

Impact of Revised Airborne Exposure Limits on Non-Stockpile Chemical Materiel Program Activities

Committee on Review and Assessment of the Army Non-Stockpile Chemical Materiel Demilitarization Program: Workplace Monitoring, National Research Council

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IMPACT OF REVISED AIRBORNE EXPOSURE LIMITS ON NON-STOCKPILE CHEMICAL MATERIEL PROGRAM ACTIVITIES

Committee on Review and Assessment of the Army Non-Stockpile Chemical Materiel Demilitarization Program: Workplace Monitoring

Board on Army Science and Technology

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^{*}GEN Keith died on September 9, 2004.

Preface

The Committee on Review and Assessment of the Army Non-Stockpile Chemical Materiel Demilitarization Program: Workplace Monitoring (see Appendix A for committee members' biographies) was appointed by the National Research Council (NRC) to evaluate the impact of then newly promulgated or proposed airborne exposure limits (AELs) for nerve agents and mustard on the program of the U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP).

The chemical demilitarization workforce and neighboring populations must be protected from the risk of exposure to hazardous materials during munition disposal operations and during facility closure. To accomplish this, a program must be in place to monitor hazardous materials in and near the workplace and to monitor workers' activities and health. A previous NRC report examined the programs in place at two stockpile facilities, the Johnston Atoll Chemical Agent Disposal System and the Tooele Chemical Agent Disposal Facility, to monitor concentrations of airborne and condensed-phase chemical agents, agent breakdown products, and other substances of concern. The report concluded that the programs then in place were adequate and recommended the pursuit of improvements in agent monitoring technologies (NRC, 2001c).

Public Law 91-121 and Public Law 91-441 require the Department of Health and Human Services to review Department of Defense plans for disposing of lethal chemical munitions and to make recommendations to protect public health. In the process of meeting these requirements, the Centers for Disease Control and Prevention (CDC) recommended new AELs for nerve agents and published these recommendations in the Federal Register in October 2003 (Federal Register, 2003a). The AELs of the nerve agents were to be monitored starting January 1, 2005. New AELs for mustard were recommended and published in the Federal Register in May 2004 (Federal Register, 2004). Monitoring of mustard will start on July 1, 2005.

The statement of task for the committee was, on its face, limited:

The NRC will establish an ad hoc committee on workplace monitoring at non-stockpile chemical materiel disposal sites and former production facilities. The committee will:

- Review and understand the basis for the Centers for Disease Control and Prevention's (CDC's) newly promulgated airborne exposure limits (AELs) for GA (tabun), GB (sarin), and VX and proposed CDC AELs for mustard agent and assess the safety and process implications of these standards.
- Review and become familiar with facility designs and operational procedures:
 - For destruction of the former production facility at Newport, Indiana, and
 - —For the use of the mobile explosive destruction system and the rapid response system.
- Assess monitoring technologies in use at the existing non-stockpile sites to determine if they are capable of measuring compliance with short- and long-term AELs and determine the degree to which these technologies can be incorporated into overall program monitoring strategies, particularly for the purposes of process verification and environmental permit compliance.
- If existing monitoring methods are not capable of determining compliance with short- and long-term AELs, evaluate the capability of other monitoring that may achieve the same goal.
- Make recommendations on
 - Application of currently used monitoring methodologies to facilitate non-stockpile activities,
 - Capability of currently used measurement technologies to meet future monitoring requirements,
 - Assessing impacts of newly promulgated AELs on worker and public safety aspects,
 - —Alternative measures (e.g., increased personal protective equipment and worker safety training

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- requirements) that may be required to compensate for inabilities to meet standards with existing equipment,
- —Impact of relevant monitoring technologies (for new AELs) and effect on ability to implement in time to meet the CWC treaty deadline, and
- —The critical path regulatory approval and public involvement issues that may arise in developing such a monitoring program.

In light of this specific charge, the committee accepted the new AELs from the CDC as a starting point for its review of the monitoring program. That is, the committee did not evaluate the process used or the end points selected by the CDC in revising the 1988 limits, nor did it take a position on the appropriateness of the 2003/2004 CDC-recommended AELs. Nevertheless, the committee expresses in Chapter 3 its belief that the new AELs will not achieve any risk benefit. This report contains a significant discussion of the 2003/2004

AELs and the differences between them and the 1988 limits, because understanding the degree of uncertainty in the new AELs was necessary to understand the role of monitoring in implementing them.

This study was conducted under the auspices of the NRC's Board on Army Science and Technology (BAST). The chair acknowledges the continued superb support of the BAST director, Bruce A. Braun, and the study director, Nancy T. Schulte. Valuable assistance was provided by Harrison Pannella, Tomeka Gilbert, and James Myska of the NRC staff and by the committee members, who all worked diligently on a demanding schedule to produce this report.

Richard J. Ayen, *Chair*Committee on Review and Assessment of the Army Non-Stockpile Chemical Materiel Demilitarization Program: Workplace Monitoring

Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Barbara Callahan, University Research Engineers and Associates,

Richard A. Conway, Union Carbide Corporation (retired), Gene Dyer, Bechtel Corporation (retired),

Eugene Kennedy, National Institute for Occupational Safety and Health,

David Mummert, Shaw Environmental, Inc., Hyla Napadensky, Napadensky Energetics, Inc. (retired), Kenneth Shuster, U.S. Environmental Protection Agency, William Tumas, Los Alamos National Laboratory, and Calvin Willhite, State of California Department of Toxic Substances Control.

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations nor did they see the final draft of the report before its release. The review of this report was overseen by Stephen Berry, University of Chicago. Appointed by the NRC, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.



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Abbreviations

ACAMS	automatic continuous agent monitoring	GDL	gross detection level
110111110	system(s)	GPL	general population limit
A/DAM	Agilent/Dynatherm agent monitor	GS	diethyl malonate
AEGL	acute exposure guideline	GTR	German Traktor rocket
AEL	airborne exposure limit		
	1	Н	sulfur mustard
CAIS	chemical agent identification set(s)	HD	sulfur mustard (distilled)
CAS	Chemical Abstract Service	HN	nitrogen mustard
CDC	Centers for Disease Control and Prevention	HT	sulfur mustard, T-mustard combination
CFR	Code of Federal Regulations	HVAC	heating, ventilation, and air conditioning
CG	phosgene		
CHPPM	(U.S. Army) Center for Health Promotion and Preventive Medicine	IDLH	immediately dangerous to life and health
CK	cyanogen chloride	L	lewisite
CMA	(U.S. Army) Chemical Materials Agency	LAMS	large area maintenance shelter
CPT	chemical process trailer	LOAEL	lowest observed adverse effect level
CWC	Chemical Weapons Convention		
CWM	chemical warfare materiel	MASP	mobile analytical support platform
		MCE	maximum credible event
DA	diphenylchloroarsine	MDU	metal decontamination unit(s)
DAAMS	depot area air monitoring system(s)	MEA	monoethanolamine
DCD	Deseret Chemical Depot (Utah)	mg	milligram
DET	detonation chamber	MINICAMS	low-level, near-real-time air monitor(s)
DF	binary chemical agent precursor	mm	millimeter
DM	adamsite	MMD	munitions management device
DPE	demilitarization protective ensemble	MPL	maximum permissible limit
		MSD	mass spectrometry detector
EA-2192	product of VX hydrolysis		
EDS	explosive destruction system(s)	NaOH	sodium hydroxide
EIS	environmental impact statement	NECD	Newport Chemical Depot
		NIOSH	National Institute for Occupational Safety
FPD	flame photometric detector		and Health
		NOAEL	no observed adverse effect level
GA	tabun (a nerve agent)	NRC	National Research Council
GB	sarin (a nerve agent)	NRT	near real time
GC	gas chromatograph	NSCM	non-stockpile chemical materiel
GD	soman (a nerve agent)	NSCMP	Non-Stockpile Chemical Materiel Product

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NSCWCC	Non-Stockpile Chemical Weapons Citizens' Coalition	SCANS SCBA SDS	single CAIS access and neutralization system self-contained breathing apparatus spent decontamination solution
O,S-DMP	O,S-diethyl methylphosphonothiolate, a by-product in the manufacture of VX	STEL	short-term exposure limit
OSHA	Occupational Safety and Health Administration	TAP TP TPA	toxicological agent protective triphosgene triphenylarsine
P&A PD	precision and accuracy phenyldichloroarsine	TRO	diethyl methylphosphonate, an oxidation product of a VX precursor
PFPD PIG PINS	pulsed flame photometric detector container for shipping CAIS portable isotopic neutron spectroscopy	TSDF TWA	treatment, storage, and disposal facility time-weighted average
PMNSCM	Product Manager for Non-Stockpile Chemical Materiel	U.S.C.	United States Code
PPE	personal protective equipment	VCS	vapor containment structure
PS	chloropicrin	VX	a nerve agent
psig	pounds per square inch gauge		
PWS	projectile washout system	WPL	worker population limit
QA/QC QL	quality assurance/quality control binary chemical agent precursor	XSD	halogen-selective detector
RAP	regulatory approval and permitting	3X	level of agent decontamination (suitable for transport for further processing)
RCRA RCWM RD&D RRS	Resource Conservation and Recovery Act recovered chemical weapons materiel research, development, and demonstration rapid response system	5X	level of agent decontamination (suitable for commercial release)

Executive Summary

The U.S. Army asked the National Research Council (NRC) to form a committee to advise the Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) on proposed plans for implementing newly recommended limits on airborne concentrations of chemical agents. The limits, called airborne exposure limits (AELs), are designed to protect demilitarization workers, the general public, and emergency responders from the toxic effects of airborne exposure to chemical agents. The Centers for Disease Control and Prevention (CDC) issued AELs in 1988 and revised them in October 2003 (for the nerve agents tabun (GA), sarin (GB), and VX) and May 2004 (for the blister agent mustard (H and HD)). The new limits were to be implemented on January 1, 2005, and July 1, 2005, respectively.

The Army's non-stockpile program is responsible for dismantling former chemical agent production facilities and destroying recovered chemical materiel.³ Assistance from the NRC was requested on means for implementing the 2003/2004 AELs in connection with two specific tasks: (1) the destruction of a former VX production facility at the

Newport Chemical Depot (NECD) in Indiana and (2) the operation of two mobile systems, the explosive destruction system (EDS) and the rapid response system (RRS). The EDS and RRS constitute the non-stockpile program's primary mobile systems for destroying recovered chemical weapons and materiel that were previously buried at military installations and other sites.

The CDC recommended new values for four types of AELs:

- The short-term exposure limit (STEL), for worker exposures of no more than 15 minutes.
- The worker population limit (WPL), for unprotected workers.
- The general population limit (GPL), for the unprotected general population.
- The immediately dangerous to life or health (IDLH) level.

In addition to specifying the length of time workers may operate safely at low levels of exposure, the AELs affect decisions about the personal protective equipment (PPE) workers should wear to avoid exposure and the monitoring equipment necessary to track ambient air concentrations. Table ES-1 further describes these four types of AELs.

COMMITTEE APPROACH

In accordance with the statement of task (see Preface), the committee reviewed facility designs and operational procedures for (1) dismantlement of the former production facility at NECD and (2) the use of the mobile EDS and RRS platforms. Committee members visited NECD to meet with Army and contractor staff tasked with destroying the former VX production facility; other committee members traveled to Dugway Proving Ground (DPG), Utah, to observe monitoring operations during use of the EDS to destroy 4.2-inch mortar rounds. To understand CDC's basis for establishing

¹In addition to former chemical agent production facilities and recovered materiel, the non-stockpile program includes buried materiel (munitions or other), components of binary chemical weapons, and miscellaneous materiel. Non-stockpile chemical materiel (NSCM) is materiel not in the current U.S. inventory of chemical munitions. Much of the NSCM was buried at current and former military installations in 31 states, the U.S. Virgin Islands, and the District of Columbia (U.S. Army, 1996).

²One feature of the chemical warfare materiel destruction program is that the Secretary of the Department of Health and Human Services is required to recommend measures as needed to protect the public health (Federal Register, 2004). In practice, these precautionary measures are determined by the CDC. Accordingly, in response to a request by the Army Surgeon General in June 2000 to review levels proposed by the U.S. Army Centers for Health Promotion and Preventive Medicine (CHPPM) and following publication in the Federal Register of proposed limits and a period of public comment, the CDC issued the new AELs (Federal Register, 2003a, 2004).

³Much of the recovered chemical materiel was buried on current and former military sites and is being recovered as the land is remediated.

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Туре	Definition
Short-term exposure limit (STEL) ^a	The level at which an unprotected worker can operate safely for one or more 15-minute periods (depending on the agent) during an 8-hour workday. The STEL was introduced as part of the 2003/2004 AELs.
Worker population limit $(WPL)^b$	The concentration at which an unprotected worker can operate safely 8 hours a day, 5 days a week, for a working lifetime, without adverse health effects. c
General population limit (GPL)	The concentration at which the unprotected general population can be exposed 24 hours a day, 7 days a week, without experiencing any adverse health effects.
Immediately dangerous to life or health (IDLH) limit	The level of exposure that an unprotected worker can tolerate for 30 minutes without experiencing escape-impairing or irreversible health effects.

^a The traditional definition of a STEL (paraphrased) is the concentration at which a worker may be exposed for 15 minutes up to four times a day with 1 hour between exposures. At the end of the work period, the established time-weighted average (TWA) must be satisfied (ACGIH, 2002).

SOURCE: Adapted from Current and Revised Airborne Exposure Limits for Chemical Warfare Agents, a chart provided by the Chemical Materials Agency at the June 2, 2004, AEL videoconference.

the new AELs for nerve and mustard agents, the committee was briefed by CDC staff, who also provided written responses to questions posed by the committee. The committee was also briefed by the Army and contractor experts and received written responses from them to its questions as well. Numerous documents pertaining to the CDC AELs and the Army's systems, technologies, processes, and procedures for ensuring worker and public safety were also reviewed.

The committee developed recommendations on analytical methods with improved selectivity and sensitivity; on various aspects of near-real-time (NRT) airborne contaminant monitoring; on operational procedures and airborne contaminant monitoring for NECD and the EDS; on the applicability of the Resource Conservation and Recovery Act (RCRA) to the non-stockpile program; and on involving workers and the public in the implementation of the new AELs. This executive summary discusses the committee's primary recommendations only; additional recommendations are included in Chapters 2 through 6.

THE 1988 AND 2003/2004 AIRBORNE EXPOSURE LIMITS

The 2003/2004 AELs were developed using generally accepted methods of setting regulatory limits. Although there are no new data on toxicity beyond those used to establish the 1988 values, the existing data were reevaluated using modified, more conservative methods that reflect present-day practices for establishing uncertainty factors (Federal Register, 2003a, 2004). Because the charge to the committee was narrowly defined, the committee accepted the new CDC-

derived AELs as the starting point for its evaluation of the monitoring program. That is, the committee did not evaluate the process used or the end points selected by the CDC in revising the 1988 limits, nor did it take a position on the appropriateness of the 2003/2004 CDC-recommended AELs. Nevertheless, the committee does express, in Chapter 3, its opinion that the new AELs will not produce a demonstrable risk benefit. This report contains a substantive discussion of the 2003/2004 AELs and the distinctions between them and the 1988 limits, because it was necessary to understand the degree of uncertainty in the new limits in order to understand the role of monitoring in implementing them. Table ES-2 presents the 1988 AELs and the revised (2003/2004) AELs.

New AELs for Nerve Agent

The 2003 WPLs and GPLs for GB were lowered from the 1988 values by a factor of 3 (an "uncertainty factor") to account for individual variability within the worker and general population (Federal Register, 2003a). Since the WPLs for GA and VX are derived from the WPL for GB, the 2003 WPLs for GA and VX were also automatically reduced by a factor of 3. The WPL for VX, however, was further reduced by an additional factor of 3 (a "modifying factor") to account for a sparse database, resulting in a 10-fold total decrease in the WPL from 1988. The CDC adjusted the GPL for VX, 3×10^{-8} mg/m³, upward by a factor of 20, to 6×10^{-7} , so as to obtain a value that was protective for humans and that could be reliably monitored by available monitoring methods (Federal Register, 2002). The CDC justified this

^bThe 1988 WPLs were issued as TWAs—8-hour time-weighted averages—but implemented as ceiling values.

^cFor purposes of quantitative risk assessment, the Occupational Safety and Health Administration considers a working lifetime to be 45 years (Federal Register, 1989).

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TABLE ES-2 1988 and 2003/2004 CDC-Recommended Airborne Exposure Limits for the Nerve Agents GA, GB, and VX (2003) and Sulfur Mustard (HD) (2004)

	Year of Recommendation ^a	Airborne Exposure Limit (mg/m³)		
AEL Type		GA/GB	VX	HD
Short-term exposure limit (STEL) (15 minutes)	1988 2003/2004	N/A 1 × 10 ⁻⁴	N/A 1 × 10 ⁻⁵	N/A 3×10^{-3}
Worker population limit (WPL) (8 hours) ^b	1988 2003/2004	1×10^{-4} 3×10^{-5}	$1 \times 10^{-5} \\ 1 \times 10^{-6}$	3×10^{-3} 4×10^{-4}
General population limit (GPL)	1988 2003/2004	3×10^{-6} 1×10^{-6}	3×10^{-6} 6×10^{-7}	$1 \times 10^{-4} \\ 2 \times 10^{-5}$
Immediately dangerous to life and health (IDLH) limit (real time) ^c	1988 2003/2004	N/A 1 × 10 ⁻¹	N/A 3×10^{-3}	N/A 7×10^{-1}

NOTE: $1 \times 10^{-4} = 0.0001$; $1 \times 10^{-5} = 0.00001$; $3 \times 10^{-3} = 0.003$, etc.

SOURCE: Adapted from Federal Register, 2003a, 2004.

increase in the allowable concentration by noting there was an expectation that any exposure would be identified and corrected within 3 days (72-hour TWA).

STELs and IDLH limits were derived in 2003 for GA, GB, and VX. A STEL of $1 \times 10^{-4} \, \text{mg/m}^3$ was determined for GA and GB, while a STEL of $1 \times 10^{-5} \, \text{mg/m}^3$ was determined for VX (Table 3-1). STELs are defined as exposures that would be acceptable for 15 minutes for unprotected workers. For GA and GB, such exposures should occur not more than four times a day, and at least 60 minutes should elapse between successive exposures. For VX, STEL exposures should occur not more than once a day (Federal Register, 2003a).

New AELs for Mustard Agent

In 2004 the CDC recommended a WPL for HD of 4×10^{-4} mg/m³. This AEL was based on both short-term human data and long-term animal data, the same data used to establish the 1988 AELs. The critical human study incorporated an exposure concentration of 0.06 mg/m³ for 8 hours per day for 3 consecutive days adjusted to a 5-day occupational work week using a factor of 3/5, resulting in a lowest observed adverse effect level (LOAEL)⁴ of 0.036 mg/m³.

In 2004, the CDC also recommended a new 12-hour GPL of 2×10^{-5} mg/m³. This AEL was established using a single

10-hour human exposure of 0.1 mg/m³ and adjusting the 10-hour exposure to 24 hours and the 1-day exposure to 7 days, resulting in a LOAEL of 6×10^{-3} mg/m³. The exposure data were those that had been used to establish the 1988 AELs.

The CDC recommended a 2004 STEL of 3×10^{-3} mg/m³ for no more than one exposure to mustard in a day.

The CDC also recommended a 2004 IDLH limit of 0.7 mg/m³, not to exceed 30 minutes of exposure. The IDLH limit was derived by CDC's National Institute for Occupational Safety and Health (NIOSH) in accordance with structured NIOSH protocols (Federal Register, 2004).

Sulfur mustard is listed as a Part A carcinogen in the National Toxicology Program's Eleventh Report on Carcinogens (DHHS, 2004) and as a Group 1 carcinogen by the World Health Organization's International Agency for Research on Cancer (IARC, 1987). The CDC GPL for sulfur mustard is a 12-hour TWA that reflects typical sampling times used in the stockpile program. The CDC considers that the 2004 GPL, 2×10^{-5} mg/m³, keeps carcinogens below thresholds of significant risk (see Chapter 3) (Federal Register, 2003b). Nevertheless, because of the uncertainties in characterizing the cancer potency of sulfur mustard, the CDC has recommended the 2004 AELs as interim values pending better understanding of the cancer potency of this agent.

Health Effects

The CDC states that the lower 2003/2004 recommended AELs do not reflect a change in or a refined understanding

^aThe CDC recommended airborne exposure limits for GA/GB and VX in 2003 and for HD in 2004.

^bThe 1988 WPLs were issued as TWAs—8-hour time-weighted averages—but implemented as ceiling values.

^cIDLH values for GB and VX were included in Army Regulation AR 385-61, "Army Chemical Agent Safety Program," dated February 28, 1997. The IDLH value for GB was 0.2 mg/m³ and the IDLH value for VX was 0.02 mg/m³. There was no IDLH value for HD prior to the 2004 CDC recommendation in the Federal Register.

⁴The LOAEL is the lowest tested dose of a substance that has been reported to have an adverse effect on the health of people or animals.

of the demonstrated human toxicity of these agents and that no overt adverse health effects have been associated with the exposure limits recommended in 1988. The 2003/2004 values are based not on new or additional scientific data on the toxicity of these nerve agents in humans or animals but on updated and minimally modified risk assessment assumptions (Federal Register, 2003a). Thus, the lower 2003/2004 AELs add a layer of safety (conservatism) to the 1988

recommended AELs that have so far been protective for

CDC's objective in developing new AELs was to protect the health of workers and others who might be exposed to these chemical agents. In response to the new, lower AELs, sufficiently capable monitors must be used. Monitoring at the new AELs at non-stockpile sites is made difficult by the need to detect small quantities of agent with a high degree of confidence, taking into account the monitor's detection limits and the presence of background interferents, to ensure that the AELs are not exceeded.

NON-STOCKPILE PROGRAM

The non-stockpile program involves the carefully planned and executed dismantlement and disposal of the former chemical agent production facility at NECD. The material removed is decontaminated, if necessary, before shipment to offsite recycling or disposal facilities. The program also encompasses the destruction of recovered munitions and chemical items, many of which had been buried at military installations. Depending on the type and condition of the recovered items, they are destroyed in one of two mobile systems—the EDS or the rapid response system (RRS), which the non-stockpile program has developed and fielded for this purpose. The Army has also developed other mobile systems for use on certain types of munitions, but these systems are beyond the scope of this study. For a review of these other systems, see the NRC report Systems and Technologies for the Treatment of Non-Stockpile Chemical Warfare Materiel (NRC, 2002).

Because of their advanced age and, frequently, their deteriorated condition, non-stockpile items require treatment different from that for items in the stockpile program, by which hundreds of thousands of various munitions that have been stored in controlled environments (e.g., storage igloos) are being destroyed in state-of-the-art fixed facilities. In contrast, former production facilities are one-of-a-kind facilities that have been in disuse for over 35 years. Recovered buried chemical munitions such as those found in Spring Valley, in northwest Washington, D.C., are frequently considered unsafe or are otherwise difficult to transport, so that mobile destruction equipment must be transported to the location where they are found.

This report focuses on the unique challenges the nonstockpile program faces in implementing lowered AELs under a schedule constrained by an international treaty deadline⁵ and subject to federal and state environmental regulatory and permitting requirements. The committee notes that at the time this report was being prepared, a second, parallel National Research Council study on issues faced by the stockpile program in implementing the revised AELs was under way.

AIR MONITORING SYSTEMS

MINICAMS and DAAMS are the primary monitoring systems used for the detection of airborne agents at non-stockpile disposal sites, at stockpile disposal sites, and at agent storage facilities. MINICAMS, an automated, near-real-time (NRT) monitoring system, is presently used to monitor for HD, GB, and VX at the CDC's 1988 TWA AELs; for GB and VX at the 1997 IDLH AELs; and for other agents of concern in the non-stockpile program. MINICAMS typically reports the concentration of agent in the air once every 3 to 10 minutes and alarms when agent is detected.

MINICAMS has also been used to monitor for HD at concentrations greater than the 1997 IDLH AEL for this agent. The use of MINICAMS to monitor for GB, HD, and VX at the CDC's 2003/2004 IDLH levels and at the 2003/2004 STELs (numerically equal to the current TWAs) should be straightforward. It will only be necessary to develop and test an analytical method for measurement at the 2004 HD IDLH level, to slightly modify operating parameters for existing IDLH analytical methods for GB and VX, and to test the modified methods.

The main problem for MINICAMS will continue to be monitoring at the STEL for VX (equal to the CDC's 1988 TWA value), especially at the NECD former VX production facility. When monitoring for VX at the TWA level at the NECD, the incidence of false positives—indications of concentrations above some given level when the actual concentrations are below that level—that are caused by phosphorus-containing compounds and other compounds with elution times similar to that of the G-analog of VX may be reduced by reconfiguring or upgrading the MINICAMS to improve its chromatographic resolution for phosphorus-containing compounds that do not undergo conversion to yield the G-analog of VX, that is, O-ethyl methylphosphono-

⁵Under the Chemical Weapons Convention, countries may apply for an extension of the deadline for the destruction of chemical weapons of up to 5 years beyond the original date of April 29, 2007. However, no provision is made for an extension of the deadline for the destruction of former production facilities, so they must be destroyed by April 29, 2007.

⁶The stockpile program uses a totally encapsulated suit with a self-contained breathing apparatus (SCBA), known as the demilitarization protective ensemble (DPE), to enter areas with known high concentrations of agent. The airborne agent concentration limit above which this suit may not be used is 100 mg/m³. ACAMS and MINICAMS have been used to monitor for HD at this concentration, which is much greater than the CDC's new 2004 IDLH value for HD (0.7 mg/m³), for many years. Thus, it should be simple to monitor at the newly defined IDLH level for HD.

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fluoridate. False positives at the TWA for VX caused by phosphorus-containing compounds other than VX that undergo conversion to yield the G-analog of VX may be eliminated by developing a MINICAMS method that can detect VX directly rather than as the G-analog. Both techniques will result in fewer interferences when monitoring for VX. Therefore, it would be preferable to monitor for VX directly and to improve chromatographic resolution. Other automated NRT monitors that have been used or tested include a system based on a thermal desorption unit connected to a gas chromatograph and a newer, improved system based on a continuous air sampler and gas chromatograph. Both are known by the acronym A/DAM. Both can be configured to achieve better chromatographic resolution and, thus, better selectivity than MINICAMS and would be expected to result in fewer false positives for phosphoruscontaining compounds and other compounds with retention times similar to that of the G-analog of VX (for phosphoruscontaining compounds that do not undergo conversion to yield the G-analog of VX). A method has been developed that allows an A/DAM system to determine the presence of VX directly, without the need for derivatization.

Recommendation 4-1: To reduce false positives when monitoring at critical locations susceptible to chemical interferences, the Army should explore ways to improve the gas-chromatographic resolution of the MINICAMS. As an alternative, at critical locations, the Army should consider using the A/DAM system, which can be configured to achieve better chromatographic resolution than the MINICAMS.

DAAMS, a manual monitoring system, is used to confirm or deny MINICAMS alarms—that is, reports of the presence of agent at concentrations greater than the alarm level. Because of its more sophisticated and longer-duration manual sampling and laboratory-based analysis, DAAMS has better gas-chromatographic resolution than MINICAMS. DAAMS has proved effective in monitoring for GB, HD, and VX at the 1988 TWA levels (numerically equivalent to the new STELs) through many years of successful use at non-stockpile and stockpile sites. Confirming or denying MINICAMS alarms at the new STELs will be no more difficult when using the DAAMS technique than confirming or denying alarms at the 1988 TWA levels.

Work is currently under way or has been completed at several stockpile and non-stockpile sites to modify DAAMS methods to meet the requirements of monitoring at the new AELs. Since much of this work appears to be taking place under the guidance of the local monitoring managers only, DAAMS methods and equipment configurations for monitoring at the new AELs could vary widely from site to site, especially because there seems to be only a limited exchange of timely information among the sites and staff at the Chemical Materials Agency (CMA).

Also, agent monitoring efforts at the sites appear to focus only on achieving adequate sensitivities to monitor at the new AELs. There appears to be little or no effort at the site level to improve the selectivity of DAAMS methods. Thus, although it is likely that agents can be detected at the new WPLs (and GPLs) using DAAMS, it is also likely that interference problems will be much more severe for DAAMS than in the past, especially for VX methods based on V-to-G conversion and, perhaps, for HD when using flame-photometric-detector (FPD)-based DAAMS systems. There is a CMA-directed study to improve the sensitivity and selectivity of DAAMS methods, but little information regarding this study is available to local sites, with the exception of the Umatilla, Oregon, stockpile site, where the CMA-modified DAAMS methods are being tested.

Recommendation 4-2: The Army should immediately convene a workshop of non-stockpile and stockpile personnel working on DAAMS methods from each site to allow them to exchange written procedures, test data, and other information regarding the CDC's 2003/2004 AELs. This workshop should also offer presentations by knowledgeable technical personnel involved in the recent CMA-sponsored effort to develop more selective DAAMS methods. Also, the Army should continue to work on improving the selectivity of DAAMS methods, especially FPD-based methods, to further reduce the number of false positive alarms.

ALTERNATIVE TECHNOLOGIES FOR MONITORING AT THE NEW AELS

The CDC's 2003 STEL level for VX, 1×10^{-5} mg/m³, corresponds to a concentration of about one part per trillion by volume. Not only must NRT monitoring systems be capable of detecting VX at this concentration, but they must also be capable of meeting quality assurance/quality control (QA/QC) requirements for concentrations as low as 0.5 part per trillion (equal to 0.50 STEL, the lowest level—other than the blank—used during P&A studies).⁷ In other words, automated detection systems used in the non-stockpile program are actually automated analytical instrument systems. The CDC's 2003 WPL for VX is 1×10^{-6} mg/m³, or about 0.1 part per trillion. The DAAMS method used to monitor at this concentration must also be capable of meeting stringent QA/QC requirements, including passing P&A studies, where the lowest test concentration is about 0.05 part per trillion. In addition to measuring VX at concentrations of less than one part per trillion and meeting QA/QC requirements, auto-

⁷Precision indicates how close together or how repeatable results are. A precise measuring instrument will give very nearly the same result each time it is used. Accuracy indicates how close a measurement is to the accepted value. Precision and accuracy (P&A) studies are used to determine whether instruments fall within required tolerances.

mated and manual methods must be amenable to reliable, long-term operation by relatively nontechnical personnel.

For the new WPL, the only systems capable of achieving the required sensitivity and meeting other stringent requirements for historical and NRT monitoring systems in the near term are systems based on sampling using porous polymers, separation using capillary gas chromatography, and detection using flame photometry. DAAMS systems using mass selective detectors with chemical ionization are also capable of detecting VX at these levels. Other technologies, especially miniature mass spectrometers, may be able to meet the sensitivity and selectivity requirements of NRT monitoring systems in the non-stockpile program at a reasonable cost within 5 years.

Other research and development programs aimed at improving sensitivity, selectivity, and reliability in monitoring for VX, GB, and mustard are under way. The stockpile sites have the largest programs because they have historically been required to monitor at lower levels than the non-stockpile sites.

Recommendation 4-3: PMNSCM should take advantage of research and development being funded by the stockpile program to develop more selective and more sensitive DAAMS methods for monitoring VX and HD at the 2003/2004 WPLs.

Recommendation 4-4: PMNSCM should conduct a paper study of the state of miniature mass spectrometer technologies and, if warranted, support the development of near-real-time (NRT) systems based on the best available technology. The paper study should be done by technical personnel with extensive hands-on experience in air monitoring at the 1988 AELs, who—along with personnel involved in the manufacture of miniature mass spectrometers—should also conduct the effort to develop or modify mass spectrometer systems for NRT monitoring.

Recommendation 4-5: For near-real-time monitoring, the non-stockpile program should meet the 2003/2004 AELs promulgated by the CDC using an approach that establishes a sufficiently high confidence level (that is, a high statistical response rate) for the detection of excursions above 1.00 AEL. The alarm levels for near-real-time (NRT) monitors should then be set to achieve the required confidence.

The purpose of alarm levels is to ensure with a high degree of confidence that an NRT monitoring system will alarm when the true concentration of agent exceeds 1.00 AEL. The non-stockpile program sometimes uses higher alarm levels than

the stockpile program, so agent excursions above 1.00 AEL are sometimes less likely to be detected by the non-stockpile program than by the stockpile program.

Recommendation 4-6: The non-stockpile program should justify sometimes using alarm levels for near-real-time monitoring systems that are different from those used by the stockpile program.

THE X CLASSIFICATION SYSTEM

The Army used the 1988 AELs to determine whether certain types of materials (e.g., contaminated tools and contaminated buildings) posed a further hazard to workers and to implement management systems for secondary waste, much of which is defined as hazardous waste under federal and state hazardous waste laws. Known as the X Classification System, this system defines levels of agent decontamination for materials and waste and defines subsequent management procedures (U.S. Army, 2002). The Army has indicated that it not only will replace the 1988 AELs with the new 2003/2004 AELs for purposes of material and waste classification but also will substantially revise the X Classification System. It says that modification of the X Classification System for decontamination is the most controversial aspect of the whole AEL implementation process and that the main stockpile demilitarization sites have already reported major schedule delays due to permit changes required by the modification.9

The committee observes that the issues involved cut across all of the Army's chemical programs. The impact on the non-stockpile program is relatively minor in comparison with impacts on the other programs. In particular, because the committee believes that the X Classification System under the new AELs is worthy of a more comprehensive examination within a larger study, it has decided not to further examine the subject in this report.

NON-STOCKPILE FACILITIES AND MOBILE TREATMENT SYSTEMS

The 1960s-era facility at NECD for the production of the nerve agent VX produced the U.S. Army's entire 4,400-ton stockpile of VX. Production of VX ceased in 1968. After production ceased, the rooms, pipes, and tanks were flushed and decontaminated using hypochlorite solution and the facility was mothballed. In August 2003, as dismantlement operations were getting under way, air monitoring in Building 143 of the NECD facility detected material suspected to be VX. Subsequent analysis of liquid samples removed from nitrogen piping showed the presence of an oxidized VX

⁸Unlike NRT monitoring systems, which can analyze samples in a matter of minutes, historical monitoring systems such as DAAMS can take as long as 12 hours of sampling to produce results. Thus, the event or situation that caused the detection of agent by DAAMS has probably been detected by other means and corrected by the time the DAAMS sample is analyzed.

⁹Cheryl Maggio, Senior Project Engineer, Chemical Materials Agency, Briefing to the committee, August 3, 2004.

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precursor and VX degradation products. As a precaution, the Army instituted safety procedures to protect workers from possible exposure to potentially toxic organophosphorus compounds, such as VX and related compounds, in Building 143.

Compounds related to VX that may be present in the atmosphere of Building 143 also pose a potential risk to NECD workers. An examination of the chromatograms from analysis of DAAMS tubes shows perhaps two dozen compounds, most of which have not been satisfactorily identified. It is likely that at least some of these compounds are related to VX. The concentrations and toxicity of these unidentified compounds are not known with certainty. Worker protection at the Level B PPE, which includes a supplied air respirator, is recommended for protection of workers dismantling the equipment and building. NECD personnel have been using Levels C and D PPE, which employ an air purifying respirator or no respiratory protection.

Recommendation 2-1: NECD personnel working in Building 143 should be protected by Level B PPE unless the background chemicals are accurately identified, their toxicity estimated, and commensurate risk established.

The alarm set points for the MINICAMS monitoring of airborne VX concentrations at NECD will not be changed after January 1, 2005 (see Chapter 4 for a full discussion of this issue). Since the committee agrees that the new AELs can be implemented for VX at the NECD facility dismantlement project without changing the MINICAMS alarm level, it does not expect an increase in the number or frequency of MINICAMS alarms. Because the new AELs have no effect on MINICAMS STEL monitoring, no process changes are required or recommended.

Recommendation 2-4: In consultation with stakeholders, including regulators, and in accordance with the new implementation guidance at all appropriate non-stockpile sites, PMNSCM should continue to take credit for the protection provided by personal protective equipment when setting alarm levels.

The CMA guidelines for selection of PPE differ from those of general industry, and non-stockpile operation managers can select from an extensive list of Army-approved PPE. The PPE being used for the dismantlement of the NECD production facility, while providing adequate protection against airborne exposure to VX, is not the most advanced in terms of minimizing operator stress and maximizing visibility. At the NECD site, the Army uses multiple layers of protection for workers and the community, including (1) double containment of the work site, (2) monitoring at the location of the dismantlement, and (3) stopping work and starting an investigation of whether corrective action is needed whenever the NRT monitors alarm. Commercial

chemical PPE that has been approved for use by the Army is listed in Appendix D.

Recommendation 2-6: The workers at NECD should be provided with state-of-the-art industrial PPE to minimize fatigue and maximize field of vision. The committee also recommends that PMNSCM consider using the best available PPE that has been certified for use with chemical agents in its other operations.

Two characteristics of the Army's mobile explosive destruction system (EDS), which can be deployed in locations with high population densities, address concerns about operating near a civilian population:

- The EDS is deployed and operated inside a vapor containment structure (VCS) under negative pressure; the VCS uses an exhaust filtration system.
- It is monitored using both near-real-time monitors (MINICAMS) and DAAMS tubes located well beyond the boundaries of the VCS and well beyond the distance at which atmospheric dispersion models predict the concentration of any released chemical agent might present a hazard.

However, the Army does not have a clear policy or set of procedures for the design of site-specific DAAMS perimeter monitoring to protect the general population living near EDS sites.

Recommendation 2-8: To reassure the public that potential agent releases are being monitored for at EDS deployment sites, PMNSCM should develop flexible, written guidelines for the deployment of perimeter air monitors at these sites.

REGULATORY APPROVAL AND PERMITTING, AND PUBLIC INVOLVEMENT

The Army has experienced significant delays in implementing the stockpile destruction program (GAO, 2004). The committee believes that the problems faced by the stockpile program could affect the non-stockpile program as well, especially with regard to environmental permitting issues and public involvement programs. As indicated in prior NRC reports on the non-stockpile program, regulatory approval and permitting (RAP) and public involvement issues have

¹⁰According to the Government Accountability Office (GAO), known as the General Accounting Office until July 2004, delays in implementing the stockpile program stemmed from "incidents during operations, environmental permitting issues, concerns about emergency preparedness, and unfunded requirements." The GAO indicates that if the Army does not resolve the problems that have caused these schedule delays, the United States risks not meeting the CWC treaty deadline to destroy the entire stockpile, even if the deadline is extended to 2012 (GAO, 2004).

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hampered the Army's ability to meet the CWC schedule and increased the cost of compliance as well (NRC, 1999, 2001a, 2001b, 2002, 2004a). The imposition of new AELs presents a new set of challenges for the non-stockpile program. The new AEL worker and community limits will involve a new round of regulatory approvals or amendments to existing approvals and have the potential to give rise to additional regulatory- and public-involvement-related delays and costs in meeting the CWC deadlines.

Constructive engagement with regulators and the public is essential to the completion of chemical materiel disposal in accordance with the CWC schedule. The committee believes that RAP and public acceptance are critical-path items. That is, if regulators or the public at any location raise significant objections regarding any program activity, it will become increasingly difficult for the Army to achieve its programmatic milestones. A proactive public involvement program would help, not only by reducing delays and other obstacles to the accomplishment of the disposal mission but also by providing the basis for resolving unexpected problems if they arise.

Recommendation 6-1: As the Army modifies its safety regulations (AR 385-61 and DA PAM 385-61) to address the new AELs, it should consider incorporating language that would clarify RCRA applicability to non-stockpile operations. In addition, to avoid reinventing the wheel in the many states where mobile treatment systems might be used, the Army should develop templates for modifying RAP when the new AELs are implemented for non-stockpile operations.

For the most part, the non-stockpile program has avoided delays caused by public concern and opposition. Its disposal strategies have earned widespread support, and through the Core Group, it maintains a constructive relationship with the activist public.¹¹

Recommendation 6-4: PMNSCM should develop, in consultation with the non-stockpile Core Group, a model for public involvement in the fielding of mobile systems and the implementation of monitoring systems to protect the general public.

¹¹Established by NSCMP in 1999, the Core Group includes Army personnel from the chemical demilitarization program, representatives of regulatory agencies, and representatives of citizens' groups; it meets twice a year to exchange information about the non-stockpile program.

1

Introduction

ANNOUNCEMENT OF NEW AIRBORNE EXPOSURE LIMITS

This report assesses the impact of newly promulgated airborne exposure limits (AELs) for nerve agents and mustard on the program of the U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP). This program, informally referred to as the non-stockpile program, consists of agent and munition disposal operations and the dismantlement and destruction of former production facilities. Operations range in scope from destruction of a single recovered chemical weapon or a few chemical agent identification sets (CAIS) to destruction of more than 1,200 recovered chemical weapons at the Pine Buff Arsenal (PBA) and dismantlement and destruction of the former VX production facility at the Newport Chemical Depot (NECD), near Newport, Indiana.¹

A much larger program is in place for the destruction of the Army's stockpiled chemical weapons (the stockpile program). The stockpile originally consisted of chemical weapons and storage containers holding over 30,000 tons of agent in eight states and on Johnston Island in the Pacific Ocean (U.S. Army, 2004a). Non-stockpile operations are in general smaller and shorter in duration than stockpile operations. Both programs fall under the direction of the U.S. Army Chemical Materials Agency (CMA), and technical oversight is provided to both programs by the NRC.

