EPA United States Environmental Protection Agency

A Literature Review of Wipe Sampling Methods for Chemical Warfare Agents and Toxic Industrial Chemicals

RESEARCH AND DEVELOPMENT

EPA/600/R-07/004
January 2007
www.epa.gov

A Literature Review of Wipe Sampling Methods for Chemical Warfare Agents and Toxic Industrial Chemicals

Contract No. GS23F0011L-3
Task Order No. 1125

Prepared for

Stephen Billets
U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Las Vegas, NV 89119

Prepared by

Battelle
Columbus, OH 43201

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

092cmb07

Notice

This document was prepared for the U.S. Environmental Protection Agency (EPA) under Contract No. GS23F0011L-3, Task Order No. 1125. The document has met the EPA's requirements for peer and administrative review and has been approved for publication. Mention of corporation names, trade names, or commercial products does not constitute endorsement or recommendation for use.

Abstract

Wipe sampling is an important technique for the estimation of contaminant deposition in buildings, homes, or outdoor surfaces as a source of possible human exposure. Numerous methods of wipe sampling exist, and each method has its own specification for the type of wipe, wetting solvent, and determinative step to be used, depending upon the contaminant of concern. The objective of this report is to concisely summarize the findings of a literature review that was conducted to identify the state-of-the-art wipe sampling techniques for a target list of compounds. This report describes the methods used to perform the literature review; a brief review of wipe sampling techniques in general; an analysis of physical and chemical properties of each target analyte; an analysis of wipe sampling techniques for the target analyte list; and a summary of the wipe sampling techniques for the target analyte list, including existing data gaps.

In general, no overwhelming consensus can be drawn from the current literature on how to collect a wipe sample for the chemical warfare agents, organophosphate pesticides, and other toxic industrial chemicals of interest to this study. Different methods, media, and wetting solvents have been recommended and used by various groups and different studies. For many of the compounds of interest, no specific wipe sampling methodology has been established for their collection. Before a wipe sampling method (or methods) can be established for the compounds discussed in this report, two steps must be taken: (1) conduct investigative research to fill in the gaps in wipe sampling knowledge, and (2) conduct method validation to optimize the methods.

Table of Contents

List of Tables

Abbreviations, Acronyms, and Symbols

ASTM	American Society for Testing and Materials
CBIAC	Chemical and Biological Defense Information Analysis Center
CHEERS	Children's Environmental Exposure Research Study
cm	centimeter
cm^2	square centimeter
cm/s	centimeter per second
CTEPP	Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants
CWA	chemical warfare agent
DCM	dichloromethane
EPA	U.S. Environmental Protection Agency
FPD	flame photometric detector
ft^2	square foot
GC	gas chromatography
HPLC	high-performance liquid chromatography
HVS3	High Volume Small Surface Sampler
IPA	isopropyl alcohol
LC	liquid chromatography
m^2	square meter
mL	milliliter
mm	millimeter
MS	mass spectrometry
MSDS	material safety data sheet
NERL	National Exposure Research Laboratory
NHEXAS	National Human Exposure Assessment Survey
NHSRC	National Homeland Security Research Center
NIOSH	National Institute for Occupational Safety and Heath
OP	organophosphate pesticide
OPCW	Organisation for the Prohibition of Chemical Weapons
OSHA	Occupational Safety and Health Agency
PBDE	polybrominated diphenyl ether
PBS	phosphate buffered saline
PBT	phosphate buffer with Tween
PCB	polychlorinated biphenyl
PCP	phencyclidine
PUF	polyurethane foam
SSP	swab sample processing
TEPP	tetraethyl pyrophosphate
TIC	toxic industrial chemical
TSA	Transportation Security Administration
USDA	U.S. Department of Agriculture

Acknowledgements

This report was prepared for the U.S. Environmental Protection Agency (EPA) under the direction and coordination of Stephen Billets of the EPA's National Exposure Research Laboratory (NERL), Environmental Sciences Division, in Las Vegas, Nevada. EPA NERL acknowledges funding support for this project from EPA's National Homeland Security Research Center (NHSRC), and specifically Oba Vincent and Rob Rothman for their contributions. The EPA NERL thanks the following peer reviewers for their review of this report: Brian Schumacher (EPA NERL); Eric Koglin (EPA NHSRC); Dan Stout (EPA NERL); and Kevin Ashley (Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health). This report was prepared for the EPA by Battelle. Acknowledgment is given to Stephanie Buehler, who was the Battelle lead author, and to Sarah Attenberger, Jane Chuang, and Amy Dindal, for their contributions to the preparation of this report.

Chapter 1
Introduction

Collection of contaminants from surfaces, referred to as "wipe sampling", is an important technique for the estimation of contaminant deposition on a variety of surfaces, including those in buildings, homes, outdoor areas, and hands (dermal wipes). Wipe sampling techniques are used for environmental sampling, industrial hygiene monitoring, monitoring of remedial processes, security monitoring, compliance monitoring, and various other related applications. Examples of wipe sampling applications include testing of household surfaces for lead; airport luggage screening for explosives; post-remediation sampling of methamphetamine houses; dermal wipe sampling techniques for personal exposure to pesticides; post-decontamination sampling; and spill clean-up verification of environmental contaminants. These are just a few of the many applications of wipe sampling techniques that are applied by government agencies and the private sector on any given day.

Procedures for the collection of contaminants from surfaces have several components in common, including the wipe sampling media, the wetting solvent, and the collection technique. However, wipe sampling procedures can vary widely, depending on the contaminant(s) of interest and the surface to be sampled. Reliability of the sample results begins with accurate collection of a sample for analysis. Thus, the wipe sampling procedures used for a particular analyte on a given surface, including the proper combination of the wipe sampling components described above, are an integral aspect of whether or not the results generated will be representative of the contamination.

The objective of this report is to concisely summarize the findings of a literature review that was conducted to identify the state-of-the-art wipe sampling techniques for a target list of compounds. This report describes the methods used to perform the literature review; a historical review of wipe sampling techniques in general; a review of chemical and physical properties of each target analyte; an analysis of wipe sampling techniques for the target analyte list; and a summary of the findings, including data gaps.

Chapter 2
Literature Search Methods

2.1 Literature Review

In the first task of this project, a two-phased approach was used to conduct a literature review to determine what is already known about wipe sampling techniques for a target list of analytes. First, a broad search was conducted that explored what general information was available on wipe sampling (i.e., how different organizations are using wipe sampling). This search did not focus on the specific compounds of interest for this project, but instead focused on what wipe sampling procedures could be found for various government agencies or other groups. Extensive internet searching was used as the primary tool for this phase of the review process. Various government agency websites were also searched using the available search options on that site using keywords such as "wipes(s)" or "wiping" and "sample(s)". The following government agency websites were included in the search: Drug Enforcement Administration, Federal Transit Administration, Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention, Bureau of Alcohol, Tobacco and Firearms, Coast Guard, Consumer Product Safety Commission, U. S. Department of Agriculture (USDA), U.S. Department of Defense, U.S. Department of Homeland Security, U.S. Department on the Interior, Agency for Toxic Substances and Disease Registry, Federal Aviation Administration, Transportation Security Administration (TSA), Federal Bureau of Investigation, Food and Drug Administration, National Aeronautics and Space Administration, National Institute of Standards and Technology, the U.S. Army Corp of Engineers, and the U.S. Environmental Protection Agency (EPA). These agencies and departments were selected because they seemed most likely to conduct wipe sampling for some branch of their operations. In spite of this effort, only limited information was obtained from this search process.

As a subset to this search, the Federal Register was explored to see if any further information could be obtained on the agencies listed above. It was determined that this approach was not productive as little practical information was found.

In the second phase of the literature search, information was sought on wipe sampling as it relates to the compounds of interest. These focused searches were conducted by using databases available through a regular library system as well as by the Chemical and Biological Defense Information Analysis Center (CBIAC), which has special access to documents related to chemical, biological, radiological, and nuclear technology information. Searches were conducted using keywords similar to the following:

wipe OR wipes OR wiping AND sample OR sampling AND compound

Each compound being investigated was included in individual searches. CBIAC searches focused on the chemical warfare agents (CWAs) and related compounds; the library database searches focused on the remaining compounds (pesticides and other toxic industrial chemicals (TICs). These searches yielded more than 140 references. The references were reviewed further for information regarding wipe sampling methodology, covering areas such as wipe material, wetting solvent, wipe procedure, and sampling surface. As a result of this further examination, only 39 citations were deemed relevant to this study and are included as references in this report.

As part of the overall reference collection effort, knowledgeable experts in the field of wipe sampling were contacted and relevant references were gathered based on their suggestions and input.

2.2 Search of Physical and Chemical Properties of Compounds

Part of the literature review also included gathering physical and chemical property information on each of the compounds of interest. Specifically, material safety data sheets (MSDSs) were collected from various publicly available internet sites as shown in Table 1. Information from the MSDSs was compiled into tables in Chapter 4. When the information contained on the MSDS seemed sparse, physical property information for a particular compound was cross-checked using CHEMINFO (through the Canadian Centre for Occupational Health and Safety (CCOHS)) and Ecotoxnet (http://extoxnet.orst.edu/). MSDS information from a subscription service (OHS at www.ohsworks.com) was also used. For the CWAs, information on chemical and physical properties was also obtained from two literature sources (*1,2*), in which detailed information on these compounds had been collected and summarized. The chemical structures for each of the compounds of interest are provided in Appendix A.

Table 1. Summary of Resources for MSDS Information for Compounds of Interest

Compound	CAS No.	Resource
Chloropicrin	76-06-2	www.e1.greatlakes.com/common/msdspdf/00026.pdf
Dichlorvos	62-73-7	http://www.cdc.gov/niosh/ipcsneng/neng0690.html
Dicrotophos	141-66-2	http://pmep.cce.cornell.edu/profiles/extoxnet/carbaryl-dicrotophos/dicrotophos-ext.html
Dimethylphosphite	868-85-9	http://www.cdc.gov/niosh/ipcsneng/neng1599.html
Distilled Mustard (HD)/Mustard Gas (H)	505-60-2	http://www.gulfweb.org/bigdoc/report/apphd.html
1,4-Dithiane	505-29-3	http://physchem.ox.ac.uk/MSDS/DI/1,4-dithiane.html
Mustard (HT)	172672-28-5	http://chppm-www.apgea.army.mil/dts/docs/detht.pdf
Ethyldichloroarsine (ED)	598-14-1	http://environmentalchemistry.com/yogi/chemicals/cn/Ethyl%A0Dichloroarsine.html
Fenamiphos	22224-92-6	http://www.cdc.gov/niosh/ipcsneng/neng0483.html
Lewisite (1)	541-25-3	http://www.uscg.mil/mlclant/KDiv/Envrn%20Hlth/IH-MSDS/MSDS/LewisiteMSDS.doc
Lewisite (2)	40334-69-8	MSDS not available; information presented from: http://www.epa.gov/opptintr/aegl/pubs/rest133.htm
Lewisite (3)	40334-70-1	MSDS not available; information presented from: http://www.epa.gov/opptintr/aegl/pubs/rest133.htm
Methyl parathion	298-00-0	http://www.cdc.gov/niosh/ipcsneng/neng0626.html
Mevinphos	7786-34-7	http://pmep.cce.cornell.edu/profiles/extoxnet/metiram-propoxur/mevinphos-ext.html
Nicotine	54-11-5	http://physchem.ox.ac.uk/MSDS/NI/nicotine.html
Phencyclidine	77-10-1	http://www.cerilliant.com/search.htm (search cat no P-001)
Phorate	298-02-2	http://www.piindustries.com/tech_main.htm
Sarin (GB)	107-44-8	http://www.gulfweb.org/bigdoc/report/appgb.html
Soman (GD)	96-64-0	http://www.gulfweb.org/bigdoc/report/appgd.html
Cyclohexyl sarin (GF)	329-99-7	MSDS not available; information presented from: Abercrombie, PL (September 2003)
Strychnine	57-24-9	http://www.cdc.gov/niosh/ipcsneng/neng0197.html
Tabun (GA)	77-81-6	http://www.gulfweb.org/bigdoc/report/appga.html
Tetraethyl pyrophosphate (TEPP)	107-49-3	http://www.segulab.com/en/t_msds.htm
Thiodiglycol	111-48-8	http://www.cdc.gov/niosh/ipcsneng/neng1601.html
1,4-Thioxane	15980-15-1	http://www.fluorochem.net/msds.asp?txtCatNo=001450&x=25&y=6 (search for cat no 001450)
Trimethyl phosphite	121-45-9	http://www.osha.gov/SLTC/healthguidelines/trimethylphosphite/recognition.html
VX	50782-69-9	http://www.gulfweb.org/bigdoc/report/appvx.html
Crimidine	535-89-7	http://yosemite.epa.gov/oswer/ceppoehs.nsf/profiles/535-89-7?opendocument
Methyl fluoroacetate	453-18-9	http://www.fluorochem.net/msds.asp?txtCatNo=006800&x=29&y=10 (search for cat no 006800)

Chapter 3
General Wipe Sampling Information

3.1 Background

Wipe sampling is one of the primary techniques for assessing surface contamination. When using the appropriate wipe sampling media coupled with an appropriate solvent (or used dry, as warranted), the type and amount of chemical on a particular surface can be identified by wiping a sufficient area of the surface and analyzing the wipe. This technique is a quick and easy means of determining what chemicals reside on a surface. Though wipe sampling is often employed, the methods and materials associated with wipe sampling vary greatly. Most wipe sampling procedures are a manual process, and the pressure applied for each wiping procedure could vary significantly among field operators. Different government agencies use different wipe methods for various compounds. Even within a particular field (such as occupational exposure assessments), variations in wipe sampling methodologies have been reported.

