ANL/EAD/TM-58

Unexploded Ordnance Issues at Aberdeen Proving Ground: Background Information

Environmental Assessment Division
Argonne National Laboratory

Operated by The University of Chicago,
under Contract W-31-109-Eng-38, for the
United States Department of Energy

Argonne National Laboratory

Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States Government, and operated by the University of Chicago under the provisions of a contract with the Department of Energy.

This technical memo is a product of Argonne's Environmental Assessment Division (EAD). For information on the division's scientific and engineering activities, contact:

Director, Environmental Assessment Division
Argonne National Laboratory
Argonne, Illinois 60439-4815
Telephone (630) 252-3107

Presented in this technical memo are preliminary results of ongoing work or work that is more limited in scope and depth than that described in formal reports issued by the EAD.

Publishing support services were provided by Argonne's Information and Publishing Division (for more information, see IPD's home page: http://www.ipd.anl.gov/).

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

ANL/EAD/TM-58

Unexploded Ordnance Issues at Aberdeen Proving Ground: Background Information

by David H. Rosenblatt

Environmental Assessment Division,
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

November 1996

Work sponsored by U.S. Department of the Army,
Aberdeen Proving Ground, Maryland
Directorate of Safety, Health, and Environment

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Distribution Restriction Statement

Approved for Public Release: Distribution is Unlimited. 1775-A-3

For further information about this document, contact:

Victoria Cwiertnie
U.S. Department of the Army
STEAP-SHER
Environmental Conservation and Restoration Division
Building 5650
Aberdeen Proving Ground
Aberdeen, MD 21005-5001

Phone: 410/278-6756 Fax: 410/278-6779
E-mail: vcwiert@eagle.army.mil

This report is printed on recycled paper.

CONTENTS

CONTENTS (Cont.)

TABLES

FIGURE

NOTATION

The acronyms, initialisms, and abbreviations that follow are found in this document.

AC	hydrogen cyanide or hydrocyanic acid
2A-4,6-DNT	2-amino-4,6-dinitrotoluene
4A-2,6-DNT	4-amino-2,6-dinitrotoluene
APG	Aberdeen Proving Ground
atm	atmosphere, unit of gas pressure
BCF	bioconcentration factor
CAS	Chemical Abstracts Service
CG	phosgene or carbonyl chloride
CK	cyanogen chloride
DESH	2-diisopropylaminoethanethiol
DIMP	diisopropyl methylphosphonate
DL	detection limit
DM	adamsite
DNB	1,3-dinitrobenzene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
DU	depleted uranium
DWEL	drinking water equivalent level
EA2192	S-(2-diisopropylaminoethyl) methylphosphonothioic acid
EA4196	bis(2-diisopropylaminoethyl) sulfide
EOD	explosive ordnance disposal
EPA	U.S. Environmental Protection Agency
ft	feet
g	gram (unit of mass)
GA	ethyl N,N-dimethylphosphoramidocyanidate (agent tabun)
gal	gallon
GB	isopropyl methylphosphonofluoridate (agent sarin)
GD	pinacolyl methylphosphonofluoridate (agent soman)
HA	Health Advisory
ha	hectare, a unit of area equal to 2.471 acres
HD	mustard

HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IMPA	isopropyl methylphosphonic acid
kg	kilogram (1,000 g)
L	liter (unit of volume, 0.001 m^3)
lb	pound
LEC	lowest effect concentration
LOAEL	lowest-observed-adverse-effect level
M	mol/L (moles per liter), an expression of concentration
m	meter
mg	milligram (0.001 g)
ml	milliliter (0.001 L)
mm	millimeter (0.001m)
mol	mole (Avogadro's number, 6.023 × 10^{23} atoms, molecules or other entities)
MPA	methylphosphonic acid
MW	molecular weight (g/mol)
NB	nitrobenzene
NOAEL	no-observed-adverse-effect level (any effects produced at this level are not considered adverse)
NOEC	no-observed-effect concentration
OSHA	U.S. Occupational Safety and Health Administration
PA	picric acid (2,4,6-trinitrophenol)
PETN	pentaerythritol tetranitrate
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RfD	reference dose
TDG	thiodiglycol
Tetryl	N,2,4,6-tetranitromethylaniline
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency (now called the Army Environmental Center)
UXO	unexploded ordnance
VX	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate
μg	microgram (0.001 mg)

GLOSSARY

Adamsite: Chlorophenarsazine.

BCF: Bioconcentration factor, ratio of concentration of a solute in tissue to the concentration in water with which the tissue is presumably in equilibrium.

DWEL: Drinking water equivalent level, the concentration of a substance in drinking water that is not expected to cause any adverse noncarcinogenic health effects in humans over a lifetime of exposure.

EC_{10}: Calculated aqueous concentration of a substance that is expected to cause effects in 10% of an experimental population of aquatic organisms.

EC_{50}: Median effects concentration, a calculated aqueous concentration of a substance that is expected to cause effects in 50% of an experimental population of aquatic organisms.

HA: Health Advisory, a document produced by the U.S. Environmental Protection Agency Office of Water in which are estimated the concentrations of a contaminant in drinking water that are not anticipated to cause any adverse noncarcinogenic effects over specific exposure durations.

Hydrolysis: Cleavage with water.

K_H: Dimensionless Henry's Law constant, concentration in air/concentration in water.

K_{oc}: Soil organic carbon/water partition coefficient, ratio of concentration of a compound in soil organic carbon to its concentration in water in a system at equilibrium.

K_{ow}: Octanol/water partition coefficient, ratio of concentration of a compound in n-octanol to its concentration in water in a system at equilibrium.

LC_{50}: Median lethal concentration, a calculated aqueous concentration of a substance that is expected to cause death in 50% of an experimental population of aquatic organisms.

LCt_{50}: Calculated product of concentration of a given substance and time of exposure by inhalation that is expected to cause death in 50% of an experimental animal population.

LD_{50}: Median lethal dose, a calculated dose of a substance that is expected to cause death in 50% of an experimental animal population.

Lewisite: 2-Chlorovinyldichlorarsine.

Mustard: Dichlorodiethyl sulfide, also mustard.

pH: The negative logarithm of the hydronium ion (proton) activity.

Picramic acid: 2-Amino-4,6-dinitrophenol.

pK_a: The negative logarithm of the acid dissociation constant, K_a.

RfD: Reference dose, a provisional estimate of the daily exposure to the human population that is likely to be without appreciable risk of deleterious noncarcinogenic effects during a portion of a lifetime (subchronic) or an entire lifetime (chronic).

Sarin: Isopropyl methylphosphonofluoridate, also GB.

Soman: Pinacolyl methylphosphonofluoridate, also GD.

Submunitions: Munitions containing incapacitating (as opposed to lethal) agents.

Tabun: Ethyl N, N-dimethylphosphoramidocyanidate, also GA.

TD_{Lo}: Toxic dose low, the lowest dose of a substance by any route other than inhalation that is reported to produce any toxic effect in humans or any tumorigenic or reproductive effect in animals or humans.

Torr: Unit of pressure, 1 mm of mercury.

Unit risk: Risk per concentration unit in air (risk/[$\mu g/m^3$]) or water (risk/[μg/L]).

UXO: Unexploded ordnance, "duds."

Zwitterion: Dipolar ion (molecule with positive and negative charge sites).

UNEXPLODED ORDNANCE ISSUES AT ABERDEEN PROVING GROUND: BACKGROUND INFORMATION

by

David H. Rosenblatt

ABSTRACT

This document summarizes currently available information about the presence and significance of unexploded ordnance (UXO) in the two main areas of Aberdeen Proving Ground: Aberdeen Area and Edgewood Area. Known UXO in the land ranges of the Aberdeen Area consists entirely of conventional munitions. The Edgewood Area contains, in addition to conventional munitions, a significant quantity of chemical-munition UXO, which is reflected in the presence of chemical agent decomposition products in Edgewood Area groundwater samples. It may be concluded from current information that the UXO at Aberdeen Proving Ground has not adversely affected the environment through release of toxic substances to the public domain, especially not by water pathways, and is not likely to do so in the near future. Nevertheless, modest but periodic monitoring of groundwater and nearby surface waters would be a prudent policy.

1 INTRODUCTION

This document was prepared in support of the Programmatic Environmental Impact Statement prepared for Aberdeen Proving Ground (APG) (see map, Figure 1) by the Environmental Assessment Division of Argonne National Laboratory. It presents currently available information about the presence and significance of unexploded ordnance (UXO) at APG. Such information should be useful for the formulation of APG's remediation policies.

The term "unexploded ordnance" refers to "dud" materiel, including gun and howitzer high-explosive ammunition, armor-defeating projectiles, bombs (up to 5,000 lb), bomblets, rockets, mines, grenades, mortar rounds, and some tank, recoilless rifle, and small arms projectiles. These munitions may be conventional or may contain chemical agents.

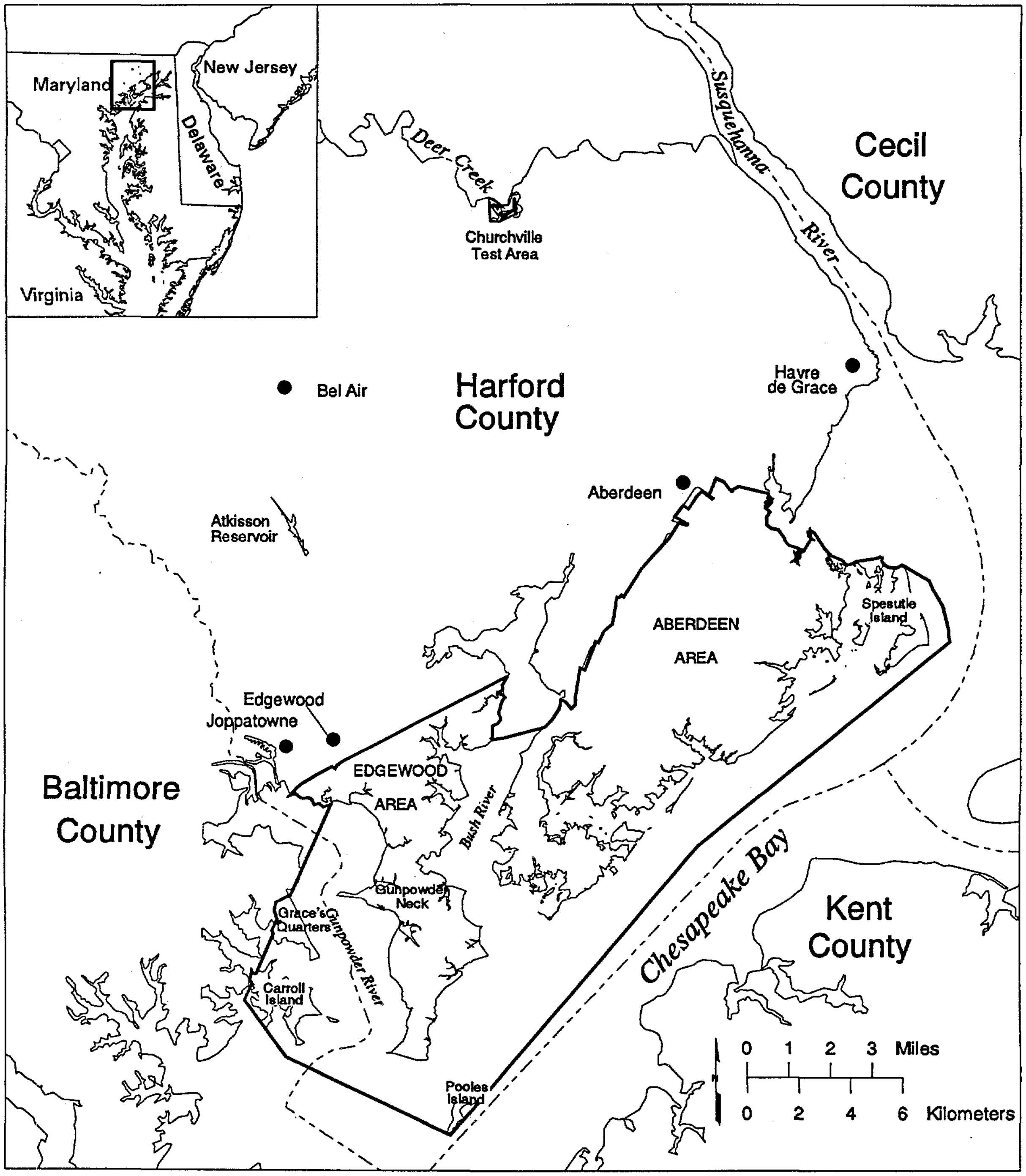

FIGURE 1 Map of Aberdeen Proving Ground, Maryland

UXO is present at sites on APG for four main reasons: (1) the sites have been target areas, (2) the sites have been part of firing or bombing ranges (with the ordnance having gone astray of the target areas), (3) UXO has been buried at the sites for disposal, or (4) accidents have caused UXO to be left at the sites. UXO is also abundantly present in sediment of the shallow waters of Chesapeake Bay, which abuts APG.

The information contained in this document will be used to assess the potential of APG to contribute to off-site water pollution through leaching of toxic UXO contents into groundwater and surface water. Section 2 of this document gives an overview of UXO detection and retrieval protocols. Section 3 summarizes the types and distribution of UXO at APG. Potentially UXO-related compounds of concern at APG are identified and their properties described in Section 4. Section 5 presents the results of past soil and water analyses for the potentially UXO-related compounds of concern at APG. Conclusions about the potential for adverse effects from UXO on and near APG are presented in Section 6.

2 UXO DETECTION AND RETRIEVAL

UXO detection and retrieval projects fall into two main categories. The first, investigation and remediation, might be undertaken to prepare a construction site, protect nearby human populations, or lessen environmental deterioration (EPA 1993). The second category, support operations, focuses on protecting site personnel from UXO hazards in their work area (EPA 1993).

Two types of personnel are involved in UXO detection and retrieval projects: the civilian UXO team and the military explosive ordnance disposal (EOD) specialists. The UXO team locates suspicious objects visually and with the aid of specialized equipment. Without disturbing the objects, this team conducts operations to expose them and attempts to characterize and identify them. If an object appears to be UXO, it is presumed to be dangerous and a military team of EOD specialists is called upon to determine what action to take and to carry out disposal if needed.

