003	p<0.0001	p<0.0001	p<0.0001	p<0.0001
Difference with fans?	Fans on=Lower persistence		Fans on=Lower persistence		No difference in persistence	
p-value	p=0.0355		p<0.0001		p=0.8131	
	DMMP					
	Carpet		Laminate		Concrete	
Duration	Fans on	Fans off	Fans on	Fans off	Fans on	Fans off
Day 1	21 \pm 4	16 \pm 3	0.8 \pm 0.2	0.4 \pm 0.4	104 \pm 22	106 \pm 6
Day 3	11 \pm 1	11 \pm 1	0.7 \pm 0.3	0.5 \pm 0.2	59 \pm 20	87 \pm 4
Day 7	7 \pm 3	7 \pm 2	0.6 \pm 0.3	0.2 \pm 0.2	54 \pm 8	99 \pm 6
Reduction over time?	Yes	Yes	Yes	Yes	Yes	No
p-value	p<0.0001	p<0.0001	p<0.0001	p<0.0001	p=0.0003	p=0.8474
Difference with fans?	No difference in persistence		Fans on=Higher persistence		Fans on=Lower persistence	
p-value	p=0.9495		p=0.0445		p<0.0001	
	TNT					
	Carpet		Laminate		Concrete	
Duration	Fans on ^{a,b}	Fans off	Fans on ^{a,b}	Fans off	Fans on ^{a,b}	Fan off
Day 1	94 \pm 9	81 \pm 7	43 \pm 5	69 \pm 11	17 \pm 6	81 \pm 19
Day 3	97 \pm 17	84 \pm 8	17 \pm 7	68 \pm 17	24 \pm 9	85 \pm 20
Day 7	89 \pm 13	61 \pm 8	12 \pm 8	45 \pm 13	43 \pm 29	57 \pm 9
Reduction over time?	No	Yes	Yes	Yes	Yes	Yes
p-value	p=0.1143	p=0.0005	p<0.0001	p=0.0006	p=0.0120	p=0.0004
Difference with fans?	Fans on=Higher persistence		Fans on=Lower persistence		No difference in persistence	
p-value	p=0.0038		p=0.0011		p=0.3254	

^a Due to anomalous data for Day 0 positive controls, the initial method recovery of TNT from concrete was substituted for the positive control.

^b TNT inadvertently spiked at 10% of planned spike amount.

The statistical analysis provides evidence that persistence is reduced after seven days for all agents, materials, and test conditions with the exception of DMMP on concrete with the fan off and TNT on carpet with the fan on. In the separate comparison of whether there is a difference in persistence for Day 7 results between the tests done with fans on and fans off, the results are mixed. For malathion, persistence with the fans on is statistically significantly lower than with the fans off for carpet and laminate, but no significant difference is detected for concrete. For DMMP, the fans-on condition results in significantly lower persistence on concrete, but not for carpet or laminate. The laminate result actually shows a statistically significantly greater persistence with the fans-on as compared to fans-off, though both fans-on and fans-off conditions exhibit very low average persistence (less than 1%). For TNT, the fans-on condition yields significantly greater persistence than with fans off on carpet. The reverse is true for laminate; the fans-on condition provides lower persistence. The results for concrete move in the same direction as the laminate result, but the variability in observed persistence is so large that the difference does not achieve statistical significance.

The statistical analysis results above are presented with the assumption that statistical significance can be concluded

whenever the p-value is less than 0.05. This approach confers 95% confidence (i.e., no more than a 5% risk) that a significant difference will not be concluded in error for a single comparison. However, over the large number of comparisons made in this evaluation, the cumulative chance of making at least one erroneous conclusion of significance becomes larger than 5%. A more conservative approach is to suppose that a maximum 5% chance of error (i.e., minimum 95% confidence) is desired for the collective set of all comparisons in the evaluation. A simple approach to achieving this outcome is to employ a Bonferroni correction to the results. Under this strategy, only p-values less than 0.0019 would be considered statistically significant. The general trend of reduced persistence after seven days would still hold. However, the statistically significant differences between fans on and fans off would be reduced. Only malathion and TNT on laminate, and DMMP on concrete would exhibit statistically significantly lower persistence with the fans on; none of the test conditions would exhibit statistically significantly higher persistence with the fans on.

Graphical representations of these trends for each TIC on the three different types of building materials are shown in Figures 4-4, 4-5, and 4-6 for malathion, DMMP, and TNT, respectively.

Figure 4-4. Mean Persistence of Malathion on Building Materials as Percentage of Time 0 Recoveries (Mean conditions fans on: 25 °C and 38% RH; fans off: 24 °C and 41% RH)

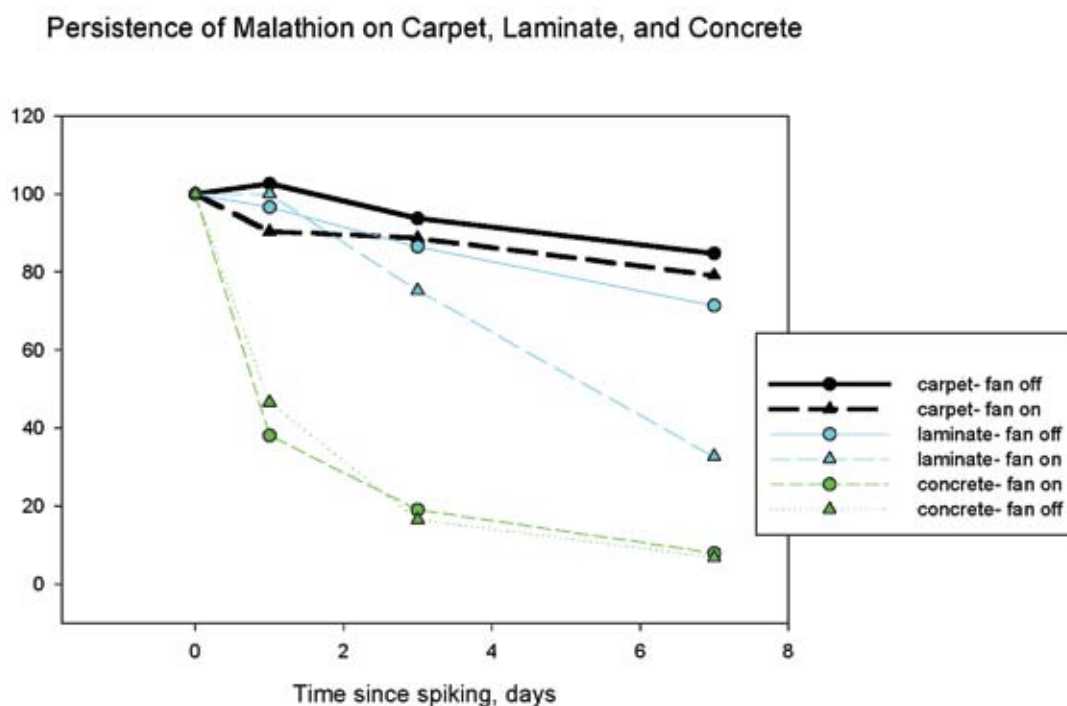


Figure 4-5. Persistence of DMMP on Building Materials as Percentage of Time 0 Recoveries (Mean conditions fans on: 25 °C and 36% RH; fans off: 24 °C and 42% RH)

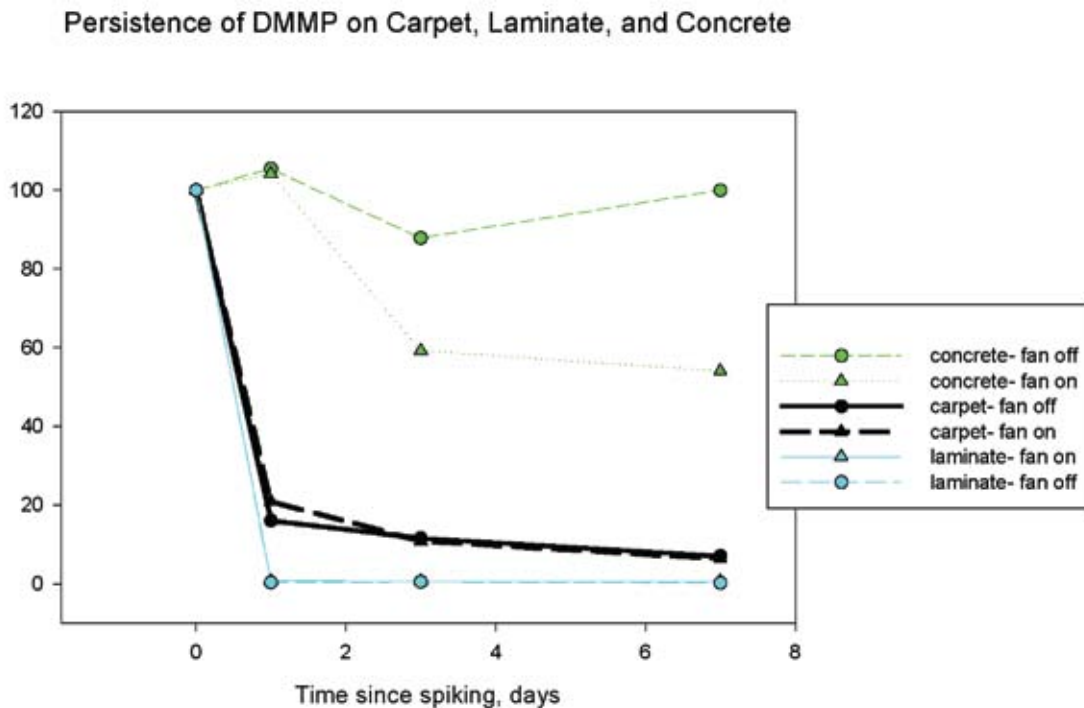
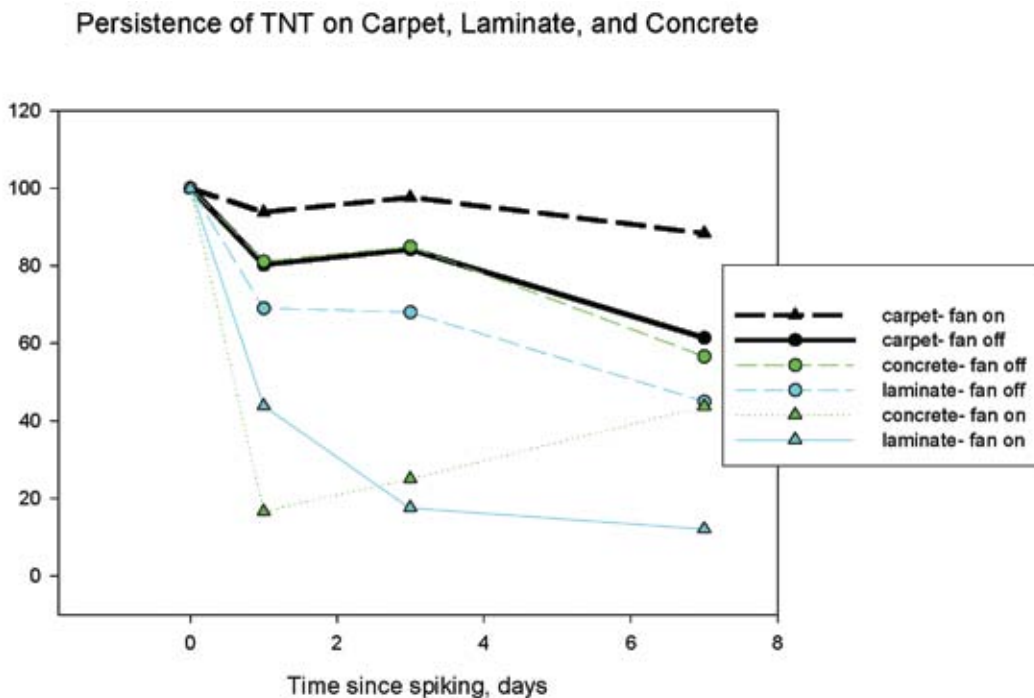


Figure 4-6. Persistence of TNT on Building Materials as Percentage of Time 0 Recoveries (Mean conditions fans on: 25 °C and 37% RH; fans off: 25 °C and 39% RH)



4.1.3 Concentrations of TICs in Test Chamber Air

Real-time APCI MS/MS was used to monitor the air concentration of each TIC in the chamber during the persistence tests. Approximately 50% of the air that was vented from the chamber to achieve 1 air exchange h^{-1} (7.5 L/min) was directed into the inlet of the APCI MS/MS instrument. Except for once daily calibration of the instrument response (needed for quantification), the MS/MS instrument monitored effluent from the chamber continuously. The time-weighted average chamber air concentrations of each TIC during the persistence tests are listed in Table 4-6. The concentrations are listed as those measured during the time when all 45 test coupons were in the chamber (Day 1 of the test), during the next 48 h period when 30 test coupons were in the chamber (Day 2–3), and during the following 96 h period when 15 test coupons were in the chamber (Day 4–7).

