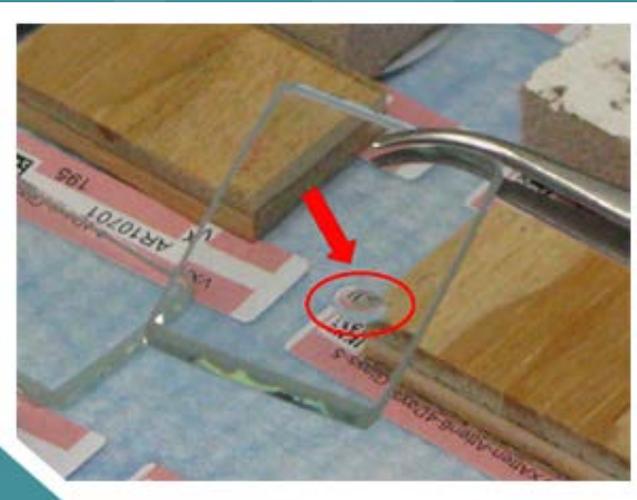
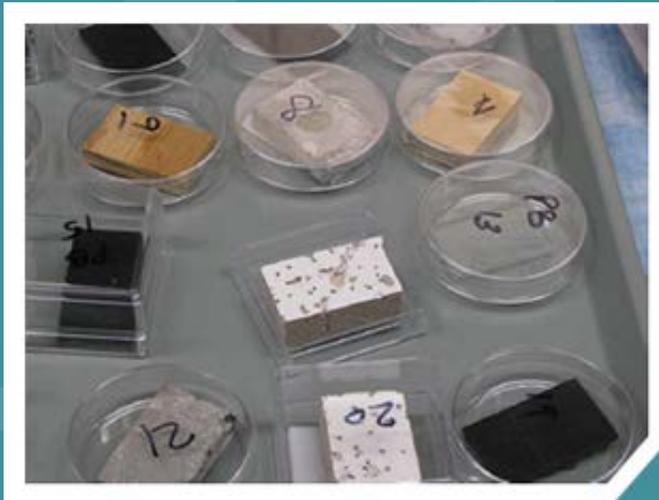


Natural Attenuation of the Persistent Chemical Warfare Agent VX on Porous and Permeable Surfaces



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Disclaimer

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Acronyms and Abbreviations

%R	percent recovery
°C	degree(s) Celsius
ANOVA	analysis of variance
CBR	chemical, biological, and radiological
CCV	continuing calibration verification
cm	centimeter(s)
CMAD	Consequence Management Advisory Division
CV	coefficient of variation
CWA	chemical warfare agent
D1	diethyl methylphosphonate (degradation product of EMPA)
D2	diethyl dimethylpyrophosphonate (degradation product of EMPA)
DIC	N,N'-diisopropylcarbodiimide
EMPA	ethyl methylphosphonic acid
EPA	U.S. Environmental Protection Agency
FID	flame ionization detector
FOD	frequency of detection
GC	gas chromatography
GLM	general linear model
HDPE	high density polyethylene
HMRC	Hazardous Materials Research Center
HS	Homeland Security
HSRP	Homeland Security Research Program
INL	Idaho National Laboratory
IS	internal standard
kHz	kilohertz
LED	light-emitting diode
µg	microgram(s)
µL	microliter(s)
µm	micrometer(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
MS	mass spectrometer(try)
NHSRC	National Homeland Security Research Center
NIST	National Institute of Standards and Technology
OEM	Office of Emergency Management
OLEM	Office of Land and Emergency Management

ORD	Office of Research and Development
PB	procedural blank
PTFE	polytetrafluoroethylene
QA	quality assurance
QAPP	quality assurance project plan
r^2	coefficient of determination
RH	relative humidity
SD	standard deviation
TSA	technical systems audit
UV	ultraviolet
VX	O-ethyl S-(2-[diisopropylamino]ethyl) methylphosphonothioate

Executive Summary

The U.S. Environmental Protection Agency (EPA) Homeland Security Research Program's (HSRP's) purpose is to protect human health and the environment from adverse impacts, including those resulting from acts of intentional contamination (including terrorist incidents) by investigating the effectiveness and applicability of remediation technologies for environmental response. Within the HSRP, EPA's National Homeland Security Research Center (NHSRC) conducts research needed to identify methods and equipment that can be used for decontamination of building surfaces contaminated with chemical warfare agents (CWAs). Previous research has indicated that natural attenuation might be an effective, low cost option for surfaces contaminated with CWAs, especially given the relatively high volatility of some of these agents. For example, natural attenuation of CWAs such as O-ethyl S-(2-[diisopropylamino]ethyl) methylphosphonothioate (VX) occurs following deposition onto relatively nonporous materials (EPA, 2016). A further study was undertaken to determine the applicability of using natural attenuation of a persistent CWA on porous or permeable materials.

This project studied the influence of temperature on the natural attenuation of VX from five types of porous/permeable materials: unsealed concrete, plywood, rubber escalator handrail, high density polyethylene (HDPE) plastic, and acoustic ceiling tile. Natural attenuation of VX was also measured on silanized glass, which served as a nonporous reference material. Testing was conducted at three different temperatures (25 degrees Celsius [°C], 10 °C, and 35 °C). Other environmental conditions such as relative humidity (RH) at 40% and air exchange (one air exchange per hour) were held constant during the testing. The test durations lasted 28 days at 25 °C, 35 days at 10 °C, and 10 days at 35 °C.

Material coupons of 4.0 centimeters (cm) × 2.5 cm were each spiked with 2 microliters (μL) of neat VX. After weathering periods (ranging from 30 minutes [min] to 35 days), VX was extracted from the coupons and quantified via gas chromatography (GC)/mass spectrometry (MS).

The natural attenuation of VX was estimated by:

$$\text{Mean VX Attenuated (\%)} = 100\% - \text{Mean VX Recovered (\%)},$$

relative to spike controls by material, temperature,
and weathering period.

Natural attenuation measured the reduction in the amount of extractable VX remaining following unaided degradation or volatilization of VX from the spiked materials. The attenuation estimates did not distinguish between VX losses attributed to volatilization, degradation, or inability to be extracted from spiked materials. VX attenuation results are shown in Figure ES-1.

As shown in Figure ES-1, natural attenuation of VX occurred on all six materials under all three temperatures tested. Natural attenuation of VX tended to occur faster at warmer temperatures. For example, at least 90% attenuation on all materials occurred within seven days at 35 °C and within 28 days at 25 °C. At 10 °C, less than 80% VX attenuation occurred on rubber escalator handrail, high density polyethylene (HDPE) plastic, and ceiling tile after 35 days (the longest duration tested).

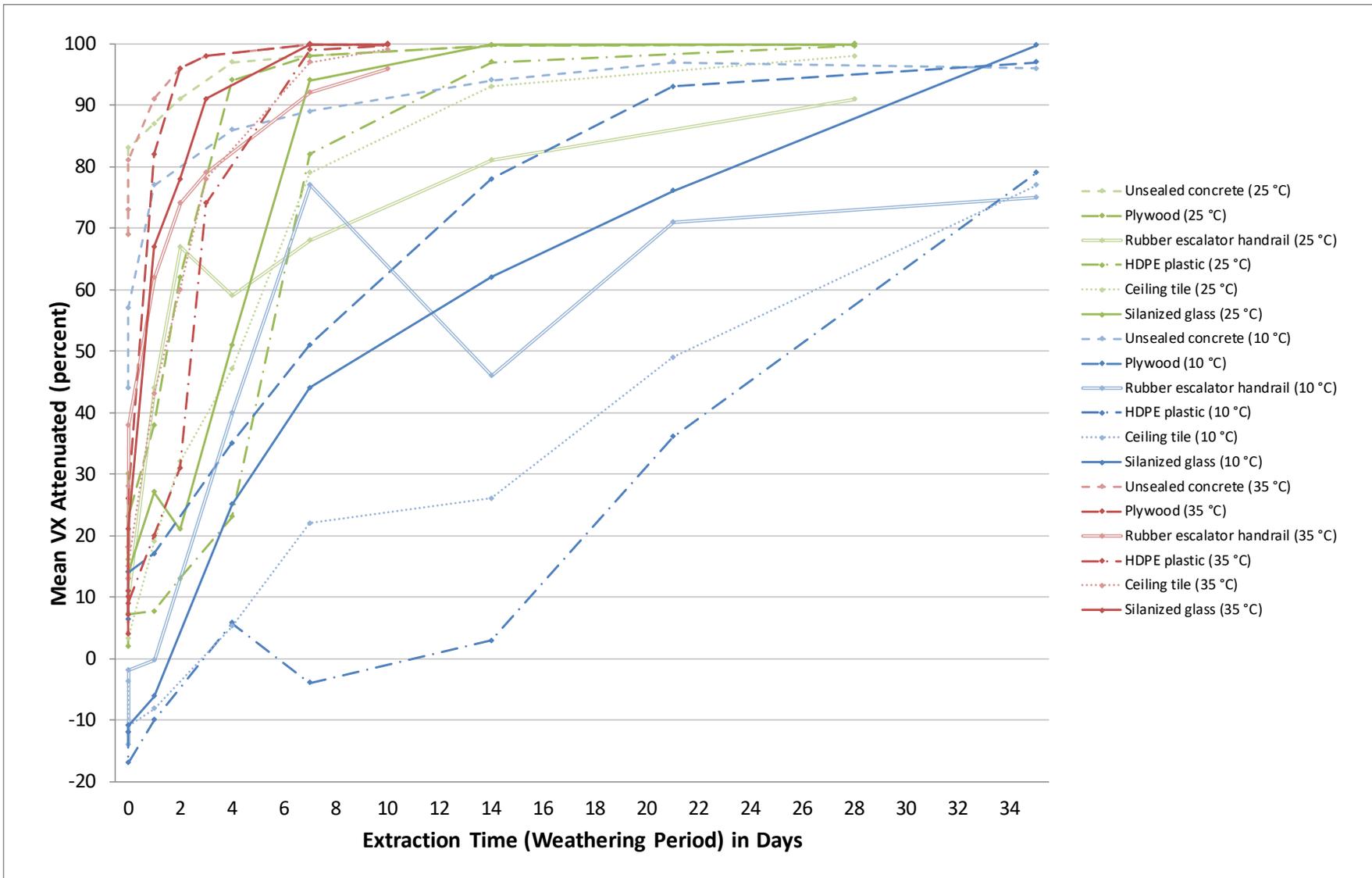


Figure ES-1. Percent of VX attenuated over time versus material and temperature (negative VX attenuation reflects instances when higher VX was recovered from the test coupons than the associated spike controls).

Natural attenuation was also influenced by the material tested. In general, VX attenuation occurred fastest on unsealed concrete (possibly associated with the inherently low VX extraction efficiencies from this material), plywood, and silanized glass. VX attenuation was slower on rubber escalator handrail, HDPE plastic, and ceiling tile. Table ES-1 shows the times that at least 90% VX attenuation was first observed for several materials and environmental conditions (test temperatures).

The natural attenuation of VX achieved >90% for all materials at all three temperatures, except the rubber escalator handrail, HDPE plastic, and ceiling tile at 10 °C, which all achieved only >70% attenuation. Despite the high levels of VX attenuation, non-detect results for all material replicates occurred for only plywood and silanized glass after a 28-day weathering period at 25 °C and a 10-day weathering period at 35 °C.

Semi-quantitative analysis for VX-associated hydrolysis product ethyl methylphosphonic acid (EMPA) confirmed VX degradation on some materials with time. This degradation product is considered to be relatively non-toxic. However, it does provide insight on the degradation of VX in addition to the evaporation process. The detection of other VX degradation products including highly toxic EA-2192 was not attempted because such an analysis would require the use of liquid chromatography/MS, which was beyond the scope of this study.

Table ES-1. Weathering Period (Time) when at Least 90% VX Attenuation was First Observed*

Material	Environmental Condition					
	1 (25 °C)		2 (10 °C)		3 (35 °C)	
	Time (days)	Actual VX Attenuation (%)	Time (days)	Actual VX Attenuation (%)	Time (days)	Actual VX Attenuation (%)
Unsealed concrete	2	91	14	94	1	91
Plywood	4	94	21	93	2	96
Rubber escalator handrail	28	91	>35 [†]	75 [†]	7	92
HDPE plastic	14	97	>35 [†]	79 [†]	7	99
Ceiling tile	14	93	>35 [†]	77 [†]	7	97
Silanized glass	7	94	35	99.7	3	91

* Coupons were extracted at eight time points (weathering periods) ranging from 30 min to 35 days; the time points differed for each of the environmental conditions. The minimum time required to achieve 90% VX attenuation may be lower.

[†] 90% VX attenuation was not achieved at the longest weathering period tested, which is identified as “>”; the actual VX attenuation is provided for the longest available weathering period.

Impact of the Study:

Based on the results obtained from this investigation, natural attenuation of persistent CWAs such as VX applied to porous/permeable materials occurs given sufficient time (days to several weeks). Natural attenuation was found to occur faster at warmer temperatures. Natural attenuation was also influenced by material type, with faster attenuation occurring on unsealed concrete, plywood and silanized glass. Slower VX attenuation occurred on rubber escalator handrail, HDPE plastic, and ceiling tile. Relatively poor extraction efficiencies of VX from unsealed concrete limits the interpretation of the natural attenuation of VX as it is not determined whether residual VX is still present in unsealed concrete. This investigation was conducted using clean and newly fabricated surfaces (except for the concrete). Aged materials and the presence of dirt, grime or other (nontoxic) chemicals may enhance or reduce the persistence of VX while the absence of ultraviolet (UV) light limits the findings of this study to indoor settings.

Trace amounts of VX may still be present weeks to months after a contamination event. These amounts should be put into context with surface concentration cleanup goals for VX. EPA has not established cleanup objectives such as surface cleanup levels. Such cleanup levels are expected to be site-specific and likely to be at or below the detection limit for VX (by GC/MS) in this study. Therefore, detectable amounts of VX on these materials, even after weeks of natural attenuation, would require surface or volumetric decontamination/neutralization to reach the expected cleanup level. The amount of VX observed on procedural blanks should be interpreted to indicate that volatilization of VX results in a redistribution of some of the VX onto originally clean surfaces; however, observed amounts were low and were also declining with time.

Clearance sampling following the implementation of natural attenuation as a decontamination strategy should also consider the analysis of VX degradation products, some of which were detected in this investigation, and some of which may have significant toxicological effects themselves. In some instances, (e.g., unsealed concrete after 10 days [all environmental conditions] and ceiling tile after seven hours [all environmental conditions]), there was no visible evidence of VX on the surface of the material, but VX was generally detected via extractive sampling methods. The potential adsorption or embedding of VX into porous or permeable materials should also be taken into consideration when selecting surface sampling methods and decontamination approaches to reach acceptable surface concentrations.

1.0 Introduction

The U.S. Environmental Protection Agency's (EPA's) Homeland Security Research Program (HSRP) serves to protect human health and the environment from the adverse impacts of a chemical, biological, or radiological (CBR) agent release. The HSRP's role is to develop tools and information that will help detect and quantify the intentional release of CBR contaminants in buildings, water systems, or the outdoor environment; contain these contaminants; decontaminate buildings, water systems or the outdoor environment; and facilitate the treatment and disposal of hazardous materials resulting from remediation/cleanup activities.

As part of the HSRP, EPA's National Homeland Security Research Center (NHSRC) investigates the effectiveness and applicability of technologies and/or approaches for homeland security (HS)-related applications by developing test plans that are responsive to the needs of the HSRP's EPA Program Office and Regional partners, conducting tests, collecting and analyzing data, and preparing peer-reviewed reports. EPA NHSRC provides high-quality information that is useful to decision makers in responding to incidents and implementing appropriate technologies to mitigate consequences to the public resulting from CBR incidents.

U.S. EPA is responsible for planning for and responding to releases of toxic chemicals into the environment, including the deliberate release of chemical warfare agents (CWAs). EPA (EPA, 2016) previously reported that natural attenuation of O-ethyl S-(2-[diisopropylamino]ethyl) methylphosphonothioate (VX) occurs following deposition onto relatively nonporous materials. Natural attenuation might provide a low cost and low impact approach for decontaminating surfaces and may also be a desirable option for structures that do not require immediate reopening/reoccupation. Further study was needed to determine the applicability of using natural attenuation for decontamination of CWAs from porous/permeable materials. This project evaluated the natural attenuation of VX after being applied as a liquid onto porous/permeable materials.

1.1 Purpose

The purpose of this project was to measure the rate and magnitude of natural attenuation of VX from various porous or permeable materials after application as a liquid at different temperatures to better inform potential decontamination options for less volatile CWAs.

1.2 Project Objectives

The project objective was to evaluate natural attenuation of VX from various porous or permeable materials including unsealed concrete, plywood, rubber escalator handrail, high density polyethylene (HDPE) plastic, and ceiling tile. Natural attenuation of VX was also studied on silanized glass, which served as a nonporous reference material similar to the previous study that investigated the natural attenuation of VX from nonporous materials (EPA 2016). Testing was conducted for 28 days at 25 degrees Celsius (°C), 35 days at 10 °C, and 10 days at 35 °C. During testing, the relative humidity (RH) was maintained at nominal 40%, and the air exchange rate was held at one volume of test chamber air per hour.

1.3 Test Facility Description

All testing was performed at the Battelle Hazardous Materials Research Center (HMRC) located on the Battelle site in West Jefferson, Ohio. The HMRC is certified to work with chemical surety material through its Bailment Agreement W911SR-10-H-0001 with the U.S. Department of the Army.

2.0 Experimental Methods

As a general overview, multiple coupons (small representative pieces) of various materials were simultaneously challenged (spiked) with neat VX for the natural attenuation investigation. All of the spiked coupons were placed in a test chamber under controlled temperature, RH, and air exchange conditions. At designated times, groups of coupons were removed from the chamber, extracted, and analyzed for VX, leaving the remainder of the coupons in the chamber for further exposure and later analysis. More specific experimental methods are provided in Sections 2.1 through 2.8.

2.1 General Experimental Design

A multiple group time-series experimental design was used, as represented below:

X_1 O_{10} O_{11} O_{12} O_{13} O_{14} O_{15} O_{16} O_{17}
 X_2 O_{20} O_{21} O_{22} O_{23} O_{24} O_{25} O_{26} O_{27}
 X_3 O_{30} O_{31} O_{32} O_{33} O_{34} O_{35} O_{36} O_{37}

For this experimental design, time passes from left to right. For $n=1, 2, 3$, X_n represents the experimental treatment (X) performed within a specified environmental condition (n). Coupons were randomly assigned to groups that were extracted and analyzed for VX after up to eight time durations (t) within the specified environmental condition. The mean masses of VX (five replicates) recovered from coupons for a given material after a given time (t) under a given environmental condition (n) were the experimental results/observations (O_{nt}).

Three hypotheses were tested:

Test #1:

- *Null hypothesis*: No decline occurs in mean recovered VX over time.
- *Alternative hypothesis*: Mean recovered VX declines over time.

Test #2:

- *Null hypothesis*: The mean rate of VX loss does not change among different environmental conditions (temperatures).
- *Alternative hypothesis*: The mean rate of VX loss differs among environmental conditions (temperatures).

Test #3:

- *Null hypothesis*: The mean rate of VX loss does not vary among different materials.
- *Alternative hypothesis*: The mean rate of VX loss does vary among different materials.