For both the stockpile and non-stockpile programs, the operations workforce and the populations in the neighborhood of these operations must be protected against the risks of exposure to hazardous materials. To accomplish this, a

program must be in place to monitor hazardous materials in and near the workplace and to monitor workers' activities and health. A previous NRC stockpile report examined the programs in place for monitoring hazardous materials at two stockpile facilities, the Johnston Atoll Chemical Agent Disposal System (JACADS) and the Tooele Chemical Agent Disposal Facility (TOCDF) (NRC, 2001c).

The Department of Health and Human Services is required by law to review Department of Defense plans for disposing of chemical munitions and to make recommendations to protect public health. Its activities include the establishment of recommended values for AELs, which are the allowable concentrations in the air for occupational and general population exposures to airborne chemical agents. Table 1-1 defines four types of AELs.

In response to a request from the U.S. Army's Office of the Surgeon General in June 2000,² the Centers for Disease Control and Prevention (CDC), in October 2003 and May 2004, recommended new AELs for certain chemical agents (Federal Register, 2003a, 2004). Their implementation by the non-stockpile program is the focus of this report.

Agent can be present in workplace air in vapor or aerosol form or both, but the AELs are independent of agent form. The committee notes that the CDC did not specify an agent's physical state in its Federal Register notices or its background materials. Similarly, Army documentation developed to implement the new AELs for workplace air monitoring did not differentiate between vapor and aerosol exposure.

The new AELs apply to all CMA activities, both stockpile and non-stockpile. However, the committee's focus was limited by the statement of task to certain non-stockpile activities: the demolition of the Army's former VX production facility at NECD and two mobile systems for the destruction

¹Recovered chemical weapons are weapons that were once buried on current and former military sites but were then recovered as the land was remediated. CAIS items, which contain chemical warfare agents, were produced for training purposes before, during, and after World War II. A CAIS holds several glass vessels, each containing a blister or choking agent. These sets were produced in large quantities (approximately 110,000) and in various configurations from 1928 through 1969.

²Letter from BG Lester Martinez-Lopez, Office of the Surgeon General, to Richard J. Jackson, Director, CDC National Center for Environmental Health, June 30, 2000.

TABLE 1-1 Types of Airborne Exposure Limits

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Type	Definition
Short-term exposure limit (STEL) ^a	The level at which an unprotected worker can operate safely for one or more 15-minute periods (depending on the agent) during an 8-hour workday. The STEL was introduced as part of the 2003/2004 AELs.
Worker population limit $(WPL)^b$	The concentration at which an unprotected worker can operate safely 8 hours a day, 5 days a week, for a working lifetime, without adverse health effects.
General population limit (GPL)	The concentration at which the unprotected general population can be exposed 24 hours a day, 7 days a week, without experiencing any adverse health effects.
Immediately dangerous to life or health (IDLH) limit	The level of exposure that an unprotected worker can tolerate for 30 minutes without experiencing escape-impairing or irreversible health effects.

^a The traditional definition of a STEL (paraphrased) is the concentration at which a worker may be exposed for 15 minutes up to four times a day with 1 hour between exposures. At the end of the work period, the established time-weighted average (TWA) must be satisfied (ACGIH, 2002).

SOURCE: Adapted from Current and Revised Airborne Exposure Limits for Chemical Warfare Agents, a chart provided by the Chemical Materials Agency at the June 2, 2004, AEL videoconference.

of recovered chemical weapons—the explosive destruction system (EDS) and the rapid response system (RRS). The committee reviewed and assessed the new recommended AELs, the techniques employed for their revision, the monitoring technologies used for determining compliance with the AELs, the demolition of the former production facility at NECD, and the operation of the two mobile destruction systems. Its assessments of and recommendations on implementing the new AELs are presented in this report.

Because the charge to the committee was narrow, the committee accepted the new CDC-derived AELs as a starting point for its evaluation of the monitoring program. That is, the committee did not evaluate the process used by the CDC in revising the 1988 limits or the end points it selected, nor did it take a position on the appropriateness of the 2003/2004 CDC-recommended AELs. Nevertheless, the committee does point out in Chapter 3 that there is no risk benefit to be gained with the new AELs. It discusses the 2003/2004 AELs at some length, along with how they differ from the prior limits, because understanding the degree of uncertainty in these just-released 2003/2004 AELs was necessary to understand the role of monitoring in implementing the AELs.

The Chemical Weapons Convention (CWC), the nonstockpile program, the NECD demolition project, the EDS, the RRS, and the assessment approach of the committee are described next.

THE CHEMICAL WEAPONS CONVENTION

For several decades, the United States maintained an extensive inventory of weapons containing chemical agents

and chemical agent in bulk storage containers. Details of this inventory were provided in previous NRC reports (NRC, 2002, 2004a). In 1985, on its own initiative, the United States instituted a program to destroy its inventory (NRC, 2004b). Then, in 1993, as a result of the United States' decision to sign and ratify the Chemical Weapons Convention (CWC),³ deadlines were established for the destruction of the entire inventory. The United States and other signatories of the CWC are now in the process of destroying all declared⁴ chemical warfare materiel (CWM) by the treaty deadlines.⁵

U.S. law and international treaties have divided CWM into two categories: stockpile and non-stockpile. Stockpile materiel includes all chemical weapons available for use in combat, plus agent stored in bulk containers. Stockpile materiel was stored at eight locations in the continental

^bThe 1988 WPLs were issued as TWAs—8-hour time-weighted averages—but implemented as ceiling values.

^c For purposes of quantitative risk assessment, the Occupational Safety and Health Administration considers a working lifetime to be 45 years (Federal Register, 1989).

³Formally, the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and Their Destruction. The treaty was signed by the United States on January 13, 1993, and ratified by the U.S. Congress on April 25, 1997. The CWC specifies the time period within which covered categories of chemical warfare material (CWM) must be destroyed.

⁴CWM that remains buried is not subject to the treaty. Once the CWM has been recovered and characterized, it must be declared under the CWC and then be destroyed as soon as possible.

⁵The treaty deadline was set as April 29, 2007, although under the CWC, countries may apply for an extension of the deadline of up to 5 years. It is anticipated that this 5-year extension will be required for destruction of the stockpile inventory. However, no provision is made in the CWC for extension of the April 29, 2007, deadline for destruction of former production facilities.

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United States and on Johnston Island, southwest of Hawaii. Destruction of the materiel stored at Johnston Island has been completed, and destruction of the materiel stored at the eight continental locations is either under way or planned.

Non-stockpile materiel is all other chemical weaponrelated items. It comprises buried CWM, recovered CWM, binary chemical weapons, former production facilities, and miscellaneous CWM. Much of this non-stockpile materiel was buried on current and former military sites but is now being recovered as the land is remediated. Some CWM also is recovered from current and former test and firing ranges. Non-stockpile items that were in storage at the time of the CWC treaty ratification in April 1997 were to be destroyed within 2, 5, or 10 years, depending on the type of chemical weapon and the type of agent. Non-stockpile CWM recovered after treaty ratification must be destroyed "as soon as possible" (U.S. Army, 2001a). In the past, recovered chemical weapons materiel (RCWM) was transported to the nearest stockpile site for safe storage. While such transportation is still an option for the NSCMP program, concerns about the safety of transporting recovered non-stockpile materiel that may be in various states of deterioration across the nation's highways, waterways, and air routes have led to decisions to treat these RCWM at or close to the site where they were discovered. The development of mobile treatment systems such as the EDS and the RRS has made this possible.

THE NON-STOCKPILE CHEMICAL MATERIEL DISPOSAL PROGRAM

Before 1991, the CWM disposal effort was limited to stockpile materiel. The Defense Appropriations Act of 1991 directed the Secretary of Defense to appoint a Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) with responsibility for the destruction of non-stockpile CWM.

Nature and Extent of Sites for Non-Stockpile Items

The most current detailed information available to the committee regarding the numbers, types of agent fills, and explosive configurations of recovered munitions currently stored at the four military sites in the United States that have the largest inventories of non-stockpile materiel is found in Appendix B. According to the CWC, these recovered items must be destroyed by April 29, 2007. About 85 percent of all RCWM in the United States is stored at PBA, in Arkansas (Table B-1, in Appendix B); smaller quantities are stored at Dugway Proving Ground, in Utah (Table B-2), Aberdeen Proving Ground, in Maryland (Table B-3), and Anniston Army Depot, in Alabama (Table B-4). Other sites have smaller quantities (NRC, 2002). Many more chemical munitions will be recovered at burial sites as current and former artillery ranges around the country are remediated; 96 suspect burial locations in 38 states, the U.S. Virgin Islands, and the District of Columbia have been identified.⁶ Whether the munitions recovered to date are representative of those that will be recovered in the future is an open question.

Former CWM Production Facilities

The CWC requires that all former CWM production facilities constructed or used after January 1, 1946, be destroyed. The United States has declared 13 former production facilities in seven states under the CWC. NSCMP was given responsibility for destroying 8 of these facilities, one of which is the former VX production and fill facility (U.S. Army, 1996).

NSCMP has made substantial progress in destroying the facilities for which it is responsible. Demolition of the former VX production facility at NECD was begun in 1998 and was 80 percent complete in January 2004. Demolition is scheduled to be complete by the CWC deadline of April 29, 2007. Since the CWC does not include a provision for extending this deadline, solving any implementation issues at NECD is urgent. Work done prior to January 2004 showed that the nitrogen piping unexpectedly contained small amounts of VX. Also, the facility was found to be contaminated with organic compounds, probably VX precursors or degradation products having analytical signals similar to the signal of VX. Both factors resulted in a higher-than-expected frequency of alarms from the ambient air monitoring system. This situation and the impact on it of the new AELs are an important focus of this report.

MOBILE TREATMENT SYSTEMS

The Army has developed mobile treatment systems to destroy the chemical weapons and chemical samples discovered at scattered sites throughout the United States and to neutralize the contained agent. Sometimes it is not practical for safety or legal reasons to move RCWM from the discovery site to a stationary non-stockpile treatment facility such as the one at Aberdeen or Pine Bluff. In such instances, it is necessary to bring mobile treatment equipment to the place where the recovered chemical item is found or stored.

The recovered chemical munitions and samples fall in two categories, each of which has characteristics that motivated the development of a specialized mobile treatment/ disposal system. The categories are these:

• Chemical weapons ranging from small bomblets to 8-inch artillery projectiles. As detailed in Tables B-1

⁶William Brankowitz, Deputy Product Manager, Non-Stockpile Chemical Materiel Product, Presentation to the Program Manager for the Elimination of Chemical Weapons (PMECW) Technology Workshop, January 28, 2004.

⁷William Brankowitz, Deputy Product Manager, Non-Stockpile Chemical Materiel Product, Presentation to the PMECW Technology Workshop, January 28, 2004.

- through B-4, many items contain explosive or energetic materials in addition to a chemical agent such as mustard blister agent or a nerve agent—for example, sarin (GB) or VX.
- CAIS, which contain small (up to 110 g per item) samples of chemical agent but no energetic component. These sets were used in the World War II era for training purposes. Over 110,000 sets were produced, but there has been no satisfactory accounting for their fate. It is believed that no sets containing nerve agents exist, but a complete set may contain up to six different agents, mainly blister agents—sulfur mustard (H), nitrogen mustard (HN), and lewisite (L)—and industrial chemicals such as phosgene (CG) and adamsite (DM). The toxic component may be present as an undiluted liquid, in a chloroform solution, or as an adsorbate on charcoal (NRC, 1999).

To deal with these two categories of recovered munitions and samples, two families of transportable treatment systems were developed (NRC, 2002).

The explosive destruction system (EDS), which is described in more detail in Chapter 2, is a versatile device that opens a munition by means of an explosive charge within a closed chamber. The explosion detonates any energetic materials in the weapon and provides access to the chemical fill, which is then destroyed by a neutralizing reagent injected into the EDS chamber. The EDS was originally developed to destroy dangerously unstable munitions that could not be transported.8 In practice, however, it has been so successful that it is also being used to destroy stable chemical weapons, whether or not they contain energetics. The Army plans to use multiple EDS units to destroy a large stockpile of recovered chemical munitions stored at PBA (NRC, 2004a).9 The original version of the EDS (EDS-1) is being supplemented by a larger version (EDS-2) that can destroy large munitions like an 8-inch projectile or multiple smaller munitions in a single operation.

The rapid response system (RRS) is a transportable system in which CAIS packages are opened in a glove box. Individual vials and bottles in the package are characterized visually and spectroscopically. Those containing industrial chemicals (e.g., CG) are repackaged and shipped to a treatment, storage, and disposal facility (TSDF) for destruction. Vessels containing blister agents—H, sulfur mustard

(distilled) (HD), HN, L—are crushed in a small reactor containing a neutralizing reagent. The neutralent and associated solid materials are packaged and shipped to a TSDF for ultimate disposal. The RRS is described in more detail in Chapter 2 and in previous NRC reports (NRC, 1999, 2001b, 2002). The RRS can be either driven or flown to locations where CAIS have been recovered. The RRS is intended to be used at sites where many CAIS vials and/or PIGs—containers for shipping CAIS—containing CAIS sets are found. If only a few CAIS vials are found at a site, PMNSCM deploys a single CAIS accessing and neutralization system (SCANS). 10

MOBILE SYSTEMS USE AND MONITORING REQUIREMENTS

In contrast to fixed facilities such as the NSCMP munitions assessment and processing system at Aberdeen Proving Ground, the mobile treatment systems are used in widely varying environments that may dictate different air monitoring requirements, especially for the protection of the general population.¹¹ The types of locations vary, from isolated military reservations, such as Dugway Proving Ground in Utah, to densely populated urban settings, such as the Spring Valley development in Washington, D.C. The need to protect workers at the site is a constant, but protective measures for the general population, such as perimeter monitoring, may vary widely. The current and projected use settings for the EDS and RRS are described below. The operational procedures and activities of the workforce are discussed in Chapter 2. Current air monitoring equipment and procedures are described in Chapter 3 in terms of both protecting workers and ensuring the health and safety of the general population.

In the course of qualifying tests and initial operations at Deseret Chemical Depot in Utah, the first RRS unit (the only one constructed to date) successfully destroyed 1,226 individual CAIS items. In its first field deployment, the RRS was used at Fort Richardson, Alaska, to destroy eight RCWM CAIS PIGs, five RCWM CAIS laboratory packs, and one 85-gallon drum of gear suspected to be contaminated.¹²

A RCRA permit application for operation of the RRS at PBA was submitted to the state of Arkansas in July 2003. The Pine Bluff site will be home base for the RRS and its operating team. When it is not deployed to field sites, it will be used to destroy the inventory of CAIS at Pine Bluff.

⁸Whether a munition can be moved is determined by Army technical escort personnel. Several factors are considered in making this decision, including (1) whether the munition is fuzed or unfuzed, (2) if fuzed, whether it is armed (i.e., if the munition was deployed as designed but failed to function properly), and (3) the severity of deterioration of the munition body and the physical state of the agent fill.

⁹John Gieseking, Group Leader, Pine Bluff Non-Stockpile Facility, Presentation to the Resource Conservation and Recovery Act (RCRA) preapplication meeting for the Pine Bluff Explosive Destruction System at Pine Bluff Arsenal, April 22, 2004.

¹⁰Operations involving SCANS were outside the scope of this report.

¹¹The general population is considered to be more sensitive to chemical agent exposure than the military population and more casualties would be expected. The reason for this is that the general population includes children, the elderly, unhealthy individuals, and a higher percentage of susceptible individuals than the military population.

¹²William Brankowitz, Deputy Product Manager, Non-Stockpile Chemical Materiel Product, Presentation to the PMECW Technology Workshop, January 28, 2004; Dave Hoffman, Rick DiMauro, Tom Rosso, and Brett Sims, Presentation to the committee, June 16, 2004.

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TABLE 1-2 1988 and 2003/2004 CDC-Recommended Airborne Exposure Limits for the Nerve Agents GA, GB, and VX (2003) and Sulfur Mustard (HD) (2004)

	Year of Recommendation ^a	Airborne Exposure Limit (mg/m³)		
AEL Type		GA/GB	VX	HD
Short-term exposure limit (STEL) (15 minutes)	1988 2003/2004	N/A 1 × 10 ⁻⁴	N/A 1 × 10 ⁻⁵	N/A 3×10^{-3}
Worker population limit (WPL) (8 hours) ^b	1988 2003/2004	1×10^{-4} 3×10^{-5}	$1 \times 10^{-5} \\ 1 \times 10^{-6}$	3×10^{-3} 4×10^{-4}
General population limit (GPL)	1988 2003/2004	3×10^{-6} 1×10^{-6}	3×10^{-6} 6×10^{-7}	$1 \times 10^{-4} \\ 2 \times 10^{-5}$
Immediately dangerous to life and health (IDLH) limit (real time) ^c	1988 2003/2004	N/A 1 × 10 ⁻¹	$N/A \\ 3 \times 10^{-3}$	N/A 7×10^{-1}

NOTE: $1 \times 10^{-4} = 0.0001$: $1 \times 10^{-5} = 0.00001$: $3 \times 10^{-3} = 0.003$, etc.

SOURCE: Adapted from Federal Register, 2003a, 2004.

BACKGROUND

Overview of New Airborne Exposure Limits

One feature of the CWM destruction program is that the Secretary of the Department of Health and Human Services is required to recommend measures as needed to protect the public health (Federal Register, 2004). In practice, these recommended precautionary measures are determined by the CDC, an agency of the Department of Health and Human Services, and include development of AELs for the general public, demilitarization workers, and emergency responders.

Specifically, AELs are issued for tabun (GA, or ethyl N,N-dimethyl-phosphoramidocyanidate, CAS 77-81-6); sarin (GB, or O-isopropyl-methylphosphonofluoridate, CAS 107-44-8); VX (O-ethyl-S-(2-diisopropylaminoethyl)-methylphosphonothiolate, CAS 50782-69-9); and sulfur mustard (H, HT, and HD, or bis(2-chloroethyl) sulfide, CAS 505-60-2). Table 1-2 presents the old (1988) and revised (2003/2004) airborne exposure limits.

In June 2000, the Army asked the CDC to review a proposal by the U.S. Army Center for Health Promotion and Preventive Medicine to reevaluate the existing 1988 AELs for chemical warfare agents and to develop new ones.¹³

Following a period of public review, the CDC issued new values for TWAs and GPLs. The TWAs for GA and GB were reduced to 1/3 of their 1988 values, the TWA for VX was reduced to 1/10 of its 1988 value, and the TWA for HD was reduced to 1/8 of its 1988 value. The GPLs for GA and GB were reduced to 1/3 of their 1988 values, the GPL for VX was reduced to 1/5 of its 1988 value, and the GPL for HD was reduced to 1/5 of its 1988 value. For H and HD, the CDC recommended "retaining the proposed GPL for perimeter monitoring stations at demilitarization facilities and evaluation of the allowable stack concentrations" (Federal Register, 2004, p. 24165). For GA, GB, and VX, the CDC recommended that the GPL "not [be] exceeded at the installation boundary as a consequence of a release ..." (Federal Register, 2003a, p. 58351). In addition, the CDC issued revised values for the immediately dangerous to life or health (IDLH) limit and for the short-term exposure limit (STEL). The IDLHs for GA/GB, VX, and HD were set at 0.10, 0.003, and 0.70 mg/m³, respectively. The STELs for GA/GB, VX, and HD were set at 1×10^{-4} , 1×10^{-5} , and 3×10^{-3} mg/m³, respectively.

Implementation of the new AEL values for the nerve agents GA, GB, and VX is required by January 1, 2005; for the blister agents H and HD it is required by July 1, 2005 (Federal Register, 2003a, 2004). See Chapter 3 for a more complete discussion of the issuance of the new AELs.

^aThe CDC recommended airborne exposure limits for GA/GB and VX in 2003 and for HD in 2004.

^bThe 1988 WPLs were issued as TWAs—8-hour time-weighted averages—but implemented as ceiling values.

^cIDLH values for GB and VX were included in Army Regulation AR 385-61, "Army Chemical Agent Safety Program," dated February 28, 1997. The IDLH value for GB was 0.2 mg/m³ and the IDLH value for VX was 0.02 mg/m³. There was no IDLH value for HD prior to the 2004 CDC recommendation in the Federal Register.

¹³BG Lester Martinez-Lopez, Office of the Surgeon General, Letter to Richard J. Jackson, Director, CDC National Center for Environmental Health, June 30, 2000.

TABLE 1-3 Equivalent Unit Nomenclatures for AEL Concentrations

Milligram Units (decimal)	Milligram Units (exponential)	Microgram Units	Nanogram Units
0.1 mg/m^3	$1.0 \times 10^{-1} \text{ mg/m}^3$	100 μg/m ³	100,000 ng/m ³
0.01 mg/m^3	$1.0 \times 10^{-2} \mathrm{mg/m^3}$	$10 \mu g/m^3$	$10,000 \text{ ng/m}^3$
0.001 mg/m^3	$1.0 \times 10^{-3} \mathrm{mg/m^3}$	$1 \mu g/m^3$	$1,000 \text{ ng/m}^3$
0.0001 mg/m^3	$1.0 \times 10^{-4} \text{ mg/m}^3$	$0.1 \mu g/m^3$	100 ng/m^3
0.00001 mg/m^3	$1.0 \times 10^{-5} \mathrm{mg/m^3}$	$0.01 \mu g/m^3$	10 ng/m ³
0.000001 mg/m ³	$1.0 \times 10^{-6} \mathrm{mg/m^3}$	$0.001 \mu g/m^3$	1 ng/m^3
0.0000001 mg/m^3	$1.0 \times 10^{-7} \mathrm{mg/m^3}$	$0.0001 \mu g/m^3$	0.1 ng/m^3

Units for Airborne Concentration Levels

Airborne concentrations for chemical agents have been reported using a variety of numerical conventions. While an individual organization tends to be more or less consistent in the manner in which it reports airborne concentrations, different organizations have used different units (milligrams, micrograms, or nanograms) and different means of expression (decimal values or exponential values). Table 1-3 shows equivalent expressions (across each row) for airborne concentrations. Each row shows a concentration 10 times less than the row above it. The first column shows decimal units in milligrams per cubic meter (mg/m³). The second column shows the equivalent concentration using an exponential expression. The third column shows the equivalent value in micrograms per cubic meter (µg/m³), and the fourth column in nanograms per cubic meter (ng/m³). Historically, the Army has most often used the unit milligrams per cubic meter (mg/m³), expressed as a decimal (see Column 1 in Table 1-3). This report gives concentration values in milligrams per cubic meter but expresses them in exponential form.

Applicability to Non-Stockpile Monitoring Environments

This report addresses the measurement of airborne concentrations of VX during the dismantlement of the Army's former VX production facility at NECD and of nerve agent and the blister agents H and HD during the operation of two mobile chemical weapon destruction systems. The workplace monitoring technologies currently in use are reviewed to determine whether they are capable of (1) reliably indicating that workers involved in these operations are not exposed to dangerous levels of airborne nerve or mustard agent, through either short-term or long-term exposure, (2) reliably indicating that the general public in the vicinity of these operations is not exposed to dangerous levels of airborne nerve or mustard agent, through either short-term or longterm exposure, and (3) verifying compliance with applicable permits and regulations. The report also addresses the adequacy of current engineering controls and personal protective equipment (PPE) to protect workers from exposure to agent in excess of allowable limits. Based on the results of these reviews, appropriate follow-on actions are recommended.

Non-Stockpile Sites Addressed

This report specifically addresses the impact of the new AELs on (1) the demolition of the former VX production facility at NECD, (2) operation of the RRS for the destruction of CAIS, and (3) operation of the EDS for the destruction of recovered chemical weapons. For the RRS, the location of interest is the Pine Bluff Arsenal. For the EDS, the locations of interest are Aberdeen Proving Ground, in Maryland; Dugway Proving Ground, in Utah; and the Pine Bluff Arsenal, in Arkansas.

STATEMENT OF TASK

The following statement of task was prepared for the National Research Council by the Army:

The NRC will establish an ad hoc committee on workplace monitoring at non-stockpile chemical materiel disposal sites and former production facilities. The committee will:

- Review and understand the basis for the Centers for Disease Control and Prevention's (CDC's) newly promulgated airborne exposure limits (AELs) for GA (tabun), GB (sarin), and VX and proposed CDC AELs for mustard agent and assess the safety and process implications of these standards.
- Review and become familiar with facility designs and operational procedures:
 - For destruction of the former production facility at Newport, Indiana, and
 - —For the use of the mobile explosive destruction system and the rapid response system.
- Assess monitoring technologies in use at the existing non-stockpile sites to determine if they are capable of measuring compliance with short- and long-term AELs and determine the degree to which these technologies can be incorporated into overall program monitoring strategies, particularly for the purposes of

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- process verification and environmental permit compliance.
- If existing monitoring methods are not capable of determining compliance with short- and long-term AELs, evaluate the capability of other monitoring that may achieve the same goal.
- · Make recommendations on
 - Application of currently used monitoring methodologies to facilitate non-stockpile activities,
 - Capability of currently used measurement technologies to meet future monitoring requirements,
 - Assessing impacts of newly promulgated AELs on worker and public safety aspects,
 - —Alternative measures (e.g., increased personal protective equipment and worker safety training requirements) that may be required to compensate for inabilities to meet standards with existing equipment,
 - —Impact of relevant monitoring technologies (for new AELs) and effect on ability to implement in time to meet the CWC treaty deadline, and
 - —The critical path regulatory approval and public involvement issues that may arise in developing such a monitoring program.

SOURCES OF INFORMATION

At its meetings, the committee received a number of briefings (see Appendix C) and held subsequent deliberations. The committee is grateful to the many individuals, particularly LTC Paul Fletcher, the Product Manager for Non-Stockpile Chemical Materiel at the time the committee was formed; William R. Brankowitz, Deputy Product Manager, and, from June 2004, Acting Product Manager, Non-Stockpile Chemical Materiel; and the NSCMP program and CMA staff members, who provided technical information and insights during these briefings. The committee received valuable briefings from Cheryl Maggio of the CMA on the rationale for the establishment of the new AELs and on various aspects of their implementation. Terry Frederick, the Tennessee Valley Authority manager for non-stockpile projects, was very helpful in developing the committee's understanding of the operations at NECD. Committee members and staff visited the former VX production facility at NECD and the Dugway Proving Ground, Utah, to observe monitoring operations during use of the EDS. Valuable information was also obtained from recent reports prepared by other organizations. These included the following:

 Evaluation of Monitoring Technologies, Phases 1 and 2-Final Report, prepared for the U.S. Army Chemical Materials Agency, Aberdeen Proving Ground, Md., FOCIS Associates Inc., October 14, 2003.

- Implementation Guidance Policy for Revised Airborne Exposures Limits for GB, GA, GD, GF, VX, H, HD, and HT, Department of the Army, Office of the Assistant Secretary of the Army, Installations and Environment, June 18, 2004.
- Final Recommendations for Protecting Human Health from Potential Adverse Effects of Exposure to Agents GA (Tabun), GB (Sarin), and VX, Federal Register, Vol. 68., No. 196, pp. 58348–58351, October 9, 2003.
- Interim Recommendations for Airborne Exposure Limits for Chemical Warfare Agents H and HD (Sulfur Mustard), Federal Register, Vol. 69, No. 85, pp. 24164–24168, May 3, 2004.
- Programmatic Monitoring Concept Plan–Final, U.S. Army Chemical Materials Agency, June 2004.
- Programmatic Laboratory and Monitoring Quality Assurance Program-Final, U.S. Army Chemical Materials Agency, June 2004.
- Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 3, National Research Council, 2003.
- Occupational Health and Workplace Monitoring at Chemical Agent Disposal Facilities, National Research Council, 1994.

This information provided a sound foundation for the committee's deliberations.

STRUCTURE OF THIS REPORT

Chapter 2 describes the former VX production site at NECD and the mobile destruction systems (the EDS and the RRS). It gives the history of the former VX production site, the main features of the facility, and the procedures being used for its demolition. It also gives more detailed descriptions of the RRS and EDS, focusing on the operational protocols for these systems and reviewing their operational history. Chapter 2 also provides information on current airborne monitoring protocols for the NECD demolition project and for operation of the EDS and the RRS. Chapter 3 addresses the reasons for establishing new AELs and their impacts on worker and public safety and health. The airborne exposure monitoring systems currently in use, including DAAMS and MINICAMS, are reviewed in Chapter 4, which also assesses the ability of the current monitoring technologies and systems to satisfy the new AELs and discusses anticipated needs for monitoring technology upgrades. The process implications of the new AELs are assessed in Chapter 5. Chapter 6 comments on regulatory approval, permitting, and public involvement issues.

2

A Non-Stockpile Facility and Two Mobile Treatment Systems

FORMER PRODUCTION FACILITY AT NEWPORT, INDIANA

The Newport (Indiana) Chemical Depot (NECD) facility for the production of the nerve agent VX was built in 1959 and 1960. During a 7-year period beginning in 1961 it produced the U.S. Army's entire 4,400-ton stockpile of VX. Weapons were shipped there, filled with VX, and then shipped to U.S. defense sites around the world. The plant complex for the four-step production of VX included a multistory production facility (Building 143); storage tanks, fill equipment, ancillary systems (located in Building 144); and scrubber towers (all are shown in Figure 2-1).

The production of VX was halted in 1968 by President Richard Nixon. The NECD facility was mothballed after the vessels and piping that were known to contain or believed to potentially have contained VX had been decontaminated. The facility was then left undisturbed for a number of years until preparations were made for its dismantlement and destruction in compliance with the Chemical Weapons Convention (CWC).

Process steps at the NECD facility were designated Steps 0, 1, 2, and 3. The first three steps produced chemicals that, when combined with sulfur in Step 3, produced VX agent. Step 3 took place in a separate enclosed building (Building 143). After manufacture, the VX was placed in bulk storage tanks from which various munitions and storage containers (e.g., ton containers) were filled using specialized filling machines that occupied a section of Building 144 (adjacent to Building 143).

In 1998, the Army began demolishing the portions of the NECD facility used for Steps 0, 1, and 2. The Step 3 equipment in Building 143 and the bulk storage tanks are being dismantled at present. When these activities, together with the destruction of the filling machines and demolition of all buildings, are finished, the dismantlement and destruction of the former VX production facility in accordance with the terms of the CWC treaty will be complete.

Condition of the NECD Facility Buildings

The following description of the NECD former production facility is based on presentations by Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) staff and contractors and on observations by some committee members during a site visit. Building 143 was reported to be in generally good condition, with double wall construction and insulation between the walls. One section of wall has been damaged by corrosion. The equipment and piping in the two upper floors (5 and 6) have been almost completely demolished and the piping and equipment in the next floor (4) have been demolished to the point where there is now adequate access to the remaining piping. The equipment and piping in the contaminated rooms in the lower floors (1, 2, and 3) remain largely intact but accessible.

The structural members of Building 143 were reported to be in excellent condition. However, some of the flooring and wall panels have been corroded by exposure to the bleach/ caustic rinse that was used during decontamination activities in the past. These corroded areas have been replaced or modified so that the building is safe to work in.

Building 144, where the munition filling machines are located, was reported to be in excellent condition. The section of Building 144 where these machines are located can be isolated from the remainder of the building.

Building 143 is being worked on. The current dismantling procedures involve the cutting of pipe, vessels, and other materials and the transfer of these materials to a storage and decontamination area. When all of the internal piping and equipment has been removed, Building 143 will have been demolished. The filling equipment will also be dismantled and Building 144 demolished as part of the project at NECD.

VX Exposure Issues

When the NECD facility was mothballed, the tanks, piping, reactors, and product storage tanks within Building 143 and

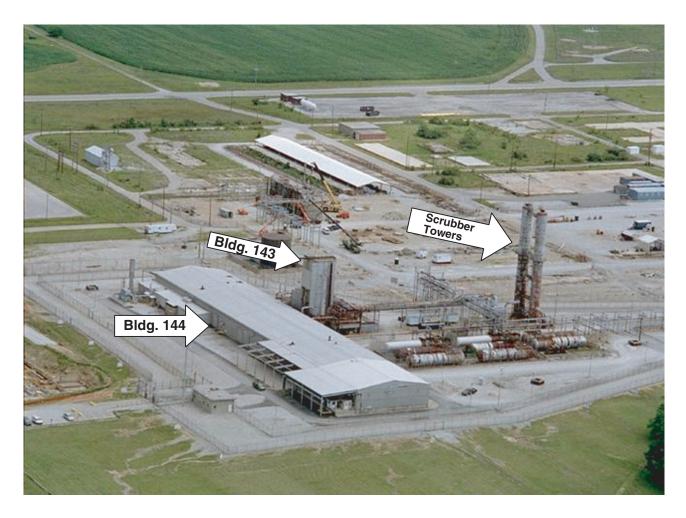


FIGURE 2-1 Former VX production facility at NECD. From left to right are Building 144, housing filling and ancillary equipment; multistory Building 143, housing the VX production facility; and scrubber towers. SOURCE: Terry Frederick, Tennessee Valley Authority, Briefing to the committee, September 14, 2004.

elsewhere in the facility that were known to contain VX or believed to possibly have contained it were flushed and decontaminated using hypochlorite (bleach) solution. This decontamination was apparently effective in removing VX from these systems. However, during the dismantling of Building 143 in August 2003, air monitoring detected material that was suspected to be VX. The source of the material was suspected to be a 0.5-inch nitrogen line. Nitrogen had been used for purging tanks and reactors throughout Building 143, for transferring liquids using pressure, and in the munitions filling process in Building 144.

Sometime between September 2003 and February 2004, a liquid sample of VX was collected from a nitrogen line in the bulk agent storage area. Ongoing monitoring confirmed the presence of the oxidized VX precursor diethyl methylphosphonate (TRO) and the degradation product O,S-diethyl methylphosphonothiolate (O,S-DMP), which was detected as VX. These compounds were thought to be the cause of

numerous and continuing MINICAMS¹ alarms in Building 143. The alarms continued to be a problem until the time when portions of the building were air conditioned (see later in this chapter for a more complete discussion of this issue).

In February 2004, the nitrogen lines in Building 143 were sampled. The analysis from the first sample location on the

¹MINICAMS is the registered trade name for a low-level, near-real-time monitor typically used to provide early warning of airborne exposure hazards. The MINICAMS unit is an automated air sampling system that collects compounds, thermally desorbs them into a capillary gas chromatography column for separation, and detects the compounds with a flame photometric detector (FPD) operated in the sulfur- or phosphorus-selective mode. At NECD, the MINICAMS is operated in the phosphorus-selective mode, which enables the device to discriminate against those compounds that do not contain phosphorus and hence cannot be VX, which contains a phosphorus atom. The combined sampling and analysis time for the MINICAMS is 3 to 10 minutes, depending on the agent being examined (U.S. Army, 2003a).

main nitrogen branch feeding the building revealed the presence of VX degradation products. At the second location, downstream of the first sample point, VX degradation products were also revealed.

Personal Protective Equipment and Worker Operations

The staff performing dismantling operations at the NECD currently wear personal protective equipment (PPE) as described in Table 2-1 and Figures 2-2 through 2-4. The type of PPE and clothing reflect current practices. When the new airborne exposure limits (AELs) promulgated by the CDC become effective in 2005, these practices may be altered. However, the *Implementation Guidance Policy for Revised Airborne Exposures Limits for GB, GA, GD, GF, VX, H, HD, and HT*, which describes implementation guidance to address the new AELs, states that the intent is not to increase the level of PPE (U.S. Army, 2004b).

TABLE 2-1 Types of PPE Currently Employed at the NECD Former VX Production Facility

Type of PPE	Description
Level B	Supplied air respirator with 45-minute SCBA, plus TAP suit—a butyl rubber suit with hood (see Figure 2-2).
Level C	Air-purifying respirator (M40 at NECD), plus disposable coveralls (may be modified to include additional dermal protection, including splash protection and head cover), hard hat, and protective work shoes (see Figure 2-3).
Modified Level D	Hard hat and protective work shoes. No respiratory protection. Skin protection selected according to the task being performed. May include disposable coveralls, chemical-resistant gloves, apron, face shield, etc. M40 mask is carried for emergency use.
Level D	No respiratory protection, protection provided for street clothes, may use reusable or disposable coveralls, hard hat, and protective work shoes. M40 mask is carried for emergency use (see Figure 2-4).

NOTE: SCBA, self-contained breathing apparatus; TAP, toxicological agent protective. Level A PPE provides the greatest amount of dermal and respiratory protection and consists of a fully encapsulating chemical protective suit and a supplied air respirator. Level A PPE is not used at the NECD former production facility because this highest level of protection is not needed for NECD dismantling operations.

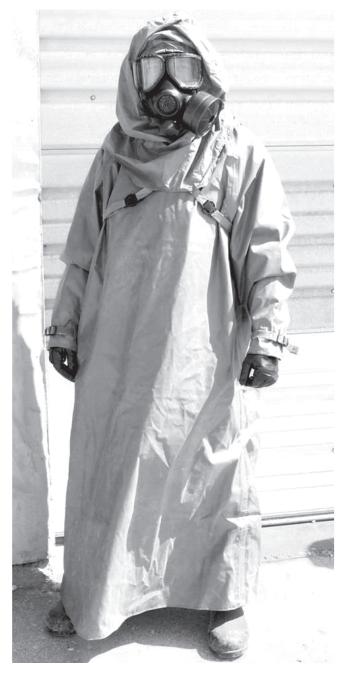
SOURCE: Committee site visit to the NECD former production facility, May 17-19, 2004.

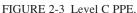


FIGURE 2-2 Level B PPE.

Issues Surrounding Pipe Removal

Concern over possible VX contamination of the nitrogen supply lines (and possibly also the process lines) prompted the Army to review the system and the precautions that ensure the safety of the workers during the dismantling process for Building 143. The Army concluded that VX could have flowed back, and probably did, into the nitrogen





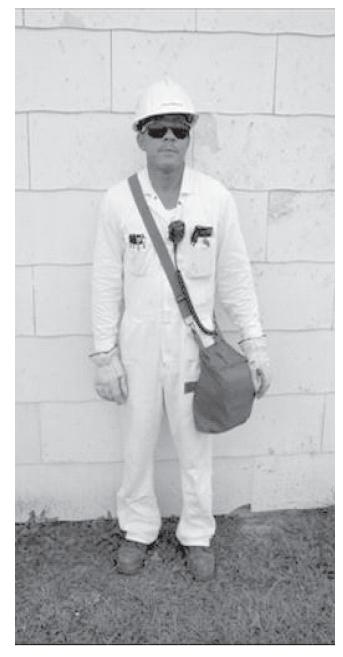


FIGURE 2-4 Level D PPE.

system at some time, or times, during the production runs.² Because the nitrogen lines were not sloped, it was possible for liquid to accumulate in the lines. Moreover, because the nitrogen piping had not been installed with straight runs but

had been field-fitted (installed without engineering drawings), it contained valves and other fittings in which liquid could accumulate.

The tanks and vessels in the system have not been monitored to determine if they are contaminated. Since the entire process was connected to the nitrogen system, there exists the possibility that some additional equipment may be contaminated. However, the bleach/caustic rinse appears to have decontaminated the process piping, so there is good reason

²Contamination of nitrogen systems is not uncommon in the petrochemical industry. It can occur if the supply pressure of the nitrogen system is not designed to be greater than the maximum system pressure or if the nitrogen supply failed during the operation of the process.

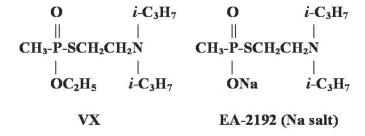


FIGURE 2-5 Structure of VX and EA-2192.

to believe that the vessels, tanks, and other equipment were also adequately decontaminated. No contamination of the process lines with VX had been confirmed at the time this report was completed. Nonetheless, the Army and its contractor are aware that additional contamination may exist within the remaining equipment and have developed procedures to ensure that exposure of workers or release of VX to the atmosphere does not occur. These procedures, and some recommended modifications, are discussed later in this chapter.

Exposure to compounds present in the atmosphere of Building 143 that may be related to VX also poses a potential risk to NECD workers. Chromatograms from the analysis of depot area air monitoring system (DAAMS) tubes show perhaps two dozen compounds, most of which have not been satisfactorily identified.³ It is likely that at least some of these compounds are related to VX since there were frequent false positive detections by the near-real-time (NRT) MINICAMS monitors. Because the MINICAMS uses phosphorus-selective flame photometric detection and so does not pick up non-phosphorus-containing compounds, the compounds responsible for the false alarms are fairly likely to possess a phosphorus atom.

