Agent Fate Study Update

Presented at

The 2007 Joint Service Chemical and Biological Decontamination Conference

24 October 2007

Dr. James Savage
JSTO-CBT-TAS Thrust Area Manager for Agent Fate
410-436-2429, james.savage@us.army.mil

What is the Objective of the Agent Fate Program?

Improve model predictions of agent persistence

Objectives:

- Measure and understand the agent/substrate interactions
- Develop predictive algorithm module

Payoffs:

- Support all capability areas:
  detection, protection, decontamination
- Augments operational and mission area analysis tools
  Joint Effects Model (JEM)
  Joint Operational Effects Federation (JOEF)
- Direct feed to Low Level Toxicology DTO (CB.51)

Providing Relevant Products To The Warfighter

Improved HD Contact Hazard Persistence Estimates

Table 1-4. Chemical agent persistency in hours on chemical agent resistant coated painted surfaces.

Temperature		Agents				
C°	F°	GA/GF[1]	GB2, 3	GD2, 3	HD1	VX 2, 3
-30	-22	*	110.34	436.69	**	***
-20	-4	*	45.26	145.63	**	***
-10	14	*	20.09	54.11	**	***
0	32	*	9.44	22.07	**	***
10	50	1.42	4.70	9.78	12	1776
20	68	0.71	2.45	4.64	6.33	634
30	86	0.33	1.35	2.36	2.8	241
40	104	0.25	0.76	1.25	2	102
50	122	0.25	0.44	0.70	1	44
55	131	0.25	0.34	0.51	1	25

NOTES:
1 For grassy terrain, multiply the number in the chart by 0.4.
2 For grassy terrain, multiply the number in the chart by 1.75.
3 For sandy terrain, multiply the number in the chart by 4.5.
* Agent persistency time is more than 1.42.
** Agent is in a frozen state and will not evaporate or decay.
*** Agent persistency time exceeds 2,000 hours.

FM 3-4

Surface	GA Tabun	GB Sarin	GD Soman	GF Cyclosarin	HD Distilled Mustard	R-33 (Russian VX Isomer)	VX
Concrete	0	0	0-0.5	0*	0	0-*	0-0.1
Asphalt	0	0	0*	0*	0*	0*	0-0.9
Grass	0	0	0*	0*	0-0.2	0*	0-33
Sand	0	0	0*	0*	0*	0*	0-0.5
Sandy Loam	0	0	0*	0*	0*	0*	0-1
Bare Ground	0	0	0*	0*	0-0.1	0*	0-1
Tar and Chip	0	0	0*	0*	0*	0*	0*
AC Topcoat	0	0	0*	0*	0-0.3	0*	0-14
CARC Paint	0	0	0*	0*	0	0*	0*
Alkyd	0	0	0*	0*	0	0*	0-1
Polyurethane	0	0	0*	0*	0	0*	0*
Glass	0	0	0-3	0*	0	0*	0*
Bare Metal	0	0	0-3	0*	0-0.8	0*	0*
Wood	0	0	0*	0*	0*	0*	0-1
Snow	0	0	0*	0*	0*	0*	0
Ice	0	0	0*	0*	0*	0*	0*

AFMAN 10-2602

(Preliminary - HD on Sand)
Based on Agent Fate DTO Data

Temp (°C)	2-m Height Windspeed (m/s) 0.5	3.0	6.0
15	>17	>17	>17
35	6	4	4
50	3	2	<1

(HD on Impermeable Surface)
Based on Agent Fate DTO Data

Temp (°C)	2-m Height Windspeed (m/s) 0.5	3.0	6.0
15	24	7	6
35	4	1	1
50	1	0.5	0.5

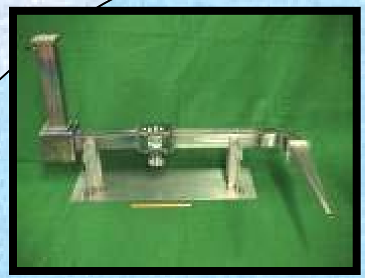
Environmental Fate of Chemical Agents

Purpose & Goal – To enhance predictive tools with high-fidelity data, quantifying the fate of chemical agents within operationally significant climates and surfaces.

Wind Tunnel Testing

Measures evaporation of agent from surface at realistic climactic conditions. Main data input stream for predictive models

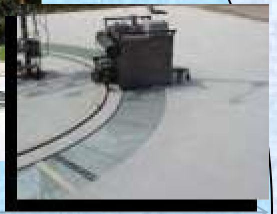
Uses combinations of vapor sampling & gravimetric analysis



Outdoor Testing

Validates model developed with wind tunnels data

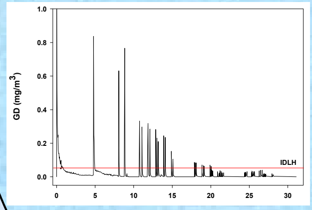
Provides "ground truth" of behavior in environment

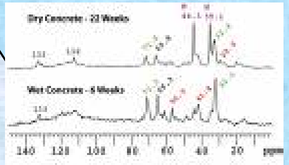


Agent/Substrate Interactions

Agent/Substrate interactions are critical component to determinations of fate.

Studies use highest fidelity methods including NMR, SPME, vapor resurgence, extractions quantitative imaging and fundamental property measurements





Modeling

Improves hazard prediction tool accuracy

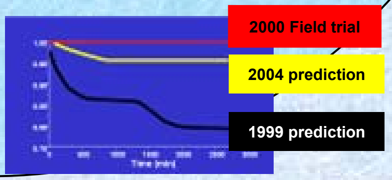
Transitions information to warfighter in a usable format

JEM

FM 3-4 Liquid	FM 3-4 Vapor
Not Avail	7 - 20+
Not Avail	20+
Not Avail	18 - 20+

FM 3-9 Liquid	FM 3-9 Vapor
Not Avail	5 - 48
Not Avail	6 - 168
Not Avail	1800 -3600

VX

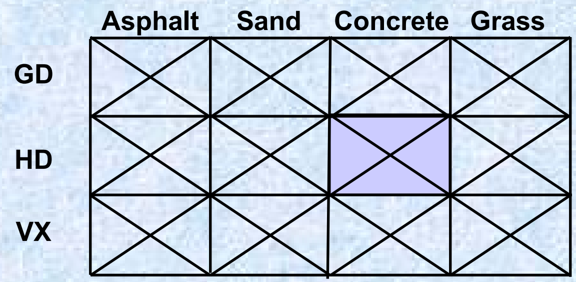


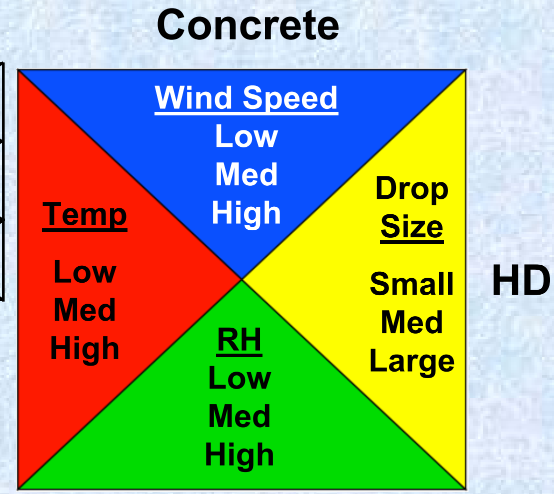
International Partners: CZ, POL, NLD, UK, and SGP

Design of Experiments Minimizes the Number of Experiments

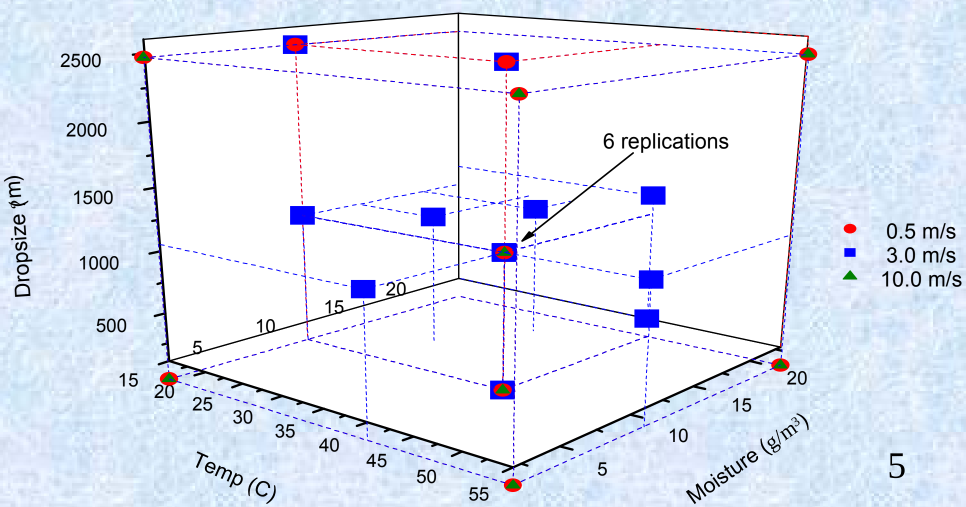
- About 10,000 experiments for full factorial approach – infeasible!
- Now, about 1500 experiments with CCD approach
    - 24 agent/substrate combinations
    - 3 levels for each parameter (temp., drop size, wind speed, humidity)