After the completion of a seven-day persistence test, the polycarbonate front panel was removed and all inner surfaces (fiberglass) were wiped with acetone. Before reassembly, the

chamber and polycarbonate front panel were allowed to air dry. Following reassembly, the chamber was purged with zero air at least 12 h before the next persistence test was begun. At the beginning of a persistence test, the background TIC concentrations were measured in real-time with APCI-MS/MS and were found to be quite low if not negligible.

Calculations based on APCI MS/MS results were used to estimate the total amount of each TIC lost from the chamber due to air exchange ventilation. This value, described as an average ventilation loss ($\mu\text{g h}^{-1}$), is listed in Table 4-7 for these three time periods.

The amount of a TIC removed from the chamber by volatilization and subsequent ventilation due to maintenance of one air exchange h^{-1} represented only a small percentage of the total amount of that TIC present in the chamber. As discussed below in Section 4.1.4, the amount of TIC removed from the chamber due to ventilation was <5% of the amount estimated to be present in the chamber.

Table 4-6. Air Concentrations of TICs During Persistence Tests

Average Air Concentration in Chamber, $\mu\text{g m}^{-3}$						
Time (Coupons in chamber)	Malathion		DMMP		TNT	
	Fans on	Fans off	Fans on	Fans off	Fans on	Fans off
Day 1 (45 coupons)	2.4	NT ^a	61	61	0.77	0.84
Day 2–3 (30 coupons)	1.6	NT	20	15	0.63	1.0
Day 4–7 (15 coupons)	0.54	NT	10	5.1	0.37	0.93

^aNT= not tested; instrument difficulties prevented monitoring during this test (see Appendix Section A.2.3 for details).

Table 4-7. Amount of TIC Vented from Chamber by Air Exchange (7.5 L/min)

Amount of TIC Vented, μg (average $\mu\text{g h}^{-1}$)						
Time (Coupons in test chamber)	Malathion		DMMP		TNT	
	Fans on	Fans off	Fans on	Fans off	Fans on	Fans off
Day 1 (45 coupons)	23 (0.96)	NT ^a	840 (35)	1100 (46)	6.5 (0.27)	7.3 (0.30)
Day 2–3 (30 coupons)	37 (0.77)	NT	320 (6.7)	390 (8.1)	11 (0.23)	26 (0.54)
Day 4–7 (15 coupons)	26 (0.27)	NT	390 (4.1)	250 (2.6)	13 (0.14)	36 (0.38)

^aNT= not tested (see Appendix Section A.2.3 for details).

4.1.4 Mass Balance of TICs

The estimates of the amount of each TIC removed from the chamber due to ventilation compared with the spiked amounts on the coupons and the measured amount remaining on the coupons indicated a significant shortfall in accounting for the mass of each TIC. Two possibilities exist for this shortfall: analytes may have been degraded to other species or the analyte may have redistributed to other surfaces in the chamber such as the walls, platform, and fans. Degradation on concrete may be a reasonable explanation for a TIC such as malathion, which is more prone to hydrolysis, because concrete retains water and has basic sites. In the majority of the cases, though, given the stability of the TICs and the neutral nature of the substrate, it is possible that much of the unaccounted for mass of each TIC was adsorbed on (or in) the walls of the chamber following initial volatilization. The interior walls of the chamber were not sampled at the end of each test to verify this hypothesis. Five of the six chamber walls were made

of fiberglass, but the front wall was constructed of polycarbonate. It is possible that this polymer would act as a sorbent for gas-phase material.

Distribution of each TIC between the measured and known compartments (coupons and air) and the unmeasured and unknown compartments (walls, degradation products) are given in Table 4-8.

The distribution of mass between known and measured compartments (coupons and air) and unknown compartments (degradation or wall losses) are shown graphically in Figures 4-7, 4-8, and 4-9 for malathion, DMMP, and TNT, respectively. The total amount in the chamber decreased over time first because five coupons of each building materials type were removed at each interval and second because of losses due to degradation or adsorption onto other compartments such as walls. Tests were not conducted to ascertain the loss mechanisms.

Table 4-8. Estimate of Distribution of TICs Among Coupons and Vented Air

			Distribution, % of Total		Mass Not Accounted for, % of Total
TIC	Fans	Time period	Coupons	Air	Unknown
Malathion	on	Day 1	79	0.1	21
		Day 2–3	64	0.3	36
		Day 4–7	42	0.4	58
	off	Day 1	84	NT ^a	17 ^b
		Day 2–3	70	NT	31 ^b
		Day 4–7	58	NT	42 ^b
DMMP	on	Day 1	36	4	60
		Day 2–3	21	2	77
		Day 4–7	18	6	76
	off	Day 1	34	5	60
		Day 2–3	29	3	68
		Day 4–7	31	4	66
TNT	on	Day 1	54	0.3	46
		Day 2–3	48	0.8	51
		Day 4–7	48	1.9	50
	off	Day 1	76	<0.1	24
		Day 2–3	79	0.2	21
		Day 4–7	54	0.5	45

^aNT= not tested; air concentration of malathion not tested with fans off.

^bBased on assumption that air level is <1%.

Figure 4-7. Accounting for Mass of Malathion

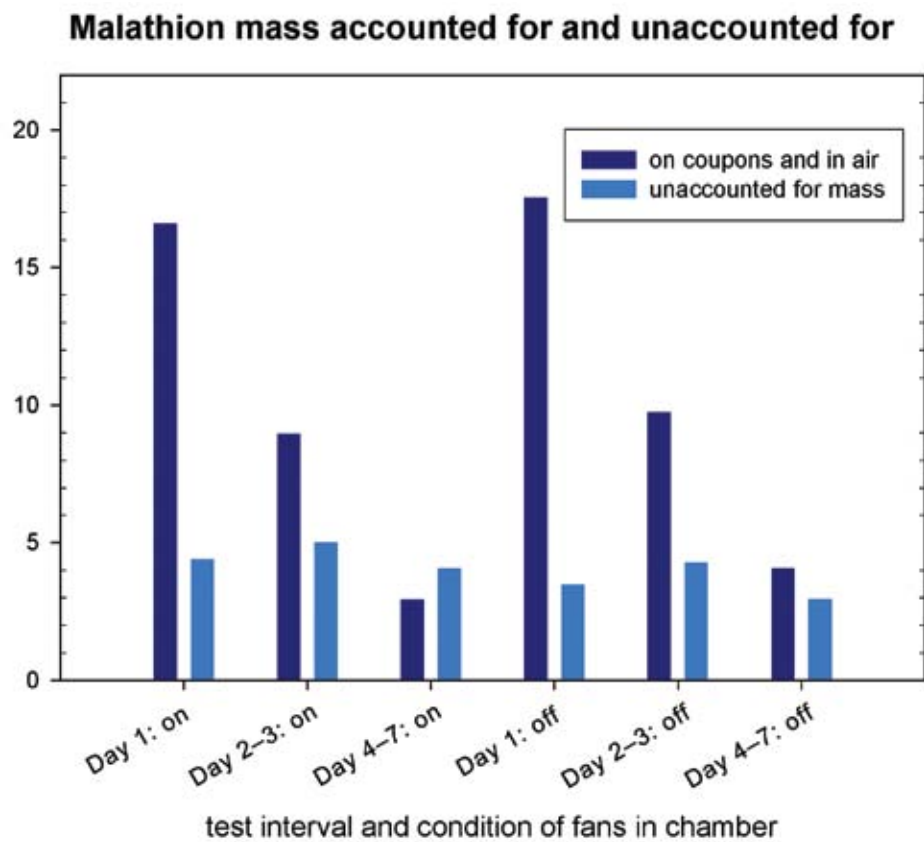


Figure 4-8. Accounting for Mass of DMMP

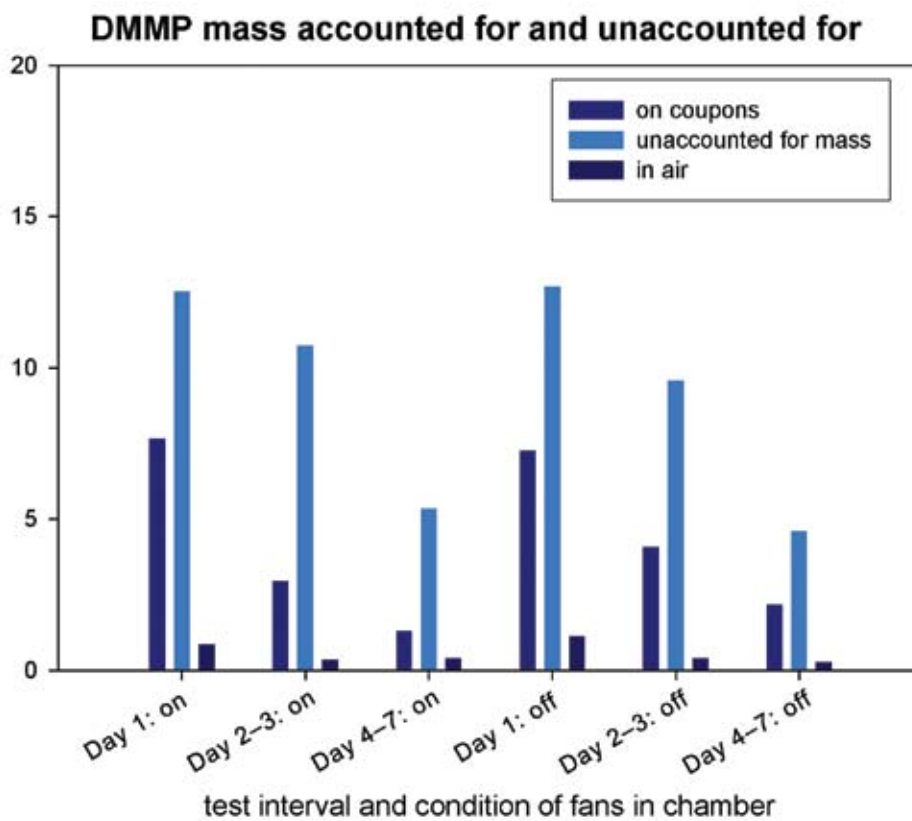
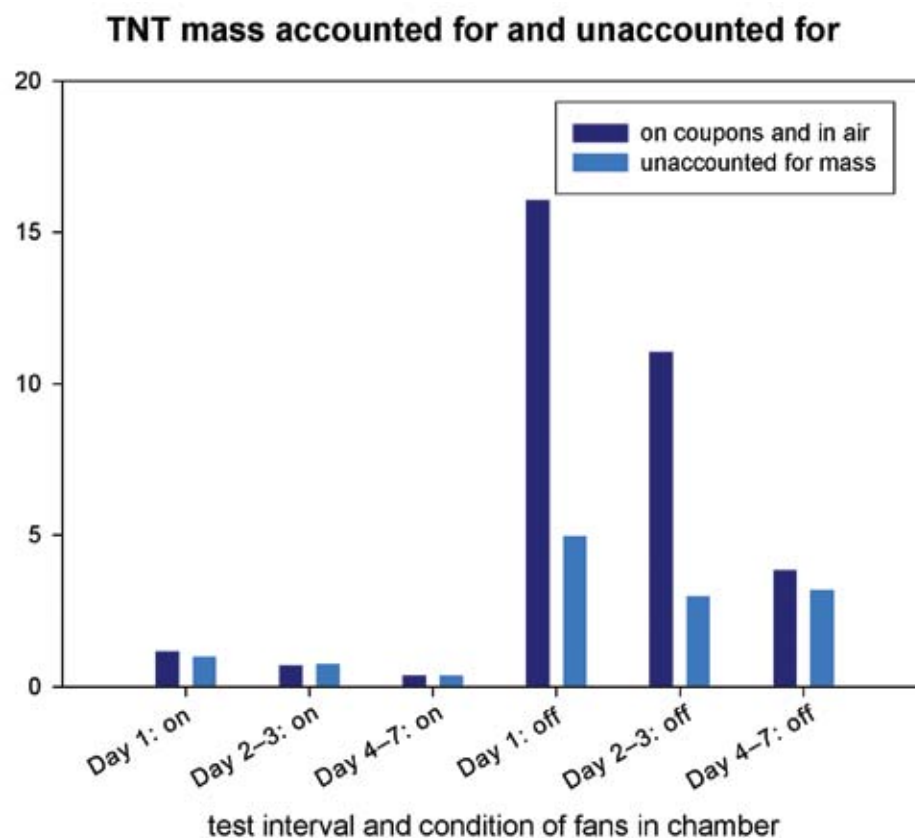


Figure 4-9. Accounting for Mass of TNT



(Note: 10% of the intended spike level was added to the concrete coupons for the test with the fans on, and thus the total amounts to be accounted for are lower in this test.)