The possibility arises that VX-related compounds are present in the NECD facility because it has been documented that VX undergoes a large number of reactions when stored for long periods of time (Witkiewicz et al., 1990; D'Agostino et al., 1987). As noted above, VX has been identified in the nitrogen lines, where it has resided since 1968. This is ample time to have allowed kinetically slow chemical reactions that could form a variety of degradation products. The majority of VX degradation reactions involve the hydrolysis of P-S and P-O bonds present in phosphonate ester: Of the initial

However, the presence of intact VX and the primary degradation products could lead to the formation of a second tier of products. The formation of methylphosphonate esters is well known-for example, O,S-DMP. The toxicity of O,S-DMP is modest: It is approximately 300 times less toxic than VX.4 However, the toxic risk posed by other compounds, such as those from the alkylation or oxidative coupling of degradation products, has not been evaluated, and the existence of substantial quantities of such reaction products cannot be dismissed out of hand. In a study of VX stored in glass for 15 years, D'Agostino and co-workers showed that only 10 percent of the sample was intact VX and noted the formation of at least 10 other compounds containing methylphosphonate or methylphosphonothiolate functional groups that could alarm the NRT monitors and also account for the toxic action of the molecule (D'Agostino et al., 1987, 1999) In addition to compounds formed from VX, VX precursors were certainly present in the past and may have migrated to areas where they could combine with VX, VX degradation products, or other compounds. This would further increase the number of compounds present.

VX hydrolysis products formed, only one, EA-2192, is known to be sufficiently toxic to warrant concern. Its intravenous toxicity is within an order of magnitude of VX toxicity. However, unlike VX (vapor pressure 0.0007 mm Hg at 25° C), EA-2192 has negligible volatility and is unlikely to contribute to the background atmosphere unless it is converted to an aerosol by mechanical operations such as sawing. Because the workers are in full PPE and the dermal toxicity of EA-2192 is relatively insignificant compared with its intravenous toxicity, localized contamination by EA-2192 aerosols is unlikely to endanger them. The structures of VX and EA-2192 are shown in Figure 2-5, and the reaction of VX and O,S-DMP with silver fluorides is shown in Box 2-1.

³DAAMS, an historical air monitoring system, is described in Chapter 4. In this report, DAAMS may refer to a single location where DAAMS tubes have been placed.

 $^{^4}$ For VX, the LD₅₀ is 0.0084 mg/kg (Munro et al., 1994). In contrast, for O,S-DMP, the LD₅₀ is 2.48 mg/kg (Alfa Aesar, 1997).

BOX 2-1 Formation of the G-Analog

The G-analog, or O-ethyl methyl phosphorofluoridate, is formed, along with the thiolamine silver salt, by reaction of VX with a silver fluoride conversion pad (Reaction 1):

The reaction is efficient for phosphonothiolate esters but not for phosphonate esters—the P-S bond cleaves while the P-OEt bond does not. For this reason, TRO does not react with the conversion pad and is unlikely to be responsible for false positive responses from the NRT monitors. In contrast, O,S-DMP, which has been identified in the background atmosphere, would be expected to respond identically to VX (Reaction 2):

Since the VX-related compounds contain structural features similar to that of VX itself, it is also reasonable to expect that they might display some fraction of the toxicity of VX. Cleavage of the O-ethyl portion of the VX molecule results in the formation of EA-2192, which does not significantly reduce the toxicity of the molecule. At least one other compound with lethal potential is known to form: Bis(O-ethyl methyl) pyrophosphonate may be thought of as the anhydride of ethyl methylphosphonic acid, and it has been reported to have a rabbit LD₅₀ that is only about 15 times greater (less toxic) than that of VX.⁵ Formation of this compound was reported under oxidative conditions similar to those used in hypochlorite decontamination processes (Yang et al., 1990).

Chemically, any ethyl methyl phosphonate compound containing a good leaving group would be expected to react identically to VX on the silver fluoride conversion pad of the MINICAMS NRT monitor, producing ethyl methylphosphonofluoridate (the G-analog that the MINICAMS uses in detecting the presence of VX) and the silver salt of

the leaving group. As noted, VX reacts in this fashion to form the G-analog, leaving behind the silver salt of diisopropylaminoethanethiolate, as shown in Box 2-1. Since identification and detection are based on the chromatographic behavior and phosphorus-specific FPD response of the G-analog, any compound that produces it would generate an alarm response identical to that for VX—namely, a false alarm. Other ethyl methylphosphonothiolates (for example those described in D'Agostino et al., 1987, 1999) would react identically to produce the G-analog, and the ethyl methylpyrophosphonate may do so also. In fact, any compound with a hydrolyzable functional group attached to the O-ethyl methylphosphono portion of the molecule has the potential to react on the silver fluoride pad on the MINICAMS, forming the G-analog and thus generating a false alarm for VX. It is noted that not all phosphonate esters will react on the silver fluoride pad. For example, the O-ethyl group is unreactive, and for this reason, the diethyl methylphosphonate, known as TRO, is not expected to produce a false positive response for VX.6

⁵The LD50, a standardized measure for expressing and comparing the toxicity of chemicals, is the dose that kills half (50 percent) of the animals tested.

⁶TRO arises from oxidation of the VX precursor bis-ethyloxymethyl phosphine.

Since the risk currently posed to the workforce by the background chemicals at NECD has not been effectively quantified, prudence dictates that workers must use appropriate PPE. If chemicals present in the background atmosphere in Building 143 are found to pose negligible chemical risk, then minimal PPE could be justified, except when cutting and handling potentially contaminated pipe and vessels. But this must be proven, given the potential for toxic chemicals to be present in the NECD atmosphere. The PPE used at the NECD former production facility was described earlier in this chapter; a list of commercial chemical PPE that has been approved for use by the Army is found in Appendix D.

Levels of protection are based on the potential for (1) inhalation, (2) skin absorption, and (3) ingestion. The use of Level B (see Figure 2-2) provides protection for all three pathways; positive-pressure supplied air gives the wearer a high level of respiratory protection (>1,000-fold) and is not dependent on the adsorption of the airborne contaminant onto a filter cartridge element as with a respirator. In order to use Level C protection (air-purifying respirator), the substance(s) must be identified, and it must be verified that the contaminant is captured by the respirator cartridge. This has not been done at NECD.

Finding 2-1: A number of chemicals are present in the NECD Building 143 atmosphere that have not been identified. Because NECD was historically used to manufacture and store VX, there is a possibility that some of these chemicals may manifest significant toxicity and thus pose a health risk to unprotected workers.

Recommendation 2-1: NECD personnel working in Building 143 should be protected by Level B PPE unless the background chemicals are accurately identified, their toxicity estimated, and commensurate risk established.

Initial Piping and Equipment Demolition Procedures

The potential for dermatological and airborne VX exposures is of concern when cutting and handling the piping. The procedure used by PMNSCM and its contractor to cut and handle potentially contaminated piping evolved as this study was being constructed. A description of the initial procedure used by PMNSCM and its contractor when removing production and nitrogen piping from Building 143 follows.⁸

To provide suitable protection, a primary containment, similar to a glove box but made of 14-mil plastic sheeting

instead of rigid material, is constructed around each section of piping to be removed. Through the plastic sheeting, rubber gloves provide access to the piping and to the powered reciprocal saws used to cut the piping. A catch tray is placed in the bottom of the primary containment to contain any liquid or debris from the tapping and cutting operations. The primary containment is maintained under negative pressure and the outlet air is purified by an activated carbon filter element (a chemical removal system that ensures that VX is not passed to the atmosphere). The operators are outside the primary containment and work on the piping using the gloved enclosure. After being cut, the piping sections are placed in plastic bags within the primary containment and then placed in drums for storage and transport to the decontamination area.

In some cases, one primary containment can be used to cut several sections of piping by sliding successive sections of pipe through and into the primary containment. In many cases, however, only one section of piping can be cut before a new primary containment must be constructed. The time needed to construct each primary containment, connect the inlet and outlet airlines, prove that negative pressure can be maintained, perform the cutting operations, and bag the piping is considerable—between 2 and 4 days per primary containment location.

Around the primary containment structure, a secondary containment area is constructed. The secondary containment is intended to provide a controlled and contained space for workers while they are performing pipe cuts. The concern in this area is the potential for airborne exposure to VX. This secondary containment area is large relative to the primary containments and, ideally, multiple primary containments can be constructed within each secondary containment area. However, the time taken to build each secondary containment area, install the inlet and outlet air supplies, and prove that it can be maintained under negative pressure, is also considerable (between 7 and 13 days for assembly and between 2 and 5 days for disassembly for each secondary containment installation).

All intrusive work (cutting and handling of piping) is done by workers in Level B PPE (see Figure 2-2). The construction of the primary and secondary containments is done by workers in Level D PPE (see Figure 2-4). The estimated total length of piping in Buildings 143 and 144 that remained to be dismantled in May 2004 was as follows: agent piping, 2,200 feet; nitrogen piping, 2,400 feet; and utility piping, 5,000 feet. The estimated number of primary containments required to dismantle this piping was 349.

The procedures described above provided adequate protection for the operating staff when cutting and handling piping. However, the time required to construct the containments resulted in schedule slippage and threatens the ability of the project to meet the April 29, 2007, CWC treaty deadline for the demolition of the NECD former production facility.

⁷PPE includes all clothing and other work accessories designed to create a barrier against workplace hazards. Examples include safety goggles, blast shields, hard hats, hearing protectors, gloves, respirators, aprons, and work boots.

⁸Terry Frederick, Manager, TVA Non-Stockpile Chemical Materiel, Briefing to the committee, September 14, 2004.

Modifications to Demolition Procedures

The use of numerous small, localized primary and secondary containment areas (see above) was the procedure in place when the committee was first briefed on the situation at NECD. On May 18-19, 2004, members of the committee visited the NECD site to receive additional briefings, inspect the facility, and discuss the problems that threatened the ability of PMNSCM to meet the CWC deadline. Subsequent to this visit, several modifications to the procedures were implemented by site management:

- The philosophy for constructing the secondary containments was modified. Instead of constructing a number of relatively small secondary containments on each floor, the new approach is to use larger secondary containments. In some cases, an entire floor in Building 143 will now be treated as a single secondary containment. In other cases, as on the first floor of Building 143, enclosed individual rooms or combinations of rooms will be treated as containment areas. A similar approach will be used in Building 144 when dismantling the filling machines and their associated piping. This modified approach to the original procedure minimizes the number of secondary containment structures to be built and shortens the time required for demolishing the piping and equipment in a safe manner.
- The enlarged secondary containment areas were airconditioned, allowing personnel to work in PPE without experiencing the heat stress that had adversely affected productivity during times of high ambient temperatures (summer and portions of spring and fall in Indiana). This modification has reportedly increased productivity and safety. In addition to the benefits to the workers, the increased ventilation and lower temperatures appear to have reduced the concentration of the compounds in the air that can give false positive MINICAMS alarms in the secondary containment areas. These alarms were disrupting operations by requiring evacuation of the workers (who were wearing Level D PPE) until the DAAMS analysis demonstrated that VX did not exceed the airborne exposure limit (AEL).

Finding 2-2: The change in operational philosophy to larger secondary containment areas and air conditioning of these areas has increased the efficiency and safety of demolition activities at the NECD VX production facility.

Recommendation 2-2: PMNSCM should continue to pursue the enlargement and air-conditioning of secondary containments for the demolition activities at the NECD VX production facility.

Recognizing that the construction of primary containment for all pipe cutting is labor- and time-intensive, PMNSCM proposed modifications to the extant demolition procedures. The use of primary containment for cutting pipe suspected to have come in contact with VX is required by the site safety and health plan and other safety documents. Any modifications to the procedures that eliminate the use of a primary containment will require the approval of the Safety Office in the Chemical Materials Agency (CMA) Risk Management Directorate.

The modifications proposed by the Army to allow eliminating the construction of primary containments are as follows:

- The addition of a vestibule for personnel entry to and exit from the large secondary containments; the vestibule will allow control of the entry of outside air into the secondary containments during personnel entry and exit.
- The use of a suction device (called a "snorkel") whose intake can be positioned close to the point where cutting is performed. This suction device would pass the air, along with any debris, liquid, or vapor generated during the cutting process, to a knock-out drum and then to an exhaust vapor containment structure (VCS).
- An alternative to the snorkel would be to introduce air into the pipe being cut upstream of the point where the cut is to be made and to apply suction to the downstream side of the cut and pass the air, with any debris, liquid, or vapor, to a knock-out drum and a VCS.

The concept of eliminating the primary containment appears feasible, and the committee believes it can be done if the following conditions are met:

- The interior of the pipe is dry, making it impossible for liquid VX agent to be released during cutting operations. This could be assured by inspection of the pipe interior using nondestructive techniques such as fiberoptic inspection. Alternatively, the geometry of the piping could be considered to determine if it would preclude the presence of liquid (as would, for example, a vertical run of piping containing no fittings).
- An area containment (formally called a secondary containment structure) is in place and is maintained under negative pressure during the cutting operation and the exhaust air is filtered.
- Workers wear appropriate PPE (Level B) to provide protection against airborne and dermal exposure to VX and related compounds.

Elimination of primary containment under the above criteria is acceptable since there is minimal possibility of a liquid VX leak. Although minor airborne emissions of VX are possible within the containment system, all workers who

could be exposed would be in Level B PPE, the atmosphere in the work area would be constantly sampled by MINICAMS, and the exhaust would be filtered. This offers the same level of protection against accidental release of agent to the atmosphere as does the standard operation of the explosive destruction system (EDS), where the overpack container is opened inside the EDS VCS. In this situation, the potential release of agent is controlled by opening the overpack inside the VCS, which is maintained under negative pressure and filtered prior to ventilation.

Finding 2-3: PMNSCM's concept of minimizing the construction of primary containments is appropriate and can be implemented without increasing the hazard to site workers.

Recommendation 2-3: The construction of primary containments should be minimized taking into consideration the orientation of the pipe being removed and information from any inspection of the pipe interior before its removal. There would have to be secondary containment under negative pressure and workers would have to wear Level B PPE.

Air Monitoring and Personal Protective Equipment

Both MINICAMS (continuous, on-line monitoring) and DAAMS tubes (time-averaged measurements) are used to monitor the primary and secondary containment areas. The NECD site currently sets the MINICAMS alarms for airborne exposure to VX with the assumption that workers are not wearing PPE. Therefore, even if workers are wearing M40 masks with respirator cartridges, or are provided with supplied breathing air, no credit is taken for the protection provided by such PPE.

As now planned, the implementation of the new AELs will not impact near-real-time monitoring with the MINICAMS at NECD. The NECD has been using the 1988 worker population limit (WPL) for VX as the basis for setting the MINICAMS alarm level. In accordance with recent Army directives (U.S. Army, 2004b), after the planned January 1, 2005, implementation of the new AELs, NECD will be using the new 15-minute short-term exposure limit (STEL) as the basis for setting the MINICAMS alarm level. Because the 1988 WPL and the new STEL have the same numerical value, the alarm level is not expected to be changed.

The impact of the implementation of the new AELs will not be zero, however. An additional level of chronic monitoring at the new WPL, which is numerically one-tenth of the 1988 WPL, should be carried out. (See Chapter 3 for a discussion of additional chronic monitoring and the use of DAAMS versus MINICAMS for this purpose). Also, as described in Chapter 6, permits and procedures must be reviewed and updated as necessary to reflect the new AELs. In consideration of the current situation at NECD and in relation to the committee's statement of task, several findings and recommendations were developed to enhance the

TABLE 2-2 VX Airborne Exposure Limits (Effective January 1, 2005) (milligrams per cubic centimeter)

VX	WPL (8 hours)	STEL (15 minutes)
No respiratory protection Air-purifying respirator Supplied-air respirator without escape bottle Supplied-air respirator with escape bottle	1×10^{-6} 5×10^{-5} 1×10^{-3} 1×10^{-2}	1×10^{-5} 5×10^{-4} 1×10^{-2} 1×10^{-1}

SOURCE: Adapted from U.S. Army, 2004b.

safety and efficiency of the project. It is important to note that most of the recommendations are synergistic, and if all are implemented, they should (1) minimize the number of alarms, (2) reduce the time required to complete demolition, (3) improve worker safety, and (4) provide additional protection to the environment and personnel outside the buildings.

The Army plans to change its operational philosophy at NECD (and throughout the chemical demilitarization program) after January 1, 2005, so that credit will be taken for PPE when determining alarm points. As indicated in Table 2-2, the Army considers that

- An air-purifying respirator provides a protection factor of 50.
- A supplied-air respirator without an escape bottle provides a protection factor of 1,000.
- A supplied-air respirator with an escape bottle provides a protection factor of 10,000.

Taking credit for PPE represents a change in the methodology for setting alarm points but one that is common in industrial practice and consistent with OSHA regulations; it is also used in Level A PPE areas of the stockpile disposal plants. Such an approach will allow operations to continue even if agent is detected above the STEL, provided that personnel are in the appropriate PPE. In addition, raising the alarm points based on PPE should minimize the number of occasions when chemical events are considered to have occurred and eliminate unnecessary delays and investigations. However, stakeholder issues on the state level may prevent PMNSCM from taking credit for PPE in some states.

⁹Army Regulation 50-6 on chemical surety defines chemical events as "chemical accidents, incidents and other circumstances where there is a confirmed or likely release to the environment, exposure of personnel, threat to the security of chemical agent materiel, or any incident of concern to the local commander" (U.S. Army, 1995, p. 36). The regulation gives examples, such as confirmed releases of agent from munitions outside a closed containment system, discovery of an actual or suspected chemical agent container or munition in a place where it is not supposed to be, and confirmed detection of agent above the threshold concentration for any period outside the primary engineering control.

TABLE 2-3 Available PPE Approved for Use at the NECD Former Production Facility

Military Unique	Commercial/Industrial				
Toxicological agent protective (TAP)	butyl				
M3 suit	Trelleborg Trellchem HPS TE and TS				
M2 apron	Kappler/Geomet CSM Responder				
M3 hood	DuPont Tychem F, Tychem (saran or polyethylene coated)				
Gloves/footwear	Gloves/footwear				
M3/M4 gloves	A number of companies provide a variety of gloves and boots				
M2A1 boots					
Respiratory protection	Respiratory protection				
M40 APR	APRs	APRs			
	North 7600	North 7600			
	MSA Ultra-twin/Advantage	MSA Ultra-twin/Advantage			
	Interspiro SCBA				

SOURCE: Adapted from John Leed, SAIC, Briefing to the committee, August 3, 2004.

Finding 2-4: In accordance with the Army's new implementation guidance policy (U.S. Army, 2004b), PMNSCM intends to take credit for the protection provided by PPE and adjust alarm levels upward when workers are in PPE.

Recommendation 2-4: In consultation with stakeholders, including regulators, and in accordance with the new implementation guidance at all appropriate non-stockpile sites, PMNSCM should continue to take credit for the protection provided by personal protective equipment when setting alarm levels.

The current Army Level B PPE—toxicological agent protective (TAP) suit, 30-minute self-contained breathing apparatus (SCBA) emergency escape bottle, etc.—and Level C PPE (M40 mask) provide adequate protection but are heavier and more tiring to wear than commercially available equipment. In addition, the M40 mask, with its two small eyepieces, provides a significantly narrower field of vision than similarly protective industrial equipment. Further, the requirement that the wearer provide the energy to draw breathing air through the M40 filter significantly increases wearer fatigue when the mask is worn for an extended period of time. Both fatigue and reduced field of vision can have significant adverse effects on safety and productivity.

Information from PMNSCM also indicates that workers in Level B PPE are equipped with a 30-minute SCBA emergency escape air bottle. ¹⁰ A 30-minute air bottle is heavy, impedes operations, and increases worker fatigue. As each

floor in Building 143 is equipped with a nearby door leading to an external stairway, the use of a 30-minute SCBA emergency escape air bottle is unnecessary because it would take only 5 minutes or so to escape from the building in the event of any interruption in the supply of breathing air from the installed manifold cascade system for Level B PPE. Industrial practice is to use small 10-minute escape bottles for emergencies. These smaller and lighter bottles are considered by OSHA to be adequate (Federal Register, 1994).

Finding 2-5: The 30-minute self-contained breathing apparatus used as an emergency escape bottle during demolition activities at the NECD VX production facility is heavy and bulky and creates unnecessary worker fatigue, which is likely to degrade overall project safety.

Recommendation 2-5: PMNSCM should specify that the 30-minute self-contained breathing apparatus bottle be replaced with a smaller 10-minute emergency escape bottle.

Table 2-3 provides details on industrial equipment approved for use at NECD.¹¹ In summary, approved industrial equipment exists that is lighter and provides equal or better protection than the military-unique PPE (TAP suits, M40 mask) presently used by the workers at NECD. Industrial respirators provide full-face vision, a significant safety advantage over the military M40 respirator. Army-approved industrial total encapsulating suits for Level B PPE have air supply fittings for providing cooling ventilation to the wearer, which will decrease heat stress (see Appendix D).

¹⁰Terry Frederick, Tennessee Valley Authority, Briefing to the committee, September 14, 2004.

¹¹John Leed, SAIC, Briefing to the committee, August 3, 2004.

Finding 2-6: The PPE being used for demolition activities at NECD, while providing adequate protection against airborne exposure to VX, is not the most advanced in terms of minimizing operator stress and maximizing field of vision.

Recommendation 2-6: The workers at NECD should be provided with state-of-the-art industrial PPE to minimize fatigue and maximize field of vision. The committee also recommends that PMNSCM consider using the best available PPE that has been certified for use with chemical agents in its other operations.

EXPLOSIVE DESTRUCTION SYSTEMS

General

EDSs are trailer-mounted mobile systems having an explosive containment vessel into which munitions are placed. The vessel door is closed and secured, shaped charges are used to open the munition and detonate any explosives within it, and chemical reagents are introduced to treat and neutralize the chemical agent within the containment vessel.

The EDSs are used to destroy recovered chemical munitions that are explosively configured and deemed unsafe to transport or store as well as to destroy chemical munitions, with or without explosive components. Primary containment of agent vapor is provided by the explosive containment vessel of the EDS itself. Secondary containment is provided by a portable VCS, within which the EDS is placed. The dimensions of the VCS may differ from site to site.

Two versions of the EDS have been developed. The smaller, original version, designated Phase 1 or EDS-1, was designed to destroy chemical munitions containing energetic materials up to 1 pound TNT equivalent. Three EDS-1 units have been built and deployed at several sites. A detailed description of the EDS-1 and its operation is found in the NRC report *Evaluation of Alternative Technologies for Disposal of Liquid Wastes from the Explosive Destruction System* (NRC, 2001b). A schematic view of the EDS-1 is shown in Figure 2-6.

The EDS developer, Sandia National Laboratories, has designed and fabricated a larger EDS, Phase 2 (EDS-2). The EDS-2 vessel will be capable of repeated-use cycles at 3 pounds TNT equivalent and occasional use at 5 pounds TNT equivalent, should such a need arise. The frequency of

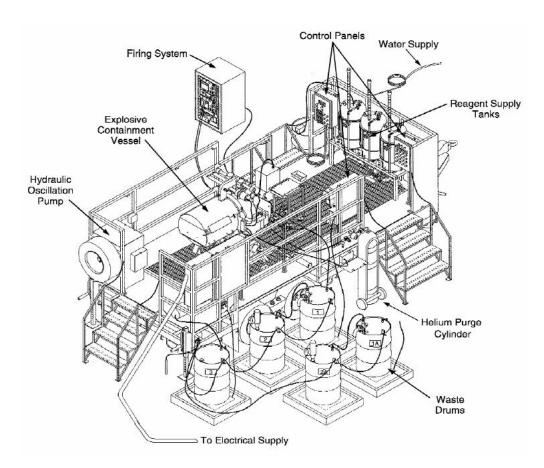


FIGURE 2-6 Diagram of the EDS-1 vessel on its trailer. SOURCE: U.S. Army, 2001b.

TABLE 2-4 General EDS Explosive Containment Vessel Specifications

EDS Weight	Explosive Rating (lb)	Inner Diameter (in.)	Inner Length (in.)	Wall Thickness (in.)	Volume (ft ³)
Phase 1 (5,200 lb) Phase 2 (18,000 lb)	1.5	20	29	2	6.7
	4.8	29	57	3.6	22

SOURCE: Adapted from John Gieseking, PMNSCM, Briefing to the RCRA Preapplication Meeting for the Pine Bluff Explosive Destruction System (PBEDS) at Pine Bluff Arsenal, April 22, 2004.

allowable use above 3 pounds has yet to be determined. This larger version of the EDS is able to dispose of munitions as large as 8-inch projectiles. Dimensions and other specifications for the containment vessels for the two versions of the EDS are given in Table 2-4.

Testing of both EDS versions has shown the capability to destroy more than one round at a time if the net explosive weight of the munition(s) and the shaped charges do not exceed the maximum explosive rating of the containment vessel. Since its first use in December 1999, 227 munitions and containers have been destroyed in both versions of the EDS. 12 Details of all EDS tests and operations are shown in Table 2-5.

EDS Workforce Tasks and Workforce Protection

The operation of the EDS units is labor-intensive and involves many manual operations, including unpacking munitions, mounting them in a fragment suppression system, attaching explosive charges, placing the assembly in the explosive containment vessel, and sealing the vessel. Subsequent operations such as detonation of the shaped charges, injection of neutralizing reagent, vapor sampling, and draining and rinsing of the vessel are manually controlled. After completion of an operation, 2 to 4 hours are required to dispose of munition fragments, clean the vessel, and refit it for the next operation. In addition to the EDS operators, the team includes people who perform analyses to confirm completion of the neutralization and people who operate the air monitoring system.

Following equipment setup, the operating team inside the VCS is made up of staff who handle the munitions upon initial receipt, who sample liquid and vapor treatment wastes, who sample solid wastes and remove metal fragments following detonation of the munition, and who transfer reagent; technicians who collect the DAAMS tubes; and decontamination personnel. With the possible exception of

Secondary Containment

During operations, each EDS has a VCS erected around it. The VCS provides environmental control of the workspace within it and secondary vapor containment in the event of an unexpected release of agent. The VCS is a modular building consisting of arched aluminum ribs connected by modular membrane panels. The VCS has a carbon-filtered exhaust system that maintains a negative pressure within it relative to the outside air. This system is intended to capture agent vapors that may result from EDS operations—for example, a leak while the munition is placed in the EDS vessel.

The exhaust filtration system for the VCS consists of prefilters, high- efficiency particulate air (HEPA) filters, and carbon filters, along with a motor, fan, and ductwork. If pressure gauges detect a head loss across a filter that exceeds a predetermined limit, then that filter will be changed. The carbon filters in the VCS filtration system contain a quantity of carbon well in excess of what is needed to contain any agent release.13

those handling leaking munitions, all of these staff are in Level C PPE. Under routine operations, no more than three people are potentially exposed to agent at any one time in the VCS erected around the EDS. PPE levels for EDS workers are specified by the Army (U.S. Army, 2004c) and are shown in Table 2-6. The same levels of PPE are expected to provide the same level of protection under the AELs promulgated by the CDC. This is so for three reasons: (1) the new 15-min STELs will be numerically equivalent to the 1988 WPL (i.e., TWA) values, (2) the new 8-hour WPLs will be lower than the 1988 recommended values, and (3) the levels of PPE in the table provide a sufficiently high degree of worker protection under the 1988 AELs.

¹²EDS treatability matrix provided to the committee by PMNSCMP, October 13, 2004; EDS update and workplace monitoring from Dave Hoffman, Systems Operations and Remediation Group Leader, PMNSCM, Briefing to the committee, June 16, 2004.

¹³Dave Hoffman, Systems Operations and Remediation Group Leader, PMNSCM; Rick DiMauro, RRS System Manager, PMNSCM; Tom Rosso, Chief Program Management Team, Edgewood Chemical and Biological Command; and Brett Sims, RRS Crew Chief, Teledyne Brown Engineering, Briefing to the committee, June 16, 2004.

TABLE 2-5 Usage Data for the EDS

Phase	Site	Month/Year	Items Destroyed	Fill
Phase 1				
Single-shot	Porton Down, U.K.	12/99-11/00	4 cylinders	CG
Single-shot		12///-11/00	7 Stokes mortars	
	(26 items)			CG
			1 cylinder	GB
			2 cylinders	Н
			8 4.2-inch mortar rounds	H
			4 4.5-inch projectiles	Н
	Rocky Mountain Arsenal, Colo. (10 items)	1/01-7/01	10 M139 bomblets	GB
	Former Camp Sibert, Ala. (1 item)	8/02	1 4.2-inch mortar round	CG
	Aberdeen Proving Ground, Md.	6/01-6/02	19 bottles and simulated munitions	Water
	(27 items)	0,01 0,02	4 cylinders	CG
	(27 Items)		•	HD
			2 cylinders	
			2 75-mm projectiles	Suspected H
	Aberdeen Proving Ground, Md.	12/02-4/03	15 75-mm projectiles	Suspected H
	(19 items)	, . ,	1 4-inch Stokes mortar	Suspected H
	(1) items)		1 8-inch Livens projectile	Suspected H
			1 E123 bomblet	Suspected GB
			1 4-inch mortar round	CG
	Spring Valley, Washington, D.C. (15 items)	5/03-6/03	15 75-mm artillery rounds	10 with H 5 no H
	Dugway Proving Ground, Utah	7/04-9/04	12 4.2-inch mortar rounds	H, suspected H
	(22 items)	,,,,,,,,,	7 DOT cylinders	Н
	(22 Items)			
			1 105-mm projectile	Probably HD
			1 M139 bomblet half	GB
			1 M125 bomblet	GB
Multiple-shot	Aberdeen Proving Ground, Md. (33 items)	5/04-8/04	3 shots, each with 3 simulated 4.2-inch mortar rounds (9 items)	Water
			3 shots, each with 3 simulated projectiles (9 items)	Water
			5 shots, each with 3 DOT bottles (15 items)	Н
Phase 2				
Single-shot	Porton Down, U.K.	2003	4 4.2-inch mortar rounds	HD
	(7 items)		3 DOT bottles	GB
	Aberdeen Proving Ground, Md.		1 cylinder	CG
	(10 items)		9 simulated rounds	Water
	(10 noms)		/ simulated rounds	vv ater
Multiple-shot	Porton Down, U.K. (27 items)	2003	2 shots, each with 3 Stokes mortar rounds (6 items)	CG
Multiple shot	,		4 shots, each with 3 British 15-lb artillery projectiles	HD
			(12 items)	1112
			3 shots, each with 3 DOT bottles (9 items)	HD
			.,	
	Aberdeen Proving Ground, Md. (30 items)	2003	10 shots, each with 3 simulated rounds (30 items)	Water

NOTE: CG, phosgene; GB, sarin; H, sulfur mustard; HD, sulfur mustard (distilled). SOURCES: Adapted from EDS treatability matrix provided to the committee by PMNSCMP, October 13, 2004; Dave Hoffman, Systems Operations and Remediation Group Leader, PMNSCM, Briefing to the committee, June 16, 2004.

TABLE 2-6 Personal Protective Equipment Levels

Task	PPE Requirement	
Emergency operations/response	Level B	
Process equipment setup	Level D	
Handling munitions/chemical-filled cylinders upon initial receipt and assessment	Level C	
Sampling liquids and vapors/sampling liquid treatment waste	Level C	
Handling cleared liquid waste drums	Level D	
Sampling solid waste and removal of munition/FSS carcass	Level C	
Transferring reagent between reagent drums and EDS tanks	Level C	
Air monitoring	Level D	
Routine and occasional maintenance	Level D	
Site operations support personnel and data collection project observers	Level D	
DAAMS technicians (when collecting tubes)	Level C	
Decontamination personnel	Level C	

NOTE: FSS, fragment suppression system SOURCE: Adapted from U.S. Army, 2004c.

Monitoring for Protection of the EDS Workforce

For both the EDS and the rapid response system (RRS) (discussed later), monitoring of the workplace air is done with MINICAMS and DAAMS. These instruments, which are described in detail elsewhere in this report, have been adapted to the special requirements of transportable systems. They must be compact enough to fit in the limited space in

air-transportable trailers and rugged enough to survive road travel. Since they may be used in remote locations, ease of maintenance is important. They must also be capable of monitoring for several agents that are not present in the stockpile program (e.g., nitrogen mustards and various arsenical agents).

The placement of MINICAMS and DAAMS monitors at a typical EDS site is shown in Figure 2-7. At all sites both

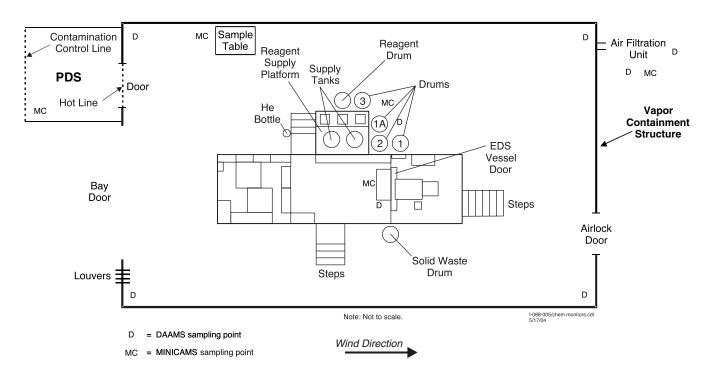


FIGURE 2-7 Typical EDS deployment layout. PDS, personnel decontamination station. SOURCE: Dave Hoffman, Systems Operations and Remediation Group Leader, PMNSCM; Rick DiMauro, RRS System Manager, PMNSCM; Tom Rosso, Chief Program Management Team, Edgewood Chemical and Biological Command; and Brett Sims, RRS Crew Chief, Briefing to the committee, June 16, 2004.

the near-real-time (NRT) monitors (MINICAMS) and the co-located confirming DAAMS are placed above the EDS vessel door, at the entry/exit door to the VCS, above the waste drums, and at the air filtration unit. DAAMS are also placed at the corners of the VCS. Other monitors used at an EDS site are noted below on a site-specific basis.

The air monitoring experience for significant EDS operations to date is summarized below.

Spring Valley

Spring Valley, in northwest Washington, D.C., is a residential neighborhood near a large university. It is also the location of the former Camp American University, a World War I-era chemical weapons research facility where a variety of munitions have been unearthed in the past several years. Between May 13, 2003, and June 10, 2003, 15 75-mm projectiles were destroyed by an EDS-1. The EDS was placed in a VCS near an interim holding facility where the recovered munitions were stored.

During EDS operations, the Army used MINICAMS to monitor for mustard (H), phosgene (CG), and chloropicrin (PS). Using the 8-hour TWA-based WPL for mustard agent $(3 \times 10^{-3} \text{ mg/m}^3)$, MINICAMS was set to alarm at 0.70 of this value $(2.1 \times 10^{-3} \text{ mg/m}^3)$. The Army also monitored for CG at its TWA of 0.4 mg/m³ and for PS at its TWA of 0.7 mg/m³. The MINICAMS were set to alarm at 100 percent of these values.

In addition to the monitoring locations shown in Figure 2-7, DAAMS tubes were placed at the personnel decontamination station and at the perimeter of the EDS site—one set of DAAMS tubes was placed upwind and the other downwind of the site for historical purposes. ¹⁴ The Army also used an open-path Fourier transform infrared spectrometer to detect and quantify the analytes of interest. For quality assurance purposes, the Army analyzed one DAAMS tube from above the EDS vessel door and one perimeter DAAMS tube for each day that the EDS was in operation. Confirmation and historical monitoring using DAAMS tubes was not done for CG and PS owing to the physical properties of these materials. Any MINICAMS alarms for CG and PS were assumed to be real.

During EDS operations at Spring Valley, there was only one alarm for mustard agent; this was at 2.2 TWA, when the EDS door was opened. The MINICAMS reading was not confirmed by analysis of the co-located DAAMS tube, however, and it was concluded that the alarm was due to an interferent (U.S. Army, 2003b).

Rocky Mountain Arsenal

Rocky Mountain Arsenal (RMA) is located 10 miles northeast of downtown Denver, Colorado, and is the site of a former GB production facility. Between October 2000 and June 2001, 10 M139 bomblets containing the nerve agent GB were unearthed in a metal scrap pile at RMA (EPA, undated). Six of these GB-filled bomblets were destroyed in an EDS-1 between January 28 and February 9, 2001, and the other four were destroyed between July 20 and July 26, 2001.

As in Spring Valley, the EDS was housed in a VCS under negative pressure. At RMA, the VCS was connected to a preexisting 300-foot-long, 75-foot-wide, 31-foot-high large-area maintenance shelter (LAMS) that covered the bomblets and the area where they were found. The LAMS provided vapor containment for the bomblets and was equipped with an exhaust filtration system fitted with carbon filters containing 14,000 pounds of activated carbon, far in excess of the amount needed to contain the agent that could be released from a bomblet.

In addition to the VCS monitor locations shown in Figure 2-7, both MINICAMS and confirming DAAMS tubes were placed at the mid-bed of the LAMS air filtration system and at the bomblet location in the LAMS that was nearest to the VCS. Monitoring was carried out for the 8-hour TWA for GB (1×10^{-4} mg/m³), and the MINICAMS was set to alarm at 0.70 TWA (0.7×10^{-4} mg/m³).

Perimeter monitoring for historical purposes was carried out at RMA through the placement of four DAAMS along the chain-link fence that surrounded the area (a boneyard) where the bomblets were found, one upwind and three downwind. Five more DAAMS were placed at air monitoring stations at the RMA perimeter, 2 to 3.5 miles from the area where the work took place. All of the historical DAAMS tubes were to be analyzed only if there was a confirmed detection of GB in the VCS or the LAMS.

During EDS operations at RMA, there was only one alarm for GB at 1.01 TWA when the EDS door was opened, but this result was not confirmed by the co-located DAAMS tube. The Army concluded that the MINICAMS reading was due to an interferent (U.S. Army, 2000a).

Dugway Proving Ground

Dugway Proving Ground (DPG) is an Army testing installation 70 miles southwest of Salt Lake City, Utah. From July to September 2004, the Army destroyed 15 munitions and 7 DOT cylinders in an EDS-1. The munitions contained GB and HD and consisted of an M139 bomblet half, an M125 bomblet, a 105-mm M60 projectile, and 12 4.2-inch mortar rounds. Some of these items contained energetics and others did not. Six of the DOT cylinders contained HD and the seventh contained HT.

At DPG the EDS was located in a VCS that provided secondary containment. Monitoring was conducted using

¹⁴Historical monitoring systems such as DAAMS can take as long as 12 hours of sampling to produce results. Thus, the event or situation that caused the detection of agent by DAAMS has probably been detected by other means and corrected by the time the DAAMS sample is analyzed. Historical monitors are used to confirm or deny the results previously taken by near-real-time monitors.

both MINICAMS and DAAMS tubes at the locations shown in Figure 2-7. In addition, a handheld detector was used for monitoring at the personnel decontamination station. The DAAMS tubes from each corner of the VCS were collected once each day during EDS operations for historical monitoring purposes.

The MINICAMS were set to alarm at 20 percent of the 8-hour TWAs for HD and GB $(3 \times 10^{-3} \text{ and } 1 \times 10^{-4}, \text{ respectively})$. During EDS operations at DPG, there were six confirmed MINICAMS alarms. Five of these were due to leaking munitions. The sixth was an alarm for HD that occurred during cleanup of the EDS vessel and was up to 2.1 TWA.

Pine Bluff Arsenal

The Army plans to use three EDS units at the Pine Bluff Explosive Destruction System facility. One of these will be an EDS-1 unit and the other two will be EDS-2 units. Each EDS will be housed in its own VCS. Both MINICAMS and confirming DAAMS tubes are expected to be placed at the locations shown in Figure 2-7.

Monitoring for Protection of the General Population

The EDS has been and will be used in a wide variety of environments, ranging from densely populated urban settings, such as Spring Valley in northwest Washington, D.C., to remote military facilities having no general population nearby, such as Dugway Proving Ground in Utah. At all sites, the EDS unit has been or will be placed in a VCS under negative pressure and will have an exhaust filtration system as described above. This secondary containment protects workers in the vicinity of the EDS should there be an agent release and also serves as an environmental safeguard for workers inside the VCS.

DAAMS tubes for perimeter monitoring are placed at distances well beyond the boundaries of the VCS and also beyond the chemical agent hazard distances estimated by atmospheric dispersion models. As previously described, this type of monitoring was carried out during the two EDS deployments to date, at Rocky Mountain Arsenal and at Spring Valley.