For example, the protection of personnel engaged in a remedial investigation/feasibility study in Edgewood Area's J-Field, which involves sampling soil and drilling monitoring wells, requires that a sufficient area be guaranteed safe before an operation begins. Because UXO disposal is typically not included in the statement of work for UXO support operations, UXO discovered in such operations is reported to the area's military EOD team, which decides what action to take. Often, in such an operation, discovery of an unexploded shell causes the operation to relocate and no attempt is made to dispose of the UXO. Clearly, nonhazardous metallic objects can be removed and disposed of by the civilian UXO team, whereas the military EOD team conducts the disposition of suspect or known-to-be hazardous UXO. The disposal of UXO during a support operation consumes a considerable amount of time (EPA 1993).

Positive identification of UXO is often difficult or impossible because (1) UXO is most often discovered in a deteriorated condition after years of exposure to the environment and (2) some UXO is of foreign origin. Such identification is even more problematic for civilian UXO specialists than for military EOD technicians because the former do not have ready access to EOD 60 series publications, reference documents that are frequently classified and give detailed guidance on the identification and functioning of specific ordnance, information that affects UXO disposal decisions.

Although exposed UXO may sometimes be identified by sight, most UXO detection operations require geophysical surveillance and excavation before UXO objects can be differentiated from harmless metal fragments or inert rounds. Geophysical detection equipment, such as metal detectors, low-sensitivity magnetometers, and high-sensitivity magnetometers, provides a nonintrusive means of detecting subsurface magnetic anomalies, which are usually caused by iron or steel objects.

Anomalies suspected to be UXO can be positively identified only after the material is excavated. Excavation does not involve removal or movement of an item (this would be part of the disposal process). UXO may be buried deep in the earth or covered by a more shallow layer of soil and vegetation. The vast majority of UXO on land is within 2 ft of the surface (EPA 1993) and gradually makes its way to the surface as a result of freeze-thaw cycles. Large projectiles and bombs can be imbedded as deeply as 10 or 20 ft; being below the frost line, they do not make their way to the surface. Common hand tools are used to excavate shallow UXO. For more deeply buried UXO, excavating equipment is used to remove overburden to within 1–2 ft, then hand tools are used to finish the excavation.

UXO disposal is within the province of the military EOD team. In general, fuzed and armed conventional UXO is unsafe to move and is therefore detonated in place, provided the location can withstand a high-order detonation. UXO that is determined safe to move is taken to a prepared disposal area (EPA 1993). UXO suspected or known to contain a chemical agent is removed to safe storage whenever possible to await disposal at a proper destruction facility. UXO with a liquid fill is presumed to contain a chemical agent unless there is good evidence to the contrary.

Difficulties in identification interfere with disposal efforts, especially for UXO containing chemical agents, where the method of disposal (unlike that for a conventional munition) depends on what agent is involved. Currently, all items at APG suspected of being agent-filled UXO are stored in the Edgewood Area's N-Field bunkers to await future disposition.

3 UXO AS A POTENTIAL SOURCE OF CONTAMINATION

3.1 TYPES AND DISTRIBUTION OF UXO AT APG

UXO at APG includes both domestic and foreign materiel, some dating back to World War I. The main explosive constituents of UXO are 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the latter containing a few percent of the even more powerful explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). These constituents can make UXO shock-, pressure-, or friction-sensitive, the main cause of concern during disposal. Some areas of the APG subsurface also contain many relatively harmless projectiles filled with inert material such as sand and wax (test or practice ammunition), toxic depleted uranium (DU) rounds, nonexplosive small arms bullets, and metallic debris. The nonexplosive items interfere with magnetometer surveys, complicating the task of searching out UXO for disposal. At a number of sites in the Edgewood Area, particularly J-Field, Old O-Field, and New O-Field, UXO filled with both chemical agents and explosive charges for agent dissemination occur; bulk storage containers of agents also occur at these sites. Among the UXO-associated agents of highest concern are mustard and sarin.

3.1.1 Conventional Munitions

Approximately three dozen ranges and impact areas at APG offer about 110 different firing positions from which conventional weapons ranging in size from small arms up to 280-mm (11-in.) artillery can be tested (Russell 1976; McMaster et al. 1981). UXO is found at fairly high density in these areas.

Researchers disagree on the size of the land area where conventional munitions testing occurred and the date munitions testing began at APG. According to McMaster et al. (1981), munitions testing occurred on 17,000 acres of land on APG and began in 1919. Russell (1976) estimates that testing began in 1917 and that projectiles impacted on about 28,000 acres of land in the Aberdeen Area, 5,000 acres of land in the Edgewood Area, and 37,000 acres of surface water areas on APG.

Both McMaster et al. and Russell estimate that 1 million live rounds and 4 million inert rounds are in the land range area, and that the water area holds 4 million live and 16 million inert projectiles. Under the Firing Records Search Program, former range control officer John Conley of Dynamic Science Inc. (Aberdeen, Md.) is searching firing records for APG dating back to World War I. Mr. Conley believes that the quantities of conventional UXO at Aberdeen Area are grossly underestimated (except for Poole's Island, for which estimates may be too high).

Russell (1976) gives a rough breakdown of the types of rounds present at APG (Table 1). If it is assumed that the contribution of chemical agent rounds is comparatively minuscule and that the small arms carry few explosives, one can use the data in Table 1 to roughly estimate the mass of explosives (as toxic pollutants) available for release to the environment. This mass comes from about 70% of the total number of projectiles, which amounts to 700,000 individual pieces on land ranges and 2.8 million under the water of Chesapeake Bay and its tributaries. Using the smaller land range area estimate of McMaster et al. (1981), one calculates a live-round density in the Aberdeen Area of about 40 large-caliber projectiles per acre of firing range land, roughly one per 1,000 ft^2. For calculation purposes, the average high-explosive loading of these large-caliber projectiles is assumed to be 11 lb, consisting of approximately equal parts of TNT and RDX. Thus, the application of high explosives to the soil, evenly spread (though it is extremely unlikely that the explosives would be evenly spread or occur in some constant ratio), would be roughly 5.5 lb/1,000 ft^2 (27 g/m^2) each of TNT and RDX. Considerably lower concentrations of such explosives as HMX (an RDX co-product) and tetryl (in some burster charges) are predicted. The density for the water-covered area would be about one projectile per 575 ft^2, or about 47 g/m^2 each of TNT and RDX.

The actual situation in any given area may differ considerably from the foregoing broad estimates. The following description from McMaster et al. (1981) illustrates the differences in activities at the various ranges:

> Large amounts of white phosphorus (WP) were tested [in the Old Bomb Field] in the 1930s and 1950s . . . DU was tested at several locations, among them the High Velocity Range, the Transonic Range, and the Defeat of Armor Range. Larger caliber weapons were apparently tested primarily at the six ranges that compose the "Main Front," covering some 11,300 ha (28,000 acres) of land and water, but also in perhaps as many as nine other ranges. About five ranges were used largely for bomb tests while other

TABLE 1 Types of Rounds Fired at APG

Type	Total (%)	Inert (%)	Live (%)
Small arms	30	90	10
Artillery mortar 60, 81, and 4.2	21	NA	NA
Howitzer 155, gun 8-in.	35	75	25
Tank mounted	14	NA	NA

NA = not available.

Source: Russell (1976).

ranges were used to test mines (about six ranges), mortars, and small arms. Spesutie Island (830 ha), with its seven test ranges and facilities, is reported to be covered with about 12,000 rounds of 20-mm to 40-mm high-explosive ammunition plus 2,000 unexploded mines containing 0.2 kg of RDX each. Poole's Island (81 ha), at 1/10 the size of Spesutie, was primarily used as an impact area, and is said to be covered with approximately 300,000 rounds, including projectiles, rockets, and unexploded cased munitions.

The total number of rounds can also be estimated using the estimated current monthly expenditure of 110,000 rounds (Russell 1976). Extrapolated back to 1917 at the same rate, this would sum to about 100 million rounds. However, for many of the 78 years since 1917, activity may have been considerably less than it was in 1976. Moreover, this estimate is considerably higher than the sum of the estimates by McMaster et al. (1981) and Russell (1976) (see above).

3.1.2 Chemical Munitions

An estimate of the number and types of chemical-agent-containing rounds in APG is unavailable. The Edgewood Area contains the bulk, if not all, of the chemical-laden UXO at APG. In one incident that seems to have occurred in 1919 (Conley et al. 1994), an explosion in the section of Aberdeen Area known as Michaelsville scattered the contents of several railroad cars containing captured German ordnance; no accounting has ever been made for this materiel. With the possible exception of articles scattered during this incident, the Aberdeen Area may be considered free of chemical agents. The types of chemical agent munitions and large storage containers that may be present in Old O-Field, a part of the Edgewood Area, are summarized in Table 2 (USATHAMA 1991). Table 3 shows the types of munitions using nerve agent fills at disposal sites throughout the country, but not necessarily at APG (USATHAMA 1991).

The total amount of chemical agents in the Edgewood Area is large enough for concern, but is probably far less than the mass of explosives contained in UXO in the entire APG area. From the point at which it first became necessary to store chemical-agent-filled UXO and other containers in Edgewood Area's N-Field bunkers (about 1988), until 1993, only 189 chemical munitions (and 700 "submunitions" with incapacitating agents) were placed in the bunkers (Army 1993; Jonas 1994). In addition, Jonas (1994) estimates as many as 50,000 agent-filled items may be buried in the Edgewood Area. Among the areas of principal concern for chemical agent UXO in the Edgewood Area are J-Field, Old O-Field, and New O-Field. These were also the sites of decontamination, burial, or open burning of chemical agents that were not contained in ordnance. Other areas of concern in the Edgewood Area are King's Creek and Carroll Island (Jonas 1994).

According to Vocelka (1994), the Edgewood Area consists of an "Industrialized/Populated Area" and a "Down Range Area" (which includes O-Field, J-Field, and other areas). Vocelka estimated the density of UXO at about 0.0526/1,000 ft^2 for the entire 5,121-acres (223 million ft^2)

TABLE 2 Chemical Agent Munitions and Large Storage Containers that May Be Present in Old O-Field

Munition/Storage Container	Agent[a]	Fill Weight (lb)
75-mm Artillery round	HD	Unknown
100-lb M47 Bomb	HD	Unknown
4.2-in. Mortar round	HD	6
115-lb M-7081	HD	60
1-ton Cylinder	HD	1,702
1-ton Cylinder	L[b]	1,702
4.2-in. Mortar round	L	10
105-mm Round	L	10
Artillery rounds	CG, CK, AC[c]	Unknown
500-lb AN-M78 Bomb	CG	205
1,000-lb AN-M79 Bomb	CG, CK, AC	415
750-lb MC-1 Bomb	CG	221
500-lb AN-M78 Bomb	CK	176
250- to 500-kg Bombs (captured munitions)	GA, GB, GD, VX	Unknown

[a] HD = mustard; L = lewisite; CG = phosgene; CK = cyanogen chloride; AC = hydrogen cyanide; GA = tabun; GB = sarin; GD = soman; VX = O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate.

[b] L is rapidly hydrolyzed by water to organic arsenic-containing products and hydrogen chloride, and thus is not an expected water contaminant. Neither L nor the organic hydrolysis products of L have been identified in Old O-Field water samples. Some of the arsenic observed in water samples could represent organic decomposition products of L.

[c] CG, CK, and AC decompose to harmless products on prolonged contact with water, and would not persist in either surface water or groundwater.

Source: USATHAMA (1991).

TABLE 3 Munitions Containing Nerve Agents Found at U.S. Army Disposal Sites

	Agent	
Munitions Type	Type	Weight (lb)
Rocket		
M55	GB[a]	10.7
M55	VX[b]	10.0
Land mine		
M23	VX	10.5
155-mm Projectile		
M121, M121A1, M122	GB	6.5
M121A1	VX	6.0
105-mm Projectile		
M360	GB	1.6
8-in. Projectile		
M426	GB or VX	14.5
500-lb Bomb		
MK-94-0	GB	108
750-lb Bomb		
MC-1	GB	220
Weteye Bomb		
MK-116	GB	347

[a] GB = Isopropyl methylphosphonofluoridate (sarin).

[b] VX = O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate.

Source: USATHAMA (1991).

of the Industrial Area, with about 10% of the estimated 11,738 UXO being liquid-filled. Thus, the Industrial Area would contain about 0.2+ liquid-filled rounds per acre, some of these filled with simulants. Only about 3% of the UXO in the Down Range Area were found to be liquid filled. Of the 749 UXO found in the Edgewood Area that were of a configuration such that they could have contained liquid fill, only 5% actually did. Altogether, only 38 liquid-filled UXO were found in the Edgewood Area during 1990–1992. (Distribution density was not estimated for the Down Range Area.)

The foregoing information is not conclusive; nevertheless, it appears that the density of UXO in the Edgewood Industrial Area is roughly 2.3 rounds per acre, compared with about 40 live rounds per acre of firing range land in APG (see Section 3.1.1). Ten percent or fewer of these are likely to contain toxic liquid agents. It would appear, then, that APG has considerably more conventional UXO than chemical UXO.

One of the most promising sources of quantitative information about the former presence of UXO on cleared sites in the Edgewood Area is Human Factors Applications Inc. (Indian Head, Maryland), which has maintained records on the clearance (complete and partial) of UXO from over 200 sites on which it worked. These records could improve the accuracy of the estimates of UXO quantities at APG.

The area most heavily affected by chemical agents, and most thoroughly studied with regard to them, would seem to be Old O-Field. According to Okusu et al. (1994), "it has been estimated that 90% of chemical warfare munitions-filled ordnance items and bulk containers at Old O-Field may contain mustard . . . between 5–10% of the remaining ordnance items and bulk containers contain phosgene, and the remainder are filled with lewisite and other materials." Other agents that may be present are adamsite and chloroacetophenone. Okusu et al. also note that empty 250-lb sarin (a nerve agent) bomb casings are supposed to have been buried in O-Field, representing approximately 0.3% of the UXO at Old O-Field.

Old O-Field is a 4.5-acre fenced site adjacent to portions of Watson Creek in the Edgewood Area of APG. According to the U.S. Army Toxic and Hazardous Materials Agency (now called the Army Environmental Center), of the compounds of concern listed in Sections 4.1.2 and 4.1.3, the following were disposed of in Old O-Field (USATHAMA 1991):

- TNT
- RDX
- HMX
- Tetryl
- 2,4-dinitrotoluene (2,4-DNT)
- 2,6-dinitrotoluene (2,6-DNT)
- 1,3,5-trinitrobenzene (TNB)
- 2,4,6-trinitrophenol (PA)
- O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)

USATHAMA's listing also includes the "munitions compound" nitromethane and several chemical agents other than VX. Records and interviews also suggest the presence at Old O-Field of the bulk high-explosive pentaerythritol tetranitrate (PETN). Some Japanese munitions originally disposed of at Old O-Field reportedly used PA in their bursters (Okusu et al. 1994). The bulk chemical agents mustard and phosgene and the antiriot agent chloroacetophenone, as well as munitions containing cyanogen chloride, chloroacetophenone, and the incapacitants adamsite, mustard, and lewisite, were also reported. Captured bombs containing the German nerve agent tabun (GA) may have been buried in Old O-Field, but this cannot be confirmed (Okusu et al. 1994). No analytical evidence indicates that tabun has ever leaked to the environment.