4.1.5 TICs on Building Material Blanks

The quantities of the TICs on the building material coupon blanks, SD, and % of spike amount are listed in Table 4-9. The limit of quantification (LOQ) of the analytical method is 0.1% of the spike amount. The amount of contamination measured on coupon blanks was in all cases at or below the LOQ of the analytical method. The most probable explanation for the small amount of TIC contamination measured on the blank coupons is slight background contamination of the analytical instrument, which manifested as coupon contamination. These small background amounts are insignificant with respect to test outcomes.

The blanks included the laboratory coupon blanks that were not exposed to the laboratory fume hood where spiking was performed and the procedural coupon blanks that were held in the laboratory fume hood and extracted at such time as the matched test coupons were extracted. Because of the similarity in blank levels on the laboratory blank coupons and the procedural blank coupons, as well as the similarity in levels for coupons from the tests with fans on or fans off, the data were averaged and presented as a single value.

Table 4-9. Amount of TICs on Building Material Coupon Blanks

Amount on Coupon Blanks, $\mu\text{g} \pm \text{SD}$ (% of spike amount), n=10			
	Carpet	Laminate	Concrete
Malathion	0.50 ± 0.18 (0.10%)	0.38 ± 0.22 (0.08%)	0.28 ± 0.17 (0.07%)
DMMP	0.12 ± 0.05 (0.02%)	0.10 ± 0.06 (0.02%)	0.12 ± 0.07 (0.03%)
TNT	0.16 ± 0.22 (0.03%)	ND, <0.04 (0.01%) ^a	0.09 ± 0.09 (0.02%)

^aND = not detected; less than the MDL.

4.1.6 Environmental Conditions During Persistence Tests

The air exchange rate through the test chamber was maintained at one exchange h^{-1} throughout all testing by using MFCs to set the total flow into the ~ 450 L chamber at 7.5 L min^{-1} . The temperature, RH, and air flow over the building material coupons were carefully controlled and monitored during all trials. The data for the environmental parameters are presented in Table 4-10.

As noted in Table 4-10, footnote b, during one test, the humid air was inadvertently turned off overnight. Dehumidification occurred immediately after Day 1 coupons were removed from the chamber and the humidity generator was refilled with DI water. The test crew inadvertently forgot to restart the flow through the humidity generator after refilling, so the chamber humidity slowly dropped overnight. Humidification was restored the next morning (after approximately 16 h) and RH quickly came back up to target level of $\sim 40\%$. The mean RH over seven days was 36%. There were no significant and consistent differences observed between fans-on and fans-off recoveries (shown in Table 4-5) that would suggest that the period of low humidity had an impact on the results.

When the anemometers were positioned 1–2 mm above the carousel platform, the air velocities were approximately 400 ft min^{-1} . However, two problems were noted with this configuration:

- The anemometers were easily disturbed when removing the coupons from the chamber.
- The measured variability in wind speed artificially increased when only a few coupons, 15 or less, remained in the test chamber.

By repositioning the anemometers to an approximate height of 8 mm above the carousel, the probes were less likely to be disturbed when coupons were removed from the chamber. A subsequent velocity mapping study was performed at the 8 mm. The study confirmed that the anemometers registered air velocities of $130\text{--}180 \text{ ft min}^{-1}$ while the air velocity over the coupons remained at $\sim 400 \text{ ft min}^{-1}$. The variability in the measured air velocity was not significantly decreased by the relocation.

For the persistence tests with no air actively directed over the coupons, the anemometers detected a small but measurable air velocity. Air was moving inside the test chamber due to the action of the mixing fan that always operated to ensure a homogeneous test chamber atmosphere. The typical background air velocity was $\sim 20 \text{ ft min}^{-1}$, or only 5% of the target air velocity with the fans activated.

Table 4-10. Temperature, RH, and Air Velocity for Persistence Tests (Average \pm SD)

Test	Temperature, $^{\circ}\text{C}$	% RH	Air Velocity, ft min^{-1}	
			Anemometer 1	Anemometer 2
Malathion - fans on	25.0 ± 0.9	37.8 ± 3.5	$356 \pm 7^{\text{a}}$	$428 \pm 2^{\text{a}}$
Malathion - fans off	23.7 ± 2.3	40.5 ± 3.9	$26 \pm 9^{\text{a}}$	$20 \pm 3^{\text{a}}$
DMMP - fans on	25.0 ± 1.8	$36.1 \pm 24^{\text{b}}$	$154 \pm 7^{\text{c}}$	$177 \pm 6^{\text{c}}$
DMMP - fans off	24.0 ± 2.4	41.7 ± 5.9	$21 \pm 11^{\text{c}}$	$23 \pm 6^{\text{c}}$
TNT - fans on	25.3 ± 1.7	37.4 ± 3.6	$138 \pm 5^{\text{c}}$	$133 \pm 5^{\text{c}}$
TNT - fans off	24.6 ± 1.6	38.9 ± 2.9	$20 \pm 8^{\text{c}}$	$23 \pm 7^{\text{c}}$

^aAnemometers positioned 1–2 mm above the carousel stage.

^bHumid air inadvertently turned off overnight, causing mean RH to drop and variability to increase.

^cAnemometers moved to 8 mm above carousel stage; with anemometers in this position a reading of $130\text{--}180 \text{ ft min}^{-1}$ indicates an air velocity 1–2 mm above the carousel stage and over the coupons of about 400 ft min^{-1} .

4.2 Results for CWAs

4.2.1 Analytical Method: Recovery of CWAs from Building Materials

As described in Section 4.1.1, the analytical method was first tested to ascertain accuracy and precision. Given the results for DMMP from TICs testing, alternate building materials (galvanized metal ductwork and ceiling tile) were evaluated for use with the CWAs in order to get adequate persistence with highly volatile GB. Galvanized metal was selected for use in place of concrete for the CWA persistence testing. The recoveries of the individual CWAs and the associated SRS from the different building materials are shown in Table 4-11. Since there was no solvent carrier for the application of CWAs, drying time was not an issue. However, the length of time between application of agent and initiation of extraction was found to be a significant factor in recovery due to the higher volatility of GB in particular.

The recovery was tested initially with the 1–7-min hold times between spiking and extraction, and was subsequently repeated for several of the materials with 0.5-min hold times. As shown

in Table 4-11, recovery of GB from ductwork was virtually 100% with a 0.5-min hold time but dropped to about 50% with a 7-min hold time. Recovery of GB from the nonporous laminate surface was about 25% after 0.5 min and dropped to less than 10% after 1 min. The recovery from the ceiling tile with a 0.5-min was approximately 30% from either the painted front side or the unpainted back side. Given the high volatility of GB, these recovery data indicated that the analytical losses were probably due to volatilization from the surface before extraction could be initiated, rather than to conventional analytical losses. It appeared that GB was not sufficiently persistent on laminate, metal ductwork, or ceiling tile to be useful for investigations of decontamination technologies; therefore, extensive persistence testing was not performed with these building materials.

Recoveries of TGD and VX were essentially 100% from all matrices with hold times as much as 5 min between spiking and extraction.

Due to the limited number of potential compounds available to use as SRS compounds, and the lengthy experience of the analysis group with the existing method, there was no attempt

Table 4-11. Mean Recovery of CWAs and SRSs from Building Materials as Percent of Expected Spike

Mean Recovery from Building Material, % ± SD				
Material	Hold time, min ^a	CWA	SRS	SRS/CWA recovery ratio ^b
		GB	TBP	
Laminate (n = 7)	0.5	23 ± 25	108 ± 5	4.7
Ductwork (n = 7)	0.5	113 ± 52	102 ± 3	0.90
Ceiling tile, front (n=7)	0.5	32 ± 14	110 ± 16	3.4
Ceiling tile, back (n=7)	0.5	32 ± 9	88 ± 22	2.8
		GB	TBP	
Carpet (n = 7)	7	91 ± 12	87 ± 14	0.96
Laminate (n = 7)	1	7 ± 11	81 ± 16	11.6
Ductwork (n = 7)	7	45 ± 18	76 ± 13	1.7
		TGD	TBP	
Carpet (n = 7)	5	88 ± 18	98 ± 11	1.11
Laminate (n = 7)	5	97 ± 8	89 ± 9	0.92
Ductwork (n = 7)	5	98 ± 11	88 ± 10	0.90
		VX	TBP	
Carpet (n = 7)	5	113 ± 9	103 ± 21	0.91
Laminate (n = 7)	5	107 ± 6	93 ± 14	0.87
Ductwork (n = 7)	5	110 ± 6	94 ± 15	0.85

^aLength of time between spiking and extraction.

^bRecovery of SRS/recovery of CWA; used to adjust for slight differences in extraction and analytical recovery between each CWA and the SRS; combined with the SRS recovery correction in every sample to adjust for analytical losses.

made to select a specifically matched SRS for each CWA. Rather, the same SRS was used for all analyses. In general, the data indicate that TGD and VX are recovered slightly more efficiently than the SRS from the building materials. For materials where GB was fully recovered, it appears that recovery of GB is also slightly greater than the recovery of the SRS.

The recoveries of the SRS in the analytical method tests and the persistence tests were generally in good agreement. The

recoveries of the SRS were higher in the persistence tests compared with the method recovery tests, but these differences are not statistically significant. The comparison between SRS recoveries in the two sets of tests is given in Table 4-12.

The MDLs for the CWAs are listed in Table 4-13. Note that the MDL on the coupon takes into account the 10-mL final volume of extracts from a coupon.

Table 4-12. Comparison of Mean SRS Recoveries by Building Material for Method Recovery Tests and Persistence Tests

SRS (CWA)	Material	Mean SRS Recovery, % \pm SD	
		Method test (n=7)	Persistence test (n=30)
TBP (GB)	Carpet	87 \pm 14	93 \pm 15
TBP (TGD)	Carpet	98 \pm 11	103 \pm 14
TBP (VX)	Carpet	103 \pm 21	124 \pm 7
TBP (TGD)	Laminate	89 \pm 9	97 \pm 9
TBP (VX)	Laminate	93 \pm 14	114 \pm 10
TBP (TGD)	Ductwork	88 \pm 10	99 \pm 12
TBP (VX)	Ductwork	94 \pm 15	116 \pm 11

Table 4-13. MDLs for CWAs

MDL			
	GB	TGD	VX
In solution	0.04 μ g/mL	0.08 μ g/mL	0.09 μ g/mL
On coupon	0.4 μ g	0.8 μ g	0.9 μ g

4.2.2 Persistence Over Time of CWAs on Building Materials

The low recovery of GB from laminate, ductwork, and ceiling tile was attributed to high volatility of GB rather than to incomplete extraction from the matrix. Because of the low recovery of GB from laminate (7% after 1 min), from ductwork (45% after 7 min), and from ceiling tile (32% after 0.5 min), comprehensive persistence testing using these building materials was not attempted. Rather, some limited data were gathered on the recovery of GB from laminate and ductwork coupons over a 30-min interval. These limited recovery data and the data from application of the controlled persistence tests of GB, TGD, and VX on other building materials are shown as a part of Table 4-14.