- Created central composite design (CCD) experimental test matrix
- Developed surface evaporation assessment tool
- Incorporated 26,115 new data elements into evaporation database



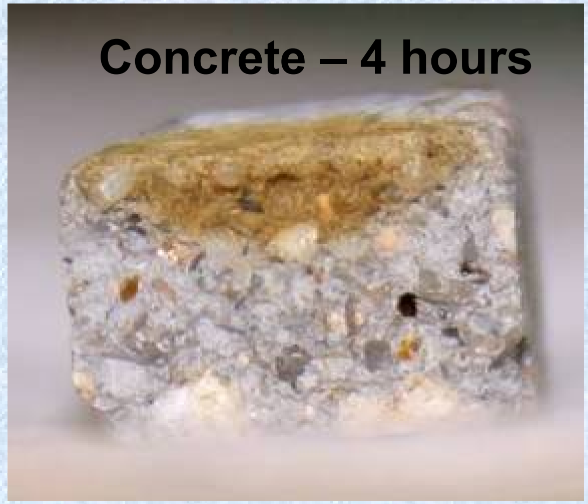


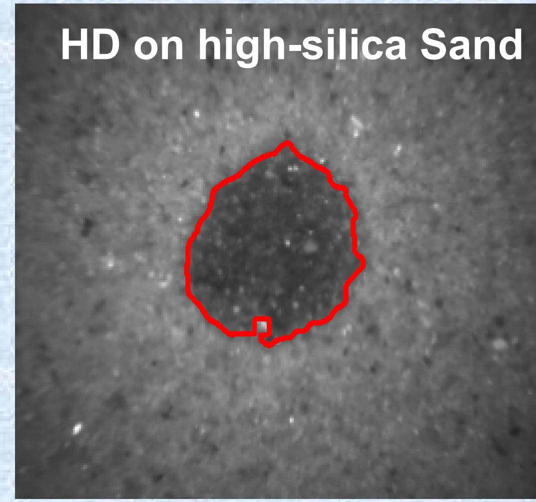
HD on Concrete CCD Experiments

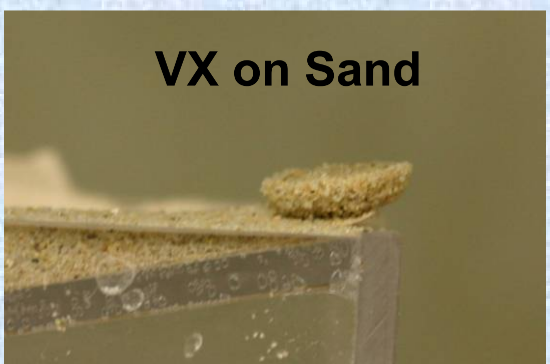


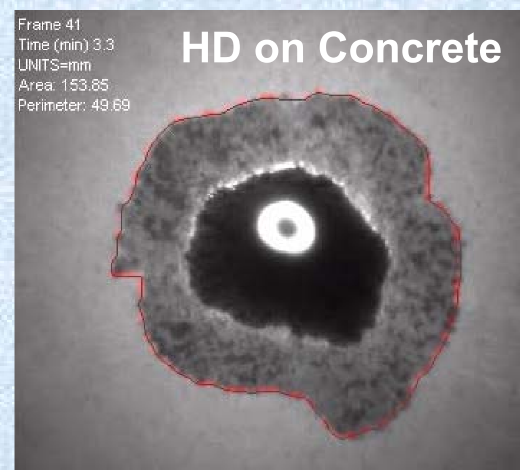
Imaging Systems Display Agent / Substrate Interactions

Imaging techniques quantify agent penetration into porous media





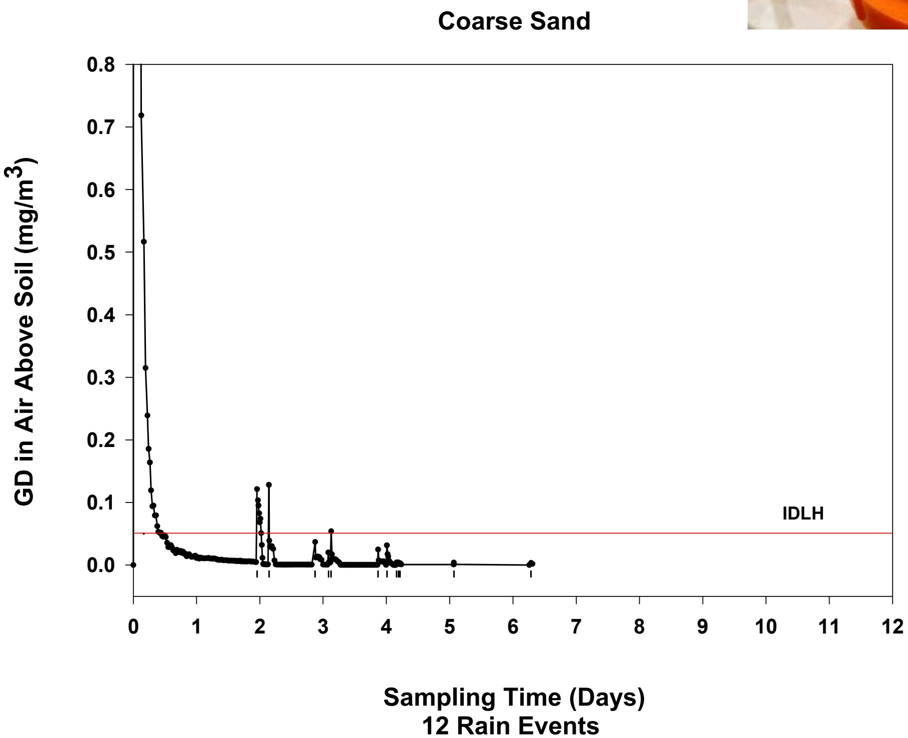


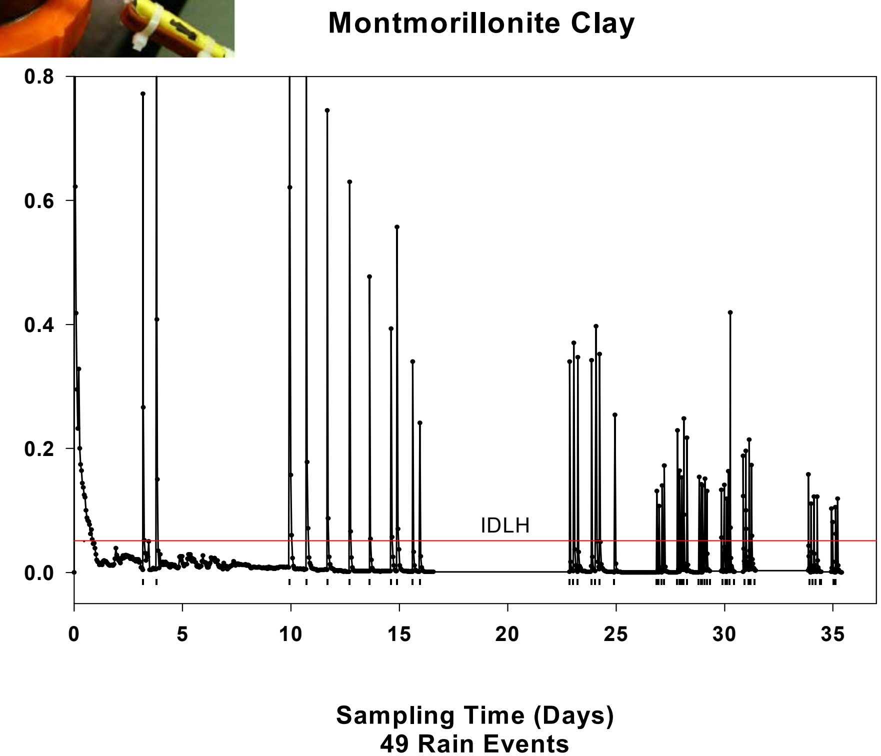


Displacement of GD by Rainfall: Sand vs. Montmorillonite Clay

0.8 – 1.2 mm

<0.002 mm





- Substantially greater GD Displacement-Peaks from Clay than Sand
- Substantially greater Total amount of GD displaced (~30x) from Clay than Sand
- Clay soil material retained displaceable-GD appreciably longer than Sand

NMR Results: Degradation of HD

• Limestone:	No reaction in 19 months
• Asphalt:	No reaction in 13 months
• Sand:	No reaction in 12 months
• Mortars:	Half-lives of weeks to years.
• Concrete:	Half-lives of weeks to years.