Each statistical test was performed by applying an analysis of variance (ANOVA) to the log-transformed residual masses of VX. The ANOVA model assumed an exponential decay over time and included effects for the duration of time from spiking to the measurement of residual

mass (i.e., eight distinct time points, treated as continuous time measurements), material type, temperature, and interactions between these terms (as they were deemed statistically significant at the 0.05 level). Each hypothesis test was associated with a test for a specific parameter in the ANOVA model:

- Test #1: Test for whether the slope parameter associated with time from initial spiking is significantly less than 0 (i.e., results in a decline in the mass measurement with increasing time).
- Test #2: Test for whether the slope parameter (rate of decline) differs significantly among different environmental conditions (temperatures).
- Test #3: Test for whether the slope parameter (rate of decline) differs significantly among different materials.

For a specific statistical test within the ANOVA, the null hypothesis was rejected for the alternative hypothesis if the p-value for the F-test performed on the given model parameter was no higher than 0.05.

2.2 Test Matrices

The test matrix for VX natural attenuation is shown in Table 1. Between attenuation tests, the test chamber and work area were cleaned, and contaminated test items and waste were disposed of. Attenuation was evaluated under controlled temperature, RH, and air exchange rates in a custom-built test chamber. Briefly, the natural attenuation investigation was conducted as follows:

- Six materials (five porous/permeable and one nonporous) were used for the attenuation investigation. The five porous/permeable materials were unsealed concrete, plywood, rubber escalator handrail, HDPE plastic, and ceiling tile. The nonporous material (silanized glass) was used as a reference material that would generally reflect the amount of VX attenuated via volatilization.
- Testing was conducted at three environmental conditions; each was run as a separate test in the chamber:
 - Environmental Condition 1: 25 ± 3 °C, $40 \pm 5\%$ RH, with one chamber volume of air exchanged per hour. Testing performed for 28 days.
 - Environmental Condition 2: 10 ± 3 °C, $40 \pm 5\%$ RH, with one chamber volume of air exchanged per hour. Testing performed for 35 days.
 - Environmental Condition 3: 35 ± 3 °C, $40 \pm 5\%$ RH, with one chamber volume of air exchanged per hour. Testing performed for 10 days.
- Environmental conditions in the chamber (with coupons present) were stabilized at specified experimental conditions for at least 24 hours prior to spiking coupons.
- On the first day of each test, 40 coupons of each material type were spiked with 2 microliters (μL) of VX as described in Section 2.5. Coupons were spiked in the test chamber. In addition, 2 μL of VX was spiked directly into hexane (five replicates) and acetone (five replicates) at time zero to serve as spike controls. The spike controls were

spiked evenly throughout the time zero spiking operation (i.e., one prior to spiking samples, one after every two weathering time sets, and the last following the spiking of all samples). Solvent volumes for the spike controls were identical to the extraction volume for the material coupons, namely, 25 mL.

Table 1. Natural Attenuation Test Matrix and Coupons Used for Each Material Type

Environmental Conditions	Materials Tested	Initial Analyses (Coupons Per Each Material)	Seven Additional Time Points (Coupons Per Each Material)
Condition 1: 25 °C, 40% RH, with one chamber volume of air exchanged per hour	Unsealed concrete*, Plywood, Rubber escalator handrail, HDPE plastic, Ceiling tile*, Silanized glass	5 spike controls (no coupons); 5 test coupons, 1 procedural blank, 1 laboratory blank (30 min after spike); 3 breakthrough controls (for unsealed concrete and ceiling tile only, used throughout all time points) [†]	5 test coupons, 1 procedural blank, 1 laboratory blank (extraction time points: 7 hours; 1, 2, 4, 7, 14 and 28 days after spike)
Condition 2: 10 °C, 40% RH, with one chamber volume of air exchanged per hour	Unsealed concrete*, Plywood, Rubber escalator handrail, HDPE plastic, Ceiling tile*, Silanized glass	5 spike controls (no coupons); 5 test coupons, 1 procedural blank, 1 laboratory blank (30 min after spike); 3 breakthrough controls (for unsealed concrete and ceiling tile only, used throughout all time points) [†]	5 test coupons, 1 procedural blank, 1 laboratory blank (extraction time points: 7 hours; 1, 4, 7, 14, 21, and 35 days after spike)
Condition 3: 35 °C, 40% RH, with one chamber volume of air exchanged per hour	Unsealed concrete*, Plywood, Rubber escalator handrail, HDPE plastic, Ceiling tile*, Silanized glass	5 spike controls (no coupons); 5 test coupons, 1 procedural blank, 1 laboratory blank (30 min after spike); 3 breakthrough controls (for unsealed concrete and ceiling tile only, used throughout all time points) [†]	5 test coupons, 1 procedural blank, 1 laboratory blank (extraction time points: 4 and 7 hours; 1, 2, 3, 7, and 10 days after spike)

* Unsealed concrete and ceiling tile test coupons were placed on top of polytetrafluoroethylene (PTFE) disks.

[†] Breakthrough controls were placed on top of M8 paper, which was intended to detect the presence of liquid VX that might seep through these coupons.

Note: all coupons (as well as PTFE disks and M8 paper) were placed in trays lined with an absorbent wipe, which helped pick up the coupons for extraction.

- For both unsealed concrete and ceiling tile, three breakthrough control coupons were spiked with 2 µL of VX and placed on top of M8 Chemical Detection Paper (M8 paper) (Luxfer Magtech, Cincinnati, OH, USA). The M8 paper was cut to the coupon dimensions and was used with the intent to detect liquid VX that might seep through the coupons. At the end of each time point, the M8 paper was checked for a color change indicating that VX had migrated through the coupon; no other chemical analysis was used for the breakthrough control coupons.
- Two of the five unsealed concrete and ceiling tile test coupons were placed on top of PTFE disks (cut to the coupon dimensions). The PTFE disks were used to capture any VX that might migrate through the coupons. If the breakthrough controls/M8 paper

indicated that VX had migrated through the material at a given time, the test coupons and PTFE disks would have been extracted and analyzed separately for VX. However, in all cases the breakthrough control coupons/M8 paper did not indicate that VX migrated through the material, so the test coupons and PTFE disks were extracted together.

- Five coupons of each material type were extracted at 30 minutes (min) after spiking plus seven additional time points (weathering periods) as shown in Table 1. The weathering periods differed for each environmental condition given the anticipated differences in the persistence of VX. The weathering periods were chosen to maximize information on the duration that VX persists under the various environmental conditions rather than generating a more uniform sampling pattern over time.
- In addition to the five test coupons, one procedural blank coupon (a coupon inside the test chamber that was not spiked with VX) of each material type and one laboratory blank coupon (a coupon kept outside the agent hood and test chamber that was not spiked with VX) of each material type were extracted and analyzed along with the test coupons at each time point.

2.3 Test Chamber

A custom-fabricated acrylic test chamber was used for testing that enabled monitoring, recording, and control of temperature, RH, and chamber air exchange. The test chamber was held within a chemical fume hood for secondary containment.

Temperature within the test chamber was adjusted with a radiator/heat exchanger (Part # 3525K25, McMaster-Carr, Aurora, OH) installed at the top of the chamber. The heat exchanger was fed by a refrigerated/heated bath circulator filled with propylene glycol heat transfer fluid (-28 °C to 150 °C operating range, ±0.1 °C temperature stability, 500 Watt cooling capacity, 1 kilowatt heating capacity). Humidity was added to the chamber air using a Nafion[®] humidification tube (Model #FC100-80, Perma Pure LLC, Toms River, NJ). House air was fed through the Nafion[®] tube to achieve the desired RH and then supplied to the chamber. The supplied house air was directed through a series of particulate filters (rated as low as 0.01 micrometers [µm]) and desiccant dryers to clean and dry the air prior to delivery to the laboratory. A redundant carbon filter and moisture trap were installed at the test chamber supply air inlet (upstream of the Nafion[®] tube) to further clean and dry the air. Chamber supply air exchange was controlled using a calibrated mass flow controller to achieve one air exchange per hour.

Process controllers integrated into the heat exchanger and Nafion[®] tube circulator baths were used to control temperature and RH. Test chamber temperature and RH was monitored and recorded using a calibrated Vaisala temperature/RH probe (HMT338, Vaisala Oyj, Helsinki, Finland). In addition, shelf-specific temperature and RH monitoring was conducted with HOBO data loggers (UX100-003, Onset Computer Corporation, Bourne, MA). A double-door-controlled access port (airlock) in the test chamber allowed for the addition or removal of coupons and supplies with minimal disturbance to the controlled environmental conditions within. Five- cm thick closed-cell foam insulation was also used to prevent chamber heat loss/gain. To minimize the exposure of the coupons to ultraviolet light, lights in the fume hood

and laboratory were turned off when not needed. Light-emitting diode (LED) bulbs emitting little to no ultraviolet light were used inside the test chamber, and black Kraft paper (Part # 883458, Staples, Columbus, OH) was used to block light at the hood face when no work was being performed. Glove ports allowed the chamber to remain sealed while operators manipulated coupons and supplies within the chamber. Circulation fans mounted inside the chamber just above the heat exchanger helped to ensure uniformity of the environmental parameters. Fans were oriented so that air flow was not directed at the coupons.

2.4 Test Materials

The natural attenuation investigation was conducted using the following six types of material coupons: unsealed concrete, plywood, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass (a nonporous reference material). Table 2 describes the materials and preparation approaches used. Coupons were cut to uniform length and width (4.0 cm × 2.5 cm) from larger pieces of material. Edges and damaged areas were avoided in cutting test coupons. Glass coupons were silanized following a modification of the method of Labit et al. (2008).

Table 2. Description of Materials Used for the Natural Attenuation Investigation

Material	Description	Supplier - Location	Coupon Length (cm) × Width (cm)	Coupon Preparation
Unsealed concrete	Type II Portland Cement was obtained from a ready-mix supplier. The cement, which met uniform building code specifications for structural walls, was delivered (to the Idaho National Laboratory [INL]) in April 2004. The cement was originally poured into 3-foot x 3-foot x 2-inch plywood molds and then troweled to form a finished surface. After curing, the cement was removed from the molds and cut into 6-inch x 6-inch blocks, some of which have been used by U.S. Department of Homeland Security, Battelle, and INL.	Unspecified supplier - Idaho Falls, ID	4.0 × 2.5 (cut to 0.5 cm thickness)	Cleaned with dry air to remove dust
Plywood	Pine subfloor plywood 23/32 CAT PS1-09 (common: 23/32-inch x 4-foot x 8-foot; actual: 0.703-inch x 47.5-inch x 95.875-inch) (Item #: 12249)	Lowe's - Hilliard, OH	4.0 × 2.5 (cut to 0.75 cm thickness)	Cleaned with dry air to remove dust
Rubber escalator handrail	Standard Otis escalator handrail (20-foot section)	Porta-Flex Manufacturing - Ajax, ON	4.0 × 2.5	Cleaned with dry air to remove dust
HDPE plastic	MacCourt drywall mud pan (Item #: 19251, Model #: AT2606)	Lowe's - Hilliard, OH	4.0 × 2.5	Cleaned with dry air to remove dust
Ceiling tile	Armstrong® random textured contractor 10-pack white textured 15/16-inch drop acoustic panel ceiling tiles (common: 48-inch x 24-inch; actual: 47.719-inch x 23.719-inch) (Item #: 55612, Model #: 933)	Lowe's - Hilliard, OH	4.0 × 2.5	Cleaned with dry air to remove dust

Material	Description	Supplier - Location	Coupon Length (cm) × Width (cm)	Coupon Preparation
Silanized glass*	Window glass (initially uncoated)	Brooks Brothers -West Jefferson, OH	4.0 × 2.5	Silanized*

* Silanized glass was used as a nonporous reference material. The process used to silanized the glass is according to Labit et al. (2008).

2.5 Chemical Agent and Spiking Coupons

All quantities of neat VX used for this project were synthesized at the Battelle HMRC in December 2015, under the Chemical Weapons Convention program guidelines, with accountability through the U.S. Army Edgewood Chemical Biological Center. All neat VX originated from the same synthesis lot and was sealed in multiple glass ampoules (i.e., one ampoule was intended to be used per test, with the sealed volume based on the anticipated need for a particular test). The ampoules used are listed below along with VX purity (if measured). VX purity was measured four times during this testing by GC/flame ionization detector (FID). The VX (ampoules) used and associated purity during this project were:

- Ampoule C063-1: VX used for the extraction recovery method demonstrations. VX purity was 95.2% as measured on February 8, 2016.
- Ampoule C063-2: VX used for spiking most coupons associated with Environmental Condition 1. VX from ampoule C063-2 was depleted after spiking all coupons and the first four spike controls. VX purity was not measured from this ampoule. For the calculation of the percent recovery of VX for the first spike controls of Environmental Condition 1, the VX purity of ampoule C063-1 was used.
- Ampoule C063-7: VX used to complete the spiking of the Environmental Condition 1. This VX was used for the remaining spike controls and purity testing. VX purity was 95.7% as measured on March 14, 2016. For the calculation of the percent recovery of VX for the spike controls (see Section 2.8, equation 4) of Environmental Condition 1, the VX purity of ampoule C063-1 was used. Ampoules C063-1 and C063-2 were sealed until being used for this testing, while ampoule C063-7 had previously been unsealed and then recapped before being used in this testing.
- Ampoule C063-3: VX used for spiking the coupons associated with Environmental Condition 2. VX purity was 95.6% as measured on May 2, 2016.
- Ampoule C063-4: VX used for spiking the coupons associated with Environmental Condition 3. VX purity was 95.7% as measured on July 5, 2016.

The coupons were visually inspected prior to spiking with the neat VX; coupons with surface anomalies such as visible scratches or divots were not used. The VX was dispensed using a Hamilton repeating dispenser (#PB600-1, Hamilton, Reno, NV) and 100 µL Hamilton syringe (#81085, Hamilton, Reno, NV). All test coupons were spiked with a single 2 µL droplet of VX. The coupons were open to the atmosphere within the test chamber. After weathering in the

environmental conditions for a given experiment and specified time, a batch of coupons was transferred from the test chamber into solvent for extraction. This process was repeated for each time point in the test matrix.

2.6 Extraction of VX from Coupons

All test and blank coupons in the test matrix were extracted by placing each coupon into a separate 60-milliliter (mL) glass bottle (05-719-257, Fisher Scientific, Pittsburgh, PA) containing 25 mL of applicable extraction solvent: hexane (H306SK-4, Fisher Scientific, Pittsburgh, PA) with the N,N'-diisopropylcarbodiimide (DIC) (AC11521-5000, Fisher Scientific, Pittsburgh, PA) VX stabilizer or acetone (A929-4, Fisher Scientific, Pittsburgh, PA) with DIC, based on the outcome of method demonstration work described in Section 2.7. The use of the DIC is intended to stabilize VX in dilute concentrations by inhibiting VX degradation (EPA, 2013). The VX stabilizer DIC was added to the extraction solvent at 1% by volume. The stabilizer also helped to improve the sensitivity of the GC/MS analysis of VX samples. The hexane and acetone extraction solvents used during this study were of Optima™ grade to ensure the highest purity possible ($\geq 99\%$). The hexane used was $\geq 95\%$ *n*-hexane and $\geq 99\%$ for all hexanes). Internal standard (IS), naphthalene- d_8 (AC17496-0010, Fisher Scientific, Pittsburgh, PA), was added to the extraction solvent stocks at a concentration of 2.5 micrograms (μg)/mL. The 4.0 cm \times 2.5 cm coupons fit lying flat within the inside diameter of the bottles, and 25 mL of liquid reached a height of approximately 1.3 cm (higher when liquid was displaced by coupons). This bottle and volume of extraction solvent were generally sufficient to submerge the coupons. For the coupon that floated (i.e., ceiling tile), the coupons were extracted with the VX-spiked side facing down. In addition, the PTFE disks associated with the unsealed concrete and ceiling tile were also extracted along with the test coupons (in the same bottle).

Following addition of coupons, the bottles were swirled by hand for approximately 5 to 10 seconds and placed into a sonicator (Branson Model 5510, Danbury, CT). Extraction bottles were sonicated at 40 kilohertz (kHz) to 60 kHz for 10 min. This coupon extraction approach was based on high recoveries for the extraction of VX from similar materials (EPA, 2011). Within 30 min of completing this process, approximately 1 mL from each extraction bottle was transferred to individual GC vials (vial P/N 21140, cap P/N 24670, Fisher Scientific [Restek Corporation], Hanover Park, IL) and sealed. Samples not analyzed the same day as extraction were stored at $-20\text{ }^\circ\text{C}$ or lower.

2.7 Extraction Recovery Method Demonstration

This method demonstration study evaluated the ability to recover VX from unsealed concrete, plywood, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass coupons 24 hours after the coupons were spiked with VX and held under ambient laboratory conditions. When considering method demonstration for extraction from hard, nonporous surfaces, a shorter time of up to 60 min is typically used. The 24 hours contact time in this study allows for permeation to occur on a longer time scale prior to extraction. The coupons were spiked with a single 2- μL droplet of VX as described in Section 2.5. During the extraction recovery testing, the coupons were placed into 60 millimeter (mm) \times 15 mm Petri dishes (AS4052, Fisher Scientific,

Waltham, MA) or 4.8 cm x 4.8 cm x 2.9 cm acrylic boxes (10172618, Michaels, Irving, TX), see Figure 1.

The lids on the dishes/boxes were loosely placed on top to prevent accidental contact with VX during the weathering time, while allowing for natural evaporation/attenuation to occur under ambient environmental conditions. The extraction approach described in Section 2.6 was employed with four different extraction solvents:

- hexane with IS
- hexane with IS and DIC
- acetone with IS and DIC
- dichloromethane (D151-1, Fisher Scientific, Pittsburgh, PA): acetone (1:1 ratio by volume) with IS and DIC.

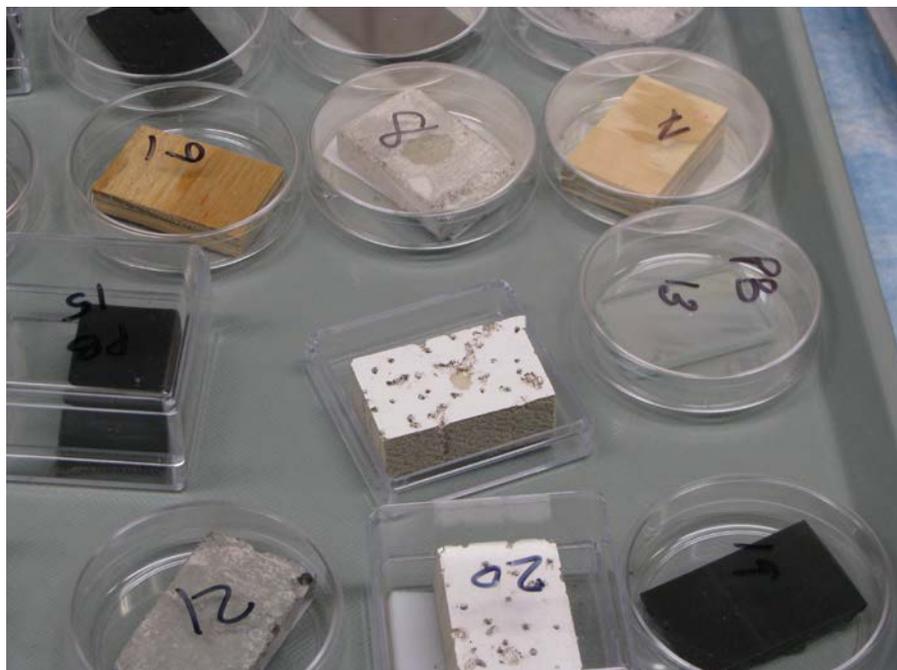


Figure 1. Photograph of coupons associated with the extraction recovery method demonstration showing use of round Petri dishes and square acrylic boxes.