The testing of the persistence of each CWA was conducted simultaneously for all of the building materials selected for that compound. The protocol included analysis of five positive control coupons, as opposed to the one positive control coupon used in the TIC persistence tests. There was, in addition, one

spike control where a 1- μ L aliquot of neat agent (identical to the volume applied to a building material coupon) was added directly to a vial containing 10 mL of the extraction solvent. The analysis of this spike control was used to determine the absolute amount of the CWA applied to all the coupons spiked at that time for a test.

For TGD and VX, a total of 90 test coupons were spiked and loaded into the test chamber. For GB (because only carpet was tested in the chamber), there were 30 test coupons spiked and loaded into the test chamber. The recoveries of the CWAs in these persistence tests are listed in Table 4-14. The percent recoveries of the spiked CWA from each building material type at initiation (Day 0) and at subsequent times were calculated as described in Section 2.1.8, using Equation 3. GB evaporates from the nonporous surfaces tested in less than 15 min and evaporates from carpeting in approximately seven days. TGD is nondetectable, or nearly so, on all three matrices in seven days; recoverable VX also decreases by seven days.

Table 4-14. Mean Recovery of CWAs from Building Materials

Mean CWA Remaining on Building Material Test Coupons as Percent of Expected Spike, % \pm SD			
Sampling Time	GB		
	Carpet	Laminate ^a	Ductwork ^a
Day 0, 0 h (n=5)	76 \pm 5	55 \pm 7 (n=2) 0.5 min	85 (n=1) 0.5 min
Day 0, 1 h (n=5)	14 \pm 3	ND ^b (n=2) 5 min	34 \pm 14 (n=2) 5 min
Day 0, 4 h (n=5)	7 \pm 3	ND (n=2) 15 min	ND (n=2) 15 min
Day 1 (n=5)	2.5 \pm 2.0	ND (n=2) 30 min	ND (n=2) 30 min
Day 3 (n=5)	1.5 \pm 0.9		
Day 7 (n=5)	0.3 \pm 0.4		
Sampling Time	TGD		
	Carpet	Laminate	Ductwork
Day 0, 0 h (n=5)	74 \pm 14	75 \pm 1	69 \pm 6
Day 0, 1 h (n=5)	62 \pm 35	13 \pm 3	28 \pm 8
Day 0, 4 h (n=5)	32 \pm 2	0.21 \pm 0.01	0.96 \pm 0.16
Day 1 (n=5)	9 \pm 1	0.08 \pm 0.03	0.63 \pm 0.09
Day 3 (n=5)	9 \pm 5	ND	0.63 \pm 0.23
Day 7 (n=5)	3 \pm 0.2	ND	0.35 \pm 0.03
Sampling Time	VX		
	Carpet	Laminate	Ductwork
Day 0, 0 h (n=5)	72 \pm 17	75 \pm 4	75 \pm 3
Day 0, 1 h (n=5)	74 \pm 6	74 \pm 5	73 \pm 4
Day 0, 4 h (n=5)	73 \pm 13	79 \pm 21	88 \pm 18
Day 1 (n=5)	63 \pm 4	39 \pm 3	67 \pm 4
Day 3 (n=5)	26 \pm 2	6 \pm 3	41 \pm 15
Day 7 (n=5)	13 \pm 0.6	3 \pm 2	18 \pm 6

^aLimited recovery data generated for highly volatile GB.

^bND = not detected; less than MDL.

Graphical representations of the recovery trends above for GB, TGD, and VX are shown in Figures 4-10, 4-11, and 4-12, respectively. Note in particular that in the three graphs for GB (Figure 4-10) that the time period for testing on carpet was

significantly different from the time period used for testing persistence on laminate and metal ductwork surfaces, with the testing on carpet being conducted over days and the testing on the other two surfaces being conducted in minutes.

Figure 4-10. Recovery of GB from Building Materials as Percentage of Time 0 Recoveries (Mean conditions fans off: 20 °C and 14% RH)

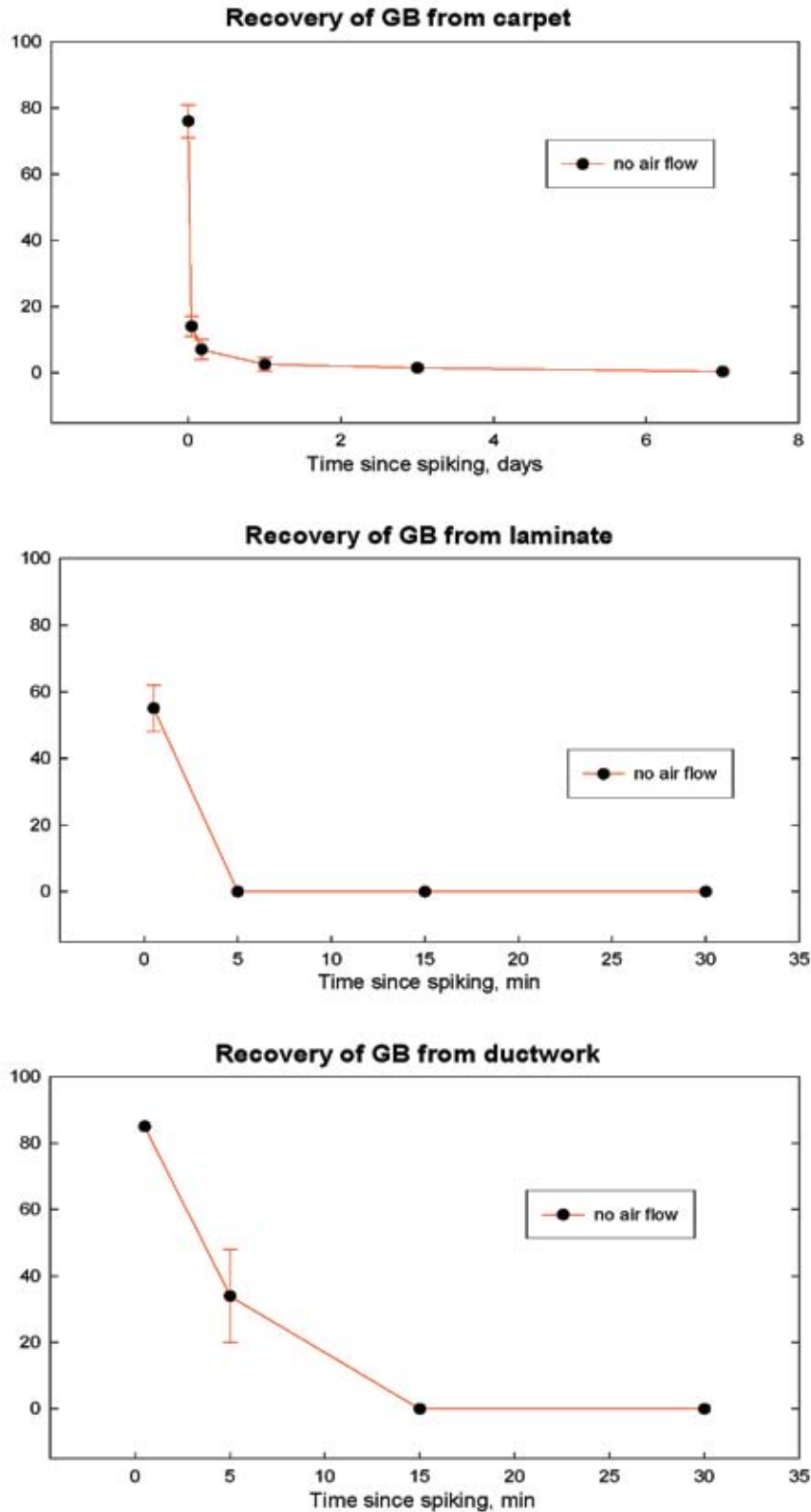


Figure 4-11. Recovery of TGD from Building Materials as Percentage of Time 0 Recoveries (Mean conditions fans off: 21 °C and 22% RH)

