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Chemistry and Chemical Engineering Division  
Department of Environmental Engineering

March 3, 1994

Department of the Army  
Huntsville Division, Corps of Engineers  
CEHND-ED-SY (Mr. Mike Robinson)  
P.O. Box 1600  
Huntsville, AL 35807-4301

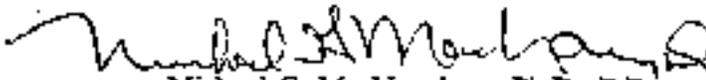
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Dear Mr. Robinson:

In accordance with the subject delivery order requirements, seven copies of the Final Report on The Environmental Decomposition of Chemical Warfare Agents are enclosed.

This completes the required deliverables for this task. Should you have any questions, please do not hesitate to call me at (210) 522-5162 or Joe Brewer at (210) 522-5168

Very truly yours,

  
Michael G. MacNaughton, Ph.D., P.E.  
Director

JHB/ltp

bcc: Polcyn (06)  
Brewer (01)



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# ENVIRONMENTAL CHEMISTRY AND FATE OF CHEMICAL WARFARE AGENTS

## FINAL REPORT

SwRI Project 01-5864

Prepared by

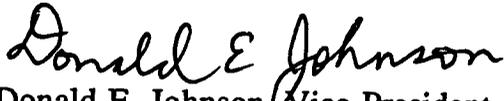
Dr. Michael G. MacNaughton  
Joseph H. Brewer

Prepared for

Department of the Army  
Corps of Engineers, Huntsville Division

March 3, 1994

APPROVED:

  
Donald E. Johnson, Vice President  
Chemistry and Chemical Engineering Division

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# 1 INTRODUCTION

The US Army Corps of Engineers (COE) has identified approximately 7,200 formerly used defense sites (FUDS) in the United States, some of which are suspected to be contaminated with chemical warfare agents (CWA). The COE has the responsibility for environmental clean-up of FUDS including site characterization, evaluation and remediation of the site. The Army Environmental Center (AEC) has responsibility for the clean-up of active Army installations. Both the COE and AEC are assisted by the USA Chemical Material Destruction Agency (USCMDA) which is responsible for the temporary storage, transportation and destruction of chemical warfare material (CWM). The AEC is responsible for the evaluation and site characterizations of most active army installations.

Thirty-four FUDS and 48 active DOD installations which may contain CWA were identified in an Interim Survey and Analysis Report by the USACMDA Program Manager for Non-Stockpile Chemical Material (NSCM). Since there are multiple burial sites on some installations there may be 215 potential burial sites at these 82 installations which require remediation. The CWA includes munitions, rockets, projectiles, drums and ton containers. The chemical agents listed include mustard (H), lewisite (L), Tabun (GA), Sarin (GB), VX, hydrogen cyanide (AC), cyanogen chloride (CK) and phosgene (CG), BZ, and CS (USACMDA, 1993).

These installations were identified in record searches as sites of CWA storage, shipping, munition filling, production, research and testing and are potential small burial site locations. NSCM is divided into five categories: buried CWM; recovered chemical weapons; former chemical agent production facilities; binary chemical weapons; and miscellaneous CWM. The assessment and remediation of buried CWM poses the greatest challenge, due to the numerous locations on and off DoD installations. These burial sites have been placed into four categories: chemical agent identification sets (CAIS); small burials sites with no explosives; small burial sites with explosives; and large burial sites with and without explosives (USACMDA, 1993).

Up until the late 1960s, open burning and burial were the acceptable methods for disposal of CWA. These burial sites on FUDS may pose a threat to the public if they are disturbed or excavated, and may contaminate groundwater or drinking water supplies.

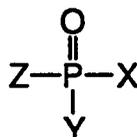
## 2 ORGANOPHOSPHORUS AGENTS

The organophosphorus (OP) agents were first developed by German scientists prior to World War II. Biologically speaking, the OP agents act by inhibiting acetylcholinesterase (AChE), a critical chemical link in the transmission of nerve impulses. AChE acts as a catalyst to inactivate acetylcholine (ACh), an important transmitter substance for nerve impulses from one motor endplate across the neuromuscular synapses. The OPs combine irreversibly with AChE, in the same manner as the ACh, and the resulting accumulation of the ACh causes breakdown of both the voluntary and involuntary nervous systems. The effects will be observed in the skeletal muscles and the central nervous system.

The first OP selected by the German scientists as a agent was Tabun (GA), ethyl N,N-dimethyl phosphoraminoxyanidate. GA was followed in rapid succession by the more toxic OPs Sarin (GB), isopropyl methylphosphonofluoridate, and Soman (GD), pinacolyl methylphosphonofluoridate. After the Second World War, the U.S. began production of GB at Rocky Mountain Arsenal, but also continued research into still more toxic agents which resulted in the development of VX, O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate. VX was produced and munitions were filled at the Newport Army Ammunition Plant (NAAP), Indiana, from 1961 to 1968.

### 2.1 Chemical Properties

The OPs are of the general structure shown in Figure 1.



where

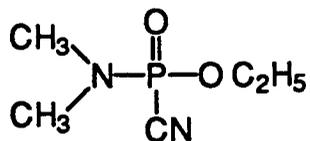
- Y is O or S
- Z is an alkyl, alkoxy alkylamino, or cycloalkyl
- X is F, CN, N<sub>3</sub>, SR', etc.

Figure 1. General Structures of Organophosphorus.

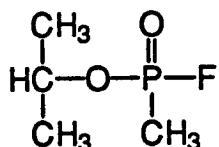
Thousands of potential OPs were screened for use as chemical agents and pesticides; however, only four are of importance in the assessment and cleanup of U.S. non-stockpile sites-GA, GB, GD and VX. The chemical/physical characteristics of the OP agents are listed in Table 1 and their structures are shown in Figure 2.

TABLE 1. CHEMICAL AND PHYSICAL PROPERTIES

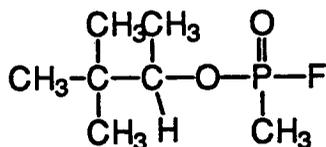
Military Name	Common Name	Chemical Name	Molecular Weight	Density (g/mL)	Vapor Pressure (mmHg)	Volatility (mg/m <sup>3</sup> )	H <sub>2</sub> O Solubility (g/L)
GA	Tabun	Ethyl N,N-dimethylphosphoramidate	162.1	1.08	0.07	610	50 - 100
GB	Sarin	Isopropyl methylphosphonofluoridate	140.1	1.09	2.9	22000	∞
GD	Soman	Pinacolyl methylphosphonofluoridate	182.2	1.02	0.40	3900	20 - 30
VX		O-ethyl S-(diisopropylamino ethyl) methylphosphonothioate	267.4	1.008	0.0007	10.5	10 - 50
HD	Distilled Mustard	Bis(2-chloroethyl) sulfide	159.1	1.27	0.165	958	0.8
L	Lewisite	Dichloro-2-chlorovinyl arsine	207.3	1.88	0.58 Trans 0.40 cis 1.562	6500	0.5 Trans 2.3 mg/l cis 4.5
CX	Phosgene Oxime	Dichloroformoxime	113.9		13 @ 40°C	22000	hydrolyzes
CG	Phosgene	Carbonyl chloride	98.9	1.37	1400	64	9



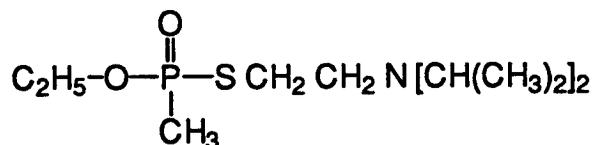
TABUN (GA) - ethyl n,n-dimethyl phosphoramidocyanidate



SARIN (GB) - isopropyl methylphosphonofluoridate



SOMAN (GD) - pinacolyl methylphosphonofluoridate



VX - O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate

Figure 2. Structure of Organophosphorus Chemical Warfare Agents.

GA, GB, GD and VX are either colorless or amber, odorless liquids which are soluble in water and many organic solvents. GB is very volatile with a vapor pressure of 2.9 mm Hg at 25°C. GD, GA and VX are successively less volatile with a vapor pressures of 0.4 mm Hg, 0.07 mm Hg, and 0.0007 mm Hg, respectively (USA FM 3-9, 1975). GB vapors are readily absorbed by most materials, however; the high volatility results in almost complete desorption in a few hours after removal from the source. This ready uptake and release presents a potential hazard if contaminated materials are placed in closed spaces where lethal concentrations could build up.

## 2.2 Hydrolysis of GB and GD

The hydrolysis of the fluorophosphonates GB or GD occurs first through the loss of a fluorine, then more slowly through the loss of the alkoxy group. The hydrolysis products, the corresponding phosphonic acids, are generally non-toxic. The hydrolysis pathways for GB/GD phosphonofluoridates are shown in Figure 3.

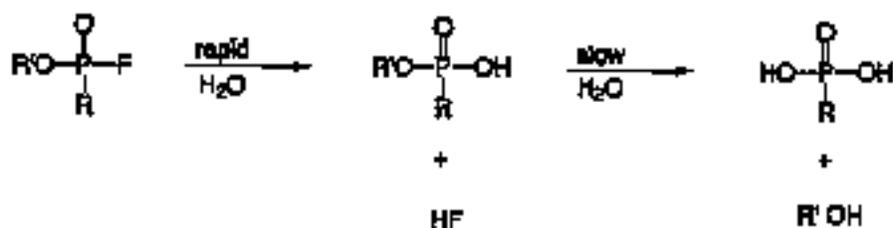


Figure 3. Hydrolysis Pathways for GD and GB.

In most reported studies on the decomposition of GB in soils, the parent and the primary and secondary hydrolysis products, O-isopropyl methyl phosphonate and methylphosphonic acid, were identified. In addition a GB impurity, diisopropyl methyl phosphonate has also been found (ASTDR, 1988). The hydrolysis products are acids or, in alkaline media, the corresponding salts. While the original fluorophosphonates can be extracted into organic solvents for analysis, the byproducts are much more hydrophilic and are not quantitatively extractable. Table 2 lists environmental contaminants which may be identified with sites previously contaminated with G type agents.

The hydrolysis rates of GB and GD are a function of the temperature and pH of the medium, with the rate being minimum between 4 and 6. Figures 4 and 5 illustrate the effect of pH on the hydrolysis half-life of GB and GD over the pH range of from 2 to 10, as reported by several investigators (Epstein 1974; Epstein and Mosher 1968; Grochowski and Korecki, 1965; Wolinski and Sawicki, 1964; USA FM 3-9 1975; Britton 1986; Forsman et al., 1979; Larsson 1957; Franke 1982). The hydrolysis rate of GD was at least equal to and maybe even exceed GB at the same temperature, in contrast to some authors contention that GD is more stable in aqueous solutions (Trapp 1985). It must be noted that  $t_{1/2}$  is the time to achieve 50% decomposition of the agent. It would take approximately 6.7 times the  $t_{1/2}$  for 99% reduction of the parent compound. Figures 6 and 7 illustrate the time necessary ( $20 \times t_{1/2}$ ) to achieve a  $1 \times 10^6$  reduction of GB or GD as a result of hydrolysis. This would result in the neat agent being degraded to below 1 ppm.