The initial degradation products on concrete were toxic sulfonium ions. These degraded to non-toxic products over a period of months to years.

Decomposition was faster on wet substrates

Interaction of VX with the Components of Concrete

Purpose:

To Determine which of the Components of Concrete is Primarily Responsible for the Hydrolytic Decomposition of VX

Conclusions:

- The active component is the Mortar, Portland Cement
- The active chemical component is Calcium Oxide
- Calcium Carbonate is ineffective in decomposing VX
- Surface Calcium Oxide is converted to Calcium Carbonate during aging

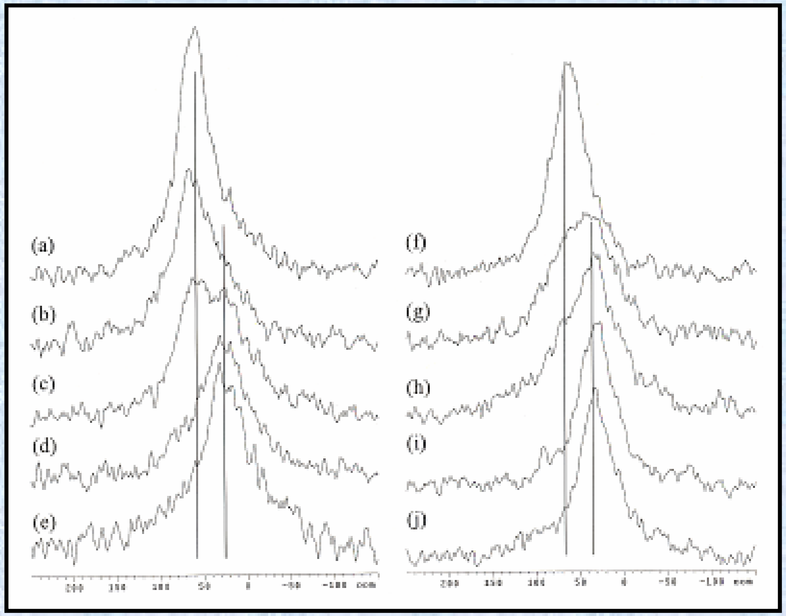
$$CaO + CO_2 = CaCO_3$$

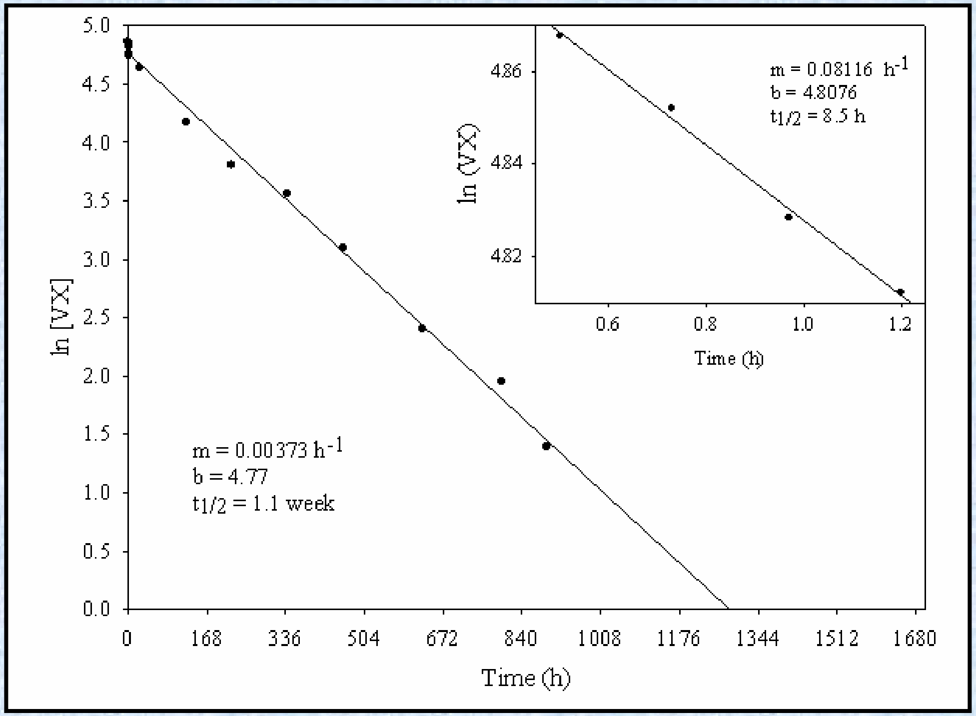
Summary:

- The experiments identify the important concrete ingredient in the decomposition of VX to be the Calcium Oxide in the Portland Cement
- Concrete is an example of a porous, reactive substrate of interest
- Further experiments continue to aid in our understanding of secondary vaporization

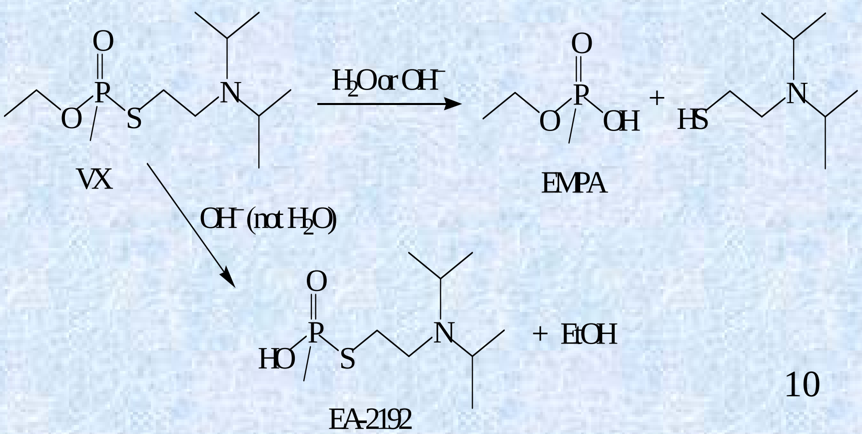
	New	Old
pH	12	8
VX	reacts faster	reacts slower
Mustard	reacts faster	reacts slower
Mustard	forms vinyl	no vinyl
Ca Species	oxide	carbonate

