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# Technical Support for Recovery Phase Decision-Making in the Event of a Chemical Warfare Agent Release

by

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## Introduction

In late 1985, Congress mandated that the U.S. stockpile of lethal unitary chemical agents and munitions be destroyed by the Department of the Army in a manner that provides maximum protection to the environment, the general public and personnel involved in the disposal program (Public Law 99-1, Section 1412, Title 14, Part b). These unitary munitions were last manufactured in the late 1960's. The stockpiled inventory is estimated to approximate 25,000-30,000 tons (Anft, 1988), and includes organophosphate ("nerve") agents such as VX [O-ethyl ester of S-(diisopropyl aminoethyl) methyl phosphonothiolate, $C_{11}H_{26}NO_2PS$] and vesicant ("blister") agents such as HD [sulfur mustard; bis (2-chloroethyl sulfide), $C_4H_8Cl_2S$]. The method of agent destruction selected by the Department of the Army is combined high-temperature and high-residence time incineration at secured military installations where munitions are currently stockpiled (eight facilities in the continental United States and one on Johnston Atoll in the South Pacific; Carnes 1989). Several of these installations are located in agricultural areas where production of livestock, pasture and row crops is important to local economies. In the unlikely event of an agent release being atmospherically transported outside the installation boundaries during continued storage or any stage of agent destruction, food, forage crops and structures will likely be suspected of surface contamination. Meat or milk could also become suspect from livestock ingestion of, or contact with, potentially contaminated forage or other materials. This issue is especially problematic for the persistent agents VX and HD, which were originally designed as "terrain denial" materials on the chemical battlefield. Due to their persistent chemical properties, they do not rapidly degrade and thus pose a potential health concern for reentry to suspect areas after an agent release.

Reproducible methods for detecting agents or their metabolites in plant or animal tissues or building materials have not been systematically established. The lack of rapid isolation techniques and low-level detection protocols has hindered development of civilian control limits for ingestion and dermal contact exposure to agents. As a result, there are currently no established analytical procedures for use in determining how long restricted public access to potentially agent-contaminated areas or agricultural resources should be maintained after release of a chemical warfare agent to the environment. Decision criteria for determining the extent and significance of potential agent contamination are needed to support several chemical warfare munition and materiel disposal activities. This logic is also needed for developing verification and compliance monitoring programs integral to the international Chemical Weapons Convention.

To support the development of environmental monitoring protocols and recovery phase planning efforts, the Office of the Assistant Secretary of the Army (Installations, Logistics and Environment) funded a multidisciplinary research program to address

1) biomonitoring of nerve agent exposure,
2) agent detection limits in meat, grain, vegetation and milk, and
3) permeation of chemical warfare agents through porous construction materials such as brick and wood.

Principal findings and applications are summarized below.

**Biomonitoring of Nerve Agent Exposure**

Biomonitoring capability by means of measuring the degree of whole blood cholinesterase (ChE) activity depression from baseline levels in sentinel livestock is potentially valuable as a biological check during routine facility operation, and as an indicator of the extent of nerve agent plume movement or deposition when timely deployment of low-level monitors is not feasible (Munro et al 1991). Monitoring of ChE activity could further serve as an indicator of the safety of previously contaminated areas for reentry by human beings, pets and livestock.

This additional monitoring capability would augment present decision criteria that rely heavily on output from atmospheric dispersion models, which are limited by their 2-dimensionality and necessarily simplified assumptions (DA 1988).

In order for livestock ChE activity to be useful as a reliable biomonitoring end point, it is first necessary to characterize the sources of ChE variability in normal, healthy animals. This is a common principle that guides monitoring of ChE activity in the blood of agricultural workers exposed to organophosphate and carbamate insecticides during the growing season (Morgan 1989). The work reported here examined the effect of age, gender, reproductive status, state of health, time of day and season as sources of biological variability in several commercial livestock species (beef and dairy cattle, sheep, horses) that would be generally available for use as sentinel species in agricultural communities hosting chemical munitions stockpiles (Halbrook et al 1992a,b). These data, the first blood ChE-activity measurements to be systematically collected over at least one reproductive cycle (for approximately 12 months) from individual healthy animals, provide new information for assessing ChE-activity depressions in livestock blood.