TABLE 2. ENVIRONMENTAL CHEMISTRY OF G-TYPE AGENTS

Agent	Chemical Name	Structure	Reg #	Source
GB	Isopropyl methyl phosphonofluoridate	$\begin{array}{c} \text{O} \\   \\ \text{IP-O-P-F} \\   \\ \text{CH}_3 \end{array}$	107-44-0	Parent Agent
IPA	Isopropyl methylphosphonic acid	$\begin{array}{c} \text{O} \\   \\ \text{IP-O-P-OH} \\   \\ \text{CH}_3 \end{array}$	1832-54-0	Hydrolysis of GB
IPr	Isopropyl	$\text{CH}_3\text{-CH-CH}_3$	-	-
GD	O-phacetyl methylphosphonofluoridate	$\begin{array}{c} \text{O} \\   \\ \text{Ph-O-P-F} \\   \\ \text{CH}_3 \end{array}$	DB 84-0 50042-24-8	Parent Agent
PMPA	O-phacetyl methylphosphonic acid	$\begin{array}{c} \text{O} \\   \\ \text{Ph-O-P-OH} \\   \\ \text{CH}_3 \end{array}$	515-52-4	Hydrolysis
DMP	Dimethyl methylphosphonate	$\begin{array}{c} \text{O} \\   \\ \text{CH}_3\text{-P-O-CH}_3 \\   \\ \text{O-CH}_3 \end{array}$	18002-90-1	Hydrolysis
PN	Pinacolyl	$\begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3)_2\text{C-C} \\   \\ \text{H} \end{array}$	-	-
GA	Ethyl n,n-dimethylphosphor amthiocyanidate	$\begin{array}{c} \text{O} \\   \\ \text{C}_2\text{H}_5\text{-O-P-CN} \\   \\ \text{N(CH}_3)_2 \end{array}$	77-81-0	Parent Agent
EDMA	o-ethyl n,n-dimethylphosphoramidate	$\begin{array}{c} \text{O} \\   \\ \text{C}_2\text{H}_5\text{-O-P-OH} \\   \\ \text{N(CH}_3)_2 \end{array}$	Not found	Hydrolysis of GA
EPC	o-ethyl phosphorocyanidate	$\begin{array}{c} \text{O} \\   \\ \text{C}_2\text{H}_5\text{-O-P-CN} \\   \\ \text{OH} \end{array}$	117529-17-0	Hydrolysis of GA
PC	Phosphorocyanidate	$\begin{array}{c} \text{O} \\   \\ \text{HO-P-CN} \\   \\ \text{OH} \end{array}$	23052-43-0	Hydrolysis of GA
PA	Dimethylphosphoramidate	$\begin{array}{c} \text{O} \\   \\ \text{HO-P-OH} \\   \\ \text{N(CH}_3)_2 \end{array}$	33070-51-5	Hydrolysis of GA
DMPAC	Dimethylphosphoramidocyanidate	$\begin{array}{c} \text{O} \\   \\ \text{HO-P-CN} \\   \\ \text{N(CH}_3)_2 \end{array}$	83917-41-0	Hydrolysis of GA

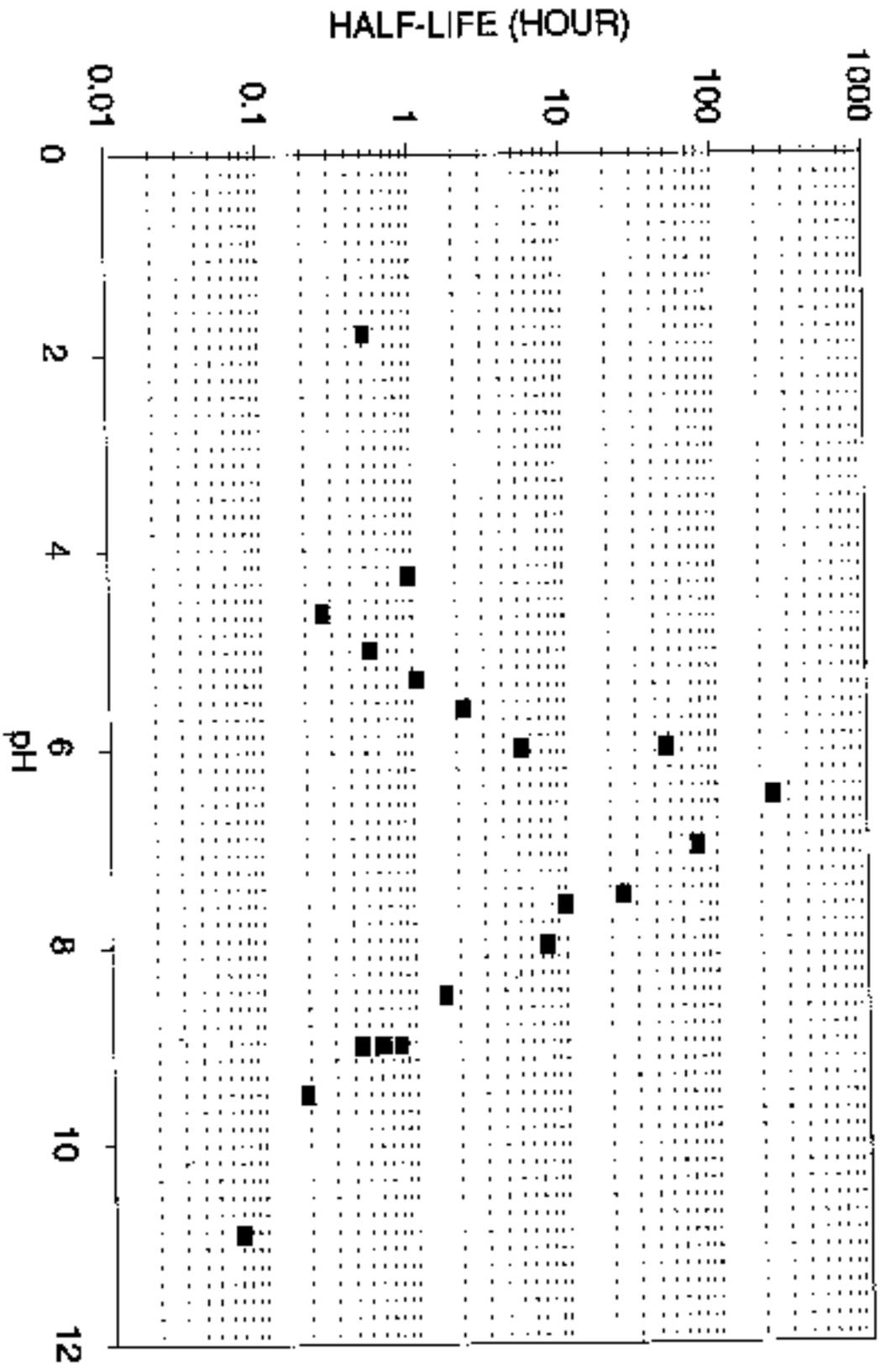


Figure 4. GB Hydrolysis VS pH.

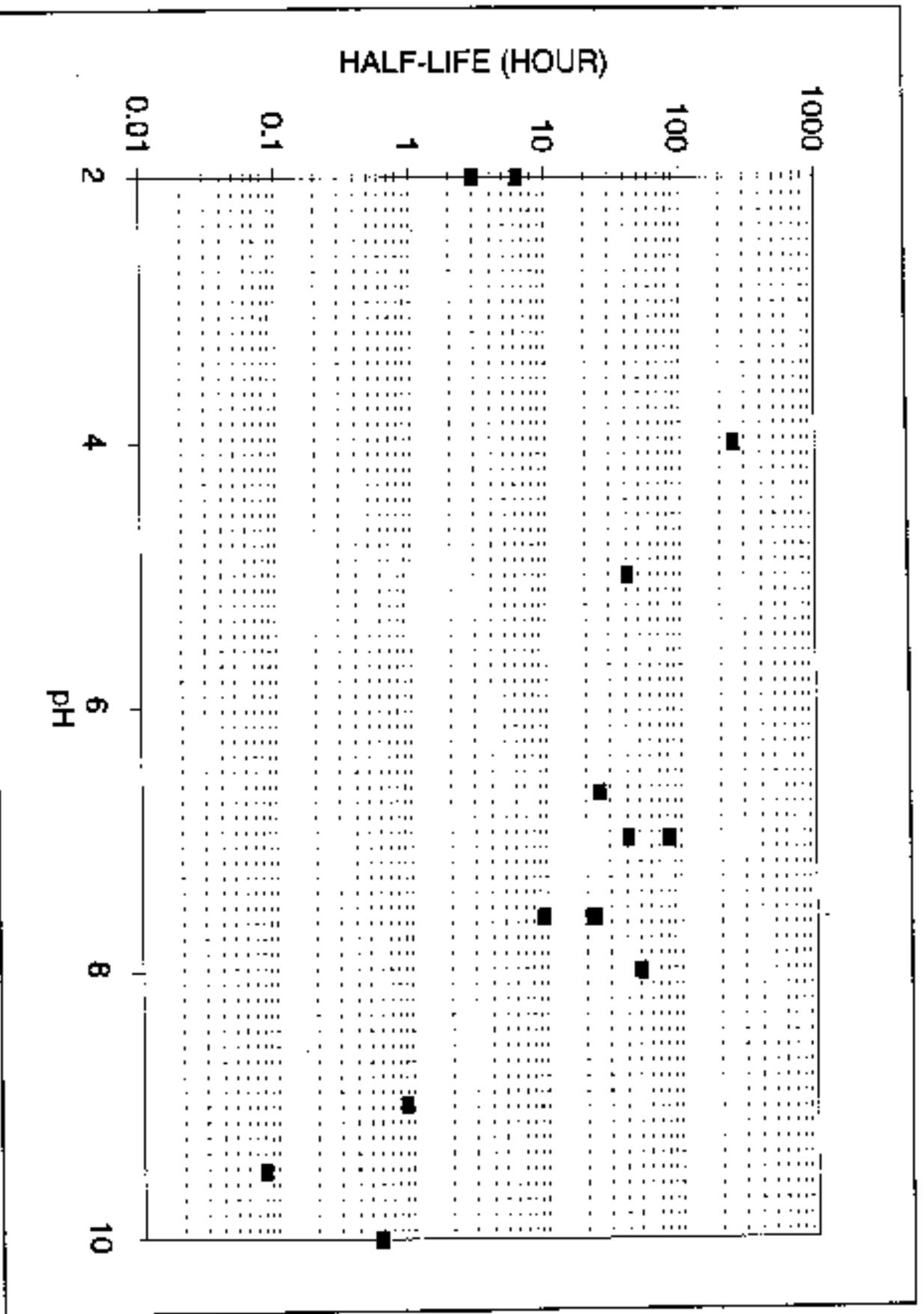


Figure 5. GD Hydrolysis VS PH.

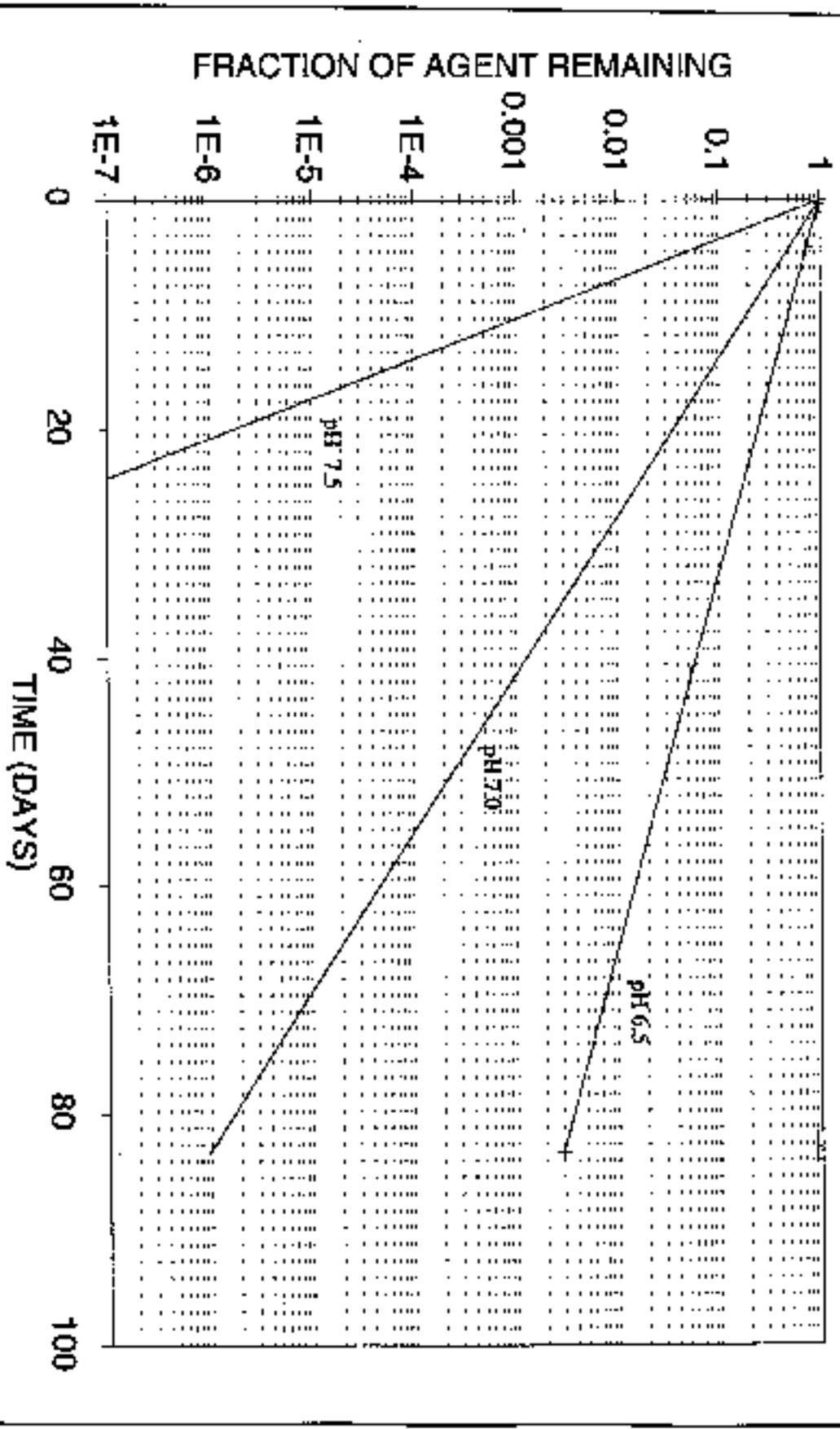


Figure 6. Degradation of GB Versus Time for Neutral pHs.