VX on Concrete Monoliths

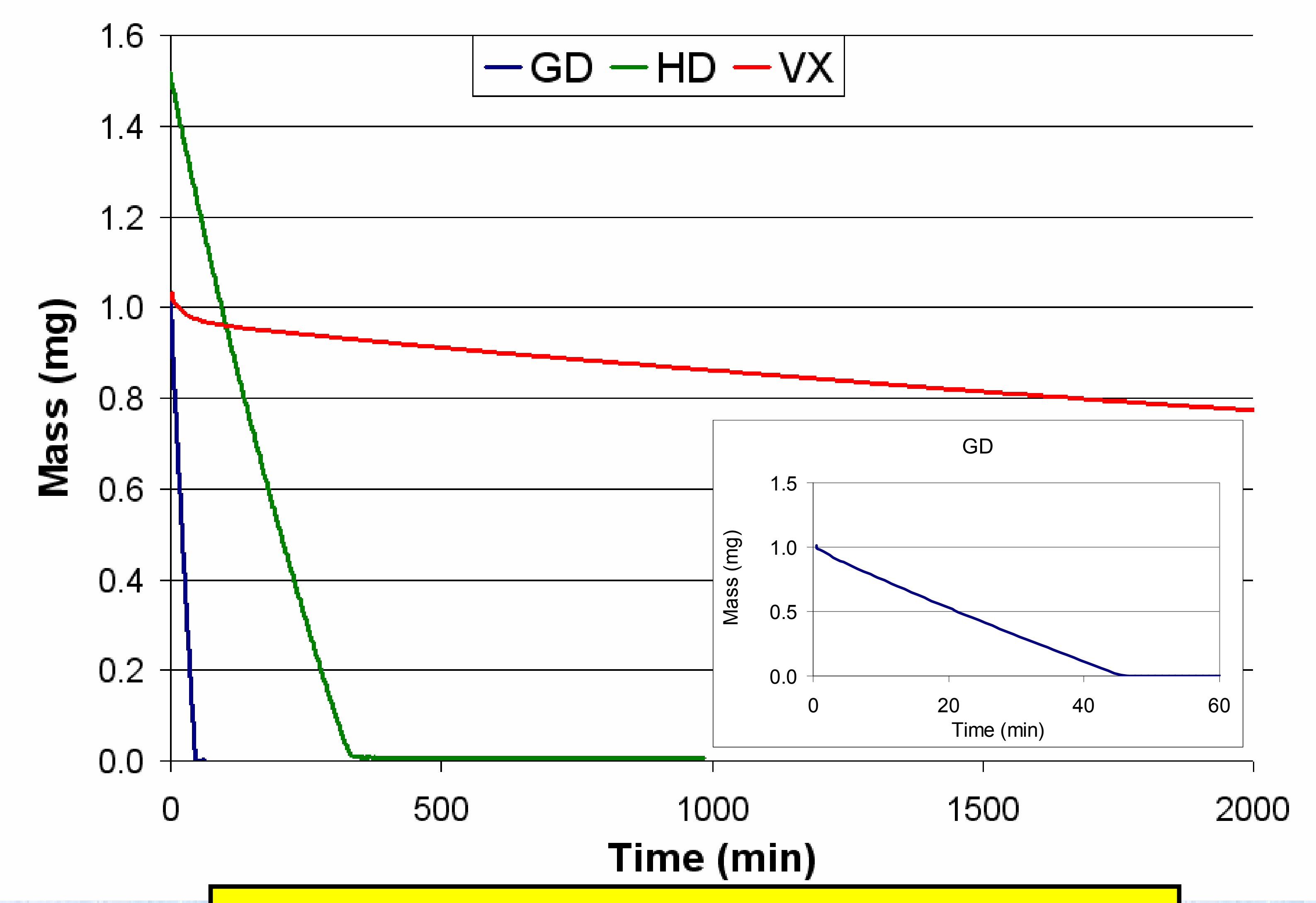




- Initial reaction in the first monolayer of VX, followed by a slower, secondary reaction
- If the VX is diluted in hexane it reacts faster
- Smaller droplets react faster
- VX degrades faster on more basic (newer) concrete

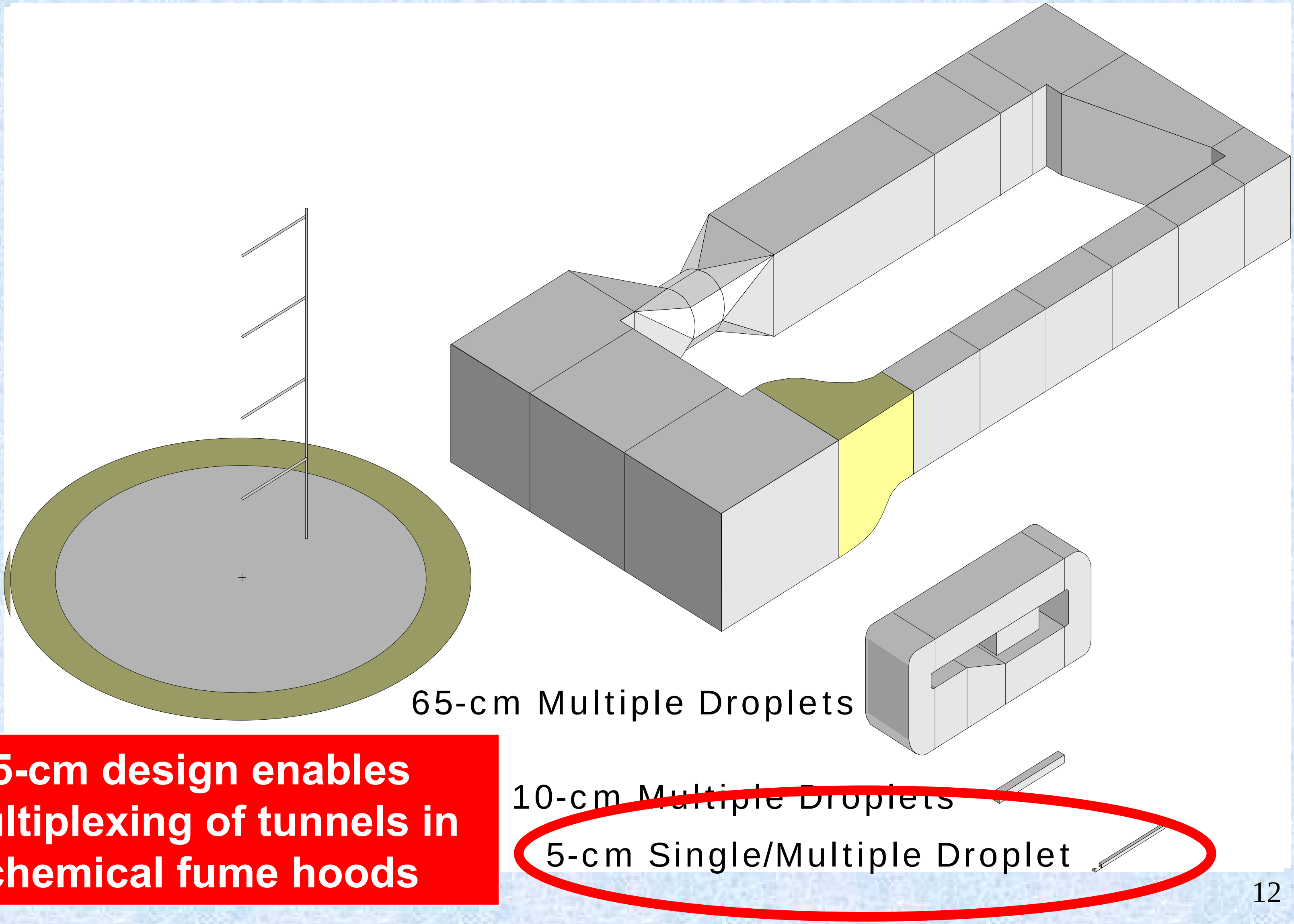


TGA Evaporation Experiments



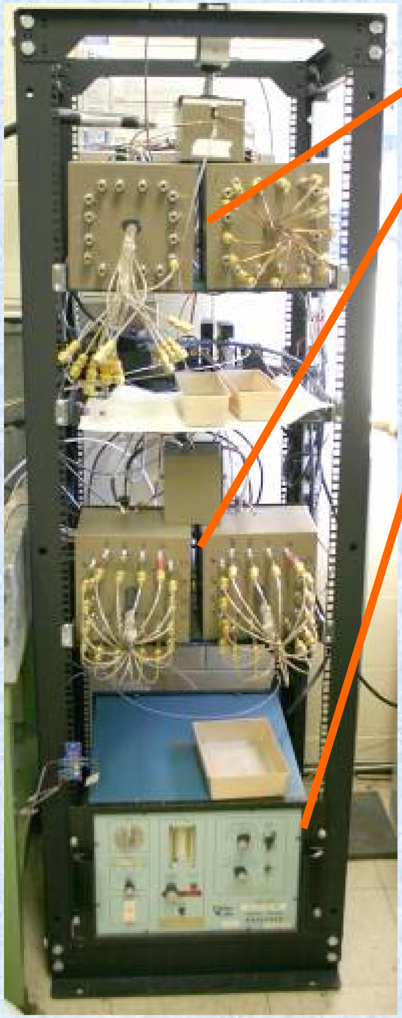
(1 µL) on TEFLON @ 30°C, 0% RH, 0.04 m/s