The research findings from the above analysis of whole-blood ChE activity in observed livestock support the following recommendations for biomonitoring near any sites where nerve agents are stockpiled, or where nerve agents have been manufactured or processed (Chemical Weapons Convention treaty verification and compliance).

1) Repeated sampling of at least once a month for 6 months is necessary to establish a stable individual baseline of mean blood ChE activity for each animal within a sentinel group.

2) Adult animals should be selected as sentinels (ChE activity is partly a function of maturation).

3) The number of animals selected as sentinels is subjective, but should be no less than 6 adult animals of the same species for each monitoring area (defined as an area that individual sentinel animals would normally enter on a daily basis).

4) Collection and analysis of whole-blood samples for ChE activity determination should be performed at least monthly during the monitoring period (more often if events warrant).

5) Of the livestock species examined, domestic sheep are the preferred sentinel species due to the fact that they
   a. possess the least variable ChE activity within-individual and across age and gender groups,
   b. are relatively easy to handle and manage, and
   c. cost less to purchase and maintain than cattle and horses

6) Refrigerate (at 4 °C) blood samples and analyze within 24 hours of collection. If samples cannot be analyzed in this time period, store in liquid nitrogen (at -197 °C).

## Agent Detection Limits and % Recovery from Food Items

Research at Oak Ridge National Laboratory (ORNL) has demonstrated the efficacy of direct sampling ion trap mass spectrometry (ITMS) for the rapid and reproducible detection of target compounds, including chemical warfare agents, in environmental and physiological samples. The objectives of ongoing efforts are to combine the minimal sample preparation steps (needed to prevent tissue components such as proteins and fats from compromising instrument operation) with a rapid method of detecting low concentrations of target compounds (Caton et al 1994; Buchanan et al, in press). Extraction and analytical methods for chemical warfare agents were developed using agent simulants, which are less toxic chemical and physical analogues of actual chemical warfare agents. The simulant compounds employed were diisopropylmethyl phosphonate (DIMP; $C_7H_{17}PO_3$) for the nerve agent VX, and 2-chloroethyl ethyl sulfide (CEES, $C_4H_9ClS$) for the blister agent HD. Verification of the developed methods will require the use of "live" warfare agent compounds at certified surety facilities.

To isolate simulant "spikes" to beef tissue, milk, wheat grain, and green alfalfa, a combination of centrifugation, filtration, dialysis, and adsorption onto solid phase sorbents was employed. Plant tissue proved to be problematic (Buchanan et al, in press). Depending on the extraction method employed, recovery rates for DIMP and CEES ranged from 50-85% (countercurrent filtration/dialysis followed by solid phase extraction) for meat, grain and milk; to 20-50% (solid phase extraction) for DIMP in meat and milk. For the sulfur mustard simulant CEES, recoveries were lower and more variable owing to the fact that CEES is more water soluble, more reactive and more volatile than DIMP. In all cases, thermal desorption ITMS proved to be a rapid and sensitive analytical procedure, with detection limits in the 50 to 100 ppb range.

Since these detection limits can be obtained with small initial sample sizes (100 mg), it is possible that this approach would be applicable to needle biopsy samples from living animals, rather than sacrificial testing. In addition, throughput is substantially increased because these new methods may be performed more quickly than conventional methods requiring substantial preparation (extraction into a suitable solvent followed by concentration via evaporation, etc.) and analysis times (combined gas chromatography and mass spectrometry).

**Permeation of Chemical Warfare Agents Through Construction Materials**

There are presently no criteria suitable for designating potentially contaminated masonry, wood, wallboard or other "porous media" as free of hazardous agent concentrations. Concepts that have been previously considered include treating the suspect item or surface as if it were a piece of military hardware being prepared for sale to the public as scrap (DA 1992, 1994 a,b), wipe sampling of the suspect surface, or enclosing the item or area in an airtight manner followed by surface heating and airstream sampling. There are sampling and interpretation problems inherent to each of these approaches, not the least of which is how to determine acceptable agent concentrations for conditions of unlimited public access. Protocols for management of military scrap are the only U.S. guidelines governing agent decontamination of material that can be released to the public (DA 1992); these protocols were never intended for application to the treatment of public or private property under civilian, not military, control.