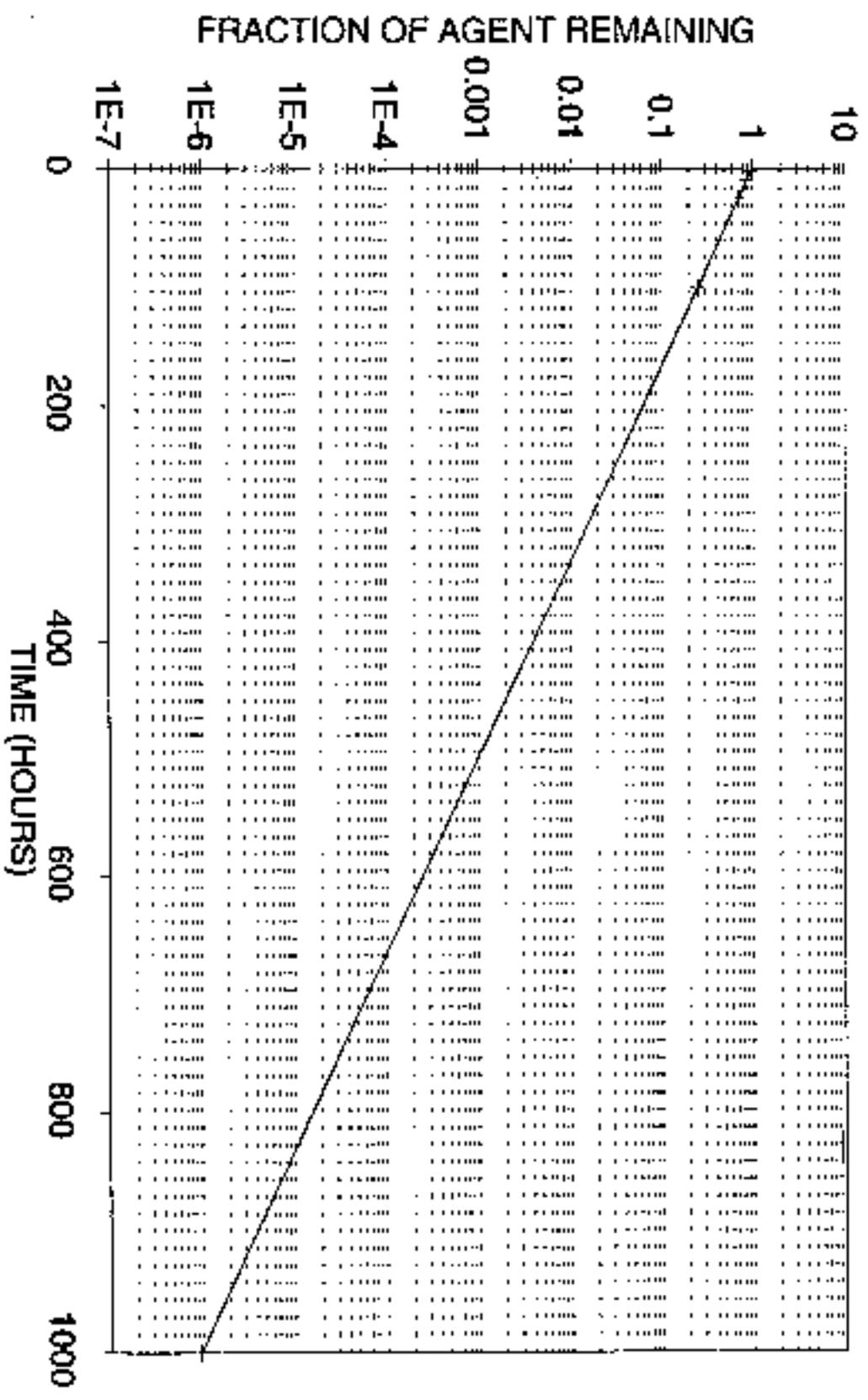


Figure 7. Degradation of GD Versus Time.

For unbuffered systems above pH 6, the GB hydrolysis reaction may be self-limiting due to the production of isopropyl methylphosphonic acid ( $pK_a = 1.96$ ) and HF ( $pK_a = 3.14$ ), both weak acids, which will reduce the pH into the 4-6 range where the hydrolysis is at a minimum. Below the neutral region, the reaction will be accelerated by the production of these acid byproducts and the resulting lowered pH of the system (Epstein, 1974; Buckles, 1947). Shih and Eilin (1984) measured the production of acid from the hydrolysis of GB and GD, and showed that in unbuffered systems the initial agent concentration will affect the hydrolysis rate. They were able to predict the concentration of GB or GD remaining by measuring the pH of the final solution.

For GD there is insufficient data to clearly determine if the hydrolysis is either acid or base catalyzed. From Figure 5, there appears to be a slight increase in the reaction rate at pH less than 4 and greater than 8. Five percent NaOH GD has a 5 minute half-life, suggesting that base catalysis does occur in more alkaline solutions (Britton, 1986). As with GB, the hydrolysis of GD results in the production of weak acids which will significantly inhibit the hydrolysis rates in unbuffered systems above pH 7. Sides et al., (1981) demonstrated that 50 ml of unbuffered water in contact with 50 mg of neat GD will quickly reach a stable concentration of 0.005 molar (0.9 g/L); whereas, the GD concentration in buffered (pH 9.6) solutions will initially increase, but will quickly begin to decrease as the GD hydrolyzes.

GD thickened with poly (methyl methacrylate) to increase the viscosity and reduce the volatility had a rate of hydrolysis equivalent to the rate of the neat agent; however, the thickened GD appeared to solubilize at a slower rate (Sides, 1981). Thus, while the rate of solution for neat GD does not appear to be rate limiting for the hydrolytic decomposition, the higher viscosity of the thickened agent may inhibit the hydrolysis of the agent under quiescent conditions.

The other two important variables in the hydrolysis rate of GB and GD are temperature and the type, and concentration of dissolved ionic species. Figure 8 illustrates the effect of temperature on GB half-life for solutions with a pH of 7.0. Epstein (1974) derived the following equation to predict the half-life as a function of pH and temperature:

$$\log t_{1/2} = \frac{5039}{T(^{\circ}K)} - 8.035 - pH$$

There is approximately a four-fold increase in the rate per  $10^{\circ}$  increase in temperature in more basic solutions ( $> pH 6.5$ ), and a two-fold increase in acidic solutions ( $< pH 4$ ) (Epstein 1974).

Many metals such as magnesium, copper, cobalt, manganese, cerium, aluminum and calcium have the ability to accelerate the hydrolysis of GB (Franke, 1982). The impact of dissolved constituents is complicated by the effect of pH on the hydrolysis of the metals which catalyze the hydrolytic decomposition of GB and GD. Interestingly, Epstein (1974; Epstein and Mosher, 1968) determined that the hydrolyzed metal cation ( $MeOH^+$ ) catalyzes the reaction rather than the unhydrolyzed, free metal species ( $Me^{++}$ ). It is postulated that this results from the electrophilic reaction of the metal hydroxo ion, which indirectly catalyzes the nucleophilic attack of hydroxide ion on the P atom, increasing the polarity of the fluorophosphate (Franke, 1982).

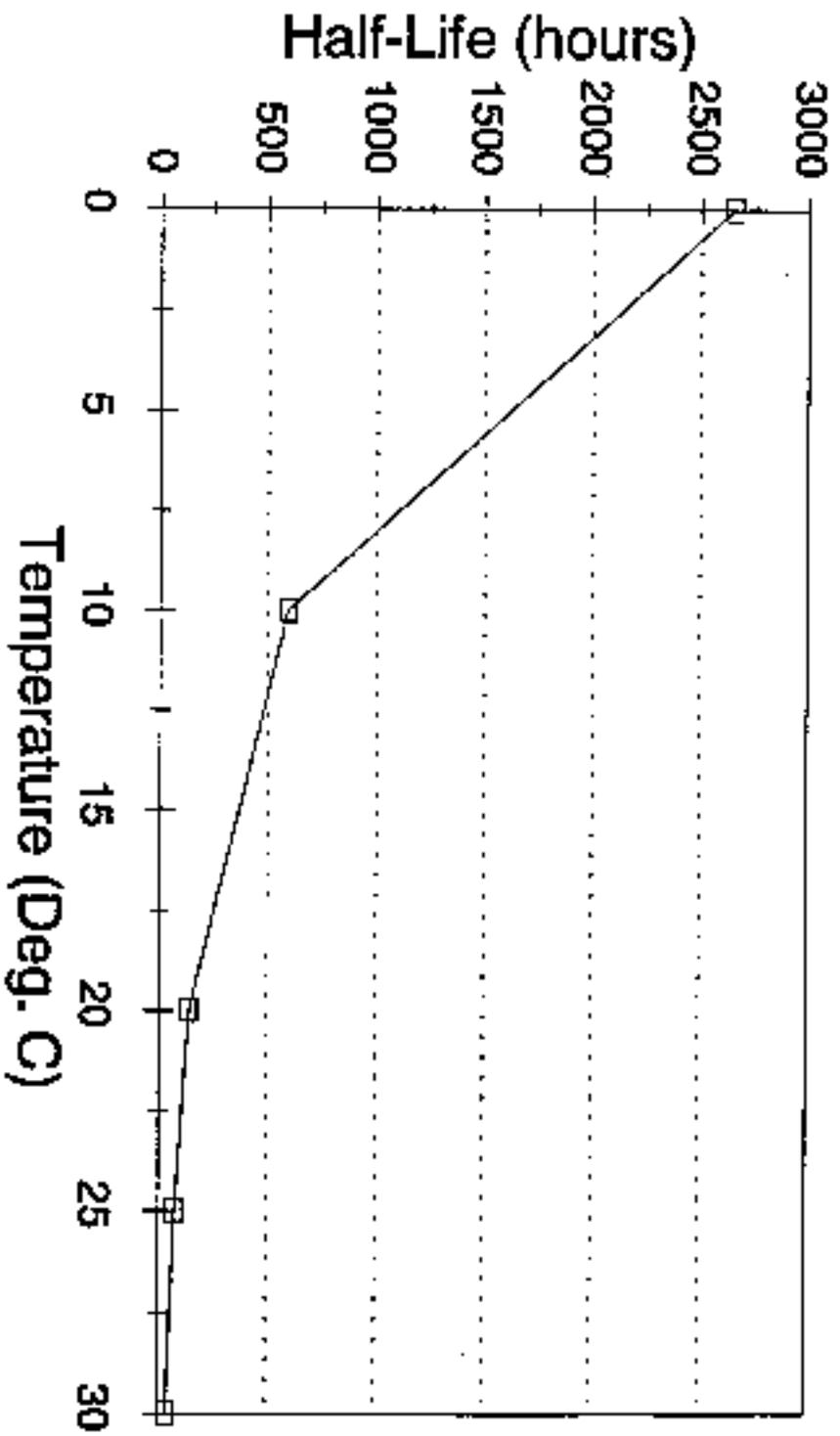


Figure 8. Effect of Temperature on Half-Life.

For the three divalent metals investigated by Epstein, the order of catalytic effectiveness copper, manganese, and magnesium reflects the order of their first hydrolysis products ( $pK_1$ ) of 8, 10.6 and 11.4, respectively. At pH values below the  $pK_1$ , the unhydrolyzed species ( $Me^{2+}$ ) predominates; and at pH values above the  $pK_1$ , the majority of the total concentration of the metal exists as the hydrolyzed species ( $MeOH^+$ ). This has also been observed with magnesium and calcium at very high pHs, and uranyl ion in dilute solutions at low pHs (Epstein and Rosenblatt 1958). The effect of copper on the half-life of GB at pHs below 7 can be estimated by the following equation (Epstein 1974):

$$t_{1/2} = \frac{5.7 \times 10^3 (H^+)}{(Cu_{tot})}$$

Above pH 7, the low solubility of copper hydroxide reduces the catalytic effect to a level where it is probably insignificant compared to the effect of pH alone. The effect of trace dissolved ions can also be seen by comparing the hydrolysis rate in seawater and distilled water. At pH 7.9 in seawater,  $t_{1/2}$  was 0.4 hour compared to approximately 7.5 hours at pH 8.0 in distilled water (Epstein 1970). Particularly in groundwater systems, the presence of metals such as iron may participate in catalytic reactions and accelerate the hydrolysis of the organophosphorous agents. This catalytic effect is also observed with metal-organo chelates. This effect has been exploited for detoxification, particularly for protecting the skin (Courtney et al., 1957 in Franke 1982).