In this section, the general uses of wipe sampling techniques by different government agencies, various researchers, and studies are described in three primary areas: environmental, occupational, and homeland security-related applications. This information is summarized in Table 2. Performance information on wipe sampling methods is provided in Section 3.6. This chapter is meant to provide only a brief overview of wipe sampling applications and performance data. It is not meant to provide exhaustive coverage of all available studies but rather a synopsis of relevant information that describes what wipe sampling methods have been performed by various organizations to help establish the credibility of wipe sampling as a useful technique.

3.2 Environmental Applications

Wipe sampling is an integral part of the sampling protocol for many environmental assessments including evaluating remedial progress, environmental compliance, and for human exposure monitoring. A review of the literature for wipe sampling techniques in these areas is described in this section.

EPA has devised wipe sampling methods for polychlorinated biphenyl (PCB) analysis (*3, 4*). This technique is used to verify PCB cleanup on hard, smooth, non-porous surfaces. In this application, filter papers (such as Whatman 40 ashless or Whatman 50 smear tabs) or a gauze pad are used for the wipe material. The wipes are wetted with a solvent, such as isooctane or hexane, held with forceps or rubber gloves, and rubbed over a 100 square centimeter (cm^2) area.

Table 2. General Uses of Wipe Sampling Techniques

Compound	Agency or Agency Affiliation	Wipe Material	Wetting Solvent	Wipe Surface	Reference
Pesticides					
polar pesticides	ASTM	cotton gauze pads	IPA	smooth, non-porous; 100 cm^2	10
malathion	ASTM	cotton gauze pads	isooctane, DCM	smooth, non-porous; 100 cm^2	10
2,4-D	EPA	gauze pads	70:30 phosphate buffer:acetonitrile; IPA	uncarpeted floors, table tops, window sills, carpet; 850cm^2 - 2m^2	12, 15, 16
chlorpyrifos	ASTM	cotton gauze pads	isooctane	smooth, non-porous; 100 cm^2	10
	EPA, New Jersey Department of Environmental Protection	gauze pads	DI water	carpet; 100 - 800 cm^2	30
	New Jersey Department of Environmental Protection and Energy	gauze pads	DI water	turf; 100 cm^2	14
chlorpyrifos, diazinon	EPA	gauze pads	IPA	hard floors, hard surfaces	12
	EPA	gauze pads	DI water	window sill	13
Other Organics					
PCBs	EPA	filter paper, gauze pad	isooctane, hexane	hard, smooth, non-porous; 100 cm^2	3, 4
	NIOSH	glass wool filter	hexane	hard, non-porous; 1 ft^2	5
	general [1]	filter paper	dry, water	floors, walls; 200 cm^2	5
	general [1]	Kleenex®	dry, water	floors, walls; 200 cm^2	5

Table 2. (continued)

Compound	Agency or Agency Affiliation	Wipe Material	Wetting Solvent	Wipe Surface	Reference
PCBs	general [1]	Cloth wipes	octane	NA	5
	general [1]	Whatman filter paper	hexane	ventilation system; 1 ft^2	5
	general [1]	Whatman smear tabs	methanol	work and tool surfaces; 100 cm^2	5
	ASTM	cotton gauze pads	hexane, isooctane	smooth, non-porous; 100 cm^2	10
organic residues	USDA	gauze pads	IPA	100 cm^2	12
tetrachlorophenol	general [1]	gauze pads	NA	wood; 231 cm^2	5
chlorophenols	general [1]	Whatman filter paper	NA	wood	5
2,4-di*tert*butylphenol	general [1]	cotton swabs	ethanol	rubber	5
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	general [1]	Whatman glass microfiber paper	none	laboratory surfaces; 625cm^2	5
Metals					
As, Cu, Cr	EPA	TexWipe TX1009 clean room wipe (100% polyester)	DI water, 0.9% saline	wood; 314 cm^2	6
Pb, Be, As, Cd, Cr, Ni	Brookhaven National Lab/NIOSH	cotton gauze pads, ashless filter paper, GhostWipes™	DI water, IPA, ethanol, methanol, hexane	metal, plastic, glass, wood, concrete; 100 cm^2	8
Pb	ASTM	Disposable towellete	pre-moistened	1 ft^2	7
	general [1]	Wash'nDry® paper towels	pre-moistened	household surfaces; 1 ft^2	5
	EPA	Swiffer® dry and wet cloths	pre-moistened	floors, window sills	9

Table 2. (continued)

Compound	Agency or Agency Affiliation	Wipe Material	Wetting Solvent	Wipe Surface	Reference
Others					
methamphetamine	MN State Department of Health	gauze sponge	methanol	dry, hard, non-porous; 100cm^2	21
	WA State Department of Health	filter paper	methanol	dry, hard, non-porous; 100cm^2	22
anthrax	general [1]	Swipe, Heavy Wipe, swab	PBT	vinyl, tile, wood laminate, metal; 929 cm^2	19
	general [1]	rayon gauze pad, swab	water, PBS	hard surface	20

[1] No particular agency was found to be affiliated with the referenced study.

NA = Not Available.
DCM = dichloromethane
IPA = isopropyl alcohol
PBT = phosphate buffer with 0.05 percent Tween
PBS = phosphate buffer saline

Other PCB wipe methods are used to determine the extent of PCB contamination. PCB contamination on walls and transformers has been determined by the National Institute for Occupational Safety and Heath (NIOSH) using glass wool filter wipes wetted with hexane over a 1 square foot (ft^2) area (*5*). Other studies by various researchers have used filter paper and Kleenex®, cloth wipes, Whatman filter paper, and Whatman smear tabs as a sampling medium. These wipes have been used dry, and saturated with octane, hexane, and methanol, respectively. The areas wiped range from 100 cm^2 to 900 cm^2 (*5*).

Wipe sampling for metals such as lead or arsenic is also routinely done. In a wipe comparison study to determine the dislodgeable arsenic, copper, and chromium residues on chromated copper arsenate treated lumber, EPA used the following wipe media: a TexWipe TX1009 clean room wipe (100 percent polyester) that was saturated with deionized (DI) water, the same polyester wipe moistened with 0.9 percent saline solutions at two times the dry weight of the wipe, and an acid-washed polyester wipe saturated with DI water, though this particular wipe was found to contain traces of the acid wash still in the wipe (*6*). Wiping was done using a 1.1 kilogram disc that was approximately 8.5 centimeter (cm) in diameter, as a wiping block.

The American Society for Testing Materials (ASTM) has a lead-specific wipe sampling standard method for collecting settled dust on surfaces in and around buildings (*7*). A packaged, disposable towellette that is pre-moistened with a wetting solvent is used for the sample collection. Overlapping "S" and "Z" patterns are used when collecting the sample from an area of 100 cm^2.

The Industrial Hygiene Group at Brookhaven National Laboratory uses NIOSH Method 9100 (posted at www.cdc.gov/niosh/nmam) to determine lead and other metals in surface residue (*8*). A range of wipe materials can be used. Either 2" x 2" or 4" x 4" cotton gauze pads; ashless filter paper (1.5 to 4 inches in diameter); or pre-moistened wipes such as GhostWipes™ are appropriate for lead, beryllium, arsenic, cadmium, chromium, or nickel sampling. Approximately 1-2 milliliters (mL) of solvent such as DI water, isopropanol (IPA), ethanol, methanol, or n-hexane is used with the wipe. A 100 cm^2 area is supposed to be sampled by this method. The solvent used does not appear to be critical for the metal collection, but can impact the sampling surface and should be chosen accordingly.

Other commercially available wipes have also been used for lead sample collection. Wash'nDry® disposable paper towels, moistened with 20 percent denatured alcohol and 1:750 benzalkanium chloride have been used to collect lead dust from general household surfaces (*5*). Other researchers have used methods similar to the NIOSH Method 9100 described previously. EPA is currently exploring the potential use of dry electrostatic cloths (Swiffer®), as well as wet Swiffer® cleaning pads, for collecting residual dust samples after lead-based paint abatement cleaning (*9*).

Sampling for organic compounds is an important component of many exposure assessments. ASTM offers a method for taking wipe samples from smooth, non-porous surfaces for organic compounds (*10*). ASTM recommends the use of sterile, surgical cotton gauze pads (7.6 cm^2) with pre-cleaning only when necessary. Wipe wetting solvents are recommended on a compound basis. For example, for PCBs and most pesticides, isooctane is recommended (54 to

80 percent recovery). Hexane can also be used in wipes for PCBs. For carbamates or polar pesticides, IPA is an appropriate solvent for use with the wipe (84 to 96 percent recovery). Acetone is not desirable because it can remove interfering compounds from the sampling surface. A 100 cm^2 wiping area is recommended as is 2 mL of any solvent that is used to wet the wipe. The area should be wiped vertically and then horizontally using firm strokes with minimal overlap.

The USDA also has a published wipe sampling method for detecting organic residues or dusts from surfaces (*11)*. As with the ASTM method, their technique uses a 3" x 3" sterile gauze pad moistened with IPA. A 100 cm^2 area is also sampled.

EPA has conducted multiple exposure studies where wipe sampling for organic compounds on household surfaces played a key role in the assessment. As part of the Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP) study assessing children's exposures to particular persistent organic pollutants, such as chlorpyrifos and polycyclic aromatic hydrocarbons, wipe samples were taken for residues on hard floors using pre-cleaned, 4" x 4" Johnson and Johnson (J&J) SOF-WICK gauze pads moistened with 2 mL of 75 percent IPA in DI water (*12*). The J&J SOF-WICK gauze pads were also used in the National Human Exposure Assessment Survey (NHEXAS) exposure study in collecting wipe samples for chlorpyrifos and diazinon from window sills. In this case, the wipes were moistened with 2 mL of DI water and were also pre-cleaned with methylene chloride prior to their use (*13*). Window sills were wiped in this study by wiping the length of the sill using moderately firm pressure. After wiping the sill in one direction, the wipe was folded in on itself and the sill was wiped in reverse.

EPA's Children's Environmental Exposure Research Study (CHEERS) pilot study also used gauze pads for wipe sampling to determine children's exposure to various pesticides, phthalates, polybrominated diphenyl ethers (PBDEs), and fluorinated compounds. At the time of this study, however, the J&J SOF-WICK gauze pads had been discontinued, so an alternative, Kendall Excilon wipes were used instead. The wipes were the same size as the J&J brand wipes and were also pre-cleaned prior to use with dichloromethane (DCM). They were saturated with 10 mL of IPA before a sample was taken. This amount of IPA has the potential to extract more of the compounds from the surface and sub-surface of the sample area than are otherwise available for human contact and thus dermal absorption.

Black et al. (*14*) also used wipe samples for measuring dislodgeable chlorpyrifos residues on Kentucky bluegrass turf. The wipes were pre-extracted 7.6 cm x 7.6 cm gauze pads sprayed with DI water. A 100 cm^2 area was sampled based on Occupational Safety and Health Agency (OSHA) methods. Specifically, the area was wiped with one pad in a single direction for 10 strokes. Wipe samples recovered 1 percent to 6 percent of the initial chlorpyrifos deposit from the turf (1 to 3 hours after application). Wipe sampling variability ranged from 37 to 74 percent between different studies performed during the research. Within a particular study, wipe sampling variability averaged 21.5 percent.

Nishioka et al. wiped uncarpeted floors, table tops, and window sills using J&J SOF-WICK cotton gauze dressing sponge moistened with 2 mL of sweat stimulant (70:30 phosphate

buffer:acetonitrile) (*15,16*). An area from 850 cm^2 to 2 m^2 was sampled by first wiping in one direction, then folding the wipe in on itself, and then wiping the same area in an orthogonal direction.