The extraction recovery method demonstration was evaluated as follows:

- For each extraction solvent and material combination evaluated, three VX-spiked test coupons, one procedural blank (an unspiked coupon handled similarly to the test coupons), and one laboratory blank (an unspiked coupon never placed inside the agent hood) were extracted. In addition, three spike controls (a spike of equal amount of VX directly applied into the extraction solvent) were used.

- Coupons were spiked as described in Section 2.5 and extracted as described in Section 2.6. Coupon extractions took place 24 hours after the test coupons were spiked. The analytical methods followed those documented in Section 2.8.
- For the unsealed concrete and ceiling tile, PTFE disks were placed underneath these coupons (to capture any VX that might migrate through the materials). The PTFE disks and coupons were extracted and analyzed together for VX.
- The acceptable recovery of VX targeted for each of the materials was 70% to 120% of the mean spike control recovery with less than a 30% coefficient of variation (CV) between triplicate samples.

2.8 Analytical Methods

2.8.1 Analysis for VX

The sample extracts were analyzed to quantify the amount of VX remaining on each coupon using GC/MS (6890 gas chromatograph and 5973 mass-selective detector, Agilent Technologies, Santa Clara, CA) operated in the full-scan mode for compounds ranging from 40 to 500 atomic mass units. VX was detected with ions 114, 72, 127, and 79. The GC/MS parameters are documented in Table 3. Example chromatograms, including one high-curve analysis and one low-curve analysis (refer to Section 4.2), are provided in Appendix A. See Section 4.2 for equipment calibration information as well as GC performance parameters and acceptance criteria that ensure the accuracy and reproducibility of the integration of the ion peaks. The integration of the target ion and qualifier ion peaks was conducted primarily by the GC/MS software, but every single peak in every sample and standard was also reviewed by the GC/MS analyst.

The lowest standard used to establish the calibration curve (quantitation limit) was above, but near, the GC/MS instrument detection limit. Samples with results below the lower calibration level (i.e., 0.10 µg/mL) were reported as less than the quantitation limit (“non-detects”).

Table 3. Gas Chromatography/Mass Spectrometry Conditions

Parameter	Description
Instrument	Hewlett Packard Model HP 6890 Gas Chromatograph equipped with HP 5973A Mass Selective Detector and Model 7683 Automatic Sampler
Column	30 meters × 0.25 mL inside diameter Rtx-5 (cross-linked methyl-silicone), fused silica capillary column, 0.25 µm film thickness (Restek Catalog Number 05223)
Carrier gas flow rate	1.2 mL/min helium (constant flow)
Column temperature	40 °C initial temperature, hold 1 min, 30 °C/min to 280 °C, hold 0 min
Injection volume/type	1 µL splitless injection (4 mm inside diameter single gooseneck quartz insert) with 0.5 min purge activation time. Split vent flow rate at 80 mL/min
Injection temperature	250 °C
Transfer line temperature	280 °C
MS quad temperature	150 °C
MS source temperature	230 °C
Ionization mode	Electron ionization
Solvent delay	3 min

The VX concentration in coupon extract samples and spike control samples was calculated by the GC/MS instrument software and is provided in units of µg/mL. The GC/MS analysis result for each extract sample was fitted to the calibration curve generated for the specific GC used to analyze the sample, and VX concentration was determined from the ratio of the VX peak area response to that of the IS peak area response. Use of an IS compensated for potential variability in sample injection volumes as well as decreasing or increasing instrument sensitivity. During the effort, VX exhibited a quadratic response over the concentration range analyzed, and thus the ratio of VX area response to the IS area response (y-axis) was plotted versus the ratio of VX concentration to IS concentration (x-axis). The quadratic VX calibration curve that was fitted to the analysis data took the following form:

$$(A_S / A_{IS}) = [a \times (C_S / C_{IS})^2] + [b \times (C_S / C_{IS})] + c \quad (1)$$

where:

A_S = area response of the target analyte

A_{IS} = area response of the internal standard

C_S = concentration of the target analyte

C_{IS} = concentration of the internal standard

a, b, c = coefficients of quadratic curve fit

VX concentrations in the coupon extracts were calculated by GC/MS instrument software and are provided in units of µg/mL. These GC concentration results (µg/mL) were converted to total mass recovered by multiplying by the extract volume:

$$M_M = C_S \times E_V \quad (2)$$

where:

M_M = calculated mass of VX recovered from an individual replicate (μg)
 C_S = GC concentration ($\mu\text{g/mL}$) from an individual replicate, see Equation 1
 E_V = extraction solvent volume (mL).

The percent recovery of VX recovered from an individual replicate relative to the mean mass measured in spike controls was calculated as follows:

$$\%R = M_M / M_{SC} \times 100\% \quad (3)$$

where:

$\%R$ = percent recovery for an individual replicate
 M_M = calculated mass of VX recovered from an individual replicate (μg)
 M_{SC} = mean calculated mass of VX recovered from spike controls (μg).

A separate $\%R$ calculation was made for recovery of VX from each replicate coupon. The mean $\%R$ was based on the mean of the $\%R$ for all applicable replicates.

The percent recovery of VX from spike controls (versus theoretical) was calculated as follows:

$$\%R_{SC} = [M_M / (D / CF_1 \times S_V \times CF_2 \times P)] \times 100\% \quad (4)$$

where:

$\%R_{SC}$ = percent recovery for an individual spike control replicate (versus theoretical)
 M_M = calculated mass of VX recovered from an individual replicate (μg)
 D = density of VX (grams/cubic centimeter)
 CF_1 = conversion factor 1 (1000 μL / cubic centimeter)
 S_V = VX spike volume (μL)
 CF_2 = conversion factor 2 (1,000,000 gram/ μg)
 P = VX purity (as a fraction)

A separate $\%R_{SC}$ calculation was made for recovery of VX from each spike control replicate. The mean $\%R$ was based on the mean of the $\%R_{SC}$ for all applicable replicates.

2.8.2 Analysis for VX Hydrolysis Product

The sample extracts were also analyzed to provide a semi-quantitative estimate of the amount of the VX hydrolysis product ethyl methylphosphonic acid (EMPA). The detection of other VX degradation products including highly toxic EA-2192 was not attempted because such an analysis would require the use of liquid chromatography/MS, which was beyond the scope of this study.

In preliminary testing, 10 $\mu\text{g/mL}$ of EMPA was not directly detected in the extraction solvents hexane or acetone via GC/MS as described in Section 2.8.1 for the analysis of VX. The solvents

might have caused a reaction with the EMPA, or EMPA might have degraded in the hot inlet of the GC; however, two degradation products of EMPA, diethyl methylphosphonate [D1] and diethyl dimethylpyrophosphonate [D2] were detected. D1 and D2 are known degradation products of EMPA and sometimes impurities associated with VX (Munro et al., 1999). The combination of detecting degradation products of EMPA, use of a single EMPA standard, and lack of information on how effective the extraction process is for EMPA from a coupon makes the EMPA analysis semi-quantitative.

The subsequent analysis of the EMPA degradation products was conducted using GC/MS (6890 gas chromatograph and 5973 mass selective detector, Agilent Technologies, Santa Clara, CA) operated in the full scan mode for compounds ranging from 40 to 500 atomic mass units, as described in Section 2.8.1. D1 was detected with ions 79, 97, and 125, and D2 was detected with ions 203, 143, and 175.

An EMPA standard at 81 $\mu\text{g/mL}$, which is equivalent to the VX concentration in the spike controls assuming 100% VX purity, was included in the analytical run (along with the VX calibration curve and the VX continuing calibration verification [CCV] standards described in Section 4.2). An intermediate EMPA standard at 3 milligrams/mL was prepared first by addition of neat EMPA (98% purity, 386561-1G, Sigma-Aldrich, St. Louis, MO) to the hexane and acetone extraction solvents containing IS and DIC. The intermediate was then diluted to the 81 $\mu\text{g/mL}$ concentration standard included in the analytical runs. The EMPA standard served as a single “calibration point” that was used to compare the EMPA-associated peaks of the test samples.

For the initial analyses associated with Environmental Condition 1, an 81 $\mu\text{g/mL}$ EMPA standard was included with the high VX calibration curve and a 10 $\mu\text{g/mL}$ EMPA standard was included with the low VX calibration curve. There was concern that using the 81 $\mu\text{g/mL}$ EMPA standard with the low VX calibration curve might cause saturation of the GC/MS detector possibly resulting in unusable data. However, chromatograms with responses exceeding as high as 700% of the low EMPA standard response were found to be of no danger to the GC/MS detector (i.e., no visual saturation in the chromatogram for EMPA byproducts) that would influence the VX response. Hence, it was acceptable to use the 81 $\mu\text{g/mL}$ EMPA standard with the low VX calibration curve.

The 81 $\mu\text{g/mL}$ EMPA standard was then used with the low and high VX calibration curves for all of the 28-day samples for Environmental Condition 1 and all the remaining tests. Using the same EMPA standard concentration with both the low and high VX calibration curves improved the comparability of the results as the reported D1 and D2 peak areas were related to the single EMPA standard. The concentrations recovered from the standard provided estimates of the maximum response from each EMPA degradant if all the VX on a particular coupon were to degrade into EMPA. Peak areas were reported for the two EMPA degradants in the standard as well as in all the samples for each analytical run.

2.9 Analysis of Variance (ANOVA) to Test Hypotheses

SAS/STAT[®] software (SAS Institute Inc., Cary NC) was used to fit an ANOVA model to the study data to test the three hypotheses noted in Section 2.1. The ANOVA model took the following form:

$$\ln(Y_{ijkn}) = \mu + \alpha_i + M_j + (\alpha M)_{ij} + (\lambda + \beta_i + \gamma_j)T_k + \varepsilon_{ijkn} \quad (5)$$

where “ln” denotes the natural logarithmic transformation, and the following notation was used:

- Y_{ijkn} is the residual mass measurement (μg) of VX recovered from the n^{th} replicate test (coupon) extracted at the k^{th} time point within the i^{th} environmental condition (temperature), where the coupon is of the j^{th} material type ($i=1, 2, 3; j=1, \dots, 6; k=1, \dots, 8; n=1, \dots, 5$),
- μ is an overall constant value,
- α_i is a constant value (added to μ) associated with the i^{th} environmental condition,
- M_j is a constant value (added to μ) associated with the j^{th} material type,
- $(\alpha M)_{ij}$ is a constant value (added to μ) associated with the specific combination of the i^{th} environmental condition and j^{th} material,
- T_k is the number of hours (from initial spiking) at which the coupon was extracted and tested,
- λ is an overall constant slope value applied to the time point value T_k ,
- β_i is a constant value (added to the slope λ) associated with the i^{th} environmental condition,
- γ_j is a constant value (added to the slope λ) associated with the j^{th} material type,
- ε_{ijkn} is random error representing the difference between the observed and model-predicted values of $\log(Y_{ijkn})$ (assumed to be normally distributed with mean 0 and variance which is constant across all environmental conditions, material types, time points, and coupons).

Only the terms Y_{ijkn} and T_k represent observed testing data; all other model terms are unknown and must be estimated by fitting the model to the $3 \times 6 \times 8 \times 5 = 720$ observed data points. This model is log-linear in nature, meaning the model on the untransformed residual mass measurement is exponential and multiplicative:

$$Y_{ijkn} = e^{\mu + \alpha_i + M_j + (\alpha M)_{ij}} e^{(\lambda + \beta_i + \gamma_j)T_k} e^{\varepsilon_{ijkn}} \quad (6)$$

This model represents exponential decay over time, with the rate of decay allowed to vary among the environmental conditions and material types. The general linear models (GLM) procedure in SAS[®] 9.4 was used to fit the log-linear model to the observed residual mass data. Only data for the six material types were included in this analysis; data for the spike controls were excluded. In

addition, any residual mass values reported as below the lower calibration limit of 2.5 μg were included in the analysis as 2.5 μg .

How the results of the ANOVA model fitting were used in performing the three sets of statistical hypothesis tests to address study objectives is detailed below. Recall that in statistical hypothesis testing, null and alternative hypotheses are specified, and the null hypothesis is assumed to hold unless the observed data (as applied to the statistical test procedure) are sufficient to support rejecting the null hypothesis for the alternative. All statistical tests were performed at a 0.05 significance level unless otherwise noted, meaning that the likelihood of incorrectly rejecting the null hypothesis for the alternative based on the observed data is no more than 5%.

Test #1:

- *Null hypothesis:* No decline occurs in mean recovered VX over time.
- *Alternative hypothesis:* Mean recovered VX declines over time.

Test #1 addressed whether the mean slope ($\lambda + \bar{\beta} + \bar{\gamma}$) associated with the time factor (i.e., the mean VX loss rate) was significantly less than 0 (i.e., an overall exponential decline occurs in the mass measurement with increasing time), where $\bar{\beta}$ and $\bar{\gamma}$ represent the mean of the incremental amounts added to the slope that are specific to the environmental condition and material type, respectively. In addition, statistical tests of whether the environmental condition-specific slope ($\lambda + \bar{\gamma} + \beta_i$) or the material-specific slope ($\lambda + \bar{\beta} + \gamma_j$) is significantly less than 0 were performed, in order to determine whether observing a significant rate of decline was dependent on either the environmental condition or material type.

Test #2:

- *Null hypothesis:* The mean rate of VX loss does not change among different environmental conditions (temperatures).
- *Alternative hypothesis:* The mean rate of VX loss differs among environmental condition (temperatures).

Because the three attenuations were distinguished by temperature, this test considered whether the attenuation effect was statistically significant on average across the time points.

Test #2 addressed whether the attenuation-specific slopes ($\lambda + \bar{\gamma} + \beta_i$) differed significantly from each other at the 0.05 level, indicating that the rate of decline in residual mass measurement of VX over time differed among the three environmental conditions. If so, then pairwise differences in these slopes (i.e., differences among the β_i values) were statistically compared at an overall 0.05 level (i.e., each test performed at a $0.05/3=0.0167$ level) to determine which of the three pairs of environmental conditions differed significantly in their rates of decline.

In addition, statistical tests were performed to determine whether the mean VX residual mass value differed among the three environmental conditions. First, the significance of the interaction term (αM)_{ij} was tested at the 0.05 level to determine whether the significance of the mean attenuation effect was dependent on the material type.

1. If this interaction term were significant, then statistical comparisons between pairs of environmental conditions were done by material type, with the overall significance level among all three pairs of the three environmental conditions being no higher than 0.05 within each material type (i.e., each test performed at a $0.05/3=0.0167$ level). No further tests were performed.
2. If the interaction term was not significant, then a test for significance of the main attenuation rate term α_i was performed at a 0.05 level.
 - a. If this test was significant, then at least one of the attenuation rates α_i differed significantly from 0. Therefore, this test was followed by pairwise tests to determine which of the three possible pairs of environmental conditions differed significantly at an overall 0.05 level (i.e., each test performed at a $0.05/3=0.0167$ level).
 - b. If this test was not significant, then on average across time points, the three environmental conditions did not differ significantly overall or for any material type.

Test #3:

- *Null hypothesis:* The mean rate of VX loss does not vary among different materials.
- *Alternative hypothesis:* The mean rate of VX loss does vary among different materials.

This test was performed in a similar manner to Test #2. First, statistical tests were performed to determine whether the material-specific slopes ($\lambda + \bar{\beta} + \gamma_j$) differed significantly from each other at a 0.05 level, indicating that the rate of decline in residual mass measurement of VX over time differed among the six material types. If so, then pairwise differences in these slopes (i.e., differences among the γ_j values) were statistically compared at an overall 0.05 level (i.e., each test performed at a $0.05/15=0.0033$ level) to determine which of the 15 pairs of material types differed significantly in their rates of decline.

Then, statistical tests were performed to determine whether the mean VX residual mass value differed among the six materials:

1. If the interaction term $(\alpha M)_{ij}$ were statistically significant at a 0.05 level (as determined within Test #2), then statistical comparisons between pairs of material types were done by environmental condition, with the overall significance level among all 15 pairs of the six material types being no higher than 0.05 within each attenuation (i.e., each test performed at a $0.05/15=0.0033$ level).
2. If the interaction term $(\alpha M)_{ij}$ was not significant, then the test for significance of the main material type effect M_j was performed at a 0.05 level.
 - a. If this test was significant, then at least one of the material types M_j differed significantly from 0. Therefore, this test was followed by pairwise tests to determine which of the 15 possible pairs of material types differed significantly at an overall 0.05 level (i.e., each test performed at a $0.05/15=0.0033$ level).

- b. If this test was not significant, then on average across time points, the six material types did not differ significantly overall or within any environmental condition.

3.0 Test Results

3.1 Extraction Recovery Method Demonstration Results

As discussed in Section 2.7, extraction recovery was determined 24 hours after spiking coupons of unsealed concrete, plywood, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass with 2 μL of VX. Four extraction solvents were tested: hexane (referred to as hexane without DIC), hexane with DIC (referred to as simply hexane), acetone with DIC (referred to as simply acetone), and dichloromethane: acetone (1:1) with DIC (referred to as dichloromethane:acetone). All extraction solvents contained the IS. The results of the recovery efficiency test are summarized in Figure 2 and Table 4. During this testing, the temperature varied from 18.1 $^{\circ}\text{C}$ to 21.3 $^{\circ}\text{C}$, and the RH ranged from <15% to 34.8%. The HOBO data logger (Onset Computer Corporation, Bourne, MA) used to monitor temperature and RH had a minimum RH reporting level of 15%. The mean spike control recoveries ranged from 82% to 102%. The spike control recoveries were calculated based on the amount and purity of VX spiked. As noted in Section 2.5, the purity of VX was 95.2% for all method demonstration tests.

Per Section 2.7, acceptable recoveries of VX were defined as having mean recoveries relative to the spike control of 70% to 120% with less than a 30% CV between samples. None of the extraction solvents tested achieved 70% VX recovery from unsealed concrete. Mean percent VX recoveries ranged from 12% to 20%, and the CV ranged from 37% to 63%. Low VX recoveries were also obtained from epoxy-sealed concrete in a companion study (EPA, 2016). The poor recoveries might be attributed to strong adsorption and/or degradation of the VX within the concrete (Groenewold et al., 2002). In fact, Groenewold et al. (2002) demonstrated the near complete VX degradation when VX was exposed to crushed concrete. Nevertheless, detectable VX was recovered with all four extraction solvents (ranging from 230 μg to 388 μg) 24 hours after spiking.