Perimeter monitoring was not carried out at other EDS sites because the Army felt that the VCS provided secure secondary containment for any agent that could have been released within it. However, the maximum credible event (MCE)¹⁶ for the Dugway EDS operations was identified as

an evaporative loss of agent during transport from the storage igloo to the VCS. Dispersion modeling for this MCE showed that elevated levels would occur over several hundred meters downwind under daytime conditions (U.S. Army, 2004d). In this case, the design of the sampling plan does not respond to the MCE identified for a specific deployment. Specifically, if the MCE occurred, there would be no monitoring data to indicate potential levels of exposure for unprotected workers immediately outside the VCS but easily within the estimated area of high exposure.

Further, the conditions assumed for the dispersion modeling for the MCE did not match the conditions that prevailed during actual operations. Dispersion was estimated based on daytime conditions, which would be conducive to high rates of dispersion, but the actual EDS operations were conducted at night, when dispersion was limited. As a result, agent released outside the VCS would not disperse as rapidly as it would during the day, and agent concentration from a release in the area immediately outside the VCS would be greater. For this reason, the dispersion modeling underestimates both the concentration of agent that would occur and worker exposure were there to be a release outside the VCS during nighttime operations. For proper design of the monitoring plan, the dispersion modeling would have to accurately reflect actual operating conditions.

Finding 2-7: Airborne exposures estimated for planning purposes are not consistent with those experienced in actual EDS operations. For example, at the EDS operation at the Dugway Proving Ground, there was little consistency between the MCE identified for that operation, the estimated exposure resulting from the MCE, the monitoring plan, and the actual EDS operation.

Recommendation 2-7: PMNSCM should develop perimeter monitoring guidelines that are consistent with the description of the MCE, the exposure estimates for the MCE, and the monitoring plan for each EDS deployment.

The perimeter monitors at RMA and Spring Valley were installed at the request of the communities involved. If, in the future, the Army includes perimeter monitoring to respond to concerns of the potentially impacted public, the PMNSCM should clearly distinguish between two cases: when such monitoring is recommended by scientific experts and when such monitoring is provided primarily to reassure the public.

Finding 2-8: Perimeter DAAMS tubes have been deployed for historical monitoring purposes at EDS sites on an ad hoc basis.

Recommendation 2-8: To reassure the public that potential agent releases are being monitored for at EDS deployment sites, PMNSCM should develop flexible, written guidelines for the deployment of perimeter air monitors at these sites.

¹⁵Personal communication between Dave Hoffman, PMNSCMP, and a committee fact-finding team at Dugway Proving Ground, August 10, 2004.

¹⁶The maximum credible event is defined as the worst single event that could occur at any time, with the maximum release of a chemical agent from a munition, container, or process as a result of an unintended, unplanned, or accidental occurrence (U.S. Army, 1999).

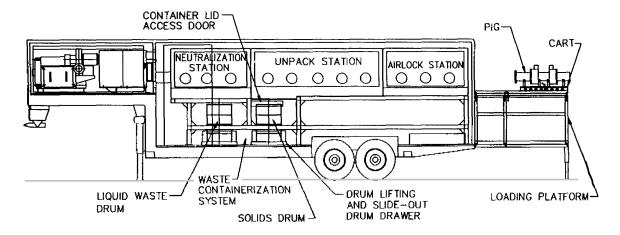


FIGURE 2-8 Side view of RRS operations trailer. SOURCE: Tripler et al., 2001.

RAPID RESPONSE SYSTEM

General

The RRS is a trailer-mounted system designed for the destruction and disposal of the chemical agent identification sets (CAIS) that are being recovered at sites throughout the United States. ¹⁷ The RRS underwent extensive testing at the Deseret Chemical Depot (DCD) in the autumn of 2000 and subsequently destroyed the entire CAIS inventory at that site. It has since been deployed to other sites. In the future, it will be transported to still other sites where significant numbers—say, several dozen—of CAIS are recovered. ¹⁸

The RRS was initially permitted under a Resource Conservation and Recovery Act (RCRA) permit by the state of Utah to conduct a test program with both simulants and chemical agents at DCD. A full-scale prototype was designed and assembled. The state approved a testing program to qualify the process, and 33 of the 60 CAIS stored at DCD were successfully destroyed during the testing program (U.S. Army, 2001c; Tripler et al., 2001). The testing operations were then converted to a production mode, and the remainder of the CAIS, more than 1,200 items, were destroyed (U.S. Army, 2001d).

After equipment modifications to correct problems encountered during the tests at DCD, the RRS was dispatched to Fort Richardson, Alaska. During a campaign ending July 24, 2003, eight PIGs and five laboratory packs of CAIS were destroyed.

A RCRA application to permit use of the RRS at Pine Bluff Arsenal (PBA) was submitted for review in July 2003 and approved in September 2004. The PBA application was to be the template for subsequent permit applications. The Army plans to base the RRS at PBA. It will be used to destroy the large inventory of CAIS stored there between deployments to other sites whenever significant quantities of CAIS are discovered.

Equipment and Operations

The complete RRS system occupies four trailers: an operations trailer, a support trailer, a utility trailer, and a mobile analytical support platform (MASP). The heart of the RRS is the operations trailer, which contains glove boxes in which CAIS are opened and the contents of the individual bottles, jars, and ampoules are identified and neutralized or repackaged. The support trailer contains spare equipment and supplies. The utility trailer carries electrical generators to allow the system to operate without commercial or host (site) power when needed. The MASP provides analytical chemistry support services.

In the operations trailer (Figure 2-8), a complete CAIS PIG or a package of individual items is introduced into an airlock. The atmosphere in the airlock compartment is monitored to detect contamination of items being brought into or out of the glove boxes. The CAIS are next moved into the unpack station, where the PIGs are cut open. The content of each glass vessel in the container is then identified by nonintrusive methods, including Raman spectroscopy. The containers of so-called industrial chemicals such as CG and PS are repackaged for dispatch to a qualified treatment, storage, and disposal facility (TSDF) for ultimate disposal. The items containing blister agents (H/HD, HN, L) are passed to the next glove box (neutralization station) for destruction. The packaging materials are decontaminated before being

¹⁷CAIS items, which contain chemical warfare agents, were produced for training purposes before, during, and after World War II. A single CAIS holds several glass vessels, each containing a blister or choking agent. These sets were produced in large quantities (approximately 110,000) and in various configurations from 1928 through 1969.

¹⁸As noted in Chapter 1, other means of disposal are used when only a few CAIS (or just a single one) are recovered.

dropped through the floor of the unpack station into a solid waste drum, which will be sent to a TSDF for disposal.

In the neutralization station, the individual glass containers are placed in a 1-gallon reactor along with an appropriate neutralization reagent based on dichlorodimethylhydantoin in an organic solvent. The reactor is sealed and the glass ampoule or bottle is broken, releasing the contents into the neutralizing solution. After the neutralization reaction is complete, the reactor contents (liquids, glass shards, and other solids) are discharged into a liquid waste drum that will be sent to a TSDF for disposal.

RRS Workforce Tasks and Workforce Protection

The RRS workforce encompasses personnel with a wide variety of skills, including glove box operators, chemists, Raman spectrometer operators, air monitoring specialists, a data entry clerk, supervisors, and site safety and health officers. During the campaign at DCD to systematize the RRS and complete destruction of the site's CAIS inventory, a team of 27 was assembled to permit operations during three shifts per day (U.S. Army, 2001d). Operations at other sites with smaller CAIS inventories may require smaller teams, but the skill requirements are similar. The minimum team on site at any time that the operations trailer is in use includes two operators, a Raman/air monitoring specialist, a supervisor, and security personnel to control access to the area. Personnel are not permitted to work alone inside the operations trailer (U.S. Army, 2001c).

The primary containment of the toxic materials handled by the operators is the battery of glove boxes in which the operations described above are performed. Because many of the CAIS items are broken or leaking, agent vapor is assumed to be present inside the glove boxes. The airlock and the glove boxes are maintained under a slight negative pressure to prevent agent and solvent¹⁹ vapors from diffusing into the work area. The air in the glove boxes is discharged through a bank of charcoal filters to remove agent and solvent vapors.

The trailer itself constitutes the secondary containment that protects personnel working outside the trailer from toxic vapors. The workspace inside the trailer, as well as in the analytical trailer, is categorized as Level D, which assumes no contact with chemical agents. Protective gear for work in the glove boxes is basically limited to extra gloves worn inside the glove box gloves and a slung M40 mask (Tripler et al., 2001). For operations such as changing waste disposal drums and packing industrial chemical items into labpacks, modified Level D PPE is worn. This includes additional PPE items such as aprons, boot covers, sleeves, and safety glasses to provide protection against splashes and spills. ²⁰ Near-real-

time monitoring of the work area in the trailers and of the air discharged from the glove boxes is accomplished with a set of MINICAMS monitors, which are backed up by DAAMS tubes for confirmation of apparent agent occurrences. The current monitoring protocols are described below.

During the CAIS disposal campaign at DCD, the operations and administration trailers of the RRS were housed in a building, both to prevent weather damage to the RRS and to provide secure storage for CAIS and waste products. The trailers were set up outdoors, adjacent to the CAIS storage facility, during work at Fort Richardson, Alaska.²¹

Current RRS Monitoring Procedures and Experience

General

The nature of the CAIS to be destroyed in the RRS significantly affects the RRS monitoring strategies. The CAIS have no associated explosive charges, 22 and the quantity of chemical agent in an individual ampoule is small. (The largest quantity in an individual CAIS vessel is the 4 ounces of mustard agent that is contained in screw-top bottles or sealed ampoules in some training kits.) For this reason, CAIS are almost always transported to a storage site on a military reservation, so in contrast to the EDS, the Army can control the presence of civilians in the immediate vicinity of the RRS. In addition, RRS operations are carried out in a trailer that provides a monitored, ventilated workspace. The air from the RRS glove boxes is exhausted through several sets of filters. As noted below, the exhaust air is monitored not only for chemical agents but also for chloroform, which is a solvent contained in some CAIS and in all the neutralization reagents used to destroy blister agents.

Because of the factors cited above—small agent quantities and no nearby civilian population—there is generally no perimeter monitoring when the RRS is in operation.²³

One complication to monitoring in and around the RRS is that the assortment of agents and chemicals in a complete CAIS requires simultaneous monitoring for eight different toxins plus the carcinogen chloroform.²⁴ For all but one of

¹⁹Many of the CAIS items, as well as the neutralizing reagents, contain chloroform, a human carcinogen.

²⁰Response from Darryl Palmer to the committee concerning PPE worn in RRS, August 12, 2004.

²¹Dave Hoffman, Systems Operations and Remediation Group Leader, PMNSCM; Rick DiMauro, RRS System Manager, PMNSCM; Tom Rosso, Chief Program Management Team, ECBC; and Brett Sims, RRS Crew Chief, Briefing to the committee, June 16, 2004.

²²The K951 sets included blasting caps to disperse the agents for identification training; however, the caps were packed and shipped in a separate container.

²³William Brankowitz, PMNSCM, Presentation to the committee, June 16, 2004.

²⁴MINICAMS may be configured to monitor each of the CAIS compounds (agents and other chemicals). However, because the AEL concentration range for CAIS compounds covers several orders of magnitude and because the chemical and physical properties of the compounds vary widely, it is not possible to configure a single MINICAMS to monitor all nine CAIS compounds simultaneously, and doing so would necessitate more than one MINICAMS.

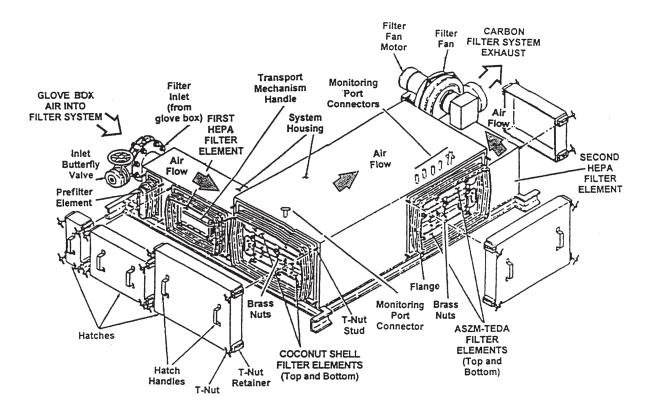


FIGURE 2-9 RRS exhaust air filtration system. SOURCE: Provided to the committee by Mitretek, June 9, 2004.

these toxins, lewisite, the MINICAMS is sufficiently versatile to meet this requirement. Lewisite, a vesicant found in some CAIS, tends to adsorb on the vapor feed lines that connect the sampling ports to the MINICAMS instrument. As a consequence, it must be derivatized (converted to a volatile form) at the sampling point by reaction with ethanedithiol to produce a volatile species that can survive the passage to the MINICAMS.²⁵ The need to derivatize the lewisite has three consequences for RRS monitoring: (1) dedicated MINICAMS must be provided to monitor for the presence of this agent; (2) vinyl chloride, a common byproduct from the neutralization of blister agents, interferes with the identification of lewisite; (3) the derivatization step leads to a long (10-minute) cycle time for the MINICAMS.²⁶

Placement of Monitors in the RRS

As configured for the RCRA permit testing at DCD, the air was tested in the following locations (Tripler et al., 2001):

- Glove box interior,
- · Operations trailer workspace,
- Glove box filtration system exhaust,
- Between the ASZM-TEDA carbon filter elements,²⁷
- Between the coconut shell carbon filter elements (for chloroform).

Air drawn from these locations was transferred through heattraced sample lines to the MINICAMS (usually equipped with halogen-specific detectors). In addition, DAAMS tubes were mounted in the workspace, between the ASZM-TEDA filter elements, and in the carbon filtration system exhaust. Figure 2-9 illustrates the configuration of the filter banks through which the exhaust air from the glove boxes is extracted.

Air exiting the glove box is drawn through a HEPA filter to remove dust and then through a pair of carbon filters to remove chloroform, chemical agents, and industrial chemicals. The monitor placed between these two filters deter-

²⁵E. Doyle, J.R. Stuff, M.S. Hulet, A.M. Schenning, and J. Horton, Presentation to Chemical Weapons Demilitarization Conference, St. Petersburg, Russia, May 2004.

²⁶William Brankowitz, PMNSCM, Presentation to the committee, June 16, 2004.

²⁷ASZM-TEDA (carbon-activated, impregnated, copper-silver-zinc-molybdenum-triethylenediamine) is a filter medium composed of military-grade activated impregnated carbon. The ASZM-TEDA coating is patented by the U.S. Army.

mines whether the first filter has become saturated with chloroform and needs to be changed. Air from the filters is drawn through a pair of carbon filters impregnated with metal complexes to remove traces of chemical agents. Again, a mid-bank monitor ensures that the first filter has not become saturated. Finally, the air is drawn through another HEPA filter before the fan discharges it into the atmosphere, where it is monitored once again for traces of agent or industrial chemicals. Monitoring the exhaust air provides protection for workers outside the operations trailer. These workers will generally carry an M40 mask and wear PPE appropriate for the tasks to be performed, such as removing wastes from the CAIS processing, packaging industrial chemicals to be shipped, or replacing the exhaust filter banks. ²⁹

The air in the glove boxes is sampled at several points with MINICAMS and DAAMS, but not continuously. To avoid overloading the sorbent columns of the MINICAMS and DAAMS, the glove-box atmosphere is sampled only as needed, for example, when cleaning up a spill or preparing to remove equipment from the airlock. Agent vapor may be present from leaking vessels or contaminated packing materials, but the workers are protected by the containment provided by the glove boxes. Colorimetric tubes specific for various agents and industrial chemicals provide confirmatory evidence for their presence (Tripler et al., 2001).

In addition to the primary containment provided by the glove boxes, the team working in the operations trailer is protected by constant monitoring of the workspace atmosphere for the relevant chemical agents and industrial chemicals. Near-real-time monitoring is done with MINICAMS adapted for multiagent capability.³⁰

During changes of the liquid and solid waste drums, the atmosphere of each waste container compartment is monitored to ensure that there are no residual agent vapors before the compartment is sealed off from the glove box overhead. The exterior access to the compartment is then unlocked and the waste handling crew (wearing garments for protection from spills) removes and securely seals the waste drum for shipment to a TSDF (U.S. Army, 2004e).

Deseret Chemical Depot Campaign

During the systemization and testing at DCD, the RRS was operated inside a building, and the air in the building was monitored for the protection of personnel working

outside the operations trailer. Besides the RRS trailer, the building housed a permitted storage area for incoming CAIS items and a temporary storage area for outgoing wastes from the processing of the CAIS. In addition to the usual six MINICAMS associated with the RRS, three additional instruments were used to monitor the storage areas.

Monitoring of three types was conducted (Tripler et al., 2001):

- Continuous near-real-time monitoring of airborne agent levels, coupled with alarms to alert staff to exceedances of the allowable TWA agent concentrations in the workspace and the exhaust air. This operation was done with MINICAMS coupled to sampling ports, as described above.
- Confirmation of MINICAMS alarms was done with DAAMS tubes for the blister agents (HD, HN, and L) and with colorimetric tubes for the industrial chemicals and chloroform.
- Historical monitoring for detection of long-term exposure effects was carried out with impingers, in which the organic components of an air stream were collected in a nonane scrubber. The contents of the impingers were then analyzed by a gas chromatography/mass spectroscopy detector (GC/MSD) in the analytical trailer. Impingers were also used to detect airborne agent in the mobile analytical support platform itself and in parts of the building not routinely monitored with MINICAMS.

As might be expected in handling damaged or improperly sealed chemical containers, numerous alarms were experienced at sampling points inside the glove boxes during the DCD campaign. There were 28 MINICAMS alarms for chloroform inside the glove boxes at levels from 0.70 to 3.87 TWA (TWA = 9.7 mg/m^3); no attempt was made to confirm them. The releases "occurred typically during waste drum sampling or handling" (Tripler et al., 2001, p. 4-42). HD was detected above 0.20 TWA (TWA = 0.003 mg/m^3) on seven occasions, six of them associated with sampling of bagged waste. Only once was there a MINICAMS alarm for HD in the workspace atmosphere; it was not confirmed by analysis of the corresponding DAAMS tube and was ascribed to an interference. One incompletely resolved incident was reported: When a container was opened, a small quantity of chloromethane was released and passed through all of the filters into the containment building. The source of the chloromethane remains unknown.

Fort Richardson, Alaska, Campaign

The monitoring setup for the RRS operation at Fort Richardson was similar to that used earlier at DCD except that the CAIS storage area did not have its own monitoring system. To protect the workers bringing samples from the

²⁸Dave Hoffman, Systems Operations and Remediation Group Leader, PMNSCM; Rick DiMauro, RRS System Manager, PMNSCM; Tom Rosso, Chief Program Management Team, ECBC; and Brett Sims, RRS Crew Chief, Briefing to the committee, June 16, 2004.

²⁹Rick DiMauro, RRS System Manager, personal communication to G.W. Parshall at a committee meeting, September 14, 2004.

³⁰Most MINICAMS sampling sites have a co-located DAAMS tube for historical/confirmatory purposes.

storage building, a sampling port connected to a MINICAMS in the RRS was installed in the storage area. No perimeter monitoring was carried out during the Fort Richardson campaign.³¹ The monitor at the exhaust of the RRS filter bank is regarded as a perimeter monitoring system since it is the only outlet for the chemicals being handled in the glove boxes.³²

Four of the five alarms that were sounded in this campaign came from the storage building. Each of the four was a false positive for cyanogen chloride (CK) and/or chloroform. In each case, a colorimetric tube failed to confirm the presence of CK. It was judged likely that interferents such as chlorinated solvents gave rise to the alarms. The one alarm coming from within the RRS was a signal for CK at 0.73 TWA (just above the 0.70 TWA alarm setting) at a filter bed midpoint. As with the storage area alarms, it was not confirmed by the colorimetric tube in place at that point. None of the alarms led to a work stoppage, but the operators donned masks.

³¹Letter from Paul Joe, Medical Officer, Chemical Demilitarization Branch, National Center from Environmental Health, CDC, to William J.B. Pringle, Chief, Environmental Monitoring Office, Program Manager for Chemical Demilitarization, January 9, 2003.

³²John Leed, SAIC, Briefing to the committee, August 3, 2004.

3

Old and New Airborne Exposure Limits

BASIS FOR ESTABLISHMENT OF AIRBORNE EXPOSURE LIMITS FOR NERVE AGENTS GA, GB, AND VX

The Centers for Disease Control and Prevention (CDC) established airborne exposure limits (AELs) in 1988 for sarin (GB), tabun (GA), and VX (Federal Register, 1988). The nerve agent GB is the most studied of these three agents; very little experimental information is available for GA and VX. Thus, in developing AELs for these three agents, experimental data on the induction of mild effects (miosis¹) were used to establish the AELs for GB and relative potency factors were used to establish the AELs for GA and VX.

The actual method of deriving the 1988 CDC worker population limit (WPL) 2 of 1×10^{-4} mg/m 3 and the general population limit (GPL) of 3×10^{-6} mg/m 3 (Table 3-1) was not specifically documented in the 1988 Federal Register or in the 1987 CDC meeting transcript "Safe Disposal of Lethal Chemical Agents." Mioduszewski et al. (1998) reported that the 1988 AELs for GB were based on recommendations proposed by McNamara and Leitnaker (1971) using a combination of acute human exposure data as well as acute animal pharmacokinetics data to predict cumulative effects of GB exposure in humans. The AELs recommended in 1988 for VX were based on the estimated relative potency of VX and GB reported by Reutter et al. (2000).

The CDC-recommended 1988 GPL for GB was 3×10^{-6} mg/m³ for a TWA over 72 hours (Table 3-1). This AEL was calculated to be 30-fold less than the 1988 WPL. The CDC did not establish a short-term exposure limit (STEL) or an immediately dangerous to life or health (IDLH) limit in 1988. The potency of GA is considered to be equal to that of GB, so the AEL values for GA are the same as those for GB (Federal Register, 2003a).

The AELs for VX were based on its potency relative to that of GB. In 1988, the CDC assumed that VX was 10 times more toxic than GB and recommended a WPL (i.e., TWA) of 1×10^{-5} mg/m³ (Table 3-1) (Federal Register, 1988).

TABLE 3-1 1988 and 2003 CDC-Recommended AELs and 2003 Acute Exposure Guidelines (AEGLs) for GA, GB, and VX (milligrams per cubic meter)

Type of Limit	Year of Recommendation	GA/GB	VX
STEL	1988	N/A	N/A
	2003	1×10^{-4}	1×10^{-5}
WPL	1988	1×10^{-4}	1×10^{-5}
	2003	3×10^{-5}	1×10^{-6}
GPL	1988	3×10^{-6}	3×10^{-6}
	2003	1×10^{-6}	6×10^{-7}
IDLH	1988	N/A	N/A
	2003	1×10^{-1}	3×10^{-3}
AEGL			
1-hr AEGL-1a		2.8×10^{-3}	1.7×10^{-4}
1-hr AEGL-2b		3.5×10^{-2}	2.9×10^{-3}
8-hr AEGL-1a		1×10^{-3}	7.1×10^{-5}
8-hr AEGL-2 ^b		1.3×10^{-2}	1×10^{-3}

^a Health effect: miosis in rats, nonhuman primates, and humans.

SOURCES: Adapted from Federal Register 1988, 2003a; NRC, 2003.

¹The earliest noticeable biological effect of exposure to a nerve agent is reduction of the pupil diameter of the eye, or miosis.

²Instead of the terms "airborne exposure limit," "general population limit," and "worker population limit," in 1988 the CDC used the terms "control limits for chemical agents" "control limits for the general population" and "control limits for workers," respectively. As noted in Chapter 1, the 1988 CDC value for "control limits for workers" was measured as an 8-hour time-weighted average (TWA) and implemented as a ceiling value. For ease of comparison, the terms AEL, GPL and WPL are used in this report to refer to both the 1988 and the 2003/2004 values. The 1988 Control Limits for Chemical Agents did not include the immediately dangerous to life and health (IDLH) limit or the short-term exposure limit (STEL), both of which came into usage some years later.

b Health effect: miosis, some dyspnea and photophobia, red blood cell cholinesterase inhibition, and subclinical single-fibre electromyographic change in humans.

However, it recommended that the GPL $(3 \times 10^{-6} \text{ mg/m}^3)$ for VX be the same as that for GB based on the limited technical capabilities of the air monitoring equipment available in 1988. STELs and IDLHs were not established for VX in 1988.

In 2003, the CDC revised the AELs for GA, GB, and VX. The revised GB WPL (3×10^{-5} mg/m³) and the GPL (1×10^{-6} mg/m³) (Table 3-1) were one-third of the 1988 values (Federal Register, 2003a). These new limits were based not on new experimental data for humans or animals but on an additional uncertainty factor of 3 that the CDC wanted to account for individual variability. For VX, the CDC adjusted the relative potency factor from 10 to 12 to reflect increased toxicity compared with GB and applied a modifying factor of 3 to account for an incomplete data set, resulting in a total composite adjustment of 36 for VX. Applying these factors resulted in a VX WPL of 1×10^{-6} mg/m³ and a calculated GPL of 3×10^{-8} mg/m³. However, CDC then adjusted the calculated GPL for VX upward, by a factor of 20, to 6×10^{-7} mg/m³ based on the technical capabilities of latter-day airmonitoring methods (Federal Register, 2003a). The CDC justified this by saying it could be expected that any exposure would be identified and corrected within 3 days (72-hour TWA).

STELs and IDLH limits were derived in 2003 for GA, GB, and VX. A STEL of 1×10^{-4} mg/m³ was set for GA and GB while a STEL of 1×10^{-5} mg/m³ was set for VX (Table 3-1) (Federal Register, 2003a). A STEL is an acceptable exposure for 15 minutes for unprotected workers.³ For GA and GB, such exposures should not occur more than four times per day, and at least 60 minutes should elapse between successive exposures. For VX, STEL exposures should occur no more than once a day (Federal Register, 2003a).

Several issues surrounding the CDC's 1988 and 2003 AELs for GA, GB, and VX deserve consideration. The CDC based its 2003 recommendations on several sources of information:

- · Comments from expert scientists,
- Risk assessment approaches used by regulatory agencies and other organizations, and
- Information provided in recent U.S. Army evaluations of AELs for chemical warfare agents.

The CDC used the U.S. Environmental Protection Agency (EPA) conventional reference dose concentration risk

assessment methodology for developing the AELs (Federal Register, 2003a). The CDC says that this methodology is conservative and does not reflect a change in the understanding of demonstrated human toxicity by these agents nor does it redefine that understanding. The CDC also indicated that no overt adverse health effects had been noted in association with the 1988 recommended exposure limits.

The EPA's risk assessment methodology is used to promulgate reference dose concentrations for airborne chemicals—that is, airborne exposure limits—for general (including sensitive) populations over a lifetime (70 years).⁴ The EPA has also developed and now manages a mechanism for establishing short-term emergency exposure limits for airborne chemicals. The process functions through the National Advisory Committee to Establish Acute Exposure Guideline Levels (AEGLs) for Hazardous Substances.⁵ AEGL values define exposures to airborne chemicals intended to protect the general public (including sensitive individuals) after single exposures ranging from 10 minutes to 8 hours. The proposed short-term AEGLs were reviewed by a National Research Council committee and ultimately issued as a National Academy of Sciences publication (NRC, 2003). EPA has not, however, developed long-term reference dose concentrations for nerve agents GA, GB, and VX. Since the CDC's recommended STELs are for a 15-minute exposure, the WPLs for 8 hours per day, and the GPLs for a lifetime based on a 24-hour TWA (albeit not one-time exposures), some of the AEGL methodology could be directly applicable to the Army for emergency responses. For

³The STEL is defined as an exposure that is acceptable for a short period of time, i.e., averaged over 15 minutes, without a respirator. Thus, the STEL recognizes that one's exposure may be higher. The STEL is set to minimize observed symptoms over a short exposure period. If there is a potential for brief airborne exposures in excess of the STEL, an industrial hygienist will assign a respirator. Emergency personnel typically select a self-contained breathing apparatus for protection until the area can be characterized correctly. Then the correct respirator, if any, can be selected.

⁴The general population is considered to be more sensitive to chemical agent exposure than the military population, and more casualties would be expected. The reason for this is that the general population includes children, the elderly, and unhealthy individuals, none of whom are represented in the military population.

⁵Acute exposure guideline levels (AEGLs) are a hazard communication measure developed by the National Advisory Committee to Establish Acute Exposure Guideline Levels for Hazardous Substances. The committee developed detailed guidelines for devising uniform, meaningful emergency response standards for the general public. The guidelines define three tiers of AEGLs as follows:

AEGL-1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL-3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

The guidelines for each level consider five exposure periods: 10 minutes, 30 minutes, 1 hour, 4 hours, and 8 hours (NRC, 2001d).

instance, the AEGL-1 for GB was derived using recent experimental vapor exposure data based on miosis in rats and nonhuman primates as well as historical data for miosis in human volunteers (Mioduszewski et al., 2002), while the AEGL-2 was based on miosis, dyspnea, and red blood cell cholinesterase inhibition in human volunteers (Baker and Sedgwick, 1996). The recommended 1-hour AEGL-1 for GB is 2.8×10^{-3} mg/m³ and the 1-hour AEGL-2 is 3.5×10^{-2} mg/m³, while the 8-hour AEGL-1 for GB is 1×10^{-3} mg/m³ and the 8-hour AEGL-2 is 1.3×10^{-2} mg/m³ (Table 3-1).

Developing long-term AELs for the nerve agents results in a fairly low calculated degree of confidence, because there are no long-term inhalation exposure data for humans and only limited animal data. For humans, almost all exposures have been for less than 60 minutes, many for only 5 or 10 minutes. The CDC used a 40-minute human study with miosis as the health end point to develop nerve agent STELs, WPLs, and GPLs. Thus, the CDC extrapolated over time from a 40-minute exposure to develop the 8-hour WPL and the GPL (Federal Register, 2002). The AEGL-1, on the other hand, was derived using recent rat and marmoset data on the presence of miosis during 4-5 hours of vapor exposure and historical human experimental data for 20-minute vapor exposures. The methods used by the CDC and the National Advisory Committee/NRC to develop AELs incorporate degrees of uncertainty and interpretive judgment. Both methods evaluated the quality and weight of evidence of the data and applied standardized uncertainty factors to establish AELs.

The CDC used a factor of 12 to represent the potency of VX compared with that of GB. The factor 12 was based on a 1971 study by Calloway and Dirnhuber that measured miosis in rabbits (Calloway and Dirnhuber, 1971). A modifying factor of 3 was also applied to account for what was considered a sparse data set, resulting in a total composite adjustment factor of 36 between the calculated exposure limits for GB and VX (Federal Register, 2003a).

The AEGL values for VX were developed by applying a relative potency factor of 4 between GB and VX based on human experimental and animal oral and intra-arterial/ intravenous administration of GB and VX with the same critical end point—a 50 percent reduction in red blood cell cholinesterase activity (NRC, 2003). A further uncertainty factor of 30 (1 for interspecies, 10 for intraspecies, and 3 for a sparse VX data set) was applied, resulting in a 1-hour AEGL-1 of 1.7×10^{-4} mg/m³ and a 1-hour AEGL-2 of 2.9×10^{-3} mg/m³, with the 8-hour AEGL-1 being 7.1×10^{-5} mg/m³ and the 8-hour AEGL-2 being 1×10^{-3} mg/m³ (Table 3-1). Thus, the two exposure limits—AELs and AEGLs—were derived using different routes of exposure (oral vs. inhalation) and health end points (red blood cell cholinesterase vs. miosis). This example demonstrates that occasionally different scientific data, exposure concentrations, and/or health end points can be selected as points of departure for risk assessment.

The CDC-recommended STELs for GB and VX are 1×10^{-4} mg/m³ and 1×10^{-5} mg/m³, respectively. The VX STEL was adjusted from a calculated 4×10^{-6} mg/m³ to 1×10^{-5} mg/m³ (not to occur more than once per day) based on the technical capabilities of existing air monitoring technologies (Federal Register, 2003a).

A question now arises about the extent to which the 2003 CDC-recommended AELs, which are lower than the 1988 CDC AELs, will impact human health. Since the 2003 WPLs and GPLs for GB were lowered by an uncertainty factor of 3 to account for individual variability (Federal Register, 2003a), the 2003 WPLs for GA and VX, which were derived from the WPL for GB, were automatically reduced by the same factor, 3. For VX, however, an additional modifying factor of 3 was applied to account for a sparse database, resulting in a 10-fold total decrease in the WPL from 1988 $(1 \times 10^{-5} \text{ mg/m}^3)$ to 2003 $(1 \times 10^{-6} \text{ mg/m}^3)$. The 2003 GPL for VX (6×10^{-7} mg/m³), on the other hand, represented a reduction by a factor of 5 of the 1988 GPL $(3 \times 10^{-6} \text{ mg/m}^3)$. The factor 5 was used to obtain a value that would be protective for humans and yet measurable by currently available monitoring methods (Federal Register, 2002). The CDC clearly states that the lower 2003 AELs do not reflect a change in or a refinement of its understanding of the demonstrated human toxicity of these agents and were not derived from new or additional scientific data on the toxicity of these nerve agents in humans or animals, and that no overt adverse health effects have been associated with the exposure limits recommended in 1988. Rather, they were a result of using updated and minimally modified risk assessment assumptions (Federal Register, 2003a) and, as such, added a layer of safety (conservatism) to the 1988 recommended AELs that have so far been protective for humans.

The U.S. Army currently sets alarm levels for near-real-time (NRT) monitors used to detect airborne nerve agents in non-stockpile and stockpile sites at 0.20, 0.50, or 0.70 of the 1988 WPL (which the Army refers to as "TWA"). In general, the non-stockpile program uses 0.70 as the alarm level, unless required by permit to use a lower alarm level. Thus, for GB and GA, 1988 WPL (TWA) concentrations at which NRT monitors alarm range from 2 \times 10⁻⁵ mg/m³ (for an alarm level of 0.20) to 7 \times 10⁻⁵ mg/m³ (for an alarm level of 0.70). The new 2003 WPL for GB and GA is 3 \times 10⁻⁵ mg/m³. For VX, 1988 WPL (TWA) concentrations at which NRT monitors alarm range from 2 \times 10⁻⁶ mg/m³ (for an alarm level of 0.20) to 7 \times 10⁻⁶ mg/m³ (for an alarm level of 0.70). The new 2003 WPL for VX is 1 \times 10⁻⁶ mg/m³.

The newly developed STELs (Federal Register, 2003a) are numerically equivalent to the 1988 WPLs (TWAs), that is, 1×10^{-4} mg/m³ for GB and GA and 1×10^{-5} mg/m³ for VX. For this reason, the readout from an NRT system for

monitoring at the new STELs is the same as the readout from the system would be if it were being used for the 1988 WPLs (TWAs), regardless of the alarm level set point.^{6,7}

The 1988 WPLs (numerically equivalent to the 2003 STELs) has been confirmed by the CDC to protect humans from the toxic effects of these agents (Federal Register, 2003a). If the Army used NRT systems (e.g., MINICAMS) to monitor at the 2003 WPLs for GB and set the alarm level to 1.00 WPL (as allowed by the CDC if certain conditions are met), then the alarm level for GB would be 3×10^{-5} mg/ m^3 versus 2×10^{-5} mg/m³ for an alarm level set at 0.20 of the 1988 WPL (TWA). Thus, it would appear that NRT monitors could be used to monitor at the 2003 WPL for GB and GA. It should be noted, however, that several problems arise if the alarm level is set at 1.00 WPL, as discussed in Chapter 4 of this report. It should also be noted that the accuracy required for a 1.00-WPL challenge of an NRT monitor is ±25 percent with 95 percent confidence and that there is no accuracy requirement for challenges of NRT monitors at a fraction of an AEL (for example, at a concentration reading of 0.20 TWA). Thus, the comparison presented in this paragraph is tenuous at best.

If the Army used NRT systems (e.g., MINICAMS) to monitor at the 2003 WPLs for VX and set the alarm level to 1.00 WPL (as allowed by the CDC, if certain conditions are met), then the alarm level for VX would be 1×10^{-6} mg/m³ versus 2×10^{-6} mg/m³ for an alarm level set at 0.20 of the 1988 WPL (TWA). Thus, it may be possible to use NRT monitors to monitor at the 2003 WPL for VX. Once again, however, it should be noted that several problems arise if the alarm level is set at 1.00 WPL.

CDC's objective in developing AELs was to protect the health of workers and others who could be exposed to nerve agents. Monitors must be capable of demonstrating the effectiveness of engineering/administrative controls and work practices and ensuring that excursions of agent concentrations above the AELs, if they occur, are detected in a timely manner. The difficulty presented by the situation at non-stockpile sites such as Newport is the pragmatic need to monitor at a level that minimizes background interference yet ensures, with a high degree of confidence, that the AELs are not exceeded.

The overall intention, and difficulty, of developing AELs for the nerve agents is to reach a balance between protecting

TABLE 3-2 1988 and 2004 CDC-Recommended AELs and 2003 AEGLs for Sulfur Mustard (HD) (milligrams per cubic meter)

	1988	2004	
STEL	NA	3×10^{-3}	
WPL	3×10^{-3}	4×10^{-4}	
GPL	1×10^{-4}	2×10^{-5}	
IDLH	NA	7×10^{-1}	
AEGL-1			
1-hour	NA	6.7×10^{-2}	
8-hour	NA	8.0×10^{-3}	
AEGL-2			
1-hour	NA	1.0×10^{-1}	
8-hour	NA	1.3×10^{-2}	

SOURCES: Adapted from the Federal Register, 1988, 2004; NRC, 2003.

humans from the health effects of these highly toxic chemicals and yet being able to adequately monitor above detection limits and against background interference to ensure safety with a reasonable degree of confidence.

BASIS FOR ESTABLISHMENT OF AIRBORNE EXPOSURE LIMITS FOR MUSTARD AGENT

Because all three forms of mustard (H, HD, and HT) are chemically and toxicologically related and can be treated as a single compound, they will be referred to as either sulfur mustard or HD in this section (Federal Register, 2003b).

The 1988 CDC-recommended worker population limit (WPL) for HD was 3×10^{-3} mg/m³, while the general population limit (GPL) was 1×10^{-4} mg/m³ (Table 3-2). These AELs were determined to be substantially below concentrations at which adverse health effects have been observed for mustard agent (Federal Register, 1988) and have proven to be protective of human health (Federal Register, 2003b).

The 2004 CDC-recommended interim occupational AELs (WPL and STEL) for HD are the same as those that were recommended by the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) in 2000. The CDC recommended a WPL⁸ of 4×10^{-4} mg/m³ (Federal Register, 2004). This AEL was based on both short-term human data and long-term animal data. The critical human study incorporates an exposure concentration of 0.06 mg/m³ for 8 hours a day for 3 consecutive days adjusted to a 5-day occupational work week using a factor of 3/5, resulting in a lowest observed adverse effect level (LOAEL)⁹ of 0.036 mg/m³.

⁶The U.S. Army Chemical Materials Agency has decided to use the STEL recommended by the CDC in 2003 as the basis for setting MINICAMS alarms levels. SOURCE: Cheryl Maggio, Chemical Materials Agency, Briefing at AEL videoconference, June 2, 2004.

 $^{^{7}}$ It is noted that an NRT monitoring system may report an agent concentration in air above the 2003/2004 WPL but below the STEL alarm level. For this reason, a STEL concentration reading equal to or greater than 0.30 STEL for GB, 0.10 STEL for VX, or 0.13 STEL for HD may indicate the presence of agent at a concentration \geq 1.00 WPL and may indicate the need to use DAAMS to monitor the area at the WPL level.

⁸The CDC recommended that the WPL be an 8-hour TWA.

⁹The LOAEL is the lowest tested dose of a substance that has been reported to have adverse health effect on people or animals.

The uncertainty factors applied were 3 to extrapolate from a LOAEL to a no observed adverse effect level (NOAEL), ¹⁰ 10 to extrapolate from short-term to long-term exposure, and 3 to accommodate additional uncertainties inherent in using acute exposure data and a small number of subjects, for a total uncertainty factor of 100 (Federal Register, 2004; U.S. Army, 2000b). ¹¹

In 2004, the CDC also recommended a new GPL of 2×10^{-5} mg/m³. This value was established using a single 10-hour human exposure of 0.1 mg/m³ and adjusting the 10-hour exposure to 24 hours and the 1-day exposure to 7 days, resulting in a LOAEL of 6×10^{-3} mg/m³. A composite uncertainty of 300 was applied to the LOAEL: 3 to account for individual human variability, 3 to extrapolate from a LOAEL to a NOAEL, 10 to extrapolate from short-term to long-term exposure, and 3 to adjust for chemical-specific or study-specific uncertainties not dealt with by the standard uncertainty factors (Federal Register, 2004).

The CDC recommended a 2004 STEL of 3×10^{-3} mg/m³ for one occurrence per day. The STEL was calculated by two approaches: the time-adjusted LOAEL approach and the probit and logistics approach (Federal Register, 2004; U.S. Army, 2000b). A total uncertainty of 10 was used in the time-adjusted LOAEL approach: 3 to extrapolate from a LOAEL to a NOAEL and 3 to extrapolate from short-term exposure data.