Okusu et al. (1994) have expressed the probability vs. magnitude of explosive events at Old O-Field in various ways, and found, for example, that the mean time between events with TNT-equivalent yields of 1–10 lb is 5–14 years.

The APG Division of Safety, Health and Environment has documentation of several small mustard disposal sites in the Edgewood Area (Jonas 1994). In particular, one of these was a detonation pit for mustard and lewisite, now covered over, in the vicinity of the sixth hole of the golf course not far from Building E1675 (between the tee-off position and the hole itself). On one occasion, according to Jonas (1994), mustard-containing rounds were removed from the golf course. This and other mustard burial areas have not yet been documented.

3.2 CORROSION, LEACHING, AND RELEASE OF MUNITIONS CONSTITUENTS

Contaminant releases to the environment by initially intact UXO can only occur after the integrity of a container has been compromised. For buried conventional munitions, this requires, at a minimum, development of openings for entry and egress of recharge water traveling downward in the vadose region or horizontally in the saturated zone, so that the explosive charges, composed of cast solids, can be leached out. Thus, even if corrosion opens small holes in conventional munitions, loss of the contents would occur only over a long period. By contrast, chemical munitions, because they are liquids in most cases (e.g., phosgene, mustard, lewisite, tabun, sarin, soman, or VX), would be released far more quickly than the explosives; it is also true, however, that these agents are more rapidly detoxified than are explosives on contact with water. Note that such incapacitants as adamsite and chloroacetophenone are solids, and so would be leached more slowly than liquid agents. Also, most chemical agent munitions depend on high explosives for agent dissemination.

Corrosion of a fresh metal surface proceeds initially at its greatest rate, but decreases to a lower and virtually uniform rate (Epstein et al. 1973). This is probably due to the formation of a protective oxide coating. The time estimates given in Table 4 for corrosion of representative agent-containing munitions are taken from Epstein et al. (1973); they depend, to a considerable extent, on the metal involved and on its thickness (note that all are made of steel except for the aluminum M55 rocket). The deep ocean (5,600-ft) figures are probably not representative of the shallow Chesapeake Bay water, where the pressure and salinity are lower, and the average temperature higher. The low temperature of deep ocean water would probably cause the rate of rusting to be lower than in Chesapeake Bay.

TABLE 4 Estimated Time to Corrosion for Munitions Found in Soil and Salt Water

	Time to Penetration of Thinnest Section (yr)	
Munition Item[a]	Munitions Found in Deep Ocean	Munitions Found in Susquehanna Clay Soil
4.2-in. Mortar shell	151	15
75-mm Shell	319	29
105-mm Shell	483	44
155-mm Shell	749	69
M70 (115-lb) Bomb	252	7
German (500-lb) bomb	125	12
German (1,000-lb) bomb	125	12
M55 Rocket	2	10
1-gal Mine	46	4
2-gal M23 Mine	47	4
Ton container[b]	539	49

[a] All items are made of steel except for the aluminum M55 rocket.

[b] Not UXO.

Source: Epstein et al. (1973).

If range use were to be discontinued, conventional munitions would still continue to release their contents to the environment very slowly over an extremely long time. Agent-containing munitions could empty more rapidly, but still over many years. It is impossible to predict how long it might take to reach the maximum rate of agent release at any given site, or what that rate might be, because of (1) the variety of ambient conditions, (2) an inadequate inventory of the types of UXO present, and (3) the lack of a scientific database.

4 COMPOUNDS OF CONCERN AT APG POTENTIALLY RELATED TO UXO

4.1 COMPOUNDS OF CONCERN

4.1.1 Basis for Selection

Which compounds in surface water and groundwater at APG might be attributable to UXO depends on the answers to the following questions:

- Is the compound associated specifically with the contents of known types of UXO (e.g., rather than propellants)?
- How frequently has the compound been detected (assuming it was properly analyzed for)?
- Can an unusual compound found at the site (and not attributable to other sources) be reasonably identified as having been derived from UXO contents?
- Can the compound survive in the aqueous environment long enough to pose a hazard?
- How toxic is the compound in question? What regulatory criteria apply?
- Is the compound mobile or does it tend to remain adsorbed to the soil?
- Is there historical evidence for the introduction of the compound at a particular location?
- For borderline cases, would analytical difficulties or costs exclude certain compounds from further consideration?

4.1.2 Compounds Related to High Explosives

The following high-explosives-related substances are listed as potential compounds of concern at APG:

- TNT—2,4,6-trinitrotoluene
- RDX—hexahydro-1,3,5-trinitro-1,3,5-triazine

- HMX—octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
- Tetryl—N,2,4,6-tetranitromethylaniline
- PETN—pentaerythritol tetranitrate
- PA—picric acid (2,4,6-trinitrophenol)
- 2,4-DNT—2,4-dinitrotoluene
- 2,6-DNT—2,6-dinitrotoluene
- TNB—1,3,5-trinitrobenzene
- 2A-4,6-DNT—2-amino-4,6-dinitrotoluene
- 4A-2,6-DNT—4-amino-2,6-dinitrotoluene
- DNB—1,3-dinitrobenzene
- NB—nitrobenzene

Of the first six compounds, all military explosives, all but picric acid are frequently found in Army ordnance and only tetryl has apparently not been detected in APG groundwater. Both 2,4-DNT and 2,6-DNT are common impurities in TNT, and have been found in association with environmental TNT. TNB is a stable end-product of TNT photolysis that occurs whenever TNT has been a soil surface contaminant or a surface water contaminant over a period of time (Rosenblatt et al. 1991). Both 2A-4,6-DNT and 4A-2,6-DNT are TNT metabolites that may be found in soil or plants. DNB and NB are possible nitration products of the benzene impurity that may have been present in toluene used to make TNT; they conceivably stay in the TNT until released by the leaching process. DNB and NB have been identified in APG groundwater, and have been assigned to the class of the other explosive compounds.

4.1.3 Compounds Related to the Chemical Surety Agents

The following substances related to chemical surety agents are listed as potential compounds of concern at APG:

- VX—O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate

- EA2192—S-(2-diisopropylaminoethyl) methylphosphonothioic acid
- DIMP—diisopropyl methylphosphonate
- IMPA—isopropyl methylphosphonic acid
- MPA—methylphosphonic acid
- TDG—thiodiglycol
- 1,4-Dithiane
- 1,4-Oxathiane
- Arsenic

The anticholinesterase (nerve agent) VX is the only chemical surety agent considered a compound of concern as the intact molecule because the other agents would rapidly hydrolyze when dissolved in water. There have been no reports of EA2192, the highly toxic cholinesterase-inhibiting hydrolysis product of VX, being detected, possibly because EA2192 is difficult to analyze for. DIMP is an intermediate product in the synthesis of the nerve agent sarin and a probable impurity in the final product. IMPA is the immediate hydrolysis product of both sarin and DIMP. MPA is the immediate hydrolysis product of IMPA and EA2192, as well as a second-generation hydrolysis product of sarin, VX, and DIMP. DIMP, IMPA, and MPA are far less toxic than VX or the nerve agents.

TDG is the hydrolysis product formed from mustard in dilute aqueous solution. The addition of small amounts of water to mustard gives rise to complex mixtures of toxic hydrolytic intermediates that can eventually transform, in large degree, to TDG; 1,4-dithiane and 1,4-oxathiane are among the products of mustard decomposition, with 1,4-dithiane probably arising from mustard by thermal, rather than hydrolytic, processes. Regardless, the presence of 1,4-dithiane and 1,4-oxathiane is a good indication that an intact mass of mustard once existed near the sampling point and may still exist there. Arsenic (presumably determined as inorganic arsenic) appears to be widespread in Edgewood Area waters at higher-than-background levels, and could be a product of the decomposition of organic arsenical agents such as lewisite or adamsite. However, inorganic arsenic could also have been applied in the area for agricultural purposes prior to military acquisition of the land in 1917.

Although suspected of having been disposed of in the Edgewood Area, neither tabun nor its hydrolysis products (O-ethyl N,N-dimethylphosphoramidic acid and ethyl phosphorocyanidic acid) have been identified in environmental media, and have therefore been omitted from the preceding list.

The incapacitants adamsite and chloroacetophenone, although considered, were not selected for discussion because neither they nor their hydrolysis products have been identified in surface water or groundwater at APG. These chemical agents are solids of low aqueous solubility and relatively low toxicity (compared with nerve agents or mustard). The lethal agents lewisite, phosgene, cyanogen chloride, and hydrogen cyanide are also not discussed because they would not persist in an aqueous solution.

4.2 PHYSICOCHEMICAL PROPERTIES OF THE EXPLOSIVES-RELATED COMPOUNDS OF CONCERN

4.2.1 2,4,6-TNT

TNT undergoes a series of photolytic reactions leading to the chemically rather stable TNB; it also is reduced to 2A-4,6-DNT and 4A-2,6-DNT, both by a variety of microbes and by multicellular organisms (Rosenblatt et al. 1991). Supplementary nutrients are required for reduction by microorganisms. In these reactions, TNT does not appear to be biodegraded (i.e., to carbon dioxide), though it is biotransformed. Metabolites were sought at various stages of wastewater treatment in an activated sludge system, and only at a very early stage was metabolite 4A-2,6-DNT found; it disappeared rapidly, and no other relevant aromatics were detected. In a tracer study with radiolabeled carbon, most of the TNT label became associated with nonextractable humic-like materials. See Table 5a for environmentally relevant properties of TNT.

4.2.2 RDX and HMX

The nitramines RDX and HMX are photolyzed slowly in sunlight to small polar fragments; photolysis seems to be the main mechanism for RDX decomposition in surface waters (Burton et al. 1993). RDX and HMX are biotransformed under anaerobic, but not aerobic, conditions, with formation of small organic fragments (Rosenblatt et al. 1991). For environmentally relevant properties of RDX and HMX, see Table 5a.

4.2.3 PA

Of all the explosives and propellants, only PA has a measured acid dissociation constant in aqueous solution, with $pK_a = 0.38$ (Weast 1979). PA is quite stable chemically in the environment

TABLE 5a Environmentally Relevant Properties of the Explosives TNT, RDX, and HMX

Property	TNT	RDX	HMX
CAS Registry No.	118-96-7	121-82-4	2691-41-0
Empirical formula	$C_7H_5N_3O_6$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$
Molecular weight, g/mol	227.15	222.15	296.20
Density, g/m	1.65	1.83	1.90
Melting point, °C	80.75	205	286
Heat of fusion, cal/g	23.5	32.86	Unavailable
Vapor pressure, torr (25°C)	5.5×10^{-6}	4.03×10^{-9}	3.33×10^{-14}
Log K_{ow}	1.8	0.86	0.06
Aqueous solubility, mg/L (25°C)	150	60	5
K_H, atm m^3/mol (25°C)	1.10×10^{-8}	1.96×10^{-11}	2.60×10^{-15}
Log K_{oc}	2.72	2.00	0.54
BCF (est., fish)	8.95	1.50	0.49

CAS = Chemical Abstracts Service; BCF = bioconcentration factor.

Source: Rosenblatt et al. (1991).

(Rosenblatt et al. 1991), though it can be converted to some degree to picramic acid (2-amino-4,6-dinitrophenol) by microorganisms (Roberts and Hartley 1992; Rosenblatt 1994). When either PA or picramic acid is administered separately to rainbow trout or to the American oyster, both compounds can be found in the tissues (Cooper et al. 1984; Burton et al. 1984); thus, it appears that these compounds are in quasi-redox equilibrium in animal tissues. For environmentally relevant properties of PA, see Table 5b.

4.2.4 DNTs and DNB

2,4-DNT, 2,6-DNT, and DNB are also quite stable chemically in the environment (Rosenblatt et al. 1991). The DNTs and DNB, unlike TNT, are biodegradable to carbon dioxide. For environmentally relevant properties of these compounds, see Tables 5c and 5d.

4.2.5 Other Compounds

Based on rate data at elevated pH, tetryl (see Table 5b) has a half-life in water of about 302 days at pH 6.8 and 20°C (without photolysis); in the dark, the main organic products are PA and

TABLE 5b Environmentally Relevant Properties of the Explosives Tetryl, PETN, and PA

Property	Tetryl	PETN	PA
CAS Registry No.	479-45-8	78-11-5	88-89-1
Empirical formula	$C_7H_5N_5O_8$	$C_5H_8N_4O_{12}$	$C_6H_3N_3O_7$
Molecular weight, g/mol	287.17	316.17	229.12
Density, g/ml	1.73	1.78	1.76
Melting point, °C	129.5	141	123
Heat of fusion, cal/g	21.6	76	20
Vapor pressure, torr (25°C)	5.7×10^{-9}	5.4×10^{-9}	7.5×10^{-7}
Log K_{ow}	1.65	3.71	2.03
Aqueous solubility, mg/L (25°C)	80	2.1[a]	12,400
K_H, atm · m^3/mol	2.69×10^{-11}	1.07×10^{-9}	Not calculated
Log K_{oc} (25°C)	1.69	3.39	2.00
BCF (est., fish)	6.3	281	12.7

CAS = Chemical Abstracts Service; BCF = bioconcentration factor.

[a] Hartley et al. (1994) give a value of 43 mg/L for the solubility of PETN.

Source: Rosenblatt et al. (1991).

methylnitramine, while photolysis produces N-methylpicramide (Kayser et al. 1984). The basic hydrolysis rate constant for PETN is probably quite low, with hydrolysis at ambient pH playing no role in its environmental fate. TNB (see Section 4.2.1 and Table 5c) is quite stable chemically in the environment and is not biodegradable to carbon dioxide (Rosenblatt et al. 1991). The undoubtedly low pK_as of the protonated forms of 2A-4,6-DNT and 4A-2,6-DNT (see Table 5e) have evidently not been measured. Little is known about the chemical stability of these aminodinitrotoluenes in the environment. NB (see Table 5d) is quite stable chemically in the environment (Rosenblatt et al. 1991).