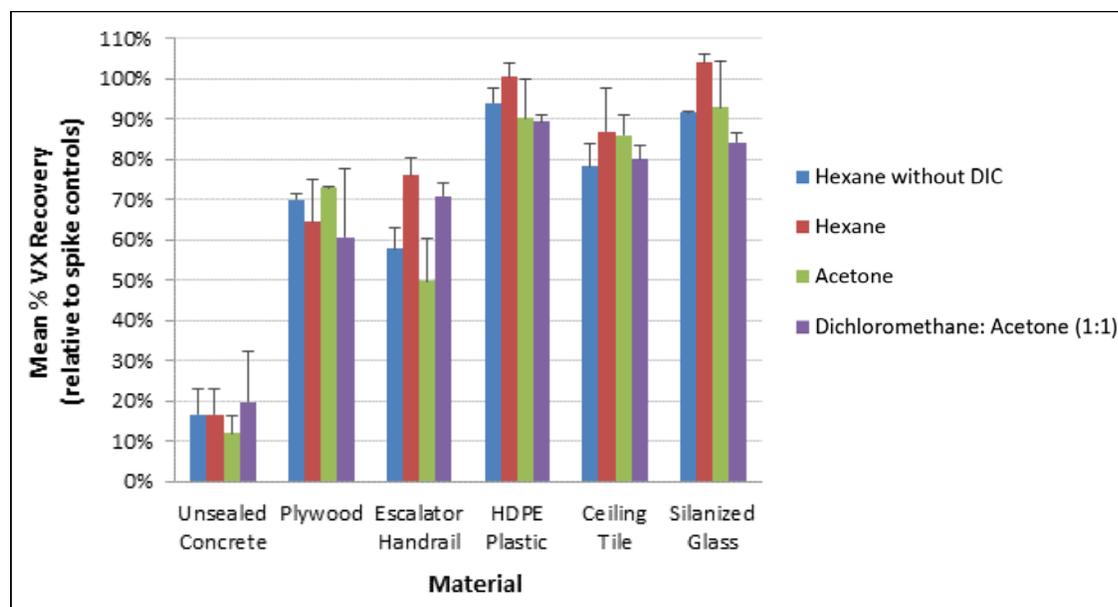


Figure 2. VX recoveries following coupon extraction in various solvents (error bars equal plus one standard deviation).

Table 4. VX Recoveries from Materials Extracted Using Different Solvents (all with IS)

Material	Measure of VX Recovery	Extraction Solvent			
		Hexane without DIC	Hexane	Acetone	Dichloromethane: Acetone (1:1)
Spike Control	Mean (µg)	1723	1577	1929	1963
	SD (µg)	128	34	81	59
	% Recovery*	90	82	100	102
	SD (%)	6.7	1.8	4.2	3.1
	CV (%)	7.4	2.2	4.2	3.0
Unsealed concrete	Mean (µg)	285	263	230	388
	SD (µg)	108	97	89	246
	% Recovery*	17	17	12	20
	SD (%)	6.3	6.1	4.6	13
	CV (%)	38	37	39	63
Plywood	Mean (µg)	1206	1016	1405	1190
	SD (µg)	27	168	9.8	338
	% Recovery*	70	64	73	61
	SD (%)	1.6	11	0.51	17
	CV (%)	2.2	17	0.70	28
Rubber escalator handrail	Mean (µg)	993	1199	960	1390
	SD (µg)	93	69	201	68
	% Recovery*	58	76	50	71
	SD (%)	5.4	4.4	10	3.5
	CV (%)	9.4	5.8	21	4.9
HDPE plastic	Mean (µg)	1620	1582	1738	1751
	SD (µg)	63	56	187	34
	% Recovery*	94	100	90	89
	SD (%)	3.6	3.6	9.7	1.7
	CV (%)	3.9	3.6	11	1.9
Ceiling tile	Mean (µg)	1347	1370	1660	1570
	SD (µg)	100	172	97	71
	% Recovery*	78	87	86	80
	SD (%)	5.8	11	5.0	3.6
	CV (%)	7.4	13	5.9	4.5
Silanized glass	Mean (µg)	1577	1639	1793	1654
	SD (µg)	3.3	36	216	43
	% Recovery*	92	104	93	84
	SD (%)	0.19	2.3	11	2.2
	CV (%)	0.21	2.2	12	2.6

SD = standard deviation of (here) the % Recovery; three replicate coupons were extracted per material and extraction solvent. All of the results were quantifiable; there were no non-detect results.

CV = coefficient of variation.

* % recovery (mean) for spike controls is relative to the theoretical recovery, and % recovery (mean) for the material samples is relative to the associated spike control.

Note: all associated laboratory and procedural blanks were non-detect for VX (<2.5 µg).

For plywood, acceptable VX recoveries relative to the spike control were obtained when using hexane without DIC (70% mean recovery and a CV of 2.2%) and acetone (73% mean recovery

and a CV of 0.7%). Lower mean VX recoveries from plywood occurred when using hexane (64%) and dichloromethane:acetone (61%).

In contrast to the results obtained with plywood, the VX recoveries from rubber escalator handrail were acceptable when using hexane or dichloromethane:acetone but not when using hexane without DIC or acetone. When using hexane, the mean VX recovery from the rubber escalator handrail was 76% with a CV of 5.8%. For dichloromethane:acetone, the mean VX recovery from the rubber escalator handrail was 71% with a CV of 4.9%. Lower mean VX recoveries from the rubber escalator handrail occurred when using hexane (58%) and acetone (50%).

For HDPE plastic, ceiling tile, and silanized glass, all mean VX recoveries relative to the spike controls were $\geq 78\%$ and all CV were $\leq 13\%$. As such, each of the extraction solvents was found to be acceptable for these materials. Silanized glass was used as a nonporous reference material to account for evaporative losses. The mean VX recoveries relative to the spike control from silanized glass ranged from 92% to 104% for all extraction solvents, except dichloromethane:acetone, which had a mean VX recovery of 84%. Considering the VX recoveries from silanized glass, some of the applied VX might be unrecoverable due to the use of an incomplete extraction process or losses associated with VX evaporation or degradation.

Based on the extraction recovery method demonstration results, hexane (with DIC) was selected as the extraction solvent for unsealed concrete, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass. Acetone with DIC was selected as the extraction solvent for plywood.

3.2 Natural Attenuation Results

3.2.1 Environmental Condition 1

The first environmental condition evaluated was 25 ± 3 °C, $40 \pm 5\%$ RH, with one chamber volume of air exchanged per hour. The actual temperature as measured by the Vaisala probe and the shelf-specific HOBO data loggers was consistently maintained within 25 ± 1 °C for all test durations. The actual RH measurements taken during this test are presented in Appendix B. In a few instances, the target RH was not maintained, but the magnitude and duration of these instances was relatively minor. The Vaisala measurement provided the overall conditions in the test chamber. The HOBO measurement on individual shelves was used to confirm that substantial differences in microenvironments did not exist between shelves.

After each weathering period (prior to extraction), the physical appearance of the coupons was noted (Table 5). Unsealed concrete and plywood were described at 30 min as having a “soak” spot, either dark or faint in color, where the VX was applied. Subsequent observations of the unsealed concrete and plywood throughout the entire exposure included faint and dark spots, but often there were no visible changes to the coupons, especially as the exposure times increased. The rubber escalator handrail initially had a “pancake” appearance (Figure 3) where the VX was applied; this area became a blister after 1 day of exposure. The HDPE plastic samples had the “pancake” appearance during the entire exposure time; at 28 days, the HDPE plastic was also described as having a hazy appearance. Dark soak spots were initially observed on some of the

ceiling tile coupons, but at the seven-hour extraction time and after, there was no VX visible. In most cases, the VX applied to silanized glass coupons had either a “pancake” appearance (Figure 3) or looked to have spread across the coupon (Figure 4). After the seven-day and longer durations, a variety of observations were noted, including: wet, hazy, or no VX visible.

None of the breakthrough control coupons (i.e., spiked unsealed concrete and ceiling tile coupons placed on M8 paper) indicated the presence of VX via a color change (i.e., the VX did not migrate through these especially porous coupons). The unsealed concrete and ceiling tile test coupons were therefore extracted along with the PTFE disks on which they were placed.

Table 5. Observations Associated with Environmental Condition 1* across Replicates

Material	Weathering Period							
	30 min	7 hours	1 day	2 days	4 days	7 days	14 days	28 days
Unsealed concrete	Soak; dark spot; faint spot	Faint spot; no VX visible	Dark Spot; no VX visible	No VX visible	No VX visible	Faint Spot; no VX visible	No VX visible	No VX visible
Plywood	Soak; dark spot	Dark spot; no VX visible	Dark spot; faint spot	Faint spot; no VX visible	No VX visible	No VX visible	No VX visible	No VX visible
Rubber escalator handrail	Pancake	Pancake	Blister; white smear	Blister	Blister	Blister	Blister	Blister
HDPE plastic	Pancake	Pancake	Pancake	Pancake	Pancake	Pancake	Pancake	Pancake; haze
Ceiling tile	Soak; dark spot; no VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible
Silanized glass	Pancake; spread	Pancake; spread	Pancake; spread	Pancake; spread	Pancake; spread; hazy	Wet; hazy; no VX visible	Wet; hazy; no VX visible	Hazy

* Differing observations (e.g., dark spot versus no VX visible) occurred on different replicate coupons. Observations were only recorded for each coupon replicate prior to extraction; repeated observations over time were not documented for the same replicate coupon.



Figure 3. Photograph of silanized glass coupon with VX having a “pancake” appearance.



Figure 4. Photograph of silanized glass coupon with VX having a “spread” appearance.

The mean spike control recoveries for VX during testing at Environmental Condition 1 were 2199 μg from the hexane spike controls and 2301 from the acetone spike controls. Hexane was

used as the extraction solvent for unsealed concrete, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass. Acetone was used as the extraction solvent for plywood.

The amount of VX recovered over time is presented in Figure 5 and Table 6. After a 30-min weathering period, the mean VX recoveries were $\geq 1537 \mu\text{g}$ for all materials, except unsealed concrete, which had a mean VX recovery of $684 \mu\text{g}$. The VX recoveries rather steadily decreased from unsealed concrete. The mean VX recovery from plywood was $871 \mu\text{g}$ after two days but rapidly decreased to $134 \mu\text{g}$ after four days. Similarly, rapid decreases in VX recoveries occurred from HPDE plastic, ceiling tile, and silanized glass which had mean recoveries $\geq 1080 \mu\text{g}$ after four days and mean VX recoveries $\leq 472 \mu\text{g}$ from these materials after seven days. The overall decrease in VX was slowest from the rubber escalator handrail, which had mean VX recoveries of $703 \mu\text{g}$ after seven days, $423 \mu\text{g}$ after 14 days, and $187 \mu\text{g}$ after 28 days. VX was recovered from at least some of the replicates of all materials tested after 14 days; the highest mean VX recoveries were from rubber escalator handrail ($423 \mu\text{g}$), ceiling tile ($152 \mu\text{g}$), and HDPE plastic ($66 \mu\text{g}$). The remaining materials had mean VX recoveries $< 10 \mu\text{g}$ after 14 days. After 28 days, VX was detected from at least one of the five replicate coupons for all materials except plywood and silanized glass. Mean VX recoveries remained above $10 \mu\text{g}$ after 28 days for the rubber escalator handrail ($187 \mu\text{g}$) and ceiling tile ($33 \mu\text{g}$).

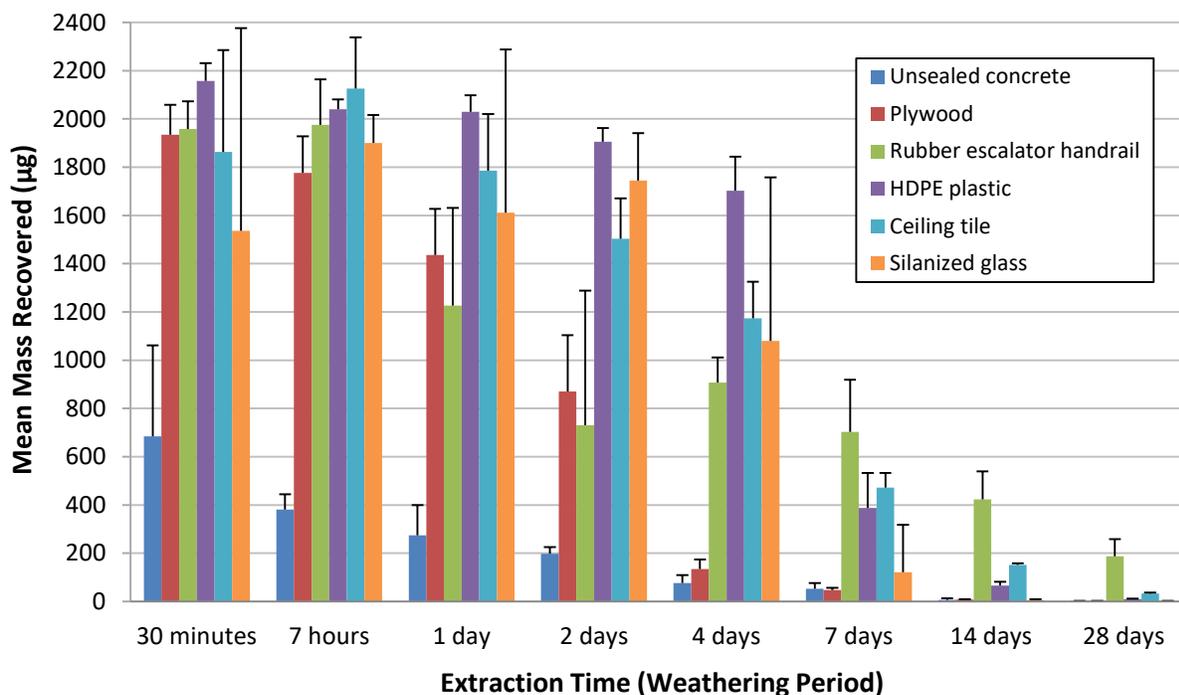


Figure 5. VX recovery at Environmental Condition 1 (error bars equal plus one standard deviation). Initial VX amount is $2200 \mu\text{g}$.

Table 6. VX Recovery at Environmental Condition 1

Material	Measure of VX Recovery	Extraction Time (Weathering Period)							
		30 min	7 hours	1 day	2 days	4 days	7 days	14 days	28 days
Unsealed concrete*	Mean (µg)	684‡	381	275	198	77	53	6.9	2.6
	SD (µg)	377	64	125	27	32	24	6.6	0.31
	CV (%)	55	17	45	14	42	46	96	12
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	3/5	1/5
	PB (µg)	<2.5	<2.5	14	17	13	4.8	<2.5	<2.5
Plywood†	Mean (µg)	1935	1776	1436	871	134	47	7.5	<2.5
	SD (µg)	123	152	192	233	40	10	1.2	0
	CV (%)	6.4	8.6	13	27	30	21	16	0
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	0/5
	PB (µg)	<2.5	<2.5	<2.5	12	29	25	18	<2.5
Rubber escalator handrail*	Mean (µg)	1959	1975	1227	731	908	703	423	187
	SD (µg)	114	189	404	558	104	216	116	71
	CV (%)	5.8	9.6	33	76	11	31	27	38
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	11	12	26	74	31	14
HDPE plastic*	Mean (µg)	2158	2040	2030	1905	1702	388	66	9.5
	SD (µg)	73	41	68	57	141	145	16	2.4
	CV (%)	3.4	2.0	3.4	3.0	8.3	37	23	26
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	<2.5	<2.5	<2.5	3.2	<2.5	<2.5
Ceiling tile*	Mean (µg)	1863	2126	1786	1504	1174	472	152	33
	SD (µg)	422	212	235	167	151	61	7.0	3.6
	CV (%)	23	10	13	11	13	13	4.6	11
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	4.0	22	21	31	36	38	7.0
Silanized glass*	Mean (µg)	1537	1900	1611	1745	1080	122	5.2	<2.5
	SD (µg)	839	117	677	196	678	196	3.7	0
	CV (%)	55	6.2	42	11	63	161	71	0
	FOD	5/5	5/5	5/5	5/5	5/5	3/5	3/5	0/5
	PB (µg)	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5

SD = standard deviation; five replicate coupons were extracted per material and weathering period.

CV = coefficient of variation.

FOD = frequency of detection (number of coupons above the quantitation limit/total number of coupons). For results less than the quantitation limit, 2.5 µg was used for the calculation of summary statistics.

PB = procedural blank; all laboratory blanks were non-detect for VX (<2.5 µg). The VX detections on the PBs were likely associated with VX volatilization and subsequent deposition/adsorption.

< = all available results were less than the quantitation limit.

* The spike control (hexane with IS and DIC) associated with these materials had a mean VX recovery of 2199 µg.

† The spike control (acetone with IS and DIC) associated with plywood had a mean VX recovery of 2301 µg.

‡ One unsealed concrete replicate had a comparatively low VX recovery (42 µg); this coupon may not have received the full VX challenge as an air bubble was noted in the syringe.

As documented on Table 6, relatively low levels of VX (≤ 74 µg or approximately 3% of amount spiked) were recovered from the procedural blanks, which are unspiked coupons held in the test chamber with the spiked coupons. VX recoveries were associated with the porous material procedural blanks but not the nonporous silanized glass procedural blanks. VX was not detected

from procedural blanks after 30 min, indicating that they were without VX at the start of the test. The porous material procedural blanks appeared to adsorb VX vapor that might have volatilized from the spiked coupons. All associated laboratory blanks (unspiked coupons never placed inside the test chamber) were non-detect for VX.

As noted in Section 2.8.2, sample extracts were also analyzed to semi-quantitatively estimate D1 and D2. These chemicals are degradation products of EMPA, which is a hydrolysis product of VX. This analysis was of particular interest for unsealed concrete, which was associated with comparatively low VX recoveries. However, neither degradation product was detected in sample extracts from the unsealed concrete. The low recovery of VX from unsealed concrete might be attributed to the highly adsorptive properties of VX, which can make it difficult to extract and analyze (Groenewold et al., 2002). Method development testing was not undertaken in this study to determine the extractability of D1 or D2 applied to concrete coupons.

As shown in Table 7, the EMPA degradation product D2 was detected from plywood (after four days), HDPE plastic (after seven days), ceiling tile (only one on replicate at seven days), and silanized glass (after 14 days). D1 was only detected from HPDE plastic after 14 days (Table 7). As footnoted in Table 7, in a few analytical runs, D1 was not detected in the associated EMPA standard; in these instances, the response from D1 was simply insufficient to provide a peak. The footnote is intended to document these instances and clarify that a semi-quantitative response for D1 was not applicable rather than indicating a 0% response. The detection of EMPA degradation products in these materials generally appeared to correspond with decreased recoveries of VX. For example, the mean VX recovery from plywood decreased from 871 µg after two days to 134 µg after four days; D2 first appeared in the plywood samples after four days.