### 2.3 Hydrolysis of VX

VX hydrolyzes very slowly except at very high pHs. In neutral aqueous solutions, the  $t_{1/2}$  for hydrolysis of VX is in excess of 2,300 hours at 25°C (Epstein et al., 1974). The reaction rate accelerates with increasing hydroxide concentration, so that at pH 13, the  $t_{1/2}$  was reported to be 16 minutes (USA FM 3-9, 1975), and 17 minutes at pH 12.9 (Epstein et al., 1974). The effect of pH on the hydrolysis half-life is shown in Figure 9. In contrast to GB, and possibly GD, the hydrolysis of VX is not accelerated at low pHs. However, it is apparent there is a substantial base catalyzed increase in the reaction rate at higher pHs. Figure 10 illustrates the time required to achieve a  $1 \times 10^6$  reduction in VX for a neutral pH.

As shown in Figure 11, different reactions predominate for the hydrolysis of VX at acid, neutral and alkaline pHs. In the acidic region below pH 7, only ethyl methyl phosphonic acid and mercaptide ion are formed; from pH 7 to 10, cleavage of P-S, O-C, and S-C bonds takes place simultaneously to form ethyl methyl phosphoric acid, S-diisopropylaminoethylmethylphosphothioic acid (or the unprotonated -thioate), S-diisopropylaminoethylmercaptan, and ethanol. A third reaction is also postulated to account for the formation of bis(diisopropylaminoethane)sulfide from the reaction of ethyleneimmonium ion and mercaptan; and above pH 10 where only P-S cleavage is observed. At pH 9, three times more bis(diisopropylaminoethane)sulfide is formed than is bis(diisopropylamino)disulfide from the oxidation of mercaptan. At pH 10, the quantities of each is approximately the same. This is attributed to competition between mercaptan oxidation and reaction

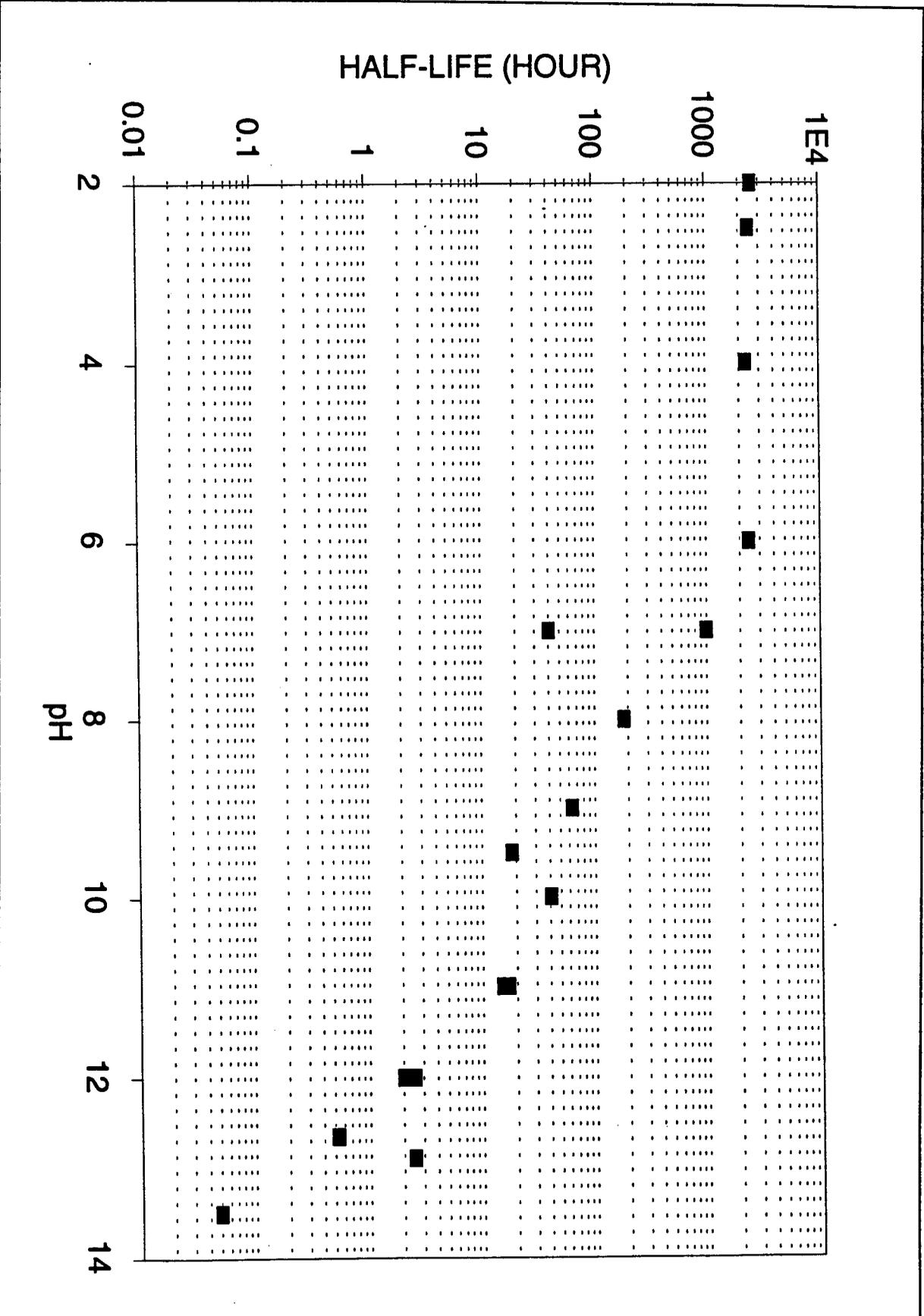


Figure 9. VX Hydrolysis VS PH.

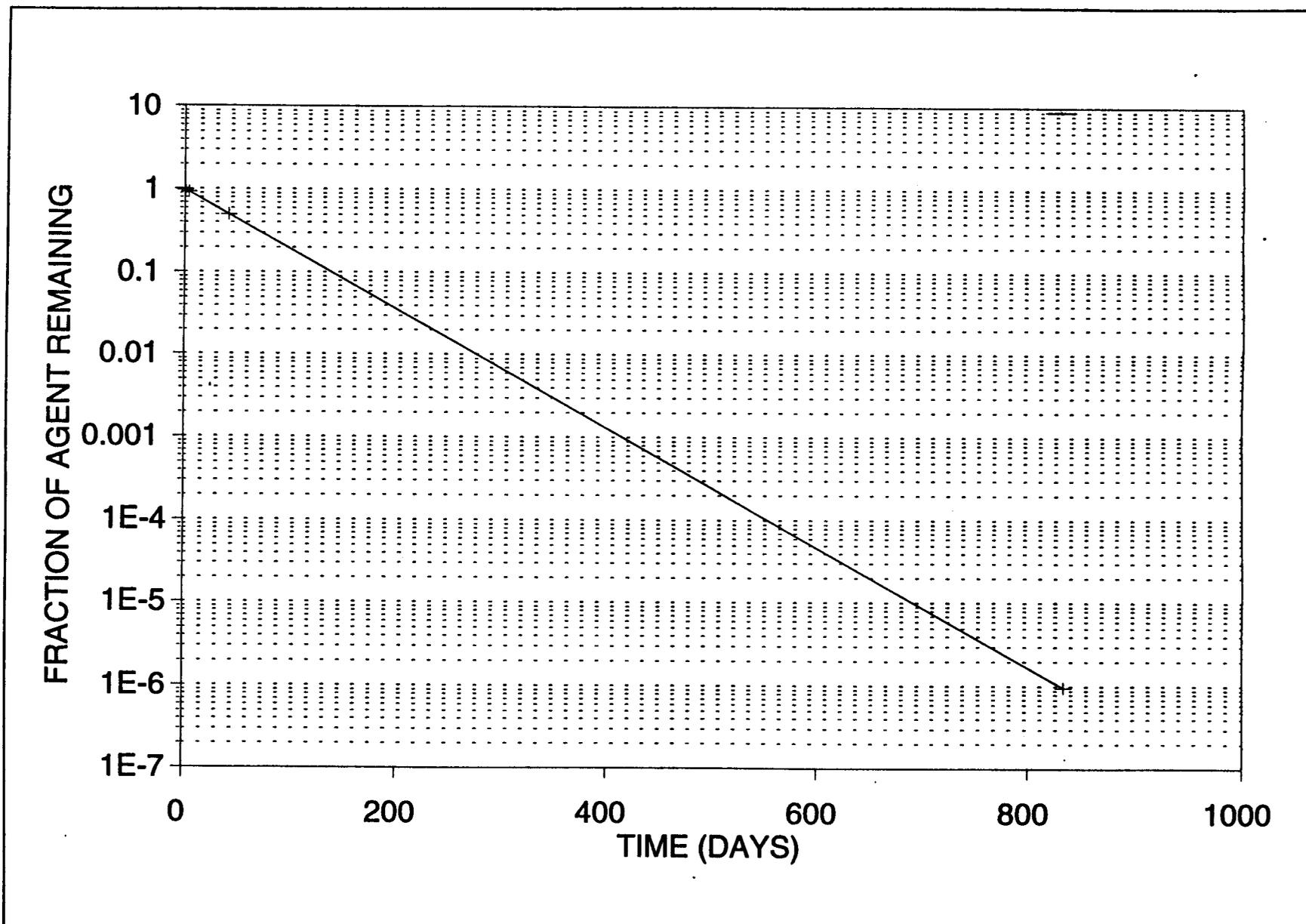


Figure 10. Degradation of VX Versus Time.

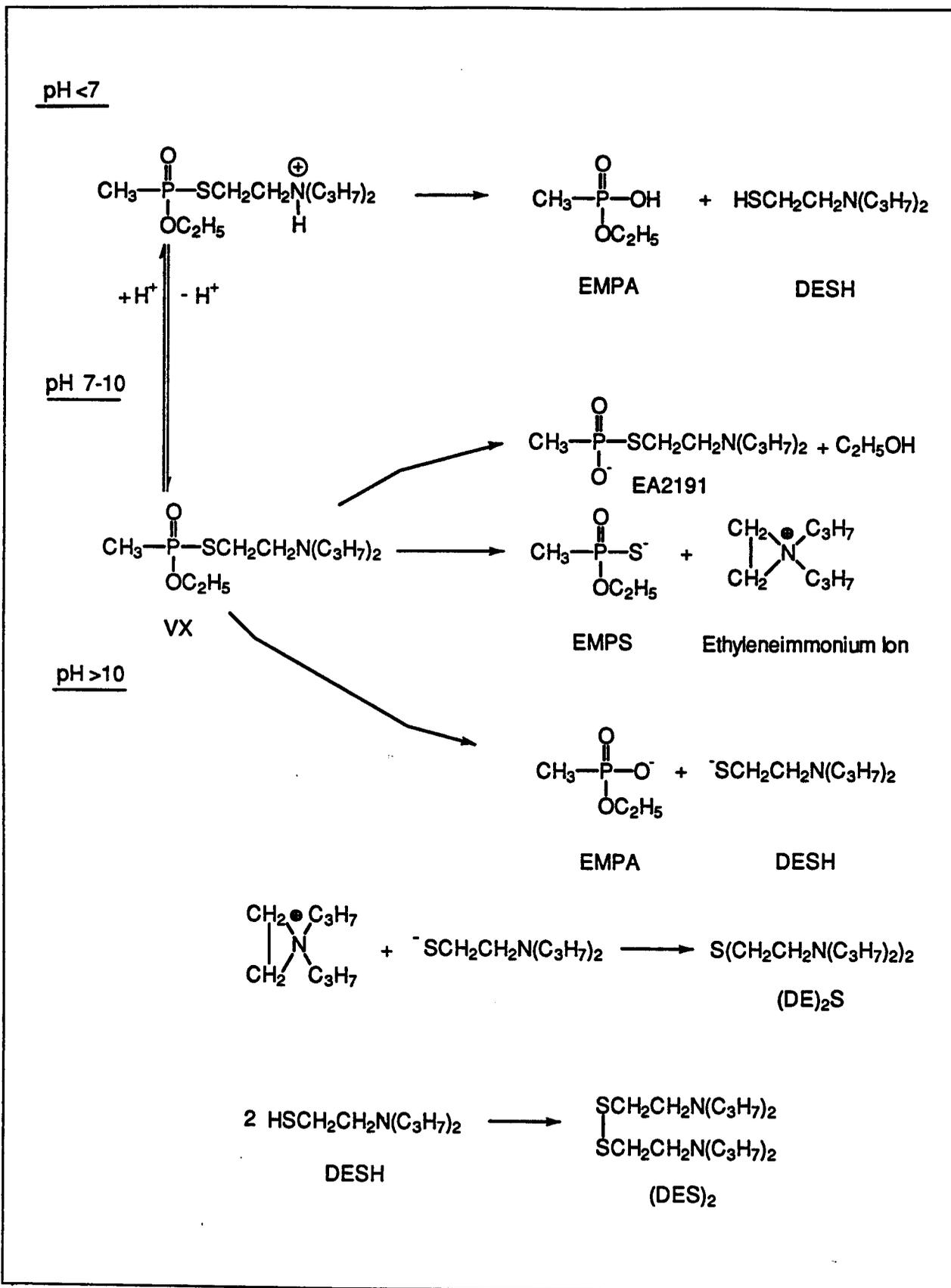


Figure 11. Hydrolysis Reactions of VX.

with ethylenimmonium ion (Epstein et al., 1974). It must also be noted that, although VX is degraded in aqueous systems, the initial hydrolysis product of VX, EA 2191, has a toxicity comparable to VX; while the other hydrolysis products are non-toxic (Forsman et al., 1979). At pH 7.2, EA 2191 can build up to 40% from the hydrolysis of VX. Table 2 lists the VX decomposition products of environmental relevance.

