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October 11, 1993

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SUBJECT: Environmental Monitoring for Chemical Warfare Agents

INTRODUCTION

This memorandum summarizes information we obtained at your request on the feasibility of sampling and analyzing water and soil for the agents HD (mustard), VX, and GB. Incineration of these chemicals is scheduled to begin at the Umatilla Depot Activity (UMDA) near Hermiston, Oregon, in 1998. Also included in Appendix A is some information to assist in planning soil surveys for pesticides which may interfere with determination of nerve agents.

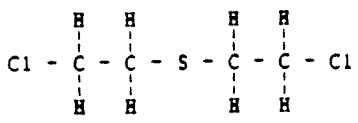
Karen Larson of the Washington State Department of Health generously provided a number of the documents reviewed on this topic. One of the most useful references on environmental monitoring for chemical warfare agents is Peterson *et al.* (1993-draft). Much of what follows is taken from this report.

GENERAL CHARACTERISTICS

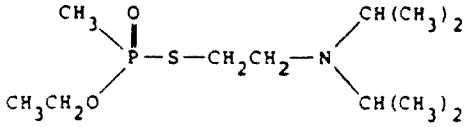
HD [bis(2-chloroethyl)sulfide; CAS no. 505-6000-2] is more commonly known as sulfur mustard, mustard gas, or mustard. Exposure causes severe blistering of skin and damage to the eyes and lungs. It is a known human carcinogen. VX [O-ethyl-S-(2 - diisopropylaminoethyl)methylphosphonothiolate; CAS no. 50782-69-9] and GB or sarin [isopropylmethylphosphonofluoridate; CAS no. 107-44-8] are organophosphate nerve agents. Like organophosphate pesticides, these are anti-cholinesterase compounds that cause over-stimulation of muscles and secretory glands; death is usually by respiratory failure. VX is approximately 1,000 - 10,000 times more toxic than commercial insecticides.

FIGURE 1. Chemical Structures

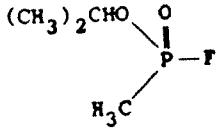
Mustard



VX



GB



Mustard is an oily pale yellow liquid. VX and GB are colorless, odorless liquids. While GB is volatile and readily hydrolyzed, mustard and VX are more persistent and the relative greater environmental concern. Quarantine times for GB may be on the order of 2 to 14 days, but weeks to months for mustard and VX. At least one breakdown product of VX [S-(2-diisopropylaminoethyl)methylphosphonothoic acid] has a toxicity similar to the parent compound.

ENVIRONMENTAL LEVELS OF CONCERN

Knowledge of safe versus hazardous concentrations of these agents is necessary to determine what level of detection is required in environmental monitoring programs. At present, control limits for the general population have only been established for air. The no-effect dose for ingestion and dermal exposure has not been determined by any regulatory agency. Limited information on aquatic toxicity indicates nerve gas LC-50s are less than 1 μg/L (parts per billion) for fish. The aquatic toxicity of mustard is unknown. Plants have a relative low sensitivity to these agents.

Watson *et al.* (1992) have proposed agent control limits for various media. Table 1 shows the lower of the limits proposed for water, soil, and vegetation (produce). The limits for mustard were calculated for a 10E-5 additional lifetime cancer risk. The nerve gas limits are based on 15% depression of red blood cell cholinesterase.

PRIORITY SAMPLING MEDIA

For purposes of making decisions to re-enter a contaminated area, environmental sampling priorities have been ranked as follows:

1) air
2) surface drinking water sources and vegetation
3) wipe samples of surfaces
4) soil
5) meat, milk
6) porous media (brick, wood, etc.) where physical contact is likely
7) non-drinking water supplies, such as sources of irrigation water

Note that vegetation has a higher sampling priority than soil. Although there is potential for long-term contamination of ground water by a spill of mustard, ground water is not given high priority for sampling.