Multiple other methods of wipe samples for various compounds have been used over the years, as noted by McArthur (*5*). Wooden surfaces (231 cm^2) were sampled for tetrachlorophenol with 12-ply surgical pads using 10 strokes for each of four samples. Chlorophenols were also collected from wooden surfaces using Whatman 1 filter paper (4.25 cm) with a 300 gram weight placed on top. Surface contamination of rubber with 2,4-di*tert*butylphenol was determined using ethanol-soaked cotton swabs. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin contamination of laboratory surfaces was found by wiping a 625 cm^2 area with dry Whatman glass microfiber paper.

3.3 Occupational Applications

Wipe sampling is an important component of occupational exposure analysis. OSHA has multiple wipe sampling methods and recommendations depending on the chemical of interest. OSHA has developed guidelines to provide chemists with a uniform method of evaluating surface sampling wipes (*17*). As part of these guidelines, information on how to properly conduct wipe sampling is presented. Among the steps is selecting a sampling medium. OSHA recommends the following list of media for wipe sampling: DURX 670 (polyester and cellulose), Pro-Wipe 880 (polypropylene), Ghost Wipes (cross linked polyvinyl alcohol), AlphaWipes (polyester), and even charcoal impregnated discs. Various wetting agents are also recommended: DI water for metals, DI water or IPA for non-volatile organics, or other solvents if the compound being sampled will react with water or IPA. The guidelines also indicate that the ideal sampling surface is a smooth and non-porous, and that the sampling area should be 100 cm^2.

OSHA has also prepared a chapter in their Technical Manual with more detailed information about wipe sampling (*18*). Similar to the previous document, each step of the wipe sampling procedure is discussed. Particular attention is paid to the media choice for sampling a surface. A filter is described as the classic wipe sampling technique. Paper filters, mixed cellulose ester filters, and smear tabs are best for metals. For things that are unstable on paper filters, polyvinyl chloride filters are recommended. Squares of a gauze material that are used either wetted (with solvent or water) or dry are purported to be best for organic compounds while volatile solvents are best sampled with charcoal impregnated pads. To sample a surface for isocyanates or aromatic amines, a filter treated with derivitizing reagent is recommended. Glass fiber filters, either wetted or dry, are recommended for many of the chemicals that will be analyzed by gas chromatography (GC) or high-performance liquid chromatography (HPLC).

3.4 Homeland-Security Related Applications

Over the last five years, the increased focus on homeland-security related techniques has generated new applications for wipe sampling. For example, airport luggage is screened by wipe sampling followed by ion mobility spectrometry analysis for explosives detection. In recent years, the detection of anthrax has become a critical analytical need. More specifically, the determination of whether or not any anthrax remains in a building after building decontamination

has become an important use for wipe sampling. Buttner et al. (*19*) tested the efficiencies of decontamination strategies for *b. anthracis* by taking wipe samples of vinyl tile, wood laminate, and metal surfaces after a simulated dispersion and subsequent decontamination. Three different kinds of wipe samples were used: (1) a Swipe (Speci-sponge) moistened with 30 mL of 0.01M phosphate buffer with 0.05 percent Tween (PBT); (2) a Heavy Wipe (Handy Wipes) moistened with 40 mL of PBT; and (3) a swab sample processing (SSP) kit moistened with 20 drops of buffer. In all cases, a 929 cm^2 area was sampled. For the Swipe and Heavy Wipe samplers, the surface was sampled by wiping the area in a horizontal direction. The wipe was then turned over and the unused surface was used to sample the same area while wiping in a vertical direction. For the SSP kit, the foam swab was used to sample the first half of the pre-moistened surface, then the swab was turned over and the remaining half of the surface was sampled. Removal efficiencies were not presented for any of the methods used in this study, but all three wipe materials collected similar levels of the *b. anthracis* surrogate used during testing, and similar levels of the bacteria were obtained from all three surfaces tested.

In another study by Sanderson et al. (*20*), two different *b. anthracis* sampling methods were tested. Wipe samples were taken using actual wipes as well as a swab. The wipe was 7.62 cm x 7.62 cm sterile rayon gauze pad that was wetted with 5 mL of sterile water. The sampling area was first wiped using vertical strokes, the wipe was then folded in on itself and the area was wiped using horizontal strokes. The swab was a sterile, rayon swab that was moistened with phosphate buffered saline (PBS) at pH 7.2. Several strokes of the area were first taken with the swab. The swab was then rotated during sampling to ensure that all of the swab was used. Dry swab samples were also taken. Samples were collected from air ducts, machinery, window boxes, and mail sorting bins from a postal facility (all non-porous surfaces). Wet swabs performed better than dry, detecting *b. anthracis* in 54 percent vs. 14 percent of the instances. Wipe sampling detected *b. anthracis* in 87 percent of the instances.

3.5 Other Applications

Illegal methamphetamine labs have become a serious problem for many cities and states. Wipe sampling methods for methamphetamines were found for two state departments, the Minnesota Department of Health (along with the Minnesota Pollution Control Agency) and the Washington State Department of Health (*21, 22*). Though both methods used 2 mL of methanol as the wetting solvent for their wipes, the wipe material itself was quite different for the two states. Minnesota used a 3" x 3" general use gauze sponge while Washington used filter paper. In both cases, a dry surface was to be sampled. The Washington State procedure specified a hard, non-porous surface be sampled; this was implied in the Minnesota protocol. An overlapping “Z” and “N” pattern are used for sampling.

3.6 Wipe Sampling Performance Information

The wipe sampling studies presented in this chapter mainly discuss applications of wipe sampling. While various applications are important in verifying the validity of the technique, it is also important to discuss and understand the validation and performance of the sampling methods. Some studies have focused on determining performance criteria for various wipe sampling methods.

Chavalitnitkul et al. (*23*) conducted an evaluation of wipe sampling variability using lead oxide dust as the test contaminant. This study aimed to evaluate wipe testing methods in general as well as the OSHA wipe testing method, more specifically, for quantitative recovery and repeatability. The study used moistened Whatman filter paper, commercial paper towels, adhesive paper labels, and adhesive tape as wipe media. Formica (a non-porous, smooth surface) and plywood (a rough, porous surface) were tested. Personal variations in performing wipe sampling were first tested using 12 different individuals to collect samples. A wide variation in removal efficiencies was found across participants, indicating potential issues in duplicating sample results between field staff. Much of the variation was caused by the pressure applied during sampling as well as the lack of a consistent sampling area. Removal efficiencies ranged from 31 percent to 212 percent across the 12 samplers in this portion of the study. The degree of sample variation decreased when the area to be sampled was measured prior to sampling, thus allowing for a consistent sampling area across all samples.

In evaluating the different wipe media and wipe surfaces, as described earlier, Chavalitnitkul et al. (*23*) found that most Whatman filter paper and moist paper towels gave similar, and good, removal efficiencies (80 to 90 percent). The surface sampled, however, was found to have a significant impact on the removal efficiency of the wipe sample. The smooth, non-porous surface (Formica) showed better removal efficiencies than the rough, porous surface (plywood). Removal efficiencies ranged from 57 percent to 91 percent across all sampling media and various applied pressures on formica, while efficiencies ranged from 30 percent to 77 percent on plywood. For plywood, the adhesive tapes gave better removal efficiencies than the paper towels or Whatman filters used. Applying the maximum pressure while sampling increased the removal efficiency of the adhesive media on both surfaces, but provided little impact for the paper towel and Whatman filter.

As part of another lead dust study, Vostal et al. (*24*) evaluated the efficacy of the wipe sampling procedure using moist, disposable paper towels on household floors. They found low variability between wipe samples and across four different investigators, indicating that the amount of lead obtained by these wipe samples could be reliably reproduced.

As McArthur describes (*5*), others have also explored the effect of wipe media, surface, and wipe techniques on the wipe sampling collection efficiency. They have determined, as Chavalitnitkul et al. (*23*) did, that wipe sampling removal efficiency decreased for rough surfaces. Variation was also found between samples taken by different individuals when the sampling area was estimated instead of measured.

Fenske et al. (*25*) evaluated the applicability of wipe sampling to determine exposure to pesticides in indoor environments. They sampled chlorpyrifos using a surgical gauze pad wetted with either distilled water or IPA. Wipe samples were taken on carpet and aluminum foil surfaces. Wipe samples were taken using a modification of the OSHA method where a 100 cm^2 area was wiped with three strokes in one direction, then a second gauze pad was used to wipe the same area in an orthogonal direction. Removal efficiency was 86 percent to 96 percent from the spiked aluminum foil samples with low variability between the different technicians taking the samples. For wipe samples taken on carpeted surface, the variability was much higher, 40

percent to 60 percent. Fenske et al. (*25*) concluded that much of this variability was related to the deposition of the pesticide onto the carpet, not the wipe sampling itself. They further concluded that wipe sampling provides a simple way of estimating the pesticide residues on a surface, but precision for the method could be improved by defining the wipe area and standardizing materials and methods.

3.7 Miscellaneous Notes on Other Surface Sampling Methods

As noted from the studies discussed in this section, wipe sampling can involve various materials and be used on a variety of surfaces. There are a couple of related sampling techniques that warrant mentioning here, but that do not address the surface wipe sampling that is the focus of this report. Dislodgeable residues from carpets can be determined using wipe sampling, as discussed previously; however, the preferred method of collecting dust samples from carpets is using vacuum sampling. For exposure studies a High Volume Small Surface Sampler (HVS3) is generally used for such a purpose. This is essentially a modified vacuum that uses cyclonic action to collect dust particles from the carpet into an attached sampling container. A sample is taken by vacuuming a given area with overlapping path lengths. An ASTM standard method is available for this technique (*26*).

EPA studies have also used a polyurethane foam (PUF) roller sampler to determine dislodgeable or transferable residues from floors (*15-16, 27-29*). The PUF roller generally consists of an aluminum frame with aluminum wheels. A PUF sleeve is the placed on the frame and the sample is taken by rolling the sampler back and forth over the selected 100 cm traverse path. This technique was used in CTEPP where a 7.6 cm thick pre-cleaned PUF was used on the roller.

One EPA study compared the PUF roller to the Dow drag sled and the California cloth roller methods to determine which was best at estimating the transfer of chlorpyrifos to carpets and vinyl flooring to skin (*27, 28*). The PUF roller used in this study is similar to the one discussed previously. The PUF sleeve used in the EPA comparison study measured 90 millimeter (mm) outer diameter x 30 mm inner diameter x 76 mm length. A 100 cm sample length was used, with sampling consisting of one forward and one backward pass of the length. The roller was operated at a rate of 10 centimeters per second (cm/s). The drag sled device consisted of a 3" x 3" piece of ¾" plywood as the base with an 8 pound weight mounted on top. A pre-cleaned 4"x 4" undyed denim cloth was used on the underside as the sampling media. The sled was pulled by a wire along a 48 inch path at a rate of 10 cm/s. The California roller device resembled a large rolling pin made of polyvinyl chloride pipe. The pipe was 63 cm long, 13 cm in diameter covered with 1 cm thick foam, and filled with steel ball bearings. A 17" x 17" pre-cleaned percale sheet cloth (50 percent cotton, 50 percent polyester) was used to collect the sample by placing the cloth on the sampling area, covering it with the plastic, and pushing the roller over it. The study found the drag sled and PUF roller to be better methods than the cloth roller technique. All three methods had reasonable precision (24 to 46 percent). Transfer efficiencies ranged from 2 percent to 7 percent, with the drag sled method averaging 2.1 percent.

Other exposure studies have also relied on the PUF roller for sampling. Nishioka et al. (*15-16, 29*) used the sampler to determine the available dislodgeable residue or surface dust of 2,4-D on indoor carpets. The PUF sleeves used were 8 cm long x 8 cm outer diameter. The PUF was pre-

cleaned before use with water and then 70:30 volume/volume acetonitrile:phosphate buffer. In one of these studies, the PUF was moistened with a 70:30 phosphate buffer:acetonitrile mixture that simulates human sweat, allowing the PUF roller to simulate a child's hand contact with the sampling surface. A 0.48 m^2 area was sampled at a rate of approximately 17 cm/s. The PUF roller provided transfer efficiencies of 0.1 percent to 0.2 percent.

In a study by Lu and Fenske (*30*), the PUF roller method was compared to wipe sampling to determine which was better at simulating hand pick-up of chlorpyrifos residues from carpet. The PUF sleeve used was 8 cm in length and sampling was conducted over a 100 cm length (total of 800 cm^2 area) using techniques similar to those described previously. The PUF sleeve was misted with DI water before use. The wipes used in this study were 12-ply 7.6 cm x 7.6 cm surgical gauze pads. They were also moistened with DI water before sampling was conducted. In this case, a 100 cm^2 area was wiped. The area was first wiped with three strokes, and then the sampling was repeated with a second pad in the orthogonal direction. Results showed that chlorpyrifos residue transfer as measured by these methods was 23 to 36 times greater than that found from normal carpet to skin transfers.