#### 2.4 Hydrolysis of GA

Tabun (GA) is unstable in neutral aqueous solutions with attacks occurring at both the P-N and P-CN bonds, as shown in Figure 12. This results in a dramatic decrease in the toxicity with time in aqueous solutions (Holmstedt, 1951). Unlike the other organophosphorous agents, GA is derived from phosphoric acid and has no P-alkyl bonds. In acidic solutions, the protonation of the N atom increases the polarity of the P-N bond and allows nucleophilic attack by the water molecule. As the pH decreases, this cleavage of the P-N bond is accelerated (Holmstedt, 1951; Franke, 1982). In alkaline solutions, nucleophilic attack by OH<sup>-</sup> results in cleavage of the P-CN bond and the release of cyanide ion. The initial reaction cleavage of the P-CN bond is rapid, but subsequent reactions are much slower (Sanches 1993). Table 3 lists the GA hydrolysis products. The influence of pH on the hydrolysis reaction is illustrated in Figure 13 (Larsson 1953, Larsson 1958, Forsman et al., 1979, Britton 1986). In the pH range of 4-5, the reported half-life for GA of 7 hours is much shorter than the other G agents (USA FM 3-9, 1975). The effect of pH on the hydrolysis half-life of GA is illustrated in Figure 13, and the time required to reduce the neat agent to below 1 ppm is shown in Figure 14.

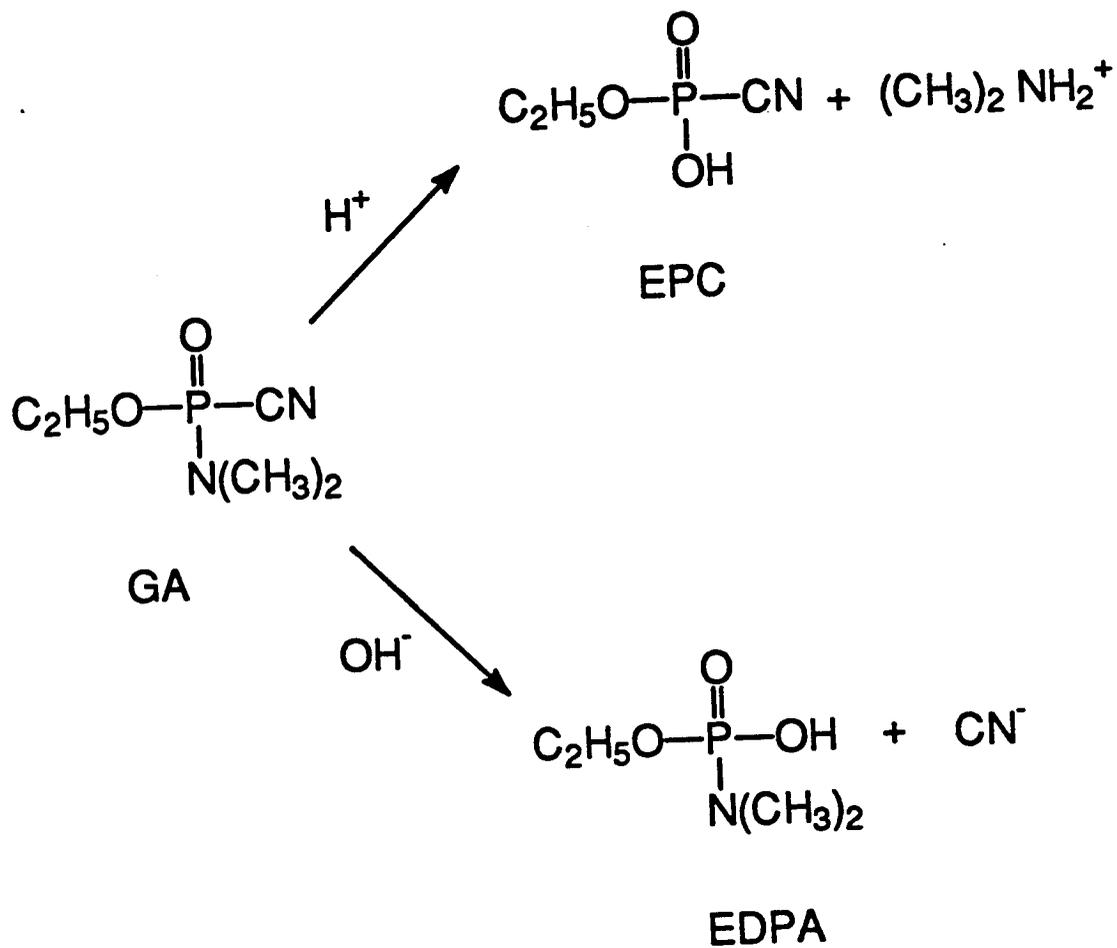


Figure 12. Hydrolysis Reactions of GA.

TABLE 3. ENVIRONMENTAL CHEMISTRY OF VX

Agent	Chemical Name	Structure	Reg #	Source
VX	O-ethyl S-(2-diisopropyl amino ethyl) methylphosphonothioate		50782-69-9 51848-47-6 53800-40-1 70938-84-0	Percent Agent
DESH	Diisopropylaminoethyl mercaptan	DIPAE-SH	5482-07-9	Hydrolysis of VX
EMPA	Ethyl methylphosphonic acid		1832-53-7	Hydrolysis of VX
EMPS	Ethyl methylphosphonothioic acid		18005-40-8	Hydrolysis of VX
DEOH	Diisopropylaminoethanol	DIPAE-OH	96-38-0	Hydrolysis of VX
DE <sub>2</sub> S	Bis(2-diisopropylaminoethyl) sulfide	DIPAE-S-DIPAE	110501-56-9	Hydrolysis of VX
DES <sub>2</sub>	Bis(2-diisopropylaminoethyl) disulfide	DIPAE-S DIPAE-S	65332-44-7	Oxidation of DESH
DDP	Diethyl dimethylpyrophosphonate		32288-17-8	Agent impurity
EA2191	S-(2-diisopropylaminoethyl) methylphosphonothioate		73207-98-4	Hydrolysis of VX
MPA	Methylphosphonic acid		993-13-3	Hydrolysis of GB, GD, and VX
DPCA	N-Chlorodiisopropylamine	(iPr) <sub>2</sub> -N-Cl	24948-81-0	Chlorination
IPCA	N-Chloroisopropylamine	iPr-N-H-Cl	26245-56-7	Chlorination
DIPAE	Diisopropylaminoethyl	(iPr) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub>	-	-
DIPC	Diisopropylcarboimide	iPr-N=C-N-iPr	693-13-0	Stablizer
DIPU	1,3 Diisopropylurea		4128-37-4	Hydrolysis of DIPC

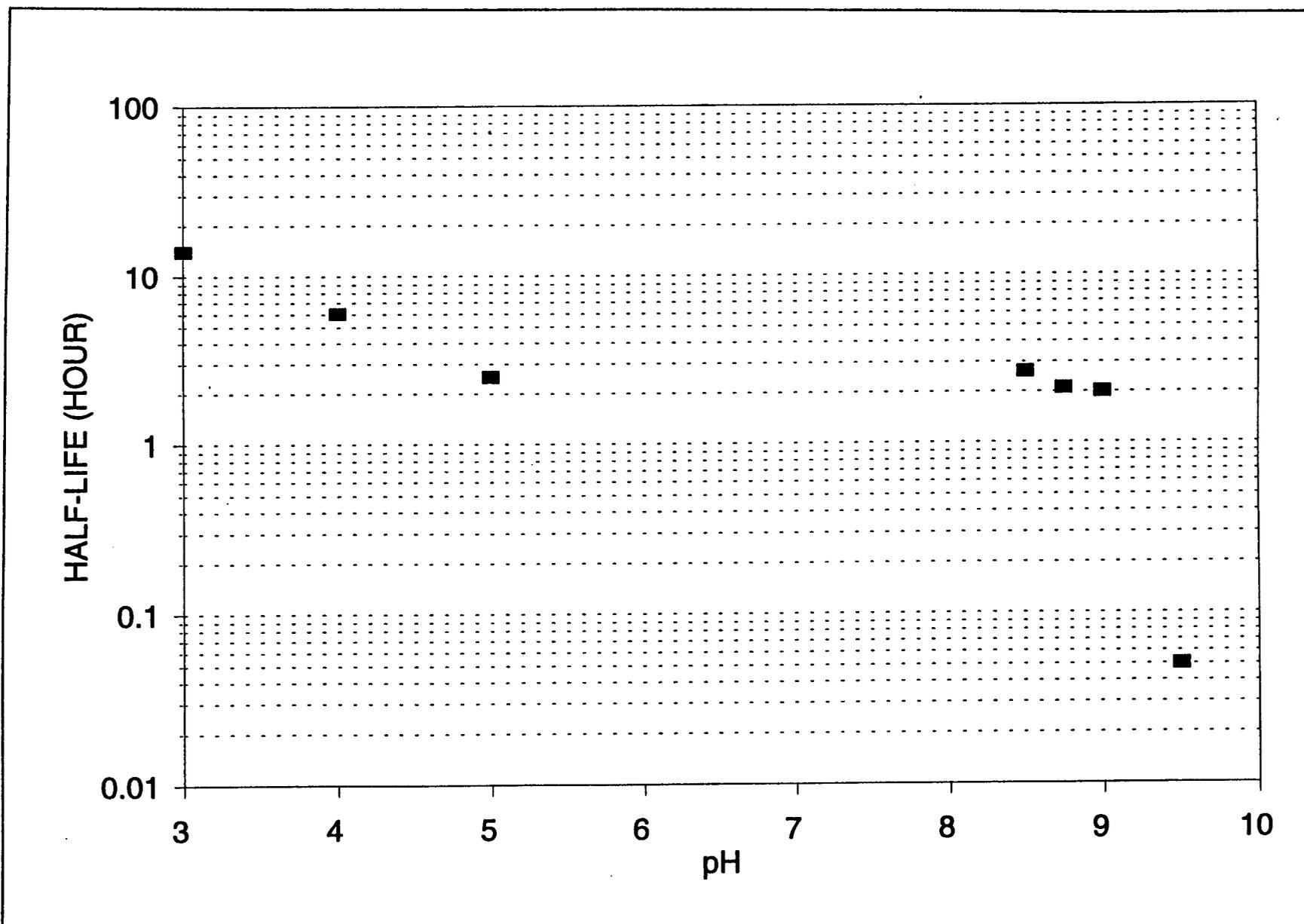


Figure 13. GA Hydrolysis VS PH.