Experimental assessment of agent simulant "spike" sorption into, and permeation through, the porous construction materials brick, cinder block, gypsum wall board, and wood (with window glass as a non-porous reference medium) at two temperatures (23 °C and 32.2 °C) has now been performed (Jenkins et al 1994). Dimethylmethyl phosphonate (DMMP; $C_3H_9PO_3$) was the test simulant for nerve agent VX, while 2-chloroethylethyl sulfide (CEES; $C_4H_9ClS$) was the test simulant for the sulfur mustard agent HD. Note that, while the chemical structures of VX and DMMP are dissimilar, DMMP is frequently used an a physical analogue for VX because both compounds are phosphonates, and possess similar volatilities.

Simulant movement through wood was found to be nearly always in the direction of the wood grain. Two-dimensional breakthrough was observed in brick and gypsum wall board. All simulants permeated to the breakthrough space of gypsum wall board in a few hours, with CEES breakthrough more rapidly (<1 hour) than other simulants. The sulfur mustard simulant broke through all test media in less than 60 min; nerve agent simulant breakthrough required several hours. All data indicate that substantial sample-to-sample variation in individual wafers of construction material exist, particularly for the coarsely porous brick and cinder block.

## Applications

Prudent host communities located near the stockpile sites have begun recovery phase planning. The results of the experimental program summarized above are included in the technical assistance currently provided to host communities by the authors. Examples of such assistance include:

Planning Guidance for recovery phase decontamination (of livestock and companion animals, personal and real property) and reentry (sampling and monitoring procedures, hazard assessment, access control). Checklists, fact sheets, material safety data sheets, pertinent technical articles, and prioritization schemes are recommended for inclusion in local emergency preparedness plans.

Recovery Plan Workbooks and Sourcebooks containing examples and necessary planning elements have been provided to host communities and stockpile installations for their use in developing coordinated recovery plans.

Reentry and Restoration Symposia are presented within individual stockpile host communities. Approximately two full days are spent communicating monitoring and technical guidance for recovery phase planning with a broad cross-section of civilian and military emergency responders, planners, environmental regulators and agriculturalists.

Reentry/Restoration Tabletop Exercises are held in "compressed" time mode as an adjunct to full scale exercises. Procedures to ensure the safety of the food supply (such as exclusion time intervals), determination of hazard zone boundaries, shelter-in-place alternatives, and the length of time necessary to provide mass care are discussed and developed

Analytical Methods for Environmental Sampling Conferences as a means of fostering exchange among investigators and end users on current efforts to standardize analytical protocols for the reliable detection of chemical warfare agents and their degradation products in soil, vegetation and other complex environmental media.

**Challenges**

Progress has been made in several recovery planning areas. However, there are still numerous challenges to be met. While there are promulgated agent control limits for chemical warfare agents in air, similar limits need to be established for other environmental media such as soil, water, milk and vegetation. As a parallel effort, the corresponding analytical methods (with detection limits) for assessing environmental media need to be documented

Reliable monitoring of agent in environmental samples is a major concern of the U.S. Army Chemical Demilitarization and Remediation Activity, which has responsibility for non-stockpile chemical materiel (NSCM). The NSCM includes buried chemical warfare materiel (primarily in the 1950's and 1960's); recovered chemical weapons; former production, storage, and processing facilities for chemical weapons; and other agent auxiliary material defined in the international Chemical Weapons Convention. A timetable for destruction of these materials and certification of the suspect area as "clean" has been established, with the year 2000 as the first target date for one category of NSCM. Similar certifications are being imposed on U.S. military facilities by installation restoration and construction site clearance requirements, even though analytical verification procedures are still under development.

It is clear that similar needs for monitoring and detection protocols are being identified by U.S. military and civilian authorities as well as the international community concerned with chemical weapons treaty compliance and verification. Consolidated efforts would best serve resolution of these issues.

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