The CDC recommended the 2004 immediately dangerous to life or health (IDLH) level to be 0.7 mg/m³ (Federal Register, 2004), not to exceed 30 minutes of exposure. It was stated in the 2003 Federal Register that the IDLH of 0.70 mg/m³ was derived by CDC's National Institute for Occupational Safety and Health (NIOSH) in accordance with structured NIOSH protocol (Federal Register, 2003b).

The 2004 recommended AELs for sulfur mustard were based on the following sources of information:

- · Comments by scientific experts,
- Latest available scientific data and technical reviews,
- · Exposure and risk assessment approaches, and
- CDC's understanding of current risk management practices associated with the U.S. Army's chemical agent demilitarization program.

The AELs proposed by the CDC reflect realistic management practices associated with chemical demilitarization and do not necessarily apply to other conceivable exposure scenarios (Federal Register, 2004).

Sulfur mustard is listed as a Part A carcinogen by the

National Toxicology Program (DHHS, 2004) and as a Group 1 carcinogen by the World Health Organization's International Agency for Research on Cancer (IARC, 1987). The CDC sulfur mustard GPL is a 12-hour TWA that reflects the typical sampling times used in the stockpile program. The CDC considers that its 2004 GPL of 2×10^{-4} mg/m³ meets carcinogenicity protection levels by keeping exposures below thresholds of significant risk (Federal Register, 2003b). Nevertheless, it recommends that its 2004 AELs should be considered as interim values pending better understanding of the cancer potency of sulfur mustard (Federal Register, 2004).

Acute exposure guidelines (AEGLs) have also been developed for sulfur mustard agent (HD). The AEGLs were developed for a one-time exposure ranging from 10 minutes to 8 hours. AEGL-1 and AEGL-2 are defined in the preceding section on nerve agents. The AEGL-1 values established for sulfur mustard are 6.7×10^{-2} mg/m³ for a 1-hour exposure and 8×10^{-3} mg/m³ for an 8-hour exposure (NRC, 2003). The 1-hour AEGL-2 is 1×10^{-1} mg/m³ and the 8-hr AEGL-2 is 1.3×10^{-2} mg/m³. The AEGL-1 levels were based on conjunctival injection and minor discomfort with no functional decrement in human volunteers, while the AEGL-2 levels were based on well-marked generalized conjunctivitis, edema, photophobia, and eye irritation in human volunteers. An intraspecies uncertainty factor of 3 was applied in developing the AEGL-1, while a composite uncertainty factor of 10 (3 for intraspecies and 3 to accommodate potential onset of long-term ocular or respiratory effects) was applied in developing the AEGL-2. The 2004 CDC WPLs and GPLs for sulfur mustard were reduced approximately 10-fold from the 1988 recommended values (Table 3-2). The 2004 AELs were derived using newer risk assessment methods and some additional toxicity data. However, the CDC stated there is no empirical evidence that the 1988 AELs for sulfur mustard are not protective of human health (Federal Register, 2003b). Thus, there does not appear to be any major change in health impact between the 1988 and 2004 WPLs and GPLs. The CDC also recommended a STEL and an IDLH limit in 2004 but did not do so in 1988 (Federal Register, 2004). The CDC did, however, state as follows: "Given the uncertainty in the risk assessment regarding cancer potency, reduce exposures to sulfur mustard to the lowest practicable level" (Federal Register, 2004, p. 24167).

The committee finds merit in the Army's adoption of the 2003 CDC-recommended STEL to replace the 1988 WPL. The 1988 WPL was used as the basis for NRT workplace monitoring and has been protective of worker health (Federal Register, 2003b). The new NRT workplace monitoring level is based on the new STEL, which is the same numerically as the old WPL and will be equally protective.

¹⁰The NOAEL is the highest tested dose of a substance that has been reported to have no adverse health effects on people or animals.

¹¹The uncertainty factor of 3 is rounded downward from 3.16, the square root of 10. Thus, $3.16 \times 10 \times 3.16 = 99.86$, for a total uncertainty factor of 100.

¹²The CDC defines significant risk as a risk level below 1 in 1 million excess cancers (Federal Register, 2003b).

Finding 3-1: The committee concurs with the non-stockpile program's plans to replace the CDC 1988 WPLs with the 2003/2004 STELs for NRT monitoring.

Recommendation 3-1: PMNSCM should continue with its plans to replace the CDC 1988 WPLs with the 2003/2004 STELs for near-real-time monitoring.

IMPACT OF THE REVISED AELS ON WORKER AND PUBLIC SAFETY

The revised AELs do not reflect any change in agent toxicity. Workers, communities, and the environment were sufficiently protected under the old AELs. The revised AELs are, however, more stringent and more in line with how these standards are established for other air toxins. This standardization should help ensure the continued safety of workers, communities, and the environment since the revised AELs are more stringent and will result in a reexamination of all aspects of the protection of these populations and the environment.

The revised AELs, including the WPL, the GPL, and the IDLH, do not offer any clear quantitative risk advantage visà-vis the 1988 AELs. The 2003/2004 AELs are slightly more conservative than the 1988 AELs, but both are low enough that any quantitative comparison between the two is overwhelmed by the uncertainty in the current understanding of

low dose effects. Further, the impacts of chronic exposures are difficult to assess owing to a lack of data.

This lack of demonstrable risk benefit is consistent with the position the CDC took when it announced the new AELs:

There is no indication that the current exposure limits, as implemented by U.S. Army PMCD, have been less than fully protective of human health. (Federal Register, 2002, p. 895)

The recommended changes in the AELs do not reflect change in, nor a refined understanding of, demonstrated human toxicity of these substances but rather the changes related from updated and minimally modified risk assessment assumptions. (Federal Register, 2003a, p. 58350)

The revision of the AELs has significant impacts on the operations at chemical agent demilitarization sites, training facilities, and laboratories. In accordance with U.S. Army guidance (2004b), the Army's monitoring program must change such that an extra level of chronic monitoring at the WPL is introduced. Other areas are also affected, such as safety and emergency response procedures, medical monitoring programs, marking and handling of contaminated materials, release of contaminated materials, and handling, treatment, and storage of waste (U.S. Army, 2004b). It is possible that some improvements in worker risk and operations will result from implementing the revised AELs. These benefits will probably come from a fresh look at operating procedures rather than from the change in AEL values.

4

Air Monitoring Systems

SYSTEMS USED TO MONITOR AT THE 1988/1997 AELS

MINICAMS, a low-level, near-real-time (NRT) air monitor, and DAAMS, a manual historical monitoring system, are used for the detection of agents that may be present in the air at non-stockpile disposal sites, at stockpile disposal sites, and at agent storage facilities. MINICAMS, an automated, near-real-time (NRT) system, is used to monitor sulfur mustard (distilled) (HD), sarin (GB), VX, and other agents of concern in the non-stockpile program using the time-weighted-average (TWA) airborne exposure limits (AELs) and the immediately dangerous to life and health (IDLH) AELs (GB and VX only) set by the Centers for Disease Control and Prevention (CDC) in 1988 and the U.S. Army in 1997. MINICAMS typically reports the concentration of agent in air once every 3 to 10 minutes (U.S. Army, 2003a).

An IDLH AEL was only recently defined for HD (Federal Register, 2004). However, HD has been monitored for many years at stockpile sites by MINICAMS and by an automatic continuous agent monitoring system (ACAMS), the predecessor of MINICAMS, at concentrations much greater than the CDC's 2004 IDLH value.¹

If the agent concentration reported by a MINICAMS exceeds a preset alarm level, the MINICAMS displays audible and visible signals to alert an operator that the concentration of agent reported for the area being monitored has

exceeded the set point.² The operator then takes actions in response to the alarm. Alarm levels for MINICAMS used at non-stockpile sites are typically set at 0.70 of the AEL of concern for the agent of concern.

DAAMS, a manual monitoring system, is used at stockpile and non-stockpile sites to confirm or deny MINICAMS TWA alarms (that is, reports of the presence of agent at concentrations greater than the alarm level) and at stockpile sites to conduct historical monitoring at the CDC's 1988 TWA and GPL AELs for HD, GB, and VX. Monitoring at GPL levels is not typically done at non-stockpile sites because non-stockpile operations involve only small quantities of agent (compared with stockpile operations) and are generally short term (U.S. Army, 2004g). Since it is highly unlikely for the general public to be exposed to agent for long periods, the general public is not considered at risk of long-term health problems from non-stockpile disposal operations.

Also, non-stockpile operations are often conducted within the perimeter of stockpile sites—for example, at the Newport Chemical Depot (NECD). In such instances, public access to non-stockpile sites is limited and the perimeter monitoring conducted in support of stockpile operations may be used to demonstrate that GPL levels are not exceeded at the perimeter, regardless of the source of agent (stockpile or non-stockpile operations).

In addition to continuous monitoring, at the time this report was written MINICAMS was used to verify decontamination to the 3X level—that is, to verify that the concentration of agent in the headspace air surrounding bagged items as a result of off-gassing does not exceed the CDC's

¹The stockpile program uses a totally encapsulated suit with a self-contained breathing apparatus (SCBA), known as the demilitarization protective ensemble (DPE)—up to the DPE use limit of 100 mg/m³ of airborne agent. ACAMS and MINICAMS have been used for more than 20 years to monitor for HD at concentrations ranging from 0.003 mg/m³ (the previous 8-hr TWA level) to 100 mg/m³ (the DPE limit). These NRT monitoring systems are able to monitor for HD over this wide concentration range simply by varying the volume of air from which agent is collected—through the adjustment of the sample flow rate and the duration of the sample period or through the use of an external fixed volume sampler (sample loop) connected to the inlet of the NRT monitor. Thus, it should be simple to monitor at the newly defined IDLH level for HD.

 $^{^2}$ Alarm level is a predetermined value for an NRT method that, when equaled or exceeded, will result in an audible and/or visual alarm at the NRT monitor. The alarm level must be set so that the statistical response rate is ≥95 percent. In other words, the probability, expressed as a percentage, that a 1.0-AEL first challenge to the NRT monitor will generate a response greater than or equal to the alarm level must be ≥95 percent (U.S. Army, 2004f).

1988 TWA AELs.³ DAAMS is used to confirm or deny any MINICAMS alarms that occur during 3X monitoring.

Both MINICAMS and DAAMS monitors are typically configured for sampling using glass tubes packed with a porous polymer. The sample is separated using temperature-programmed capillary gas chromatography, and detection is done using a flame photometric detector (FPD). The FPD may be operated in a phosphorus-specific mode for the detection of GB and VX or in a sulfur-specific mode for the detection of HD. The FPD in the MINICAMS may be replaced with either a pulsed flame photometric detector (PFPD), which may be operated in a phosphorus- or sulfur-specific mode, or with a halogen-selective detector (XSD), which is sensitive only to chlorinated and brominated compounds. A mass selective detector (MSD), in addition to the FPD, may be installed in the laboratory-grade gas chromatographs used in the DAAMS method.

MINICAMS provides a more rapid warning, but there is generally a greater risk of false positives (for MINICAMS and NRT monitors in general) than there is with DAAMS. This is true because MINICAMS typically has poorer gaschromatographic resolution than the more time-consuming and more sophisticated manual sampling, laboratory-based analysis, and reporting methods on which DAAMS is based.⁴ Also, DAAMS signal-to-noise ratios are typically greater than those for MINICAMS because the volume of air sampled by DAAMS tubes is greater, making the mass of agent collected for a given AEL setting greater as well.

Other automated NRT systems that have been used or tested at various storage and disposal sites are essentially automated DAAMS, commonly known by the acronym A/DAM (Agilent/Dynatherm agent monitor). The A/DAM system consists of a Dynatherm ACEM 900 sorbent-based sampling system connected to an Agilent 6890 gas chromatograph or, in its latest configuration, a Dynatherm IACEM 980 sorbent-based sampling system connected to an Agilent 6852 gas chromatograph. Both A/DAM systems are configured for sampling using a glass tube packed with a porous polymer, separation using a temperature-programmed capillary gas chromatograph (GC), and flame photometric detection. Both the 6890- and the 6852-based A/DAM systems can be configured to achieve better chromatographic resolution than MINICAMS, so in certain situations, they

may experience fewer false positives. In addition, the A/DAM system can be configured with two separate GC columns and with two separate FPDs, which improves selectivity with respect to chemical interferences.

Monitoring systems (and their associated written methods) used at non-stockpile and stockpile disposal sites must be certified before use in accordance with requirements stated in the Chemical Materials Agency's (CMA's) Programmatic Laboratory and Monitoring Quality Assurance Plan (U.S. Army, 2004f). Certification generally includes passing a 4-day precision-and-accuracy (P&A) study using liquid standard solutions to estimate the performance of monitoring systems when they sample actual agent vapor. Note that P&A studies for DAAMS and MINICAMS are usually conducted over a relatively narrow concentration range, typically 0.20 to 1.50 AEL in the past and now 0.50 to 2.00 AEL (as presented in the latest version of the *Program*matic Laboratory and Monitoring Quality Assurance Plan (U.S. Army, 2004f)). The goals of a P&A study are (1) to demonstrate that when used for the detection of a true agent concentration of 1.00 AEL, the monitoring system (and its associated written method) is predicted to report a found concentration in the range of 0.75 to 1.25 AEL (that is, 75 to 125 percent recovery) with a precision of ± 25 percent with 95 percent confidence and (2) to document the precision and accuracy of the monitoring system at all concentrations used in the study (U.S. Army, 2001e). Monitoring systems and written methods are generally not tested formally outside the concentration range required for the P&A study (U.S. Army, 2004f). Thus, the accuracy of a given monitoring system for concentrations outside the range tested is generally uncertified. This fact is important to keep in mind when extrapolating the performance of monitoring systems and methods at the 1988 CDC 0.20 to 1.50 AEL concentration range to the 2003/2004 CDC 0.50 to 2.00 AEL concentration range.

This chapter does four things: (1) it documents technologies used before 2005 in the non-stockpile program or available to monitor at the CDC's 1988 AELs; (2) it assesses the ability of these monitoring systems and associated methods to monitor at the CDC's 2003/2004 AELs; (3) it recommends upgrades to existing monitoring systems and identifies technologies recommended for further development; and (4) it addresses alarm levels and their relationship to AELs.

MINICAMS

MINICAMS is an automated NRT monitor for the detection of GB, HD, or VX that, as previously noted, is typically configured with a sampling tube, a capillary GC column, and an FPD. During the sampling period, chemicals present in the air stream pulled into the MINICAMS are trapped in the sampling tube, which is usually a glass tube packed with particles of HayeSep D (for G and VX agents) or Tenax-TA (for HD). After the sampling period, an inert carrier gas

³Known as the X Classification System, this system, which is described in Chapter 5, defines levels of agent decontamination for materials and waste and defines subsequent management procedures (U.S. Army, 2002). 3X is applied to materials or waste that have been surface decontaminated such that they do not produce a vapor concentration in excess of the agent-specific AEL for an unmasked worker.

⁴Letter from Vickie H. Paul, Dynatherm Sales Manager, CDS Analytical, Inc., to John Decker, CDC National Center for Environmental Health, June 28, 2002; Personal communication between Vickie H. Paul, Dynatherm Sales Manager, CDS Analytical, Inc., and Gary Sides, committee member, August 20, 2004.

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(helium or nitrogen) is allowed to flow through the sampling tube and into the GC column. The sorbent bed in the tube is then heated to desorb the collected chemicals, which are swept into the GC column by the flow of carrier gas. The chemicals are then separated on the GC column, which is temperature programmed. Ideally, the agent of interest exits the GC column into the detector at a time, known as the retention time, when no other chemical is entering the detector. That is, the agent of interest should have a GC retention time that does not overlap the retention time for any other chemical exiting the GC column. The agent can then be detected without interference by measuring light emitted from the species HPO* (phosphorus emission) for G and V agents or by measuring light emitted from the species S_2^* (sulfur emission) for HD.5

Before use, each MINICAMS must be calibrated. Calibration consists of injecting known masses of agent into the inlet of the MINICAMS during successive instrument cycles—specifically, microliter volumes of a dilute solution of agent are injected. Thus, the response (detector signal) versus mass of agent ratio can be determined. After calibration, the responses obtained during subsequent MINICAMS cycles can be converted to detected masses and to detected concentration readings, which are then reported by the MINICAMS. The calibration procedure is covered in greater detail later in this section.

GB and HD are sampled and detected directly by MINICAMS. Because of its low volatility and high affinity for irreversible adsorption on surfaces, however, VX is first derivatized by reaction with silver fluoride to yield the more volatile and less reactive G-analog of VX, which is then sampled and detected by MINICAMS.

The derivatization of VX is accomplished in real time by installing a V-to-G conversion pad on the inlet of the MINICAMS or on the distal end of a heated sample line connected to the inlet. The conversion pad consists of a polyester felt pad impregnated with potassium fluoride and silver nitrate.

$$\begin{array}{c} \text{HPO*} \rightarrow \text{HPO} + hv \\ \text{S}_2^* \rightarrow \text{S}_2 + hv \end{array}$$

where hv represents a photon of light with a wavelength centered at about 526 nm for the HPO* emission and at about 396 nm for the S_2^* emission.

As noted previously, the FPD may be operated in a phosphorus-specific mode (by monitoring HPO* emissions through a 525-nm, narrow-bandpass optical filter) or in a sulfur-specific mode (by monitoring S₂* emissions through a 396-nm, narrow-bandpass optical filter). In the phosphorusspecific mode, the FPD is about 10,000 times more sensitive to phosphorus than to carbon on the basis of signal per unit mass. In the sulfur-specific mode, the FPD is also about 10,000 times more sensitive to sulfur than to carbon for the mass range of interest when monitoring for HD at its STEL (Thurbide and Aue, 1994). The FPD is less selective for phosphorus versus sulfur than for phosphorus versus carbon or phosphorus versus hydrocarbons. Thus, despite the selectivity of the FPD, sulfur emissions (resulting from the formation of S_2^* in the FPD) and hydrocarbon emissions (resulting, for example, from the formation of CH*) can cause interference (false positives) in the phosphorusspecific mode. Also, two kinds of organophosphorus compounds can cause false positives in the phosphorus-specific mode: (1) organophosphorus compounds that are not agents but have the same retention time as GB or the G-analog of VX and (2) organophosphorus compounds other than VXfor example, certain pesticides—that also undergo V-to-G conversion to yield the G-analog of VX. In addition, hydrocarbons can quench (reduce) sulfur and phosphorus emissions, causing false negatives. For example, a concentration of only a few parts per million of a hydrocarbon, present in an area sampled by MINICAMS and with the same retention time as the agent being monitored, can result in the quenching of phosphorus or sulfur emissions by about 50 percent (Aue and Sun, 1993).

During one recent 22-month period at the former production facility at NECD (March 2002 through December 2003), about 1.5 percent of the VX readings reported by MINICAMS, corresponding to 80 different events, were greater than or equal to the alarm level set point (0.70 TWA). DAAMS samples collected to confirm or deny the MINICAMS alarm events showed that all but one of these events were due to false positives.⁶ At least some of the false positives were thought to have been caused by O,S-diethyl methylphosphonothioate (O,S-DMP), diethyl methylphosphonate (TRO), or related phosphorus-containing compounds in the air at the facility. In addition, false positives caused by plasticizers (hydrocarbons) have occurred at the NECD former production facility. Recent changes in operations at the NECD facility, especially better ventilation (that is, a higher rate of air exchange) in Building 143, greatly reduced the rate of false positives.8

 $^{^5}$ The asterisks in HPO* and S_2 * refer to the electronically excited states for HPO and S_2 . Light is emitted from these excited states and detected by the photomultiplier tube in the FPD as follows:

⁶Tom Hoff, NECD Project Manager, and William Rogers, Tennessee Valley Authority (TVA) Quality Officer, Briefing to the Department of Health and Human Services, March 11, 2004; William Rogers, TVA Quality Officer, Briefing to the committee, August 3, 2004.

⁷Terry Frederick, TVA, Briefing to the committee, September 14, 2004. ⁸Terry Frederick, TVA, Briefing to the committee, September 14, 2004.

False positives and false negatives caused by chemicals with the same retention time as the agent being monitored can sometimes be eliminated by installing a detector not subject to the same interferences. For example, false positives caused by the presence of sulfur-containing compounds with the same retention time as HD can be eliminated by replacing the FPD with an XSD. The XSD detects the chlorine in HD, but it does not detect the sulfur present in HD or in other sulfur-containing compounds that may interfere with the detection of HD when using the FPD. Of course, a MINICAMS configured with an XSD in place of the FPD may then be subject to false positives caused by the presence of chlorine-containing compounds other than HD in the area being monitored.

The XSD also has the advantage of a linear response for HD, in contrast to the FPD's quadratic response, and the XSD can detect lower levels of HD than the FPD. The response of the XSD, however, is less stable than that of the FPD, and the XSD requires more frequent maintenance and service than the FPD. For example, the XSD for MINICAMS is usually sold with a spare reactor probe assembly, which must be replaced after a few months of operation. By comparison, the FPD may be operated for years without requiring maintenance or repair. Again, only one detector at a time (FPD, PFPD, or XSD) can be installed in the MINICAMS.

As noted previously, MINICAMS may also be configured with a pulsed flame photometric detector (PFPD). The PFPD is more selective than the FPD for phosphorus emissions than for sulfur and hydrocarbon emissions (Cheskis et al., 1993). Thus, the PFPD operated in the phosphorus-specific mode can result in fewer false positives caused by organosulfur compounds and by hydrocarbons than the FPD operated in the phosphorus-specific mode. The PFPD, however, is still susceptible to false positives caused by organophosphorus compounds and to false negatives (quenching) caused by hydrocarbons (Cheskis et al., 1993). In addition, the PFPD is more complex and more costly than the FPD (FOCIS, 2003a).

To certify MINICAMS as a monitor for a given agent at a specific AEL (TWA or IDLH limit), a method that describes the proper analytical use of the monitor must first be written, reviewed, and approved. At least two MINICAMS must then pass a 4-day precision-and-accuracy (P&A) study, during which the monitors are operated and maintained by two different trained operators in accordance with the written method. A P&A study consists of first calibrating the MINICAMS and then conducting two series of challenges of the monitor each day over a 4-day period using dilute solutions of the agent. Each series of challenges consists of injecting microliter volumes of the agent solution into the inlet of the MINICAMS so that the mass of agent injected corresponds to the mass of agent that would be collected if the monitor were sampling air containing agent at the following concentrations: 0.00 (blank), 0.20, 0.50, 0.80, 1.00, and 1.50 AEL (or, as stated in Table 10-2 of the latest version of the Programmatic Laboratory and Monitoring Quality Assurance Plan, 0.00, 0.50, 0.75, 1.00, 1.50, and 2.00 AEL) (U.S. Army, 2004f). At the end of the 4-day test period, the concentrations reported by the MINICAMS are analyzed statistically to determine whether the monitor passed the certification test. As noted previously, they are analyzed (1) to demonstrate that, when used for the detection of a true agent concentration of 1.00 AEL, the monitoring system (and associated written method) will report a found concentration in the range of 0.75 to 1.25 AEL (that is, 75 to 125 percent recovery) with a precision of \pm 25 percent and 95 percent confidence and (2) to document the precision and accuracy of the monitoring system at all of the concentrations used in the P&A study.

Many P&A studies of MINICAMS have been conducted successfully by non-stockpile and stockpile staff during the past 10 years. 9 These studies have shown that MINICAMS are capable of reporting GB, VX, and HD concentrations with an accuracy of ±25 percent and a precision of ±25 percent with 95 percent confidence at true concentrations of 1.00 TWA and 1.00 IDLH for each agent and have documented the precision and accuracy of the monitoring system at the concentrations used in the P&A studies in the ranges 0.20 to 1.50 TWA and 0.20 to 1.50 IDLH. Although MINICAMS will report agent concentration readings below 0.20 AEL and above 1.50 AEL, these concentration reports are not "certified." That is, MINICAMS used in the field typically have not passed P&A studies that encompass agent challenge concentrations below 0.20 AEL or above 1.50 AEL. However, over the last 10 years, P&A studies and baseline studies—another type of certification test defined in the CMA Programmatic Laboratory and Monitoring Quality Assurance Plan (U.S. Army, 2004f)—have shown that if a MINICAMS reports an agent concentration greater than the P&A study range, there is confidence that the true concentration of agent is greater than 1.50 AEL. Thus, MINICAMS reliably warns of agent concentrations greater than 1.50 AEL even though it is generally not certified for accuracy at concentrations greater than 1.50 AEL.

During the past 10 years, hundreds of MINICAMS have been certified for operation in the range 0.20 to 1.50 TWA for HD, GB, and VX and in the range 0.20 to 1.50 IDLH limit for GB and VX. MINICAMS have also been certified and used successfully to monitor at HD concentrations greater than the CDC's IDLH limit for this agent. Successful operation for these agents and in these concentration ranges has been demonstrated repeatedly during the past 10 years for a wide variety of environments and facilities. It is thus reasonable to assume that the MINICAMS has been proved reliable during field operation. This is illustrated in Figures 4-1 and 4-2, where it is labeled "1988/1997 MINICAMS."

⁹In this report, "precision-and-accuracy study" refers to the practice of using liquid standard solutions to estimate the performance of monitoring systems when the systems are used to sample actual agent vapor.

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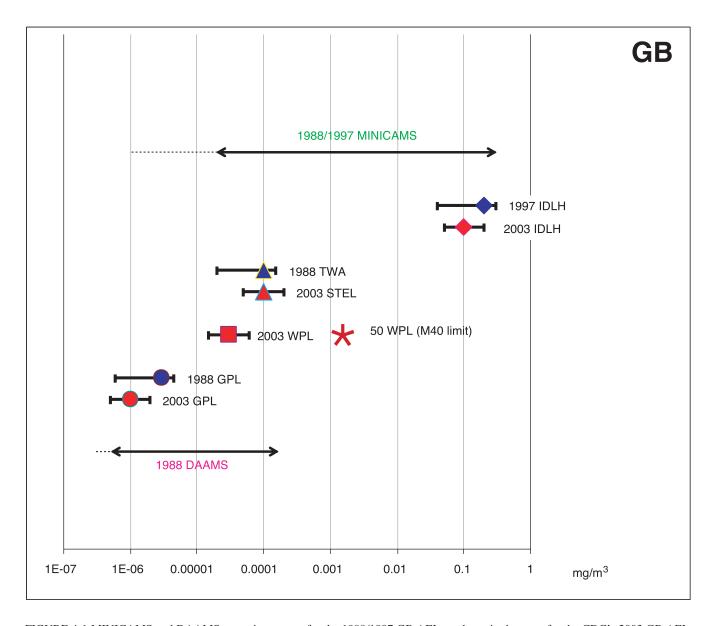


FIGURE 4-1 MINICAMS and DAAMS operating ranges for the 1988/1997 GB AELs and required ranges for the CDC's 2003 GB AELs. NOTES: (1) The 1988/1997 AEL concentration ranges for GB over which MINICAMS and DAAMS have been certified and operated for many years at various sites are indicated by horizontal lines that end in arrows. (2) The "1988/1997 MINICAMS" line includes a dotted line to its left. Although MINICAMS has not been certified or used to monitor for GB in the concentration range represented by the dotted line, its performance when monitoring for VX in the range 0.20 to 1.50 TWA indicates that it should be possible to calibrate and certify MINICAMS for monitoring GB at phosphorus-equivalent concentrations corresponding to 0.20 to 1.50 TWA of VX; (3) The "1988 DAAMS" line also has a dotted line to its left. Although DAAMS has not been certified or used to monitor for GB in the concentration range represented by the dotted line, its performance when monitoring for VX in the range 0.20 to 1.50 of the CDC's 1988 GPL for VX indicates that it should be possible to calibrate and certify DAAMS for monitoring GB at phosphorus-equivalent concentrations corresponding to 0.20 to 1.50 of the 1988 GPL for VX; (4) The IDLH AELs are represented by diamonds. The IDLH concentration range used in the past when certifying MINICAMS, 0.20 to 1.50, and the concentration range required in the future, 0.50 to 2.00, are represented by range bars on the diamonds; (5) The CDC's 1988 TWA AEL and the CDC's 2003 15-minute STEL for GB (numerically equivalent to the 1988 TWA AEL) are represented by triangles with range bars; (6) The CDC's 2003 WPL for GB is represented by a square with a range bar, and the 1988 and 2003 GPLs are represented by circles with range bars; (7) The GB concentration limit above which negative-pressure respirators, such as the M40 mask, may not be worn is marked by an asterisk and labeled "50 WPL (M40 limit)"; and (8) Limits for supplied-air respirators (1,000 WPL) and SCBA (10,000 WPL) are not shown.

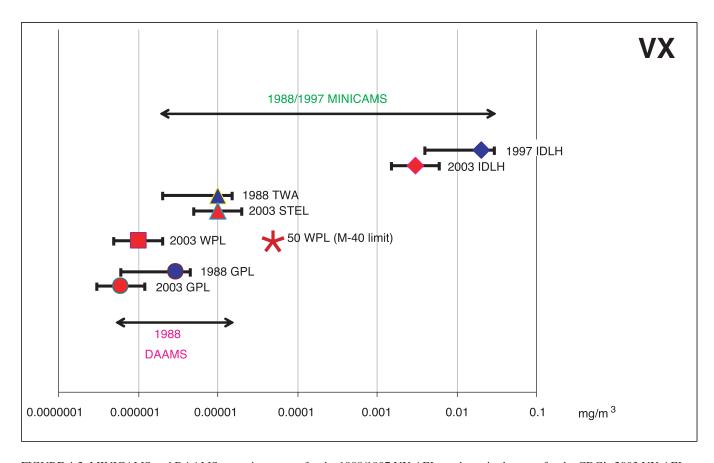


FIGURE 4-2. MINICAMS and DAAMS operating ranges for the 1988/1997 VX AELs and required ranges for the CDC's 2003 VX AELs. NOTES: (1) The 1988/1997 AEL concentration ranges for VX over which MINICAMS and DAAMS have been certified and operated for many years at various sites are indicated by horizontal lines that end in arrows. (2) The IDLH AELs are represented by diamonds. The IDLH concentration range used in the past when certifying MINICAMS, 0.20 to 1.50, and the concentration range required in the future, 0.50 to 2.00, are represented by range bars on the diamonds; (3) The CDC's 1988 TWA AEL and the CDC's 2003 15-minute STEL for VX (numerically equivalent to the 1988 TWA AEL) are represented by triangles with range bars; (4) The CDC's 2003 WPL for VX is represented by a square with a range bar, and the 1988 and 2003 GPLs are represented by circles with range bars; (5) The VX concentration limit above which negative-pressure respirators, such as the M40 mask, may not be worn is marked by an asterisk; and (6) Limits for supplied-air respirators (1,000 WPL) and SCBA (10,000 WPL) are not shown.

The 1988/1997 MINICAMS and current DAAMS concentration ranges shown in Figures 4-1 through 4-3 reflect the performance of these systems when monitoring at the CDC's 1988 AELs (and at the Army's 1997 IDLH limits for GB and VX), performance proven at many different nonstockpile and stockpile sites during the past 10-15 years. The CDC's 2003/2004 AELs and required operating ranges for GB, VX, and HD are also presented in Figures 4-1 through 4-3. The projected and actual performance (as of the date of preparation of this report) for MINICAMS and DAAMS when monitoring at the CDC's 2003/2004 AELs is discussed in the next section.

Note that VX is detected as its G-analog, which differs from GB only by the presence of an ethyl group in place of an isopropyl group. Thus, it is likely that MINICAMS could be successfully certified for GB at concentrations at least an order of magnitude less than the lower limit shown for the 1988/1997 MINICAMS range in Figure 4-1. (This extension of the GB lower detection limit vis-à-vis the 1988/1997 MINICAMS range for VX is shown by the dotted line to the left of the 1988/1997 MINICAMS line at the top of Figure 4-1.)

DAAMS

Manual DAAMS samples are collected by pulling air through glass sampling tubes packed with a porous polymer for periods of time ranging from a few minutes for NRT confirmation samples to as long as 12 hours for GPL historical monitoring. Sampling tubes are placed at various locations within a given site. Most of the sampling tubes are co-located with NRT monitors such as MINICAMS. DAAMS samples

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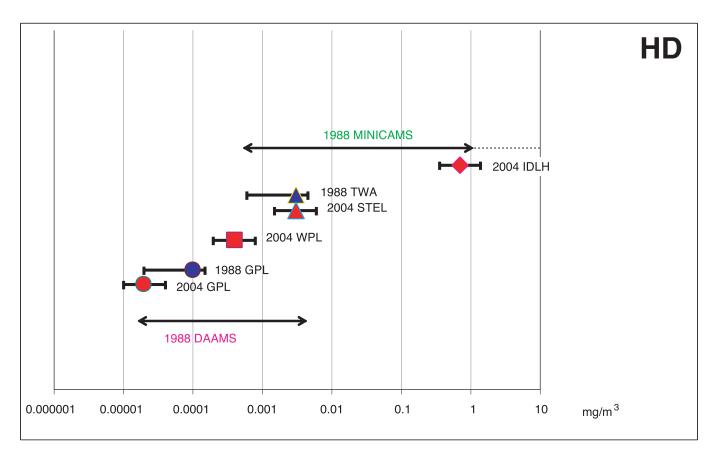


FIGURE 4-3 MINICAMS and DAAMS operating ranges for the 1988 HD AELs and required ranges for the CDC's 2004 HD AELs. NOTES: (1) The 1988 AEL concentration ranges for HD over which MINICAMS and DAAMS have been certified and operated for many years at various sites are indicated by horizontal lines that end in arrows. (2) The "1988 MINICAMS" line includes a dotted line to its right. This dotted line represents the fact that even though an IDLH AEL for HD was not defined until recently, MINICAMS has been used for many years to monitor for HD at concentrations up to and far above the CDC's 2004 IDLH AEL for HD; (3) The CDC's 2004 IDLH AEL for HD is represented by a diamond. The IDLH concentration range required in the future when certifying MINICAMS, 0.50 to 2.00, is represented by range bars on the diamond; (4) The CDC's 1988 TWA AEL and the CDC's 2004 15-minute STEL for HD (numerically equivalent to the 1988 TWA AEL) are represented by triangles with range bars; (5) The CDC's 2004 WPL is represented by a square with a range bar, and the 1988 and 2004 GPLs are represented by circles with range bars; and (6) Limits for supplied-air respirators (1,000 WPL) and SCBA (10,000 WPL) are not shown.

are currently analyzed for agent to provide historical monitoring data for TWA AELs and, where applicable, for GPL AELs. DAAMS samples are also analyzed to confirm or deny TWA alarms sounded by NRT monitoring systems.

The analysis of DAAMS samples is accomplished using an Agilent Model 6890 GC connected to a Dynatherm ACEM 900 or a Dynatherm IACEM 980 thermal desorption system, which is configured to receive and desorb manually collected samples. For samples collected and analyzed in support of historical monitoring, the DAAMS GC is usually configured with an FPD. DAAMS GCs used to confirm or deny NRT monitoring alarms may also be configured with a mass spectroscopy detector (MSD) or with an FPD and an MSD.

Because the analysis of DAAMS samples is based on the use of laboratory-grade GCs, which may be configured in many different ways, the configuration of DAAMS GCs may vary widely. Most DAAMS GC systems in use at stockpile and non-stockpile sites include a precolumn and an analytical column in series. In this configuration, low-boiling compounds and agents are first allowed to pass from the precolumn into the analytical column. The flow of carrier gas within the precolumn is then reversed to allow high-boiling compounds to be backflushed from the precolumn to clean and ready it for the next sample to be analyzed. While the precolumn is being backflushed, carrier gas continues to flow through the analytical column and into the detector, allowing the detection of agents of interest.

The initial step in the analysis of a DAAMS sample consists of inserting the sampling tube into a port on the Dynatherm thermal desorption unit. Agent desorbed from the sampling tube is first collected on a sorbent bed in a

small-bore focusing tube within the Dynatherm unit. Agent is then desorbed from the small-bore tube into the precolumn within a narrow band. For this reason, the DAAMS typically achieves better chromatographic resolution than MINICAMS and thus is more selective and experiences fewer false positives (interferences) than MINICAMS. This enables DAAMS monitors to be used effectively to confirm or deny the presence of agent in areas monitored by MINICAMS.

As with MINICAMS, each DAAMS system must be calibrated before use. Calibration consists of injecting known masses of agent in dilute microliter volumes of solution into the inlets of DAAMS sampling tubes while ambient air is flowing through the tubes. Each tube is then analyzed for agent to yield the response (detector signal) versus the mass of agent. After calibration, the responses obtained for subsequent DAAMS samples can be converted to detected masses and detected concentrations, which are then reported by the DAAMS system.

At most sites, DAAMS relies on the direct detection of GB and HD and the detection of VX as its G-analog. A DAAMS configured only with an FPD, however, is susceptible to the same types of false positives (interferences) as MINICAMS. For example, in the phosphorus-specific mode of operation, false positives may be caused by any hydrocarbon, organosulfur compound, or organophosphorus compound that has the same retention time as GB or the G-analog of VX. However, DAAMS generally experiences far fewer false positives for a given AEL than MINICAMS. This is due to the superior (relative to MINICAMS) chromatographic resolution possible using laboratory-grade gas chromatographs and the larger mass of agent that can be collected using DAAMS methods, which results in a greater signal-to-noise ratio. For example, as noted previously, during one 22-month period at the NECD FPF, about 1.5 percent of the VX readings reported by MINICAMS, corresponding to 80 different events, were greater than or equal to the alarm level set point (0.70 TWA). DAAMS samples collected to confirm or deny the MINICAMS alarms showed that all but one of these events were due to false positives caused by chemical interferences.

Despite the better resolution of DAAMS compared with MINICAMS, DAAMS is susceptible to false positives caused by organophosphorus compounds that undergo V-to-G conversion to yield the G-analog of VX, whether the DAAMS GC is configured with an FPD, an MSD, or both. For example, O,S-DMP will interfere with the DAAMS determination of VX when the V-to-G conversion method is used. ¹⁰ At NECD, a DAAMS method that collects and analyzes VX directly has proven effective in eliminating false positives caused by O,S-DMP and similar compounds.

At first, this method could only be used for sampling times up to about 1 hour because of poor VX recoveries observed for longer sample periods. 11 Recent work at NECD, however, has resulted in a direct VX DAAMS method for the CDC's 2003 VX WPL that has passed P&A studies with a sample period of 6 hours. 12

Like MINICAMS, DAAMS instruments and methods must be certified before use by conducting 4-day P&A studies. At the end of the 4-day test period, the concentrations detected using DAAMS are analyzed statistically to determine whether a given instrument or method passed the certification test—that is, whether the instrument or method will report a found concentration in the range of 0.75 to 1.25 AEL (that is, 75 to 125 percent recovery) with a precision of ±25 percent and 95 percent confidence—and, also, to document the precision and accuracy of the DAAMS method at all concentrations used in the study (typically in the range 0.20 to 1.50 AEL).

During the past 20 years, hundreds of DAAMS systems have been certified for operation and used successfully to monitor GB, VX, and HD manually in the range 0.20 to 1.50 TWA and 0.20 to 1.50 GPL. Successful operation for these agents and in these concentration ranges has been demonstrated repeatedly during this period in a wide variety of environments and facilities. It is thus reasonable to assume that the DAAMS has been field proven in the concentration noted above. This is illustrated in Figures 4-1 through 4-3, where these ranges are labeled "1988 DAAMS."

Other Monitoring Systems (A/DAM)

Other automated NRT monitors that have been used or tested at various storage and disposal sites include a monitor based on the Dynatherm ACEM 900 thermal desorption unit connected to an Agilent 6890 GC and a newer, improved NRT monitor based on the Dynatherm IACEM 980 unit and the Agilent 6852 GC. Both monitoring systems are known by the same acronym, A/DAM. Both are typically configured for sampling using a glass tube packed with a porous polymer, separation using a temperature-programmed capillary GC, and flame photometric detection. Both the 6890- and the 6852-based monitoring systems can be configured to achieve better chromatographic resolution (and thus better selectivity) than MINICAMS and may therefore experience fewer false positives for phosphorus-containing compounds and other compounds with retention times similar to that of the G-analog of VX (for phosphoruscontaining compounds that do not undergo conversion to yield the G-analog of VX).

¹⁰Tom Hoff, NECD Project Manager, and William Rogers, TVA Quality Assurance Officer, Briefing to the Department of Health and Human Services, March 11, 2004; William Rogers, TVA Quality Assurance Officer, Briefing to the committee, August 3, 2004.

¹¹Tom Hoff, NECD Project Manager, and William Rogers, TVA Quality Assurance Officer, Briefing to the Department of Health and Human Services, March 11, 2004; William Rogers, TVA Quality Assurance Officer, Briefing to the committee, August 3, 2004.

¹²Terry Frederick, TVA, Briefing to the committee, September 14, 2004.