Table 7. EMPA Degradation Product Recovery at Environmental Condition 1*

Material and Replicate	Extraction Time (Weathering Period)							
	4 days		7 days		14 days		28 days	
	% Response [†]	EMPA Standard [‡]	% Response [†]	EMPA Standard [‡]	% Response [†]	EMPA Standard [‡]	% Response [†]	EMPA Standard [‡]
D2								
Plywood 1	2.2	High	114	Low	11	Low	0.3	High
Plywood 2	3.0	Low [#]	21	Low	74	Low	1.0	High
Plywood 3	2.6	High	104	Low	44	Low	0.2	High
Plywood 4	3.3	High	102	Low	39	Low	0.9	High
Plywood 5	4.9	High	129	Low	55	Low	0.3	High
HDPE plastic 1	--	--	9.2	High	15	High	21	High
HDPE plastic 2	--	--	0	High	15	High	16	High
HDPE plastic 3	--	--	10	High	20	High	7.8	High
HDPE plastic 4	--	--	16	High	20	High	14	High
HDPE plastic 5	--	--	13	High	15	High	12	High

Table 7. EMPA Degradation Product Recovery at Environmental Condition 1* (continued)

Material and Replicate	Extraction Time (Weathering Period)							
	4 days		7 days		14 days		28 days	
	% Response [†]	EMPA Standard [‡]	% Response [†]	EMPA Standard [‡]	% Response [†]	EMPA Standard [‡]	% Response [†]	EMPA Standard [‡]
D2								
Ceiling tile 1	--	--	0	High	--	--	--	--
Ceiling tile 2	--	--	0	High	--	--	--	--
Ceiling tile 3	--	--	8.2	High	--	--	--	--
Ceiling tile 4	--	--	0	High	--	--	--	--
Ceiling tile 5	--	--	0	High	--	--	--	--
Silanized glass 1	--	--	--	--	0	Low	1.1	High
Silanized glass 2	--	--	--	--	4.8	Low	2.0	High
Silanized glass 3	--	--	--	--	0	Low	0.5	High
Silanized glass 4	--	--	--	--	0	Low	0.5	High
Silanized glass 5	--	--	--	--	0	Low	0	High
D1[§]								
HDPE plastic 1	--	--	--	--	7.7	High	11	High
HDPE plastic 2	--	--	--	--	7.6	High	10	High
HDPE plastic 3	--	--	--	--	7.5	High	2.8	High
HDPE plastic 4	--	--	--	--	8.8	High	8.9	High
HDPE plastic 5	--	--	--	--	8.1	High	8.6	High

* Detections (semi-quantitative) of D2 and D1 from test coupons; detections did not occur at other weathering times or materials.

[†] The percent of the applicable standard peak area for D2 or D1.

[‡] The low EMPA standard was 10 µg/mL, and the high EMPA standard was 81 µg/mL.

[#] This sample was the only plywood replicate reanalyzed using the low VX curve and was thus the only replicate based on the low EMPA standard.

[§] In some cases D1 was not detected in the associated EMPA standard, so it was not possible to semi-quantitatively detect D1 from the test coupons specifically: unsealed concrete (at two days), plywood (at four, seven, and 14 days), rubber escalator handrail (at two days), HDPE plastic (at two days), ceiling tile (at two days), and silanized glass (at two days).

-- = D2 or D1 was not detected on any replicate.

3.2.2 Environmental Condition 2

The second environmental condition evaluated was 10 ± 3 °C, 40 ± 5% RH, with one chamber volume of air exchanged per hour. The target temperature was consistently maintained and ranged from 8.9 °C to 12.2 °C throughout the study as measured by the Vaisala probe and shelf-specific HOBO data loggers.

The RH data are presented in Table 8 and Appendix B. As shown in Table 8, which presents summaries of the shelf-specific HOBO data loggers that collected RH measurements at five min intervals, the mean RH was above the target level at 30 min (52.4% RH) and at seven hours (47.1% RH); all other mean RH levels were within the target range of 35% to 45% RH. The RH became elevated during test initiation when the chamber was opened for a period of time to allow the VX to be brought into the chamber for coupon spiking. The RH returned to the target RH level relatively quickly after spiking (Appendix B). On May 10, 2016, the RH level nearly

reached 65%; during this time, corrective action was being taken to reverse the trend of increasing RH, but the bypass valve on the Nafion[®] humidification tube was inadvertently turned the wrong way increasing the air flow through the humidifier. This error was quickly identified, and the bypass valve was turned the correct way to introduce drier air into the chamber. As shown in Appendix B, other instances of relatively minor or brief RH deviations from the target level occurred. In some instances, these events were likely associated with the opening of the chamber to remove samples.

Table 8 also estimates the amount of time the samples were above and below the target RH levels. The mean RH at 30 min exceeded the target RH level for the entire 30 min duration. For the seven-hour test, the RH target level was exceeded for 50% of the time. For all other tests, relatively small portions of the weathering period (<12%) were outside the target RH range.

Table 8. Relative Humidity during Environmental Condition 2 Testing

Measurement	Extraction Time (Weathering Period)							
	30 min	7 hours	1 day	4 days	7 days	14 days	21 days	35 days
Minimum RH (%)	50.5	41.2	34.9	35.3	32.7	33.0	30.0	29.8
Mean RH (%)	52.4	47.1	39.4	40.5	38.5	40.3	40.3	40.3
Maximum RH (%)	53.4	59.6	56.3	57.7	55.7	63.0	61.9	63.0
Estimated Time RH was Above the Upper Limit (45%)*	30 min (100%)	3.5 hours (50%)	2.3 hours (9.7%)	3.0 hours (3.1%)	2.4 hours (1.4%)	19.8 hours (5.9%)	21.2 hours (4.2%)	25.7 hours (3.1%)
Estimated Time RH was Below the Lower Limit (35%)*	--	--	--	--	11.3 hours (6.7%)	19.6 hours (5.8%)	35.3 hours (7.0%)	36.3 hours (4.3%)

Note: Based on test/shelf-specific RH measured with HOBO data loggers during the weathering periods only. Lower and higher designations are used to indicate the amount of time below or above the target RH level.

* Results are presented as time, i.e., in min or hours, and as a percentage of the weathering period; estimates of time above or below RH limits were made based on RH measurements rounded to whole numbers.

-- RH was not below the lower limit.

After each weathering period (prior to extraction), the physical appearance of the coupons was noted (Table 9). Unsealed concrete and plywood were initially observed at 30 min and were described as having a “soak” spot, either dark or faint in color, where the VX was applied. Subsequent observations of the unsealed concrete and plywood throughout the entire exposure included faint and dark spots, but often there were no visible changes to the coupons. The rubber escalator handrail initially had a “bead” appearance where the VX was applied; this area was consistently described as being a blister after four days of exposure. The HDPE plastic samples generally had a “bead” or “pancake” appearance during the entire exposure time. Dark soak spots were initially observed on all of the ceiling tile coupons, but at the 7-hour extraction time and after there was no VX visible. On silanized glass, VX initially had a “pancake” appearance. Instances of the VX having a “spread” appearance in contrast to a well-defined pancake appearance occurred during the seven-hour through 21-day exposure durations. The VX on

silanized glass began to appear dry in some cases at seven days and these observations continued until all coupons appeared dry or hazy at 35 days.

Table 9. Observations Associated with Environmental Condition 2* across Replicates

Material	Extraction Time (Weathering Period)							
	30 min	7 hours	1 day	4 days	7 days	14 days	21 days	35 days
Unsealed concrete	Spread; soak; dark spot; faint spot	Dark Spot; no VX visible	No VX visible	No VX visible	Faint spot; no VX visible	No VX visible	No VX visible	No VX visible
Plywood	Soak; dark spot	Faint spot	Faint spot; no VX visible	Faint Spot; no VX visible	No VX visible	Faint spot; no VX visible	No VX visible	Faint Spot; no VX visible
Rubber escalator handrail	Bead	Bead	Bead	Blister	Blister	Blister	Blister	Blister
HDPE plastic	Bead	Bead; pancake	Bead	Pancake	Pancake	Pancake	Pancake	Pancake; wet
Ceiling tile	Soak; dark spot	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible
Silanized glass	Pancake	Pancake; spread	Pancake; spread; wet	Pancake; spread; wet	Spread; wet; dry spot	Pancake; spread; wet; dry spot	Pancake; spread; wet; dry spot	Hazy; dry spot

* Differing observations (e.g., dark spot versus no VX visible) occurred on different replicate coupons. Observations were only recorded for each coupon replicate prior to extraction; repeated observations over time were not documented for the same replicate coupon.

None of the breakthrough control coupons (i.e., spiked unsealed concrete and ceiling tile coupons placed on M8 paper) indicated the presence of VX via a color change (i.e., the VX did not migrate through these especially porous coupons). The unsealed concrete and ceiling tile test coupons were therefore extracted along with the PTFE disks on which they were placed.

The mean spike control recoveries for VX during testing at Environmental Condition 2 were 1880 µg from the hexane spike controls and 2073 µg from the acetone spike controls. Hexane was used as the extraction solvent for unsealed concrete, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass. Acetone was used as the extraction solvent for plywood. The mean VX recovery from the hexane spike controls (1880 µg) was lower than expected, because one of the spike control replicates had a lower recovery (1240 µg) compared to the other four replicates with VX recoveries ranging from 1765 µg to 2280 µg. No observations were made at the time of testing to explain the lower recovery. For rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass, mean VX recoveries were sometimes higher than the theoretical recoveries obtained from the spike controls, especially within the first day of testing.

The amount of VX recovered from the various materials over time is presented in Figure 6 and Table 10. After a 30-min weathering period, the mean VX recovery was ≥1940 µg for all

materials except unsealed concrete, which had a mean VX recovery of 1050 μg . The VX recoveries decreased rather steadily for unsealed concrete, but VX remained detectable after 35 days with a mean VX recovery of 78 μg . The mean VX recoveries from the other materials remained ≥ 1128 μg for at least four days. For plywood and silanized glass, the mean VX recoveries remained ≥ 1026 μg after seven days but then decreased to levels lower than those recovered from unsealed concrete at 35 days (≤ 52 μg). The VX recoveries from rubber escalator handrail, HDPE plastic, and ceiling tile were ≥ 1015 μg after 14 days and remained ≥ 391 μg for the entire study duration. The mean VX recovery from rubber escalator handrail was noticeably lower at seven days (427 μg) than observed at four days (1128 μg) and 14 days (1015 μg). The reason for this lower result is unknown, but a similar incidence of lower VX recovery from rubber escalator handrail also occurred at Environmental Condition 1, where the mean VX recovery at two days (731 μg) was lower than the recovery at one day (1227 μg) and four days (908 μg) (see Table 6).

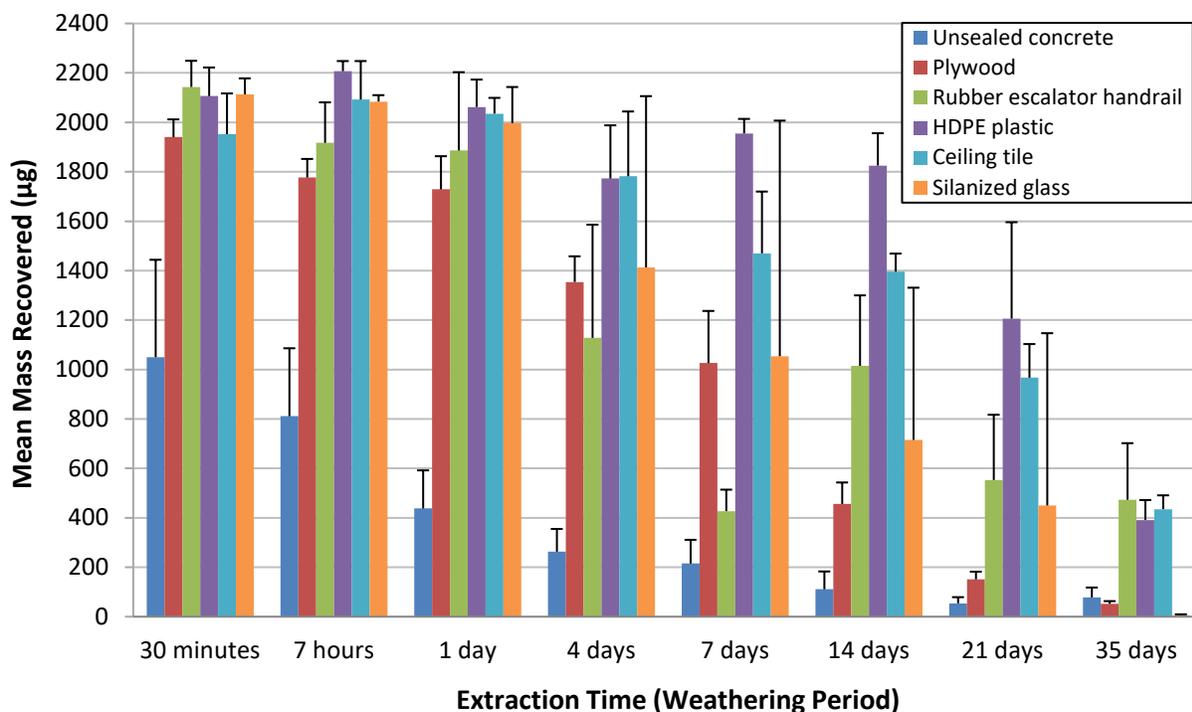


Figure 6. VX recovery at Environmental Condition 2 (error bars equal plus one standard deviation). Initial spiked VX amount is 1900 μg except for plywood (2100 μg).

Table 10. VX Recovery at Environmental Condition 2

Material	Measure of VX Recovery	Extraction Time (Weathering Period)							
		30 min	7 hours	1 day	4 days	7 days	14 days	21 days	35 days
Unsealed concrete*	Mean (µg)	1050	811	438	263	215	111	54	78
	SD (µg)	394	275	154	92	96	72	25	40
	CV (%)	38	34	35	35	45	65	46	52
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	<2.5	<2.5	9.3	10	3.1	5.7
Plywood†	Mean (µg)	1940	1777	1729	1354	1026	456	151	52
	SD (µg)	72	75	134	104	211	87	31	11
	CV (%)	3.7	4.2	7.8	7.7	21	19	20	22
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	<2.5	16	16	32	29	16
Rubber escalator handrail*	Mean (µg)	2143	1917	1886	1128	427	1015	553	473
	SD (µg)	106	164	317	458	87	285	264	229
	CV (%)	4.9	8.5	17	41	20	28	48	48
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	2.7	27	50	44	32	39
HDPE plastic*	Mean (µg)	2106	2207	2062	1773	1955	1825	1206	391
	SD (µg)	116	41	111	215	59	131	390	81
	CV (%)	5.5	1.9	5.4	12	3.0	7.2	32	21
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	3.2	<2.5
Ceiling tile*	Mean (µg)	1952	2092	2035	1782	1470	1396	967	435
	SD (µg)	165	156	64	262	250	73	136	56
	CV (%)	8.4	7.5	3.1	15	17	5.2	14	13
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	<2.5	4.4	10	16	14	25	29
Silanized glass*	Mean (µg)	2113	2084	1997	1413	1054	715	450	5.9
	SD (µg)	65	26	146	693	953	616	697	3.6
	CV (%)	3.1	1.3	7.3	49	90	86	155	61
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	4/5	4/5
	PB (µg)	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5

SD = standard deviation; five replicate coupons were extracted per material and weathering period.

CV = coefficient of variation.

FOD = frequency of detection (number of coupons above the quantitation limit/total number of coupons). For results less than the quantitation limit, 2.5 µg was used for the calculation of summary statistics.

PB = procedural blank; all laboratory blanks were non-detect for VX (<2.5 µg). The VX detections on the PBs were likely associated with VX volatilization and subsequent deposition/adsorption.

< = all available results were less than the quantitation limit.

* The spike control (hexane with IS and DIC) associated with these materials had a mean VX recovery of 1880 µg; one of the replicates had a comparatively low VX recovery (1240 µg); a definitive cause was not identified.

† The spike control (acetone with IS and DIC) associated with plywood had a mean VX recovery of 2073 µg.

The VX recoveries associated with silanized glass were associated with the highest CVs (e.g., from 86% to 155% over 7 to 21 days), while the CVs were ≤65% in all other cases (Table 10). Interestingly, the VX descriptions on silanized glass for these weathering times (Table 9) covered a wide range of appearances from well formed “pancake” shapes, to coupons that remained wet with VX spread across the coupon, to an apparently dry VX residue on the coupon.

As shown in Table 11, VX recoveries within a given weathering period were lowest where the coupon was described as being dry, higher when the coupons were described as having a wet appearance, and highest when the coupons retained VX in a “pancake” shape. The visual descriptions may reflect the amount of agent volatilization/degradation that has occurred with silanized glass coupons appearing dry having the most VX loss, while VX retaining the “pancake” appearance is associated with the lowest amount of attenuation. Similar relationships between the VX appearance on silanized glass coupons and the amount of VX recovered also occurred with Environmental Condition 1 at four and seven days (data not presented). Other researchers have reported relationships between CWA drop size and evaporation rates and degradation rates. For example, Jung and Lee (2014) reported the evaporation rate of sulfur mustard from aluminum and stainless steel increased linearly with increasing drop size. Wagner et al. (2004) found that the degradation rate of larger VX droplets on concrete was slower than for smaller droplets. When Wagner et al. (2004) dissolved a large droplet of VX in hexane and uniformly distributed the VX across the concrete surface, the degradation rate increased similar to the degradation rate associated with the smaller droplets. For the current study, the reason for VX presenting differently on silanized glass is not known.

Table 11. VX Recoveries from Silanized Glass at 7, 14, and 21 Days at Environmental Condition 2

Silanized Glass Replicate	Extraction Time (Weathering Period)					
	7 Days		14 Days		21 Days	
	Description*	VX Recovery (µg)	Description*	VX Recovery (µg)	Description*	VX Recovery (µg)
1	Wet; spread	1781	Wet; spread	644	Dry Spot	188
2	Dry spot	3.2	Dry spot; spread	6.3	Dry Spot	<2.5
3	Wet; spread	1827	Pancake	1582	Dry Spot	4.0
4	Wet; spread	1637	Dry spot; spread	313	Wet; Spread	394
5	Dry spot	21	Wet; spread	1029	Pancake	1663

* Observations were recorded for each coupon replicate prior to extraction; repeated observations over time were not documented for the same replicate coupon.

Relatively low levels ($\leq 50 \mu\text{g}$) of VX were recovered from the procedural blanks (unspiked coupons held in the test chamber) (Table 10). As with the testing conducted under Environmental Condition 1, VX was only recovered from the porous/permeable material procedural blanks and not from the silanized glass procedural blanks. The porous materials appear capable of adsorbing vaporous VX that might have volatilized from the spiked coupons. VX was not detected from any of the laboratory blanks, which are unspiked coupons never placed inside the test chamber.

As noted in Section 2.8.8, sample extracts were also analyzed to semi-quantitatively estimate D1 and D2, which are degradation products of VX by way of EMPA degradation. As shown on Table 12, D2 was detected from plywood at 7, 14, 21, and 35 days and detected from HDPE

plastic at 21 and 35 days. As footnoted in Table 12, in a few analytical runs D1 was not detected in the associated EMPA standard; in these instances, the response from D1 was simply insufficient to provide a peak. The footnote is intended to document these instances and clarify that a semi-quantitative response for D1 was not applicable rather than indicating a 0% response.

Table 12. EMPA Degradation Product Recovery at Environmental Condition 2*

Material and Replicate	Extraction Time (Weathering Period)			
	7 days % Response [†]	14 days % Response [†]	21 days % Response [†]	35 days % Response [†]
D2				
Plywood 1	0	1.3	2.2	0.6
Plywood 2	0	5.2	3.3	0.9
Plywood 3	0	1.3	3.2	1.0
Plywood 4	0.3	1.5	3.3	1.3
Plywood 5	0	2.0	4.3	1.7
HDPE plastic 1	--	--	0.8	4.6
HDPE plastic 2	--	--	0.7	4.0
HDPE plastic 3	--	--	0	4.7
HDPE plastic 4	--	--	3.9	3.1
HDPE plastic 5	--	--	0.3	4.2

* Detections (semi-quantitative) of D2 from test coupons; detections did not occur at other weathering times or materials. D1 was not detected from the test coupons; however, in some cases D1 was not detected in the associated EMPA standard either, so it was not possible to semi-quantitatively detect D1 from: unsealed concrete (at 30 min, seven hours, and one day), rubber escalator handrail (at 30 min, seven hours, and one day), HDPE plastic (at 30 min, seven hours, and one day), ceiling tile (at 30 min, seven hours, and one day), and silanized glass (at 30 min, seven hours, and one day).