Range of Wind Tunnel Sizes Used in Agent Fate



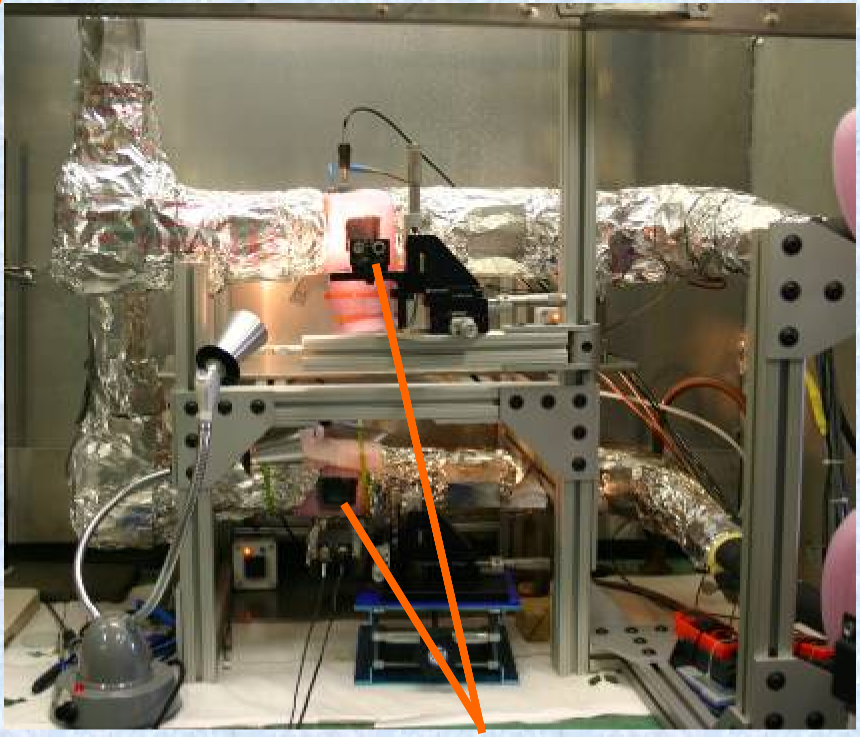
5-cm design enables multiplexing of tunnels in chemical fume hoods