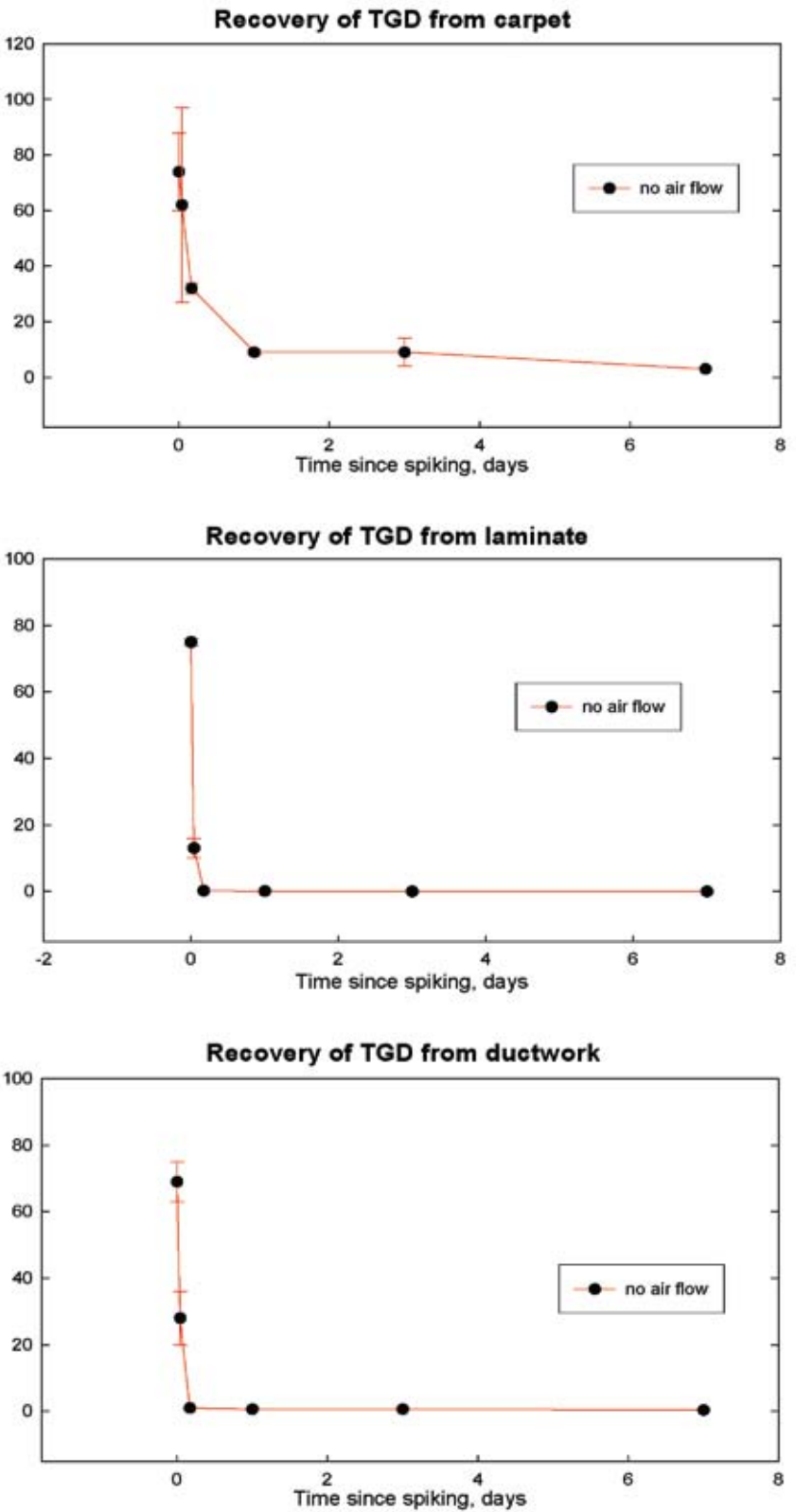
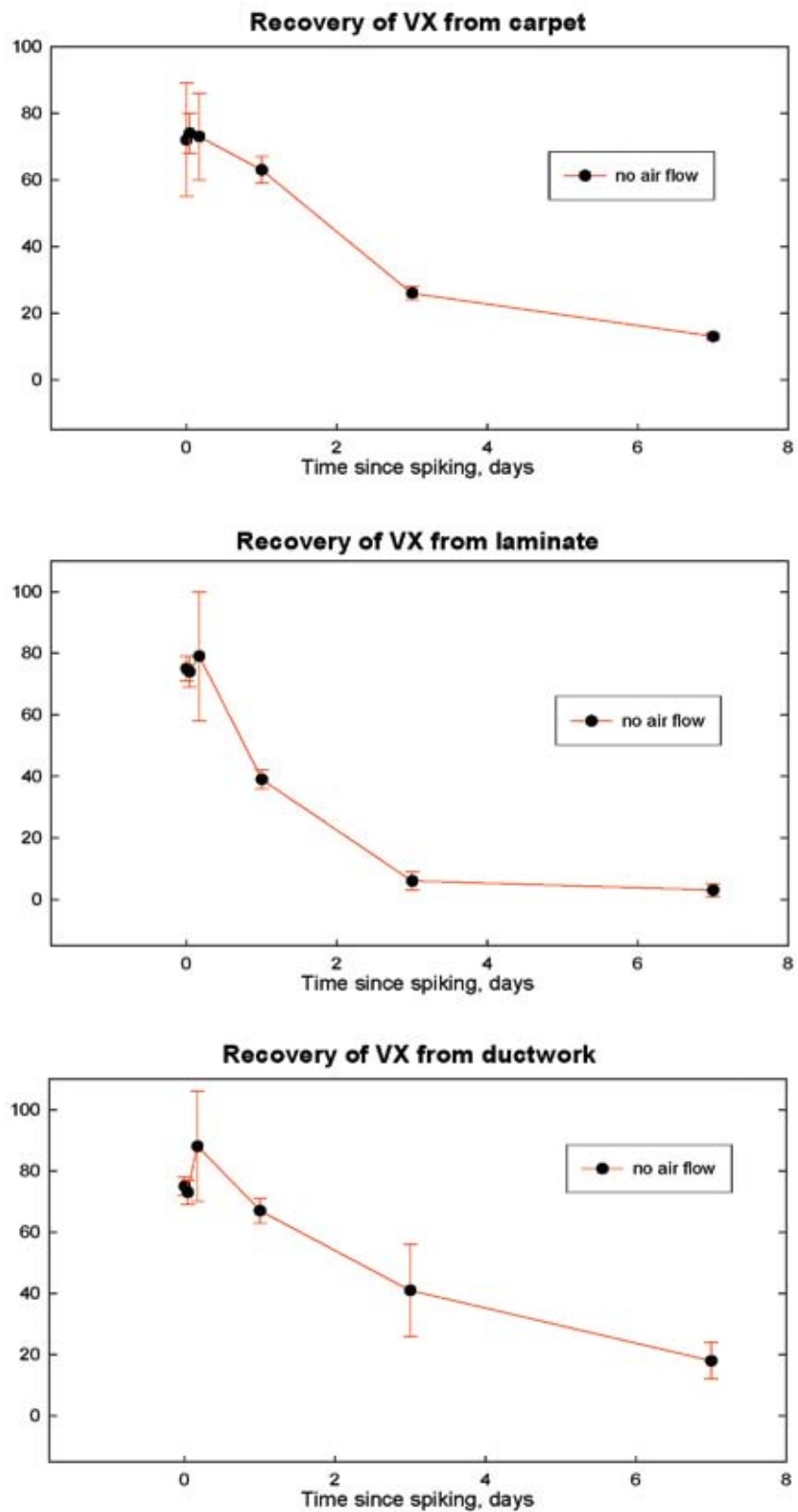


Figure 4-12. Recovery of VX from Building Materials as Percentage of Time 0 Recoveries (Mean conditions fans off: 21 °C and 12% RH)



The recovery data were corrected by the recovery on the Day 0 positive control coupons to determine persistence. The persistence of the CWAs over time is given in Table 4-15.

Clearly, the volatility of these agents played a major role in the amount that was retained on these building materials. In three out of nine cases, no CWA was detected in the coupon extract at

the end of the test regimen; in four out of nine cases, the amount remaining was less than 5% of the original spiked quantity; in the remaining two cases (of nine) the amount remaining was less than 25% of the original amount.

Graphical representations of these trends for each CWA on the three types of building materials are shown in the three panels of Figure 4-13 for GB, TGD, and VX.

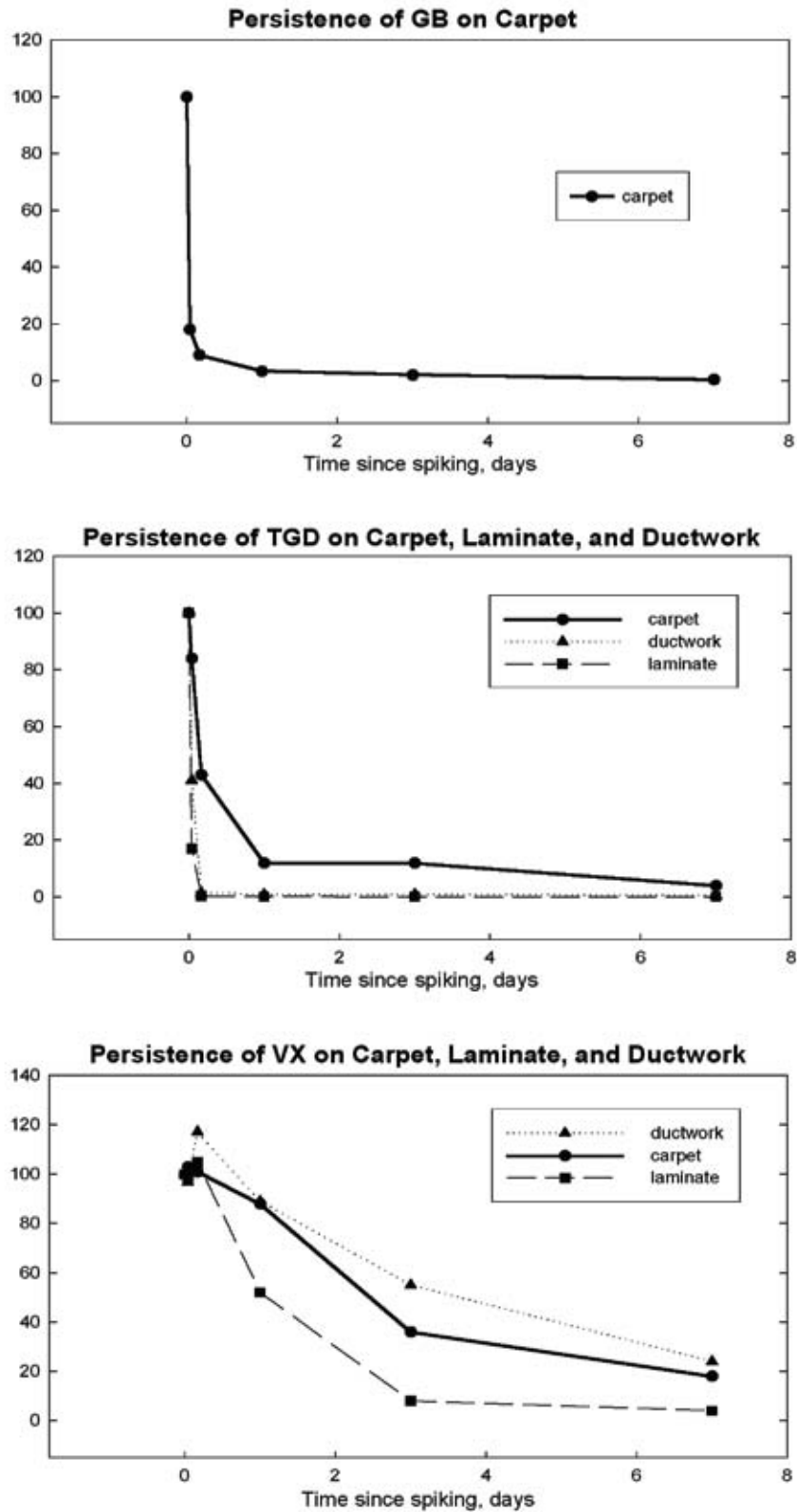
Table 4-15. Persistence of CWAs on Building Materials over Time as Percent of Day 0 Spike Recovery

CWA Persistence on Building Material Test Coupons, % ± SD					
Duration	GB				
	Carpet	Laminate ^a		Ductwork ^a	
1 h	18 ± 4	ND ^b , <0.05	5 min	40 ± 16	5 min
4 h	9 ± 4	ND, <0.05	15 min	ND, <0.05	15 min
Day 1	3.3 ± 3	ND, <0.05	30 min	ND, <0.05	30 min
Day 3	2.0 ± 1				
Day 7	0.4 ± 0.5				
Duration	TGD				
	Carpet	Laminate		Ductwork	
1 h	84 ± 47	17 ± 4		41 ± 12	
4 h	43 ± 3	0.28 ± 0.01		1.4 ± 0.2	
Day 1	12 ± 1	0.11 ± 0.04		0.91 ± 0.1	
Day 3	12 ± 7	ND, <0.1		0.91 ± 0.3	
Day 7	4 ± 0	ND, <0.1		0.51 ± 0.04	
Duration	VX				
	Carpet	Laminate		Ductwork	
1 h	103 ± 8	99 ± 7		97 ± 5	
4 h	101 ± 18	105 ± 28		117 ± 24	
Day 1	88 ± 6	52 ± 4		89 ± 5	
Day 3	36 ± 3	8 ± 4		55 ± 20	
Day 7	18 ± 1	4 ± 3		24 ± 8	

^aLimited persistence data for highly volatile GB.

^bND = not detected; less than detection limit converted to percentage of spike amount.

Figure 4-13. Persistence of GB, TGD, and VX on Building Materials Compared to Percentage of Spike Amount Recovered at Time 0



4.2.3 Concentrations of CWAs in Test Chamber Air

The accuracy (recovery) and precision (reproducibility) of the analysis methods for the sorbent-collected air samples of the CWAs are listed in Table 4-16. These data were determined by spiking a known amount of CWA onto the sorbent. The sorbent was spiked with a known amount of CWA, and then clean air was passed through the tube for 1 h. The tube was extracted and extracts were analyzed and recoveries calculated.

Table 4-16. Method Recovery of CWAs from Carboxen™ Sorbent

Recovery of CWA from Sorbent Tube, % ± SD (n=6)		
GB	TGD	VX
90 ± 9	79 ± 13	61 ± 13

The concentrations of the CWAs in the test chamber air at the time intervals during persistence testing and the numbers of coupons in the test chamber at each interval are listed in Table 4-17.

The total amounts of each CWA vented from the test chamber, due to air exchange, during each time interval of persistence

testing, and the conversion of this value to an hourly rate, are listed in Table 4-18.

The amount of the CWA in the gas phase accounts for relatively little of the total amount of the agent in the chamber at any given time. Again, the high volatility of GB and TGD and the sorptive nature of the polymeric chamber walls may together form a plausible explanation for the fate of the CWAs. Distribution of the CWA mass between the known compartments (coupons and air) and the unknown compartments (walls, degradation products, or other) for the first 1 h time period are listed in Table 4-19. These distributions were calculated as described in Sections 2.1.8 and 2.2.8.

By the time the Day 7 samples were taken, the CWA (GB or TGD) was not detected. The chamber was essentially free of agent prior to the testing using each subsequent agent.

As shown in Table 4-19, the amount in the air accounts for 2%, at most, of the total amount of the CWA in the test chamber. As discussed below (see Section 4.2.4), a small amount of the unaccounted for mass was found on the procedural blank coupons that were held in the test chamber along with the spiked coupons.