The Minnesota Children's Pesticide Exposure Study compared two different surface sampling methods to determine which better represents realistic estimates of exposure (*31*). Malathion, atrazine, diazinon, and chlorpyrifos were measured using the Edwards and Lioy (EL) sampler and the Lioy, Wainman, and Weisel (LWW) surface wipe sampler. The EL sampler is a press sampler designed to collect surface dust from carpets or other surfaces. C18 filters were used and a 150 cm^2 area was sampled. Samples were collected from both carpet and another non-carpeted surface. The LWW sampler consisted of a C18 impregnated Teflon filter wetted with IPA and placed on a pressure plate. A sample was taken by sliding the sampler the length of a 100 cm^2 template three times. Wipe samples from smooth surfaces were collected in this manner. The LWW sampler was determined to not be representative of pesticide residues found on a child's hand from dermal contact with contaminated surfaces. The EL sampler, because it uses only a single hand press, represents what dislodgeable residues are available via one hand contact on the surface, not the total amount that might end up on a child's hand.

Other techniques for assessing surface contamination include directly applying a sensing instrument at or near the surface. Some examples of direct sensing techniques include: X-ray fluorescence devices for metals detection, radiation meters for determining radioactivity, and portable photoionization monitors for detecting volatile organic compounds. The application of these direct-sensing techniques is usually limited to: qualitative (e.g., presence/absence) results, higher detection limits, analyte selectivity, and availability of detection capability for the target analyte. For these reasons, wipe sampling techniques are typically used in conjunction with or instead of direct sensing techniques. For example, as noted previously, the TSA often collects wipe samples of passengers' luggage and then tests the wipes for explosives residue using ion mobility spectrometry, a direct-sensing technique. Because we regard this as more of a direct-sensing method rather than a wipe sampling method, this technique was not researched as part of this report.

For many studies, it is important to understand what amount of contaminants a person has transferred from the surface to his hands. Hand wipe samples or dermal wipes have therefore

played a major role in many exposure studies. Dermal wipes generally consist of some sort of gauze sponge or cloth being used as the wipe, the wipe being wetted, and then the hand being thoroughly wiped. For the CTEPP study, pre-extracted gauze pads, the same as those used for surface wipes, were wetted with 2 mL of 75 percent IPA in DI water and used for hand wipe samples (*12*). NHEXAS dermal wipes were similar but used 4 mL of IPA (*13*). OSHA recommends the use of glass fiber filters, mixed cellulose ester filters or smear tabs, gauze sponges, or charcoal impregnated pads moistened with either DI water or a 50 percent solution of IPA in water (*18*). McArthur (*5*) notes the use of ethyl alcohol for dermal wipe samples. Though dermal wipes do not measure the contaminated surface, they can provide a more accurate assessment of a person's exposure to a chemical.

3.8 Summary

Numerous wipe sampling methods were found for different government agencies, such as EPA, OSHA, and NIOSH, and for various sampling studies that have been conducted by different researchers. Wipe media ranged from gauze sponges to Whatman filters to pre-wetted, commercially-available wipes. Wipe sampling methods were found for various compounds, such as metals, PCBs, drugs, and pesticides.

Wipe sampling provides a simple way of testing for contamination on a particular surface and can provide information on the mass of a contaminant on the surface. However, variability in reproducibility and removal efficiencies can result from the lack of standardization within a particular wipe sampling method as well as across various other methods. Simply clearly measuring the area to be sampled can significantly lower this variability. Different surface characteristics can also affect wipe sampling efficiency. It is therefore important that a wipe sampling method be fully validated before it is used so that such performance parameters, as discussed here, can be determined and improved.

Chapter 4
Physical and Chemical Properties

4.1 Chemical Agents and TICs of Interest

Wipe sampling methods exist for a variety of situations and a diverse number of chemicals. The focus of this report, however, is on a select set of compounds. Table 1 lists the compounds of interest to EPA that are the subject of this literature review. The ultimate goal of this review is to determine what wipe sampling methods are available and have been used for these compounds. Before that can be done, however, it is important to better understand the compounds listed in Table 1. To this end, the physical and chemical properties of each of the compounds of interest listed in Table 1 have been obtained, as available, for this report. The chemical structure of each compound has also been collected. The structures are provided in Appendix A.

Tables 3 through 7 provide a summary of some of the physical properties listed in the MSDS information that was obtained. Characteristics that are provided where available include the chemical family that the compound belongs to; the physical state of the compound; its molecular weight and formula; boiling, freezing, and melting points; vapor pressure and density; and solubility. The information listed in Tables 3 through 7 was gathered from the MSDSs listed in Table 1, two other primary references that were used to fill in gaps in the information (*1, 2*), and those references discussed in Chapter 2.

There are essentially two major classes of compounds in the following tables: organophosphate (OP) pesticides and CWAs and related compounds (e.g., CWA precursors and degradation products). A couple other compound classes round out the list, such as rodenticides and controlled substances, but the OP pesticides and CWAs and related compounds comprise 83 percent of the compounds of interest to this literature review. Within the group of CWAs, there are two different types: blister agents (see Table 3) and nerve agents (see Table 4). HD, H, HT, Lewisite, and ED are all blister agents. Blister or vesicant agents produce burns and blisters on the skin of those who come in contact with them. The mustard agents (HD, H, and HT) are chemically stable. They are not very soluble in water, but that which does dissolve in water can hydrolyze very quickly. HT is actually a mixture of 60 percent H and 40 percent T (a closely related mustard). Lewisite and ED are organic arsenicals. They have similar properties to the mustard agents but they contain arsenic instead of the sulfur found in mustard agents. Lewisite is often found as a mixture of isomers (Lewisite 1, 2, and 3) and is only slightly soluble in water.

Table 3. Physical/Chemical Properties of CWAs – Blister Agents

Compounds	CAS #	Chemical Class	Physical State	Molecular Weight	Molecular Formula	Boiling Point	Freezing Point	Melting Point	Vapor Pressure	Vapor Density (air =1)	Specific Gravity (water =1)	Water Solubility	Solvent Solubility
Mustard Gas (H)/ Distilled Mustard (HD)	505-60-2	organic sulfur compounds	liquid	159.08	$C_4H_8Cl_2S$	423 ºF (217 ºC)	57 ºF (14 ºC)	NA	0.09 mmHg @ 30 ºC	5.5	1.2741	very slightly soluble; hydrolysis $t_{1/2}$ = 5min @ 25 ºC only for what dissolves	fats, oils, organic solvents
Mustard (HT)	172672-28-5	organic sulfur compounds	liquid	263.3 (T)	$C_8H_{16}Cl_2S_2O$ (T)	> 228 ºC	NA	0.0 - 1.3 ºC	0.077 mmHg @ 25 ºC	6.5	NA	negligible	most organic solvents
Ethyldichloroarsine (ED)	598-14-1	halogenated, aliphatic	liquid	174.89	$C_2H_5AsCl_2$	NA	< -65 ºC	NA	2.29 mmHg @ 21.5 ºC	6	1.742 @ 14 ºC	decomposes/hydrolyzes immediately	ethyl chloride, alcohol, ether, benzene, acetone, kersone, cyclohexane
Lewisite (1)	541-25-3	halogenated, aliphatic	liquid	207.31	$C_2H_2AsCl_3$	159.8 ºC	32.2 ºF (0.1 ºC)	NA	0.395 mmHg @ 20 ºC	7.1	1.88 @ 20 ºC	decomposes/hydrolyzes rapidly	ether, alcohol, organic solvents
Lewisite (2)	40334-69-8	halogenated, aliphatic	liquid	233.36	$C_4H_4AsCl_3$	230 ºC	NA	NA	0.108 mmHg @ 20 ºC	NA	1.702 @ 20 ºC	NA	NA
Lewisite (3)	40334-70-1	halogenated, aliphatic	liquid	259.39	$C_6H_6AsCl_3$	215.4 ºC	NA	NA	0.217 mmHg @ 25 ºC	NA	1.572 @ 20 ºC	NA	NA

NA = Not Available

Table 4. Physical/Chemical Properties of CWAs – Nerve Agents

Compounds	CAS #	Chemical Class	Physical State	Molecular Weight	Molecular Formula	Boiling Point	Freezing Point	Melting Point	Vapor Pressure	Vapor Density (air =1)	Specific Gravity (water =1)	Water Solubility	Solvent Solubility
Sarin (GB)	107-44-8	esters, halogens, phosphine	liquid	140.11	$C_4H_{10}FO_2P$	297 ºF (147 ºC)	-71 ºF (-57 ºC)	NA	2.9 mmHg @ 25 ºC	4.86	1.10 @ 20 ºC	miscible; hydrolysis under acidic conditions; $t_{1/2}$ = 80hr @ 20 ºC, pH7	organic solvents
Soman (GD)	96-64-0	esters, halogens, phosphine, organophosphorus	liquid	182.19	$C_7H_{16}FO_2P$	333 ºF (167 ºC)	-94 ºF (-70 ºC)	NA	0.401 mmHg @ 25 ºC	6.3	1.026	2.1g GD/100g @ 20 ºC; hydrolysis, $t_{1/2}$ = 45hr @ pH 6.65	organic solvents
Cyclohexyl sarin (GF)	329-99-7	esters, halogens, phosphine	liquid	180.16	$C_7H_{14}FO_2P$	228 ºC	-30 to -50 ºC	NA	0.0927 mmHg @ 25 ºC	6.2	1.128 @ 25 ºC	3.7g GF/100g @ 20 ºC; hydrolysis, $t_{1/2}$ = 42hr @ 20 ºC in DI water	organic solvents
Tabun (GA)	77-81-6	organophosphorus, phosphoryls, amides	liquid	162.13	$C_5H_{11}N_2O_2P$	248 ºC	-51 ºF (-46 ºC)	NA	0.07 mmHg @ 25 ºC	5.63	1.073 @ 25 ºC	7.1g GA/100g @ 20 ºC; hydrolyzes, $t_{1/2}$ = 8.5 hr @ 20 ºC, pH 7	organic solvents
VX	50782-69-9	phosphono, sulfur compounds	liquid	267.36	$C_{11}H_{26}NO_2PS$	568 ºF (298 ºC)	< -60 ºF (< -51 ºC)	NA	0.0007 mmHg @ 25 ºC	9.2	1.0083 @ 25 ºC	30 g/L @ 25 ºC; miscible @ 9.4 ºC; hydrolysis, varies $t_{1/2}$ = 17 - 42 days @ 25 ºC, pH 7	lipids; organic solvents

NA = Not Available

Table 5. Physical/Chemical Properties of CWA Precursors and Degradation Products

Compounds	CAS #	Chemical Class	Physical State	Molecular Weight	Molecular Formula	Boiling Point	Freezing Point	Melting Point	Vapor Pressure	Vapor Density (air =1)	Specific Gravity (water =1)	Water Solubility	Solvent Solubility
Dimethyl phosphite	868-85-9	phosphoryls, esters, alkyl phosphite	liquid	110.05	$C_2H_6O_3P^+$	336-342 ºF (169-172 ºC)	NA	NA	<1.0 mmHg @ 20 ºC	NA	1.2	hydrolyzes	organic solvents
1,4-Dithiane	505-29-3	heterocyclic, sulfur, hydrocarbons	solid	120.24	$C_4H_8S_2$	390-392 ºF (199-200 ºC)	NA	226-235 ºF (108-113 ºC)	NA	NA	NA	slightly soluble	alcohol, carbon tetrachloride, ethanol, ether
Thiodiglycol	111-48-8	hydroxyls, aliphatic, mercaptans	liquid	122.18	$C_4H1_0O_2S$	541 ºF (283 ºC)	3 ºF (-16 ºC)	NA	1.3 mmHg @ 42 ºC	4.2	1.1852	soluble	ethanol, acetone, methanol, chloroform; **Slightly Soluble:** ether, benzene, carbon tetrachloride
1,4-Thioxane	15980-15-1	ethers, alicyclic, sulfur compounds, ethers	liquid	104.17	C_4H_8OS	297 ºF (147 ºC)	1 ºF (-17 ºC)	NA	NA	3.59	1.1174	NA	N/A
Trimethyl phosphite	121-45-9	organic, alkyl phosphites	liquid	124.09	$C_3H_9O_3P$	232-234 ºF (111-112 ºC)	-108 ºF (-78 ºC)	NA	17.0 mmHg @ 20 ºC	4.3	1.052	reacts	hexane, benzene, acetone, alcohol, ether, carbon tetrachloride, kerosene, organic solvents