ANALYSIS AND COST

Laboratory (as opposed to field) analysis is required to detect the low concentrations of VX, GB, and mustard shown in Table 1. Methods and laboratory availability to analyze chemical warfare agents are reviewed in Peterson *et al.* (1993-draft) and Nesbitt and Zimmerman (1991). Because some of this information appeared outdated or in error, we contacted three of the commercial laboratories with the most experience in this type of work (pers. comm., Elijah Jones, Rocky Mountain Arsenal) and discussed the current feasibility of analyzing low levels of VX, GB, and mustard. A hypothetical sample set of 20 each water and soils was proposed:

1) Southern Research Institute (SRI)
2000 Ninth Avenue, South
P.O Box 55305
Birmingham, AL 35255-5305
Dr. Bill Fowler
(205) 581-2305

SRI claims capability to analyze VX, GB, and mustard at a detection limit of 1 ppb in water and soil. Routine detection limits are 20 ppb for VX/GB and 200 ppb for mustard (combat standard for drinking water). A minimum sample size of 250 mL is recommended.

A cost of $30,000 was estimated for analyzing all three agents in 20 samples each of water and soil. Analysis is by GC/FPD. GC/GC-MS confirmation of hits was not included in the cost. Turn-around time from submission of samples to receipt of data was 30-45 days.

QA/QC deliverables include results of matrix spikes, instrument calibration, procedural blanks, and a cover letter discussing analytical problems (if any) and procedures. The laboratory will also conduct a preliminary evaluation of extractability of sample soils and provide written sampling instructions. Pre-cleaned sample containers, packaging, and chain-of-custody forms can be provided at extra cost.

The laboratory has some capability to analyze metabolites and degradation products, but their methods are less sensitive for these compounds. Analytical capabilities and cost for vegetation samples are similar to soil.

Costs were not provided on a per sample basis because of the expense of gearing up for this type of work. SRI estimated only about 30% of their cost was for sample preparation and analysis, the remainder being in complying with health, safety, disposal, and other regulations. Therefore, sample size could be increased without greatly affecting the cost.

2) Battelle - Columbus Laboratory
505 King Avenue
Columbus, OH 43201
Dr. John M. Smith
(614) 424-5392
Dr. Tim Moore
(614) 424-7956

Battelle proposed to conduct the requested task in three phases: 1) Program Plan preparation, which would include detailed descriptions of the sample handling and control, QA/QC, and analytical protocols to be used, 2) sample analysis, and 3) report generation.

For preliminary screening, Battelle would use a modification of EPA Method 608 for all GC analyses and requires 30 grams for each soil sample and one liter for each water sample. Triplicates of each sample will be prepared. One will be analyzed by GC. Any samples which generate peak heights and retention times consistent with either HD, VX, or GB will be rerun by GC to verify the identification. If both samples produce similar results, the third will be analyzed by GC/MS for positive identification and quantification using a modified EPA Method 846. Confirmation analysis is done by a modification of EPA GC/MS Method 8270.

Because Battelle was unfamiliar with the types of soil and water in question, they were not comfortable in claiming detection limits below 250 ppb. Their more intensive approach to the proposed project resulted in an estimated cost of $3,500 per sample.

3) Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110-2299
Dr. Barry Knier
(816) 753-7600 ext. 621

Midwest Research Institute can perform the analyses for VX, GB, and mustard in water and soil. They also have the capability to analyze a number of decomposition products including: ethyl methyl phosponic acid (EMPA, from VX), ispopropyl phosphonic acid (IMPA, from GB), methyl phosphonic acid (MPA, from both VX and GB), and dithiane, oxathiane, and thiodiglycol (from mustard).

Detection limits for VX and GB in water and soil samples are 20 ppb with 200 ppb for mustard. Detection limits in the 1 ppb range are possible, although additional method development and QA would be required.

Analysis is by GC/FPD with solid sorbent preconcentration. Confirmation is usually done using a second column approach because GC/MS is 5-to-10 times less sensitive, resulting in five-fold differences between primary and confirmational detection limits.

No prices could be quoted until the nature and extent of work is detailed.