Table 4-17. Air Concentration of CWAs During Persistence Tests

Time Period	Number Coupons in Test Chamber		Average Air Concentration, µg m ⁻³		
	GB ^a	TGD or VX ^b	GB	TGD	VX
Day 0, 1 h	25	75	16,000	60,000	ND ^c , <4
Day 0, 2-4 h	20	60	850	16,700	43
Day 0, 5-24 h	15	45	20	1350	46
Day 2-3	10	30	5	340	52
Day 4-7	5	15	ND, <4	90	51

^aTesting was performed only on carpet coupons.

^bSimultaneous testing was performed on carpet, laminate, and ductwork coupons.

^cND= not detected; less than identified MDL.

Table 4-18. Amount of CWA Vented from Chamber by Air Exchange

Time Period	CWA Vented, µg			CWA Vented, µg h ⁻¹		
	GB	TGD	VX	GB	TGD	VX
Day 0, 1 h	326	1224	ND ^a , <0.08	326	1224	ND, <0.08
Day 0, 2-4 h	52	1022	2.6	17	340	0.9
Day 0, 5-24 h	8	550	19	0.41	28	0.9
Day 2-3	5	333	51	0.10	7	1.1
Day 4-7	ND, <8	176	100	ND, <0.08	2	1.0

^aND = not detected; less than identified MDL.

Table 4-19. Distribution of CWA Mass Between Known and Unknown Compartments During First (Day 0, 1 h) Sampling Period

	Distribution in Compartments, %		
	Coupons	Air	Unknown
GB	14	1	85
TGD	34	2	64
VX	74	0	26

4.2.4 CWAs on Building Material Blanks

In contrast to the persistence tests for the TICs, the procedural building material blank coupons for the CWAs persistence tests were placed in the chamber during the persistence tests. The blank building material coupon corresponding to Time 0, though, was not placed in the chamber and is, therefore, a laboratory matrix blank sample. The amounts of the CWAs measured on these two different types of blank coupons, and those amounts as a calculated percentage of the spike level applied to an individual test coupon, are listed in Table 4-20 for the different agents and building materials. The calculation and expression of the blank level as a percentage of the amount that was spiked onto an individual coupon was used to show that when detectable, levels on blanks were quite low.

As shown in Table 4-20 for the Time 0 laboratory blank coupons (not placed in the test chamber), no CWA was detected. That is, no background levels of CWA were detected. However, the results for the building material blank coupons that were placed in the test chamber indicate that the CWAs redistribute to adsorptive media in the chamber. The percentage of the spike listed in Table 4-20 corresponds to the detected amount relative to the spike amount applied to any single coupon. When the amount found on the procedural blank coupons was normalized to the total amount of the CWA in the chamber at a time, approximately 0.4%–1.3% of the total mass was found on the procedural blanks. Given the relatively small area of the coupons compared with the overall area of the chamber, it seems plausible to assume that the majority of the unaccounted for mass may have been adsorbed onto the chamber walls. In addition, the unaccounted for mass may have become reaction degradation products. However, neither of these possible explanations were tested.

Table 4-20. Amount of CWA on Laboratory and Procedural Blank Coupons

CWA	Time	Type of Coupon Blank ^a	Amount on Laboratory and Procedural Blank Coupon, µg (% of single coupon spike amount) ^b		
			Carpet	Laminate	Ductwork
GB	0	Lab	ND ^c (<0.05%)	NT ^d	
	1 h	Procedural	37 (4%)		
	4 h	Procedural	9.0 (1%)		
	Day 1	Procedural	1.8 (0.2%)		
	Day 3	Procedural	0.80 (0.1%)		
	Day 7	Procedural	ND (<0.05%)		
TGD	0	Lab	ND (<0.1%)	ND (<0.1%)	ND (<0.1%)
	1 h	Procedural	170 (20%)	ND (<0.1%)	ND (<0.1%)
	4 h	Procedural	190 (23%)	ND (<0.1%)	ND (<0.1%)
	Day 1	Procedural	53 (6%)	ND (<0.1%)	ND (<0.1%)
	Day 3	Procedural	27 (3%)	ND (<0.1%)	ND (<0.1%)
	Day 7	Procedural	15 (2%)	ND (<0.1%)	ND (<0.1%)
VX	0	Lab	ND (<0.2%)	ND (<0.2%)	ND (<0.2%)
	1 h	Procedural	17 (3%)	19 (3%)	ND (<0.2%)
	4 h	Procedural	17 (3%)	21 (4%)	25 (4%)
	Day 1	Procedural	27 (5%)	ND ^a (<0.2%)	ND ^a (<0.2%)
	Day 3	Procedural	44 (8%)	1.6 (0.3%)	ND ^a (<0.2%)
	Day 7	Procedural	45 (7%)	2.2 (0.3%)	ND ^a (<0.2%)

^aLab blank = laboratory blank coupon, not spiked and not exposed to test chamber; procedural blank = coupon not spiked, but adjacent to test coupons during spiking or placed in the test chamber during persistence testing.

^bBlank level expressed as a percentage of the amount that was spiked to an individual coupon; used to show that when detectable, blank levels were quite low.

^cND = not detected (MDL expressed as percentage of the spike level used on an individual coupon).

^dNT = not tested.

5.0 Summary

For the three TICs and three CWAs tested, the amounts persisting on the building materials decreased over time when held at environmental conditions typical of those that may be found inside an office building or subway. As expected, the persistence was significantly different for the different compounds in contact with different building materials, and these differences may be rationalized in terms of physicochemical properties such as vapor pressure, hydrolysis rate, and solubility in organic-like matrices (as indicated by the octanol:water partition coefficient). For example, persistence of relatively nonvolatile malathion and TNT on industrial carpet was approximately 61%–85% over the seven-day period tested; in contrast, the persistence of the higher volatility compounds (DMMP, GB, and TGD) was 7% on industrial carpet. For these highly volatile compounds, persistence on the nonporous laminate surface or on the metal ductwork was 0%–0.7%. VX is considered a nonvolatile agent — it has the lowest vapor pressure of all of the conventional CWAs. VX, with intermediate volatility between the highly

volatile compounds and the relatively nonvolatile compounds like malathion, exhibited an intermediate persistence of 18% on carpet and 25% on ductwork over the seven-day period tested. The general trends in persistence on the different building materials are summarized below in Table 5-1.

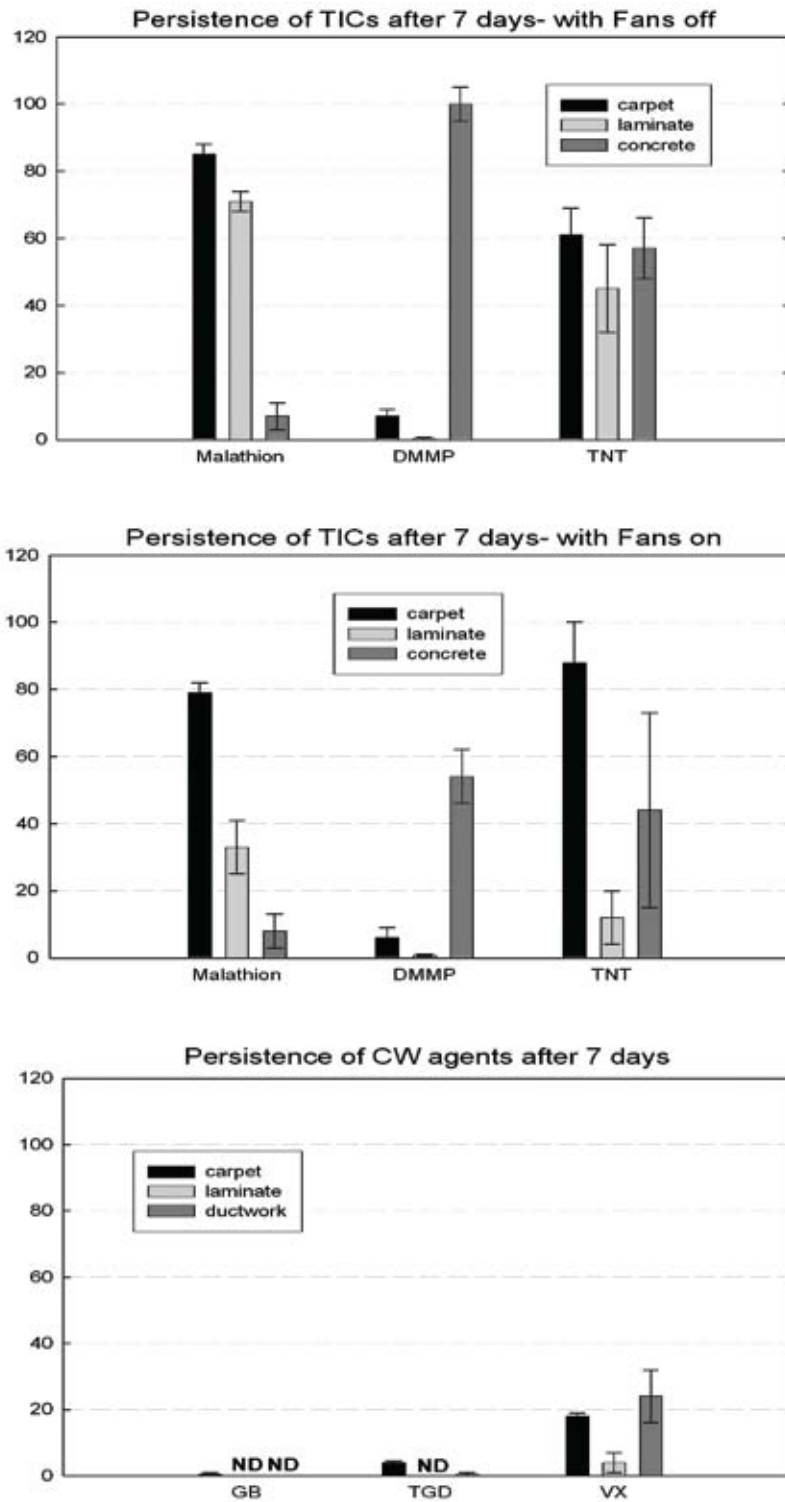
As shown in Table 5-1, TICs and CWAs on carpet generally exhibited the most persistence; TICs and CWAs on laminate generally exhibited the least persistence. For the persistence testing with the TICs, which was determined with fans either on or off in the test chamber, the persistence of lower volatility malathion and TNT was greater when the fans were turned off. For higher volatility DMMP, the persistence was approximately the same whether fans were on or off.

The amounts of TICs or CWAs in the test chamber air accounted for relatively little of the total mass of the applied compounds. Distribution of the TICs and CWAs to other compartments, e.g., absorption to walls or conversion to degradation products, was not determined.

Table 5-1. Trends in Persistence of TICs and CWAs on Building Materials

Compound	Persistence on Building Material, Highest to Lowest
DMMP	Concrete > carpet > laminate
TNT	Carpet > concrete > laminate
Malathion	Carpet > laminate >> concrete
GB	Carpet > laminate \cong metal ductwork
TGD	Carpet > metal ductwork > laminate
VX	Metal ductwork > carpet > laminate

Figure 5-1. Mean Persistence (as % of the Day 0 Recovery) of TICs and CWAs on Building Material Coupons After Seven Days (Error bars are 1 SD)



6.0 References

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APCI MS/MS: Method Development and Real-Time Monitoring for Gas-Phase TICs

During persistence testing, a PE-Sciex APCI-365 tandem MS (APCI MS/MS) quantified in real time the concentration of TICs present in the gas phase in the atmosphere of the test chamber. The development of the APCI monitoring method, the procedures to monitor TIC concentrations in real time including calibration procedures and instrument performance and sensitivity checks, and a brief synopsis of the data reduction methodology are presented in this appendix. In addition, the results obtained for real-time monitoring of the gas-phase TIC concentrations using the APCI MS/MS technique are presented.