NA = Not Available

Table 6. Physical/Chemical Properties of OP Pesticides and Other Pesticides

Compounds	CAS #	Chemical Class	Physical State	Molecular Weight	Molecular Formula	Boiling Point	Freezing Point	Melting Point	Vapor Pressure	Vapor Density (air =1)	Specific Gravity (water =1)	Water Solubility	Solvent Solubility
Chloropicrin	76-06-2	nitro, halogenated, aliphatic	liquid	164.38	CCl_3NO_2	234 F (112 ºC)	-83 ºF (-64 ºC)	NA	20 mmHg @ 20 ºC	5.7	1.7	0.2% @ 20 ºC	alcohol, ether, acetone, benzene, acetic acid
Dichlorvos	62-73-7	heterocyclic, organophosphorous	liquid	220.98	$C_4H_7Cl_2O_4P$	183 F (84 ºC) @1 mmHg	NA	NA	0.012 mmHg @ 30 ºC	15.3	1.415 @ 25 ºC	1%; hydrolysis, $t_{1/2}$ = 20 to 80hrs @ pH 9 to pH 4	organic solvents
Dicrotophos	141-66-2	organophosphorus	liquid	237.21	$C_8H_{16}NO_5P$	266 ºF (130 ºC) @ 0.1 mmHg	NA	NA	NA	NA	1.216	miscible; hydrolysis, $t_{1/2}$ = 50 days @ 38 ºC pH 9.1	acetone, alcohol, isobutanol, hexylene glycol, xylene
Fenamiphos	22224-92-6	organophosphorus	solid	303.39	$C_{13}H_{22}NO_3PS$	NA	NA	120 ºF (49 ºC)	negligible	NA	1.14	770 ppm @ 20 ºC; hydrolysis, $t_{1/2}$ = 4hrs @ pH 7	dichloromethane, isopropanol, organic solvents; **Insoluble:** aliphatic solvents
Methyl parathion	298-00-0	organophosphorus	solid	263.22	$C_8H_{10}NO_5PS$	228 ºF (109 ºC) @ 0.05 mmHg	NA	97 ºF (36 ºC)	0.000097 mmHg @ 20 ºC	NA	1.358	55-60 ppm @ 25 ºC; hydrolysis, 100% degradation in seawater, lakes and rivers in 1 week to 1 month	dichloromethane, isopropanol, organic solvents; **Slightly Soluble:** aliphatic solvents, light petroleum, mineral oils

Table 6. (continued)

Compounds	CAS #	Chemical Class	Physical State	Molecular Weight	Molecular Formula	Boiling Point	Freezing Point	Melting Point	Vapor Pressure	Vapor Density (air =1)	Specific Gravity (water =1)	Water Solubility	Solvent Solubility
Mevinphos	7786-34-7	organophosphorus	liquid	224.16	$C_7H_{13}O_6P$	617 ºF (325 ºC)	-69 ºF (-56 ºC)	NA	0.003 mmHg @ 20 ºC	7.5	1.25	miscible; hydrolysis, $t_{1/2}$ = 35 days @ pH 7	acetone, carbon tetrachloride, chloroform, alcohol, benzene, toluene, xylene; **Slightly Soluble:** petroleum ether, kerosene, carbon disulfide; **Insoluble:** hexane
Phorate	298-02-2	organophosphorus	liquid	260.39	$C_7H_{17}O_2PS_3$	244-248 ºF (118-120 ºC) @ 0.8 mmHg	<5 ºF (< -15 ºC)	NA	0.00084 mmHg @ 20 ºC	NA	1.156	50ppm; hydrolysis, $t_{1/2}$ = few days to few weeks in acidic water	carbon tetrachloride, dioxane, xylene, alcohols, esters, ethers, vegetable oils, methyl cellosolve, dibutyl phthalate
Tetraethyl pyrophosphate	107-49-3	organophosphorus	liquid	290.22	$C_8H_{20}O_7P_2$	255 ºF	NA	NA	0.00047 mmHg @ 30 ºC	NA	1.185	soluble; hydrolysis, $t_{1/2}$ = 6.8 hrs @ pH 6	alcohol, benzene, acetone, glycerol, ethylene glycol, propylene toluene, xylene, organic solvents; **Insoluble:** petroleum oils

NA = Not Available

Table 7. Physical/Chemical Properties of Rodenticides and Controlled Substances

Compounds	CAS #	Chemical Class	Physical State	Molecular Weight	Molecular Formula	Boiling Point	Freezing Point	Melting Point	Vapor Pressure	Vapor Density (air =1)	Specific Gravity (water =1)	Water Solubility	Solvent Solubility
Crimidine	535-89-7	pyrimidines	solid	171.63	$C_7H_{10}ClN_3$	284-297 ºF (140-147 ºC) @ 4 mmHg	NA	189 ºF (87 ºC)	<0.00001 mmHg @ 20 ºC	NA	NA	1% @ 20 ºC	alcohol, organic solvents
Methyl fluoroacetate	453-18-9	ester, acetic acid	NA	92.07	$C_3H_5FO_2$	104.5 ºC	NA	-35 ºC	30.8 mmHg @ 25 C	NA	1.17 @ 20 ºC	150 g/L; 2.5% hydrolized in 60 hrs @ 22-24 ºC DI water	NA
Nicotine from nicotine sulfate	54-11-5	pyridinyl	liquid	162.23	$C_{20}H_{30}N_4O_4S$	247 ºC	NA	-79 ºC	0.045 mmHg @ 25 ºC	NA	1.01 g/mL	soluble	alcohol, ether
Phencyclidine	77-10-1	heterocyclic	solid	243.39	$C_{17}H_{25}N$	275-279 ºF (135-137 ºC) @ 1 mmHg	NA	115-117 ºF (46-47 ºC)	NA	NA	NA	soluble	alcohol
Strychnine	57-24-9	heterocyclic, nitrogen, alkaloids	solid	334.42	$C_{21}H_{22}N_2O_2$	NA	NA	547-550 ºF(286-288 ºC)	0 mmHg @ 20 ºC	NA	1.36	0.02%	chloroform; **Slightly Soluble:** alcohol, benzene, ether, toluene, methanol, glycerol, amyl alcohol, petroleum ether

NA = Not Available

The nerve agents (G-series and VX compounds, see Table 4) have a high acute toxicity and inhibit acetylcholinesterase throughout the body, disrupting the nervous system. They are structurally similar OP compounds and, thus, are quite similar to OP pesticides. However, the nerve agents contain a C-P bond that is not found in OP pesticides and that bond is very resistant to hydrolysis (*1*). The nerve agents differ somewhat in the remainder of their structure. VX contains sulfur while GB, GF, and GD contain fluorine; GA has a cyanide group. The G-series nerve agents are more volatile than VX and present a vapor hazard. Furthermore, GA, GB, and GF are more miscible in water, while VX and GD are less soluble (*1*). As Table 4 indicates, hydrolysis rates also differ amongst the nerve agents, with VX having the longest half-life (17 to 42 days at 25 ºC, pH 7). Though the C-P bond in nerve agents may resist hydrolysis, the overall hydrolysis half-lives for these compounds is much shorter than those for the OP pesticides discussed in this report (see Table 6). The P-F bond is the first to hydrolyze for GB, GD, and GF; the P-CN bond for GA; and the P-S bond is prone to hydrolysis for VX. Two of the compounds from Table 1 are precursors to the manufacturing of G-series nerve agents. These are trimethyl phosphite (TMP) and dimethyl phosphite, both of which are alkyl phosphites (see Table 5). TMP can also be used as an intermediate in the manufacturing of OP pesticides.

The degradation of mustard agents can produce multiple compounds. Table 5 provides information on the degradation and hydrolysis products from the list of compounds of concern. 1,4-Thioxane is a degradation product of mustard gas; 1,4-dithiane is a thermal degradation product of HD (*1*). Thiodiglycol is also known to be a product of the hydrolysis of HD. This chemical, though, is also a precursor to the production of sulfur-based blister agents.

These degradation products are only a small portion of the overall number of degradation products associated with the CWAs identified in this report. Not only do CWAs break down in the environment, but the agents themselves are full of impurities which can also make their way into the environment in the event of a CWA distribution. In fact, the sulfur mustard agents alone (H, HD, and HT) have over 40 associated degradation products, hydrolysis products, and impurities (*1*). Lewisite has seven reported impurities and degradation products, while GA has 22, GB has nine, and GD has seven reported impurities and degradation products; VX alone has over 30 (*1*). A table of the known toxic and persistent degradation products of the aforementioned CWAs can be found in Munro et al. (*1*).

Dichlorovos, dicrotophos, fenamiphos, methyl parathion, mevinphos, phorate, and tetraethyl pyrophosphate (TEPP) are all OP pesticides (see Table 6). OP pesticides work similarly to the CWA nerve agents, inhibiting acetylcholinesterase in the insects they target. They can also act as acetylcholinesterase inhibitors in humans. OP pesticides are used on many fruit and vegetable crops as well as in and around buildings, though their residential uses have been voluntarily withdrawn by the manufacturers. Most OP pesticides are only slightly soluble in water, have a low volatility, and undergo hydrolysis. However, there are some exceptions to the rule. For example, dicrotophos is considered miscible in water but does not undergo hydrolysis quickly. Dichlorovos, on the other hand, is not as soluble but can hydrolyze rather quickly under the right conditions. Mevinphos and TEPP are also soluble in water, but their hydrolysis rates in neutral water differ greatly. For mevinphos, the half-life in water can be up to 35 days. The hydrolysis half-life for TEPP in neutral waters is closer to seven hours, with that time decreasing down to minutes as the pH increases. Phorate and methyl parathion have similar solubility in water as

well as similar hydrolysis rates. Fenamiphos is more soluble than these OP pesticides, and its hydrolysis rate is also much quicker.

Though the basic structural building block is consistent in all of the OP pesticides, each compound has a slightly different overall structure that separates it from the rest. As the name implies, dichlorovos has two chlorine atoms, while phorate has three sulfur atoms. Both methyl parathion and fenamiphos have a benzene ring, a sulfur atom, and a nitrogen atom, but they are not oriented in the same way. Dicrotophos has a nitrogen atom along with multiple methyl groups, while mevinphos has oxygen atoms with methyl groups. TEPP is set apart from all of the other OP pesticides by having two phosphorous atoms in its structure. These structural differences allow for the physical property differences discussed previously.

The remaining compounds from the list are somewhat diverse. Chloropicrin is a pesticide (see Table 5) and is used as an insecticidal fumigant. It is also blended with several other toxic fumigants for insect control, but also has roots as a chemical weapon in World War I, where it was known as PS. Chloropicrin has also been described as an irritant and something that has been used for riot control as a tear gas. As with ED, chloropicrin is aliphatic and halogenated, but it contains nitrogen instead of arsenic. As with many other compounds in Tables 3 through 7, this contaminant is not very water soluble. Crimidine and strychnine are both rodenticides (see Table 7) that act on cells in the brain and spinal cord to cause convulsions. Strychnine, however, is a very large molecule compared to crimidine, and is even less water soluble, though both are barely soluble. Nicotine (see Table 7) is a nerve poison that acts on the nicotinic acetylcholine receptors. Nicotine sulfate is an insecticide and nicotine can be generated from it. Nicotine shares one similarity with crimidine as well as phencyclidine (PCP) in that they all have nitrogen rings in their structure. Nicotine is also considered a drug, as is PCP. PCP (see Table 7) is a dissociative drug and is also a neurotoxin. Both compounds are readily soluble in water, as some of the compounds previously discussed are. As with the other compounds, methyl fluoroacetate (see Table 7) is considered a toxin; it has rodenticidal properties. Fluoroacetates, in fact, were considered as potential CWAs at one point. As with some of the nerve agents, the hydrolysis half life for methyl fluoroacetate is quite long (2.5 percent in 60 hours).

4.2 Summary

A good understanding of the properties of each of the compounds of interest is important in selecting an appropriate wipe sampling method for them. As such, Tables 3 through 7 provide a synopsis of the physical and chemical properties of the compounds listed in Table 1. The CWA blister agents are presented in Table 3, CWA nerve agents in Table 4, CWA precursors and degradation products in Table 5, OP and other pesticides in Table 6, and the remaining compounds (rodenticides and controlled substances) in Table 7. Within each compound class, similarities and differences exist, as noted in this chapter. Many of the descriptions in this chapter reference the chemical structure of each compound to elucidate a better understanding of the compound classes. The chemical structures of each of the compounds listed in Table 1 can be found in Appendix A.