[†] The percent of the applicable standard peak area for D2; only the high EMPA standard (81 µg/mL) was used.

-- = D2 was not detected on any replicate.

3.2.3 Environmental Condition 3

Environmental Condition 3 was defined as: 35 ± 3 °C, 40 ± 5% RH, with one chamber volume of air exchanged per hour. The actual temperature as measured by the Vaisala probe and the shelf-specific HOBO data loggers was consistently maintained within 35 ± 1 °C for all test durations. Similarly, the actual RH values, when rounded to whole numbers, ranged from 35% to 43%, which was within the target RH level range. Technically two RH measurements made with the Vaisala probe (34.99% and 34.69%) were slightly less than the lower RH target of 35%, but none of the RH measurements made with the HOBO data loggers were below 35%.

After each weathering period (prior to extraction), the physical appearance of the coupons was noted (Table 13). Unsealed concrete and plywood were initially observed at 30 min and were described as having a dark “soak” spot where the VX was applied. Subsequent observations of the unsealed concrete and plywood included faint and dark spots or no visible changes to the coupons. The rubber escalator handrail initially had a “pancake” appearance where the VX was applied; this area was consistently described as being a blister after 1 day of exposure. With the exception of one “wet/spread” observation at 30 min, all HDPE plastic samples were described as having a “pancake” appearance. Some dark soak spots or stains were initially observed after

30 min on the ceiling tile coupons, but subsequent observations were described as no VX visible. On silanized glass, VX initially had a “pancake” or “wet/spread” appearance. Observations indicative of the VX becoming dry or hazy began to be reported after one day of weathering, and in some cases, there was no VX visible on the silanized glass coupons.

None of the breakthrough control coupons (i.e., spiked unsealed concrete and ceiling tile coupons placed on M8 paper) indicated the presence of VX via a color change (i.e., the VX did not seep through these especially porous coupons). The unsealed concrete and ceiling tile test coupons were therefore extracted along with the PTFE disks on which they were placed.

Table 13. Observations Associated with Environmental Condition 3* across Replicates

Material	Extraction Time (Weathering Period)							
	30 min	4 hours	7 hours	1 day	2 days	3 days	7 days	10 days
Unsealed concrete	Soak; dark spot	Dark spot; no VX visible	Dark spot; no VX visible	Faint spot; no VX visible	No VX visible	No VX visible	No VX visible	No VX visible
Plywood	Soak; dark spot	Dark spot; faint spot; no VX visible	Faint spot	Faint spot; no VX visible	Faint spot; no VX visible	No VX visible	No VX visible	No VX visible
Rubber escalator handrail	Pancake	Pancake; Blister	Pancake; Blister	Blister	Blister	Blister	Blister	Blister
HDPE plastic	Pancake; wet; spread	Pancake	Pancake	Pancake	Pancake	Pancake	Pancake	Pancake
Ceiling tile	Soak; dark spot; stain; No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible	No VX visible
Silanized glass	Pancake; wet; spread	Pancake; wet; spread	Pancake; wet; spread	Wet; spread; hazy; dry spot; no VX visible	Pancake; hazy; dry spot	Wet; spread; hazy; dry spot; no VX visible	Hazy; dry spot; no VX visible	Hazy; dry spot; no VX visible

* Differing observations (e.g., dark spot versus no VX visible) occurred on different replicate coupons. Observations were only recorded for each coupon replicate prior to extraction; repeated observations over time were not documented for the same replicate coupon.

The amount of VX recovered over time is presented in Figure 7 and Table 14. The mean spike control recoveries for VX during testing at Environmental Condition 3 were 2104 µg from the hexane spike controls and 2218 µg from the acetone spike controls. Hexane was used as the extraction solvent for unsealed concrete, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass. Acetone was used as the extraction solvent for plywood.

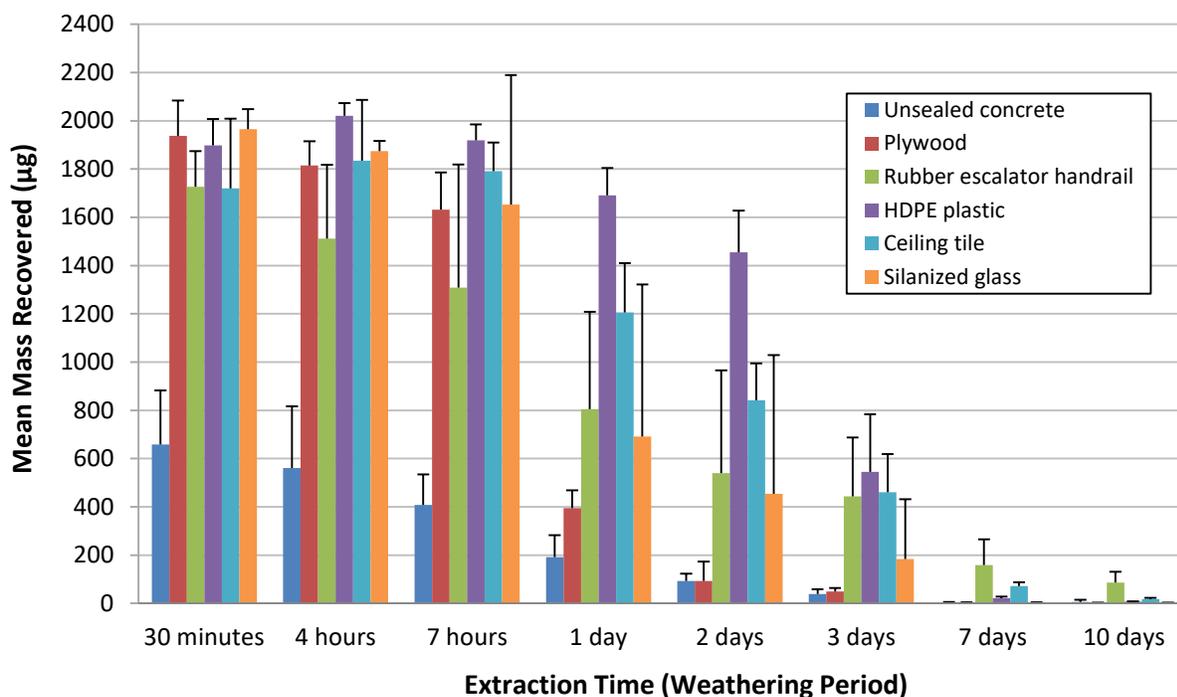


Figure 7. VX recovery at Environmental Condition 3 (error bars equal plus one standard deviation). Initial spiked VX amount is 2100 µg except for plywood (2200 µg).

The mean VX recoveries after 30 min were ≥ 1720 µg for all materials, except unsealed concrete, which had a mean VX recovery of 659 µg. VX recovery from unsealed concrete rather steadily decreased with only one or two replicate coupons detecting VX at seven days and 10 days of exposure (the associated mean VX recoveries were ≤ 6.2 µg). The mean VX recoveries remained ≥ 1308 µg for all other materials after seven hours. For plywood, the mean VX recovery dramatically decreased between seven hours (1631 µg) and one day (395 µg); the VX recoveries from plywood continued to decrease until becoming completely non-detect at 10 days. Similar decreases in mean VX recovery were associated with HDPE plastic between two days (1455 µg) and three days (545 µg) and silanized glass between seven hours (1653 µg) and one day (691 µg). The VX remained detectable from HDPE plastic at low levels (mean VX recovery 7.1 µg) at 10 days, but VX was not detected from silanized glass at 10 days. The mean VX recoveries at seven days and 10 days were highest from rubber escalator handrail (159 µg and 86 µg, respectively) and ceiling tile (71 µg and 18 µg, respectively).

Table 14. VX Recovery at Environmental Condition 3

Material	Measure of VX Recovery	Extraction Time (Weathering Period)							
		30 min	4 hours	7 hours	1 day	2 days	3 days	7 days	10 days
Unsealed concrete*	Mean (µg)	659	561	408	192	93	38	3.6	6.2
	SD (µg)	223	256	126	91	30	21	1.7	8.3
	CV (%)	34	46	31	47	33	57	46	133
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	2/5	1/5
	PB (µg)	<2.5	4.4	36	12	4.1	20	<2.5	<2.5
Plywood†	Mean (µg)	1937	1815	1631	395	93	49	3.7	<2.5
	SD (µg)	147	100	155	73	80	14	0.39	0
	CV (%)	7.6	5.5	9.5	19	86	28	11	0
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	0/5
	PB (µg)	<2.5	8.5	19	23	22	33	2.8	<2.5
Rubber escalator handrail*	Mean (µg)	1726	1511	1308	805	540	443	159	86
	SD (µg)	148	306	511	403	425	244	107	45
	CV (%)	8.6	20	39	50	79	55	67	53
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	6.6	17	41	31	24	14	33
HDPE plastic*	Mean (µg)	1898	2021	1919	1691	1455	545	22	7.1
	SD (µg)	110	53	66	113	173	238	5.4	1.2
	CV (%)	5.8	2.6	3.5	6.7	12	44	25	18
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	3.7	3.6	<2.5	8.7	2.9	<2.5	<2.5
Ceiling tile*	Mean (µg)	1720	1835	1791	1205	842	460	71	18
	SD (µg)	289	251	119	205	152	159	16	5.3
	CV (%)	17	14	6.7	17	18	35	23	29
	FOD	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
	PB (µg)	<2.5	5.7	17	24	55	66	28	10
Silanized glass*	Mean (µg)	1965	1874	1653	691	454	184	3.0	<2.5
	SD (µg)	83	43	537	631	575	247	1.2	0
	CV (%)	4.2	2.3	32	91	127	135	39	0
	FOD	5/5	5/5	5/5	3/5	5/5	4/5	1/5	0/5
	PB (µg)	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5

SD = standard deviation; five replicate coupons were extracted per material and weathering period.

CV = coefficient of variation.

FOD = frequency of detection (number of coupons above the quantitation limit / total number of coupons). For results less than the quantitation limit, 2.5 µg was used for the calculation of summary statistics.

PB = procedural blank; all laboratory blanks were non-detect for VX (<2.5 µg). The VX detections on the PBs were likely associated with VX volatilization and subsequent deposition/adsorption.

< = all available results were less than the quantitation limit.

* The spike control (hexane with IS and DIC) associated with these materials had a mean VX recovery of 2104 µg.

† The spike control (acetone with IS and DIC) associated with plywood had a mean VX recovery of 2218 µg.

Relatively low levels (≤ 66 µg) of VX were recovered from the procedural blanks (unspiked coupons held in the test chamber) (Table 14). As with the testing conducted under Environmental Conditions 1 and 2, VX was only recovered from the porous/permeable material procedural blanks and not from the silanized glass procedural blanks. The porous or permeable materials appear capable of adsorbing VX that might have volatilized from the spiked coupons.

VX was not detected from any of the laboratory blanks, which are unspiked coupons never placed inside the test chamber.

Sample extracts were also analyzed to semi-quantitatively estimate D1 and D2, which are degradation products of VX by way of EMPA degradation. As shown on Table 15, D2 was detected from plywood, HDPE plastic, ceiling tile, and silanized glass at seven and 10 days. D2 was also detected earlier from plywood (after one, two, and three days) and HDPE plastic (after two and three days). D1 was only detected from HDPE plastic after seven and 10 days.

Table 15. EMPA Degradation Product Recovery at Environmental Condition 3*

Material and Replicate	Extraction Time (Weathering Period)				
	1 day % Response [†]	2 days % Response [†]	3 days % Response [†]	7 days % Response [†]	10 days % Response [†]
D2					
Plywood 1	1.4	0	2.9	1.8	1.0
Plywood 2	1.2	3.7	1.5	2.2	1.2
Plywood 3	1.9	1.0	3.8	1.2	1.7
Plywood 4	1.1	0	3.7	1.2	1.3
Plywood 5	2.2	5.3	1.5	1.2	1.0
HDPE plastic 1	--	0.3	3.5	87	6.6
HDPE plastic 2	--	0	2.5	111	11
HDPE plastic 3	--	0	4.1	51	7.2
HDPE plastic 4	--	0	14	65	11
HDPE plastic 5	--	0	3.2	85	14
Ceiling tile 1	--	--	--	2.6	0.1
Ceiling tile 2	--	--	--	1.0	0.1
Ceiling tile 3	--	--	--	0	0.1
Ceiling tile 4	--	--	--	0	0.2
Ceiling tile 5	--	--	--	1.0	0.1
Silanized glass 1	--	--	--	0	0.7
Silanized glass 2	--	--	--	12	0
Silanized glass 3	--	--	--	0	0.3
Silanized glass 4	--	--	--	0	0
Silanized glass 5	--	--	--	2.4	0
D1					
HDPE plastic 1	--	--	--	57	1.9
HDPE plastic 2	--	--	--	77	2.9
HDPE plastic 3	--	--	--	46	2.8
HDPE plastic 4	--	--	--	50	3.6
HDPE plastic 5	--	--	--	58	4.3

* Detections (semi-quantitative) of D2 and D1 from test coupons; detections did not occur at other weathering times or materials.

[†] The percent of the applicable standard peak area for D2 or D1; only the high EMPA standard (81 µg/mL) was used.

-- = D2 or D1 was not detected on any replicate.

3.3 ANOVA Results

The results of applying the log-linear ANOVA model presented in Section 2.9 above to the observed (log-transformed) residual VX mass measurement data to test the three sets of statistical hypotheses of interest were as follows:

Test #1:

- *Null hypothesis:* No decline occurs in mean recovered VX over time.
- *Alternative hypothesis:* Mean recovered VX declines over time.

The (declining) time trend was highly statistically significant overall and for each of the three environmental conditions and six material types ($p < 0.0001$ for each test), meaning the null hypothesis can be rejected in favor of the alternative.

The overall mean slope estimate ($\lambda + \bar{\beta} + \bar{\gamma}$) was -0.01141 (with standard error 0.00027). Thus, at T hours following spiking, the model-predicted average residual mass of VX (μg) is some multiple of $e^{-0.01140T} = (0.9887)^T$.

The environmental condition-specific slope estimates ($\lambda + \bar{\gamma} + \beta_i$) were as follows:

- Environmental Condition #1 (25 ± 3 °C): -0.00791 (with standard error 0.00028)
- Environmental Condition #2 (10 ± 3 °C): -0.00335 (with standard error 0.00022)
- Environmental Condition #3 (35 ± 3 °C): -0.02230 (with standard error 0.00073)

The material-specific slope estimates ($\lambda + \bar{\beta} + \gamma_j$) were as follows (each having standard error 0.00046):

- Unsealed concrete: -0.01134
- Plywood: -0.01328
- Rubber escalator handrail: -0.00824
- HDPE plastic: -0.01093
- Ceiling tile: -0.00973
- Silanized glass (reference material): -0.01490

All of these estimates are negative, implying a decline in residual mass over time. The larger the slope estimate in absolute value, the greater the rate of decline in the hours immediately following spiking.

Test #2:

- *Null hypothesis:* The mean rate of VX loss does not change among different environmental conditions (temperatures).

- *Alternative hypothesis:* The mean rate of VX loss differs among environmental conditions (temperatures).

The ANOVA model fitting determined that significant differences existed between the three environmental condition-specific slopes ($\lambda + \bar{\gamma} + \beta_i$) ($p < 0.0001$), indicating the rate of decline in residual mass measurement of VX over time differed significantly among the three environmental conditions. These estimates were given above in the results for Test #1: Environmental Condition #3 had the largest slope in absolute value, about 2.8 times the value of the next-highest slope, for Environmental Condition #1, which in turn was twice the value of the slope for Environmental Condition #2. To determine which of these three slopes differed significantly from each other, pairwise differences among each of these three slopes (i.e., differences among the β_i values) were statistically compared at an overall 0.05 level (i.e., each test performed at a $0.05/3 = 0.0167$ level). All three pairs differed significantly from each other ($p < 0.0001$).

Statistical tests were also performed to determine whether the mean VX residual mass value (across time) differed among the three environmental conditions. Because the interaction term $(\alpha M)_{ij}$ was statistically significant ($p < 0.0001$), the significance of the mean attenuation effect was dependent on the material type. Therefore, statistical comparisons between pairs of attenuations were done by material type, with the overall significance level among all three pairs of the three environmental conditions being no higher than 0.05 within each material type (i.e., each test performed at a $0.05/3 = 0.0167$ level). The following pairs of environmental conditions differed significantly in their mean residual mass values for the following material types:

- Unsealed concrete: Environmental Condition 1 vs. 2
- Plywood: Environmental Condition 1 vs. 2, 2 vs. 3
- Rubber escalator handrail: Environmental Condition 2 vs. 3
- Silanized glass: Environmental Condition 1 vs. 3, 2 vs. 3

Test #3:

- *Null hypothesis:* The mean rate of VX loss does not vary among different materials.
- *Alternative hypothesis:* The mean rate of VX loss does vary among different materials.

The ANOVA model fitting determined that significant differences existed between the six material-specific slopes ($\lambda + \bar{\beta} + \gamma_j$) ($p < 0.0001$), indicating that the rate of decline in residual mass measurement of VX over time differed significantly among the three environmental conditions. These estimates were given above in the results for Test #1 (and are repeated below in Table 16): the largest slope estimate in absolute value (for silanized glass, the nonporous reference material) was approximately 80% higher than the smallest estimated slope in absolute value (for rubber escalator handrail). To determine which of these six slopes differed significantly from each other, pairwise differences in these slopes (i.e., differences among the γ_j values) were statistically compared at an overall 0.05 level (i.e., each test performed at a $0.05/15 = 0.0033$ level).

Table 16. ANOVA Test Results for Mean Rate of VX Loss (Slope Estimate) from Different Materials (among the Three Environmental Conditions Tested)

Material	Material-Specific Slope Estimates	Vertical Lines Connect Materials whose Estimates do not Differ Significantly	
Silanized glass (reference material):	-0.01490		
Plywood	-0.01328		
Unsealed concrete	-0.01134		
HDPE plastic	-0.01093		
Ceiling tile	-0.00973		
Rubber escalator handrail	-0.00824		

As shown in Table 16, the rate of decline for silanized glass differs significantly from each of the porous/permeable materials except plywood. In turn, the rate of decline for rubber escalator handrail differed significantly from all but ceiling tile.