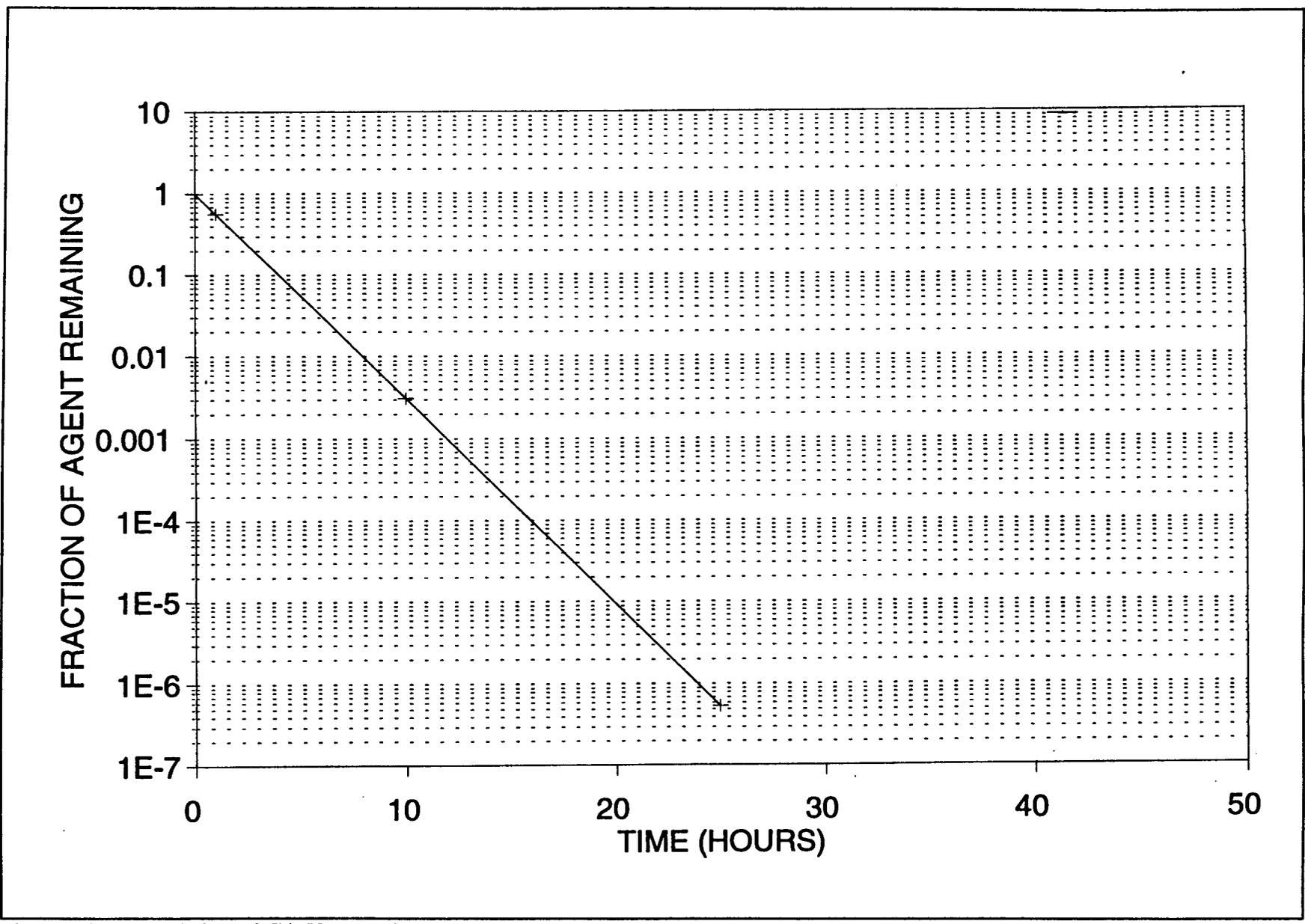


Figure 14. Degradation of GA Versus Time.

### 3 MUSTARD AGENTS

The sulfur mustard family of vesicants were one of the first chemical warfare materials used in World War II. In the US and England, the bis(2-chloroethyl)thioether or bis(chloroethyl)sulfide is called "mustard gas" because of its odor. After its use near Ypres France, it is identified as "Yperite" in some early publications. Commercial sulfur mustard (H) is normally a mixture of a large number of homologs with a  $\text{ClC}_2\text{H}_4\text{S}$ - moiety which is more toxic than distilled mustard (HD). Oxygen mustard (T), 1,2 bis(2chloroethylthio)ether, is the other important sulfur mustard agent identified as a possible contaminate at FUDS (USACMD 1993). HT is a mixture of 60% HD and 40% T, and has a greater persistence, lower freezing point and is more stable than HD (USA FM 3-9, 1975).

Pure sulfur mustard is a colorless, odorless, oily liquid; however, the commercial product has a yellow/brown color with a sweet odor due to contaminants (Franke, 1982). Heating mustard to its boiling point results in thermal degradation and the formation of products with a strong garlic and mustard odor. HD is classified as a persistent agent due to its low vapor pressure (0.165 mm Hg). HD has a low solubility in aqueous solutions, but it dissolves readily in organic solvents. Mustards can penetrate into many materials including rubbers, plastics, wood and concrete and still retain its toxic properties. Therefore, unless decontaminates can penetrate into the materials, the hazard of vapor exposures and skin contact will still remain.

#### 3.1 Hydrolysis of H

Because of the low aqueous solubility of mustards, the rate of hydrolysis is dependent on the rate of solvation. This will be controlled by the surface area exposed to the solvent which in turn is a function of particle size and turbulence. Complicating the picture is the tendency, in quiescent conditions, of mustards to polymerize at the mustard/solution interface, further shielding the bulk of the agent from hydrolysis reactions. Experience has demonstrated that mustards can remain stable under water for years if there is little turbulence or mixing (Sanchez 1993, Trapp 1985, Franke 1982). Small (1984) calculated it took 867 hours for a 1 cm diameter HD droplet in quiescent water at 18°C to decrease by one half. Demek et al., (1970) determined that the dissolution rate for HD in flowing seawater would be approximately ten times as high as in quiescent seawater. The effect of temperature on the solution rate (S) of mustard in distilled water can be calculated from the following equation (Rosenblatt et al., 1975).

$$S = 233.7 \times e^{-\frac{6215}{T}}$$

The hydrolysis of H is pH-dependent, with reversible reactions taking place in acidic solutions and decomposition accelerated in neutral and basic mediums. The hydrolysis of mustard takes place in two stages (Franke 1982). In the first stage, a heterocyclic sulfonium cation is formed (Figure 15). These onium compounds are highly reactive, and their interaction with enzymes, DNA and proteins is the basis for the skin toxicity of mustards (Trapp 1985). As illustrated in Figure 16, in the second stage the sulfonium cation initiates series of reactions between water and intermediate products.

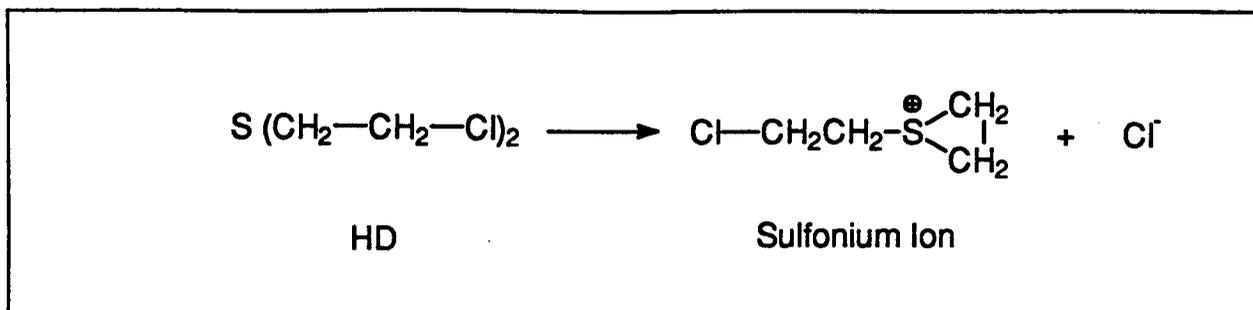


Figure 15. Formation of Sulfonium Ion in First Stage of HD Hydrolysis.

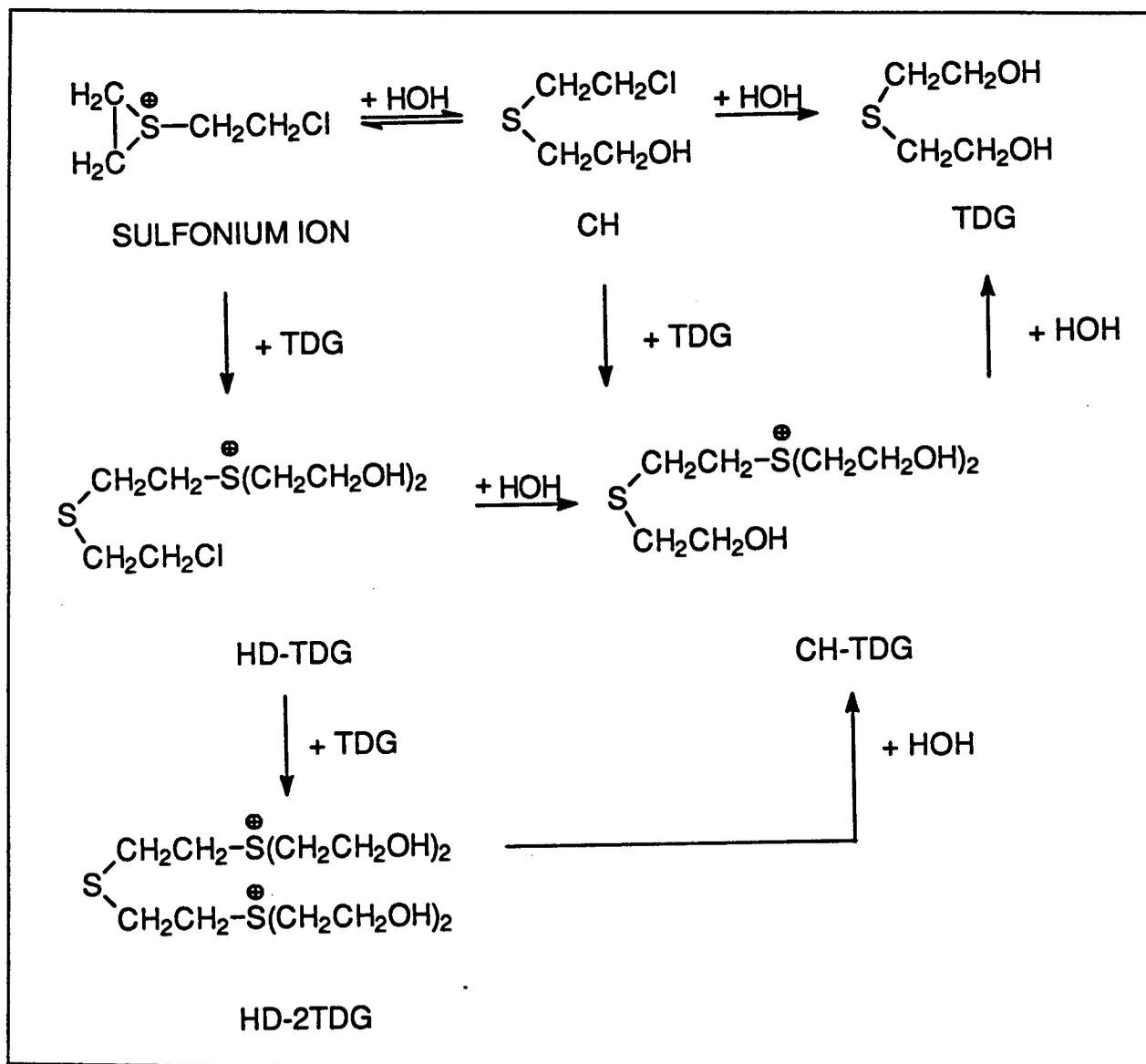


Figure 16. Second Stage of HD Hydrolysis.

The formation of the first intermediate is the rate limiting step in hydrolysis; however, the overall decomposition is still controlled by the dissolution rate. Anything that increases the solution rate, i.e., mixing or addition of a cosolvent such as alcohol or acetone, will increase the apparent hydrolysis rate. The maximum rate of hydrolysis is reported to be 104 mg/min/L at 25°C for mustard gas in equilibrium with water (Forsman 1979).

The rate of HD hydrolysis is difficult to predict due to the dependence on the rate of solvation. Although mustard in solution can undergo a relatively rapid hydrolysis, the slow solvation can inhibit the observed decomposition in natural environments. The relative amounts of water also affect the distribution of the hydrolysis byproducts. In dilute aqueous solutions, thiodiglycol (TDG) is the dominant byproduct; whereas, in cases of limited water, the TDG reacts with the intermediates to form the toxic intermediates HD-TDG, HD-2TDG and CH-TDG (Rosenblatt et al., 1975). In the absence of sufficient mixing, the TDG formed would concentrate at the mustard/water interface and form sulfonium salts with the dissolving mustard. These products and the other oligomers would shield the bulk mustard and reduce solvation (Small 1984). These linear polymers are biologically active and display much of the same vesicant properties as HD.

There is significant variation in the reported hydrolysis rates of mustard in aqueous solution, as would be expected with the dependence on the mixing rate and concentration. In his review, Small (1984) reported half-lives from 7.4 to 15.8 minutes for 20°C, and from 3.9 to 8 minutes for 25°C. Figure 17 shows the half-life versus temperature as reported by Franke (1982).

Table 4 is from Sanches (1993) who summarized half-life data versus temperature from Ward and Seiders (1984) and from Finish studies for both the first and second hydrolysis products. Sides et al., (1981) reported a half-life for HD of 4.9 minutes at pH 9.5 at 25°C.

T (°C)	$t_{1/2}$ (min) 1st Hydrolysis Product	$t_{1/2}$ (min) 2nd Hydrolysis Product
10	31	52
21	6	15
30	2.5	3

As would be expected from Figure 15, increased chloride inhibits the formation of the sulfonium cation. This effect of chloride on the hydrolysis rate was investigated by Bartlett and Swain (1949), who showed that the intermediate sulfonium ion preferably reacts with a nucleophilic reagent such as Cl<sup>-</sup> to reform mustard. This is observed as an apparent reduction in the hydrolysis rate. Thus, the calculated hydrolysis rate in freshwater is 2.5 times faster than in seawater (Rosenblatt et al., 1975).