4.3 PHYSICOCHEMICAL PROPERTIES OF THE CHEMICAL-SURETY-AGENT-RELATED COMPOUNDS OF CONCERN

Except for VX (Table 6), far less is known about compounds related to chemical surety agents than of the high-explosives-related compounds.

TABLE 5c Environmentally Relevant Properties of the Explosives 2,4-DNT, 2,6-DNT, and TNB

Property	2,4-DNT	2,6-DNT	TNB
CAS Registry No.	121-14-2	606-20-2	99-35-4
Empirical formula	$C_7H_6N_2O_4$	$C_7H_6N_2O_4$	$C_6H_3N_3O_6$
Molecular weight, g/mol	182.15	182.15	213.12
Density, g/ml	1.52	1.38	1.63
Melting point, °C	72	66	122
Heat of fusion, cal/g	26.1	22.5	16.0
Vapor pressure, torr (25°C)	2.17×10^{-4}	5.67×10^{-4}	3.03×10^{-6}
Log K_{ow}	1.98	2.02	1.18
Aqueous solubility, mg/L (25°C)	280	208	385
K_H, atm · m^3/mol (25°C)	1.86×10^{-7}	4.86×10^{-7}	2.21×10^{-9}
Log K_{oc}	2.40	1.89	1.30
BCF (est., fish)	3.8-11.6	9.8	2.65

CAS = Chemical Abstracts Service; BCF = bioconcentration factor.

Source: Rosenblatt et al. (1991).

4.3.1 VX

VX is a good skin penetrant and fairly persistent because of its low vapor pressure; its evaporation rate is about 1/1,500 that of water (Army et al. 1990). Nevertheless, the literature indicates that, most conservatively, 90% of VX applied to soil would be lost in 15 days (Small 1983). VX hydrolysis rates tend to be fairly slow; at pH 10 and 25°C, the half-life of VX in water is 2,432 minutes (converted data from Epstein et al. 1974). At pH 5 and 25°C, the half-life was reported elsewhere as 2,342 hours (Clark 1989). VX is not subject to acid-catalyzed hydrolysis but does undergo water- and hydroxyl-ion-catalyzed hydrolysis. Complex mixtures of hydrolysis products are formed, involving ethoxy cleavage from the phosphorus to form EA2192 and ethanol, P-S cleavage at the sulfur to give ethyl methylphosphonic acid and 2-diisopropylaminoethanethiol (DESH), and C-S cleavage that yields diisopropylaminoethanol and O-ethyl methylphosphonothioic acid (Epstein et al. 1974). Bis(2-diisopropylaminoethyl) disulfide (EA4196) is formed by air oxidation of the primary cleavage product DESH. The toxic product of ethoxy cleavage, EA2192,is discussed below. At loadings up to 1%, VX was said to degrade in soil at a rate of about 50% per day (Kingery and Allen 1995).

TABLE 5d Environmentally Relevant Properties of the Explosives DNB and NB

Property	DNB	NB
CAS Registry No.	99-65-0	98-95-3
Empirical formula	$C_6H_4N_2O_4$	$C_6H_5NO_2$
Molecular weight, g/mol	168.12	123.11
Density, g/ml	1.575	1.2037/20°C[a]
Melting point, °C	90	5.7
Heat of fusion, cal/g	28.97	22.4[b]
Vapor pressure, torr (25°C)	1.93×10^{-4}	0.15/20°C 1/44.4°C[c]
Log K_{ow}	1.49	1.85
Aqueous solubility, mg/L (25°C)	533	1,900/20°C
K_H, atm · m^3/mol (25°C)	8.01×10^{-7}	2.44×10^{-5}
Log K_{oc}	1.56	1.49-2.57
BCF (est., fish)	4.7	6-15

CAS = Chemical Abstracts Service; BCF = bioconcentration factor.

[a] Weast (1979).

[b] Richter (1930).

[c] EPA (1990).

Sources: Rosenblatt et al. (1991) and Howard (1989).

TABLE 5e Environmentally Relevant Properties of Explosive Metabolites 2A-4,6-DNT and 4A-2,6-DNT

Property	2A-4,6-DNT	4A-2,6-DNT
CAS Registry No.	35572-78-2	19406-51-0
Empirical formula	$C_7H_7N_3O_4$	$C_7H_7N_3O_4$
Molecular weight, g/mol	197.15	197.15
Melting point, °C[a]	176	171

CAS = Chemical Abstracts Service.

[a] Channon et al. (1944).

Sources: Rosenblatt et al. (1991) and Channon et al. (1944).

In addition to environmentally relevant data in Table 6, the following temperature relationships were reported for vapor pressure (P) and density (d) for VX (Samuel et al. 1983):

$$\log P \text{ (torr)} = 7.28100 - 2{,}072.10/(172.5 + t\ [^\circ\text{C}]) ,$$

and

$$d \text{ (g/ml)} = 1.0290 - (0.00083\ t[^\circ\text{C}]) ,$$

where t = temperature in degrees Celsius. The pK_a of protonated VX at 25°C has been given as 8.60 (Epstein et al. 1974) and 9.1 (Demek et al. 1970).

TABLE 6 Environmentally Relevant Properties of VX

Property	Data	Quality	Reference
CAS Registry No.	50782-69-9		
Empirical formula	$C_{11}H_{26}NO_2PS$		
Molecular weight, g/mol	267.38		
Density, g/ml (25°C)	1.0083	Good	Samuel et al. (1983)
Melting point, °C	-50	Fair	Samuel et al. (1983)
Boiling point, °C	298.4	Good	Samuel et al. (1983)
Heat of fusion, cal/g	23.9 (estimated)	Fair	Penski and Domalski (1987)
Heat of vaporization, cal/g	80.8	Good	Samuel et al. (1983)
Vapor pressure, torr (25°C)	6.2×10^{-4}	Good	Samuel et al. (1983)
Log K_{ow}	2.36 (estimate)	Poor	Britton and Grant (1988)
	2.09 (estimate)	Poor	Small (1984)
	1.992 (estimate)	Poor	Sage and Howard (1989)
Aqueous solubility, g/L (25°C)	30	Fair	Army (1974)
K_H, atm · m^3/mol (25°C)	7.2×10^{-9}	Poor	[a]
Log K_{oc}	1.18[b]	Poor	Sage and Howard (1989)
BCF (fish)	19	Poor	Sage and Howard (1989)

CAS = Chemical Abstracts Service; BCF = bioconcentration factor.

[a] Author's estimate.

[b] Small (1984) estimated a value of 2.5.

4.3.2 EA2192

EA2192, one of the VX hydrolysis products, is S-(2-diisopropylaminoethyl) methylphosphonothioic acid ($C_9H_{22}NO_2PS$, CAS Registry No. 73207-98-4). Its molecular weight [MW] is 239.32 and its melting point is 138-140°C (Durst et al. 1988). EA2192 is about 3,700 times as stable as VX toward alkaline hydrolysis in 1 M sodium hydroxide (Yang et al. 1993). It is completely stable in distilled water for at least 1,000 hours (Kingery and Allen 1995). The higher (ammonio) pK_a of EA2192 is cited by Kingery and Allen (1995) as 11.2 and by Michel et al. (1962) as 10.6. The lower (phosphonate) pK_a was reported as 0.6 (Michel et al. 1962). The compound exists as a zwitterion in neutral aqueous solution, and must be quite hydrophilic. Its vapor pressure, and especially its Henry's Law constant (K_H), should be considerably less than those of VX. EA2192 is formed when VX decomposes in soil, but its rate of disappearance is evidently greater than that of VX (Kingery and Allen 1995).

4.3.3 DIMP

DIMP ($C_7H_{17}O_3P$, CAS Registry No. 1445-75-6, MW 180.18) is a colorless liquid. Its density is 0.976 g/ml at 25°C (Rosenblatt et al. 1975), it boils at 174°C, and it is reported to have an empirical vapor pressure (Rosenblatt et al. 1975) of:

$$\log P \text{ (torr)} = 9.8571 - 3105/T(°\text{K}) ,$$

where T = temperature in degrees Kelvin. This equation gives a vapor pressure of 0.28 torr at 25°C, compared with a vapor pressure of 1.49 torr estimated by the method of Fishtine (as presented by Lyman et al. 1990). Although an aqueous solubility estimate of 1–2 g/L was reported for DIMP (Rosenblatt et al. 1975), a crude experiment indicated that DIMP and water are infinitely miscible (Major 1990). On that basis, a dimensionless Henry's Law constant of 2.71×10^{-7} at 25°C (or 6.63×10^{-9} atm · m^3/mole) was derived (Appendix A). Major (1989) evaluated two reported octanol-water partition coefficients (K_{ow}) and selected what he considered the better value, log K_{ow} = 1.35. The estimated hydrolysis half-life in water at 10°C was 687 years (Rosenblatt et al. 1975). The half-life in soil was estimated as two years (Spanggord et al. 1979). In contact with Rocky Mountain Arsenal sandy loam at room temperature, aqueous DIMP showed no hydrolysis; under comparable conditions, Lakewood sand catalyzed hydrolysis with a half-life of about 300 hours (Kingery and Allen 1994). Thus, some soils catalyze decomposition while others do not.

4.3.4 IMPA

IMPA ($C_4H_{11}O_3P$, CAS Registry No. 1832-54-8, MW 138.09) is a colorless liquid that arises from the facile hydrolysis of the nerve agent sarin, or the slower hydrolysis of DIMP (see above). Its specific gravity is 1.1091 at 20°C, and it boils at 123–125°C/0.2 torr (Rosenblatt et al. 1975). The pK_a of IMPA was determined to be 2.41; the K_{ow} observable at around pH 7 would be vanishingly small because the compound would be almost entirely in the anionic form (Major 1989). The half-life of hydrolysis of IMPA to MPA is evidently much longer than that of DIMP to IMPA (Rosenblatt et al. 1975); for example, Kingery and Allen (1994) have estimated a half-life in water at pH 4 and 25°C of 9,100 years. Tests on five soils at ambient temperature (2 g soil, 50 ml of 4-mg/L IMPA solution) showed very diverse hydrolytic half-lives (Kingery and Allen 1994):

Dugway Proving Ground sandy clay loam	Infinite
Rocky Mountain Arsenal sandy loam	Infinite
Lakewood, N.J., sand	58 hours
Woodston sandy loam (Gunpowder State Park, Md.)	40 hours
Fort McClellan clay loam	2.9 hours

IMPA is biodegraded (hydrolyzed) very slowly by certain microorganisms, apparently nitrifying bacteria; microorganisms would not significantly affect the rates of reaction in the soil systems (Kingery and Allen 1994).

4.3.5 MPA

MPA (CH_5O_3P, MW 96.0, CAS Registry No. 993-13-5) is a solid with a melting point of 107–107.5°C (Rosenblatt et al. 1975). Sarin, DIMP, soman, the simulant dimethyl methylphosphonate, and VX can all undergo hydrolysis to the corresponding alkyl methylphosphonate, which may then be hydrolyzed to MPA. MPA itself does not undergo hydrolysis and is in general very stable to chemical attack, but may undergo slow metabolism to inorganic phosphate by aerobic microorganisms such as *Agrobacter radiobacter*, which contains the as-yet-unisolated enzyme C-P lyase (Kingery and Allen 1995). MPA has two dissociable protons with pK_a values of 2.38 and 7.74 (Rosenblatt et al. 1975). MPA has been found to be very soluble in water (Williams et al. 1987).

4.3.6 TDG

TDG ($C_4H_{10}\,O_2S$, MW 122.19, CAS Registry No. 111-48-8) melts at -10°C and boils at 164°C/20 torr (Rosenblatt et al. 1975) or 280°C at atmospheric pressure (Nemeth 1989). The density of this syrupy colorless liquid is 1.22 g/ml at 20°C (Rosenblatt et al. 1975). It is infinitely miscible with water (Nemeth 1989). The value of log K_{ow} is -0.08 (Major 1989). TDG is by far the most important final hydrolysis product of mustard "gas," from which it forms rapidly when in dilute aqueous solution. Though it does not hydrolyze further, TDG can undergo environmental biotransformation (e.g., to oxidation products) (Nemeth 1989).

4.3.7 1,4-Dithiane

1,4-Dithiane ($C_4H_8S_2$, MW 120.25, CAS Registry No. 505-29-3) melts at 111–112°C, and boils at 199–200°C (Weast 1979). The value of log K_{ow} is 1.85 (Major 1989). Berkowitz et al. (1978) estimated an aqueous solubility of 11,800 mg/L. This compound is reported to have an empirical vapor pressure (Berkowitz et al. 1978) of:

$$\log P\ (\text{torr}) = 7.99 - (2{,}410/T[^\circ\text{K}]).$$

Thus, the vapor pressure at 25°C is approximately 0.8 torr. The heat of vaporization was estimated as 10,200 cal/mol (Berkowitz et al. 1978). 1,4-Dithiane is a groundwater contaminant associated with mustard "gas" storage and deposits; the occurrence of 1,4-dithiane is thought to result from mustard degradation (presumably thermal) because the level increases with storage time (Roberts and Hartley 1992; Berkowitz 1982).

4.3.8 1,4-Oxathiane

1,4-Oxathiane (C_4H_8OS, MW 104.18, CAS Registry No. 15980-15-1) is a liquid freezing at -17°C and boiling at 147–150°C (Berkowitz et al. 1978). The value of log K_{ow} is 0.77 (Major 1989). Berkowitz et al. (1978) calculated an aqueous solubility of approximately 167,000 mg/L. This compound is estimated to have a vapor pressure of 5.3 torr at 25°C (Berkowitz et al. 1978). The heat of vaporization was calculated as 9,020 cal/mol (Berkowitz et al. 1978). 1,4-Oxathiane is a groundwater contaminant associated with production and demilitarization of mustard "gas," probably from hydrolytic decomposition (Roberts and Hartley 1992).

4.3.9 Arsenic

Arsenic occurs in a variety of forms in the environment. In studies of the Edgewood Area, analytical tests may have failed to discriminate between inorganic arsenic and organic chemical agents that contain arsenic or their organic breakdown products. This could be important, because only inorganic arsenic appears to be carcinogenic, and carcinogenicity is a driving force in the establishment of health-based cleanup criteria. Inorganic arsenic may occur as part of the natural background, or it may have been applied as an agricultural pesticide. Also, it may have been formed from organic arsenical agents that were once present. Depending on pH and redox potentials, inorganic arsenic may occur in the +5 valence state (most oxidized), the +3 state, or the -3 state (arsine), the latter under strongly reducing conditions. The arsines, which are formed microbiologically, are both inorganic (namely, AsH_3) and organic (i.e., the methylated arsines); unlike other reasonably stable arsenicals, arsines are volatile (Wood 1974). Inorganic arsenic, in the form of arsenate and arsenite ions, may be present in precipitated or chemisorbed forms, or may travel dissolved in groundwater. It is not possible to predict arsenic's behavior in soil without considerable information about site conditions.