Statistical tests were also performed to determine whether the mean VX residual mass value (across time) differed among the six materials. Because the interaction term $(\alpha M)_{ij}$ was statistically significant ($p < 0.0001$), the significance of the mean attenuation effect was dependent on the environmental condition. Therefore, statistical comparisons between pairs of materials were done by environmental condition, with the overall significance level among all 15 pairs of the six material types being no higher than 0.05 within each environmental condition (i.e., each test performed at a $0.05/15 = 0.0033$ level). The following pairs of materials differed significantly in their mean residual mass values for the following environmental conditions (Table 17):

- Environmental Condition 1:
 - [plywood and unsealed concrete] versus all other materials (with the exception of plywood versus silanized glass).
- Environmental Condition 2:
 - unsealed concrete versus all other materials (with the exception of rubber escalator handrail);
 - rubber escalator handrail versus [HDPE plastic and plywood].
- Environmental Condition 3:
 - rubber escalator handrail versus all other materials (with the exception of ceiling tile)
 - [plywood, silanized glass, and unsealed concrete] versus [ceiling tile and HDPE plastic]
 - plywood versus unsealed concrete.

Table 17. ANOVA Test Results Identifying Pairs of Materials with Significantly Different Mean Residual Mass under Identified Environmental Conditions

Material	Material				
	Plywood	Unsealed concrete	HDPE plastic	Ceiling tile	Rubber escalator handrail
Silanized Glass		E1, E2	E3	E3	E3
Plywood		E1, E2, E3	E1, E3	E1, E3	E1, E2, E3
Unsealed concrete			E1, E2, E3	E1, E2, E3	E1, E3
HDPE plastic					E2, E3
Ceiling tile					

E1, E2, E3: Environmental Condition 1, 2, 3

4.0 Quality Assurance/Quality Control

4.1 Control of Monitoring and Measuring Devices

Quality control requirements and results are shown in Table 18 and includes checks of the measurement methods for temperature, RH, time, volume, spike controls, IS, VX recovery from silanized glass, and laboratory blanks. Attainment of these data quality indicator results limited the amount of error introduced into the investigation results.

Table 18. Quality Control Requirements and Results

Parameter	Measurement Method	Data Quality Indicators	Results
Temperature, °C	Thermometer	Compared against calibrated National Institute of Standards and Technology (NIST)-traceable thermometer once before testing, agree ± 1 °C	At each environmental condition, the HOBO data loggers were generally within ± 1 °C of the NIST-traceable Vaisala instrument.
RH, %	Hygrometer	Compared against calibrated NIST-traceable hygrometer once before testing, agree $\pm 10\%$ (full scale)	At each environmental condition, the HOBO data loggers were generally within $\pm 5\%$ of the NIST-traceable Vaisala instrument.
Time, second	Timer/data logger	Compared against calibrated NIST-traceable timer once before testing; agree ± 2 seconds/min.	Deviation of 0 second/min
Volume, μL	Repeating dispenser/syringe	Repeating dispenser/syringe was checked for accuracy and repeatability one time before use by determining the mass of water delivered. The syringe was considered acceptable if the range of observed masses for five droplets was $\pm 10\%$ of expected.	Ten measurements were made with tolerances (percent errors) of 4.84, 9.85, 0.17, 10.19, 9.85, 9.85, 9.85, 0.17, 0.17, and 9.85%.
Spike control	GC/MS	The mean of the spike controls included with each day of testing should be within 70% to 120% of the target application.	The mean spike control recoveries (for hexane and acetone separately) were within 70% to 120% of the theoretical recoveries.

Table 18. Quality Control Requirements and Results (continued)

Parameter	Measurement Method	Data Quality Indicators	Results
IS, naphthalene-d ₈	Extraction, GC/MS	The mean of the IS quantity included with each day of testing should be within 70% to 120% of the expected mass.	Every sample's IS response was compared to the mid-point standard. Anything outside the specification was flagged and re-run.
VX on silanized glass with immediate extraction, µg/mL	Extraction, GC/MS	The mean percent recovery for a known quantity of VX added to silanized glass coupons must fall within the range of 70% to 120% of the spike control and have a CV of <30% between replicates.	The mean VX recovered from silanized glass (after a 30-min weathering period) was within 70% to 120% of the VX recovered from the associated spike controls and the CVs were <30% between replicates, except for Environmental Condition 1 when the CV was 55%.
VX on laboratory blank coupons, µg/mL	Extraction, GC/MS	Laboratory blanks (coupons without applied VX maintained outside the testing hood) should have <1% of the amount of analyte compared to that found on spike controls.	No measurable VX detected on laboratory blank coupons.

4.2 Equipment Calibrations

The instrumentation used to quantify VX and semi-quantify D1 and D2 from the material extracts is identified in Section 2.8. The equipment needed for the analytical methods was maintained and operated according to the quality requirements and documentation of the Battelle HMRC. All equipment was calibrated with appropriate standards and at the frequency specified in Table 19.

GC/MS calibration ranged from 0.1 µg/mL to 125 µg/mL. To accommodate accurate analysis over this broad range, two separate calibration curves were generated – a “low” curve ranging from 0.1 µg/mL to 10 µg/mL, and a “high” curve ranging from 5.0 µg/mL to 125 µg/mL. Each curve was constructed using five distinct calibration levels. Range of each curve and selection of the specific calibration points included in each curve were determined based on general GC/MS performance in analysis of VX in hexane and acetone as well as on the observed quadratic response nature of VX. A quadratic regression (coefficient of determination [r^2] >0.990) curve fit was applied to the calibration data. Any sample exceeding the upper calibration limit of the high curve would have been diluted to a concentration within the calibration range and reanalyzed. However, no such case occurred. Sample results below the high curve lower calibration limit

were analyzed against the low curve. Sample results below the low curve lower calibration limit were reported as < 0.1µg/mL. The GC/MS was tuned daily. A tune check was performed before running each batch using decafluorotriphenylphosphine. A 12-hour tune time was not employed.

Table 19. Equipment Calibration Schedule

Equipment	Frequency
Calibrated pipette and repeating dispenser/syringe	Prior to the investigation and every six months thereafter
Calibrated hygrometer/thermometer	Prior to the investigation and annually thereafter
GC/MS	Beginning of each batch of test samples (calibration curve) and a calibration verification standard after every five samples and at the end of a batch of samples

Following analysis of the calibration standards at the beginning of each analytical run, a solvent blank sample (e.g., hexane with IS and DIC or acetone with IS and DIC) was analyzed to confirm that no VX carryover was occurring. Solvent blank sample analysis results were below the value of the lowest calibration standard.

Independently prepared CCV standards were analyzed prior to sample analysis, following every five samples, and at the end of each batch of samples. Two CCV concentrations were used, one of which was equal to the low calibration standard and the other(s) within the calibration range. Measured CCV concentration was required to fall within 35% of the nominal concentration for the lowest level CCV used and within 20% of the nominal concentration for all other CCVs for test sample extract VX analysis results to be considered valid. Samples analyzed prior to or following CCVs that were outside acceptance limits were reanalyzed.

Neat VX was used to create calibration standards encompassing the appropriate analysis range. Calibration standards were kept and used for no longer than six months from the date of creation. CCV standards were kept and used for no longer than one month from the date of creation. The GC was recalibrated if the r^2 from the regression analysis of the standards was <0.98.

Limits were placed on the percent bias observed in the standards.

$$\text{Percent bias} = \frac{R-C}{R} \times 100\% \quad (5)$$

where:

R = expected value from calibration curve

C = observed value from standard.

The percent bias for the low standard required <25%, and the percent bias for the remaining standards required <15%.

As stated above, one CCV standard was run for every five samples. The percent bias for the low CCV standard was required to be <35%, and the percent bias for the remaining CCV standards had to be <20%. Additionally, every 10th test sample extract was immediately reinjected and analyzed following the original. The result from the reanalysis of every 10th sample was used strictly as an additional confirmation to the analyst of adequate GC performance. The reanalysis result was required to fall within 20% of the result of the original analysis of the sample (see Table 19). The 10th sample reanalysis results were included only in the primary raw analysis data generated by the analyst and excluded from calculations and reported data (only the original analysis result was used for calculation and reporting purposes). Criteria for evaluation of the GC performance are shown in Table 20.

CCV standards or test sample extract reinjections/reanalyses that did not meet the above analysis results quality criteria were flagged, and all test sample extracts analyzed prior to and following the non-compliant standard (to the next compliant standard) were reanalyzed. All reported data (data included in calculations and attenuation performance summaries) were generated from analyses that met the criteria described in Table 20.

Table 20. Gas Chromatography Performance Parameters and Acceptance Criteria

Parameter	Criterion
Coefficient of determination (r ²)	>0.99
% bias for the lowest calibration standard	<25%
% bias for remaining calibration standards (except lowest standard)	<15%
Solvent blank sample	< lowest calibration standard
% bias for the lowest CCV	<35%
% bias for remaining CCVs (except lowest CCV)	<20%
Differences between replicate samples (10 th sample reanalysis)	<20%

4.3 Technical Systems Audit

The Quality Assurance (QA) Officer performed a technical systems audit (TSA) at the HMRC facility in West Jefferson, Ohio, during the first day of testing at Environmental Condition 2. The purpose of the TSA was to ensure that testing was performed in accordance with the Quality Assurance Project Plan (QAPP). The QA Officer reviewed the investigation methods, compared test procedures to those specified in the QAPP (and the associated amendments), and reviewed data acquisition and handling procedures. The QA Officer did not identify any findings that required corrective action.

4.4 Performance Evaluation Audit

A performance evaluation audit was conducted as summarized in Table 21. Acceptable tolerances were volume ($\pm 10\%$), time (± 1 second/min), chemical mass ($\geq 85\%$), IS ($\pm 10\%$), temperature (± 1 °C), and RH ($\pm 10\%$).

Table 21. Performance Evaluation Results

Parameter	Audit Procedure	Expected Tolerance	Results
Volume	Syringe used for dispensing chemical agent was checked for accuracy and repeatability one time before use by determining the mass of water delivered	±10%	Ten measurements were made with tolerances (percent errors) of 4.84, 9.85, 0.17, 10.19, 9.85, 9.85, 9.85, 0.17, 0.17, and 9.85%.
Time	Compared time to independent NIST-traceable timer one time before use	±1 second/min	0 second/min
Compound mass	Used GC/MS to determine mass of VX delivered as 2 µL droplet into 25 mL of hexane and acetone and compared to target application level one time	≥85% of spike target	All mean spike control VX recoveries were ≥85% of the target spike amount; only one replicate (a hexane spike control from Environmental Condition 2) had a VX recovery <85% (64%).
IS	Used GC/MS to measure from a secondary source and compare to the primary source one time	±10%	1.9% (relative percent difference)
Temperature	Compared against calibrated NIST-traceable thermometer one time before use	±1 °C	At each environmental condition, the HOBO data loggers were generally within ±1 °C of the NIST-traceable Vaisala instrument.
RH	Compared against calibrated NIST-traceable hygrometer one time before use	±10%	At each environmental condition, the HOBO data loggers were generally within ±5% of the NIST-traceable Vaisala instrument.

4.5 Data Quality Audit

The QA Manager audited at least 10% of the investigation data and traced the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All data analysis calculations were checked.

4.6 Deviations

Two deviations were noted for this project:

- The purity of the VX used for most of the coupon spiking associated with Environmental Condition 1 was not directly confirmed because the ampoule of VX being used was depleted before the purity sample was collected. Purity was obtained from the same synthesis lot as the VX used for most of the spiking. Impact to the project was minimal. The VX purity was expected to be the same because the ampoules of VX originated from the same synthesis lot.

- The RH levels sometimes deviated from the target RH levels during Environmental Conditions 1 and 2. The deviations are documented in this report (see Appendix B1 and B2) and are generally minor with regard to the magnitude of the deviation and/or the duration of time the target RH level was not maintained. The mean RH (based on the longest weathering periods) were within the target range of $40 \pm 5\%$ RH for Environmental Conditions 1 and 2.

5.0 Summary

The objective of this research effort was to investigate the natural attenuation of VX on various porous or permeable materials under controlled environmental conditions. Test conditions were consistent with an indoor environment as, for example, possible degradation by UV light was not part of this project. Testing was conducted with unsealed concrete, plywood, rubber escalator handrail, HDPE plastic, ceiling tile, and silanized glass (a nonporous reference material). Except for the unsealed concrete, all materials were new and considered to be clean. Unsealed concrete was poured in 2004. Three environmental conditions were tested with temperatures of 25 °C, 10 °C, or 35 °C, and 40% RH and one volume of chamber air exchanged per hour. Coupons of the test materials were spiked with 2 µL of neat VX and allowed to weather for various periods (ranging from 30 min to 35 days). The weathered coupons were then immersed in hexane or acetone solvent and sonicated to extract the VX. The sample extracts were quantified via GC/MS for VX.

Natural attenuation was estimated by:

$$\text{Mean VX Attenuated (\%)} = 100\% - \text{Mean VX Recovered (\%)}, \text{ relative to spike controls by material, temperature, and weathering period.}$$

Natural attenuation measured the reduction in the amount of extractable VX remaining following unaided degradation or volatilization of VX from the spiked materials. The VX natural attenuation results are shown in Figure 8. The percent of VX naturally attenuated is also presented in Table 21 by environmental condition, material, and weathering period. It is apparent that natural attenuation of VX occurred on all six materials under all three environmental conditions. Natural attenuation occurred fastest at warmer temperatures. For example, >90% natural attenuation occurred with all materials tested by seven days at 35 °C, by 28 days at 25 °C, and longer than 35 days at 10 °C (i.e., 90% attenuation was not yet achieved on rubber escalator handrail, HDPE plastic, or ceiling tile at the longest duration tested).

The time required for the natural attenuation of VX to achieve a given attenuation level was also material-dependent. Unsealed concrete was consistently the first material to reach 90% attenuation, followed by plywood, and then silanized glass. Longer amounts of time were consistently required to achieve 90% natural attenuation when associated with rubber escalator handrail, HDPE plastic, and ceiling tile.

The various mechanisms possibly contributing to the observed attenuations, such as volatilization, chemical degradation, or inability to extract were not explicitly investigated or quantified. However, evidence of chemical degradation was shown with the semi-quantitative analysis of the degradation products of EMPA that were detected from plywood, HDPE plastic, ceiling tile, and silanized glass. The detection of other toxic degradation products such as EA-2192 was not attempted because such an analysis would require the use of liquid chromatography/MS, which was beyond the scope of this study. Volatilization (and subsequent reabsorption/deposition) was also likely occurring as shown with the VX detections observed with many of the procedural blanks. In addition, relatively low VX recoveries occurred at 30 min with unsealed concrete, indicative of extraction challenges and/or chemical degradation. The extractability of the EMPA from any material was not investigated in this study.

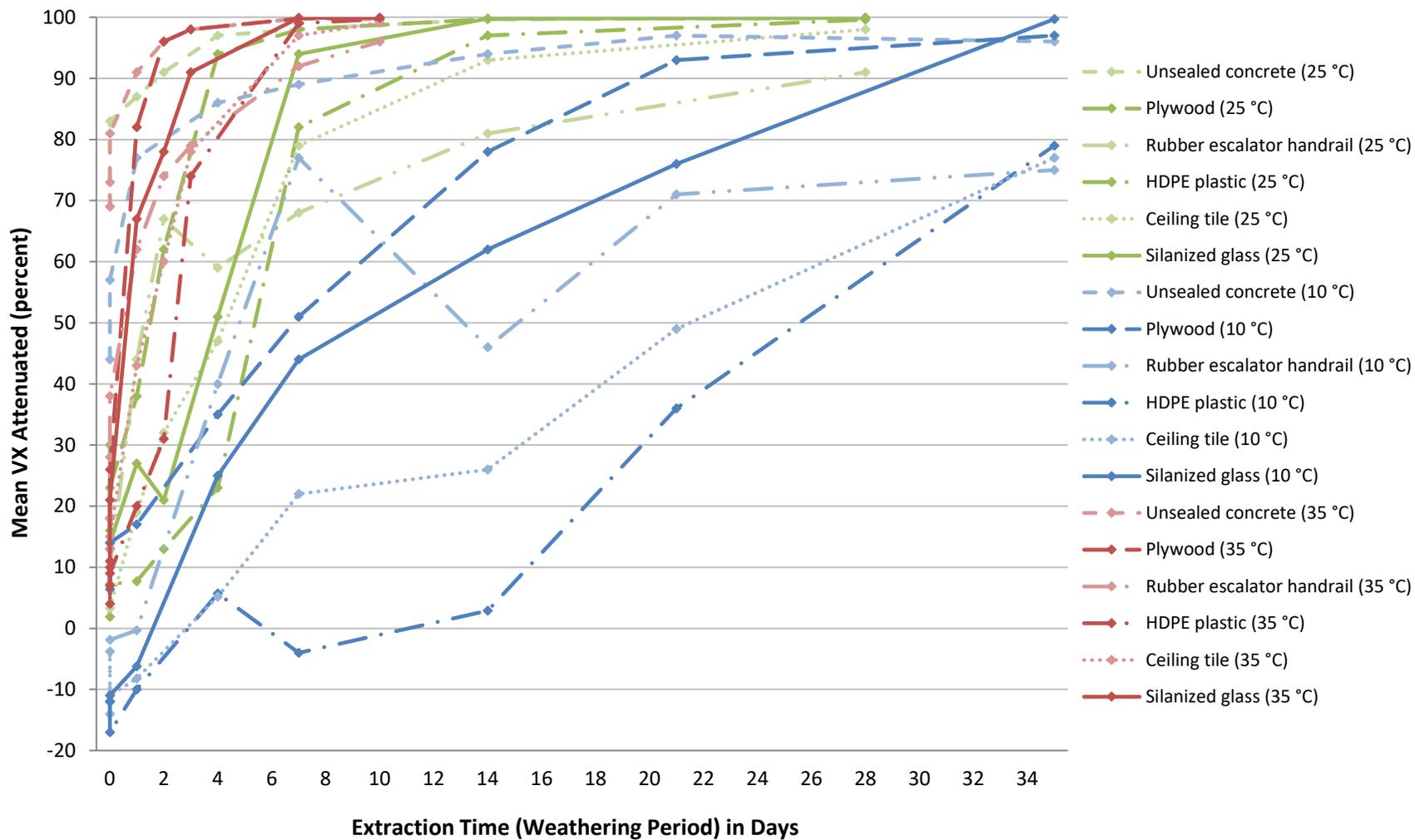


Figure 8. Percent of VX attenuated over time by material and temperature (negative VX attenuation reflects instances when higher VX was recovered from the test coupons than the associated spike controls).

Table 22. Percent of VX Naturally Attenuated over Time by Environmental Condition

Material	Percent of VX Attenuation at Extraction Time (Weathering Period)*												
	Min 30	Hours 4 7		Days 1 2 3 4 7 10 14 21 28 35									
Environmental Condition 1: 25 °C, 40% RH, with One Volume of Air Exchanged per Hour													
Unsealed concrete	69	--	83	87	91	--	97	98	--	99.7	--	99.9	--
Plywood	16	--	23	38	62	--	94	98	--	99.7	--	99.9 [†]	--
Rubber escalator handrail	11	--	10	44	67	--	59	68	--	81	--	91	--
HDPE plastic	1.9	--	7.2	7.7	13	--	23	82	--	97	--	99.6	--
Ceiling tile	15	--	3.3	19	32	--	47	79	--	93	--	98	--
Silanized glass	30	--	14	27	21	--	51	94	--	99.8	--	99.9 [†]	--
Environmental Condition 2: 10 °C, 40% RH, with One Volume of Air Exchanged per Hour													
Unsealed concrete	44	--	57	77	--	--	86	89	--	94	97	--	96
Plywood	6.4	--	14	17	--	--	35	51	--	78	93	--	97
Rubber escalator handrail	0 [‡]	--	0 [‡]	0 [‡]	--	--	40	77	--	46	71	--	75
HDPE plastic	0 [‡]	--	0 [‡]	0 [‡]	--	--	5.7	0 [‡]	--	2.9	36	--	79
Ceiling tile	0 [‡]	--	0 [‡]	0 [‡]	--	--	5.2	22	--	26	49	--	77
Silanized glass	0 [‡]	--	0 [‡]	0 [‡]	--	--	25	44	--	62	76	--	99.7
Environmental Condition 3: 35 °C, 40% RH, with One Volume of Air Exchanged per Hour													
Unsealed concrete	69	73	81	91	96	98	--	99.8	99.7	--	--	--	--
Plywood	13	18	26	82	96	98	--	99.8	99.9 [†]	--	--	--	--
Rubber escalator handrail	18	28	38	62	74	79	--	92	96	--	--	--	--
HDPE plastic	10	4	9	20	31	74	--	99	99.7	--	--	--	--
Ceiling tile	18	13	15	43	60	78	--	97	99.1	--	--	--	--
Silanized glass	7	11	21	67	78	91	--	99.9	99.9 [†]	--	--	--	--

* Attenuation estimated by 100% - mean percent VX recovery relative to spike controls.