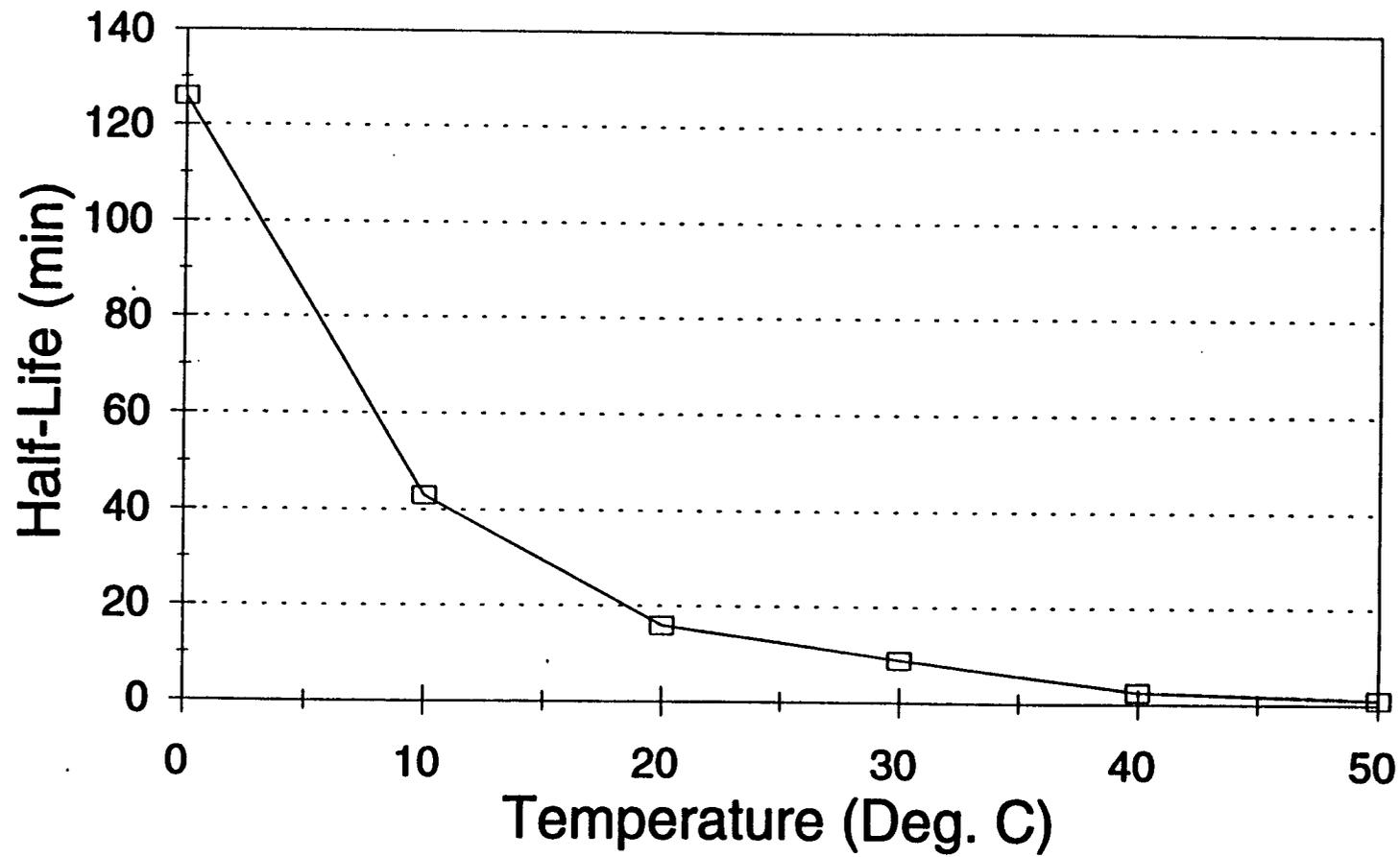


Figure 17. Effect of Temperature on HD Half-Life.

Two other common products that have been identified on surfaces and groundwater at Rocky Mountain Arsenal are 1,4 dithiane and 1,4 oxathiane (Sanches 1993). As illustrated in Figure 18, these are formed due to the de-chlorination of mustard and the half-mustard. 1,4 dithiane is a thermal degradation product, and 1,4 oxathiane is a principal contaminant found on concrete contaminated with H. The half-life for 1,4 oxathiane is reported to be 1,747 hours (Sanches 1993). The compounds of environmental interest for mustard are listed in Table 5.

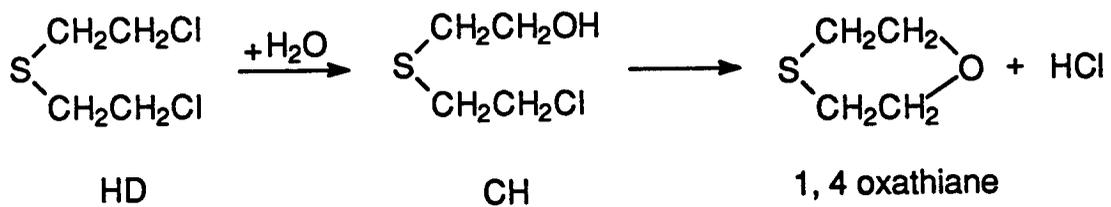
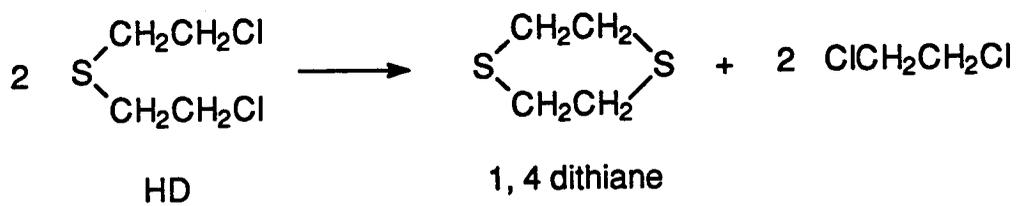


Figure 18. Non-Hydrolytic Degradation Products.

TABLE 5. ENVIRONMENTAL CHEMISTRY OF MUSTARD

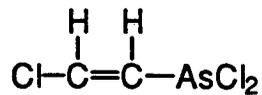
Symbol	Name	Structure	Reg #	Source
HD	Sulfur mustard	$\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-Cl}$	505-60-2	Agent
CH	Hemi-mustard	$\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-OH}$	693-30-1	Hydrolysis
HT	2,2-Bis(2-Chloroethyl thioethyl) ether	$\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-O-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-Cl}$	63918-89-8	Agent
TDG	Thiodiglycol	$\text{HO-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-OH}$	111-48-8	Hydrolysis
CVS	2-Chloroethyl vinyl sulfide	$\text{Cl-C}_2\text{H}_4\text{-S-CH=CH}_2$	81142-02-1	Dechlorination of HD
DVS	Divinyl sulfide	$\text{CH}_2=\text{CH-S-CH=CH}_2$	627-51-0	Dechlorination of HD
HO	Mustard sulfoxide	$\text{Cl-C}_2\text{H}_4\text{-S(=O)-C}_2\text{H}_4\text{-Cl}$	5819-08-9	Oxidation of HD
HO <sub>2</sub>	Mustard sulfone	$\text{Cl-C}_2\text{H}_4\text{-S(=O)}_2\text{-C}_2\text{H}_4\text{-Cl}$	471-03-4	Oxidation of HD
CVSO	2-Chloroethyl vinyl sulfoxide	$\text{Cl-C}_2\text{H}_4\text{-S(=O)-CH=CH}_2$	40709-82-8	Dechlorination of HD
DVSO	Divinyl sulfoxide	$\text{CH}_2=\text{CH-S(=O)-CH=CH}_2$	1115-15-7	Dechlorination of HD
HVS	2-Hydroxyethyl vinyl sulfide	$\text{HO-C}_2\text{H}_4\text{-S-CH=CH}_2$	3090-56-0	Dechlorination of CH
CVSO <sub>2</sub>	2-Chloroethyl vinyl sulfone	$\text{Cl-C}_2\text{H}_4\text{-S(=O)}_2\text{-CH=CH}_2$	7327-58-4	Dechlorination of HO <sub>2</sub>
DVSO <sub>2</sub>	Divinyl sulfone	$\text{CH}_2=\text{CH-S(=O)}_2\text{-CH=CH}_2$	77-77-0	Dechlorination of HO <sub>2</sub>
HD-TDG	Bis(2-hydroxyethyl)-2-(2-chloroethylthio) ethyl-sulfonium	$\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-S}^+(\text{C}_2\text{H}_4\text{OH})_2$	64036-91-5	Hydrolysis of HD
HD-2TDG	Bis-2-(bis(2-hydroxyethyl)-sulfonium ethyl) sulfide	$\text{S-C}_2\text{H}_4\text{-S}^+(\text{C}_2\text{H}_4\text{OH})_2\text{-C}_2\text{H}_4\text{-S}^+(\text{C}_2\text{H}_4\text{OH})_2$	64036-78-9	Hydrolysis of HD
CH-TDG	Bis(2-hydroxyethyl)-2-(2-hydroxyethylthio) ethyl-sulfonium chloride	$\text{HO-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-S}^+(\text{C}_2\text{H}_4\text{OH})_2$	107327-27-5	Hydrolysis of HD
DT	1,4-Dithiane	$\text{S-C}_2\text{H}_4\text{-S-C}_2\text{H}_4$	505-29-3	Thermal
OT	1,4-Oxathiane	$\text{C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-O-C}_2\text{H}_4$	15980-15-1	Dechlorination of CH
HDLP	HD Linear polymer	$\text{Cl-C}_2\text{H}_4\text{-(S-C}_2\text{H}_4\text{)}_n\text{-S-C}_2\text{H}_4\text{-Cl}$	--	

## 4 LEWISITE (L)

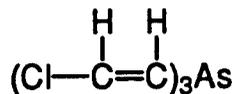
Lewisite or dichloro-2-chlorovinylarsine, is an organic arsenic compound in which the trivalent arsenic is the toxic moiety, which causes an effect similar to the sulfur and nitrogen mustards. The commercial product is a dark, oily liquid with a strong geranium odor and contains both isomers of dichloro-2-chlorovinylarsine, tris(2-chlorovinyl)arsine, bis(2-chlorovinyl)chloroarsine, and arsenic trichloride, as shown in Figure 19 (Sanches 1993). Lewisite is absorbed rapidly through the skin and causes injury immediately upon contact (Franke 1982). The vapor pressure of L is slightly higher than GD (0.58-1.6 mm Hg), and undergoes rapid hydrolysis in the gas phase (USA FM 3-9, Rosenblatt et al., 1975, Whiting, 1948). The range in the vapor pressure is due to the significant difference between the *cis* and *trans* isomers. It is readily soluble in polar and non-polar hydrocarbon solvents such as alcohols, gasoline and chlorocarbons. L supposedly has a solubility of 0.5 g/L; however, the high rate of hydrolysis makes this virtually meaningless (Rosenblatt et al., 1975).

Methyl and ethyl dichloroarsines cause both skin necrosis and a general toxic effect due to the trivalent arsenic. The contact hazards of lewisite are similar to HD, but is adsorbed through the skin more rapidly than HD. Skin damage from L is more extreme than HD; however, the healing takes place more quickly (Franke 1982). Ingestion of L causes immediate symptoms: severe salivation, nausea, vomiting, and bloody diarrhea, and can be fatal in a few hours. Systemic arsenic intoxication can also occur.

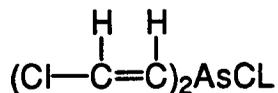
The dichloroarsine group,  $-AsCl_2$ , and the vinyl double bond contribute to the instability of lewisite. Stabilizers are normally added to prevent the decomposition of L in munitions due to reaction with iron. The hydrolysis of L is illustrated in Figure 20, and occurs through the cleavage of HCl forming 2-chlorovinylarsine oxide, which is a blood toxin and irritates the skin (Franke 1982). The hydrolysis of L is complex with a number of reversible reactions. The first stage of the hydrolysis is very rapid, forming a water soluble dihydroxy arsine. The following reactions are slower, eventually ending in the polymerized arsenic oxide. Dissolved L hydrolyzes rapidly with weak alkaline solutions promoting the formation of the arsine oxide. Strong bases form the arsenite salt and acetylene from the *trans* isomer, even in cold solutions; however, the *cis* isomer must be heated to over 40°C to react with hydroxide solutions. In the presence of sulfide ion, arsine sulfide,  $As_2S_3$ , is formed. Above pH 10 the *trans* isomer hydrolysis reaction should be complete in a day (Waters and Williams 1950). The environmental degradation products of L are listed in Table 6.



Lewisite (L) dichloro-2-chlorovinylarsine



Lewisite Impurity (L-1) Tres (2-chlorovinyl)arsine



Lewisite Impurity (L-2) Chloro-Bis (2-chlorovinyl)arsine

Figure 19. Structure of Lewisite Chemical Warfare Agents.