Based on the above, it appears feasible to analyze VX, GB, and mustard in water and soil at detection limits of 1 ppb. None of the laboratories were confident in their ability to achieve detection limits lower than 1 ppb--the level of detection needed to determine compliance with some but not all of the proposed agent control limits shown in Table 1. Inquiries resulting in this information were necessarily preliminary in nature. A request for formal, technical proposals would be required for a clear understanding of laboratory capabilities and cost.

SAMPLE COLLECTION AND HANDLING

Apart from the rigorous requirements in the aftermath of an accident for personnel protection & safety (Dept. Army, 1987), sample collection and handling for these agents is relatively straightforward. The procedures are essentially the same as when sampling water and soil for other organic contaminants (e.g., the EPA Priority Pollutants).

EPA guidelines are generally followed for sampling packaging and handling (e.g., EPA 1989). Sample containers for agent analysis should be amber glass with teflon-lined lids. Commercially available sample bottles, precleaned for trace organics analysis according to

EPA protocols, are suitable. Equipment used to collect soil and water should be made of glass, teflon, or stainless steel. Core samplers are recommended for soil to obtain uniform samples, rapidly and with minimum contamination.

To safeguard against cross-contamination between samples, decontaminate sampling equipment with sodium hypochlorite (bleach) or other appropriate solution.

Each sample should be bubble-wrapped and placed in a polyethylene bag. Samples should be put on ice (4°C) immediately on collection and kept out of sunlight. Ideally, samples should be extracted or analyzed within a few hours, although this is not always possible. The Army follows EPA limits for sample holding times.

Sadusky (1992) gives detailed guidance on collecting, handling, and preserving soil samples for analysis of chemical warfare agents, including recommendations on depth, location, and number of samples to collect. Similar information is provided in Simini (1992) for vegetation samples.

If a state or local agency were to undertake their own effort to monitor these agents, logistics and cost of sample transport may pose problems. Samples intended for agent analysis, even if collected outside UMDA, are assumed to contain agent unless proved otherwise. Among other things, field monitoring and sample custody by the Army may be required in order to transport samples to the analyzing laboratory (pers. comm., Dr. John M. Smith, Battelle). Resolution of this question was not pursued.

SUMMARY OF FINDINGS

Due to their persistence, VX and mustard are of more environmental concern than GB. Environmental monitoring programs should target detection limits of 1 ppb or less for VX, GB, and mustard in water, soil, and vegetation.

Commercial laboratories are available with experience in analyzing all three agents. Detection limits of 1 ppb are reportedly feasible. Limited information obtained on cost of sample analysis showed a range of $750 - $3,500 per sample.

Apart from health and safety concerns, sample collection, preservation, and handling is similar to that for other chemical contaminants of surface waters and soil. The logistics of obtaining regulatory approval and transporting samples may pose significant problems for state or local agencies wishing to do environmental monitoring for chemical warfare agents.

AJ:DS:blt
Attachments

Table 1. Selected Control Limits Proposed by Watson et al., (1992)
(parts per billion)

Agent	Drinking Water*	Soil (dermal exposure)	Produce
GB	1.5 – 3.0 (adult) 0.14 – 0.29 (infant)	none proposed	0.02 – 10**
VX	1.5 – 3.0 (adult) 0.14 – 0.29 (infant)	85 – 1500	0.02 – 10
Mustard	0.023 (adult) 0.0022 (infant)	0.6 – 11	0.015 (adult) 0.0045 (infant)

* @ 2 liters/day
** varies with type of produce

Table 2. Summary of Analytical Capabilities for VX, GB, and Mustard

Laboratory	Media	Method	Detection Limits	Cost/Sample*
Southern Research Inst.	water & soil	GC/FPD	1 ppb	$750
Battelle – Columbia	water & soil	GC/FPD; GC/MS	250 ppb	$3,500
Midwest Research Inst.	water & soil	GC/FPD	20 ppb VX/GB 200 ppb mustard	N/A