4.4 TOXICOLOGY AND REGULATORY INFORMATION ON THE CONVENTIONAL MUNITIONS COMPOUNDS OF CONCERN

4.4.1 2,4,6-TNT

TNT poisoning fatalities among munitions workers in World War II were due mainly to aplastic anemia and toxic hepatitis; however, a large variety of other symptoms were observed among nonfatally exposed individuals. Gastrointestinal symptoms were often reported as the first indication of toxicity. Median lethal doses (LD_{50}) of TNT in rats and mice are shown in Table 7. On the basis of a lowest-observed-adverse-effect level (LOAEL) in a 26-week study in the dog, and an uncertainty factor of 1,000, the U.S. Environmental Protection Agency (EPA) determined a chronic oral reference dose (RfD) of 0.5 μg/kg/d, and a lifetime drinking water Health Advisory (HA) value of 2 μg/L. As a result of animal studies, TNT is classified in EPA group C as a possible human carcinogen. At the lifetime HA level of 2 μg/L, the upper 95% confidence limit on cancer risk was estimated as 2×10^{-6} (Roberts and Hartley 1992). TNT is generally more toxic to fish (fathead minnow) than to duckweed or invertebrates (Burton et al. 1993). Whereas the static 96-hour median lethal concentration (LC_{50}) for this species is 2.9 mg/L (Rosenblatt et al. 1991), the lowest chronic no-effect concentration of TNT for the full life cycle test is 5 μg/L (Burton et al. 1993).

4.4.2 RDX

Acute and chronic exposure to RDX causes epileptiform convulsions in humans. On the basis of a no-observed-adverse-effect level (NOAEL) in a 24-month study in the rat and an uncertainty factor of 100, EPA determined a chronic RfD of 3 μg/kg/d and a lifetime drinking water HA value of 2 μg/L. As a result of animal studies, RDX is classified in EPA group C as a possible human carcinogen. At the HA level of 2 μg/L, the estimated upper 95% confidence limit on cancer risk is estimated as 7×10^{-6} or more, depending on the risk model employed (Roberts and Hartley

TABLE 7 Median Oral Lethal Doses of TNT and Two of Its Metabolites in Rats and Mice

	LD_{50} (mg/kg)		
Animal/Sex	TNT	2A-4,6-DNT	4A-2,6-DNT
Rat/male	1,010 1,320	2,240	1,360
Rat/female	820 794	1,394	959
Mouse/male	1,004 660	1,722	1,342
Mouse/female	1,009 660	1,522	1,495

Source: Roberts and Hartley (1992).

1992). The lowest 96-hour no-observed-effect concentration (NOEC) of RDX for any alga, namely growth reduction in the green alga, was <0.32 mg/L. The lowest credible 96-hour LC_{50} for RDX in fathead minnows is 4.5 mg/L, while the life cycle NOEC for fathead minnows is 3.2 mg/L, and that for the cladoceran *Ceriodaphnia dubia* is 3.6 mg/L (Burton et al. 1993). (Note: It is not clear from the text of Burton et al. [1993] whether the cited 96-hour LC_{50} for RDX [Liu et al., 1984] is static or flow-through. This difference can affect the average level of test compound to which the organism is exposed, as evidenced when the compound became depleted during a static test.)

4.4.3 HMX

Though chemically related to RDX, HMX is almost 100 times less toxic than RDX on oral administration. HMX, at high enough doses, causes convulsions in animals. On the basis of a NOAEL in a 13-week feeding study in the rat, and an uncertainty factor of 1,000, EPA determined the chronic oral RFD at 500 μg/kg/d, and the lifetime drinking water HA value at 400 μg/L. Because of the dearth of long-term animal studies, HMX is classified in EPA group D, "not classifiable as to human carcinogenicity" (Roberts and Hartley 1992). No toxic effects were noted on aquatic organisms from HMX up to the solubility limit of 5 mg/L (Rosenblatt et al. 1991).

4.4.4 Tetryl

Very little quantitative information is available on the toxicity of tetryl. Among munitions workers, the compound has been reported to cause fatigue, headache, anorexia, abdominal complaints, nausea and vomiting, weight loss, nose bleeds and coughing, contact dermatitis (including allergic dermatitis), a general yellow pigmentation of skin and hair, and at least two deaths. The Occupational Safety and Health Administration (OSHA) permissible exposure limit values for workers exposed by inhalation are 1.5 mg/m^3 for both tetryl and TNT (Roberts and Hartley 1992). The smallest fatal dose of tetryl was 500 mg/kg given to a dog subcutaneously in olive oil as five daily doses of 100 mg/kg each; the dog lived 15 days (Wells et al. 1920). This total dose is roughly half the oral LD_{50} values reported for TNT in rats. There are no drinking water criteria for tetryl. Based on the skimpy evidence available, the present author recommends using the lifetime drinking water HA developed for TNT (2 μg/L) for this study.

4.4.5 PETN

A 1-year no-observed-effect level (presumably by oral dosing) for PETN is given as 2 mg/kg/d for rats (Rosenblatt et al. 1991). No evidence of toxicity was seen in rats or mice fed up to 10,000 ppm of PETN in their diet for 14 days (Hartley et al. 1994); this dosage is equivalent to about 600 mg/kg/d in rats and 1,200 mg/kg/d in mice. Dermatological effects (TD_{Lo}) were noted upon continuous human oral ingestion of 1,669 mg/kg of PETN for eight years (Sweet 1987). The usual human medical dose of PETN as a vasodilator is 0.6 to 2.3 mg/kg (Hartley et al. 1994). These sparse data suggest that PETN should not pose a toxicity problem, especially in view of its low solubility in water.

4.4.6 PA

No adverse effects (including carcinogenesis) were noted in Wistar rats fed 500 ppm of PA in the diet for 2.5 years. Nevertheless, the compound is rated as extremely toxic to humans, with a probable oral LD_{50} of between 5 and 50 mg/kg. Acute poisoning (1–2 g) is accompanied by headache, progressive stupor, coma, and death. Other symptoms include severe gastroenteritis, intravascular hemolysis, and hemorrhagic nephritis. The OSHA-permissible exposure level for inhalation is 0.1 mg/m^3 (Roberts and Hartley 1992). In rainbow trout, a 96-hour LC_{50} of 110 mg/L was reported for PA, but exposure to <0.001 LC_{50} for 42 days caused petechial lesions on the skin. At PA concentrations as low as 0.05 mg/L, American oysters showed considerable PA uptake and growth inhibition (Rosenblatt et al. 1991). There are no drinking water criteria for PA. For lack of sufficient data, and in view of the similarity of PA to TNT, the lifetime drinking water HA value developed for TNT (2 μg/L) might be used for PA.

4.4.7 2,4-DNT

Occupational exposures to 2,4-DNT involve the presence of DNT isomers; symptoms arising from exposure to production-grade DNT are caused by mixtures in which the 2,4-isomer predominates. Symptoms of poisoning include an unpleasant metallic or slightly bitter taste, muscular weakness, fatigue, headaches, loss of appetite, dizziness, nausea, and tremors. The chief clinical findings are pallor, cyanosis, and normocytic-normochromic anemia (Rosenblatt 1980; Hartley et al. 1994). On the basis of a LOAEL in a two-year study in dogs and an uncertainty factor of 100, EPA determined a chronic oral RfD of 2 µg/kg/d (EPA 1994a; Hartley et al. 1994) and a drinking water equivalent level (DWEL) of 100 µg/L (EPA 1994b; Hartley et al. 1994). For a noncarcinogen, the lifetime HA value would normally be calculated as 20% of the DWEL (in this case, 20 µg/L). 2,4-DNT has been considered a pure cancer promotor but not an initiator, and a much less potent carcinogen than the 2,6-isomer (Rosenblatt et al. 1991). DNT (technical grade) has been classified in EPA group B2 as a probable human carcinogen; however, an epidemiological study of workers exposed to crude DNT (containing 19% of the 2,6-isomer) or to DNT containing no more than 1% of the 2,6-isomer showed no excess cancer deaths but did demonstrate an elevated mortality due to heart and circulatory diseases of atherosclerotic origin (Rosenblatt et al. 1991). (Note that the hypothetical lifetime HA value of 20 µg/L would entail a calculated cancer risk of 4×10^{-4}, based on a risk of 10^{-4} for 0.005 mg/L of technical-grade DNT [EPA 1993]. In any event, EPA did not recommend a lifetime HA because 2,4-DNT is classified as a probable human carcinogen [Hartley et al. 1994].) The 96-hour static LC_{50} for 2,4-DNT in the fathead minnow is 32.8 mg/L and the estimated criterion for continuous exposure is 0.2 mg/L (Rosenblatt et al. 1991).

4.4.8 2,6-DNT

Cyanosis and ataxia were the chief symptoms observed in rodents acutely dosed with 2,6-DNT. Testicular degeneration was also observed (Roberts and Hartley 1992; Hartley et al. 1994). On the basis of a LOAEL in a 13-week study in dogs and an uncertainty factor of 3,000, EPA determined a chronic oral RfD of 1 µg/kg/d (EPA 1994a; Hartley et al. 1994), and a DWEL of 40 µg/L (EPA 1993; Hartley et al. 1994). For a noncarcinogen, the lifetime HA value would normally be calculated as 20% of the DWEL (in this case, 8 µg/L). 2,6-DNT has been characterized as a complete hepatocarcinogen, that is, both a cancer initiator and promotor, and a significantly more potent carcinogen than 2,4-DNT (Rosenblatt et al. 1991; Roberts and Hartley 1992). (Note that the hypothetical lifetime HA value of 8 µg/L would entail a calculated cancer risk of 1.6×10^{-4}, based on a risk of 10^{-4} for 0.005 mg/L of technical-grade DNT [EPA 1993]. In any event, the EPA did not recommend a lifetime HA because 2,6-DNT is classified as a probable human carcinogen [Hartley et al. 1994].) The 96-hour static LC_{50} for 2,6-DNT in the fathead minnow is 18.5 mg/L (Rosenblatt et al. 1991).

4.4.9 1,3,5-TNB

Little information is available about the toxicity of TNB. Orally in rats and mice, it is roughly twice as acutely toxic as TNT; in the fathead minnow, the ratio is about 3:1 (Rosenblatt et al. 1991). TNB has been rated an "extremely toxic compound," with a lethal dose in humans of between 5 and 50 mg/kg (Roberts and Hartley 1992) (but this toxicity is nowhere near that of VX, with an estimated human median lethal dose 0.0064 mg/kg; see Section 4.5.1). EPA developed a chronic oral RfD for TNB of 5×10^{-5} mg/kg/d based on the toxicity of DNB, but with a larger uncertainty factor (EPA 1991) (Section 4.4.11). By the same token, the lifetime HA value should be 0.5 µg/L, half that for DNB.

4.4.10 Aminodinitrotoluenes

Virtually nothing other than acute toxicities is known about the mammalian toxicity of the aminodinitrotoluenes (2A-4,6-DNT and 4A-2,6-DNT) (see Table 7). From the near equivalency of the LD_{50} findings in rodents with those for TNT (Table 7), and from the fact that they are TNT metabolites, it is surmised that the aminodinitrotoluenes are of about the same order of chronic toxicity as TNT and should be assigned, for present purposes, a lifetime drinking water criterion of 2 µg/L.

4.4.11 1,3-DNB

DNB has also been rated as an "extremely toxic compound." It has a lethal dose in humans between 5 and 50 mg/kg (which, like TNB, would still be some three orders of magnitude less toxic than VX). Symptoms include cyanosis, anemia, palpitations, dizziness, and fatigue; recovery is slow (Roberts and Hartley 1992). The oral LD_{50} in female rats (81 mg/kg) is about one-tenth that of TNT (see Table 7). On the basis of a LOAEL in a 16-week study in rats and an uncertainty factor of 3,000, EPA determined a chronic oral RfD of 10^{-4} mg/kg/d and a lifetime drinking water HA value of 1 µg/L. Due to lack of information, the compound was assigned by the EPA to group D, "not classified as to human carcinogenicity" (Roberts and Hartley 1992). Static 96-hour LC_{50}s for fathead minnows of 7.0 and 16.8 mg/L were cited for DNB (Rosenblatt et al. 1991).

4.4.12 NB

NB can cause death by respiratory failure, and has been rated as an "extremely toxic compound." Its mean oral lethal dose in humans of 1–5 g makes NB still some one or two orders of magnitude less toxic than VX. Symptoms and effects of nitrobenzene poisoning to workers (primarily by inhalation and absorption through the skin) include headaches, vertigo, and methemoglobinemia, but the effects on liver and kidneys have not been adequately evaluated (EPA 1990). From an LOAEL in 90-day inhalation studies in mice and rats and an uncertainty factor of 10,000, EPA has set a chronic oral RfD of 0.5 μg/kg/d for NB (EPA 1990). On the basis of the chronic oral RfD value, a DWEL of 17.5 μg/L and a lifetime drinking water criterion (analogous to an HA) of 20% of the DWEL (i.e., 3.5 μg/L) can be derived when NB is considered a noncarcinogen (a question yet to be determined). It is somewhat surprising, then, that the human health ambient water quality criterion for water and fish consumption was set by EPA at 30 μg/L when using organoleptic endpoints, and at 19.8 mg/L when derived from the available toxicity data (EPA 1990). An acute literature-lowest-effect concentration (LEC) value of 27 mg/L is given for freshwater organisms and the LEC for marine organisms is 6.68 mg/L (EPA 1990).

4.5 TOXICOLOGY AND REGULATORY INFORMATION ON THE CHEMICAL-SURETY-AGENT-RELATED COMPOUNDS OF CONCERN

4.5.1 VX

VX, a nerve agent, exerts its physiologic effects through its powerful inhibition of the enzyme acetylcholinesterase, which is required for nerve and muscle function in multicellular animals. Individuals poisoned by ingestion of VX may show the following symptoms (Army 1974; Army et al. 1990):

- Difficulty in breathing, tightness of chest;
- Drooling and excessive sweating;
- Nausea, vomiting, cramps, loss of bladder/bowel control;
- Twitching, jerking, and staggering;
- Headache, confusion, drowsiness, coma, and convulsion; and
- Death.