A.1 Method Development

For each of the three TICs, the response of the APCI MS/MS was first maximized by optimizing the potentials on the instrument's

various ion optics and the focus of the first and third quadruples (Q1 and Q3). The TICs were introduced into the MS ionization source either directly as a vapor or were infused into the source as a dilute aqueous solution. Separate sets of optimized MS acquisition parameters were created for each TIC and are shown in Table A-1.

An MS spectrum and an MS/MS spectrum were obtained under the optimized conditions for each compound's appropriate mass-to-charge ratio. See Table A-2 for the transitions that were optimized and then monitored for real-time measurements. Also shown in Table A-2 are the names and MS transitions of the IS compounds used to correct for variations in MS response over the course of a single seven-day experiment. This procedure is explained in further detail below.

Table A-1. APCI MS/MS Acquisition File Settings

Acquisition File Parameters	Malathion Values	DMMP Values	TNT Values
Ion Mode	Positive	Positive	Negative
Nebulizer Gas Flow ^a	0	0	0
Curtain Gas Flow ^a	12	12	12
Collision Activated Dissociation Gas Flow ^a	3	3	3
Needle Current, kilovolts	5	5	-7
Orifice Plate, volts	3	12	-20
Ring Electrode, volts	180	100	-60
Quad 0 Rod Offset, volts	-4	-5	2.5
Inter Quad 1 Len, volts	-4	-6	7
Stubbies, volts	-10	-8	20
Rod Offset 1, volts	-5	-9	12
Inter Quad 2, volts	-15	-15	14
Rod Offset 2, volts	-40	-25	12.8
Inter Quad 3, volts	-55	-55	15
Rod Offset 3, volts	-45	-45	26
Deflector, volts	-300	-300	300
Multiplier, volts	2400	2400	2600

^aThe number corresponds to the dial setting. The relationship between the dial setting and measured flow rates is not established.

Table A-2. Primary and Secondary Transitions for TICs and APCI IS

Analyte	Primary Ion Transition	Secondary Ion Transition
Malathion	331 > 99	331 > 125
Dimethyl methylphosphonate (DMMP)	125.1 > 111	125.1 > 93
Diisopropyl methylphosphonate (DIMP) (IS)	181 > 97	NA
2,4,6-Trinitrotoluene (TNT)	227 > 210	227 > 193
1,3,5-Trinitrobenzene (TNB) (IS)	213 > 183	NA

A.2 Real-Time Monitoring

Throughout each test, approximately 4 L min⁻¹ of air from the test chamber was continuously withdrawn and introduced to the APCI. The response of the APCI to a given TIC was averaged and recorded over 30 time intervals. To ensure the proper operation of the instrument, its mass calibration and response sensitivity were periodically checked as described below.

A.2.1 External Calibration for Quantification of TICs

Multipoint calibration curves, consisting of a minimum of six points, were generated at the beginning and end of each seven-day test period for each TIC. For calibration, known amounts of a specific TIC were delivered to the APCI at a known rate; the delivery method depended on the volatility of the TIC. For malathion and TNT, dilute aqueous solutions of varying concentration (typically from 0.1 to 10 µg mL⁻¹) were prepared and directed into the MS source through a custom-built vaporizer at a known flow rate (typically 5 to 15 mL h⁻¹) using a syringe pump. As the air flow into the APCI MS/MS was constant, variation of the aqueous concentration and liquid delivery rate allowed for different gas-phase concentrations to be delivered to the MS. For the higher volatility DMMP, the effluent from a diffusion tube, containing neat chemical maintained at a constant temperature in a permeation oven, was introduced to the MS source in varying amounts through a heated transfer line. That is, in order to generate a multipoint calibration curve, the amount of DMMP delivered to the APCI inlet was adjusted by varying the fraction of the oven air stream that was vented away from the transfer line and replaced with DMMP-free makeup air. Calibration was performed before and after each of the six TIC experiments; the responses of the two curves were averaged and the resultant mean response factor was used to quantify the compound. All calibration curves generated had a correlation coefficient of 0.985 or greater.

A.2.2 Mass Calibration Checks

A daily calibration of the mass scale of the APCI MS/MS was performed during real-time monitoring in order to verify the accuracy of the mass assignments of the MS/MS system. Mass calibration was performed by disconnecting the instrument from the test chamber and allowing compounds of known mass to charge ratios (*m/z*) to be introduced to the MS source. This procedure calibrated both mass resolving quadrupoles (Q1 and Q3) over the mass range of the selected TICs. The mass accuracy was acceptable when within ±0.2 atomic mass units for

both Q1 and Q3. If the mass calibration was unacceptable, the instrument acquisition parameters were adjusted and the mass calibration procedures repeated until the calibration was within the acceptance criteria.

A.2.3 MS Response: Sensitivity Checks and Tracking

To track and correct for short-term variation in the response of the MS/MS detector, sensitivity checks were performed. For malathion, sensitivity checks were performed daily by introduction of a known amount of malathion in the gas phase from a constant-temperature diffusion tube (for the fans-on trial) and by infusion of malathion in an aqueous solution with a vaporizer (for the fans-off trial). Although useful for tracking the change in detector response, the concentration of these daily checks was in general higher than the test chamber malathion concentration. Following the completion of the checks, the measured test chamber malathion concentration tended to remain high and only gradually decreased to levels indicative of the test chamber concentration observed prior to the checks. This is possibly due to malathion carryover in the sampling lines or APCI inlet, as malathion is a semi-volatile compound. Carryover was especially problematic during the fans-off trial and caused such disturbance and variation in the measured test chamber malathion concentration that the data for this run were inconsistent and thus not reported. Therefore, the daily sensitivity checks were discontinued in favor of simultaneous real-time monitoring of an IS for the DMMP and TNT trials. To generate a known constant IS gas concentration, the outlet of a permeation oven containing the IS compound in a diffusion tube was teed into the APCI sampling line downstream from the test chamber so that the IS was continually bled into the APCI inlet. The IS response was monitored throughout the experiment to assess the day-to-day sensitivity changes of the MS system and to adjust the TIC concentration over the test period. Diisopropyl methylphosphonate (DIMP) was the IS used for DMMP and 1,3,5-trinitrobenzene (TNB) was the IS used for TNT. The transitions monitored for these compounds are shown in Table A-2.

A.3 Data Reduction

The TIC concentration was calculated using the measured MS response and the mean response ratio from the appropriate calibration curves. Periods in the monitoring record where the APCI had been disconnected to perform mass or MS sensitivity checks were interpolated using a linear method with respect to time. The DMMP and TNT concentrations were then multiplied by a correction factor determined using the corresponding IS response. The correction factor was calculated as the ratio of the initial IS response (averaged over several hours at the beginning of a trial) to the MS response to the IS at the time when the correction was performed. TIC concentrations were plotted with respect to time, and the mass measured over several time intervals (Days 0 to 1, 1 to 3, 3 to 7, and total) were determined by appropriately integrating the area under the concentration vs. time curve.

A.4 Results from Air Sampling with APCI MS/MS

The concentration of the TICs in the gas-phase in the test chamber was monitored in real time during each of the six trials using the APCI MS/MS. The primary objective of this real-time monitoring was to investigate whether the APCI-365 could be used to detect the TICs of interest in the gaseous atmosphere of the test chamber. If the gaseous TICs could be detected, additional objectives were to:

- Observe how the gas-phase concentration of the TICs changes over the course of the seven-day test periods.
- Perform a mass balance calculation by quantifying the amount of gas-phase TIC and comparing it to the amount lost from the coupons as measured by extraction and GC/MS.

The real-time monitoring results obtained during the TICs persistence investigation are presented graphically in Figures A-1 through A-5. Designated in the figures are the times at which the coupons were removed from the test chamber on Days 1, 3, and 7. As described in Section A.2.3, a plot for malathion with fans off is not available because of difficulties with the APCI MS/MS.

For all trials, the gas-phase TIC concentration in the test chamber began to increase immediately when the coupons were placed in the chamber at the start of a given trial. Furthermore, in all cases the gas-phase concentrations were observed to decrease over the duration of the trial. The results appear consistent with volatilization of TICs from the coupons and removal of coupons (spiked with TICs) from the test chamber over the seven-day test periods.

The results obtained for malathion, shown in Figure A-1, indicate that the gas-phase concentrations of malathion peaked at nearly 0.2 ppb shortly before the Day 1 coupons were removed from the test chamber. With the fans on, the malathion concentration decreased gradually from Day 1 through Day 7.

Among the three TICs, the DMMP volatilized the most readily, a fact that was confirmed using real-time APCI MS/MS monitoring. With the fans on, DMMP concentrations peaked at 62 ppb, but the maximum concentration reached was greater at 101 ppb with the fans off. Although the maximum concentration was higher, the peak concentration was reached more quickly with the fans on: ~ 20 min for fans on compared to ~ one h for fans off. Thus real-time monitoring suggests that increased air velocity decreases DMMP persistence by accelerating volatilization of the DMMP from the coupon surfaces.

Moreover, for both the fans-on and fans-off trials, DMMP concentrations quickly decreased within hours after placing the coupons in the test chamber and remained relatively low for the remainder of the seven-day test period. This rapid rise in gas-phase concentration of DMMP and subsequent steep decline is in agreement with the GC/MS results for DMMP extracted from coupons: during the first 24 h of the extraction experiments, all of the DMMP was lost from the laminate and only 15%–20% persisted on the carpet.

The TNT had the lowest gas-phase concentrations measured during testing, with a peak of ~0.09 ppb shortly after the commencement of the fans-on trial and concentrations approaching 0.14 ppb during the second day of testing with the fans off. The low gas-phase concentration with the fans on is most likely explained by the fact that only 10% of the spike amount of TNT (0.1 g m⁻²) was applied to the coupons as compared to those used in the fans-off trial (1 g m⁻²). Thus, less TNT was present to volatilize from the coupon surfaces, resulting in lower gas-phase concentrations. With the fans on, gas-phase TNT concentrations rose rapidly upon placement of the coupons into the test chamber, peaked within the first 24 h, and then decreased over time. With the fans off, TNT concentrations climbed throughout the first two days, peaked broadly during Days 2 and 3, and gradually decreased through Day 7. Without air passing over the coupons, it appears that TNT volatilization was suppressed, as the persistence of TNT on the laminate coupons indicates, causing TNT to accumulate in the gas phase more slowly. The real-time monitoring results for TNT, shown in Figures A-4 and A-5, support the assertion that increased air velocity over the coupons generally decreases TNT persistence.