*based on sample load of 20 each water and soil

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APPENDIX A. SOME GUIDANCE ON SURVEYING OP PESTICIDES IN SOIL

Peterson *et al.* (1993-draft) and the Response Plan for the Washington Chemical Stockpile Emergency Preparedness Program (CSEPP) recommend obtaining baseline data on occurrence of organophosphate (OP) pesticides in soil. Because of structural similarity to VX and GB, OP pesticides may interfere with agent analysis. Malathion, for example, was identified as an interference in previous analytical methods (now revised) employed for nerve agents at Southern Research Institute (pers. comm., Dr. Bill Fowler).

Contrary to statements in the CSEPP Plan, the Washington State Department of Agriculture apparently does not have background data on OP pesticides in soils (pers. comm., Cliff Weed, Program Manager for Compliance). The Department sometimes, however, analyses soil for pesticides during investigation of complaints.

A starting point for planning a soil survey for OP pesticides would be to consider a stratified random sampling design. This scheme is useful for allocating sampling efforts and increases the accuracy of estimating average concentrations.

In this approach, the area of concern (e.g., the portion of Benton County within the 20-km zone) would be divided into non-overlapping subareas (strata) such that variability of pesticide residues would be expected to be less within a given strata than for the survey area as a whole. Possible strata might include agricultural land, undeveloped land, urban areas, Columbia River (sediments), etc. If interest was limited to agricultural land, subdivision may be appropriate by crop type or amount and variety of OP pesticides used.

For a fixed analytical budget, sampling effort could be apportioned by land area. If estimates were available on residue variability within strata (from other studies or preliminary sampling), the allocation scheme could be optimized by factoring in a standard deviation for each strata. This results in sampling effort getting focused on the more variable areas. Obviously, more effort should be devoted to sampling agricultural areas than undeveloped land (which may largely be non-detects).

Sampling sites within strata should be selected randomly, and each sample collected as a composite rather than single grab. Material taken for sample should be restricted to the surface layer (e.g., top 2 cm) and be consistent between sampling sites. Interpretation of results would be aided by analyzing total organic carbon ($50/sample) and grain size ($75/sample).

Table A.1 summarizes sampling, analysis, and cost information for OP pesticides. Although more expensive than the routine GC/FPD analysis, GC/AED has the potential advantages of avoiding interferences often encountered in GC/FPD and the ability to detect non-target compounds. Detection limits vary with compound and may vary between samples. At least 5 percent of samples should be analyzed in duplicate. Add the cost of 2 additional samples for a matrix spike and matrix spike duplicate to each set of 20 samples.

Table A.1. Sampling and Analysis of Soil for OP Pesticides
(Ecology Manchester Environmental Laboratory)

Minimum Volume Required: 250 grams

Sample Container: 8 oz. glass jar (organic-free w/ teflon lid liner)

Preservation: Cool to 4 degrees C

Holding Times: 14 days to extraction: 40 days to analyze extract

Analytical Methods: *1) GC/AED w/ confirmation by GC/MS; EPA Method 1618*
2) GC/FPD w/ dual column confirmation; EPA Method 8141

Detection Limits: 0.01 - 10 ppb

Approximate Cost per Sample: 1) $400
2) $320

Analytes (Method 1618):

Demeton-O	*Fenthion*
Demeton-S	*Parathion*
Sulfotepp	*Fensulfothion*
Fonofos	*Sulprofos*
Disulfoton	*Imidan*
Methylchlorpyrifos	*Azinphos*
Fenitrothion	*Coumaphos*
Malathion	*Dichlorvos*
Chlorpyrifos	*Mevinphos*
Merphos	*Dioxathion*
Ethion	*Propetamphos*
Carbophenothion	*Methylparaoxon*
EPN	*Phosphamidan*
Ethylazinphos	*Tetrachlorvinphos*
Ethoprop	*Fenamiphos*
Phorate	*Butifos*
Dimethoate	*Abate*
Diazinon	*Ronnel*
Methylparathion	