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In addition, the 6852-based A/DAM system can be configured with two separate GC columns and two separate FPDs. Gas streams exiting the IACEM 980 can be split between the two analytical channels. If the two columns have liquid phases that are sufficiently dissimilar (for example, nonpolar and polar), a given agent will be detected at two different retention times on the two different analytical channels. Other potential interferences (for example, hydrocarbons) are unlikely to exhibit the same retention times as the agent on the two different columns. In this manner, a much higher degree of selectivity is possible than for MINICAMS.

Agilent recently introduced enhancements to the FPD that resulted in a twofold to fivefold improvement in the signal-to-noise ratio. ¹³ In addition, Agilent has developed a method for the IACEM 980/Agilent 6852 system that allows determining VX directly, without derivatization. Although often difficult to implement for routine use, if successful, a direct method for VX should result in fewer interferences (false positives) in comparison with the V-to-G conversion method for VX.

The ACEM 900/Agilent 6890 and the IACEM 980/Agilent 6852 A/DAM systems have been proven capable of monitoring at the CDC's 1988 TWA levels for GB, HD, and VX at several sites during the past 10 years. The primary barriers to the more widespread use of these systems have been their greater cost, size, weight, and complexity compared with the MINICAMS. However, their greater analytical flexibility might offset these barriers in the future, especially when monitoring sites or operations where MINICAMS has produced numerous false positives.

ABILITY OF SYSTEMS USED FOR MONITORING AT THE 1988/1997 AELS TO MONITOR AT THE 2003/2004 AELS

The Army plans to use MINICAMS to monitor at non-stockpile sites for GB, HD, and VX at the 2003/2004 STELs and, when necessary, at the IDLH levels. DAAMS will be used at non-stockpile sites for historical monitoring at the CDC's 2003/2004 WPLs and to confirm or deny MINICAMS alarms at the CDC's 2003/2004 STELs (equal to the CDC's 1988 TWA AELs). (Since the Army does not currently conduct GPL monitoring at non-stockpile sites, the reductions in the GPL levels are not expected to impact non-stockpile operations.)

One other issue that must be considered is the protection factor of 50 that is assigned for negative-pressure respirators, such as the M40 mask. This means the M40 can be used in environments with GB or VX present at concentrations up to 50 times their WPLs for 8 hours and in environments with agent present at concentrations up to 50 times the STELs for not more than 15 minutes. Because HD is suspected to be a

carcinogen, the concentration limit for the use of negativepressure respirators for this agent is 1.00 STEL (equal to 7.50 WPL).

MINICAMS

The use of MINICAMS to monitor for GB, HD, and VX at the 2003/2004 IDLH levels and at the 2003/2004 STELs (numerically equal to the CDC's 1988 TWAs) should be straightforward in view of its performance in monitoring at the 1988 AELs. It will only be necessary to develop and test a method for the 2004 HD IDLH level, to make minor modifications in operating parameters for existing IDLH methods for GB and VX, and to test the modified methods.

The main problem for MINICAMS will continue to be monitoring at the STEL for VX (equal to the CDC's 1988 TWA value)—especially at the NECD former production facility. False positives for VX at the TWA level at the NECD caused by phosphorus-containing compounds and other compounds with elution times similar to that of the G-analog of VX may be reduced by reconfiguring or upgrading the MINICAMS to improve its chromatographic resolution (for phosphorus-containing compounds that do not undergo conversion to yield the G-analog of VX, that is, O-ethyl methylphosphonofluoridate). False positives for VX at the TWA level caused by phosphorus-containing compounds other than VX that undergo conversion to yield the G-analog of VX may be eliminated by developing a MINICAMS method that can detect VX directly rather than as the G-analog. Both techniques will decrease interferences when monitoring for VX, so it would be preferable to monitor for VX directly and to improve chromatographic resolution. The dual-tube sampling system now available as an accessory for the MINICAMS results in a larger sample volume and, accordingly, the collection of a larger mass of agent for a given AEL, improving the signal-to-noise ratio but not the chromatographic resolution of the MINICAMS.

As noted previously, the use of the PFPD in place of the FPD in MINICAMS results in improved selectivity for phosphorus-containing agents (GB and VX) versus hydrocarbons and sulfur-containing compounds (which may cause false positives). The PFPD, however, is more costly and complex to operate and maintain than the FPD (FOCIS, 2003a). Moreover, it would not solve the main problem with MINICAMS at the NECD former production facility—namely, the false positives caused by the presence of phosphorus-containing compounds, especially compounds that may undergo conversion to yield the G-analog of VX. In fact, a MINICAMS with a PFPD was recently tested at NECD, and there was no reduction in false positives. 14

¹³Letter from Wayne Abrams, Senior Consultant, Agilent Technologies, to John Decker, CDC National Center for Environmental Health, May 31, 2002

¹⁴Tom Hoff, NECD Project Manager, and William Rogers, TVA Quality Assurance Officer, Briefing to the Department of Health and Human Services, March 11, 2004; William Rogers, TVA Quality Assurance Officer, Briefing to the committee, August 3, 2004.

Because MINICAMS will be used in the non-stockpile program to monitor at the 2003/2004 STELs, which are numerically equivalent to the 1988 TWA levels, there is no need to improve the sensitivity of MINICAMS, at least based on the Army's near-term monitoring requirements. Nonetheless, in anticipation of a possible future need for NRT monitoring at the 2003/2004 WPLs, the Army recently completed a laboratory study of the performance of MINICAMS and A/DAM systems modified to monitor for GB, HD, and VX at the 2003/2004 WPLs (FOCIS, 2003a). MINICAMS modified to include a PFPD and an external dual-tube sampler passed 4-day laboratory P&A studies for GB, VX, and HD. It passed 20-day laboratory baseline studies for GB and HD but failed the baseline study for VX because chemical interferences were present in the atmosphere being sampled during part of the baseline test period. A 4-day field P&A study and a field baseline study for all three agents at the 2003/2004 WPLs was recently conducted using MINICAMS and A/DAM systems at the Anniston, Alabama, stockpile site, and a report on this test is currently in preparation.¹⁵

Finding 4-1: MINICAMS, with only minor modifications to methods used to monitor at the 1988/1997 AELs, is capable of monitoring for GB, HD, and VX at the CDC's 2003/2004 IDLH values and at the CDC's 2003/2004 STELs, which are numerically equivalent to the CDC's 1988 TWA AELs. Interference problems (false positives), especially those caused by organophosphorus compounds and plasticizers when monitoring for VX, will continue to occur for the current low-resolution MINICAMS configuration, especially when using the V-to-G conversion method. The A/DAM system can be configured to achieve better chromatographic resolution than the MINICAMS, to confirm agent detection automatically (using two independent analytical channels), and, although difficult to implement routinely, to detect VX directly (that is, without conversion of VX to the G-analog).

Recommendation 4-1: To reduce false positives when monitoring at critical locations susceptible to chemical interferences, the Army should explore ways to improve the gaschromatographic resolution of the MINICAMS. As an alternative, at critical locations, the Army should consider using the A/DAM system, which can be configured to achieve better chromatographic resolution than the MINICAMS.

DAAMS

Confirming or denying MINICAMS alarms at the 2003/2004 STELs will be no more difficult for the DAAMS than confirming or denying alarms at the CDC's 1988 TWA levels. The CDC's 2003 WPL for GB is greater than the

CDC's 1988 GPL for GB and greater than the CDC's 1988 TWA level for VX, concentrations that have been monitored using DAAMS for many years. Thus, from the standpoint of sensitivity, it should be possible to use DAAMS techniques for monitoring at CDC's 1988 AELs with only minor modifications for monitoring at CDC's 2003 WPL for GB. Similarly, because the CDC's 2004 WPL for HD is greater than the CDC's 1988 GPL for HD, which has been monitored using DAAMS for many years, only relatively minor changes should be necessary with respect to sensitivity to allow DAAMS to monitor for HD at the new level. These statements assume that the sampling period for DAAMS, when sampling at the WPLs, is no less than 8 hours. (The typical DAAMS sample period used to monitor at the 1988 GPL for HD is 12 hours.)

The response of the DAAMS FPD to sulfur-containing compounds, such as HD, is approximately quadratic. Thus, although DAAMS configured with an FPD appears to have the sensitivity to monitor at the CDC's 2004 WPL for HD, the signal obtained will be about 50 times weaker than the signal at the CDC's 1988 TWA AEL (for the same sample volume). Because the concentrations of potential chemical interferences in the environments being sampled will, of course, be unaffected by changes in the regulatory limits for HD, it is likely that a much higher rate of false positives will be observed when using DAAMS to monitor for HD at the CDC's 2004 WPL rather than at the CDC's 1988 TWA AEL.

If interferences (false positives) increase for the CDC's 2004 HD WPL and HD GPL—compared with the CDC's 1988 AELs—installing an XSD in DAAMS in place of or in addition to the FPD may be a solution. The XSD has a linear response to HD, is more sensitive than the FPD, and is less susceptible to false positives from hydrocarbons than the FPD. Of course, the XSD is susceptible to false positives caused by chlorine-containing compounds.

Almost all sites use the V-to-G conversion method when sampling for VX. Concentration ranges for DAAMS methods used to monitor at 1988/1997 AELs for VX are shown in Figure 4-2. The CDC's 2003 WPL value for VX is less than the CDC's 1988 GPL for VX, but it falls within the concentration range over which current DAAMS methods must be certified for monitoring at the CDC's 1988 VX GPL. Detection limits for VX for current DAAMS have been reported to be as low as 30 picograms. 16 For a sample flow rate of 1 liter per minute, a sample period of 8 hours, and a concentration of 1.00 WPL for VX (1 picogram per liter), 480 picograms of VX would be sampled. This mass is about 16 times greater than the lowest detection limit reported. MINICAMS and A/DAM systems have demonstrated the ability to detect VX at the CDC's 2003 WPL with instrument cycles of 15 minutes or less. Both MINICAMS and the A/DAM are based on the same technologies as the historical

¹⁵Personal communication between Rob O'Neil, FOCIS Associates, Inc., and Gary Sides, committee member, August 24, 2004.

¹⁶Letter from Michael McNaughton, Southwest Research Institute, to John Decker, Centers for Disease Control and Prevention, June 28, 2002.

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DAAMS method. Because sample periods for DAAMS may be 8 hours or more, DAAMS should collect a greater mass of agent when sampling at the WPLs and thus be able to achieve much higher signal-to-noise ratios than MINICAMS or the A/DAM system. From the standpoint of instrument sensitivity, therefore, it appears that DAAMS methods used to monitor at the 1988 AELs can be modified to determine VX at the CDC's 2003 WPL.

It is anticipated, however, that interference problems are likely to be much greater when using DAAMS based on V-to-G conversion to monitor at the CDC's 2003 VX WPL than at the CDC's 1988 VX TWA level, which is 10 times greater. The types of interference expected are those caused by hydrocarbons, sulfur-containing compounds, and phosphorus-containing precursors, impurities, and breakdown or decontamination products. At some sites, interferences caused by compounds such as O,S-DMP, which undergo V-to-G conversion to yield the G-analog of VX, may be a serious problem. For example, interferences from March 2002 through December 2003 resulted in MINICAMS readings >0.10 TWA (equal to 1.0 WPL) 24 percent of the time in Building 143 at the NECD former production facility. Non-stockpile staff anticipate that chemical interferences will be a serious problem at this facility if a V-to-G-based DAAMS method must be used for routine monitoring at the CDC's 2003 VX WPL.17

Staff at the NECD former production facility have developed a DAAMS method that allows VX to be detected directly (without V-to-G conversion), as long as the sample period is less than about 6 hours. (Poor recoveries of VX were obtained for sample periods greater than 6 hours.) If successful in routine use, this direct DAAMS method for VX is expected to result in improved selectivity and fewer false positives.

In anticipation of the implementation of the CDC's 2003/2004 AELs, the Army has conducted tests of modified DAAMS methods at various sites. For example, at the NECD stockpile facility, a DAAMS configured with an IACEM 980 connected to an Agilent 6890 GC configured with a precolumn and an analytical column, to an Agilent heart-cut system, and to an FPD has been used successfully to determine VX at the CDC's 2003 WPL and GPL.¹⁸

A DAAMS configured with a heart-cut valve is usually more selective than systems configured using only a backflush valve; that is, interferences caused by chemical compounds other than agents are greatly reduced with the heart-cut approach. The heart-cut-based DAAMS/FPD system at the NECD stockpile facility, which relies on V-to-G conversion for the detection of VX, has passed 4-day P&A studies and baseline studies for VX WPL and GPL methods (with a sample period of 12 hours for both methods).

In addition to developing DAAMS/FPD-based methods, the staff at the NECD stockpile facility has successfully developed confirmation methods for the CDC's 2003 VX WPL and its 2003 VX GPL using a DAAMS configured with an FPD and an MSD. Although DAAMS/FPD and DAAMS/FPD/MSD methods for VX have been certified at NECD, staff at the NECD stockpile facility expect more false positives at the CDC's 2003 VX WPL and GPL than have been observed for VX in the past.

Staff at the TOCDF stockpile site (Tooele, Utah) have also developed DAAMS methods to monitor at the CDC's 2003 VX and GB WPLs. These methods have been submitted to the CDC for review and approval.

In addition to the recent work at the Tooele and NECD stockpile sites, the Army's CMA has undertaken a study with the goal of modifying DAAMS methods to meet the requirements of monitoring at the CDC's 2003 WPLs and GPLs for GB and VX (FOCIS, 2003b). The study was recently expanded to include HD. It aimed not only to achieve the sensitivities necessary to detect the agents at the various AELs but also to reduce the potential for interferences at the CDC's 2003/2004 AELs by improving the selectivity of the DAAMS. This work addressed both FPD-based screening systems used for routine DAAMS monitoring and FPD/MSD-based DAAMS, which are typically used to confirm the detection of agent by other DAAMS or by NRT monitors.

Various technologies have been incorporated into the development work on DAAMS methods begun by the CMA about 2 years ago. These technologies and upgrades include the following:

- More extensive use of heart-cut methods;
- Upgrades of the backflush technique;
- Cryogenic cooling to narrow chromatographic peaks to improve chromatographic resolution (using a tank of compressed, liquid carbon dioxide connected to a cryotrap surrounding a short length of the GC column);
- Use of a convex lens to increase the signal-to-noise ratio for the FPD; and
- Faster sample flow, made possible by using 8-mmdiameter sampling tubes in place of the 6-mmdiameter tubes that had been used at most sites.

The new DAAMs methods developed in the effort noted above have successfully passed laboratory P&A and baseline

¹⁷Tom Hoff, NECD Project Manager, and William Rogers, TVA Quality Assurance Officer, Briefing to the Department of Health and Human Services, March 11, 2004; William Rogers, TVA Quality Assurance Officer, Briefing to the committee, August 3, 2004.

¹⁸The key component of the heart-cut system is a Dean switch, which allows the effluent of the precolumn to be directed into the analytical column only during a short period, from the time just before the agent of interest begins to exit the precolumn to the time just after the agent has exited the precolumn. At all other times, before and after this agent window, the carrier-gas effluent from the precolumn vents through a restrictor column to the atmosphere (or to a second detector installed to monitor the effluent from the precolumn). The liquid phase of the analytical column generally differs greatly in polarity from the liquid phase of the precolumn.

studies. They are now undergoing P&A and baseline studies at the Umatilla stockpile site (UMCDF) (FOCIS, 2004).

Finding 4-2: Work is currently under way or has been completed at several stockpile and non-stockpile sites to modify DAAMS methods to meet the requirements of monitoring at the CDC's 2003/2004 AELs. The DAAMS methods and equipment configurations used to enable monitoring at the CDC's 2003/2004 AELs vary widely from site to site, however. Also, the methods that are being developed at those sites appear to be focusing on achieving adequate sensitivities to monitor at the new AELs. Although it is likely that agents can be detected at the CDC's 2003/2004 WPLs (and GPLs) using DAAMS, it is also likely that interference will be a bigger problem than it was for DAAMS in the past.

Recommendation 4-2: The Army should immediately convene a workshop of non-stockpile and stockpile personnel working on DAAMS methods from each site to allow them to exchange written procedures, test data, and other information regarding the CDC's 2003/2004 AELs. This workshop should also offer presentations by knowledgeable technical personnel involved in the recent CMA-sponsored effort to develop more selective DAAMS methods. Also, the Army should continue to work on improving the selectivity of DAAMS methods, especially FPD-based methods, to further reduce the number of false positive alarms.

A/DAM

A/DAM has been used routinely at a few sites to monitor for GB, HD, and VX at CDC's 1988 TWA AELs and for GB and VX at the IDLH levels. Thus, the use of A/DAM to monitor for GB, HD, and VX at the CDC's 2003/2004 IDLH levels and STELs (equal to the CDC's 1988 TWAs) should be straightforward. However, the use of the A/DAM system as an NRT monitor has not been widespread because it is more expensive, larger, heavier, and more complex than MINICAMS.

Because no IDLH level had been defined for HD before May 2004, a method must be developed and certified for the determination of the IDLH levels of this agent by the A/DAM system. This task should be straightforward using an A/DAM configured with an external loop sampler.

Testing of the A/DAM for monitoring at the STEL for VX (equal to CDC's 1988 TWA level) at the NECD former production facility is planned.¹⁹ The A/DAM will determine VX directly (instead of as the G-analog). It is anticipated that the A/DAM system, configured for the direct determination of VX, will not experience the relatively high rate of false positives that has sometimes plagued MINICAMS at the NECD former production facility, which was thought

to be caused by phosphorus-containing compounds (TRO or related compounds, O,S-DMP, etc.).

As it did for MINICAMS, the Army recently completed laboratory studies of the performance of A/DAM at the CDC's 2003/2004 WPLs for GB, HD, and VX (FOCIS, 2003a). The A/DAM (6852-based) system passed 4-day P&A studies and baseline studies for each agent during laboratory tests, with VX determined using the V-to-G conversion. Finally, A/DAM systems recently underwent both 4-day P&A and baseline studies at the Anniston (ANCDF) stockpile facility. A report describing the results of these tests is in preparation.²⁰

ALTERNATIVE TECHNOLOGIES FOR MONITORING AT THE 2003/2004 AELS

The CDC's 2003 STEL level for VX, 1×10^{-5} mg/m³, corresponds to a concentration of about one part per trillion by volume. Not only must NRT monitoring systems be capable of detecting VX at this concentration, but NRT systems used prior to 2005 also had to be capable of meeting quality assurance/quality control (QA/QC) requirements for concentrations as low as about 0.50 parts per trillion (equal to 0.50 STEL, the lowest level—other than the blank—used during P&A studies). In other words, automated detection systems used in the non-stockpile program are actually automated analytical instrument systems. The CDC's 2003 WPL for VX is 1×10^{-6} mg/m³, or about 0.1 parts per trillion. The DAAMS method used to monitor at this concentration must also be capable of meeting stringent QA/QC requirements, including those of P&A studies, where the lowest test concentration is about 0.05 parts per trillion. In addition to measuring VX at concentrations of less than one part per trillion and meeting QA/QC requirements, automated and manual methods must be amenable to reliable, long-term operation by personnel with minimal technical skills.

For VX concentrations as low as 0.05 parts per trillion, the only technologies mature enough to be considered for use in the non-stockpile program in the next 3 years are sorbent-based sampling, temperature-programmed capillary gas chromatography, and detection using the FPD, PFPD, XSD, MSD, or FPD/MSD. Such technology has also proved capable of meeting the requirement for reliable long-term operation by relatively nontechnical personnel. Given these discriminators, the near-term choice in NRT systems is the MINICAMS (configured with an FPD, a PFPD, or an XSD) or a 6852-based A/DAM system (configured with an FPD).²¹

¹⁹William Brankowitz, PMNSCM, Information provided to the committee, May 6, 2004.

²⁰Personal communication between Rob O'Neil, FOCIS Associates, Inc., and Gary Sides, committee member, August 24, 2004.

²¹It should be possible to configure the A/DAM system with a PFPD or an XSD, but—to the best of the committee's knowledge—these configurations have not been tested. It should also be possible to configure the A/DAM system with an MSD or with an FPD and an MSD, but these configurations are not practical for routine NRT monitoring, primarily because of cost and complexity.

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Some of the advantages of the MINICAMS compared with the A/DAM are the availability of more selective detectors for routine monitoring (PFPD and XSD) and MINICAMS's greater simplicity, lower cost, lighter weight, and smaller size. Some of the advantages of the A/DAM system compared with the MINICAMS are dual columns/dual detectors to enhance selectivity, a more flexible analytical system, heart-cut capability (using the Dean switch to enhance selectivity), and FPD enhancements for a greater signal-to-noise ratio.

MINICAMS, compared with the A/DAM, is severely limited by its relatively rigid analytical system. For example, it is not possible to use backflush, heart-cut, or dual columns/detectors with MINICAMS—all techniques that would improve selectivity. Poor chromatographic resolution is the main disadvantage of MINICAMS, and this makes it more susceptible to false positives than the A/DAM system.

Repackaging of MINICAMS or A/DAM technology to eliminate their "faults" would require at least 3 years to complete engineering, laboratory testing, field testing, production, and integration of the changes into the non-stockpile program.

Although DAAMS configured with FPDs appear adequate for detecting VX and HD at the CDC's 2003/2004 AELs, they are not expected to be sufficiently selective to pass published P&A requirements, to pass initial and continuing baseline certification requirements, and to achieve the required statistical response rate at reportable limits when they are used to monitor at the 2003/2004 WPLs for these agents.²² Thus, although sensitive enough to detect the WPLs and pass P&A requirements for the agents alone, the presence of chemical interferences (and associated false positives) will make it difficult to pass P&A certification requirements. The main problem anticipated by the committee is the high false positives rates for primary DAAMS tubes analyzed using a GC configured with an FPD and the resulting need to analyze backup DAAMS tubes by alternative methods (for example, a separate GC configured with a column of significantly different polarity or configured with a different detector). Work is currently under way to improve the selectivity of DAAMS systems used for historical monitoring and systems used to confirm or deny alarms reported by NRT monitors. To fully implement the DAAMS modifications now being developed to improve selectivity will take 2 or 3 years from the time that field tests of these modifications are completed.

Finding 4-3: The committee observes that although DAAMS methods used to monitor at the 1988 AELs may currently be capable of monitoring at the 2003/2004 WPLs for VX and HD, improvements in the sensitivity and selectivity of the DAAMS would make it easier to pass published precision and accuracy certification requirements, to pass initial and continuing baseline certification requirements, and to achieve the required statistical response rate at reportable limits.

Recommendation 4-3: PMNSCM should take advantage of research and development being funded by the stockpile program to develop more selective and more sensitive DAAMS methods for monitoring VX and HD at the 2003/2004 WPLs.

During the past year, several technical meetings have included or have been dedicated to the detection of chemical agents. These meetings covered the following technologies:

- Conventional Fourier-transform ion mobility spectrometry (IMS), differential IMS, and dual-cell IMS;
- Cylindrical ion-trap mass spectrometry and IMS/timeof-flight mass spectrometry;
- Surface-enhanced Raman microwave spectroscopy, terahertz and millimeter-wave microwave spectroscopy, and Fourier-transform microwave spectroscopy;
- · Cavitands and liquid crystals;
- Ceramic-metallic (cermet) solid state sensors, surfaceacoustic-wave (SAW) solid state sensors, and metalinsulator/metal-ensemble (MIME) solid state sensors;
- Fluorescent indicating chromophores (fluorescent reporters); and
- · Enzyme-based methods.

The developers of most of these technologies are focusing on homeland security applications, which require the detection of agents at concentrations like the IDLH AELs or, perhaps, an order of magnitude less. Thus, the concentrations of interest to most developers are several orders of magnitude greater than the STEL and WPL AELs of interest in the non-stockpile program. Although a few of the technologies presented at the meetings listed might be able to detect agents at concentrations of parts per trillion, this capability has not been demonstrated. Also, most of these technologies are in the research and development phase, and monitoring systems suitable for use in the non-stockpile program generally are at least 3-5 years from being commercially available. Finally, many of the researchers involved in these technologies are focusing on automated point-detection systems that are simply meant to sound an alarm when agent is detected as opposed to the automated analytical instruments needed by the non-stockpile program, which will accurately determine and report the concentrations of agents, meet stringent QA/QC requirements, and activate alarms.

²²The Army defines reportable limit as "a predetermined value for historical method, that when equaled or exceeded will be reported as chemical materiel that may have exceeded the monitoring level" (U.S. Army, 2004f, p. B-9). For a Class I historical method (that is, a manual method such as DAAMS), the reportable limit must be set so that the statistical response rate at the reportable limit is greater than or equal to 95 percent—that is, the probability, expressed as a percentage, that a 1.0-Z QP challenge will generate a response greater than or equal to the reportable limit must be equal to or greater than 95.

Although the detection limits and stringent QA/QC requirements for NRT monitoring systems and for manual DAAMS methods seem to preclude modifying other technologies for use in the non-stockpile program in the near term, rapid advances in the miniaturization of mass spectrometers may allow them to meet non-stockpile program requirements for NRT monitors and manual historical/confirmation methods at a reasonable cost within about 5 years. It should be emphasized that the NRT monitoring systems used in the non-stockpile program to monitor at the 1988/1997 AELs generally have adequate sensitivity but need much better selectivity. Mass spectrometers are currently the holy grail in the verification of agent alarms at stockpile and non-stockpile facilities.

One existing technology that may enable the development of small, affordable mass spectrometers is an instrument based on a simple cylindrical ion trap that is capable of the direct detection of toluene in air at a concentration as low as 17 parts per billion by volume (Griffin Analytical Technologies, West Lafayette, Indiana). Membrane-based concentration methods currently enable such mass spectrometers to detect methyl salicylate at about 300 parts per trillion. The use of a porous-polymer-based trap on the front end of the mass spectrometer should enable the detection of toluene at concentrations approaching 20-30 parts per trillion. Further improvements might allow cylindrical ion traps to detect less than one part per billion.

Finding 4-4: The CDC's 2003 STEL for VX corresponds to a concentration of less than one part per trillion by volume. DAAMS systems utilizing mass selective detectors with chemical ionization sources are currently capable of detecting VX at these levels. Other technologies, especially miniature mass spectrometers, might be able to meet the requirements of the non-stockpile program for parts-pertrillion sensitivity and improved selectivity at a reasonable cost within a 5 years.

Recommendation 4-4: PMNSCM should conduct a paper study of the state of miniature mass spectrometer technologies and, if warranted, support the development of near-real-time (NRT) systems based on the best available technology. The paper study should be done by technical personnel with extensive hands-on experience in air monitoring at the 1988 AELs, who—along with personnel involved in the manufacture of miniature mass spectrometers—should also conduct the effort to develop or modify mass spectrometer systems for NRT monitoring.

ALARM LEVELS FOR NEAR-REAL-TIME MONITORS

NRT monitors have been used in the non-stockpile program for many years to detect agent at true concentrations that equal or exceed 1.00 TWA and then to sound an alarm that warns workers to take action in a timely manner. The

CDC's 1988 TWA airborne exposure limit for each agent is intended to ensure the absence of long-term health effects, even for workers not wearing respiratory protection, for exposures up to 8 hours per day (Federal Register, 1988). The same numerical values defined by the CDC in 1988 as TWA levels were recently renamed "short-term exposure limits" (STELs) (Federal Register, 2003a, 2004).

It is desirable that an alarm sound each and every time the true concentration of agent in an area being monitored equals or exceeds 1.00 STEL and never when the true concentration is less than 1.00 STEL.²³ Because of measurement errors, however, the concentration of agent reported by an NRT system is typically not the same as the true concentration of the agent in the area being monitored. In fact, the most stringent certification requirement for NRT systems published by the Army requires an accuracy of only ±25 percent and a precision of ±25 percent with 95 percent confidence for challenges at 1.00 STEL (U.S. Army, 2004f). As an example, a certified NRT system may report an agent concentration of 0.75 STEL even though the true agent concentration in the area being monitored is 1.00 STEL or greater. Thus, it is clearly not possible to set the alarm level for an NRT monitor to sound an alarm only when the true concentration of agent equals or exceeds 1.00 STEL and to avoid sounding an alarm whenever the true concentration is less than 1.00 STEL.

Currently, in the non-stockpile program, the statistical uncertainty of NRT systems is usually accounted for by setting the alarm level at 0.70 STEL. Thus, an alarm is sounded and required actions are taken any time the concentration of agent reported by an NRT monitor exceeds 70 percent of the STEL. Past experience with NRT systems and the statistical analysis of data from numerous certification studies during the past 20 years have shown that any time the true concentration of agent in the area being monitored equals or exceeds 1.00 STEL, NRT systems in use by the Army (that is, ACAMS and MINICAMS) typically have at least an 80 percent probability of reporting a concentration ≥0.70 STEL and sounding an alarm. The Army's stockpile program has long used (and in some states the non-stockpile program may also be required to use) alarm levels as low as 0.20 STEL. At this alarm level, NRT systems in use by the Army typically have at least a 99 percent probability of reporting a detected concentration greater than or equal to 0.20 STEL and of sounding an alarm any time the true concentration of agent in the area being monitored equals or exceeds 1.00 STEL.

 $^{^{23}}$ The discussion in this section focuses on alarm levels for NRT monitoring systems used for monitoring at the 2003/2004 STELs. It should be noted, however, that an NRT monitoring system may report an air agent concentration above the 2003/2004 WPL but below the STEL alarm level. For this reason, a STEL concentration reading ≥0.30 STEL for GB, ≥0.10 STEL for VX, or, ≥0.13 STEL for HD may indicate the presence of agent at a concentration ≥1.00 WPL and may indicate the need to use DAAMS to monitor the area at the WPL level.

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Note that the target concentration of concern when using an NRT monitor is 1.00 STEL, no matter the set point for the alarm level. Also, the accuracy of an NRT monitor, its minimum detection limits, its certification requirements, and its operation are not affected in any way by the choice of alarm level. That is, NRT monitors used in the non-stockpile program are certified to demonstrate that they meet QA/QC requirements for 1.00 STEL; are typically calibrated only at 1.00 STEL; and are challenged at least once a day at 1.00 STEL to make certain that they respond properly—again, no matter whether the alarm level is set at 0.20 STEL or 0.70 STEL. The alarm level, in effect, simply defines the probability that an alarm will be sounded if the true concentration of agent in an area being monitored is 1.00 STEL or greater—that is, it is an indication of how certain the Army is that an agent excursion above 1.00 STEL will be detected and an alarm sounded.

The CDC's 2003 Federal Register announcement regarding AELs for G and V agents states as follows: ²⁴

In implementing the WPLs, STELs, and GPLs, specific reduction factors for statistical assurance of action at the exposure limits are not needed because of safety factors already built into the derivation of the exposure limit. This recommendation assumes that the sampling and analytical methods are measuring within ±25 percent of the true concentration 95 percent of the time. If this criterion is not met, an alarm level or action level below the exposure limit may be required. (Federal Register, 2003a, p. 58349)

Furthermore, written clarification received by the committee from the CDC on August 3, 2004, makes it clear that, for GB and VX, the CDC recommends that the alarm level for an NRT system be set at 1.00 AEL as long as "the sampling and analytical methods are measuring within ±25 percent of the true concentration 95 percent of the time." If this condition cannot be met, then the CDC says that an alarm level below the AEL may be required, but the CDC did not provide any guidance on how to determine that level.

With regard to HD, the CDC announcement (Federal Register, 2004, p. 24167) reads as follows: "Although the CDC does not specifically recommend additional reduction factors for statistical assurance of action at the exposure limit, expo-

sures to sulfur mustard should be minimized given the uncertainties in risk assessment, particularly as related to characterizing carcinogenic potency." There, the CDC seems to say it is acceptable to set the alarm level at 1.00 AEL, but at the same time the CDC requires procedures to minimize exposures to mustard—two directives that seem somewhat in conflict.

The Army apparently used the CDC recommendations for guidance and states in the most recent *Programmatic Laboratory and Monitoring Quality Assurance Program* (U.S. Army, 2004f, Table 10-3) that the alarm levels for GB, VX, and HD can be set one of two ways:

- If the first-challenge pass rate is ≥95 percent for the NRT monitor, the alarm level may be set at 1.00 AEL.
- If a first-challenge pass rate of ≥95 percent cannot be achieved, the alarm level must be set to a value that results in a statistical response rate of ≥95 percent, and a first-challenge pass rate of ≥75 percent must be maintained.

In other words, for a given NRT monitor, according to the CDC, the alarm level may be set at 1.00 AEL if at least 95 percent of the first 1.00-AEL daily quality control (QC) challenges of the monitor over a defined period of time result in concentration readings between 0.75 and 1.25 AEL, which corresponds to ±25 percent accuracy. The requirement for a first-challenge pass rate of ≥95 percent must be met during an initial 28-day baseline study and during successive measured operational intervals (weekly, monthly, etc.), which were not defined in the Programmatic Laboratory and Monitoring Quality Assurance Program (U.S. Army, 2004f). If a first-challenge pass rate of ≥95 percent cannot be achieved during the initial baseline study or during continuing operations for a given NRT monitor, then (1) the alarm level for the monitor must be set so that there is a ≥95 percent probability (statistical response rate) that a 1.00-AEL challenge results in an alarm and (2) a first-challenge pass rate of \geq 75 percent must be maintained. Based on past performance data for NRT monitoring systems, if a first-challenge pass rate of ≥95 percent cannot be achieved, it is likely that the alarm level will have to be set to a value well below 0.70 AEL to achieve a statistical response rate of ≥95 percent.

It is important to understand that the operation of NRT systems is not affected by the alarm level selected. The probability of sounding an alarm in response to a true agent concentration at or above 1.00 AEL, however, is clearly affected by the choice of the alarm level. As an example, for an unbiased, normal distribution (that is, a bell-shaped distribution with the maximum at 1.00 AEL) and with the alarm level set at 1.00 AEL, an alarm would be sounded only 50 percent of the time that the true agent concentration in the area being monitored is at or just above 1.00 AEL. In reality, distributions of agent concentration are not perfectly unbiased or normal. A series of 1.00-AEL challenges made

²⁴The Army defines an action level as a predetermined value, usually for an NRT method, that, when equaled or exceeded, indicates the need to conduct a series of required actions in response to the apparent detection of agent. An action level is typically less than the alarm level for an NRT monitor. Actions taken when the action level is exceeded (but the alarm level is not exceeded) may include checking to ensure that the NRT monitor is functioning properly, locating and correcting a leak before the concentration of agent at the location being sampled exceeds the alarm level, etc. (Personal communication between Robert Durgin, Chief, Monitoring Team, Office of the Program Manager for CMA; Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA; and Gary Sides, committee member, November 30, 2004)

just after calibration and in subsequent days would often result in all reported agent concentration readings being less than 1.00 AEL. In this case, no alarms would be sounded in response to 1.00-AEL QC challenges conducted over several days. The instrument would then appear to be malfunctioning—that is, challenge after challenge at a true concentration of 1.00 AEL would result in no alarms.

Because of variations in the distribution of agent concentration readings, if the alarm levels are set to 1.00 AEL, the percentage of 1.00-AEL challenges that result in an alarm will vary widely from instrument to instrument and from day to day. This is illustrated by the 1.00-TWA challenge data shown in Table 4-1, which were generated during 4 weeks of operation of two different MINICAMS at the Center for Domestic Preparedness' COBRA Training Facility, Anniston, Alabama. During this period, each MINICAMS was calibrated about once a week and used to monitor for GB and VX continuously at the CDC's 1988 TWA levels for these agents (except when 1.00-TWA test challenges were

made). For an alarm level of 1.00 TWA, the 4 weeks of 1.00-TWA challenges for VX would have resulted in alarms 24 percent of the time for Instrument 1 and 28 percent of the time for Instrument 2. For GB, Instrument 1 would have alarmed 9 percent of the time and Instrument 2 would have alarmed 16 percent of the time. On this basis, it appears that the NRT monitors performed poorly. If the alarm level had been set to 0.70 TWA, however, the 1.00-TWA challenges would have resulted in alarms 100 percent of the time for both agents for both instruments, which would correctly reflect the excellent performance of the MINICAMS during the 4-week test period.

The only possible benefit to be gained by raising the alarm level from 0.70 to 1.00 AEL for the non-stockpile program is a reduction in the rate of false positives, which can be achieved only at the expense of increasing the rate of false negatives (that is, failure to sound an alarm even though the true agent concentration equals or exceeds 1.00 AEL). As an example of the impact of raising the alarm level, the

TABLE 4-1 TWA Concentrations Reported by Two Different MINICAMS for 1.00-TWA Challenges Made During 4 Weeks of Operation (August 2004)

	llenge Data –	Instrument 1									
1.03	0.87	0.96	0.97	0.90	0.91	0.82	0.78	0.88	0.83	1.02	0.94
0.87	0.84	0.77	0.71	0.82	0.97	1.10	1.00	0.95	0.91	0.88	0.83
0.83	1.09	1.05	0.97	0.96	0.87	1.02	0.91	1.01	0.92		
24 perce	nt of challeng	ges result in a	alarm with ala	ırm level at 1	.00 TWA						
100 perc	ent of challer	nges result in	alarm with a	larm level at	0.70 TWA						
GB Cha	lenge Data –	Instrument 1									
0.99	0.84	0.93	0.89	0.86	0.85	0.78	0.73	0.80	0.75	0.98	0.90
0.85	0.84	0.76	0.76	0.85	0.93	1.00	0.94	0.90	0.85	0.83	0.81
0.80	1.05	1.00	0.93	0.92	0.86	0.96	0.90	0.97	0.88		
100 perc											
	llenge Data –	Instrument 2	2								
VX Cha	llenge Data –	Instrument 2	1.02	1.05	1.03	1.04	1.03	0.90	1.00	0.92	0.97
VX Cha				1.05 0.98	1.03 1.02	1.04 0.95	1.03 0.97	0.90 0.98	1.00 0.83	0.92 0.97	0.97 0.98
0.96 0.99	1.00 0.93 0.96	1.06 0.90 0.94	1.02 0.89 0.86	0.98 0.98	1.02 0.93						
VX Cha 0.96 0.99 0.96 28 perce	1.00 0.93 0.96 nt of challeng	1.06 0.90 0.94 ges result in a	1.02 0.89	0.98 0.98 arm level at 1	1.02 0.93 .00 TWA	0.95	0.97				
0.96 0.99 0.96 28 perce	1.00 0.93 0.96 nt of challeng	1.06 0.90 0.94 ges result in a	1.02 0.89 0.86 alarm with ala	0.98 0.98 arm level at 1	1.02 0.93 .00 TWA	0.95	0.97				
0.96 0.99 0.96 28 perce	1.00 0.93 0.96 nt of challeng	1.06 0.90 0.94 ges result in a	1.02 0.89 0.86 alarm with ala	0.98 0.98 arm level at 1	1.02 0.93 .00 TWA	0.95	0.97				
VX Cha 0.96 0.99 0.96 28 perce 100 perc GB Chai	1.00 0.93 0.96 nt of challeng ent of challer	1.06 0.90 0.94 ges result in a nges result in Instrument 2	1.02 0.89 0.86 alarm with ala alarm with a	0.98 0.98 arm level at 1 larm level at	1.02 0.93 .00 TWA 0.70 TWA	0.95 0.98	0.97 0.94	0.98	0.83	0.97	0.98
VX Cha 0.96 0.99 0.96 28 perce 100 perc GB Chal	1.00 0.93 0.96 nt of challeng ent of challer lenge Data –	1.06 0.90 0.94 ges result in a nges result in Instrument 2	1.02 0.89 0.86 alarm with ala alarm with a	0.98 0.98 urm level at 1 larm level at	1.02 0.93 .00 TWA 0.70 TWA	0.95 0.98	0.97 0.94	0.98	0.83	0.97	0.98
VX Cha 0.96 0.99 0.96 28 perce 100 perc GB Chai	1.00 0.93 0.96 nt of challeng ent of challer lenge Data – 0.97 0.88 0.94	1.06 0.90 0.94 ges result in a nges result in Instrument 2 1.01 0.86 0.93	1.02 0.89 0.86 alarm with ala alarm with a	0.98 0.98 urm level at 1 larm level at 1.01 0.93 0.93	1.02 0.93 .00 TWA 0.70 TWA 1.01 0.97 0.90	0.95 0.98 1.02 0.95	0.97 0.94 0.94 0.92	0.98	0.83	0.97	0.98

SOURCE: Information provided to the committee by the Department of Homeland Security, Center for Domestic Preparedness, COBRA Training Facility, Anniston, Alabama, October 2004.

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MINICAMS TWA concentration data for Building 143 at the NECD former production facility for the period March 2002 through December 2003 showed that agent concentration exceeded the alarm level of 0.70 TWA during only 288 of 18,675 total cycles.²⁵ It should be noted that the 288 cycles during which the NRT monitors alarmed represented 80 different apparent chemical events (periods of time), and that only one of these events was confirmed as caused by VX. If the alarm level had been set to 1.00 TWA during this period, 209 cycles out of 18,675 total cycles would have resulted in alarms. This seems to be a relatively minor reduction in the rate of false positives (false alarms), achieved by increasing the probability of a false negative for a true agent concentration of 1.00 TWA from about 20 percent to about 50 percent (for an unbiased, normal distribution).