Figure A-1. Real-Time Gas-phase Malathion Concentration in the Test Chamber with the Fans On

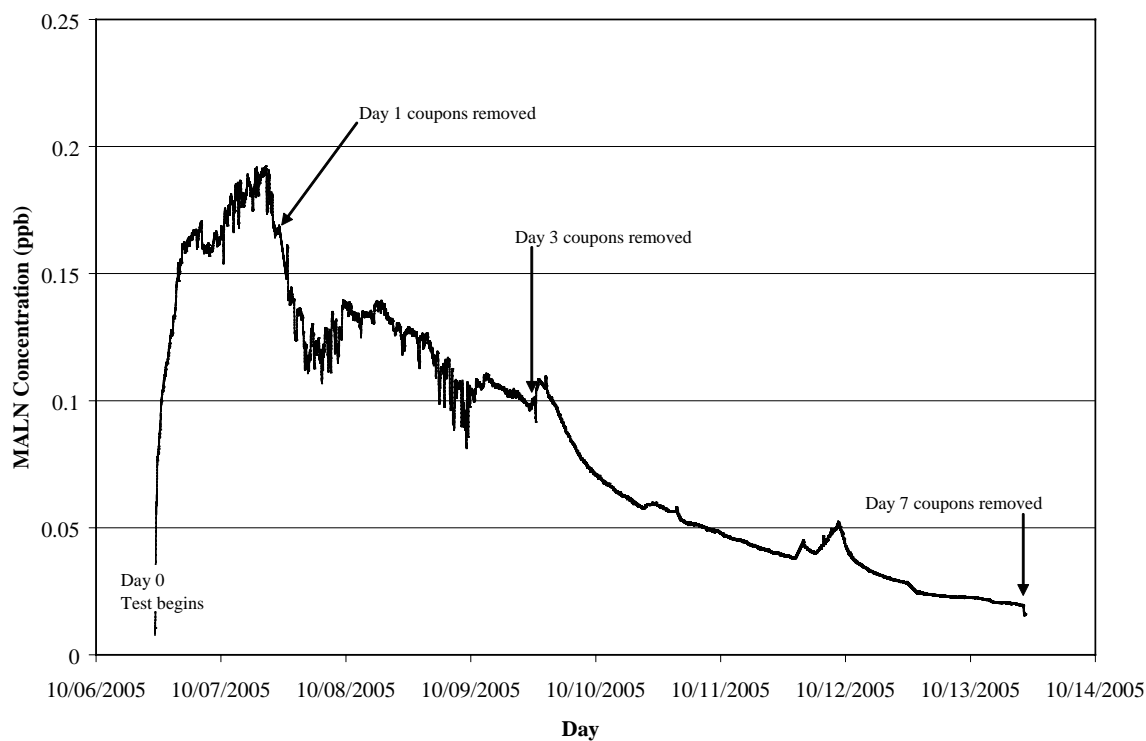


Figure A-2. Real-Time Gas-phase DMMP Concentration in the Test Chamber with the Fans On

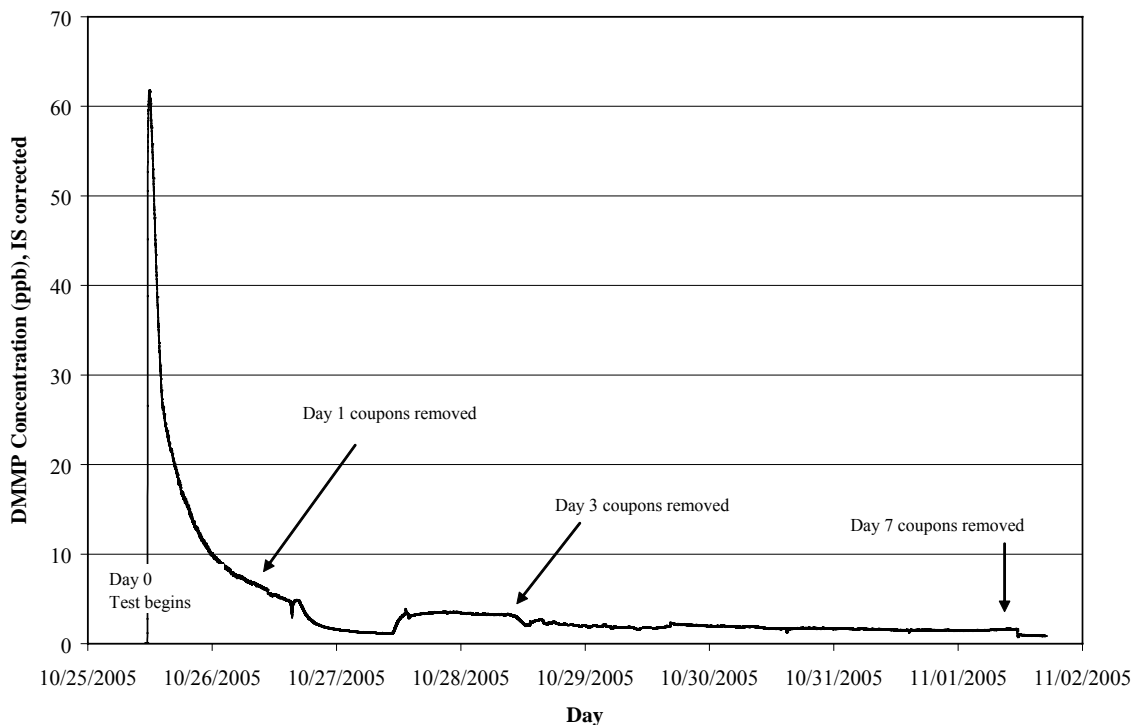


Figure A-3. Real-Time Gas-phase DMMP Concentration in the Test Chamber with the Fans Off

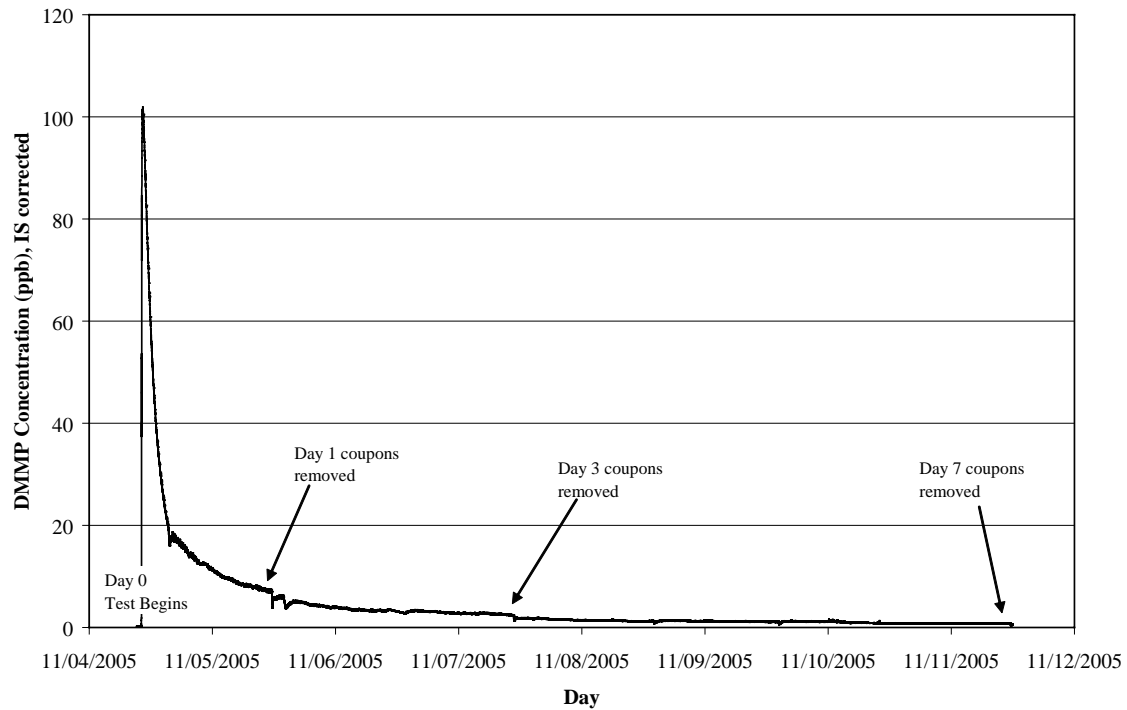


Figure A-4. Real-Time Gas-phase TNT Concentration in the Test Chamber with the Fans On

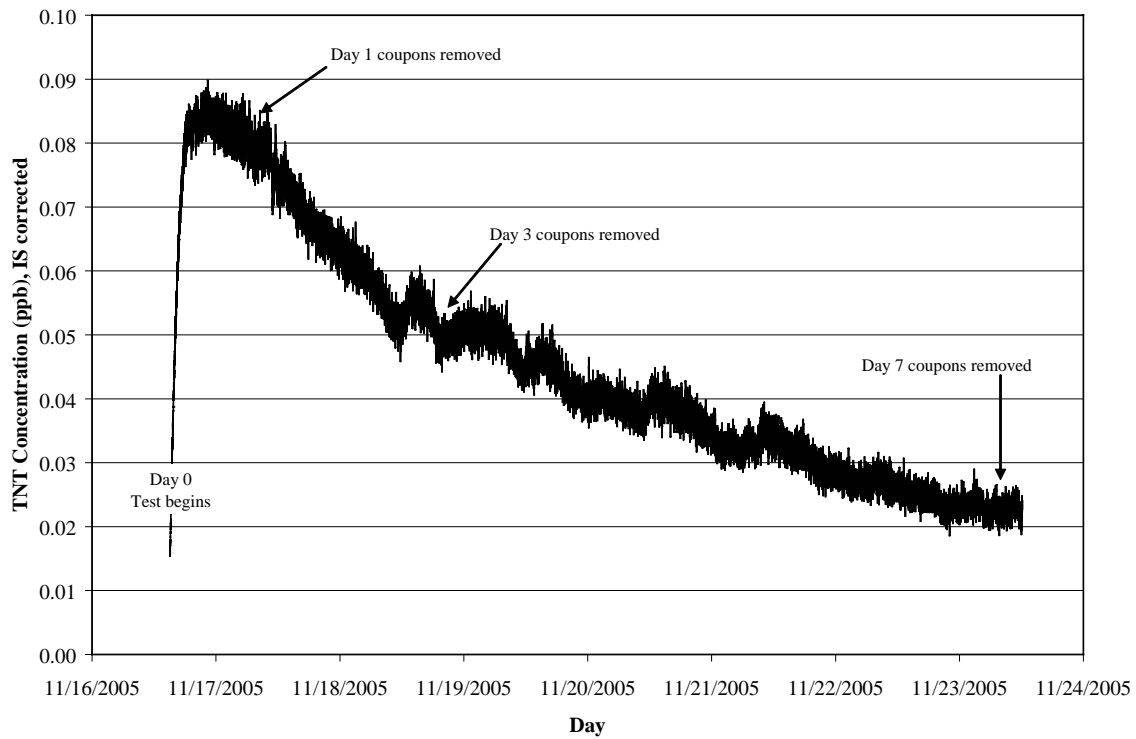
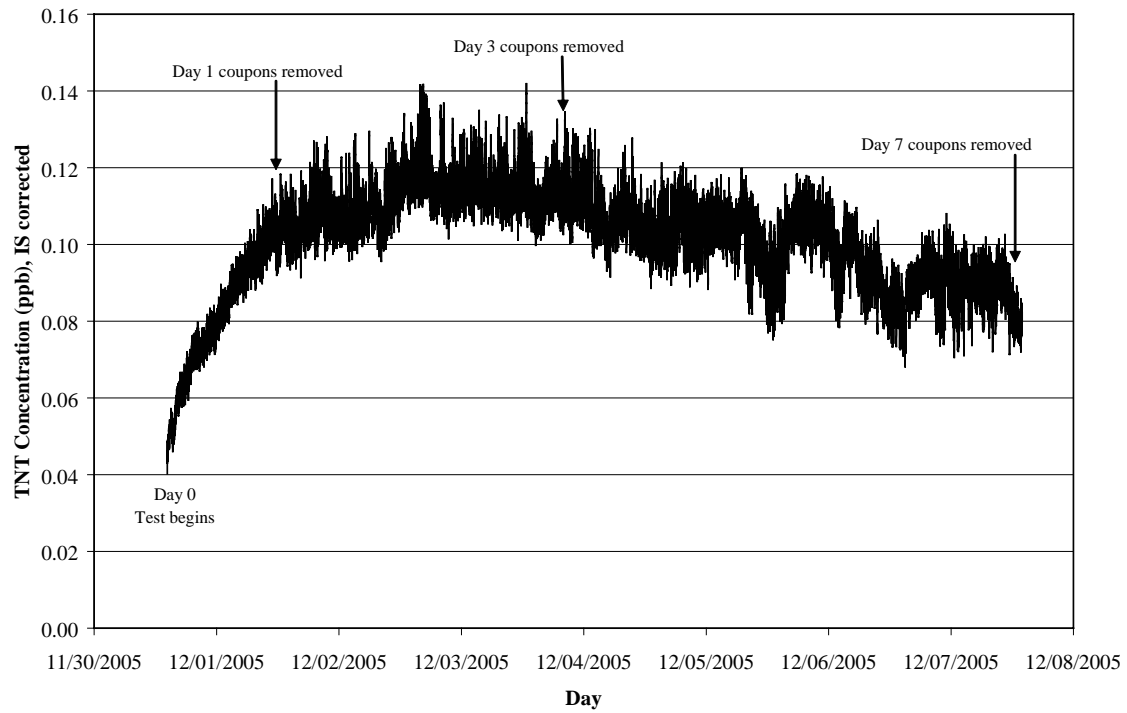


Figure A-5. Real-Time Gas-phase TNT Concentration in the Test Chamber with the Fans Off





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