Chapter 5
Wipe Sampling Methods for Chemical Warfare Agents and Toxic Industrial Chemicals

A variety wipe sampling techniques have been used for some of the compounds listed in Table 1. A summary of the wipe sampling information for the compounds of interest is provided in Table 8. Information regarding the analyte, wipe material, wetting solvent, wipe surface, and determinative step are provided, including the reference where this information was obtained. Information gaps are designated as "NA" in the table, and as shown in Table 8, limited specific wipe sampling information was found for many of the compounds of interest. The literature information which was available and summarized in Table 8 is described in this section, organized by chemical class.

5.1 OP Pesticides/Pesticides

Surface wipe sampling for methyl parathion was conducted in a number of different studies. In a study of 18 pesticides (including methyl parathion) by Lemley et al. (*32*), living room dust wipe samples were taken, usually from a window sill or table, using two Whatman filter papers. One wipe was moistened with water and the other with aqueous methanol solution. Approximately 0.031 m^2 was sampled by wiping across the area with each wipe. Methyl parathion was found in one of the 15 wipe samples taken.

In a study by Clark et al. (*33*), methyl parathion wipe samples were collected to assess the potential exposures and health risks of a population, provide a basis for enforcement action, and determine which properties needed decontamination. Wipes consisted of gauze pads wetted with IPA. A 100 cm^2 area was wiped in this study. Surface sampled included baseboards, counter splashboards, and under the kitchen sink. Similar wipe sampling methods were used by Wasley et al. (*34*) for methyl parathion sampling in another study. Specific wipe sampling information was not found for the remaining OP pesticides (dichlorovos, dicrotophos, fenamiphos, mevinphos, and phorate).

Though chloropicrin is considered a pesticide (though not an OP pesticide), it is also listed as a Scheduled (Schedule 3) chemical by the Organisation for the Prohibition of Chemical Weapons' (OPCW's) Chemical Weapons Convention (www.opcw.org). Details on sampling methods for Scheduled chemicals are discussed in the next section.

Table 8. Summary of Wipe Sampling Information Found in the Literature for the Compounds of Interest

Compound Class	Compound	Wipe Material	Wetting Solvent	Wipe Surface	Determinative Step	Reference
OP Pesticides/ Pesticides	Chloropicrin	lint-free cotton	DCM, methanol	NA	NA	35
	Dichlorvos	NA	NA	NA	NA	NA
	Dicrotophos	NA	NA	NA	NA	NA
	Fenamiphos	NA	NA	NA	NA	NA
	Methyl parathion	filter paper	water or aqueous methanol	Window sills or tables	GC/MS	32
		gauze pad	IPA	Kitchen (baseboards, backsplash, under sink), bathroom (baseboard)	GC/MS or GC/FPD	33, 34
	Mevinphos	NA	NA	NA	NA	NA
	Phorate	NA	NA	NA	NA	NA
	Tetraethyl pyrophosphate	NA	NA	NA	NA	NA
CWAs - Blister Agents	Distilled Mustard (HD)	Q-tip, cotton cloth, felt, filter paper	acetone, IPA, ethyl acetate, DCM	painted metal, concrete	GC/MS	35
		Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36
	Mustard Gas (H)	lint-free cotton	DCM, methanol	NA	NA	36
	Mustard (HT)	lint-free cotton	DCM, methanol	NA	NA	36
	Ethyldichloroarsine (ED)	NA	NA	NA	NA	NA
	Lewisite (1)	Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36

Table 8. (continued)

Compound Class	Compound	Wipe Material	Wetting Solvent	Wipe Surface	Determinative Step	Reference
CWAs - Blister Agents	Lewisite (2)	Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36
	Lewisite (3)	Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36
CWAs – Nerve Agents	Sarin (GB)	Q-tip, cotton cloth, felt, filter paper	acetone, IPA, ethyl acetate, DCM	painted metal, concrete	GC/MS	35
		Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36
	Soman (GD)	Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36
	Cyclosarin (GF)	lint-free cotton	DCM, methanol	NA	NA	36
	Tabun (GA)	Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
		lint-free cotton	DCM, methanol	NA	NA	36
	VX	Woven polyester/cotton blend	IPA	NA	GC/MS	37, 38
CWA Precursors and Degradation Products	1,4-Dithiane	NA	NA	NA	NA	NA
	Thiodiglycol	lint-free cotton	DCM, methanol	NA	NA	36
	1,4-Thioxane	NA	NA	NA	NA	NA
	Trimethyl phosphite	lint-free cotton	DCM, methanol	NA	NA	36
	Dimethyl phosphite	lint-free cotton	DCM, methanol	NA	NA	36

Table 8. (continued)

Compound Class	Compound	Wipe Material	Wetting Solvent	Wipe Surface	Determinative Step	Reference
Rodenticides	Crimidine	NA	NA	NA	NA	NA
	Methyl fluoroacetate	NA	NA	NA	NA	NA
	Strychnine	NA	NA	NA	NA	NA
Controlled Substances	Nicotine	NA	0.1% ascorbic acid	non-upholstered living room and bedroom furniture; 10 cm x 10 cm	GC/MS	39
	Phencyclidine	NA	NA	NA	NA	NA

NA = Information not available in the literature
DCM = dichloromethane
IPA = isopropyl alcohol
GC/MS = gas chromatography/mass spectrometry
GC/FPD = gas chromatography/flame photometric detector

5.2 CWAs, CWA Precursors, and CWA Degradation Products

In a Norwegian study, different types of wipe samples for collecting HD and GB on solid surfaces were used after the chemical agents had been applied to the area (*35*). Q-tips, cotton cloth (10 cm^2), felt (1.5 cm diameter), and filter paper (1.5 cm diameter) were used as the wipe media. Acetone, IPA, ethyl acetate, and DCM were used as the wetting solvent with each wipe media. Two surfaces were tested as part of this experiment: a painted metal surface with combined layers of epoxy, polyurethane, and alkyd paint (similar to a military vehicle) and a concrete surface (to simulate a building). An artery clamp was used to hold the cotton cloth during sampling while disposable pincers were used for the filter paper and felt. Wipe materials were wetted with one of the aforementioned solvents, and wipe samples were taken from the sampling surface at 5 minutes, 6 hours, and 24 hours after the CWA application. Wipe samples were also taken using dry wipe media. For surface samples contaminated with HD, ethyl acetate-wetted Q-tips had the highest recoveries from painted metal surfaces (between 50 percent and 60 percent). Cotton cloths, however, are recommended by the OPCW (*36*). Higher recoveries were seen for wet over dry wipes after six and 24 hours. Recoveries were less than 0.5 percent for dry Q-tips after six hours and 0.003 percent after 24 hours. Recoveries for Q-tips wetted with ethyl acetate were between 2 percent and 6 percent after six hours and 0.05 percent after 24 hours. Other wetting solvents gave recovery rates similar to that of ethyl acetate.

On concrete surfaces, ethyl acetate wetted wipes gave recoveries of < 6 percent after 5 minutes for both HD and GB. Recovery rates were even lower after 6 hours (< 1 percent for HD). There were no significant differences between Q-tip and cotton cloth wipe recovery rates for HD from concrete surfaces. The Q-tip, however, proved to be easier to use in the field.

Overall, the Q-tip was viewed to be the best medium for sampling solid surfaces for HD and GB (*35*). Better recoveries were found with wetted versus dry wipes, and ethyl acetate was the solvent of choice. It was also discovered that an increase in the amount of time that transpires between the initial application of the CWA and the wipe sample leads to lower recoveries of the agent from the surface. Recovery rates for HD using a Q-tip wetted with ethyl acetate dropped from 44 percent after five minutes on a painted metal surface to 2.4 percent after six hours to 0.05 percent after 24 hours. Thus, the condition of the solid surface as well as the length of time after a contamination would influence the ability to determine the presence of CWAs.

Various other wipe sampling methods have been employed for CWAs. The U.S. and Finland Joint Document describes the use of wipe samples for GA, GB, GD, HD, VX, and Lewisite using a 3" x 3" portion of as well as full Texwipe Clean Cotton Wipes, which are a polyester/cotton blend (*37*). Further sampling details were not provided. In an extension of the U.S./Finnish study evaluating the method's ability to extract all of the CWAs from one wipe, a 9" x 9" TX™ 1020 polyester/cotton blend wipe was used (*38*). The wipe was moistened with IPA before spiking tests were performed.

The OPCW provides guidance for inspectors in collecting on-site wipe samples for scheduled chemicals. Scheduled chemicals include HD, H, HT, Lewisite 1, Lewisite 2, Lewisite 3, GB, GD, GF, GA, thiodiglycol, trimethyl phosphite, dimethyl phosphite, and chloropicrin. OPCW

indicates that a packaged wipe from the sample collection kit should be used for the wipe material (*36*). This is usually an adsorbent wipe made of lint-free cotton. Some of the wipes are wetted with 2 mL of DCM while other are wetted with 2 mL of methanol. To take a sample, a DCM-wetted wipe is held with tweezers or haemostats and rubbed with force in a circular motion over the surface of interest. As necessary, the procedure is repeated with a methanol-wetted wipe.

5.3 Rodenticides

No wipe sampling information was found in the literature for crimidine, methyl fluoroacetate or strychnine.

5.4 Controlled Substances

Matt et al. (*39*) collected wipe samples for nicotine analysis from living room and bedroom (non-upholstered) furniture using pre-screened wipes. The wipes were soaked in 0.1 percent (weight/volume) ascorbic acid. A 100 cm^2 area was sampled. No information was found for PCP.

5.5 Summary

Table 8 summarizes the wipe sampling methods found in the literature for the compounds of interest listed Table 1. Unfortunately, much of the information that was sought for this report was not found in the literature, as indicated by the large number of "NA" designations in the table. In these instances, "NA" indicates that a particular category of information was not found in the reference that is cited. In many cases, only the sampling method was presented in the paper, not the analytical techniques required to test a given sample. Furthermore, most of the cited articles did not specify a particular surface on which to perform the wipe sampling. While most wipe sampling is generally performed on smooth, hard, non-porous surfaces, samples are often taken from many other surface types, as discussed in Chapter 3. Not providing a sampling surface in the referenced documents in Table 8 most likely indicates that the robustness of a particular sampling method beyond general non-porous surface sampling has not been explored. Before these methods could be used on different or novel surface types, surface residue extraction efficiencies would have to be investigated.

Chapter 6
Summary and Data Gaps

6.1 Summary of Available Wipe Sampling Information for Compounds of Interest

Limited wipe sampling information was found in the literature for the compounds of interest presented in Table 1. This section summarizes the literature information that was found by compound class. Information found in the literature summarized in Chapter 5 is used to discuss reasonable extrapolations as to what types of wipe, wetting agents, and techniques might be appropriate for the compounds for which no literature information was found. A general discussion of the information found throughout the report is also presented.

6.1.1 OP Pesticides

As shown in Table 8, literature information was only available for chloropicrin and methyl parathion. The wipe materials used in these studies were lint-free cotton, filter paper, and gauze pads; the wetting solvents used were DCM, methanol, water, and IPA. Surfaces wiped were only noted for methyl parathion wipe samples; the surfaces wiped in those studies were smooth and non-porous.

Specific wipe sampling information was not found for the remaining OP pesticides of interest to this study. However, multiple wipe sampling methods were discussed for chlorpyrifos in Section 3.2. Chlorpyrifos is an OP pesticide. Thus, it would be expected that sampling methodologies for chlorpyrifos could also be applied to other OP pesticides. However, the literature does not provide a consensus on which wipe sampling method is appropriate for all OP pesticides. The chlorpyrifos sampling methods included the use PUF rollers and cotton gauze pads moistened with water, IPA, and isooctane. The use of a cotton gauze pad, wetted with IPA has been used by more than one study and is the current method supported in multiple EPA studies.

6.1.2 CWAs, CWA Precursors, and CWA Degradation Products

The literature on CWAs and their precursor and degradation products indicated that cotton or polyester/cotton blend wipes, as well as Q-tips, have been used for sampling these compounds. The wetting solvents included mostly IPA, DCM, and methanol; with the exception of one study for Sarin (GB) and Mustard (HD) which also used acetone, IPA and ethyl acetate. Water could not be used for CWA wipe samples due to rapid hydrolysis. The studies cited in Table 8 did not agree on what wipe materials and wetting agents were preferable for CWAs. Limited performance data were only available for one study that only focused on wipe sampling for HD and GB (*35*).

Surfaces wiped were only noted in one study by Opstad et al. where painted metal and concrete were sampled. This study determined that an increase in the amount of time that transpires between the initial application of the CWA and the wipe sample leads to lower recoveries of the agent from the surface. This implies that the condition of the solid surface as well as the length of time after a contamination would influence the ability to determine the presence of CWAs.