[†] VX was not detected from any of the replicate coupons.

[‡] In cases where higher VX recovery occurred from the material than the spike control (i.e., the mean percent VX recovery relative to the spike controls was >100%), a “0” was used on this table rather than presenting a negative percent VX attenuation value.

-- = not sampled.

As can be derived from Figure 8, trace amounts of VX may still be present weeks to months after a contamination event. These amounts should be put into context with cleanup objectives and surface concentration cleanup levels for VX which have not been established. Such cleanup levels are expected to be site-specific and likely to be at or below the detection limit for VX (by GC/MS) in this study. Therefore, detectable amounts of VX on these materials, even after weeks of natural attenuation, would require decontamination/neutralization to reach the expected cleanup level. The amount of VX observed on procedural blanks should be interpreted to indicate that volatilization of VX results in a redistribution of some of the VX onto originally clean surfaces; however, observed amounts were low and were also declining with time.

6.0 References

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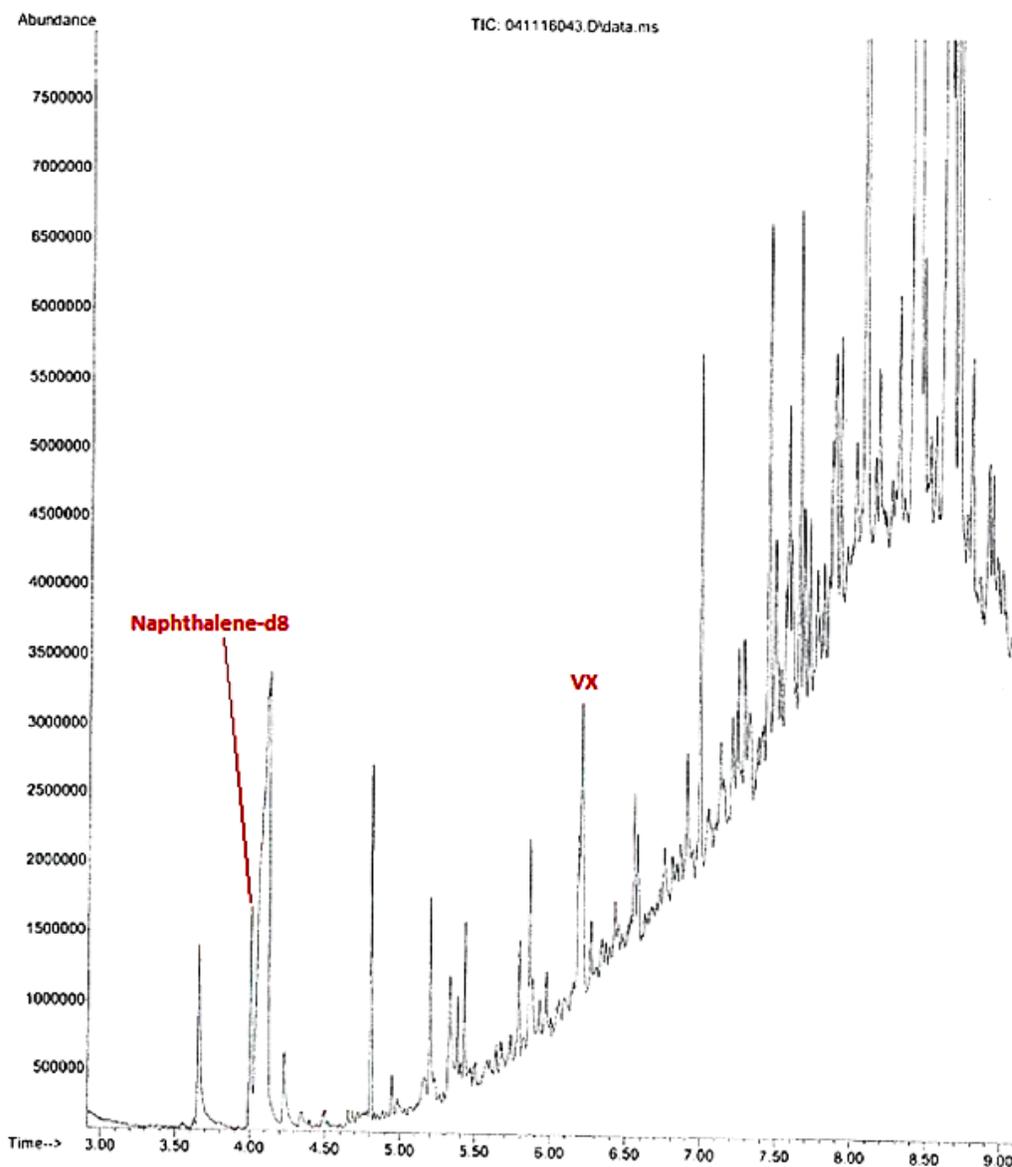
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Appendix A

VX Analysis by GC/MS, Sample Chromatograms

File :C:\msdchem\1\data\EPA\11\APR16\041116043.D
Operator : AWE
Acquired : 12 Apr 2016 3:25 using AcqMethod EPA LOW.M
Instrument : 602
Sample Name: AQ37841
Misc Info :
Vial Number: 38



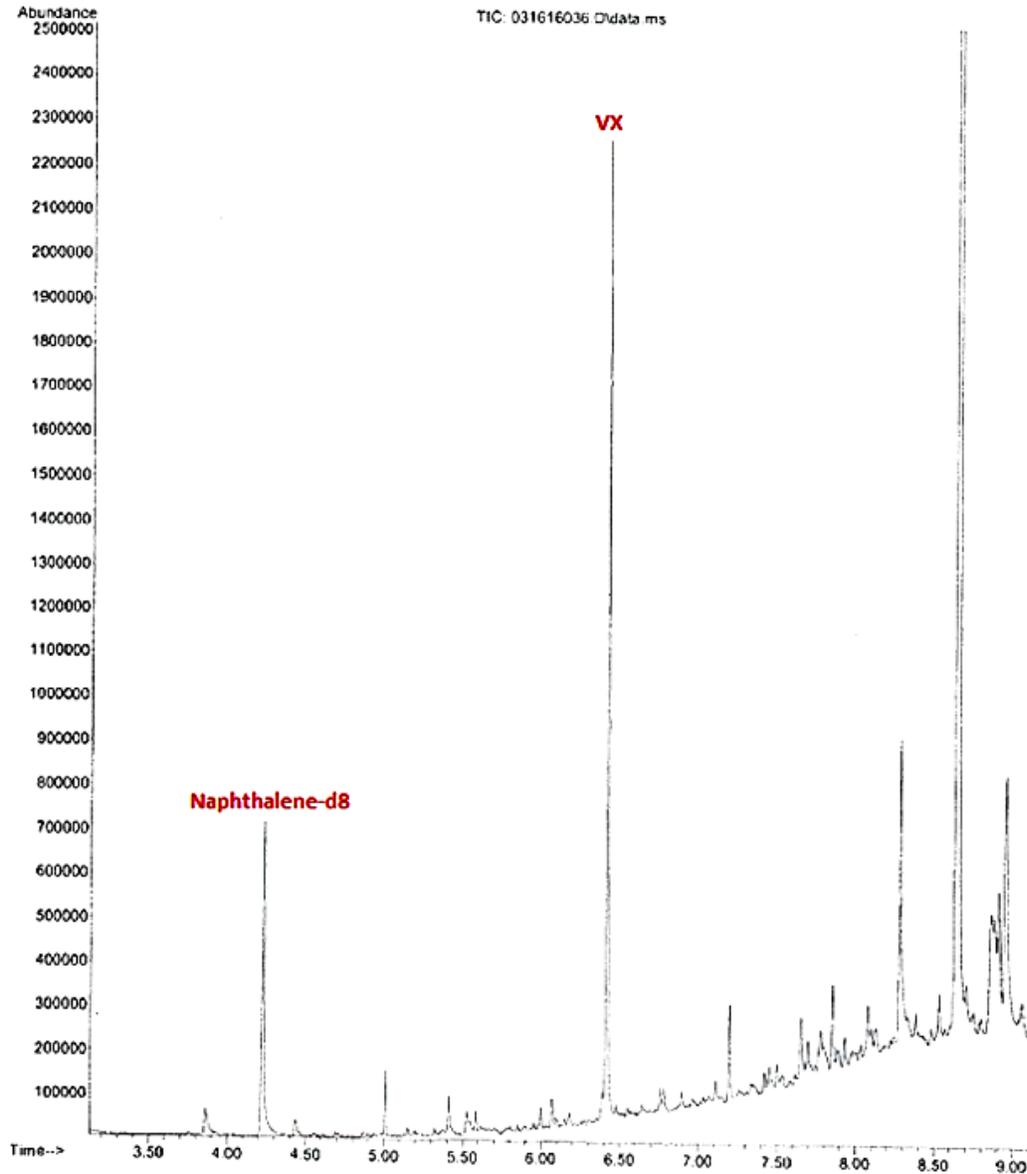
Test – EPA-VX-Attenuation-5 (25°C, 40% RH)

Sample Number – AQ37841 (rubber escalator handrail coupon #5, extracted at 28 days)

Result – 4.2 µg/mL

VX and IS peaks are identified in the chromatogram

File :C:\msdchem\1\data\EPA\16MAR16\031616036.D
Operator : AWE
Acquired : 17 Mar 2016 2:39 using AcqMethod EPA HIGH.M
Instrument : 602
Sample Name: AQ39181
Misc Info :
Vial Number: 31



Test – EPA-VX-Attenuation-5 (25°C, 40% RH)

Sample Number – AQ39181 (rubber escalator handrail coupon #5, extracted at 30 minutes)

Result – 74 µg/mL

VX and IS peaks are identified in the chromatogram

Appendix B

Relative Humidity during Environmental Conditions 1 and 2 testing

Figure B1: Relative humidity during Environmental Condition 1

Additional notes: The RH briefly (approximately 5 min) dipped to 33% RH on March 31, 2016 (as measured by the Vaisala). The RH was periodically 46% on April 6 and 7, 2016 (total time at 46% RH was approximately 60 min) as measured by the HOBO located on Shelf 2, which was associated with the 28-day samples. Only the 28-day samples were present in the chamber when the 46% RH occurred.

Figure B2: Relative humidity during Environmental Condition 2

Additional notes: None

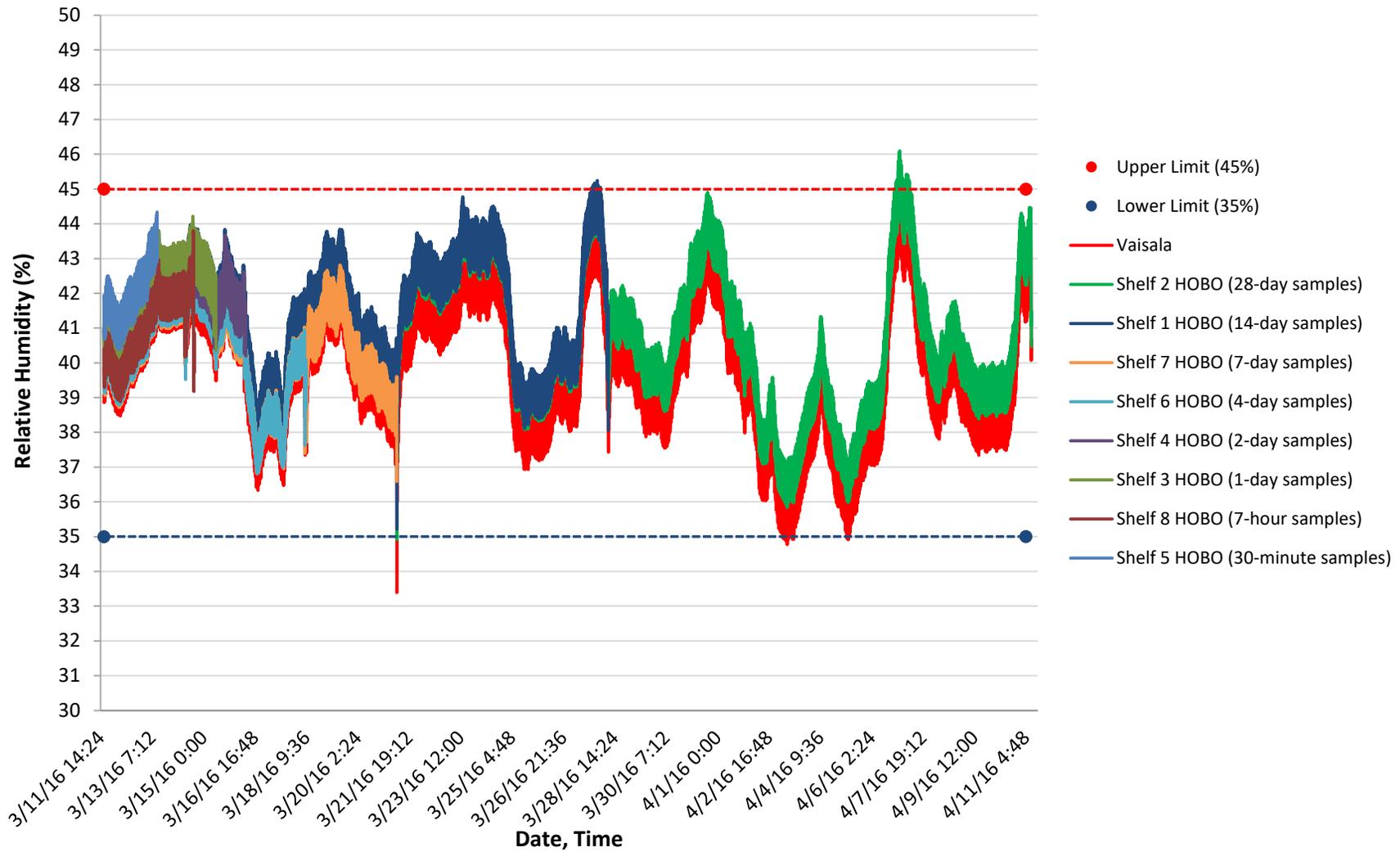


Figure B1. Relative humidity during Environmental Condition 1 testing (environmental conditioning was initiated on March 11, 2016; actual testing began on March 14, 2016 and continued until April 11, 2016).

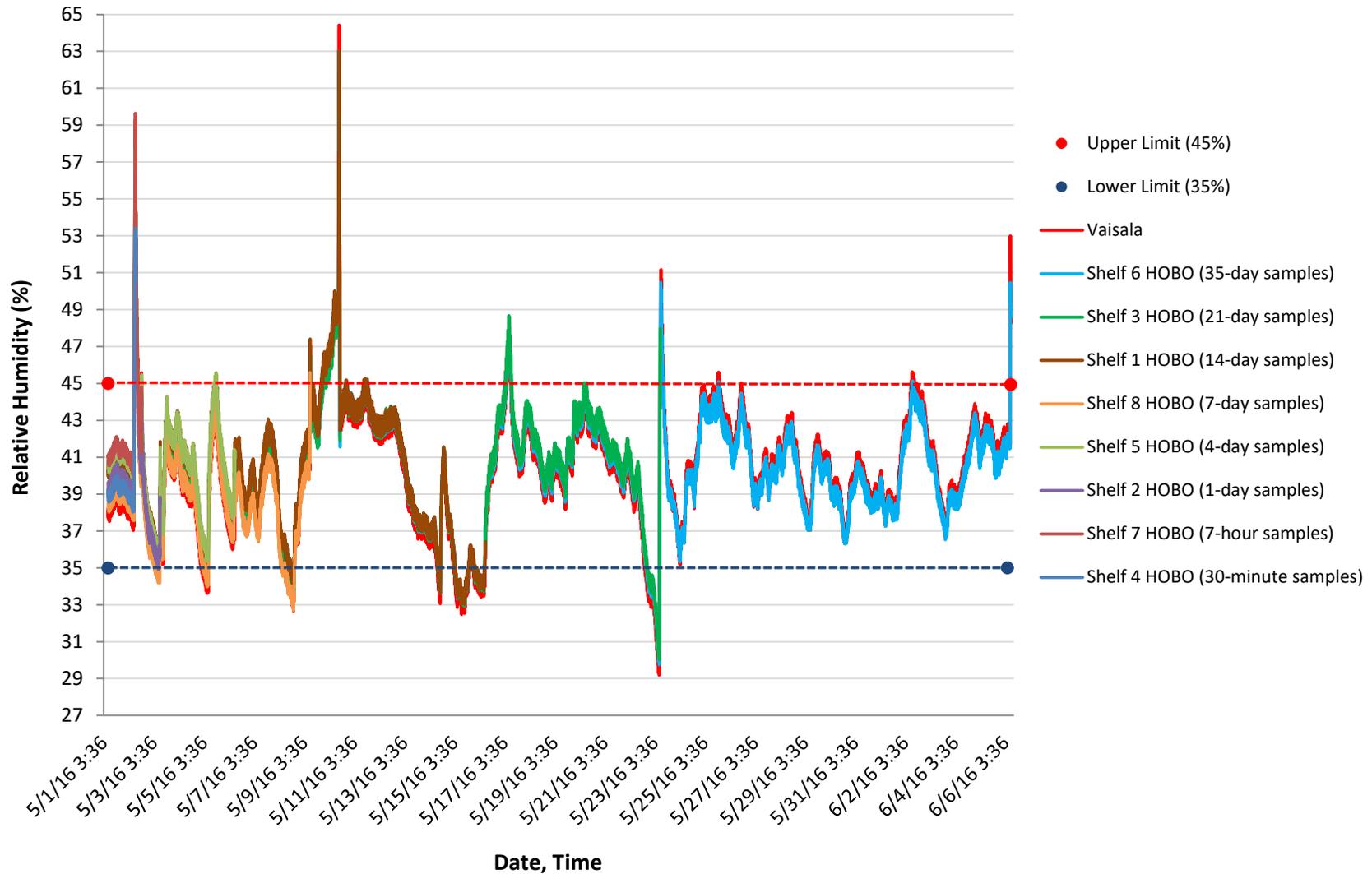


Figure B2. Relative humidity during Environmental Condition 2 testing (environmental conditioning was initiated on May 1, 2016; actual testing began on May 2, 2016 and continued until June 6, 2016).



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