5 x 5-cm Wind Tunnel Operational Arrangement



Variable Tube Sampler (VTS) x2

HYFED

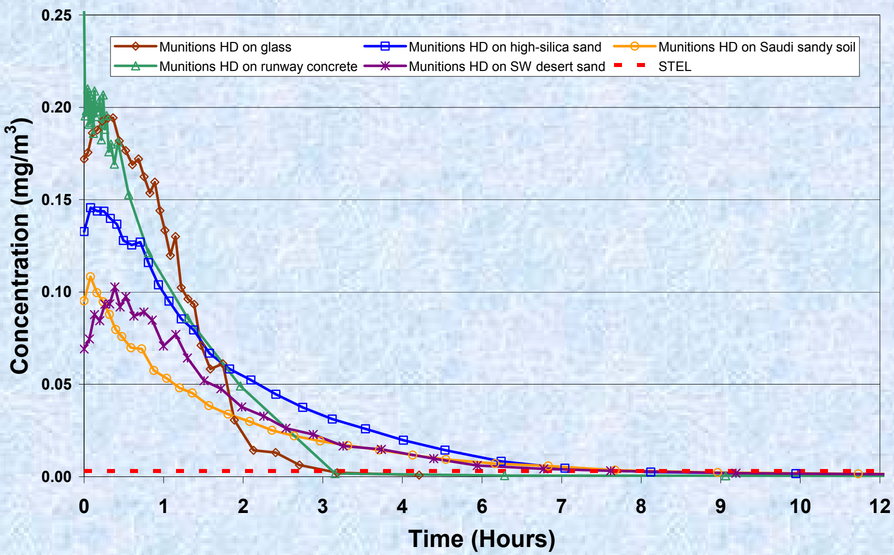


Control System Computer

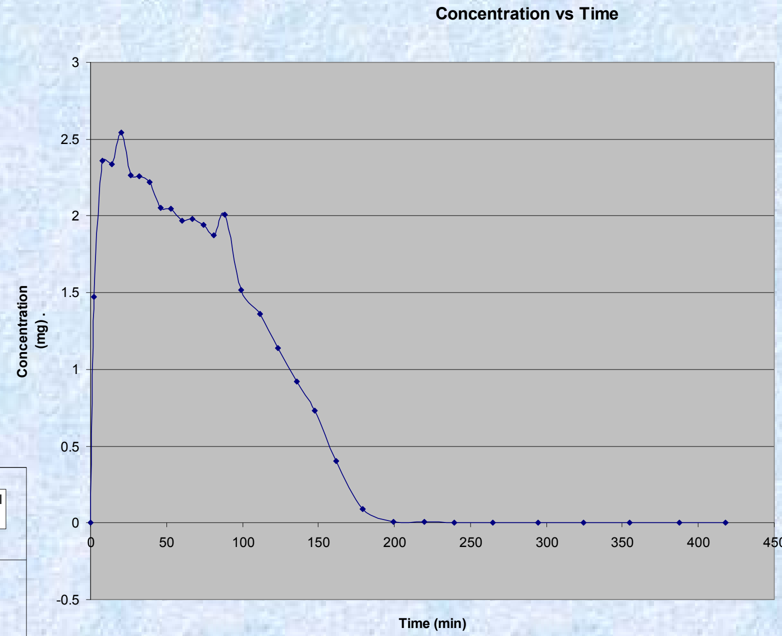
Agent/Substrate Sample

ECBC Lab Wind Tunnel Results

Comparison of Mustard on Different Substrates



6 µL Drop Size, 35 °C, 3 m/s Wind Speed at 2 m, ~0% Relative Humidity



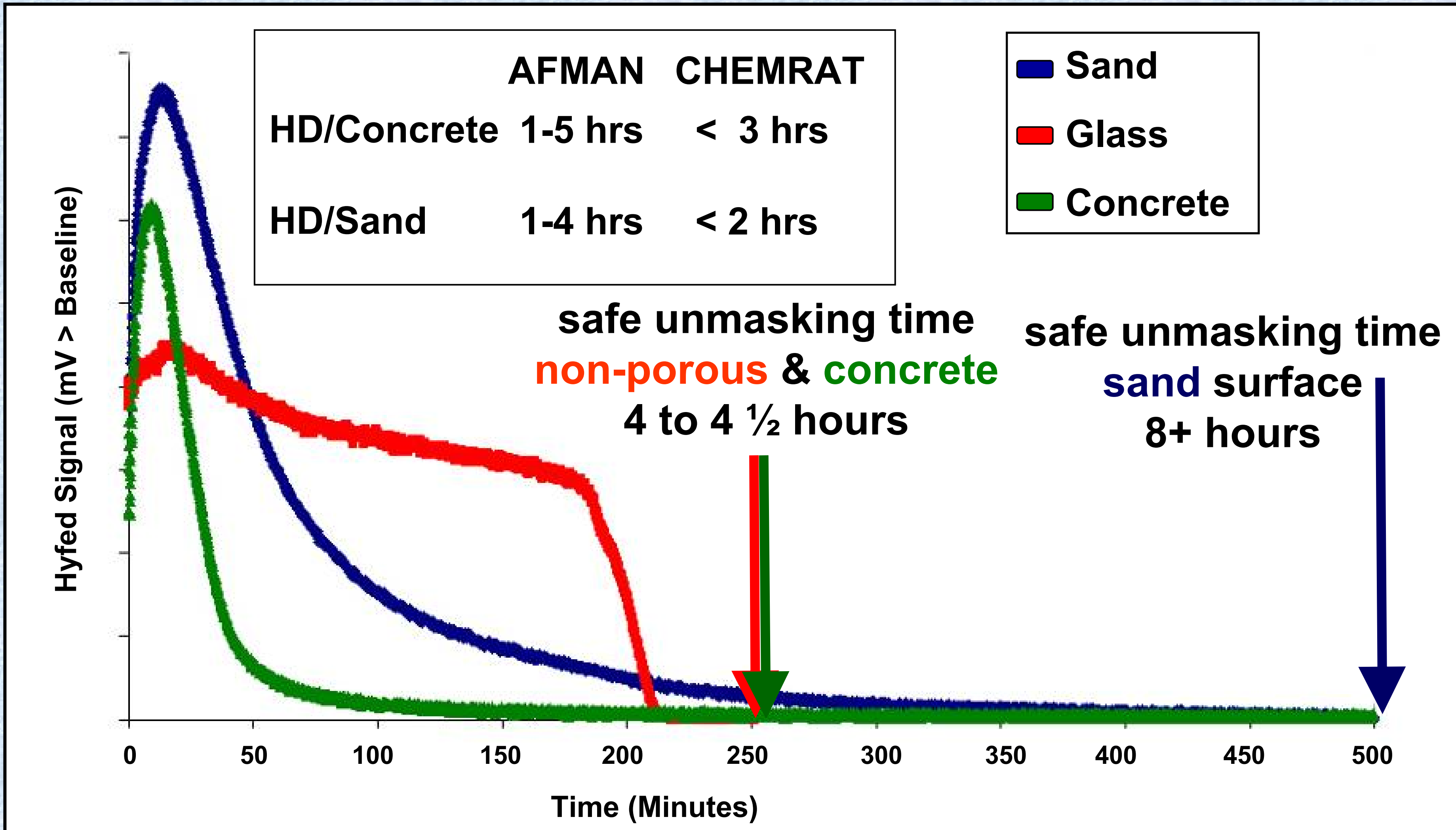
15C
9uL
1/2 m/s
50% RH

CUBRC
38 GD on SS
7 HD on Glass

GD on Stainless Steel

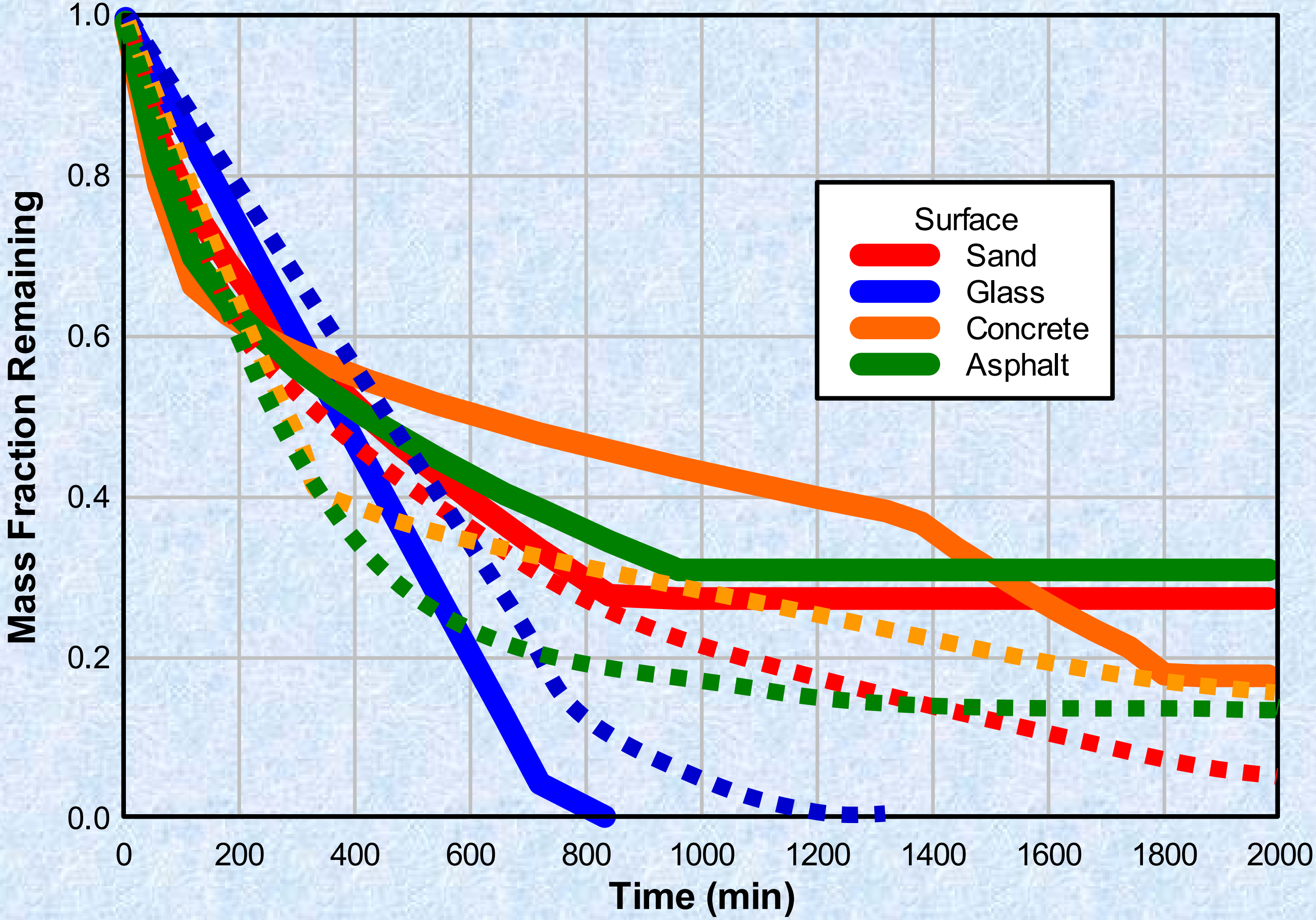
Preliminary Persistence Estimates HD on Concrete / Sand Vapor Hazard

Preliminary comparisons of evaporation from operationally relevant substrates



	AFMAN	CHEMRAT
HD/Concrete	1-5 hrs	< 3 hrs
HD/Sand	1-4 hrs	< 2 hrs

Comparison of HD Evaporation Model Predictions To Experimental Data

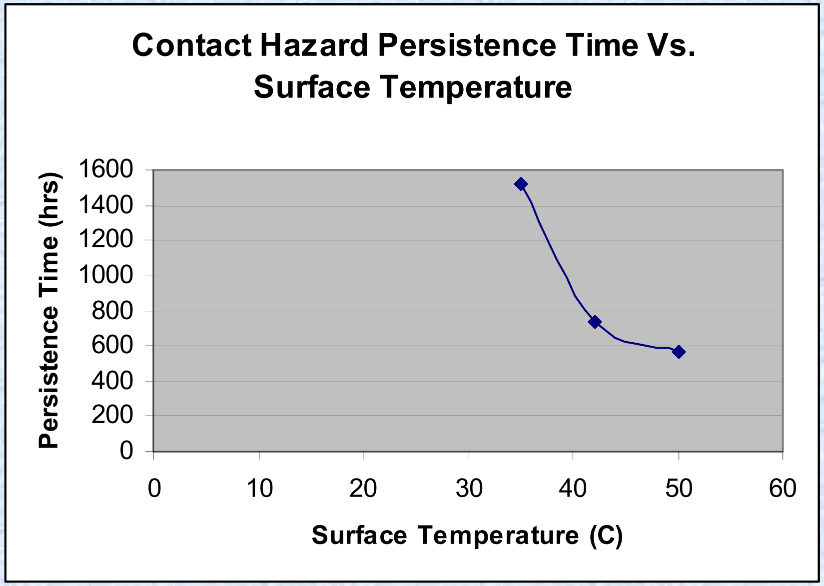


Agent Fate Product

As of Sept 2007

- 364 datasheets
- Agents
  - HD, GD, VX
- Substrates
  - Asphalt
  - Concrete
  - Glass
  - UK Sand
  - Stainless Steel

VX Contact Hazard Estimates



Ungloved, 2-Hand Touch Percutaneous Liquid Contact Hazard (Severe ED_{50} Effects)

Based on VX data on an Impermeable Surface from Agent Fate DTO

Surface Temperature (°C)	Full Transfer	Partial Transfer*
35	2770	1520
42	1470	740
50	990	570

Time (min)

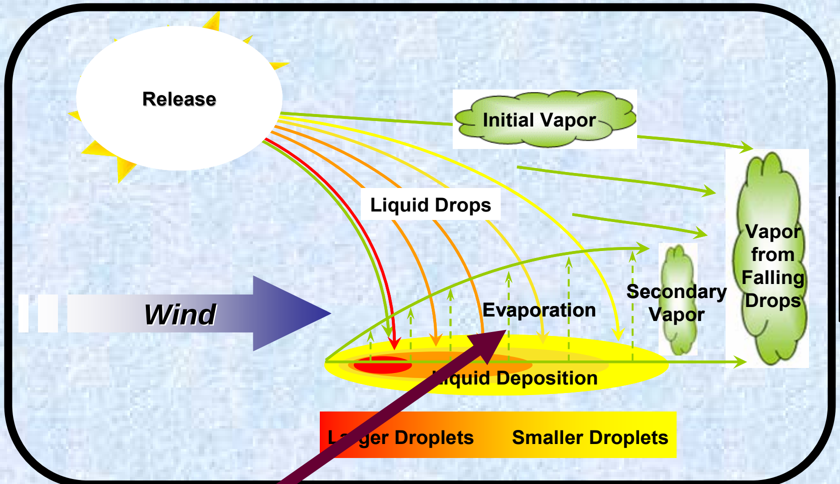
* Partial Transfer = 50% transfer from surface to hand, 25% transfer through skin

1 g/m^2 deposition
90% agent purity (900 mg/m^2 agent deposition)
Mono-dispersed 6-uL drops (~ 2.3mm spherical drop diameter)

From Data to Operational Utility

ATTACK INPUTS

Threat Environment



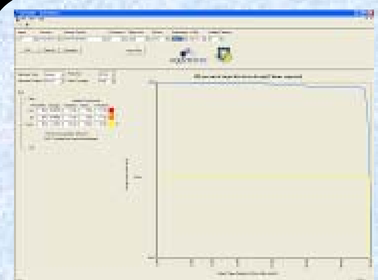
CWA CHALLENGE

Concentration
Dosage
Residual liquid

Agent Fate Data → Agent Fate Models

Hazard Prediction Model (e.g., JEM)