CWA nerve agents are also OP compounds and behave similarly to OP pesticides. This would seemingly indicate that wipe sampling methods for OP pesticides could be used for the nerve agents in Table 1. In fact, the joint U.S./Finnish method tested wetting the CWA sampling wipes with IPA, the same wipe solvent used in multiple EPA studies (e.g., CTEPP and CHEERS) and is recommended in the ASTM method (*10*).

6.1.3 Rodenticides

No information was found on wipe sampling for the two rodenticides on the target compound list. The ASTM method (*10*) for organic compounds, however, specifies using a gauze wetted with IPA, which could be appropriate for these compounds as well.

6.1.4 Controlled Substances

As described in Section 5.4, only literature on wipe sampling for nicotine was found: cotton gauze, wetted with 0.1 percent ascorbic acid. Non-upholstered furniture were sampled in the cited study. This technique works well for nicotine because of its basic properties. Since PCP is also considered a basic drug, this wipe sampling method could be appropriate for it, too.

6.1.5 General Thoughts on Available Wipe Sampling Information

The literature review of each compound class indicated that cotton wipes are most commonly used. Most hard surface collection techniques for chlorpyrifos (and other OP pesticides) involve the use of some type of gauze pad. The OPCW recommends the use of a cotton cloth for CWA wipe sampling. Cloth or gauze wipes are easily transported, readily wetted, and are convenient for sampling most surfaces. Wipe samples that use cloth or gauze can even be used on more uniquely shaped surface areas. Of course, surfaces such as cement could snag or tear such a wipe material. In these instances, filters, cotton swabs or Q-tips, found to be the best performers in a CWA residue study (*35*), might be better. However, the amount of area that a swab could cover might be problematic. As the ASTM method (*11*) alludes to, gauze pads have been found to contain high background concentrations of potential interferents, depending on what chemical is to be sampled. In such instances where there is an interference, the wipes must be pre-cleaned, removing the potential interferent, before any sampling can occur. This can be costly and time-consuming. In this case, Q-tips or even filters might be better, alternative wipe media to avoid this issue.

As Table 3 indicates, most of the target compounds are readily soluble in organic solvents. The use of water as a wetting agent would then not be desirable, if not for this reason then for the reason that it would cause many of these chemicals to hydrolyze, eliminating the parent compound and leaving behind the hydrolysis products. Alcohol can be used as a suitable solvent for many of the compounds, and IPA appears to have the potential to be a reasonable wiping

solvent for most of the compounds of interest. Even for studies like CHEERS, the IPA wipe was intended not only for sampling of OP pesticides, but also for collecting PBDEs, other pesticides, pesticide metabolites, and perfluorinated compounds. The ASTM method also notes IPA's utility in collecting other compounds besides OP pesticides. Thus, IPA might also be an appropriate solvent for many of the compounds used in Table 1.

One issue of potential concern with IPA-wetted wipes is that heavily wetted wipes are thought to extract chemical residues from within the sampling surface, not just residues on top of the surface. However, when sampling for the chemicals in Table 1, particularly after an attack or decontamination effort, this sampling effect may not be a concern.

IPA was chosen for many studies because of its low toxicity, familiarity to study participants, and ability to not disturb most furniture finishes, because it was to be used mainly around children in EPA studies and on or near people for other studies. If the compounds in Table 1 are to be sampled in a less sensitive environment, then stronger solvents could potentially be used. DCM and methanol are recommended by the OPCW for collecting residual CWAs on surfaces. Ethyl acetate was determined to be a good wipe wetting solvent for the collection of HD and GB from surfaces. This solvent has also proven robust for sampling pesticides and other organic contaminants in exposure assessments, but is not often used because it can mar furniture finishes. Ethyl acetate wipes can, however, be easier to extract than those containing IPA. Given its past performance and ability to work for CWA sampling, ethyl acetate could also be a good wipe wetting solvent for most of the compounds in Table 1. Other solvents, including acetone and DCM, were also found to work reasonably well. These solvents could likely be applied to wipes for other CWAs or pesticides from Table 1, especially if the toxicity of the solvent or the possible destruction of furniture finishes is not a concern.

6.2 Gaps

As described throughout this report, many gaps still exist in determining the best wipe sampling method for the compounds listed in Table 1. Specific wipe sampling information, such as the wipe material and wetting solvent, was not available for many of the compounds of interest. Furthermore, details on the precise wipe method used as well as the performance of the method were often lacking. Before a wipe sampling method can be used for these compounds, existing methods must be fully validated and the gaps that exist must be filled in.

Besides wipe sampling information being missing for many of the compounds of interest (see Table 8), one of the largest data gaps that was found was information on the effects of various surfaces. Wipe samples could potentially be taken from a variety of surfaces. Limited information was obtained from the literature on what techniques or materials are best on different surfaces, or even if there are any surface characteristics (e.g., porous versus non-porous) that might affect or interact with the compounds of interest and affect what is available for collection by a wipe. Gauze pads can be used on most surfaces, and they have been used extensively in the past (and present) to sample multiple household surfaces, toys, furniture, carpet, and hands among others. As noted in Section 3.7, PUF roller samplers have been used for turf and carpet sampling. Most of the sampling methods that were obtained for the compounds in Table 1,

however, do not explore the usefulness of that method on various surfaces. Wiping surfaces from a building decontamination effort would include a large array of different surfaces that would need to be sampled. Thus, it is important to understand how different surfaces might affect the wipe sampling process as well as potentially the compound being sampled. Along these lines, it is also important to also determine the extraction efficiency of the wipe sampling method to determine which is appropriate to use either for a given surface, a given compound, or a combination of the two.

A complicating issue for collecting wipe samples for CWAs (mainly nerve agents and some OP pesticides) is the fact that these compounds can undergo hydrolysis and other environmental breakdown, leaving behind degradation products in place of the parent compound. The wipe sampling discussed in this report focused on the parent compound, not sampling for degradation products, which can also be toxic. Munro et al. *(2)* contains a literature review of chemical agent degradation products and impurities, which can be numerous for a given chemical agent. In this article, a list of known persistent or toxic degradation products for many of the CWAs is provided. Degradation products included in the list that are not part of the target list for this study include diisopropyl methylphosphonate, EA 2192 (S-2-diisopropylaminoethyl methylphosphonothionic acid), ethylmethyl phosphonic acid, isopropyl methylphosphonic acid, and methylphosphonic acid. These degradation products tend to be small molecules and are more polar than the parent compounds. It is possible, however, that the wiping method for the parent compounds could be applied for the degradation products (i.e., IPA would most likely be the appropriate solvent). Any efforts to implement a wipe sampling method for CWAs will need to consider the hydrolysis products and how they fit into the overall sampling and analysis scheme.

Wipe sampling methods have varied across studies found for this report. Some of the methods rely on vertical and horizontal strokes, while others recommend "S" or "Z" patterns, while still others call for more or less wipes per area. Sampling specifics for the compounds in Table 1 are very sparse, if not non-existent. Sampling areas are provided in a couple of studies. For a wipe method to be used properly and provide dependable and repeatable results, specific sampling steps must be followed, including how many wipes will constitute a sample, how much solvent to apply to the wipe, what pattern the area should be wiped in, and the amount of area that should always be wiped. This review did not attempt to investigate sampling designs, or data quality objectives, as this was outside the scope of this study, but these are aspects that must also be considered when applying a wipe sampling method.

6.3 Conclusions

Based on the findings of this literature review, it is clear that there is not an overwhelming consensus on how to take a wipe sample for collecting CWAs, OP pesticides, and other TICs from surfaces. Different methods, media, and wetting solvents have been recommended and used by various groups and studies. Many of the compounds in Table 1 do not even have a specific wipe sampling methodology for their collection. If the goal is to establish a wipe sampling method (or methods) for the compounds discussed in this report, then the next steps in this process must be research to investigate and fill in the gaps in wipe sampling knowledge that exist, followed by method validation to optimize the methods.

Chapter 7
References

1. Munro, N. B., S. S. Talmage, G. D. Griffin, L. D. Waters, A. P. Watson, J. F. King, and V. Hauschild, 1999. The Sources, Fate and Toxicity of Chemical Warfare Agent Degradation Products. *Environmental Health Perspectives.* 107: 933-97.

2. Abercrombie, P. L., 2003. *Physical Property Data Review of Selected Chemical Agents and Related Compounds: Updating Field Manual 3-9.* ECBC-TR-294.

3. Boomer, B. A., M. D. Erikson, S. E. Swanson, G. L. Kelso, D. C. Cox, and B. D. Schultz, 1985. *Verification of PCB Spill Cleanup by Sampling and Analysis*. EPA-560/5-85-026. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC.

4. Kelso, G. L., M. D. Erickson, and D.C. Cox, 1986. *Field Manual for Grid Sampling of PCB Spill Sites to Verify Cleanup*. EPA-560/5-86-017. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC.

5. McArthur, B., 1992. Dermal Measurement and Wipe Sampling Methods: A Review. *Applied Occupational and Environmental Hygiene.* 7(9): 599-606.

6. ARCADIS G&M, Inc., 2005. *Evaluation of the Effectiveness of Coating in Reducing Dislodgeable Arsenic, Chromium, and Copper from CCA-Treated Wood*. Prepared for U.S. Environmental Protection Agency, Air Pollution Prevention and Control Division, Research Triangle Park, NC.

7. ASTM, 2003. E1728-03 Standard Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Lead Determination. *Annual Book of Standards*. Vol. 04.12.

8. Brookhaven National Laboratory, 2006. *Surface Wipe Sampling Procedure*. IH75190. www.bnl.gov/esh/shsd/sop/pdf/IH_SOPS/IH75190.pdf.

9. Federal Register, 2006. Vol. 71, No. 6. 40 CFR Part 745. January 10, 2006.

10. American Society for Testing Materials, 2001. D6661-01 Standard Practice for Field Collection of Organic Compounds from Surfaces Using Wipe Sampling, May 2006. *Annual Book of Standards*. Vol. 11.04.

11. U.S. Department of Agriculture, 2003. *Collecting Wipe Samples for Residue Analysis*. SOP No. EM-24.

12. Morgan, M. K., L. S. Sheldon, C. W. Croghan, J. C. Chuang, R. A. Lordo, and N. K. Wilson. *A Pilot Study of Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP)*. U.S. Environmental Protection Agency, Air Pollution Prevention and Control Division, Research Triangle Park, NC. (http://www.epa.gov/heasd/ctepp/index.htm).

13. Gordon, S., P. Callahan, M. Nishioka, M. Brinkman, M. K. O'Rourke, M. Lebowitz, and D. Moschandreas, 1999. Residential environmental measurements in the National Human Exposure Assessment Survey (NHEXAS) pilot study in Arizona: preliminary results for pesticides and VOCs. *Journal of Exposure Analysis and Environmental Epidemiology.* 9: 456-470.

14. Black, K. G., and R. A. Fenske, 1996. Dislodgeability of Chlorpyrifos and Fluorescent Tracer Residue on Turf: Comparison of Wipe and Foliar Wash Sampling Techniques. *Archives of Environmental Contamination and Toxicology.* 31: 563-570.

15. Nishioka, M., H. Burkholder, M. Brinkman, S. Gordon, and R. Lewis, 1996. Measuring Transport of Lawn-Applied Herbicide Acids from Turf to Home: Correlation of Dislodgeable 2,4-D Turf Residues with Carpet Dust and Carpet Surface Residues. *Environmental Science & Technology*. 30(11): 3313-3320.

16. Nishioka, M., R. Lewis, M. Brinkman, H. Burkholder, C. Hines, and J. Menkedick, 2001. Distribution on 2,4-D in Air and on Surfaces inside Residences after Lawn Applications: Comparing Exposure Estimates from Various Media for Young Children. *Environmental Health Perspectives.* 109(11):1185-1191.

17. U.S. Department of Labor Occupational Safety & Health Administration. *Evaluation Guidelines for Surface Sampling Methods.* OSHA Salt Lake City Technical Center, Salt Lake City, UT.

18. U.S. Department of Labor Occupational Safety & Health Administration. *OSHA Technical Manual.* TED 01-00-015 [TED 1-0.15A]. OSHA Salt Lake City Technical Center, Salt Lake City, UT.

19. Buttner, M.P., P. Cruz, L. D. Stetzenbach, A. K. Klima-Comba, V. L. Stevens, and T. D. Cronin, 2004. Determination of the Efficacy of Two Building Decontamination Strategies by Surface Sampling with Culture and Quantitative PCR Analysis. *Applied and Environmental Microbiology*. 70(8):4740-4747.

20. Sanderson, W. T., M. J. Hein, L. Taylor, B. D. Curwin, G. M. Kinnes, T. A. Seitz, T. Popovic, H. T. Holmes, M. E. Kellum, S. K. McAllister, D. N. Whaley, E. A. Tupin, T. Walker, J. A. Freed, D. S. Small, B. Klusaritz, and J. H. Bridges, 2002. Surface Sampling Methods for *Bacillus anthracis* Spore Contamination. *Emerging Infectious Diseases*.