Based on the uncertainty in the toxicity and health effects data used by the CDC to establish the 2003/2004 AELs, no significant additional health risk would be created by increasing the alarm level from 0.70 AEL, currently used at most sites in the non-stockpile program, to 1.00 AEL. However, a number of potentially serious problems involving worker perception, public perception, and logistics or tracking could result from using an alarm level of 1.00 AEL in place of the previous value of 0.70 AEL. These problems include the following:

- The Army has renamed the CDC's 1988 TWA, adopting the more traditional occupational safety terminology "short-term exposure limit (STEL)," kept the same numerical value, and changed the allowed exposure time from 8 hours to 15 minutes. With an alarm level of 0.70 TWA, there was at least an 80 percent probability of an alarm sounding when the true agent concentration in an area being monitored was at or just above 1.00 TWA. Now, Army documents (for example, U.S. Army, 2004f) allow alarm levels to be set at 1.00 STEL, which will cause NRT monitors to sound an alarm only 50 percent of the time at 1.00 STEL (for an unbiased, normal distribution). It makes little sense to reduce the exposure time, which implies that these concentrations are now greater hazards than previously thought, while changing the alarm setting from 0.70 to 1.00 STEL, which reduces the probability than an alarm will sound.
- The Army has specified actions that must be taken in response to an excursion of agent above a given AEL.
 The actions that must be taken were presumably based on the primary intent of the CDC's recommendations—to define concentration boundaries above which workers needed added respiratory protection.

- With the alarm level set at 1.00 AEL, a given NRT system will sound an alarm only 50 percent of the time when the true concentration of agent in the area being monitored is at or just above 1.00 AEL (for an unbiased, normal distribution of reported concentrations), whereas set at 0.70 AEL, an alarm will sound at least 80 percent of the time. Thus, the probability of false negatives is much greater with the alarm level set at 1.00 AEL rather than 0.70 AEL.
- Because the distributions of concentrations reported by MINICAMS are typically biased and are not normal over an operating period of several days, the percentage of 1.00-AEL challenges that result in an alarm will vary widely from instrument to instrument, from day to day, and from week to week. It is entirely possible that if the alarm level is set to 1.00 AEL, the percentage of 1.00-AEL QC challenges that result in alarms will vary within the range 0 to 100 percent for a given group of instruments monitoring the same agent in the same facility. Thus, it will appear that some instruments work properly and that others do not.
- Workers have calibrated NRT monitoring systems at 1.00 TWA (or 1.00-IDLH limit) and then conducted daily challenges at 1.00 TWA (or 1.00-IDLH limit). Because the alarm levels used were 0.70 TWA and the instruments used for GB, VX, and HD were required to maintain an accuracy of ±25 percent with 95 percent confidence, almost every time an operator conducted a daily 1.00-TWA challenge, an alarm sounded. With the alarm level set at 1.00 STEL, the NRT monitoring system will alarm, at best (for an unbiased, normal distribution), 50 percent of the time—even if functioning perfectly—and often much less frequently (for other distributions) in response to 1.00-STEL challenges. This will be perceived by the worker as a reduction in worker safety.
- The two different ways that the Army allows the alarm level to be set for the CDC's 2003/2004 AELs will be confusing at best. It is likely that some instruments will be able to achieve ±25 percent accuracy ≥95 percent of the time for 1.00-AEL challenges; the alarm level for these instruments will be set to 1.00 AEL. Other instruments will not be able to meet this requirement, and their alarm levels will have to be set so that ≥95 percent of 1.00-AEL challenges will result in an alarm. This may result in some instruments at a single site being set at an alarm level of 1.00 AEL and the remainder of the instruments being set at a level less than 0.70 AEL (for example, 0.50 AEL). In addition, because the technique required to determine the proper alarm level must be based on the value of the firstchallenge pass rate achieved for each continuing baseline test period, the technique used may be different for a given monitor from week to week or month to month. Tracking alarm levels and challenge data that

²⁵Tom Hoff, NECD Project Manager, and William Rogers, TVA Quality Assurance Officer, Briefing to the Department of Health and Human Services, March 11, 2004; William Rogers, TVA Quality Assurance Officer, Briefing to the committee, August 3, 2004.

- must be analyzed in two different ways to justify specific alarm levels from instrument to instrument and from baseline period to baseline period will be confusing to operators of NRT monitors.
- By stating that exposures to sulfur mustard, unlike to GB and VX, "should be minimized given the uncertainties in risk assessment, particularly as related to characterizing carcinogenic potency" (Federal Register, 2004, p. 24167), CDC would seem to imply that the alarm level should be set at the lowest practical value to obtain the maximum practical probability of sounding an alarm when the true concentration of HD in the area being monitored exceeds 1.00 AEL. Raising the alarm level from 0.70 to 1.00 AEL, thereby reducing the probability of sounding an alarm from 80 percent to 50 percent (for an unbiased, normal distribution), seems at odds with the CDC's statements on minimizing exposure to HD.
- GB, VX, and HD have been monitored successfully by NRT monitoring systems at concentrations equal to the CDC's 1988 TWA values and at the IDLH levels for more than 20 years—with alarm levels set at 0.70 AEL or less. The alarm levels used in the past ensured at least an 80 percent probability of sounding an alarm when the true concentration of agent in the area being monitored exceeded 1.00 AEL. The CDC's 2003/2004 IDLH values are between one-half and one-sixth of the 1997 IDLH values, but they are still several orders of magnitude above the detection limits for NRT monitoring systems. There is no logical justification for or any significant benefit to raising the alarm level from 0.70 IDLH to 1.00 IDLH and thereby reducing the probability of sounding an alarm at a true concentration of 1.00 IDLH from 80 percent to 50 percent. The TWA concentrations are new in name only: STEL. The numerical values of the CDC's 2003/2004 STELs are identical to the 1988 TWA limits. Again, there is no good reason for raising the alarm level when the numerical concentrations being monitored have not changed and given that the Army has successfully monitored at these levels for more than 20 years with the alarm level set at 0.70 TWA or less.
- The Army has relied on a statistical approach to setting alarm levels for more than 20 years. It has briefed the public many times during this period and repeatedly assured the public and workers that if an agent excursion above a given AEL value occurs, there is an 80 percent or greater probability of detecting the agent and sounding an alarm. If the Army's statistical approach to setting alarm levels is abandoned and alarm levels are allowed to be set to 1.00 AEL, the Army will have to admit that it has adopted a policy that results in a 50 percent or greater chance that an agent excursion could occur without an alarm being sounded to alert workers or the general public.

Finding 4-5: The Army's plan to allow alarm levels to be set at 1.00 of the CDC-recommended AELs (especially for the CDC's 2003/2004 STEL and IDLH levels) has the potential to be perceived by workers and the general public as significantly reducing worker safety, for four reasons: (1) the alarm levels will be higher than the alarm levels used historically, (2) the percentage of QC challenges that yield alarms will vary widely from instrument to instrument and from day to day and week to week, (3) the probability will increase that a worker might be exposed to unacceptable levels of the carcinogen HD, and (4) there is a greater likelihood that the Army will not respond properly or in a timely manner to the presence of agents at true concentrations above the AELs. The rationale for such a large change in the alarm level will be difficult to explain to regulators, auditors, judges, and the general public, especially because concentrations have not changed and remain orders of magnitude above detection limits for NRT monitors and because the Army has a sterling record monitoring at these levels during the past 20 years with the alarm level set to 0.70 AEL or less. The only perceived benefit of raising the alarm level to 1.00 AEL is a reduction in false positives, but this benefit is gained at the expense of a higher probability of false negatives, which is unacceptable.

Recommendation 4-5: For near-real-time monitoring, the non-stockpile program should meet the 2003/2004 AELs promulgated by the CDC using an approach that establishes a sufficiently high confidence level (that is, a high statistical response rate) for the detection of excursions above 1.00 AEL. The alarm levels for near-real-time (NRT) monitors should then be set to achieve the required confidence.

Finding 4-6: The purpose of adjusting alarm levels is to ensure a sufficiently high degree of confidence that an NRT monitoring system will sound an alarm any time that the true concentration of agent in the area being monitored exceeds 1.00 AEL. The non-stockpile program sometimes uses alarm levels that are greater than those used by the stockpile program, making it seem that the non-stockpile program is less likely to detect agent excursions above 1.00 AEL than the stockpile program.

Recommendation 4-6: The non-stockpile program should justify sometimes using alarm levels for near-real-time monitoring systems that are different from those used by the stockpile program.

The issues raised in this section of Chapter 4 regarding alarm levels for NRT monitoring systems also apply to reportable limits for manual monitoring methods such as DAAMS. However, the committee chose to limit the discussion here to NRT monitoring systems for the following reasons:

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- Typically, more than 90 percent of the agent concentration reports at non-stockpile sites are obtained using NRT monitoring systems.
- NRT monitoring systems provide an immediate warning to workers to allow them to take proper actions to protect themselves and to get the situation under control, and the setting of an alarm level is the key
- determinant of the probability of detecting and reporting true agent concentrations above 1.00 AEL.
- All DAAMS results are essentially historical; the event or situation that caused the detection of agent by DAAMS has likely been detected by other means and corrected by the time the DAAMS sample is analyzed.

5

Process Implications of the New AELs

NEWPORT CHEMICAL DEPOT

The alarm points for the MINICAMS monitoring airborne VX concentrations at the Newport Chemical Depot (NECD) will not be changed after January 1, 2005. Since the committee agrees that the new airborne exposure limits (AELs) can be implemented for VX at the NECD facility demolition project without changing the MINICAMS alarm level, no increase in the number or frequency of MINICAMS alarms is expected. The Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) has also demonstrated to the committee that VX at concentrations equal to the worker population limit (WPL) can be detected using the depot area air monitoring system (DAAMS) for VX. Therefore, the new AELs do not necessitate any process changes for demolition activities at the VX former production facility at NECD.

IMPACT ON THE OPERATIONS OF MOBILE TREATMENT SYSTEMS

As described in Chapter 2, the explosive destruction system (EDS) and the rapid response system (RRS) share many features, such as the use of MINICAMS and DAAMS monitors for near-real-time and confirmatory/historical monitoring, respectively. As summarized from Chapter 2 in Table 5-1, both systems provide primary and secondary control of agent vapor emissions.

In both systems, it is assumed that the primary containment area becomes contaminated during the processing of munitions but that this contamination is reduced or eliminated by decontamination procedures. Progress in decontaminating the explosion containment vessel or glove boxes is monitored following agent neutralization. The vapors in the primary containments are vented through multiple activated-carbon beds.

In both systems, all process vapor emissions are passed through activated carbon and monitored before being released to the ambient environment. In effect, the carbon bed exhaust monitors serve as perimeter monitors. However, as discussed in Chapter 2, more remote perimeter monitors are deployed when the EDS is operated in proximity to a civilian population.

The impact of the new AELs will be most pronounced for the EDS, which is used to destroy munitions containing H/HD/HT, GB, and VX as well as some of the less common blister and choking agents. Because there are believed to be no chemical agent identification sets (CAIS) containing nerve agents still in existence, the main impact on RRS operations will be during the processing of mustard agents.

EDS Operations

The EDS has processed and will continue to process a variety of munitions and agent-filled containers holding both blister and nerve agents—primarily H/HD and GB and occasionally VX. Existing equipment should be able to monitor at the worker population limits (WPLs) and short-term exposure limits (STELs) listed by the Centers for Disease Control and Prevention (CDC) for these agents (see Figures 4-1 through 4-3), although using DAAMS to monitor at the new WPLs may be time consuming and expensive, especially if numerous DAAMS samples must be collected and analyzed in order to have confidence that the new WPLs are not exceeded. A requirement to obtain and analyze several (rather than one) DAAMS samples each day for the purpose of determining whether or not the WPL has been exceeded is expected to adversely impact worker productivity, especially if normal daily operations are interrupted as a consequence of the retrieval and analysis of DAAMS tubes. Costs will also increase owing to the need for additional monitoring and analysis staff, monitoring equipment, and analytical capabilities.

Expenses incurred as a result of monitoring at the new AELs will also increase if state regulators require that MINICAMS alarm set points and DAAMS reportable limits are set at some percentage of the new AELs. Even if these values fall within the certification ranges of the monitors,

TABLE 5-1 EDS and RRS Containment Features

System	Primary Containment/Venting ^a	Secondary Containment/Work Area Rating
EDS RRS	ECV/vents into VCS Glove boxes/vent to environment	Vapor containment structure (VCS)/Level C b Operations trailer/Level D

NOTES: ECV, explosion containment vessel; VCS, vapor containment structure.

the frequency of NRT alarms due to the detection of interferents is expected to increase, as will the need to obtain and analyze DAAMS tubes to confirm the alarms.

If state regulators require lower alarm set points (for MINICAMS) and reportable limits (for DAAMS)—for example, at 50 percent or 20 percent of the AELs—then the probability of false positives due to the detection of interferents will increase further. Moreover, these alarm set points and reportable limits might be below the lower ends of the current certification ranges for MINICAMS and DAAMS monitors, respectively. This is discussed on an agent-specific basis next.

H, HD

For the blister agent mustard (H and HD, for example), the 15-minute STEL will be the same as the 1988 timeweighted average (TWA) of 3×10^{-3} mg/m³, which is well within the monitoring capabilities of MINICAMS (Federal Register, 2003b). The new 8-hour WPL will be 4×10^{-4} mg/m³ and is measurable with DAAMS tubes. If, in the worst case, some states require that the alarm set point for the MINICAMS be 0.20 STEL (or 6×10^{-4} mg/m³), this will still be within the certification range for MINICAMS, but the incidence of false positives and their associated costs will increase. If states require that the DAAMS reportable limit for the 8-hour WPL be a fraction of the WPL, for example, 0.50 WPL (or 2×10^{-4} mg/m³), this will be within the current certification range for DAAMS under the current version of the Programmatic Laboratory and Monitoring Quality Assurance Program (U.S. Army, 2004f).

Finding 5-1: To summarize, it should be technically possible for the Army to continue to monitor as at present under the new AELs for HD. However, both cost and schedule impacts are expected, depending in part on the MINICAMS alarm set points and the DAAMS reportable limits that are used.

GB

For GB, the 15-minute STEL will be 1×10^{-4} mg/m³, well within the MINICAMS capability. The new WPL will be 3×10^{-5} mg/m³, also within DAAMS capabilities (Fed-

eral Register, 2003a). Alarm set points for the MINICAMS that are as low as 20 percent of the STEL will fall within the certification range for MINICAMS shown in Figure 4-1, although the probability of alarming due to interferents will increase, along with cost and schedule impacts. DAAMS monitors having a reportable limit as low as 20 percent of the WPL— 6×10^{-6} mg/m³—should be able to detect at this level since this is at the lower end of the current DAAMS certification range for GB.

Finding 5-2: If the Army is required to monitor at the GB WPL—at 3×10^{-5} mg/m³—then it may be possible to use MINICAMS for this purpose rather than DAAMS monitors since this is slightly above the lower limit of the MINICAMS certification range and would provide near-real-time WPL monitoring.

PMNSCM hopes to use monitoring levels and alarm set points that are consistent with the level of PPE that is used. For example, in its final Programmatic Monitoring Concept Plan (U.S. Army, 2004g), the Army gives 8-hour WPLs and 15-minute STELs that are up to four orders of magnitude higher than those for unprotected workers, depending on the degree of worker protection. If PMNSCM were to take credit for PPE and to use the correspondingly higher WPLs and STELs, then MINICAMS alarm set points and DAAMS reportable limits that are even a small fraction of these values will fall well within the certification ranges of existing monitoring equipment. Using GB as an example, the 8-hour WPL for unprotected workers is 3×10^{-5} mg/m³, but for workers using air-purifying respirators (Level C PPE), the 8-hour WPL, in effect, increases 50-fold, to 1.5×10^{-3} mg/m³ (U.S. Army, 2004g).1

VX

The EDS may be used to process non-stockpile items containing VX. For VX, the 15-minute STEL will be 1×10^{-5} mg/m³, within the capability of MINICAMS, although moni-

^aProcess emissions are vented through multiple activated carbon beds.

^bIn the event of a leak or spill, Level A personal protective equipment (PPE) is employed.

¹The value of 50 is the protection factor assigned for negative-pressure respirators.

toring at this level at NECD has resulted in false positives caused by phosphorus-containing compounds. The new WPL will be 1×10^{-6} mg/m³, within the capability of DAAMS monitors (see Figure 4-2). If however, states require that the MINICAMS alarm set point be at a low fraction of the 15-minute STEL—for example, at 2×10^{-6} mg/m³—then this is close to the lower end of the VX certification range for MINICAMS (see Figure 4-2) and it may not be possible for MINICAMS to reliably distinguish between VX and interferents at this level. As a result, the number of MINICAMS alarms is expected to increase, along with the number of confirming DAAMS tubes to be analyzed. Higher fractional alarm set points for VX— 5×10^{-6} mg/m³—will, however, fall within the MINICAMS certification range and are expected to result in fewer false positive MINICAMS alarms.

Also, low fractional reportable limits for DAAMS—for example, 2×10^{-7} mg/m³, or 20 percent of the new WPL—will present problems in confirmation monitoring since the lower end of the certification range for VX using DAAMS monitors is on the order of 6×10^{-7} mg/m³, as shown in Figure 4-2.

In summary, although both MINICAMS and DAAMS are capable of monitoring at the new STELS and WPLs, respectively, it would be helpful if the use of PPE were taken into consideration when the MINICAMS alarm set points and DAAMS reportable limits are selected, as noted in Recommendation 2-4. If credit for the use of PPE cannot be taken, then fractional MINICAMS alarm set points and DAAMS reportable limits are expected to be set that do not require the monitors to alarm at agent concentrations below the lower ends of their certification ranges.

RRS Operations

RRS operations will be largely unaffected by the new AEL standards. The primary impact of the new AELs will occur when the RRS is processing CAIS items containing sulfur mustard agent. Based on the Pine Bluff Arsenal environmental assessment for the destruction of CAIS sets (U.S. Army, 2003c), at least 83 percent of the items contain H or HD; the total might exceed 90 percent.

In considering the impact of the new AELs, the requirement for NRT monitoring at the 15-minute STEL should be largely unaffected because the new target is approximately equivalent to the 1988 TWA of 3×10^{-3} mg/m³. Because the current MINICAMS monitors meet this target routinely, implementing this new requirement should present few challenges other than modest changes in recordkeeping, instrument maintenance, and operator training.² For a mobile system such as the RRS, which will operate in many differ-

ent environments, instrument maintenance may be especially important. Similarly, measurements at the newly defined immediately dangerous to life and health (IDLH) level of 0.7 mg/m³ are within the capability of the MINICAMS. Confirmatory and historical monitoring of H/HD concentrations at the STEL level using DAAMS tubes should also be accomplished readily.

Monitoring for sulfur mustard at the new WPL of 4×10^{-4} mg/m³ is more challenging. This concentration is below the level routinely accessible with the MINICAMS but well within the capability of the DAAMS, which will be analyzed daily to monitor worker exposures relative to the WPL. Since an 8-hour TWA is necessarily retrospective, the delayed response while a DAAMS sample is acquired and the adsorbate in the DAAMS tube is analyzed does not seem to pose a technical problem. The main problematic aspect that will require remediation concerns personnel who discover that they have been exposed to agent at levels above the WPL during the preceding shift.

Because the RRS will be used at military facilities and the limited quantities of agent do not pose a significant risk to any civilian population, there appears to be no reason to institute perimeter monitoring for RRS operations. Hence, it is unlikely that there will be any need to monitor at the new GPL. To monitor at the new GPL of 2×10^{-5} mg/m³ would require significant development work on the DAAMS operating protocol.

Finding 5-3: There appears to be no reason to institute perimeter monitoring for RRS operations.

DECONTAMINATION OF AGENT-CONTAMINATED MATERIALS: THE X REQUIREMENT

The Army used the 1988 AELs to determine whether certain types of materials posed a further hazard to workers (e.g., contaminated tools, contaminated buildings) and to implement management systems for secondary waste, much of which is defined as hazardous waste under federal and state hazardous waste laws. Known as the X Classification System, these standards determine decontamination requirements and define subsequent management procedures. The old X Classification System is contained in Department of the Army pamphlet (DA PAM) 385-61 (U.S. Army, 2002). Under this DA PAM, the decontamination status of possibly agent-contaminated materiel is defined as follows:

- 1X (X) indicates that a material or waste has been partially decontaminated but needs further treatment before it can be shipped or handled without special arrangements for worker protection.
- 3X (XXX) is applied to materials or waste that have been surface-decontaminated such that they do not produce a vapor concentration in excess of the agent-specific AEL for an unmasked worker (the old TWA). Many provisos

²Personal communication between Donald Spina, Teledyne Brown Engineering, and Douglas Medville, committee member, August 10, 2004.

apply, but 3X materials or wastes can generally be handled or shipped as long as they remain under government control. For example, wastes may be sent off-site for treatment and/or disposal in government or commercial permitted RCRA waste treatment, storage, and disposal facilities (TSDFs).

• 5X (XXXXX) indicates that the materiel or waste is decontaminated completely of the indicated agent. The only approved 5X decontamination (DA PAM 385-61) protocol is thermal treatment at a minimum of 1000°F (538°C) for a minimum of 15 minutes. 5X materials may be released from government control and disposed of as nonhazardous waste or may be sold as scrap to the general public.

The Army is planning to revise DA PAM 385-61, as well as the regulation on which it is based, to incorporate the new AELs. In addition, the Army has indicated (U.S. Army, 2004b, 2004g) that not only will it replace the 1988 AELs with the new 2003/2004 AELs for purposes of material and waste classification, but it will also substantially revise the X Classification System. Because the X Classification System defines management systems for secondary waste, including hazardous waste management systems, these standards have been incorporated into all regulatory approval and permitting (RAP) documents established for non-

stockpile (and stockpile) operations. Hence, RAP requirements pertaining to waste management requirements will have to be modified to incorporate the new requirements.

The Army has indicated that the modification of the X Classification System for decontamination is the most controversial aspect of the whole AEL implementation process and that the main stockpile demilitarization sites have already reported long schedule delays due to the required permit changes.³ Considering the potential for continuing delays, changing RAP documents to incorporate the new material and waste management systems is a critical path regulatory issue.

The committee observes that the issues involved cut across all of the Army's chemical programs. The impact on the non-stockpile program is relatively minor in comparison with the impacts on the stockpile programs. In particular, the committee believes that an examination of the X Classification System under the new AELs is worthy of a more comprehensive evaluation as part of a larger study. It has therefore decided not to further examine the subject in this report. The provisions outlined in the *Implementation Guidance Policy* (U.S. Army, 2004b) and in the *Programmatic Monitoring Concept Plan* (U.S. Army, 2004g) may change as the requirements are clarified.⁴

³Cheryl Maggio, Senior Project Engineer, CMA, Briefing to the committee, August 3, 2004.

⁴Cheryl Maggio, CMA Operations Division, PMECW, Briefing to the CMA Monitoring Committee, October 5, 2004.

6

Regulatory Approval and Permitting, and Public Involvement

INTRODUCTION

The regulation of chemical agent destruction processes and public involvement in some of the decisions surrounding these processes were discussed in several earlier National Research Council (NRC) reports on the Non-Stockpile Chemical Materiel Product (NSCMP) (NRC, 2002, 2004a). However, the Army has experienced significant delays in implementing the stockpile destruction program (GAO, 2004). The committee believes that the problems faced by the stockpile program could affect the non-stockpile program as well, especially with regard to environmental permitting issues and public involvement programs. As indicated in earlier NRC reports on the non-stockpile program, regulatory approval and permitting (RAP) and public involvement issues have hampered the Army's ability to meet the CWC schedule and increased the cost of compliance as well (NRC, 1999, 2001a, 2001b, 2002, 2004a). The imposition of new airborne exposure limits (AELs) presents a new set of RAP and public involvement challenges for the non-stockpile program. The new AELs for workers and the community will involve a new round of regulatory approvals or amendments to existing approvals and have the potential to give rise to additional regulatory- and public-involvement-related delays and costs in meeting the CWC deadlines.

Constructive engagement with regulators and the public is essential to the completion of chemical materiel disposal in accordance with the CWC schedule. The committee believes that RAP and public acceptance are critical path items. That is, if regulators or the public at any location present significant objections to any program activity, it will become increasingly difficult for the Army to achieve its programmatic milestones.

REGULATORY PROGRAMS

Implementation of the new AELs must be carried out within the federal and state regulatory and legal framework established for protection of workers and for protection of human health and the environment. There are actually two separate regulatory programs in operation here, one for worker protection and the other for protection of human health and the environment. There is a significant amount of overlap between the two programs, and both have implications for cost and the Army's ability to meet the CWC schedule for non-stockpile operations.

Worker Protection

Historically, workplace protection standards for general industry have been the purview of the U.S. Occupational Safety and Health Administration (OSHA). OSHA does not, however, develop or administer worker protection standards within the U.S. military.² The authority for establishing and implementing worker protection within the military has been delegated to the DOD.

Within the Army, the Office of the Assistant Secretary for Installations and Environment establishes policies and procedures for worker and environmental protection. The

¹According to the Government Accountability Office (GAO), known as the General Accounting Office until July 2004, delays in implementing the stockpile program have stemmed "from incidents during operations, environmental permitting issues, concerns about emergency preparedness, and unfunded requirements" (GAO, 2004, summary). The GAO indicates that if the Army does not resolve the problems that have caused these schedule delays, the United States risks not meeting the Chemical Weapons Convention (CWC) treaty deadline to destroy the entire stockpile, even if the deadline is extended to 2012 (GAO, 2004). Of course, delays and increased costs have also been due to many of the Army's own policies and problems with integrating the role of the NSCMP, the Army Corps of Engineers, and, where appropriate, the base commander (NRC 2002, 2004a). As a result, the NRC recommended that the regulators and the public "should 'see' only one Army across all chemical agent programs" (NRC, 2002, p. 62).

²The U.S. military may nevertheless request guidance from OSHA, as appropriate.

Chemical Materials Agency's (CMA's) Risk Management Directorate carries out this function for chemical agent operations. Specific policies and procedures applicable to the Army's chemical agent programs are established in Army Regulation (AR) 385-61 (U.S. Army, 2001a) and Department of the Army pamphlet (DA PAM) 385-61 (U.S. Army, 2002).³ AR 385-61 was last issued on October 12, 2001, and DA PAM 385-61 was last issued on March 27, 2002. Neither of these regulatory documents describes how standards for worker safety interact with standards for protection of human health and the environment. The Army plans to revise its safety regulations to incorporate the new AELs. This provides an opportunity to incorporate language that would clarify the applicability of safety regulations to standards intended to protect human health and the environment.

With the advent of the Army's chemical demilitarization program, Congress directed, within the defense appropriations bill, the U.S. Department of Health and Human Service's Centers for Disease Control and Prevention (CDC) to establish chemical agent AELs for worker protection (P.L. 99-145, November 8, 1985). The CDC first issued the AEL standards in 1988 (Federal Register, 1988). While Congress directed the CDC to develop the AEL standards and required the CDC to review the "particulars and plans" and provide recommendations for transportation and disposal of chemical warfare agents, it provided no direct oversight or enforcement responsibilities to the CDC. The legislation, however, imposes restrictions on the expenditure of funds if CDC recommendations are not implemented. Thus, the CDC directives are a hybrid—somewhat more than a recommendation but somewhat less than a traditional regulatory requirement.

Protection of Human Health and the Environment

Many of the Army's non-stockpile operations are permitted or have received other types of regulatory approval under the Resource Conservation and Recovery Act (RCRA).⁴ RCRA, enacted in 1976, established a cradle-to-grave management system for hazardous waste (40 CFR Part 260-282), primarily to protect human health and the environment from indiscriminant hazardous waste management practices. The applicability of RCRA to non-stockpile operations is reviewed in *Systems and Technologies for the Treatment of Non-Stockpile Chemical Warfare Materiel* (NRC, 2002).

The RCRA regulations apply the substantive OSHA regulations to state and local government employees engaged in hazardous waste operations, as defined in 29 CFR Part 1910.120(a), but not to federal employees (40 CFR Part 311). Federal employees at cleanup sites have protection limits that are at least "comparable to Federal OSHA standards."

Worker Protection Standards and RCRA Integration Issues

In some states, but not all, worker protection AELs have been incorporated into RCRA permits and regulatory approvals, including those under development. The RCRA statute does not provide explicit authority to the Environmental Protection Agency (EPA) or the authorized state programs to regulate workplace exposures. In fact, EPA indicates, in a memorandum dated December 1983, as follows:

A related issue that has arisen in some of the first permit reviews is whether RCRA permit writers should insert permit conditions which would require permittees to meet requirements established under other Federal laws and regulations. Permit writers should realize that the RCRA regulations have been specifically written to avoid duplication of coverage with other Federal authorities. The supporting information behind the Part 264 regulations points out that the Agency has excluded from the regulations many proposed Part 264 standards that would have required permittees to meet other Federal laws and regulations (see 45 FR 33171, May 19, 1980). Therefore, as a general matter, permit writers should not include the RCRA permits conditions based on other Federal authorities merely for repletion or emphasis. Such conditions should only be used if the permit writer decides they are needed to meet RCRA regulatory requirements. (Weddle, 1983, p. 1)

Nevertheless, RCRA provides, under its omnibus provisions (RCRA 3005(c)(3)), the authority to permit writers to incorporate conditions into RCRA permits that are not specifically described in 40 CFR Part 264 if it can be demonstrated that the additional standards are necessary to protect human health and the environment. Under this authority (or similar state authority) some state-authorized RCRA programs have incorporated agent-associated worker protection standards into operating permits or other regulatory approvals.

³Army Regulation 385-61 can be found at http://www.army.mil/usapa/epubs/pdf/r385_61.pdf, and DA PAM 385-61 at http://www.army.mil/usapa/epubs/pdf/p385_61.pdf.

⁴Other types of regulatory approvals are issued pursuant to removal and remedial actions under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). In some cases, permits for certain operations have also been established under provisions of the Clean Air Act (CAA).

⁵MaryAnn Garrahan, OSHA, Office of Health Compliance Assistance, Briefing to the RCRA National Meeting, January 17, 2002.

⁶As described in *Systems and Technologies for the Treatment of Non-Stockpile Chemical Warfare Materiel* (NRC, 2002), the RCRA program was intended by Congress to be a state-implemented program, and many of the states, and all of the stockpile states, have received authorization from EPA to administer the RCRA program within their boundaries.

Finding 6-1a: AELs have been incorporated into RCRA permits and other regulatory approvals for many of the Army's non-stockpile operations, and their implementation is also regulated by the worker protection authorities within the Army. Worker protection standards are then implemented and enforced, pursuant to multiple regulatory authorities.

Because the AELs are incorporated into RAP documentation for some non-stockpile operations, RAP documentation will require significant changes, including permit modifications, to accommodate the new AELs. Considering the number of non-stockpile operations in progress or planned, the effort required to support the changes to RAP documentation will be substantial.

Finding 6-1b: Permit modifications and modification to other RAP documentation will be required for all existing and planned operations.

Using Lower Alarm Levels and Reportable Limits

In incorporating AELs into RCRA permits and other regulatory approvals, some states (e.g., Utah) have determined that the Army's practice of setting the alarm level for NRT monitors at 0.70 AEL for non-stockpile program operations would not be consistent with stockpile operations, where alarm levels as low as 0.20 AEL are often used. These state regulators have urged the Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) to examine the feasibility of using an alarm level of 0.20 AEL for nonstockpile operations, for consistency with stockpile operations.⁷ Non-stockpile operations in these states would then have alarm levels 3.5 times lower than alarm levels in other states. Although using an AEL of 0.20 rather than 0.70 would increase the probability of detecting agent excursions above 1.00 AEL, it would also increase the frequency of false positives.

The same conclusion applies to reportable limits using the DAAMS monitoring technology. Here again, if reportable limits are set below the relevant AEL (e.g., WPL or GPL) to achieve a higher probability of detecting agent excursions above 1.00 AEL, the frequency of false positives would be expected to rise.

Finding 6-1c: Some state regulators have urged PMNSCM to examine the feasibility of using NRT alarm levels as low as 0.20 AEL for non-stockpile operations, to be consistent with stockpile operations in the same states. Similarly, reportable limits using the DAAMS technology could be set at lower levels.

Recommendation 6-1: As the Army modifies its safety regulations (AR 385-61 and DA PAM 385-61) to address the new AELs, it should consider incorporating language that would clarify RCRA applicability to non-stockpile operations. In addition, to avoid reinventing the wheel in the many states where mobile treatment systems might be used, the Army should develop templates for modifying RAP when the new AELs are implemented for non-stockpile operations.

In addition, although the committee believes that more stringent standards would be warranted if they significantly reduce risk, the non-stockpile mission would also benefit from uniform standards and procedures, particularly for its mobile systems. Further, to facilitate state and public acceptance of revised Army regulations, RAP templates, and consistent standards, the Army should consider establishing a collaborative group made up of state regulators and members of the public. For example, the Army might establish a collaborative arrangement based on the existing Core Group or on an existing outside organization, such as the Interstate Technology and Regulatory Council (ITRC).^{8,9}

Relationship of AELs to the RCRA Contingency Plan

All RCRA permit applications contain a RCRA contingency plan—see, for example, the Newport Chemical Depot's (NECD's) former production facility RCRA permit modification application, March 2004, Attachment G3. ¹⁰ The purpose of the contingency plan is to minimize hazards to human health or the environment from fires, explosions, or unplanned releases of hazardous waste or hazardous waste constituents. In Army terms, such events, if they involved exceedance of the STEL, would be termed chemical events that are reportable under AR 50-6 (U.S. Army, 1995).

In the past, RCRA contingency plans were nonspecific with respect to the magnitude of a release of hazardous waste or hazardous waste constituents that might cause their activation. In addition, a contingency plan is written broadly so that it applies to releases to the outside environment as well as within confined structures (such as NECD Building 144). Presumably, therefore, the release of any amount of agent, either inside a building or to the outside environment, might

⁷Communication between William Brankowitz, Product Manager, Non-Stockpile Chemical Materiel Product, and the committee, June 16, 2004.

⁸Established by NSCMP in 1999, the Core Group includes Army personnel from the chemical demilitarization program, representatives of regulatory agencies, and representatives of citizens' groups; it meets twice a year to exchange information about the non-stockpile program.

⁹The ITRC is a state-led coalition working with industry and stakeholders to achieve regulatory acceptance of environmental technologies. ITRC consists of 40 states, the District of Columbia, multiple federal partners, industry participants, and other stakeholders, cooperating to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources.

¹⁰This permit can be obtained from the Newport Chemical Depot, Newport, Indiana.

activate the contingency plan. Because activation of a MINICAMS alarm above the STEL might signal an agent release, it would presumably activate the RCRA contingency plan. However, as indicated earlier in this report, MINICAMS alarms are often confirmed as false positive readings by the DAAMS.

Finding 6-2: The relationship between MINICAMS alarms and DAAMS confirmation, on the one hand, and activation of a RCRA contingency plan, on the other, is unclear.

Recommendation 6-2: PMNSCM should describe, within the RCRA contingency plan, specific criteria that would activate the plan. These criteria should address MINICAMS alarms and DAAMS confirmation and should consider the frequency of false positive confirmations.

PUBLIC INVOLVEMENT

Constructive engagement with the public is essential to the timely completion of chemical materiel disposal. In fact, the committee believes that public acceptance, like regulatory approval, is a critical path item. That is, if the public at any location turns against any program activity, including off-site secondary waste disposal, then it becomes difficult for the Army to achieve its programmatic milestones.

For the most part, the non-stockpile program has avoided delays caused by public concern and opposition. Its disposal strategies have earned widespread support, and, through the Core Group, it maintains a constructive relationship with the activist public. Further, before each deployment of its transportable treatment systems, it conducts activities to involve the local public. However, given the intense public concern about chemical weapons, this largely successful experience should not allow complacency. A single incident could easily reverse the positive relationship.

The committee believes that public involvement at nonstockpile program sites is and should be based on the program's activities at each of those sites. Since those activities differ significantly, the potentially impacted public varies as well. This study covers sites of three types:

- The disassembly of former production facilities—for example, Building 143 at the Newport Chemical Depot (Indiana)—containing small amounts of VX and its by-products.
- The use of mobile destruction systems, such as the EDS and RRS, within large military facilities, such as Pine Bluff Arsenal (Arkansas), the Dugway Proving Ground (Utah), and Dover Air Force Base (Delaware)
- The use of those same mobile systems in populated nearby areas, such as Denver, Colorado (Rocky Mountain Arsenal), or the Spring Valley neighborhood in Washington, D.C.

At NECD, the surrounding community is unlikely to show much interest in monitoring potential releases from the dismantling of the former production facility. The small quantities of VX trapped in old piping are dwarfed by the 1,269 tons of liquid VX in the Newport stockpile that await neutralization.¹¹ Any monitoring designed to protect people living in the vicinity of stockpile storage and treatment should be more than adequate to address non-stockpile risks.

Those affected at the NECD former production facility at Newport are, therefore, primarily the workers. They are the people whose health and safety directly depend on the accuracy and reliability of the monitoring system. Further, these same workers understand both the benefits of and challenges posed by personal protective equipment (PPE), the use of which may serve to allay concerns about (1) problems with the monitoring technologies and (2) the possibility of more false positive alarms.

During the summer of 2004, the Army's Center for Health Promotion and Preventive Medicine (CHPPM) conducted a series of focus groups with workers in five states, including one at NECD for stockpile demilitarization, stockpile storage, and non-stockpile program workers. The committee's observation of the CHPPM focus group in Newport reinforces the Army's conclusion that communication between Army management and the contractor workforce needs strengthening. At the time of the focus groups, workers did not understand, but were concerned about, the impact of the new AELs on their work:

There was general concern . . . that revising AELs will directly impact the way workers perform theirs jobs. Concern about job impacts far outweighed health and safety concerns. Of particular note about job impacts was that some workers expressed concern that revised AELs could lead to a culture of false positives and result in workers taking alarms less seriously. In addition, participants consistently pointed out that these changes would impact schedules and wanted to know if the schedules would be extended to accommodate the requirements of the revised AELs. (U.S. Army, 2004h, p. 5)

The committee commends the Army's focus groups as a first step in consulting workers about potential changes in monitoring strategy. It agrees with CHPPM's recommendations for improved training and communications, including the suggestion that the CMA "provide avenues for individuals to express concerns, raise issues, and ask questions about implementing the AEL changes directly to CMA HQ" (U.S. Army, 2004h, p. 13).

Further, both the contractor teams and the technical escort units that operate and support the EDS, the RRS, and other non-stockpile operations are highly trained and prepared. The committee believes that they, too, should be consulted should there be any significant changes in the Army's monitoring strategy.

¹¹See http://www.globalsecurity.org/wmd/facility/newport.htm.

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While workforce concerns are generally the same in populated areas as on remote military installations, public involvement takes on an important new dimension when chemical weapons are recovered in or near areas where people live. The Army has identified 96 suspected chemical weapon burial locations in 38 states, the Virgin Islands, and the District of Columbia. Thus, it is likely that the mobile disposal equipment will be brought in to numerous areas where civilians reside, work, study, or enjoy outdoor recreation.

The discovery of what many citizens consider weapons of mass destruction in or near populated areas, regardless of their source, is likely to trigger fear and mistrust. To dispose of recovered chemical materiel in a timely fashion, it is prudent that the Army go to great lengths to ensure that the potentially impacted public is comfortable with Army efforts to mitigate the risks of exposure. In addition to meeting the regulatory requirements described in the preceding section, a proactive public involvement program will not only help to reduce delays and other obstacles to the accomplishment of the disposal mission but will also provide the basis for resolving unexpected problems if they arise. That is, to be effective, the non-stockpile program must be seen as part of the solution, not part of the problem.

When chemical ordnance or identification kits are discovered in a community, there is rarely time to build a public involvement strategy from scratch. Communities do not necessarily know in advance the extent of the removal or remedial actions, intrusive work, and monitoring that will be needed, or even that chemical warfare material (CWM) treatment/disposal operations will probably be required. The Army's current strategy, which includes scheduling, publicizing, and conducting open houses or public meetings before finalizing destruction plans, is a good start. Still, it is advisable that the Army work with the Core Group to establish a public involvement model that it can roll into town along with the RRS or the EDS. A satisfactory model would include established monitoring protocols describing how communities would be warned of any hazardous release from the chemical materiel, and it would lay out ground rules for communicating with the public, including at public meetings, where the local population has the opportunity to influence monitoring and other plans. With such proactiveness, communities are likely to facilitate rapid completion of the nonstockpile mission and to participate more constructively in overcoming unanticipated problems. Also, early public involvement often facilitates the investigation, especially at formerly used defense sites, because citizens may recall previous finds, suspicious areas, health problems, or other potentially relevant information that could help the investigators.