Low Level Tox



Agent Toxicity
Exposure Duration
Protection
Route of Entry
Risk
Physical Exertion Effects
CONOPS & TTPs

Operational Effects Model (e.g., JOEF, CHEMRAT)

Hazard Persistence
Operational MOE

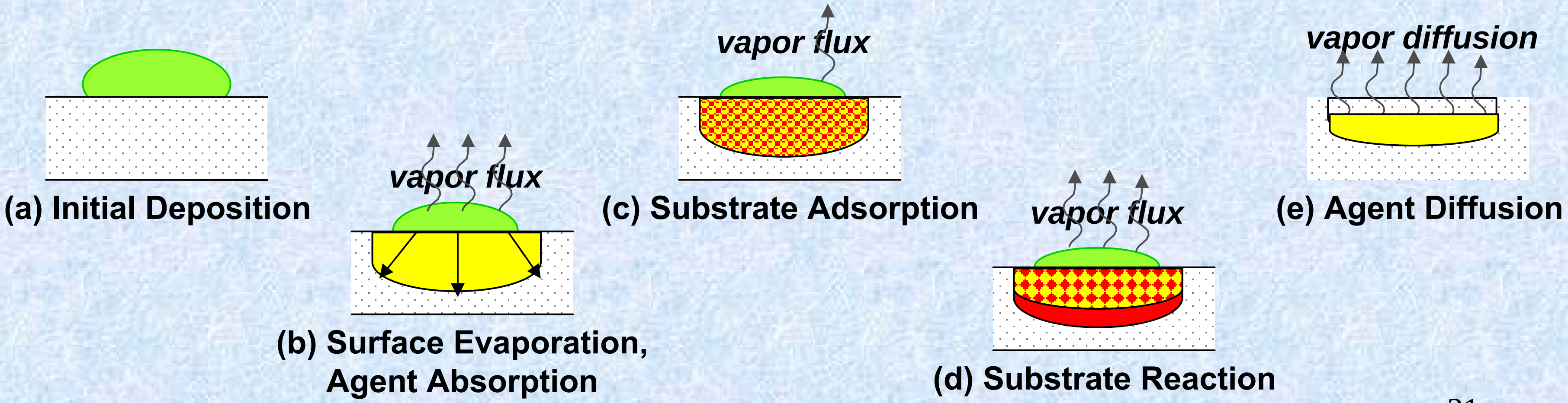
CONOPS
TTPs
Guidance
Acq Rqmts
Studies & Analyses

Summary

- Environmental Fate of Chemical Agents DTO CB.42 successfully completed in 2006 ECBC-TR-532
- CWA evaporation and reaction kinetics data delivered to modelers to improve hazard prediction estimates
  - Updated AFMAN 10-2602; TTP's; VLSTRACK; CHEMRAT
- Data being processed to deliver secondary evaporation model to JEM 3rd quarter FY08 under TTA IS12
- Future work: Thickened Agents on operational substrates

What is the source term?

- The *source term* is defined as follows:
  - (a) amount of agent deposited on the surface
  - \- (b) amount of agent evaporated
  - \- (c) amount of agent that 'irreversibly' binds to substrate
  - \- (d) amount of agent that reacts with the substrate
  - \+ (e) amount of agent that diffuses back to the surface