The LCt_{50} (concentration × time that is expected to cause death to 50% of a population) value for VX, estimated for humans breathing at the rate of 15 L/min, was 30 $mg \cdot min/m^3$ (Army 1974). Assuming that the compound is completely absorbed and acts systemically, the corresponding LD_{50} value would be 0.0064 mg/kg. VX is a somewhat cumulative poison; repeated exposure to low (subacute) concentrations, if not too far apart, may produce symptoms (Army et al. 1990).

If a victim recovers from acute VX poisoning, the recovery will be complete unless anoxia and convulsions have gone unchecked for so long that irreversible central nervous system changes have occurred (Army et al. 1990).

A review of the histories of human volunteers exposed to anticholinesterase agents (i.e., nerve agents) concluded that:

> no evidence has been developed (to date) that any of the anticholinesterase test compounds surveyed carries long-range adverse human health effects in the doses used. Exposures to low doses of OP [organophosphorus] compounds have been reported (but not confirmed) to produce subtle changes in EEG, sleep pattern, and behavior that persist for at least a year (NRC 1982).

The dietary oral LD_{50} of VX for steers has been estimated at 0.026 mg/kg, and for the common mouse at 0.25 mg/kg (USATHAMA 1991). The 96-hour LC_{50} of VX to striped bass has been estimated at 0.3 µg/L on the basis of experimental data (USATHAMA 1991). Adverse changes to plants occur at an aqueous VX concentration of 10 mg/L (USATHAMA 1991).

4.5.2 EA2192

EA2192, a cholinesterase-inhibiting product of VX hydrolysis, has a mean intravenous LD_{50} in two species of 0.015 mg/kg (Army, undated), while VX has a median subcutaneous LD_{50} in four species of 0.014 mg/kg (Lewis 1992); thus, the assertion that EA2192 is almost as toxic as VX (Sage and Howard 1989) is quite appropriate. While the routes noted above are not strictly comparable, prudence dictates assigning EA2192 the same drinking water criterion as for VX (assuming only the drinking water exposure route in each case).

4.5.3 DIMP

There is no evidence for toxicity of DIMP to man. Acute oral LD_{50} in several species ranges from 503 mg/kg in female mink to 1,490 mg/kg in mallard ducks. In the mink, clinical signs of acute intoxication included salivation, lethargy, weakness, immobilization, and vomiting. On the basis of a NOAEL at the highest administered dose in a 90-day study in dogs and an uncertainty factor of 1,000, EPA set the chronic oral RfD at 80 µg/kg/d, the DWEL at 2.8 mg/L, and the lifetime drinking water HA value at 600 µg/L. Due to lack of information, the compound was assigned by the EPA to group D, "not classified as to human carcinogenicity" (Roberts and Hartley 1992).

Bentley et al. (1976) performed 96-hour DIMP aquatic organism toxicity studies that found essentially no bioconcentration in bluegills (as cited in Dacre and Rosenblatt 1987).

4.5.4 IMPA

There is no evidence that IMPA is toxic to man. Acute oral LD_{50}s range from 5,620 mg/kg in male mice to 7,650 mg/kg in male rats. The mice showed evidence of soft or liquid stools, reduced motor activity, ataxia, and prostration. On the basis of a NOAEL at the highest administered dose in a 13-week study in rats, EPA promulgated a chronic oral RfD of 100 µg/kg/d, a DWEL of 4 mg/L, and a lifetime drinking water HA value of 700 µg/L (Roberts and Hartley 1992; EPA 1993).

4.5.5 MPA

According to Williams et al. (1987), a Material Data Safety Sheet prepared by Thiokol/ Ventron Division in 1980 states, "MPA is a skin and eye irritant that may be toxic by skin absorption, ingestion, or inhalation." However, preliminary data indicate acute oral toxicities in rats and mice of 5,000 mg/kg or more. Among aquatic organisms, the LC_{50}s were 3 g/L for daphnids and >10 g/L for fathead minnows and bluegills; chronic sensitivity was demonstrated by multispecies protozoan communities at around 600 mg/L (Williams et al. 1987). Thus, MPA appears have a rather low toxicity for aquatic species. It seems logical that the IMPA drinking water criterion of 700 µg/L could be applied to MPA.

4.5.6 TDG

What little is known of the biological effects of TDG indicates a very low toxicity. The oral LD_{50}s for rats and guinea pigs are 6,610 mg/kg and 3,960 mg/kg, respectively, with relatively steep dose-response curves (ICF Kaiser and Clement 1991; Rosenblatt et al. 1975). In lieu of more definitive information, a criterion analogous to a chronic oral RfD can be estimated at the 95% confidence level by multiplying the rat LD_{50} by 1.5×10^{-6} (Layton et al. 1987). This results in a very conservative oral RfD analogue estimate of 0.01 mg/kg/d for TDG. Hence, one can derive a DWEL of 0.35 mg/L and a lifetime HA value of 70 µg/L.

The lowest of a group of estimates for TDG aquatic toxicities was the 96-hour saltwater toxicity to the sheepshead minnow of 684 mg/L (USATHAMA 1991).

4.5.7 1,4-Dithiane

Vapors of 1,4-dithiane are reported to be irritating to the oral cavity and upper respiratory tract in humans (ICF Kaiser and Clement 1991). The oral LD_{50} to rats (combined male and female) of 3,473 mg/kg indicates fairly low toxicity. Crusty eyes, nose, or muzzle; hyperactivity; tremors; emaciation; ataxia; and irregular breathing were among the antemortem observations (ICF Kaiser and Clement 1991; Roberts and Hartley 1992). In a 90-day gavage study in rats, the NOAEL was found to be 105 mg/kg/d (Roberts and Hartley 1992). This value and an uncertainty factor of 1,000 and a modifying factor of 10 were used to derive an RfD of 0.01 mg/kg/d (Hartley et al. 1994). Hence, the DWEL is 0.4 mg/L and the lifetime HA value is 0.08 mg/L (Hartley et al. 1994).

Regression equations relating toxicity for aquatic species to log K_{ow} (1.85) indicated that dithiane should not be very toxic to these organisms. The most sensitive species, the saltwater sheepshead minnow, was estimated to have a 96-hour LC_{50} of 26.5 mg/L (USATHAMA 1991).

4.5.8 1,4-Oxathiane

No information is available on the effects of 1,4-oxathiane in humans. High oral LD_{50} values are reported for rats (2,830 and 3,000 mg/kg in separate studies; Roberts and Hartley 1992) and guinea pigs (3,960 mg/kg; ICF Kaiser and Clement 1991). Antemortem observations in the rat studies included coma, ataxia, lacrimation, dyspnea, cyanosis, squinting, paralysis, and hunched posture. Comparison of the LD_{50} values with those of 1,4-dithiane suggests that, as with 1,4-dithiane, 0.08 mg/L would be a safe value for a lifetime HA for 1,4-oxathiane.

4.5.9 Arsenic

In animals, acute oral toxicities for soluble inorganic arsenic compounds are in the LD_{50} range of 10 to 70 mg/kg. Soluble arsenites show an LD_{50} of 150 mg/kg in rats by skin contact. No animal data are available for inhalation toxicity. The principal target organs following repeated oral exposures are the liver and kidneys (Fielder et al. 1986). Arsenic carcinogenicity has not been consistently demonstrated in test animals (EPA 1994c).

In adult humans, 70–300 mg of inorganic arsenic in a single dose are usually fatal. Dermatitis has frequently been observed in workers exposed to appreciable levels of arsenic dust by skin contact. Ingestion of 1–5 mg of arsenic per day for prolonged periods has frequently been associated with the development, after a latent period, of hyperpigmentation and hyperkeratosis, and some evidence of peripheral neuropathy (Fielder et al. 1986). The chronic oral RfD for noncarcinogenic effects is 0.3 μg/kg/d; no RfD value has been given for inhalation toxicity (EPA 1994c).

Inorganic arsenic belongs to the Group A cancer category, which makes it a definite human carcinogen by both the oral (skin cancer) and inhalation (lung cancer) routes. For drinking water, the unit risk is 5×10^{-5} $(\mu g/L)^{-1}$ (EPA 1994c). The maximum contaminant level for drinking water is 50 μg/L (EPA 1994b), which corresponds to a cancer risk of 2×10^{-3}. The reason for this relatively high allowable level of exposure is that arsenic is considered a possibly essential nutrient (EPA

1994c). The inhalation unit cancer risk is 4.3×10^{-3} $(\mu g/m^3)^{-1}$; rounded off, a concentration of 0.02 $\mu g/m^3$ corresponds to a cancer risk of 10^{-4} (EPA 1994c).

Arsenic(V) appears to be more toxic than arsenic(III) to algae. The freshwater species most sensitive to arsenic(V) was *Scenedesmus obliquus*, with a 14-day EC_{50} of 48 µg/L; the most sensitive saltwater species was *Skeletonema costatum*, which showed growth inhibition at 13 µg/L (USATHAMA 1991).

Apparent effects thresholds for arsenic-containing sediments were 57 mg/kg for amphipods and 93 mg/kg for oysters (USATHAMA 1991).

The 28-day EC_{50} (based on death and deformity) for freshwater embryo-larval rainbow trout exposed to arsenic(III) is 550 µg/L, and the EC_{10} is 134 µg/L (USATHAMA 1991). A seven-day early-life-stage EC_{50} of 40 µg/L of arsenic(III) was reported for the narrow-mouthed toad (USATHAMA 1991). These numbers represent what has been reported for the most sensitive ends of the toxicity scales for fish and amphibia. EPA has established a chronic (four-day average concentration) criterion for arsenic(III) of 190 µg/L for freshwater aquatic species and 36 µg/L for marine species (EPA 1994c).

5 RESULTS OF SOIL AND WATER ANALYSES

Environmental investigations have been conducted for several compounds of concern at APG. The results discussed in this section are only for those compounds of concern suspected of being related to UXO.

5.1 ABERDEEN AREA

Although inorganic arsenic would be a possible product of arsenical agent decomposition, the inorganic arsenic found in the Aberdeen Area probably arose from other sources. In any event, only four Aberdeen Area water samples showed detectable amounts: Mosquito Creek Site CRW-H (0.005 mg/L) and on-post Chesapeake Bay Water Sites BAYW-A (0.005 mg/L), BAYW-B (0.009 mg/L), and BAY-C (0.005 mg/L) (Phillips 1994). The highest-testing site sediment sample, showing 8.3 mg/kg, contained only about twice as much arsenic as the highest-testing background sample (4.4 mg/kg). Similarly, the highest-testing site soil sample, showing 8.0 mg/kg, contained only about 2.2 times as much as the highest-testing background sample (3.6 mg/kg). These values may be of use for evaluating excesses of inorganic or total arsenic in Edgewood Area soils.

None of the identified high-explosives-related compounds of concern was detected in surface water, sediment, or soil samples collected from the Aberdeen Area (Phillips 1994). RDX and HMX were detected in Aberdeen Area groundwater (Table 8); however, only RDX exceeded its drinking water HA value.

TABLE 8 Compounds of Concern Detected in Aberdeen Area Groundwater

	Compound of Concern	
Parameter	RDX	HMX
Frequency of detection	4/30	2/30
Range of detection (μg/L)	14.0–16.0	8.1–9.0
Detection level (μg/L)	0.30	6.0
Background level (μg/L)	8.7	Undetected
Acceptable regulatory level[a] (μg/L)	2.0	400

[a] Lifetime Drinking Water Health Advisory.

Source: Phillips (1994).

The following are a series of issues that are also pertinent to the concern about UXO:

- Certain firing point surface soil samples contained HMX, RDX, 2,4-DNT, and/or nitroglycerin (Phillips 1994). The last two compounds are linked with propellants rather than with high-explosive charges.
- Soil and water in the vicinity of the shell washout facility (Building 700B) were found to contain TNT. The soil also contained RDX, while the water contained detectable amounts of 2,6-DNT and the TNT metabolites 2A-4,6-DNT and 4-A-2,6-DNT. Though analyses were conducted for PA (as the ammonium salt), none was found, despite a history that included the washout of shells containing ammonium picrate (Derryberry et al. 1990). Note that analyses are not usually conducted for PA.
- DU was test-fired and is "reportedly" present at Aberdeen Area as particulates (McMaster et al. 1981).
- White phosphorus (possibly contained in UXO) is also of concern, especially in sediments off Black Point, a feature of the APG coastline (EPA 1993; McMaster et al. 1981).

5.2 EDGEWOOD AREA

5.2.1 J-Field

The compounds listed in Table 9 were detected in 1990 groundwater sampling at J-Field in the Edgewood Area (USATHAMA 1991). More recently, Martino (1994) found RDX above detection limits in J-Field groundwater and surface water, as shown in Table 10.

Only arsenic was detected in surface water in the 1990 sampling (frequency 3/20; range 3.6–5.0 μg/L) (USATHAMA 1991). Martino (1994) reported the following three chemical surety agent degradation products in one of seven J-Field surface water samples (JFSW10): DIMP at 0.45 μg/L (detection limit [DL] = 0.43 μg/L); 1,4-dithiane at 2.49 μg/L (DL = 1.57 μg/L); and oxathiane at 12.2 μg/L (DL = 2.55 μg/L).

TABLE 9 Compounds of Concern Detected in J-Field Groundwater in 1990 Sampling

Compound	Frequency of Detection (μg/L)	Range of Detection (μg/L)	Acceptable Regulatory Level (μg/L)
RDX	3/12	0.5–1.2	2[a]
PETN	1/11	15.9	NA
NB	1/11	0.9	3.5[a]
1,4-Dithiane	2/49	2.1–8.2	80[a]
1,4-Oxathiane	1/49	8.2	NA
Arsenic	14/51	2.7–60.0	50

NA = not available.

[a] Lifetime Drinking Water Health Advisory.

Source: USATHAMA (1991).

TABLE 10 RDX in J-Field Groundwater and Surface Water in 1994 Sampling

Sample No.	Concentration (μg/L)[a,b]	Medium
DGD-1	3.8	Groundwater
DGD-2	3.1	Groundwater
94-153	2.9	Surface water
94-173	1.5	Surface water
94-JF83	8.5	Surface water

[a] Detection Limits vary somewhat, but are usually 1.7 μg/L.

[b] Lifetime Drinking Water Health Advisory is 2 μg/L.

Source: Martino (1994).