Given the fear associated with chemical munitions, it is reasonable to expect that some communities will want more monitors or more stringent notification levels than outside experts recommend. The committee notes that even when the outside experts indicate a certain level of monitoring is sufficient, the Army may decide to take local factors into consideration.

The non-stockpile program has good relations with the communities in which it operates, and the committee believes that with a moderate, proactive public involvement strategy, it can maintain those relations in other communities into which it is called.

Finding 6-3: Workers whose safety depends on prompt, reliable warnings of airborne exposures to chemical agent are concerned about the impact that the new AELs will have on their work.

Recommendation 6-3: PMNSCM management should continue or expand its efforts to consult with the non-stockpile workforce before implementing any changes in agent monitoring or the use of personal protective equipment.

Finding 6-4: Public acceptance is critical to the smooth, timely use of mobile destruction devices in populated areas. The non-stockpile program's proactive community relations program has thus far been effective, but the potential for controversy remains.

Recommendation 6-4: PMNSCM should develop, in consultation with the non-stockpile Core Group, a model for public involvement in the fielding of mobile systems and the implementation of monitoring systems to protect the general public.

¹²William Brankowitz, Product Manager for Non-Stockpile Chemical Materials, Briefing to the committee, September 14, 2004.

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Appendixes



Appendix A

Biographical Sketches of Committee Members

Richard J. Ayen, Chair, a member of the NRC Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons (I and II), received his Ph.D. in chemical engineering from the University of Illinois. Dr. Ayen, now retired, was director of technology for Waste Management, Inc. He managed all aspects of Waste Management's Clemson Technical Center, including treatability studies and technology demonstrations for the treatment of hazardous and radioactive waste. His experience includes 20 years at Stauffer Chemical Company, where he was manager of the Process Development Department at Stauffer's Eastern Research Center. Dr. Ayen has published extensively in his fields of interest. He has extensive experience in the evaluation and development of new technologies for the treatment of hazardous, radioactive, industrial, and municipal wastes.

Martin Gollin, a process design engineer affiliated with Carmagen Engineering, Inc., and, before that, with ARCO Chemical Co., has over 20 years of experience in process engineering and management of capital projects, risk assessment, process safety, loss prevention, and product development. From 1988 to 1999 he served as process design manager, environment, health, and safety manager, and principal engineer at ARCO Chemical Co. As an independent consultant Mr. Gollin has participated in various activities involving chemical demilitarization programs and facilities. He earned a B.S. and an M.S. in chemical engineering from Loughborough University of Technology. Mr. Gollin has expertise in process design and process safety.

Gary S, Groenewold has conducted research in surface chemistry, gas-phase chemistry, and secondary ion mass spectrometry at the Idaho National Engineering Environmental Laboratory (INEEL) since 1991. His research has focused on determining the speciation of adsorbed toxic metals (e.g., Hg, Al, and Cu) and organic compounds (e.g., VX, G agents, HD, organophosphates, amines, and sulfides).

Prior to this, Dr. Groenewold served 3 years in line management at the INEEL and as the technical leader of an environmental organic analysis group. Before coming to the INEEL, Dr. Groenewold worked in anticancer drug discovery for Bristol-Myers, using mass spectrometry as an identification tool. He received his Ph.D. in chemistry at the University of Nebraska, where he studied ion-molecule condensation and elimination reactions in the gas phase. He has authored 50 scientific publications on these subjects. Dr. Groenewold has expertise in monitoring instrumentation.

Frederick T. Harper is a Distinguished Member of the Technical Staff at Sandia National Laboratories in the High Consequence Assessment and Technology Department. He manages and performs research in the following areas: (1) explosive aerosolization of nuclear materials from nuclear weapons and other nuclear sources (experimental and analytical), including materials in metal, ceramic, powder, and liquid forms; (2) effects of chemical and biological releases from explosive and nonexplosive dissemination mechanisms (experimental and analytical); and (3) the energetic dissipation of shock waves in an aqueous foam medium (experimental and analytical). Dr. Harper is a deployable member of the DOE emergency response team that uses tools developed from the above research. Recently, he served as a substantive expert in the area of explosive aerosolization and effects of aerosol releases for several national and international counterterrorism exercises and workgroups. He has a bachelor's degree in physics from Yale University, a master's in nuclear engineering from the University of Virginia, and a Ph.D. in nuclear engineering from the University of New Mexico.

Paul F. Kavanaugh, Brigadier General (retired), is an engineering management consultant. Before that, he was the director of government programs for Rust International, Inc., and director of strategic planning for Waste Management Environmental Services. In the Army, he served with the

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Army Corps of Engineers, the Department of Energy, and the Defense Nuclear Agency and managed projects at the U.S. Army Chemical Demilitarization Program at Johnston Atoll. General Kavanaugh earned a B.S. in civil engineering from Norwich University and an M.S. in civil engineering from Oklahoma State University. He has expertise in military and civil works design and construction.

Todd A. Kimmell is principal investigator with the Environmental Assessment Division at the U.S. Department of Energy's Argonne National Laboratory. He is an environmental scientist and policy analyst with more than 25 years of experience in solid and hazardous waste management, permitting and regulatory compliance, cleanup programs, and environmental program and policy development. Mr. Kimmell has supported the Army's chemical weapons storage programs and has contributed to the Army's Assembled Chemical Weapons Assessment Program and the Chemical Stockpile Emergency Preparedness Program. Mr. Kimmell also has a strong background in analytical and physicochemical test method development and in analytical quality assurance and control. He presently serves the EPA Water Protection Task Force Core Group on environmental test methods for chemical, biological, and radiological assessment technologies. Mr. Kimmell also has extensive experience in environmental cleanup programs and is involved in environmental cleanup programs at chemical weapons disposal sites. He has also supported a number of environmental permitting programs at Army chemical weapons storage sites and at open burning/open detonation sites. Mr. Kimmell graduated from the George Washington University with an M.S. in environmental sciences. He has expertise in environmental assessment and regulatory and permitting issues.

Loren D. Koller is an independent consultant and former professor and dean of the College of Veterinary Medicine at Oregon State University. His research interests include the toxicologic, pathologic, and immunologic effects of toxic substances and the effect of environmental contaminants on tumor growth and immunity. Dr. Koller is a former member of the NRC Committee on Toxicology and participated on several of its subcommittees, including the Subcommittee on Immunotoxicity and the Subcommittee on Zinc Cadmium Sulfide. He is currently serving on the Institute of Medicine's Committee on the Assessment of Wartime Exposure to Herbicides in Vietnam. Dr. Koller received his D.V.M. from Washington State University and his Ph.D. in pathology from the University of Wisconsin. His expertise is in toxicology.

Brian Lamb, Boeing Distinguished Professor of Environmental Engineering, Washington State University, has been involved in atmospheric pollutant transport and dispersion studies for more than 20 years. His work on an automated vertical sampling system for sulfur hexafluoride that was

deployed in a large Homeland Security urban dispersion study in Oklahoma City and his work on a real-time urban air quality forecast system for the Puget Sound region involved the development of detailed emission inventories and the evaluation of model performance using an array of available monitoring data. Mr. Lamb has expertise in modeling and measuring air plumes.

Benjamin Y.H. Liu (NAE), Regents' Professor Emeritus, University of Minnesota, is CEO and president of MSP Corporation. Dr. Liu directed the Particle Technology Laboratory at the University of Minnesota and conducted aerosol science research in a variety of disciplines and applications, including contamination control in microelectronics manufacturing, air pollution, gas cleaning, industrial hygiene, respiratory devices, and atmospheric sciences. He has authored or co-authored more than 300 publications, edited four books, and held 22 patents. He has extensive experience with the development of novel aerosol instrumentation and with studies of fine particle behavior.

Douglas M. Medville retired from MITRE as program leader for chemical materiel disposal and remediation. He has led many analyses of risk, process engineering, transportation, and alternative disposal technologies and has briefed the public and senior military officials on the results. Mr. Medville led the evaluation of the operational performance of the Army's chemical weapon disposal facility on Johnston Atoll and directed an assessment of the risks, public perceptions, environmental aspects, and logistics of transporting recovered non-stockpile chemical warfare materiel to candidate storage and disposal destinations. Before that, he worked at Franklin Institute Research Laboratories and General Electric. Mr. Medville earned a B.S. in industrial engineering and an M.S. in operations research, both from New York University. He has expertise in process and design engineering.

Barbara Paldus, chief technology officer at Picarro, is responsible for technology strategy and research innovation. Her expertise is in cavity ring-down spectroscopy (CRDS) and its application in diverse technology fields. Dr. Paldus has been issued 12 patents and written over 40 articles and conference papers on the application of CRDS and tunable lasers. In 2001, she was awarded the Aldolph Lomb Medal from the Optical Society of America. Previously, Dr. Paldus worked at Stanford on applications of MEMS to communication and display technologies. Dr. Paldus received her Ph.D. and her M.S.E.E. from Stanford University. She received her B.S. in electrical engineering and applied mathematics from the University of Waterloo, Canada. She has expertise in monitoring.

George W. Parshall (NAS) is a consultant for E.I. DuPont de Nemours & Company, having retired from there in 1992

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after a career at the company spanning nearly 40 years. From 1979, he served as director of chemical science in Central Research and Development. Dr. Parshall is a past member of the NRC Board on Chemical Science and Technology and took part in earlier NRC chemical demilitarization studies. He continues to play an active role in National Research Council activities. He graduated from the University of Illinois with a Ph.D. in organic chemistry. He has experience in organic and inorganic chemistry and catalysis and in conducting and supervising chemical research.

James P. Pastorick is president of Geophex UXO, Ltd., an unexploded ordnance (UXO) consulting firm based in Alexandria, Virginia, that specializes in UXO planning and management consulting to state and foreign governments. Since he retired from the U.S. Navy as an explosive ordnance disposal officer and diver in 1989, he has been working on civilian UXO clearance projects. Prior to starting his company, he was the senior project manager for UXO projects at UXB International, Inc., and the IT Group. He is a masterrated unexploded ordnance technician with over 18 years of experience in explosive ordnance disposal. Mr. Pastorick has been responsible for the management and supervision of numerous projects involving the investigation and remediation of sites contaminated with unexploded ordnance. He has expertise in explosives and ordnance handling; transport, disassembly, and disposal; and workforce protective ensembles.

Charles F. Reinhardt, who has an M.D. from the Indiana University School of Medicine and an M.Sc. in occupational medicine from the Ohio State University School of Medicine, retired after more than 30 years with the DuPont Company's Haskell Laboratory, where he was a physiologist, then chief of the physiology section, and then research manager for environmental sciences. In 1971 he became assistant director of the laboratory and in 1976 was named its director, a position he held until his retirement in 1996. Dr. Reinhardt has served on numerous National Research Council panels and committees, including the Committee on Toxicology. He has expertise in occupational medicine and toxicology.

Gary D. Sides, senior scientist and director of government marketing for the Gas Technology Institute, Des Plaines, Illinois, has 25 years of experience in the development of automated and manual methods and the manufacture of automated monitoring systems to determine sarin (GB), VX, mustard, and other agents at the current worker protection levels and at the proposed CDC airborne exposure levels. Following the receipt of his Ph.D. in physical chemistry from the University of Florida in 1975, Dr. Sides conducted, and later directed, research, development, testing, and evaluation of automated and manual monitoring systems and accessories for the near-real-time detection of chemical warfare agents. His efforts in this area have included the

design, development, and manufacture of ACAMS; the design, development, manufacture, and support of the MINICAMS; and the development of improved DAAMS methods. These three automated and manual methods form the basis of the Army's agent monitoring technology currently used in the non-stockpile and stockpile programs. His work in air monitoring during the past 25 years has been conducted not only at CMS Research Corporation, which he founded and ran for 12 years, but also at Southern Research Institute, from which he retired in 2003. Dr. Sides has expertise in monitoring and instrumentation.

Leonard M. Siegel is director of the Washington, D.C.based Center for Public Environmental Oversight (CPEO), a project of the Tides Center that facilitates public participation in the oversight of military environmental programs, federal facilities cleanup, and brownfields revitalization. One of the environmental movement's leading experts on military facility contamination, he serves on numerous advisory committees in that area, including the Interstate Technology Regulatory Council's work teams on vapor intrusion and perchlorate, the Moffett Field (formerly the Moffett Naval Air Station) Restoration Advisory Board, the National Environmental Justice Advisory Council's Federal Facilities Working Group, and the Outreach Advisory Committee of the Western Region Hazardous Substance Research Center. Mr. Siegel moderates and writes regularly for CPEO's Military Environmental Forum listserv. He has expertise in public participation in environmental programs.

Robert Snyder, associate dean of the School of Pharmacy at the Rutgers University College of Pharmacy, served as director of toxicology of the Environmental and Occupational Health Sciences Institute, Piscataway, New Jersey. He received a Ph.D. in biochemistry from the State University of New York at Syracuse. Dr. Snyder's research focuses on mechanisms for the toxic and carcinogenic effects of benzene, the role played by benzene metabolites, and mechanisms for the formation of these metabolites. Other scholarly interests include solvent toxicology, the mechanisms of hepatic toxicology, factors that control the dose-response relationship, and establishment of levels of exposure to chemicals that minimize the risks of toxicity. Dr. Snyder has expertise in toxicology and occupational health.

Billy R. Thomas is vice president of the Consulting Division of Integrated Environmental Management, Inc., in Findlay, Ohio. He is board-certified in industrial hygiene and has served as the health and safety manager for both IT Corporation and OH Services, where he worked at the sites of spills or transportation emergencies where chemicals posed hazards to technicians. Mr. Thomas, who holds an M.S. degree in environmental health from the University of Oklahoma, has expertise in industrial hygiene in connection with the demolition of buildings, as well as a comprehensive back-

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ground in protective clothing and the use of supplied air equipment.

William J. Walsh is an attorney in the Washington, D.C., office of Pepper Hamilton LLP. Prior to joining Pepper, he was section chief in the EPA Office of Enforcement. His legal experience includes environmental regulatory advice and advocacy and defense of environmental injury litigation involving a broad spectrum of issues pursuant to a variety of environmental statutes, including the Resources Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA). He represents trade associations, including the Rubber Manufacturers Association and the American Dental Association, in rule-making and other

public policy advocacy. He has negotiated protective yet cost-effective remedies in pollution cases involving water, air, and hazardous waste and advised technology developers and users on taking advantage of the incentives for using innovative environmental technology and eliminating the regulatory barriers to its use. He previously served on NRC committees concerned with Superfund and RCRA corrective action programs and the use of appropriate scientific groundwater models in environmental regulatory programs and related activities. Mr. Walsh holds a J.D. from the George Washington University Law School and a B.S. in physics from Manhattan College. He has expertise in environmental and regulatory law.

Appendix B

Non-Stockpile Inventories

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TABLE B-1 Inventory of Non-Stockpile Items at the Pine Bluff Arsenal

		No. Contair	ning a Cher	nical(s)							
Item	No. Empty	H/HD/HN/ HS/HT	GA/GB/ GD	VX	DM/L	CG/CK	DF	QL	Other	Unknown	Total No. of Items
Munition											
4.2-in. mortar round	596^{a}	99a				1^b				36^{a}	732^{a}
75-mm projectile	4^a	9^a									13^{a}
200-mm Livens											
projectile	3^a	5^a				3^b					11^{a}
4.7-in. projectile		1^a									1^a
155-mm projectile	1^a										1^b
105-mm projectile										1^a	1^b
M70A1 bomb (poss.											
explosive)	6^a	3^a									9b
150-mm German	_	_									
Traktor rocket											
w/expended motor	224^{a}	184^{a}									408^{a}
150-mm German	227	104									700
Traktor rocket											
w/unexpended motor	13^a	18^a									31^a
150-mm German	15"	100									31"
Traktor rocket	260	127									20.4
w/warhead only	26a	12a				4.1-				25-	38a
Subtotal	873^{a}	331^{a}				4^b				37^a	$1,245^{a}$
Chemical sample container ^c		- 1									
Ton container		2^d	2^d								4 ^d
4-in. cylinder		2^d									2^d
Lab sample container			14^{d}	7^d							21^{d}
Vial (L)					1^b						1^b
Subtotal		4^d	16^d	7^d	1^b						28^d
Chemical agent ID set (CAIS)											
Mustard (H/HD/HS)		$5,764^{b}$									$5,764^{b}$
Nitrogen mustard											
(HN-1 and -3)		50^{b}									50^{b}
Lewisite (L)					397^{b}						397^{b}
Chloropicrin (PS)									396^{b}		396^{b}
Phosgene (CG)						396^{b}					396^{b}
Chloroacetophenone (CN)									17^{b}		17
Adamsite (DM)					17^{b}				-,		17^{b}
Triphosgene (TP)					- ,				17^{b}		17^{b}
Cyanogen chloride (CK)						33^{b}			1,		33^b
Diethyl malonate, etc.						55					55
(GS)									33^b		33^b
Subtotal		$5,814^{b}$			414^{b}	429^{b}			463 ^b		$7,120^{b}$
		3,014			414"	427			403		7,120
Binary agent precursor							56761d				56 76 Ad
M20							56,764 ^d 7 ^d	201d			56,764 ^d
Drum								291^d			298 ^d
Subtotal					4 27.5 b		56,771 ^d	291^{d}			$57,062^d$
Empty ton container ^e	0724	(1460	ah	2h	$4,375^b$	422h	56 7714	2014	162h	274	4,375 ^b
Total	873 ^a	$6,146^a$	2^b	2^b	$4,789^{b}$	433^{b}	56,771 ^d	291^{d}	463^{b}	37^a	$69,830^d$

^aData from Verrill and Salcedo, 2001.

SOURCE: Provided to the committee by PMNSCM.

^bProvided to the Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel Disposal Program by the Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) on July 10, 2001.

^cInventory consists of individual CAIS items, not complete CAIS.

^dProvided to the committee by Darryl Palmer, Office of the PMNSCM, on February 14, 2005.

eSampling of some of these containers indicated that they may be contaminated with lewisite, arsenic, and/or mercury.

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TABLE B-2 Inventory of Non-Stockpile Items at Dugway Proving Ground (DPG) and Deseret Chemical Depot (DCD), Utah

		Chemical Fill				
Item	Location	H/HD/HN/HT/HS	GA/GB/GD	Lewisite	VX	Total No. of Items
Explosive munitions						
(4.2-inch mortar rounds)	DPG	8^a				
Chemical sample						
Containers						
Ton container	DCD	1				1
Containers, bottles, vials	DPG				18	18
Containers (39 HD, 5 HT)	DCD	45				45
Ampoule	DCD		1			1
Total		54	1	1	18	65

^a Scheduled for transport to DCD.

SOURCE: Provided to the committee by PMNSCM on November 19, 2004.

TABLE B-3 Inventory of Non-Stockpile Items at Aberdeen Proving Ground, Maryland

	Chemical Fill						
Item	HD/HT/HS	GB/GA/GD	VX	Lewisite	CG	Total	
Chemical sample containers							
55-gallon drum (pumpkins)	10					10	
30-gallon bucket (pumpkins)		5	5			10	
5-pint can (vials or bottles)	3		16			19	
Steel cylinder		12				12	
Multipack bottles, vials		8		9		17	
DOT bottle			1			1	
Ton container		1				1	
Total	13	26	22	9		70	

SOURCE: Provided to the committee by PMNSCM on November 19, 2004.

TABLE B-4 Inventory of Non-Stockpile Items at Anniston Chemical Activity, Alabama

	Chemical Fil	1		
Item	HD/HT	GB	VX	Total
Chemical sample container	s			
Vials		36		36
DOT bottles	5		7	12
Ton containers		2		2
Total	5	38	7	50

SOURCE: Provided to the committee by PMNSCM on November 19, 2004.

REFERENCE

D. Verrill and J. Salcedo. 2001. X300P90 Characterization Project. Preliminary Data Review, May 14. Aberdeen Proving Ground, Md.: Product Manager for Non-Stockpile Chemical Materiel.

Appendix C

Committee Meetings and Other Activities

MEETINGS

First Committee Meeting, May 6-7, 2004, Aberdeen, Maryland

Product Manager's Overview of Army Non-Stockpile Program LTC Paul Fletcher, product manager, Non-Stockpile Chemical Materiel Command

Airborne Exposure Limit (AEL) Implementation Cheryl Maggio, senior project engineer, Chemical Materials Agency

Newport Former Production Facility Status

Tom Hoff, project officer, Non-Stockpile Chemical Materiel Former Production Facilities

Terry Frederick, manager, TVA Non-Stockpile Chemical Materiel

The Impact of Revised AELs on Operations at the Former VX Production Facility in Newport, Indiana *George Bizzigotti*, senior principal scientist, Mitretek Systems

Revised Exposure Limits for Chemical Warfare Agents John Decker, team leader, Chemical Weapons Elimination, Centers for Disease Control and Prevention

Harvey Rogers, environmental engineer, Chemical Weapons Elimination, Centers for Disease Control and Prevention

Paul Joe, chief medical officer, Environmental Public Health, Centers for Disease Control and Prevention

Second Committee Meeting, June 16-17, 2004, Washington, D.C.

Airborne Exposure Limit Briefing to the National Research

Cheryl Maggio, senior project engineer, Chemical Materials Agency

Explosive Destruction System (EDS) and Rapid Response System (RRS) Update and Workplace Monitoring

Dave Hoffman, group leader, Systems Operations and Remediation PMNSCM

Tom Rosso, chief, Program Management Team, Edgewood Chemical and Biological Command

Third Committee Meeting, August 3-4, 2004, Washington, D.C.

Airborne Exposure Limit Implementation

Cheryl Maggio, senior project engineer, Chemical Materials

Agency

Newport Chemical Depot Former Production Facility Demolition: Revised Schedule

Terry Frederick, manager, TVA Non-Stockpile Chemical Materiel

Personal Protective Equipment Selection and Use John Leed, safety engineer, Non-Stockpile Chemical Materiel/ SAIC

Monitoring During Explosive Destruction System and Rapid Response System Operations

John Leed, safety engineer, Non-Stockpile Chemical Materiel/SAIC

Program Manager Non-Stockpile Chemical Materiel Site Monitoring Approach at NECD

William Rogers, TVA quality assurance officer, Tennessee Valley Authority

APPENDIX C 83

Fourth Committee Meeting, September 14-15, 2004, Irvine, California

Non-Stockpile Chemical Materiel Product Overview William Brankowitz, acting product manager, Non-Stockpile Chemical Materiel Product

Newport Chemical Depot Former Production Facility
Demolition: Baseline Schedule Overview

Terry Frederick, manager, TVA Non-Stockpile Chemical Materiel

Addressing NRC Requests for Information on NECD-FPF Terry Frederick, manager, TVA Non-Stockpile Chemical Materiel

Fifth Committee Meeting, October 26, 2004, Washington, D.C.

Writing meeting

OTHER ACTIVITIES

Newport, Indiana, Former VX Production Facility, May 17-19, 2004

Site team

Martin Gollin, committee member James Pastorick, committee member Billy Thomas, committee member Nancy Schulte, study director

Newport, Indiana, Focus Group Meeting, June 30, 2004

Site team

Leonard Siegel, committee member Nancy Schulte, study director

Dugway Proving Ground EDS Site Visit, August 10-11, 2004

Site team

Brian Lamb, committee member Douglas Medville, committee member Nancy Schulte, study director

Technologies for Chemical Agent Detection, Washington, D.C., August 23-24, 2004

Site team

Todd Kimmell, committee member Gary Sides, committee member Nancy Schulte, study director

EDS Open House, Dover, Delaware, October 6, 2004

Site team

George Parshall, committee member Leonard Siegel, committee member Nancy Schulte, study director

Appendix D

Approved Personal Protective Equipment



DEPARTMENT OF THE ARMY
OFFICE OF THE CHIEF OF STAFF
200 ARMY PENTAGON
WASHINGTON DC 20310-0200

DACS-SF

1 May 2003

MEMORANDUM FOR SEE DISTRIBUTION

SUBJECT: Generic Approval of Commercial Chemical Protective Equipment

- 1. Reference:
- a. DACS-SF memorandum dated 11 Apr 94, subject: Use of Commercially Available Chemical Protective Clothing.
- b. DACS-SF memorandum dated 30 Dec 98, subject: Revised Policy for the Use of NIOSH-Certified Commercial Respirators with Chemical Agents.
 - c. DACS-SF memorandum dated 28 Feb 02, subject as above.
- 2. This memorandum supercedes reference "c." Reference "c" presented a list of clothing and respirators approved by the U.S. Army Materiel Command Chemical Agent Safety and Health Policy Action Committee (CASHPAC), on behalf of the Director of Army Safety, for specific chemical agents and use scenarios and with specific limitations. The enclosure contains the updated list of approved commercial chemical protective equipment coupled with appropriate scenarios, limitations, and chemical agents.
- 3. Use of CASHPAC-approved chemical protective clothing/respirator approved for the specific agent and in the specific use scenario listed on the attached eliminates the need to use the CASHPAC approval process outlined in reference "a" and "b." Note that under the following situations the CASHPAC approval process outlined in reference "a" and "b" must be used:
- a. An installation/activity wants to use a commercial EPA Level A or B/C ensemble/respirator that has not been approved and listed by the CASHPAC.
 - b. A different use scenario is desired.
- c. An installation/activity desires to use the commercial EPA Level A or B/C ensemble/respirator with chemical agent for which it has not been tested.
- d. An installation/activity desires to use a commercial EPA Level A or B/C ensemble/respirator beyond its approved limitations.

1 May 2003 SUBJECT: Generic Approval of Commercial Chemical Protective Equipment

logic (listing potential agent exposures and use scenarios) to DACS-SF for future reference. The installation/activity shall also maintain a copy of their decision logic for chemical protective equipment will furnish a copy of the equipment selection decision review by any Department of Army Pre-Operational Inspection Team and include it in An installation/activity planning to use CASHPAC approved/listed commercial applicable chemical warfare materiel safety submissions.

JAMES A. GIBSON Senior Safety Manager

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Office of the Director of Army Safety

Deputy Assistant Secretary of the Army (Environment, Safety and Occupational DISTRIBUTION:

Project Manager for Non-Stockpile Chemical Materiel, ATTN: SFAE-CD-N, Aberdeen Health), 110 Amy Pentagon, Washington, DC 20310-0110 Project Manager for Chemical Stockpile Disposal, ATTN: SFAE-CD-SQ, Aberdeen Proving Ground, MD 21010-5401

Proving Ground, MD 21010-5401 Chief, National Guard Bureau, Army Aviation and Safety Directorate, Arlington Hall Readiness Center, ATTN: NGB-AVN-S, 111 South George Mason Drive, Arlington, VA 22204-1382

Commander, U.S. Army Materiel Command, ATTN: AMCSF, 5001 Eisenhower Avenue, Alexandria, VA 22333-0001 Commander, U.S. Army Soldier, Biological and Chemical Defense Command, Commander, U.S. Army Soldier, Biological and Chemical Defense Command, ATTN: AMSBC-RA, Aberdeen Proving Ground, MD 21010-5423

Director, Edgewood Chemical Biological Center, ATTN: AMSCB-ODR-S, Aberdeen ATTN: AMSBC-SO, Aberdeen Proving Ground, MD 21010-5423 continued

Commander, U.S. Forces Command, ATTN: AFPI-SO, Fort McPherson, GA Proving Ground, MD 21010-5423 30330-6000

Commander, U.S. Army Corps of Engineers, ATTN: CESO-ZA, WASH DC

SUBJECT: Generic Approval of Commercial Chemical Protective Equipment

1 May 2003

DISTRIBUTION, conf.

Director, U.S. Army Nuclear and Chemical Agency, ATTN: ATNA-CM, 7150 Heller Commander, U.S. Army Training and Doctrine Command, ATTN: ATBO-S, Fort Monroe, VA 23651-5000

Loop, Suite 101, Springfield, VA 22150-3198

Commander, U.S. Army Center for Health Promotion and Preventive Medicine,

Commander, U.S. Army Test and Evaluation Command, 4501 Ford Avenue, Alexandria, ATTN: MCHB-TS-OFS, Aberdeen Proving Ground, MD 21010-5422

Director, U.S. Army Technical Center for Explosives Safety, ATTN: JMCAC-ES, VA 22302-1458

McAlester, OK 7450'

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Manufacturer: Dupont and Dupont-licensed suppliers

Model: Tyvek "F"

BCC Level: Agent(s): G-series, VX, HD, L

Use Scenario(s):

1. Intrusive excavation using, heavy machinery, hand tools, by hand, sifting equipment,

- Environmental sample collection such as soil, sludge, water, etc. Decontamination of agent contaminated media. For example, soil, debris, etc.
 - - Operation of a PDS or EPDS.
- Assessment, packaging, unpackaging and removal of excavated items.
 - Well drilling/installation.
- General site work such as, equipment maintenance, cylinder change-out, other routine tasks as defined in the applicable safety submission. 6
 - Disposal of HD ton containers.

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Reuse: Not reusable if contaminated with vapor and/or liquid chemical agent. This is also a one-time use suit.

Limitations/Additional Requirements:

- Must be removed immediately if contaminated with liquid chloroform/HD or GB and the wearer decontaminated within 30 minutes
 - if workers encounter leaking CAIS they will immediately evacuate the area and don other approved chemical protective clothing.

 - May not be used if fire is expected (suit is not NFPA certified for flame resistance) CPU must be worn for HD operations.
 - Have a heat stress plan developed, approved, and workers trained prior to use. 7.60.57
- Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of Suit must be thoroughly inspected before and during use for signs of wear.
- suit material swatches to ensure consistent materiel quality over time and between production lots

Manufacturer: GEOMET (via Kappler)

Model: Geomet Responder CSM

Level: NB

Agants) messenes was the first

Emergency response into an area in which an unplanned release of chemical agent Use Scenario(s). has occurred.

Operation of a PDS/EPDS.

CAIRA operations such as, clean up of spills, air monitoring set up, first entry after engineering control failure, containment of open agent

Operations conducted in igloos or test chambers involving suspect chemical agent Demilitarization of CAIS (unpacking, segregating, storing, preparing, etc.)

items.

Destruction/dismantling of contaminated buildings and equipment.
 Isolation of leaking munitions.
 Emergency back-up entries into IDLH areas.
 Confined space entry into toxic/hazardous environments.
 Confined first entry monitoring into outdoor or indoor agent storage areas/igloos.
 Sampling and removal (manually or mechanically) of potentially contaminated soil

and/or items from remediation sites.

Decontamination/treatment of soil samples.
 Disposal of HD ton containers.

Reuse: Not reusable if contaminated with vapor and/or liquid chemical agent. Otherwise, if not contaminated, this is a limited use suit.

<u>Limitations/Additional Requirements:</u>
1. May not be used if fire is expected (suit is not NFPA certified for flame resistance) unless the silver over-shield is worn

Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of suit material swatches to ensure consistent materiel quality over time and between Have a heat stress plan developed, approved and workers trained prior to use.

Pass-through (if worn tethered) must be compatible with airline system. 4

Manufacturer: Trelleborg Industri

Model: TRELLCHEM HPS

Level:

Agent(s): G-series, HD, L, VX

Use Scenario(s):

Working within a vapor containment structure (VCS).

Decontamination of a VCS.

CAIRA operations such as, clean up of spills, air monitoring set up, first entry after engineering control failure, containment of open agent.

Operations conducted in igloos or test chambers involving suspect chemical agent Routine first entry monitoring into outdoor or indoor agent storage areas/igloos.

items.

 Destruction/dismantling of contaminated buildings and equipment.
 Isolation of leaking munitions.
 Emergency back-up entries into IDLH areas.
 Confined space entry into toxic/hazardous environments.
 Operation of the PDTDF (decontamination of interior and work conducted in agent environment).

containment chamber (ECC); decontamination of the ECC; opening munition Operation of the MAPS facility (removal of drill/cut box from the explosion overpack in process room; decontamination of the process room).

12. Operation of the solvated electron technology (SET''') with in a chemical agent test 13. Sampling and removal (manually or mechanically) of potentially contaminated soil

and/or items from remediation sites.

Decontamination/treatment of soil samples.
 Disposal of HD ton containers.

Reuse: Not reusable if contaminated with liquid agent; reusable if contaminated with vapor agent

Limitations/Additional Requirements:

Have a heat stress plan developed, approved and workers trained prior to use.

Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of suit material swatches to ensure consistent materiel quality over time and between production lats.

Pass-through (if worn tethered) must be compatible with airline system.

Manufacturer: Trelleborg Industri Model: TRELLECHEM TLU

Level: A

Agent(s): G-series, HD/L, VX

Use Scenario(s): CAIRA operations such as, clean up of spills, air monitoring set up, first entry after engineering control failure, containment of open agent.

Reuse: Not reusable if contaminated with vapor and/or liquid chemical agent. Otherwise, if not contaminated, this is a limited use suit.

Limitations/Additional Requirements:

May not be used if fire is expected (suit is not NFPA certified for flame resistance). Have a heat stress plan developed, approved and workers trained prior to use.

Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of suit material swatches to ensure consistent materiel quality over time and between production lots.

Pass-through (if worn tethered) must be compatible with airline system.

Manufacturer: GEOMET

Model: Commercial STEPO

Ø Level: Agent(s): G-series, HD/L, VX

Use Scenario(s): CAIRA operations such as, clean up of spills, air monitoring set up, first entry after engineering control failure, containment of open agent.

Reuse: Not reusable if contaminated with vapor and/or liquid chemical agent.

Limitations/Additional Requirements:

Have a heat stress plan developed, approved and workers trained prior to use. Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of suit material swatches to ensure consistent materiel quality over time and between production lots

Manufacturer: Trelleborg Industri Model: TRELLCHEM HPS-TS

Level:

Agent(s): G-series, HD/L, VX

Working within a vapor containment structure (VCS) Use Scenario(s).

Decontamination of a VCS.

CAIRA operations such as, clean up of spills, air monitoring set up, first entry after engineering control failure, containment of open agent.

Operations conducted in igloos or test chambers involving suspect chemical agent Routine first entry monitoring into outdoor or indoor agent storage areas/igloos.

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items.

 Destruction/dismantling of contaminated buildings and equipment.
 Isolation of leaking munitions.
 Emergency back-up entries into IDLH areas.
 Confined space entry into toxic/hazardous environments.
 Operation of the PDTDF (decontamination of interior and work conducted in agent environment).

 Operation of the MAPS facility (removal of drill/cut box from the explosion containment chamber (ECC); decontamination of the ECC; opening munition overpack in process room; decontamination of the process room)

12. Operation of the solvated electron technology (SETTM) with in a chemical agent test

Sampling and removal of potentially contaminated soil and/or items from remediation sites Reuse: Not reusable if contaminated with liquid agent; reusable if contaminated with /apor agent.

<u>-imitations/Additional Requirements:</u>
. Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of suit material swatches to ensure consistent materiel quality over time and between production lots

Manufacturer: Kappler®

Model: Kappler® Coverall Style 41250 FV

Ϋ́ Level: Agent(s): GB, HD, L, VX

Use Scenario(s):

Routine disposal of the industrial and warfare chemicals found in CAIS sets.

Reuse: Not reusable if contaminated with liquid or vapor agent.

Limitations/Additional Requirements:

- 1. The Kappler® Coverall is approved for use as a replacement for the Army Level B
- Prior to use of suit, manufacturer shall provide validation of QA/QC batch testing of suit material swatches to ensure consistent materiel quality over time and between
- Must have a complete inspection program in place and employed to ensure that damaged coveralls are not reused.

Manufacturer: North

Model: North 7600-8A NIOSH-Certified Full Facepiece Air-Purifying Respirator with North 7583/P100 Organic Vapors/Acid Gases Cartridge/Filter

Level: N/A

Agent(s): Specific chemical agents listed in AR 50-6.

Use Scenario(s):

- 1. Added protection in chemical agent laboratory operations when chemical agent is inside a certified chemical agent laboratory ventilation hood.
 - Emergency-escape from a chemical agent laboratory.

Reuse: Respirators and cartridges that have been exposed to chemical agents will be decontaminated, monitored, and disposed of.

Limitations/Additional Requirements:

- MUC is the assigned protection factor of the respirator (50) multiplied times the Airborne Exposure Limit (AEL) for the agent. The MUC for mustard and Lewisite will Near Real Time (NRT) monitoring must be conducted to ensure agent levels do not exceed the Maximum Use Concentration (MUC) for the specific agent involved. The not exceed 0.003 mg/m3.
 - The user's Respiratory Protection Program will meet the requirements of 29 CFR 1910.134, to include establishing filter/canister change-out schedules. Additional personal protective clothing and equipment will be adequate for the work
 - being performed

Manufacturer: North

Model: North 7600 Series NIOSH-Certified Full Facepiece Air-Purifying Respirator with North 7583/P100 Organic Vapors/Acid Gases Cartridge/Filter

X Level:

Agent(s): Specific chemical agents listed in AR 50-6.

Use Scenario(s)

- Environmental sampling
- Excavation into anomalies.
- Operations where personnel are responsible for decontaminating personnel and
- Emergency escape for personnel working outside the exclusion zone but within the No Significant Effects zone, in the event the near real time (NRT) monitoring devices
- Emergency escape from chemical area
- Industrial chemical operations in support of MMD-1 operations. Maintenance operations
- Processing of munitions/container carcasses already processed in the MMD-1 50000
- Agent treatment process liquid and/or vapor sampling filter unit, and gas reactor carbon replacement in support of MMD-1 operations.

Respirators and cartridges that have been exposed to chemical agents will be decontaminated, monitored, and disposed of. Reuse:

Limitations/Additional Requirements.

- exceed the Maximum Use Concentration (MUC) for the specific agent involved. The Airborne Exposure Limit (AEL) for the agent. The MUC for mustard and Lewisite will Near Real Time (NRT) monitoring must be conducted to ensure agent levels do not MUC is the assigned protection factor of the respirator (50) multiplied times the not exceed 0.003 mg/m3.
 - The user's Respiratory Protection Program will meet the requirements of 29 CFR 1910.134, to include establishing filter/canister change-out schedules. ć,
- Additional personal protective clothing and equipment will be adequate for the work being performed

Manufacturer: MSA

Model: MSA Ultra-Twin NIOSH-Certified Full Facepiece Air-Purifying Respirator with MSA GME Super Cartridges/P100 Filters

N/A Level: Agent(s): Specific chemical agents listed in AR 50-6.

Use Scenario(s):

- Environmental sampling. Excavation into anomalies.

3 4.

- Operations where personnel are responsible for decontaminating personnel and equipment.
- Emergency escape for personnel working outside the exclusion zone but within the No Significant Effects zone, in the event the near real time (NRT) monitoring devices
- Emergency escape from chemical area.
 - Maintenance operations,

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Respirators and cartridges that have been exposed to chemical agents will be Reuse: Respirators and cartridges that have decontaminated, monitored, and disposed of.

Limitations/Additional Requirements:

- Maximum Use Concentration (MUC) for the specific agent involved. The MUC is the assigned protection factor of the respirator (50) multiplied times the Airborne Exposure Limit (AEL) for the agent. The MUC for mustard and Lewisita will not NRT monitoring must be conducted to ensure agent levels do not exceed the exceed 0.003 mg/m3.
 - The user's Respiratory Protection Program will meet the requirements of 29 CFR 1910.134, to include establishing filter/canister change-out schedules. Additional personal protective clothing and equipment will be adequate for the work 2
 - e,

Manufacturer: MSA

Model: MSA Advantage 1000 NIOSH-Certified Full Facepiece Air-Purifying Respirator with MSA GME Super Cartridges/P100 Filters

N/A Level:

Agent(s): Specific chemical agents listed in AR 50-6.

- <u>Use Scenario(s):</u> 1. Industrial chemical operations where there is a potential for chemical agent
- Operation of the Emergency Personnel Decontamination Station (EPDS)

Operation of Rapid Response System (RRS).

- Maintenance and housekeeping operations.
 - Emergency escape from chemical area.
- Industrial chemical operations in support of MMD-1 operations.

 Processing of munitions/container carcasses already processed in the MMD-1
- Agent treatment process liquid and/or vapor sampling filter unit, and gas reactor carbon replacement in support of MMD-1 operations. Process Trailer.

Reuse: Respirators and cartridges that have been exposed to chemical agents will be decontaminated, monitored, and disposed of.

Limitations/Additional Requirements:

- NRT monitoring must be conducted to ensure agent levels do not exceed the Maximum Use Concentration (MUC) for the specific agent involved. The MUC is the assigned protection factor of the respirator (50) multiplied times the Airborne Exposure Limit (AEL) for the agent. The MUC for mustard and Lewisite will not
- The user's Respiratory Protection Program will meet the requirements of 29 CFR 1910-134, to include establishing filter/canister change-out schedules. Additional personal protective clothing and equipment will be adequate for the work
 - being performed.

exceed 0.003 mg/m3.