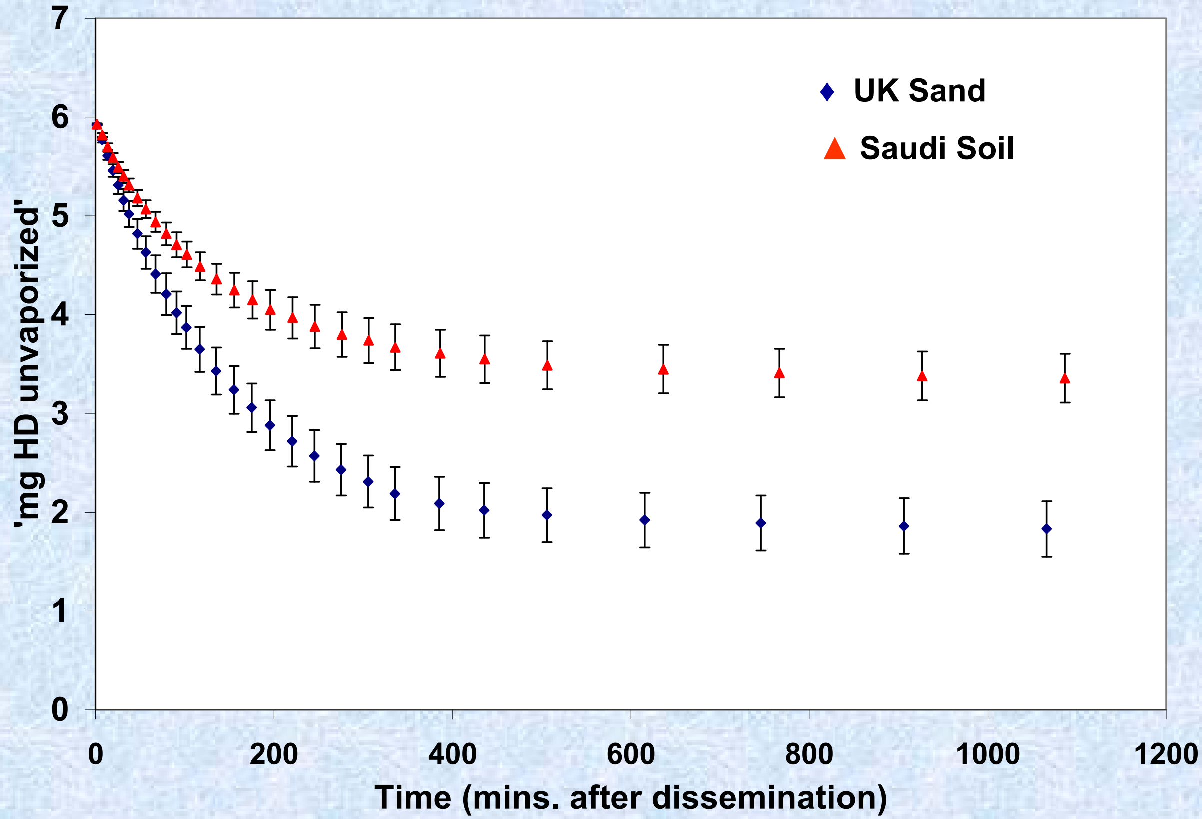


Need to Determine Scope of Agent/ Substrate Interactions

Royal Saudi Air Base

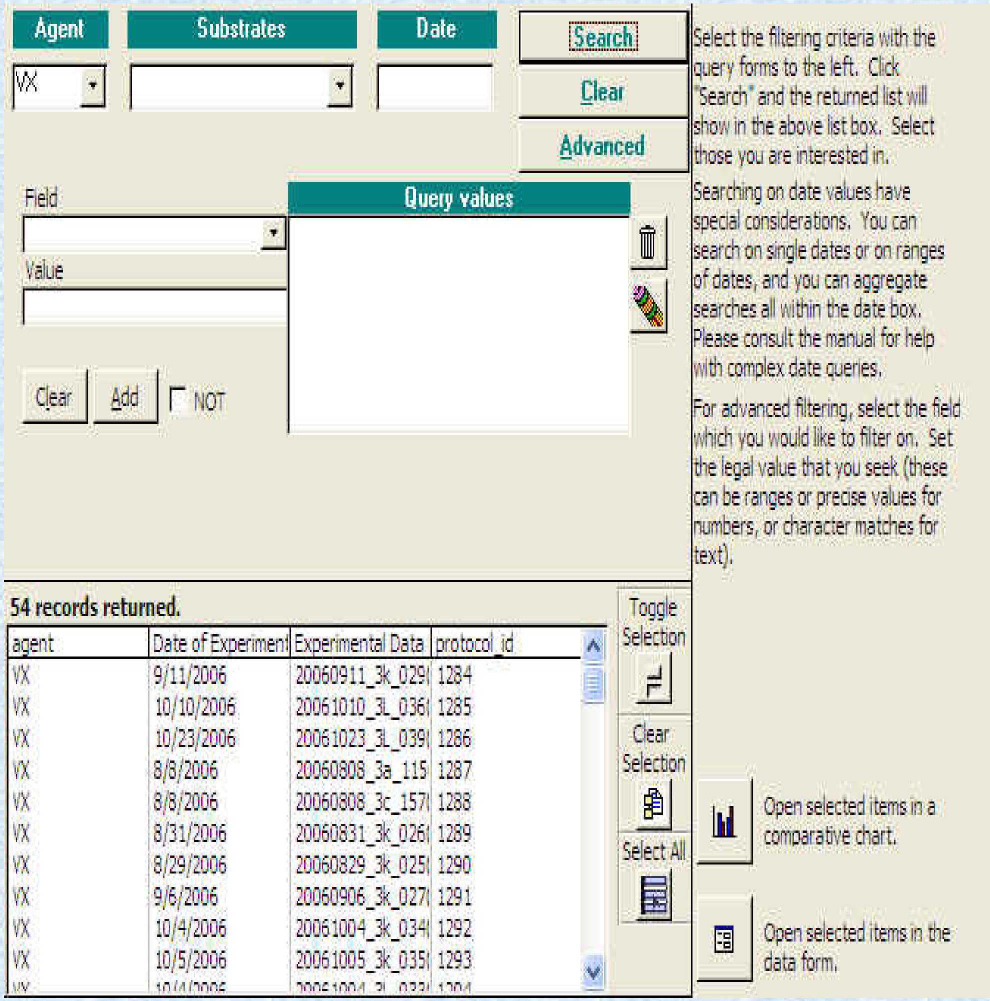
Dhahran

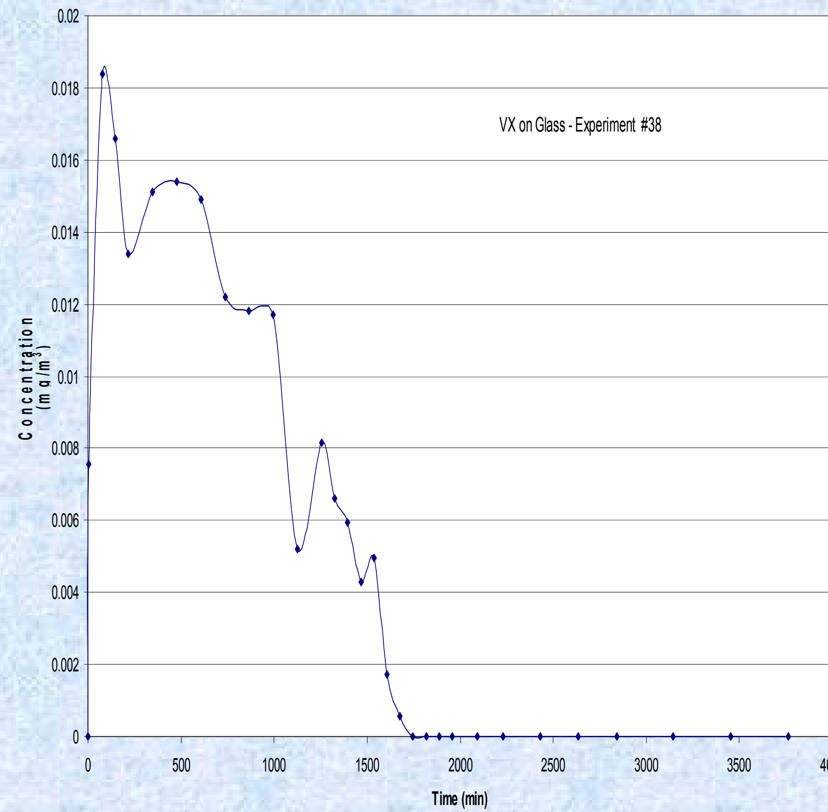
Torrispsamments Plain soil type represents 3 different sites



T (°C)	WS m/s	DS µL	RH%
35	1.5	6	0

Agent Fate Database





Agent Fate Database

Data Sheet Droplet Evaporation in ECBC Wind Tunnel

Tunnel:	3K			
Date:	October 16, 2006			
Experiment Number:	38			
File Name:	20061016_3k_038			
Substrate				
type of substrate :	Glass			
substrate sample size (mm):	36.6	0.00105 m^2		
Agent				
test agent:	VX_CASARM			
agent grade::	CASARM			
agent purity:	91.0%	Date/Chem:	KS	12/21/2006
actual density:	1.01	mg/uL		
Contamination				
number of drops:	1			
nominal drop volume:	6	µL		
actual calculated drop volume:	6.000	µL		
weight of clean substrate:	0.000	mg		
weight of contaminated substrate:	0.000	mg		
mass of agent disseminated:	6.060	mg		
corrected mass on 100% agent purity:	5.515	mg		
actual contamination density:	5.76	g/m^2		
actual contamination density based on 100% agent purity:	5.24	g/m^2		
Control Parameters				
Miller Nelson temperature:	0.0	°C	0.0	
air flow temperature:	41.7	°C	0.3	
Aalborg Flowmeter air flow rate:	181.64	SLPM	1.1	
transition section wall temperature:	41.9	°C	0.4	
fetch section wall temperature:	42.3	°C	0.6	
substrate temperature:	42.0	°C	0.4	
piston zone temperature:	42.7	°C	0.5	
post-test section wall temperature:	45.1	°C	0.3	
mixing box wall temperature:	50.1	°C	0.4	
sampling duct wall temperature:	50.0	°C	0.1	
test section air flow speed:	1.64	m/s	0.0	
air flow relative humidity:	0.00	%	0.0	
Sampling Parameters				
sampling technique:	VTS#06			
introduction technique:	UNITY/ULTRA			
analysis technique:	GCMSD			

Master | **Protocol Sheet** | Vapor | TGA | VX | Conditions | Temps | TubeData | DATA | Tracking | Report

Summary Data Sheet - Wind Tunnel Experiment

Test Facility:	**ECBC**
Date of Experiment (mm/dd/yy):	**10/16/06**
Wind Tunnel Descriptor:	**3K**
Original Data File Name:	**20061016_3k_038(0 0 0_a_2)VX_G**

Substrate	**Glass**	
substrate code:	G001	
Agent	**VX**	
agent type (neat/thickened):	CASARM	
agent purity - weight %:	91.00%	
*density of pure agent - mg/µL:	1.01	
nominal density of test agent - mg/µL:	nd	
targeted drop volume - µL:	6.00	
actual drop volume - µL:	nd	
targeted drop mass - mg:	6.060	
actual drop mass - mg:	nd	
number of drops disseminated:	1	
total mass disseminated - mg:	6.060	
total mass of agent disseminated (corrected for purity) - mg:	5.515	

Experimental Variables	**Targeted**	**Actual (Avg/StdDev)**	
air flow temperature - °C:	35	41.7	0.323
substrate temperature - °C:	35	42.0	0.354
air flow relative humidity - %:	0	0.00	0.000
air flow speed above drop - m/s:	1.77	1.64	0.013
air flow speed measurement height - cm:	1		
enter theoretical air flow speed at 2 m height - m/s:	3.250	3.033	

Evaporation Measurement Technique	**Vapor Collection**
reference code for experimental method:	ECBC X-SOP v.06
Vapor Collection Data	
total mass of agent vapor collected - mg:	3.233
Gravimetric Data (not provided by ECBC)	
initial weight of uncontaminated test substrate - g:	nd
weight of contaminated test substrate - g:	nd
initial mass of agent deposited on test substrate - mg:	nd
initial weight of uncontaminated test substrate - g:	nd
weight of test substrate after evaporation - g:	nd
residual mass of agent in test substrate after evaporation - mg:	0.000

Evaporation Data

Data Point	*Elapsed Time	GC Tube Conc.	Vapor Collected
#	min	mg/m3	mg
0	0.00	0.0000	0.0000
1	5.82	0.0075	0.0040
2	75.87	0.0184	0.1689
3	145.92	0.0166	0.3914
4	215.97	0.0134	0.5824
5	346.02	0.0151	0.9196
6	476.07	0.0154	1.2797
7	606.10	0.0149	1.6370
8	736.15	0.0122	1.9567
9	866.20	0.0118	2.2399
10	996.25	0.0117	2.5175
11	1126.30	0.0052	2.7172
12	1256.35	0.0081	2.8748
13	1326.40	0.0066	2.9686
14	1396.45	0.0060	3.0484
15	1466.50	0.0043	3.1136
16	1536.55	0.0050	3.1726
17	1606.60	0.0017	3.2151
18	1676.65	0.0006	3.2296
19	1746.70	0.0000	3.2332
20	1816.75	0.0000	3.2332
21	1886.80	0.0000	3.2332
22	1956.85	0.0000	3.2332
23	2091.90	0.0000	3.2332
24	2231.95	0.0000	3.2332
25	2428.67	0.0000	3.2332
26	2635.38	0.0000	3.2332
27	2842.10	0.0000	3.2332
28	3142.15	0.0000	3.2332
29	3452.20	0.0000	3.2332