8(10):1145-1151.

21. Minnesota Department of Health, Minnesota Pollution Control Agency, 2006. *Clandestine Drug Lab General Cleanup Guidance*. (July 2006).

22. Washington State Department of Health, 2005. *Guidelines for Environmental Sampling at Illegal Drug Manufacturing Sites*. (November 2005).

23. Chavalitnitkul, C., and L. Levin, 1984. A Laboratory Evaluation of Wipe Testing Based on Lead Oxide Surface Contamination. *American Industrial Hygeine Association Journal*. 45(5):311-317.

24. Vostal, J.J., E. Taves, J.W. Sayre, and E. Charney, 1974. Lead Analysis of House Dust: A Method for the Detection of Another Source f Lead Exposure in Inner City Children. *Environmental Health Perspectives*. 7:91-97.

25. Fenske, R.A., P.B. Curry, F. Wandelmaier, and L. Ritter, 1991. Development of Dermal and Respiratory Sampling Procedures for Humans Exposure to Pesticides in Indoor Environments. *Journal of Exposure Analysis and Environmental Epidemiology*. 1(1):11-30.

26. American Society for Testing Materials, 2006. D5438-05 Standard Practice for Collection of Floor Dust for Chemical Analysis, October 2006. *Annual Book of Standards*. Vol. 11.03.

27. Camann, D., H. Harding, P. Geno, and S. Agrawal, 1996. *Comparison of Methods to Determine Dislodgeable Residue Transfer from Floors*. EPA/600/SR-96/089. U.S. Environmental Protection Agency, National Exposure Research Laboratory, RTP, NC (August 1996).

28. Fortune C., 1998. *Round-Robin Testing of Methods for Collecting Dislodgeable Residues from Carpets*. EPA/600/SR-97/107. U.S. Environmental Protection Agency, National Exposure Research Laboratory, RTP, NC (January 1998).

29. Nishioka, M., H. Burkholder, M. Brinkman, and R. Lewis, 1999. Distribution of 2,4-Dichlorophenoxyacetic Acid in Floor Dust throughout Homes Following Homeowner and Commercial Lawn Applications: Quantitative Effects of Children, Pets, and Shoes. *Environmental Science and Technology.* 33(9): 1359-1365.

30. Lu, C., and R. Fenske, 1999. Dermal Transfer of Chlorpyrifos Residues from Residential Surfaces: Comparison of Hand Press, Hand Drag, Wipe, and Polyurethane Foam Roller Measurements after Broadcast and Aerosol Pesticide Applications. *Environmental Health Perspectives.* 107(6): 463-467.

31. Lioy, P. J., R. D. Edwards, N. Freeman, S. Gurunathan, E. Pellizzari, J. L. Adgate, J. Quackenboss, and K. Sexton, 2000. House dust levels of selected insecticides and a herbicide measure by the EL and LWW samplers and comparisons to hand rinses and urine

metabolites. *Journal of Exposure Analysis and Environmental Epidemiology.* 10: 327-340.

32. Lemley, A. T., A. Hedge, S. K. Obendorf, S. Hong, J. Kim, T. M. Muss, and C. J. Varner, 2002. Selected Pesticide Residues in House Dust from Farmers' Homes in Central New York State, USA. *Bulletin of Environmental Contamination and Toxicology.* 69: 155-163.

33. Clark, J. M., J. Bing-Canar, S. Renninger, R. Dollhopf, J. El-Zein, D. Star, D. Zimmerman, A. Anisuzzaman, K. Boylan, T. Tomaszewski, K. Pearce, R. Yacovac, B. Erlwein, and J. Ward, 2002. Methyl Parathion in Residential Properties: Relocation and Decontamination Methodology. *Environmental Health Perspectives.* 110(6): 1061-1070.

34. Wasley, A., L. A. Lepine, R. Jenkins, and C. Rubin, 2002. An Investigation of Unexplained Infant Death in Houses Contaminated with Methyl Parathion. *Environmental Health Perspectives*. 110(6): 1053-1056.

35. Opstad, A. M., B. Pedersen, and J. A.Tornes, 1999. *Sampling of Solid Surfaces After an Alleged Use of Chemical Warfare Agent*. FFI/RAPPORT-99/04423. Norwegian Defense Research Establishment, Kjeller, Norway.

36. Swahn, I., 2000. QDOC/LAB/WI/SC005. *Work Instruction for Collection of Wipe Samples On-Site*. Organization for the Prohibition of Chemical Weapons.

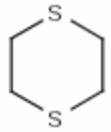
37. *Sample Preparation Method for GC/MS Analysis On Site Joint Document: United States/Finland, Volume 1 February 1996 – December 1997.* Prepared for Defense Threat Reduction Agency, U.S. Department of Defense.

38. Rohrbaugh, D. K., K. B. Sumpter, and M. W.Ellzy, 2003. *Chemical Weapons Convention Verification Technology Research and Development. Evaluation of a Proposed Joint US/Finnish Method for Extraction of Chemical Agents and Their Degradation Products from Wipe Samples*. ECBC-TR-315. Prepared for Defense Threat Reduction Agency, Fort Belvoir, VA. (May 2003).

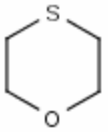
39. Matt, G. E., P.J.E. Quintana, M. F. Hovell, J. T. Bernert, S. Song, N. Novianti, T. Juarez, J. Floro, C. Gehrman, M. Garcia, and S. Larson, 2004. Households contaminated by environmental tobacco smoke: sources of infant exposures. *Tobacco Control*. 13:29-37.

APPENDIX A

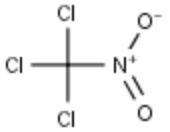
CHEMICAL STRUCTURES FOR THE COMPOUNDS OF INTEREST



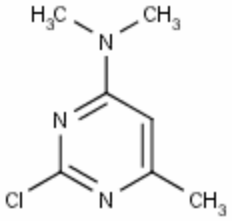
1,4-Dithiane



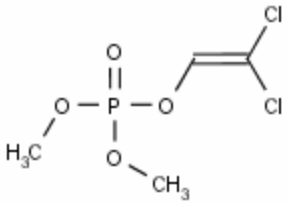
1,4-Thioxane



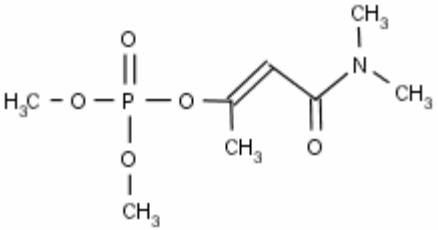
Chloropicrin



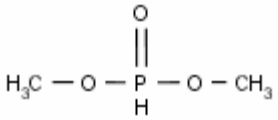
Crimidine



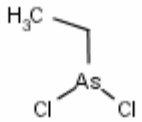
Dichlorovos



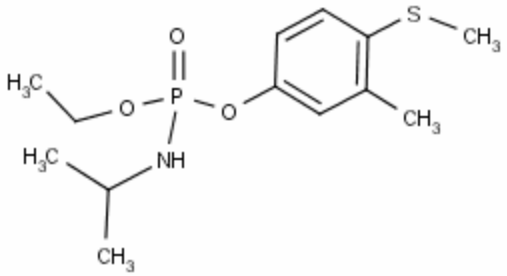
Dicrotophos



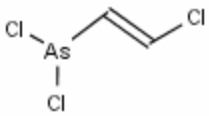
Dimethyl Phosphite



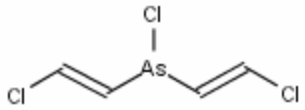
Ethyldichloroarsine (ED)

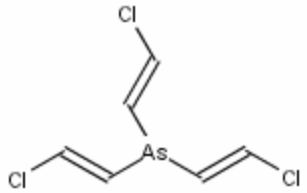


Fenamiphos

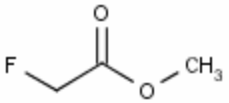


Lewisite (1)

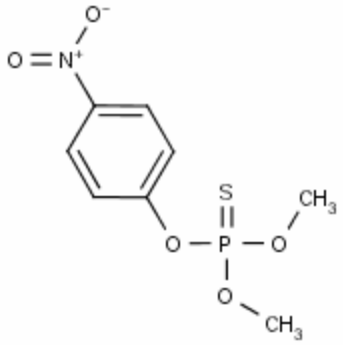




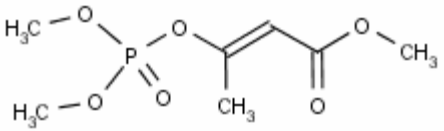
Lewisite (3)



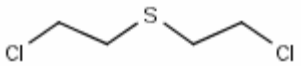
Methyl Fluoroacetate



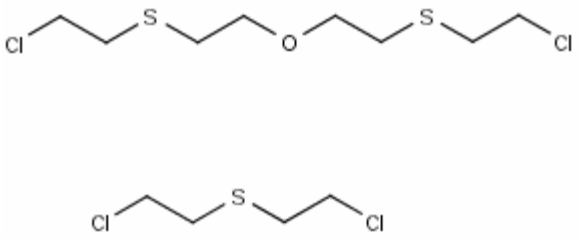
Methyl Parathion



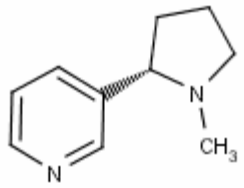
Mevinphos



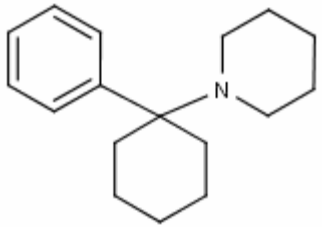
Mustard Gas (H)/
Distilled Mustard (HD)



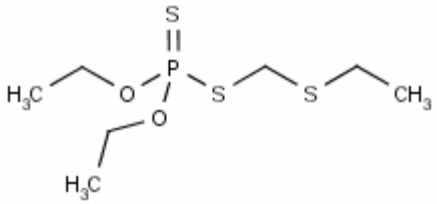
Mustard (HT)



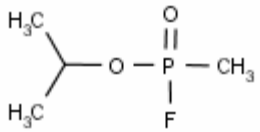
Nicotine



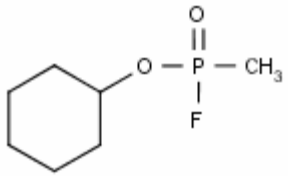
Phencyclidine (PCP)



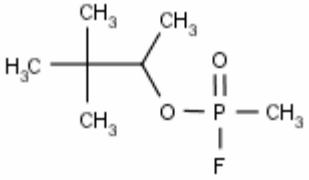
Phorate



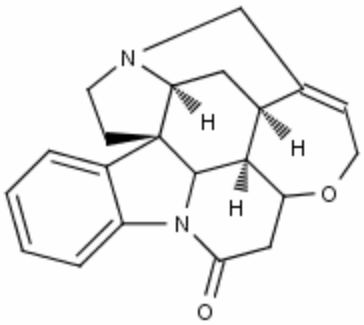
Sarin (GB)



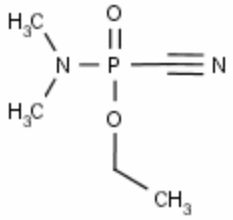
Cyclohexyl sarin (GF)



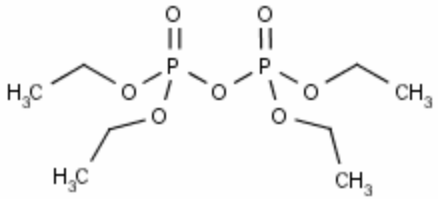
Soman (GD)



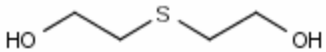
Strychnine



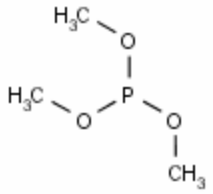
Tabun (GA)



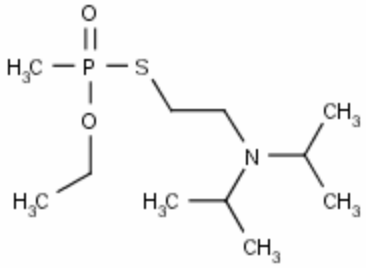
Tetraethyl pyrophosphate (TEPP)



Thiodiglycol



Trimethyl phosphite



VX

United States
Environmental Protection
Agency

Office of Research
and Development (8101R)
Washington, DC 20460

Please make all necessary changes on the below label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐; detach, or copy this cover, and return to the address in the upper left-hand corner.

PRESORTED STANDARD
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use
$300

EPA/600/R-07/004
January 2007
www.epa.gov