5.2.2 Old O-Field

Groundwater samples were collected from selected wells in Old O-Field in 1986–1987. The following compounds of concern were analyzed for: TNT, 2,4-DNT, 2,6-DNT, HMX, RDX, TNB, DNB, NB, tetryl, VX, IMPA, MPA, TDG, and arsenic. 1,4-Dithiane was tentatively identified even though it was not analyzed for. Table 11 summarizes the results of the sample analysis (USATHAMA 1991). The highest concentrations of three of the chemical-agent-related contaminants of concern were detected in the water table aquifer. Tables 12 and 13 summarize the sampling results for the water table and the upper confined aquifers. The O-Field feasibility study by Zirps et al. (1990) contains maps with numbered well locations and water table and upper confined aquifer plumes for arsenic, TDG, and 1,4-dithiane.

Arsenic concentrations in the surface water of Watson Creek ranged from 13 to 126 μg/L and in the Gunpowder River near the mouth of Watson Creek the range was 70–96 μg/L (Zirps et al. 1990). With the exception of arsenic, none of the compounds of concern was detected in surface water or sediment at Old O-Field (USATHAMA 1991).

Arsenic was the only compound of concern analyzed for in four subsurface soil samples collected at Old O-Field during the 1988-1989 USATHAMA investigation. The range detected was between 0.38 and 22.4 mg/kg, compared with a "background" concentration of 6.0 mg/kg (USATHAMA 1991).

5.2.3 New O-Field

Groundwater samples collected in 1988-1989 from four shallow downgradient wells in New O-Field contained MPA, DIMP, 1,4-dithiane, and arsenic. Results are shown in Table 14 (USATHAMA 1991). New tests were conducted in 1993 on water from the 3 background and 23 groundwater wells of the New O-Field area (Williams et al. 1994). Five organic chemical surety agent degradation products were detected, as shown in Table 15. The detection of IMPA in water from one background well and six otherwise clean wells may indicate that the results for this compound are unreliable. Except for arsenic, none of the compounds of concern was detected in surface water or Watson Creek sediment during 1985 sampling at New O-Field (USATHAMA 1991).

5.2.4 Canal Creek

Twenty-four groundwater samples were collected from the Canal Creek Area and the results were reported (Wrobel 1994). Compounds of concern were detected in four samples, probably from an unconfined aquifer (Table 16).

TABLE 11 Compounds of Concern Detected in Old O-Field Groundwater

Compound	Detection Frequency	Range of Detection (μg/L)	Acceptable Regulatory Level (μg/L)
Shallow Aquifer			
DNB	2/4	23.3–71.8	1[a]
MPA	1/12	10,000	NA
TDG	10/12	1,000–1×10^6	NA
TNT	18	22.1	2[a]
1,4-Dithiane (tentative)	14/18	3–5,150	80[a]
Arsenic	14/19	1.7–1,250	50
Deep Aquifer			
Arsenic	2/2	1.2–4.0	50

NA = not available.

[a] Lifetime Drinking Water Health Advisory.

Source: USATHAMA (1991).

TABLE 12 **Compounds of Concern Detected in the Water Table Aquifer of Old O-Field**

Compound	Highest Detected Level (μg/L)	Acceptable Regulatory Level (μg/L)
Inorganic arsenic	2,243	50
Organic arsenic	47	NA
1,4-Dithiane	5,154	80[a]
TDG	1×10^6	NA
TNT	22,100[b]	2[a]
TNB	71,800[b]	NA

NA = not available.

[a] Lifetime Drinking Water Health Advisory.

[b] Found in the groundwater of the water table aquifer east of the disposal area near Watson Creek (Zirps et al. 1990). These values, however, should probably be 1,000 times smaller (i.e., 22.1 μg/L and 71.8 μg/L), as given in the report by USATHAMA (1991), and shown in Table 11 of the present document.

Source: Zirps et al. (1990).

TABLE 13 **Compounds of Concern Detected in the Upper Confined Aquifer of Old O-Field**

Compound	Highest Detected Level (μg/L)	Accepted Regulatory Level (μg/L)
Inorganic arsenic	92	50
Organic arsenic	1.6	NA
1,4-Dithiane	150	80[a]
TDG	1,000–2,000	NA

NA = not available.

[a] Lifetime Drinking Water Health Advisory.

Source: Zirps et al. (1990).

TABLE 14 Compounds of Concern Detected in New O-Field Groundwater (Shallow Aquifer)

Compound	Detection Frequency	Range of Detection (μg/L)	Acceptable Regulatory Limit (μg/L)
MPA	1/2	>10,000	NA
DIMP (tentative)	2/4	24–32	600[a]
1,4-Dithiane (tentative)	1/4	4.1	80[a]
Arsenic	2/4	2.2–6.7	50

NA = not available.

[a] Lifetime Drinking Water Health Advisory.

Source: USATHAMA (1991).

TABLE 15 Chemical Surety Agent Degradation Compounds Detected in New O-Field Groundwater

Well No.	Compound	Concentration (µg/L)[a, b]	Acceptable Regulatory Level (µg/L)[c]
Water Table Aquifer Wells			
OF23A[d]	IMPA	213	700
OF16A	MPA	3,120	NA
OF26A	IMPA	187	700
OF27A	MPA	139	NA
	1,4-Dithiane	2	80
	1,4-Oxathiane	2.97	NA
	DIMP	17.7	600
	IMPA	309	700
	MPA	2,840	NA
OF28A	IMPA	186	700
OF29A	IMPA	233	700
OF30A	IMPA	114	700
OF31A	MPA	1,750	NA
OF31AX	MPA	2,310	NA
OF32A	IMPA	118	700
Upper Confined Aquifer Wells			
OF16B	1,4-Dithiane	2.47	80
	DIMP	44.6	600
	IMPA	442	700
OF25B	IMPA	302	700
OF26B	IMPA	490	700
OF27B	1,4-Dithiane	1.85	80
	1,4-Oxathiane	2.77	NA
	IMPA	457	700
	MPA	1,920	NA
OF28B	MPA	143	NA
OF31B	DIMP	38.2	600
	IMPA	377	700
	MPA	401	NA

NA = not available.

[a] Certified reporting limits: 1,4-dithiane, 1.11; 1,4-oxathiane, 1.98; DIMP, 10.5; IMPA, 100; MPA, 128.

[b] Source: Williams et al. (1994).

[c] Section 4.5

[d] One of two water table aquifer background wells.

TABLE 16 Compounds of Concern Detected in Canal Creek Groundwater

Well No.	Compound	Concentration (µg/L)[a]	Detection Limit (µg/L)[a]	Acceptable Regulatory Level (µg/L)
CC25A	1,4-Oxathiane	24	2.1	NA
	1,4-Dithiane	16	2.2	80[b]
CC33B	1,4-Dithiane	3	2.1	80[b]
CC112A	NB	140	10	3.5[c]
CC120A	NB	370	10	3.5[c]

NA = not available.

[a] Source: Wrobel (1994).

[b] Section 4.5.7.

[c] Section 4.4.12.

6 POTENTIAL FOR ADVERSE EFFECTS FROM UXO ON GROUNDWATER AND SURFACE WATER

Whereas known UXO in the land ranges of the Aberdeen Area consists entirely of conventional munitions, the Edgewood Area contains both conventional munitions and a variety of chemical munitions.

Current data suggest that the rate of deterioration of conventional UXO has been so slow that release of moderately toxic and in some cases carcinogenic high-explosive compounds, especially TNT and RDX, has been negligible. In part, this is because such explosives are solids and thus cannot leak from their casings. These substances would only be accessible to the dissolving action of rainwater or groundwater after the casings had disintegrated. It is possible, however, that explosive fills in munitions would eventually release increasing amounts of explosives to the environment. A relatively moderate but indefinitely extended monitoring effort would permit timely remedial action to be instituted before dangerous levels were released, thereby protecting drinking water supplies and Chesapeake Bay.

UXO with chemical fill presents the twin dangers of physical damage or injury by explosion and death or incapacitation by extreme toxicity. To exacerbate the situation, the more common and lethal chemical agents, such as mustard and the nerve agents, are liquids. Even pinholes in chemical-agent-filled ordnance would permit leakage into the surrounding media. This tendency to leak, however, is mitigated by the rather rapid hydrolysis of these agents once they dissolve in water; thus, only five relatively benign decomposition products of mustard and the nerve agents, not the parent compounds, have been detected through groundwater and surface water sampling and analysis. The occurrence and sources of arsenic might be attributable to UXO, but until the arsenic is characterized as either inorganic or particular organic arsenicals, this question remains unsettled. As with conventional UXO, it does not appear that there have been significant releases of toxic agents from UXO to the aquatic environment; nevertheless, modest periodic monitoring would be prudent.

Explosions of conventional UXO also represent no hazard to the public. Nevertheless, without extensive cleanup, it will be necessary to restrict public access to much of APG indefinitely. Potential danger to site workers, unauthorized visitors, and the general public from accidental or spontaneous explosions of chemical UXO is perhaps of greater concern.

7 REFERENCES

AMC: See U.S. Army Materiel Command

Army: See U.S. Department of the Army

Bentley, R.E., et al., 1976, *Acute Toxicity of Diisopropyl Methylphosphonate and Dicyclopentadiene to Aquatic Organisms*, Contract No. DAMD17-75-C-5073, EG&G Bionomics, Wareham, Mass.

Berkowitz, J.B., et al., 1978, *Literature Review—Problem Definition Studies on Selected Chemicals, Final Report, Volume II: Chemistry, Toxicology and Potential Environmental Effects of Selected Organic Pollutants*, Contract No. DAMD17-77-C-7037, prepared by Arthur D. Little, Inc., Cambridge, Mass., for U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, Md., June.

Berkowitz, J.B., 1982, *Literature Review—Problem Definition Studies on Selected Chemicals, Final Report, Volume IV: Site Specific Evaluation of Selected Organic Pollutants at Rocky Mountain Arsenal as of 1979*, Contract No. DAMD17-77-C-7037, prepared by Arthur D. Little, Inc., Cambridge, Mass., for U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, Md., March.

Britton, K.B., and C.L. Grant, 1988, *Prediction of Octanol-Water Partition Coefficients of Organophosphonates: Evaluation of Structure-Function Relationships*, Special Report 88-11, U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory, Hanover, N.H., Aug.

Burton, D.T., et al., 1984, "Uptake, Elimination, and Metabolism of ^{14}C-PA and ^{14}C-Picramic Acid in the American Oyster (*Crassostrea virginica*)," *Archives of Environmental Contamination and Toxicology* 13:653-663.

Burton, D.T., et al., 1993, *Toxicity of Nitroguanidine, Nitroglycerin, Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-Trinitrotoluene (TNT) to Selected Aquatic Organisms*, Final Report, Contract No. N00039-88-C-5301, prepared by The Johns Hopkins University Applied Physics Laboratory, Laurel, Md., for the U.S. Navy, April.

Channon, H.J., et al., 1944, "The Metabolism of 2:4:6-Trinitrotoluene (α-T.N.T.)," *The Biochemical Journal* 38:70-85.

Clark, D.N., 1989, *Review of Reactions of Chemical Agents in Water (Task 80)*, Final Report, prepared by Battelle Columbus Division, Columbus, Ohio, for the U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, Md., under Army Project No. 88PP8847.

Conley, J.H., 1994, personal communication from Conley (formerly Aberdeen Proving Ground Range Control Officer, now with Dynamic Science, Inc., Aberdeen, Md.), to D.H. Rosenblatt (Argonne National Laboratory, Argonne, Ill.), Oct. 12.

Cooper, K.R., 1984, "Bioconcentration and Metabolism of PA (2,4,6-trinitrophenol) and Picramic Acid (2-amino-4,6-trinotrophenol) in Rainbow Trout (*Salmo Gairdneri*)," *Journal of Toxicology and Environmental Health* 14:731-747.

Dacre, J.C., and D.H. Rosenblatt, 1987, *Drinking Water Criteria for the Groundwater Pollutant Diisopropyl Methylphosphonate (DIMP)*, Technical Report 8610, U.S. Army Biomedical Research & Development Laboratory, Fort Detrick, Frederick, Md.

Demek, M.M., et al., 1970, *Behavior of Chemical Agents in Seawater*, Edgewood Arsenal Technical Report EATR 4417, Edgewood Arsenal Research Laboratories, Edgewood Arsenal, Md.

Derryberry, N.A., et al., 1990, *RCRA Facility Assessment: Other Areas, Aberdeen Proving Ground, Volume I: Main Text,* prepared by Waterways Experiment Station, Vicksburg, Mich., for the Environmental Management Division, Directorate of Safety, Health and Environment, Aberdeen Proving Ground, Md., Sept.

Durst, H.D., et al., 1988, *Support for the Delisting of Decontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources (State) MD02 in COMAR 10.51.02.16-1*, CRDEC-TR-009, Research Directorate, Chemical Research, Development & Engineering Center, Aberdeen Proving Ground, Md., Nov.

EPA: See U.S. Environmental Protection Agency

Epstein, J., et al., 1973, *Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations*, EASP 1200-12, Headquarters, Edgewood Arsenal, Md., Jan.

Epstein, J., et al., 1974, "The Kinetics and Mechanisms of Hydrolysis of Phosphonothiolates in Dilute Aqueous Solution," *Phosphorus* 4:157-163.

Fielder, R.J., 1986, *Inorganic Arsenic Compounds, Toxicity Review 16*, Her Majesty's Stationery Office, U.K.

Hartley, W.R., 1994, *Drinking Water HA: Munitions II*, Professional Administrative Services, Washington, D.C.

Howard, P.H., 1989, *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Lewis Publishers, Chelsea, Mich., pp. 421-430.

ICF Kaiser Engineers and Clement International Corporation, 1991, *Baseline Risk Assessment for Eight Selected Study Areas at Aberdeen Proving Ground—Draft Document*, prepared under Task Order No. 11, Remedial Investigations/ Feasibility Studies Contract Number DAAA15-88-D-0009, by ICF Kaiser Engineers and Clement International Corporation, Fairfax, Va., for the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Md., Jan.

Jonas, L., 1994, personal communication from Jonas (Directorate of Safety, Health and Environment, Aberdeen Proving Ground, Md.) to D.H. Rosenblatt (Argonne National Laboratory, Argonne, Ill.), concerning numbers and locations of nonstockpile munitions and containers (mostly buried) with chemical agent fills, Sept. 14.

Kayser, E.G., et al., 1984, *Kinetics of Hydrolysis and Products of Hydrolysis and Photolysis of Tetryl*, NSWC TR 84-68, Naval Surface Weapons Center, Silver Spring, Md., Oct.

Kingery, A.F., and H.E. Allen, 1995, "The Environmental Fate of Organophosphorus Nerve Agents: A Review," *Toxicology and Environmental Chemistry* 47:155-184.

Kingery, A.F., and H.E. Allen, 1994, *Environmental Fate of Alkyl Methylphosphonates Arising from Chemical Surety Material (CSM) and Potential Non-CSM Sources in Soil and Aqueous Media*, Final Report, prepared by the Department of Civil Engineering, University of Delaware, Newark, Del., for the U.S. Army Environmental Center under Contract No. DAAL03-86-D-0001, Delivery Order 2871-TCN 91429, March.

Layton, D.W., et al., 1987, "Deriving Allowable Daily Intakes for Systemic Toxicants Lacking Chronic Toxicity Data," *Regulatory Toxicology and Pharmacology* 7:96-112.

Lewis, R.J., Sr., 1992, *Sax's Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold Publishing Co., New York.

Liu, D.H.W., et al., 1984, *Toxicity of TNT Wastewaters to Aquatic Organisms, Volume I: Acute Toxicity of LAP Wastewater and 2,4,6-Trinitrotoluene*, Final Report, AD A142144, SRI International, Menlo Park, Calif.

Lyman, W.J., et al., 1990, *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*, American Chemical Society, Washington, D.C.

Major, M.A., 1989, *Octanol Water Partition Coefficients of Surface and Ground Water Contaminants Found at Military Installations*, Technical Report 88-10, U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, Md., Nov.

Major, M.A., 1990, personal communication from Major (U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, Md.) to D.H. Rosenblatt (Argonne National Laboratory, Argonne, Ill.) concerning miscibility of DIMP with water, Dec. 4.

Martino, L.E., 1994, personal communication from Martino (Argonne National Laboratory, Argonne, Ill.) to D.H. Rosenblatt (Argonne National Laboratory, Argonne, Ill.), concerning recent results of analyses of J-Field groundwater for explosives and chemical agent-related compounds, Aug.

McMaster, B.N., et al., 1981, *Installation Assessment of Aberdeen Proving Ground—Aberdeen Area,* Report No. 301, Environmental Science & Engineering, Inc., Gainesville, Fla., Feb.

Michel, H.O., et al., 1962, *EA2192, A Novel Anticholinesterase (U)*, CRDLR 3135, Chemical Research and Development Laboratories, Edgewood Arsenal, Md., May.

National Research Council, 1982, *Possible Long-Term Health Effects of Short-Term Exposure to Chemical Agents, Volume 1, Anticholinesterases and Anticholinergics*, PB83-181271, prepared by the National Research Council, National Academy Press, Washington, D.C., for the Office of Naval Research, Arlington, Va., June.

Nemeth, G., 1989, *RCRA Facility Assessment Report—Edgewood Area, Aberdeen Proving Ground, Maryland,* No. 39-26-0490-90, Waste Disposal Engineering Division, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, Md., Nov.

NRC: See National Research Council

Okusu, N., et al., 1994, *Aberdeen Proving Ground Focused Feasibility Study, Old O-Field Source Area, Final Document*, prepared by ICF Kaiser Engineers, Fairfax, Va., for the U.S. Army Aberdeen Proving Ground Support Activity, Task Order No.6, Contract Number DAAA15-91-D-0014, June.

Penski, E.C., and E.S. Domalski, 1987, *Estimation of the Heats of Formation and Other Thermodynamic Properties. I. Organophosphorus Agents and Related Compounds*, Technical Report ERDEC-TR-87063, Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, Md., Aug.

Phillips, L., 1994, *Effects of Active Firing Range Activities on Environmental Media, Aberdeen Proving Ground—Aberdeen Area, Maryland, 31 January–30 November 1993*, Wastewater Management Study No. 32-24-HP16-94, U.S. Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, Md.

Richter, F. (editor), 1930, *Beilsteins Handbuch der Organischen Chemie, First Supplement, Nitrobenzene*, System No. 465, Julius Springer Verlag, Berlin, Germany.

Roberts, W.C., and W.R. Hartley, 1992, *Drinking Water HA: Munitions*, Lewis Publishers, Boca Raton, Fla.

Rosenblatt, D.H., 1980, "Toxicology of Explosives and Propellants," in S.M. Kaye (editor) *Encyclopedia of Explosives and Related Items*, Volume 9, Picatinny Arsenal Technical Report (PATR) 2700, Large Caliber Weapon Systems Laboratory, U.S. Army Armament Research and Development Command, Dover, N.J., pp. T-332–T-345.

Rosenblatt, D.H., 1994, personal recollection of PA/picramic acid burial site contamination described during tour of Bangor Naval Submarine Base in 1981.

Rosenblatt, D.H., et al., 1975, "Mustard Gas/Thiodiglycol," Appendix A in *Problem Definition Studies on Potential Environmental Pollutants, II: Physical, Chemical, Toxicological, and Biological Properties of 16 Substances*, Technical Report 7509, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Md., Dec.

Rosenblatt, D.H., et al., 1991, "Organic Explosives and Related Compounds" in O. Hutzinger (editor), *The Handbook of Environmental Chemistry,* Volume 3, Part G, Springer-Verlag, Heidelberg, Germany, pp. 196-234.

Russell, W.A., Jr., 1976, *Installation Environmental Impact Assessment—Aberdeen Proving Ground, Maryland 21005,* 3rd Edition, U.S. Army Materiel Command, Test and Evaluation Command, Aberdeen Proving Ground, Md., Sept.

Sage, G.W., and P.H. Howard, 1989, *Environmental Fate Assessments of Chemical Agents HD and VX*, CRDEC-CR-034, prepared by Syracuse Research Corporation, Syracuse, N.Y., for the Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, Md., June.

Samuel, J.B., et al., 1983, *Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures (U)*, Special Publication ARCSL-SP-83015, Chemical Systems Laboratory, Aberdeen Proving Ground, Md., June.

Small, M.J., 1983, *Soil Detection Limits for Potential Chemical Warfare-Related Contaminants at Fort McClellan Alabama*, Technical Report 8208, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Md., May.

Small, M.J., 1984, *Compounds Formed from the Chemical Decontamination of HD, GB, and VX and their Environmental Fate*, Technical Report 8304, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Md., June.

Spanggord, R.J., et al., 1979, *Studies of Environmental Fates of DIMP and DCPD*, Final Report, Contract DAMD 17-78-C-8053, prepared by SRI International, Menlo Park, Calif., for the U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, Md.

Sweet, D.V. (editor), 1987, *Registry of Toxic Effects of Chemical Substances (RTECS),* 1985–1986 edition, DHHS (NIOSH) Publication No. 87-114, prepared by Advanced Engineering and Planning Corp., Inc., Rockville, Md., for the National Institute for Occupational Safety and Health under Contract No. 200-84-2768.

U.S. Army Materiel Command, 1987, *Safety Regulation for Chemical Agents H, HD, HT, GB, and VX*, AMC Reg. No. 385-131, Headquarters, Alexandria, Va., Oct.

U.S. Army Toxic and Hazardous Materials Agency, 1991, *Baseline Risk Assessment for Eight Selected Study Areas at Aberdeen Proving Ground*, Draft Document, Task Order No.11, Remedial Investigations/Feasibility Studies, Contract Number DAAA15-88-D-0009, prepared by ICF Kaiser Engineers and Clement International Corporation, Abingdon, Md., for the U.S. Army Corps of Engineers, Jan.

USATHAMA: See U.S. Army Toxic and Hazardous Materials Agency

U.S. Department of the Army, undated, *Material Safety Data Sheets*, U.S. Army Chemical, Research, Development and Engineering Center, Aberdeen Proving Ground, Md. [Note: Each "Safety Sheet" is actually a packet of sheets and normally consists of 10 sections. An individual information packet has been prepared for each chemical of interest to CRDEC and is updated at irregular intervals.]

U.S. Department of the Army, 1974, *Chemical Agent Data Sheets, Volume I*, Edgewood Arsenal Special Report EO-SR-740001, Aberdeen Proving Ground, Md., Dec.

U.S. Department of the Army, et al., 1990, *Potential Military Chemical/Biological Agents and Compounds,* Army Field Manual No. 3-9, U.S. Army Chemical School, Fort McClellan, Ala., Dec.

U.S. Department of the Army, 1991, *Interim Action, Record of Decision, Old O-Field Site, Aberdeen Proving Ground, MD, Final Report*, Aberdeen Proving Ground, Md., Sept.

U.S. Department of the Army, 1993, *Non-Stockpile Chemical Materiel Program: Survey and Analysis Report*, U.S. Army Chemical Materiel Destruction Agency, Aberdeen Proving Ground, Md., Nov.

U.S. Environmental Protection Agency, 1990, *Integrated Risk Information System (IRIS)*, data retrieval on nitrobenzene, Jan.

U.S. Environmental Protection Agency, 1991, *Health Effects Summary Tables, Annual FY-1991*, Publication 9200.6-303(91-1), Office of Solid Wastes and Emergency Response, Washington, D.C., Jan.

U.S. Environmental Protection Agency, 1993, *Handbook: Approaches for the Remediation of Federal Facility Sites Contaminated with Explosive or Radioactive Wastes*, EPA/625/R93/013, Office of Research and Development, Washington, D.C., Sept.

U.S. Environmental Protection Agency, 1994a, *Health Effects Summary Tables, FY-1994 Annual*, Publication 9200.6-303(94-1), EPA540/R-94/020, Office of Solid Wastes and Emergency Response, Washington, D.C., March.

U.S. Environmental Protection Agency, 1994b, *EPA Drinking Water Regulations and Health Advisories*, EPA 822/F-93-011, U.S. Environmental Protection Agency Office of Drinking Water 4304, Washington, D.C., May.

U.S. Environmental Protection Agency, 1994c, *Integrated Risk Information System (IRIS)*, data retrieval on inorganic arsenic, Jan.

Vocelka, R.R., August 1994, *Risk Estimates for Potential Liquid-Filled Unexploded Ordnance Incidents at the Edgewood Area of Aberdeen Proving Ground*, Draft Final Report, General Physics Corporation, Aberdeen Proving Ground, Md.

Watson, A.P., et al., 1992, *Estimated General Population Control Limits for Unitary Agents in Drinking Water, Milk, Soil, and Unprocessed Food Items—For Use in Reentry Decision-Making*, ORNL/TM-12035, prepared by the Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., for the Office of the Assistant Secretary for Installations, Logistics, and Environment, U.S. Department of the Army, under Interagency Agreement DOE No. 1769-1354-A1, Jan.

Weast, R.C., 1979, *CRC Handbook of Chemistry and Physics,* 60th edition, CRC Press, Inc., Boca Raton, Fla.

Wells, H.G., et al., 1920, "Observations on the Toxicity of Tetranitromethylaniline (Tetryl), Tetranitroxylene (T.N.X.), Tetranitroaniline (T.N.A.), Dinitrochlorobenzene (Parazol), and Metanitraline," *Journal of Industrial Hygiene* 2:247-252.

Williams, R.T., et al., 1987, *Environmental Fate and Effects of Tributyl Phosphate and Methyl Phosphonic Acid,* DRDEC-CR-87103, prepared by Roy F. Weston, Inc., West Chester, Pa., for Chemical Research, Development & Engineering Center, Aberdeen Proving Ground, Md., under Task Order 1, Contract DAAA15-85-D-0020.

Williams, T., et al., 1994, *Aberdeen Proving Ground Remedial Investigation Report for the O-Field Area—Phase I Draft Report*, prepared by ICF Kaiser Engineers, Abingdon, Md., for the U.S. Army, Aberdeen Proving Ground, Md., under Contract No. DAAA15-91-D-0014, Task Order No. 6.

Wood, J.M., 1974, "Biological Cycles for Toxic Elements in the Environment," *Science* 183:1049-1052.

Wrobel, J., 1994, personal communication from Wrobel (Aberdeen Proving Ground, Md.) to D.H. Rosenblatt (Argonne National Laboratory, Argonne, Ill.) concerning results of April/May 1994 Canal Creek groundwater analysis by Jacobs Engineering Group, Inc., Aug 16.

Yang, Y.-C., et al., 1993, "Perhydrolysis of Nerve Agent VX," *Journal of Organic Chemistry* 58:6964-6965.

Zirps, N.A., et al., 1990, *Aberdeen Proving Ground Baseline Risk Assessment—Focused Feasibility Study of Groundwater Treatment Alternatives for Old O-Field, Aberdeen Proving Ground*, Final Report, Task Order No. 11, Remedial Investigations/Feasibility Studies, Contract Number DAAA15-88-D-0009, prepared by ICF Technology, Inc., Fairfax, Va., for the U.S. Army Corps of Engineers, March 22.

APPENDIX A:

ESTIMATION OF THE DIMENSIONLESS HENRY'S LAW CONSTANT FOR DIMP

APPENDIX A:

ESTIMATION OF THE DIMENSIONLESS HENRY'S LAW CONSTANT FOR DIMP

In December 1990, Dr. Michael Major of the U.S. Army Biomedical Research and Development Laboratory at Fort Detrick (Frederick, Maryland) demonstrated that diisopropyl methylphosphonate (DIMP) is miscible in all proportions with water. This provided the basis for the reevaluation of the air-water equilibrium constant for DIMP.

Assumption: The solute exhibits ideal behavior at very low concentrations so that the activity coefficient approaches unity.

Equation Development:

R = 62.36 torr × L/(mol × K) [K = temp., degrees Kelvin]

P = vapor pressure in torr for pure DIMP = 0.28 torr, based on the equation log

P(torr) = 9.851 – 3105/T, where T is in degrees Kelvin

Pp = partial pressure (in torr) of dissolved DIMP

C = number of moles of solution in 1 L, which is essentially equivalent to the solvent concentration when the solute concentration is very low (i.e., 55.55 mol/L)

T = temperature, K = 298° K

C_{air} = Concentration of DIMP in air (mol/L) at equilibrium with the concentration in water

C_{water} = Concentration of DIMP in water (mol/L)

The dimensionless Henry's Law Constant, K_H, is defined as the ratio of the compound's concentration in air to that in water, both in the same concentration units (i.e., $K_H = C_{air}/C_{water}$).

Under the ideality assumption, the partial pressure of the dissolved (very dilute) compound is equal to the mole fraction of the compound times the vapor pressure of pure DIMP:

$$(P_p = [C_{water}/C] \times P).$$

The corresponding concentration in air is:

$$C_{air} = P_p/RT = (C_{water}/C) \times P/(R \times T);$$

hence,

$$\mathrm{K_H} = P/(C \times R \times T).$$

Calculation of $\mathbf{K_H}$ for DIMP:

$$\mathrm{K_H} = 0.28/(55.55 \times 62.36 \times 298.16) = 2.71 \times 10^{-7} \text{ at } 298^\circ \text{ K, which is } 25^\circ\text{C.}$$