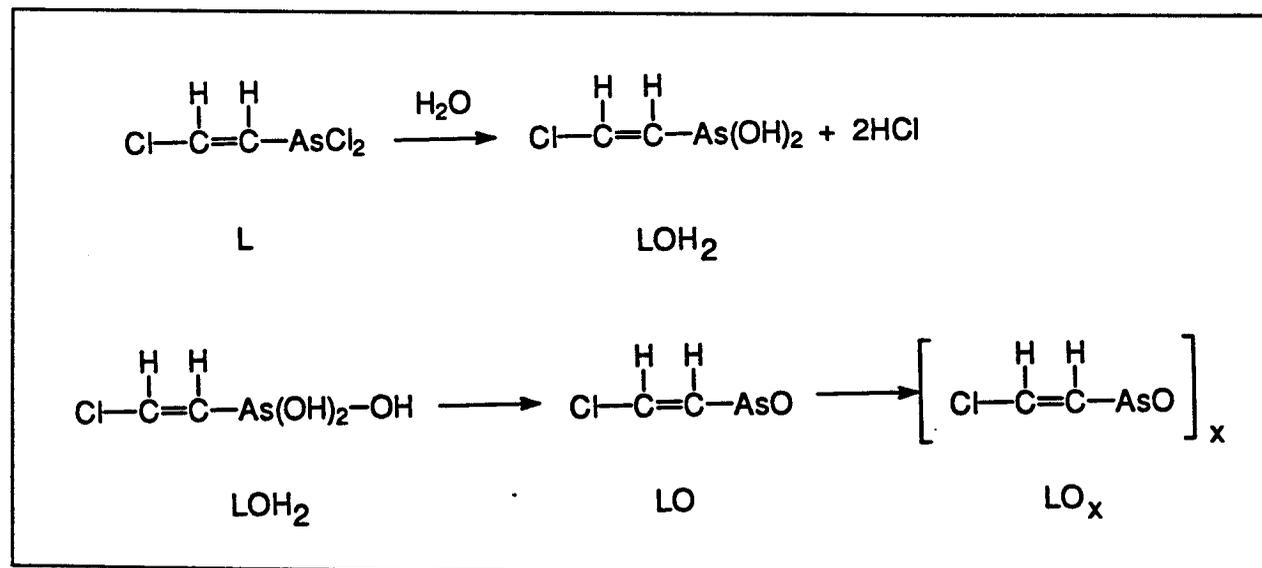


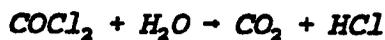
Figure 20. Hydrolysis of Lewisite.

TABLE 6. ENVIRONMENTAL CHEMISTRY OF L, CG, and CX

Agent	Chemical Name	Structure	Reg #	Source
L	Dichloro-2-chlorovinylarsine	$\text{ClCH}=\text{CH}-\text{As}(\text{Cl})_2$	541-25-3	Parent Agent
LOH	Dihydroxy-2-chlorovinylarsine	$\text{C}_2\text{H}_3\text{ClO}_2\text{As}$	85090-33-1	1st Hydrolysis product
LO	2-Chlorovinyl Arsenicoxide	$\text{ClCH}=\text{CH}-\text{AsO}$	123089-28-1	2nd Hydrolysis product
LO <sub>n</sub>	LO polymer	$[\text{ClCH}=\text{CH}-\text{AsO}]_n$	--	
LA	2-Chlorovinyl arsonic acid	$\text{Cl}-\text{CH}=\text{CHAsO}(\text{OH})_2$	64038-44-4	Oxidation product
	Sodium arsenite	$\text{Na}_2\text{As}(\text{O})_2$	11137-68-1	Alkaline decon product
CG	Carbonyl chloride	$\text{OC}(\text{Cl})_2$	75-44-5	Parent Agent
CX	Dichloroformaxime	$\text{Cl}_2\text{NOH}$		Parent Agent

## 5 PHOSGENE (CG)

Phosgene (CG),  $\text{COCl}_2$ , is a colorless gas which condenses at  $8.2^\circ\text{C}$ . The vapors have an odor of "rotting fruit" (Franke 1982). The vapor pressure at  $25^\circ\text{C}$  is 1,379 mm Hg. The solubility of CG in water is limited, but is readily absorbed in polar and nonpolar hydrocarbon solvents. CG hydrolyzes rapidly in water, even at low temperatures. At  $0^\circ\text{C}$ , 1 g of CG is completely hydrolyzed in 100 g of water in 20 seconds, forming  $\text{CO}_2$  and  $\text{HCl}$  (Franke 1982).



In the vapor phase CG is relatively stable, decreasing noticeably only after several hours. From a starting concentration of 12.5 ppm, and a water vapor concentration of 20,000, 24% of the CG was still unhydrolyzed after 22 hours (Franke 1982). Hydrolysis is promoted by bases with the formation of  $\text{NaCO}_3$  and  $\text{NaCl}$ .

## 6 PHOSGENE OXIME (CX)

Phosgene oxime, dichloroformoxime ( $\text{CCl}_2\text{NOH}$ ), is a low melting-point solid or a yellowish brown liquid. The melting point is in the range of  $39^\circ\text{--}40^\circ\text{C}$ , and the boiling point is  $129^\circ\text{C}$  (Franke 1982). CX is a powerful irritant which produces an immediate effect upon contact (USA FM 3-9, 1975).

CX is hygroscopic and tends to polymerize in the presence of water and light. No rate data was in the literature; however, it is reported to dissolve slowly but readily in water, forming  $\text{CO}_2$ ,  $\text{HCl}$ , and hydroxylamine hydrochloride ( $\text{NH}_3\text{OHCl}$ ). The hydrolysis is promoted by both acids and bases. Halogenated oximes react vigorously with strong bases such as alkali hydroxides, ammonia and carbonates (Franke, 1982).



## 7 DECONTAMINANT REACTIONS

Disposal methods used for chemical agents and agent filled munitions used at many installations in the past were only partially effective. In some cases the munitions were punctured and placed in a pit or ditch with a decontaminant such as sodium hypochlorite, or in other instances, the munitions were explosively detonated or burned with gasoline or some other fuel. It is expected that in many, if not most cases, these techniques were inefficient and incomplete, and produced a variety of byproducts. Some of these byproducts have short half-lives and would not be expected to exist over extended periods of time. Others are stable and water soluble and would, therefore, be expected to be indicators of past contamination, and alert the investigator that there may be undestroyed agent presence. Yurow (1981) conducted a literature review of the decontamination methods for HD, GB and VX, which provides information on many of the techniques used from 1918 to 1978.

### 7.1 Hypochlorite

Hypochlorite or STB (Super Tropical Bleach) has been used extensively for decontamination of HD. Theoretically, HD can be completely decomposed to sulfate, chloride and carbon dioxide; however, due to the low solubility of HD in aqueous solutions, poor mixing, or non-stoichiometric proportions, other products such as the sulfoxide (HO) or sulfone (HO<sub>2</sub>) are produced (Yurow, 1981). According to Franke (1982), the oxidation products of HD, HO<sub>2</sub>, and HD-2TDG are also damaging to the skin. The reaction of HD and hypochlorites is pH dependant. In alkaline media the reactions are primarily oxidative, while in acid and neutral solutions, chlorination takes place. The required quantities of hypochlorite are always in excess of that required to form the sulfone as a result of chlorination and other secondary reactions (Franke, 1982). The lower the hypochlorite concentration, the greater the proportion of sulfoxide will be formed. Excess hypochlorite will oxidize the sulfoxides to sulfones. The chlorination products of HD do not retain the vesicant properties. The all-purpose decontaminant DS2 (70% diethylenetriamine, 28% 2-methoxyethanol, and 2% sodium hydroxide) converts HD to divinyl chloride (Yurow 1981). If the reaction is incomplete, then 2-chloroethyl vinyl sulfide (CVS) may also be recovered (Small 1984).

Calcium hypochlorite has also been used to decontaminate VX. The reaction is reported to have a half-life of 1.5 minutes and produce ethyl methyl phosphonate (Yurow 1981). GB reactions with hypochlorite are also expected to produce the same product, isopropyl methylphosphonate, as the hydrolytic reaction.

### 7.2 Thermal Destruction

HD is completely decomposed during proper incineration. The products formed during the combustion include dithiane and 2,2'-dichloroethyldisulfide (Yurow, 1981). Thermal destruction of GB and VX produces methylfluorophosphoric acid and O-ethyl O-(2-diisopropylaminoethyl)methylphosphonate.

## 8 SOIL SYSTEMS

The fate and migration of chemical agents and their decomposition products in the subsurface soil environment will be controlled by many factors including the chemical properties and concentration of the agent, time since the agents were buried, presence of other chemicals such as decontaminants, depth, temperature cycles, location of groundwater table, annual precipitation, soil type, pH, trace inorganic constituents, organic content, and microbial populations. Because each site will have a unique combination of these factors, and most of the required information for environmental fate models will not exist, predictions will, at best, be rough approximations. The following information on parameters which control the persistence and environmental fate will assist the environmental professional to estimate the extent and potential risks associated with remedial investigation and site remediation of suspected burial sites. The report by Small (1984) is an excellent summary of the chemistry and other properties which would control the degradation and environmental fate of the agents and degradation products. Since data on the chemical and physical properties of many of the decomposition products is lacking, Small used accepted theoretical methods to estimate them. In lieu of experimental results, calculated properties can be used to estimate the environmental fate of these compounds.

Most agents have a reasonable water solubility, but some sorption to clays and soil humic materials is expected through hydrogen bonding, columbic attraction and ligand exchange. Little data is available on the sorption of agents or agent byproducts to soil or soil components; although, there is a wealth of data on the adsorption of organophosphorus pesticides such as chlorpyrifos and diazinon (Macalady and Wolf 1984). The affinity of soils for organic material is generally a function of the clay content, with smectites having the highest affinity and kaolinite the lowest. The interaction of the soil with organics is dependant on the location of the surface charge of the mineral. Clays with charge localized on the tetrahedral sheet bind weak organic bases stronger than those with the charge on the octahedral sheet. In addition, those clays susceptible to swelling may allow the organic molecules to penetrate between the basal planes and be bound by near-field electrostatic and Van der Waals-London Forces (Morrill, 1985).

Soil environments, except in arid regions, can be expected to have relative humidities in excess of 90%, and therefore, most chemical agents can be expected to undergo hydrolysis reactions. While data is generally available on the hydrolysis rates of chemical agents in pure water, this data is not appropriate for the heterogenous and diverse soil environment. The data on the fate of chemical agents in soil is generally limited to studies which investigated the fate of agents on the ground surface or in "closed-containers." These studies were designed to understand the persistence of agents applied under realistic wartime situations, and have minimal relevancy to understanding the fate of agents buried several meters below ground. In addition, the relative agent to soil ratios studied have been in the range of mg per g of soil, rather than the high concentrations that might be expected for burial sites of partially decontaminated munitions.

As described in Section 2, all the chemical agents undergo hydrolytic decomposition to some degree in the presence of moisture. The rate of these hydrolytic reactions depend on the type agent, pH, the concentration of metal and other aqueous ions, and temperature. Generally, other things being equal, degradation rates in soil should be faster than in single phase systems, due to the

presence of trace metal ions and catalytic effects of clay edges; however, if a chemical is strongly bound to the clay or soil organic matter, then degradation may proceed more slowly.

There is limited data on the interaction of CWA in soil systems; however, based on studies with pesticides and other compounds of similar structure, a few general conclusions can be drawn:

- Increased soil organic content will increase the retention of CWA.
- Adsorption of CWA will increase as the soil pH increases.
- The lower the water content of soil the higher the capacity of the soil to retain CWA.
- Hydrolysis reactions will be accelerated in soil systems due to catalytic effects.
- Microbial metabolism may take place, however, would not be expected to play a predominant role in degradation

The following summarizes the literature on reactions of CWA in soil:

GB-The decomposition of GB on  $\gamma$ -alumina were studies done by Kuiper et al., 1976. GB was strongly adsorbed to the  $\gamma$ -alumina and the hydrolysis was promoted by the basic surface sites. The hydrolysis product was identified as isopropyl methylphosphonic acid. The half-life of GB adsorbed to soil was reported to be 4 hours (20°C) (Sinkensen, 1952). Using a dynamic flow system, moist air was passed over soil contaminated with GB, and 15% of the GB was hydrolyzed after 20 minutes. Assuming the pH of the soil was 6-7, this is considerably less than the 170 hours reported by Epstein (1974).

VX-Verneij and Boter (1976) found that only 0.1% of VX applied to soil was remaining after 3 weeks. The phosphorous degradation pathways produced ethyl methyl phosphonic acid (EMPA), which slowly deesterified to methylphosphonic acid (MPA). In one test, 40% of EMPA applied to a humic soil (pH 5.3) was hydrolyzed to MPA in one day and 80% was converted in 12 days. At Dugway Proving Grounds, analysis of soil samples which had been previously contaminated with VX showed only MPA. The MPA was detected down to a depth of 102 cm, due to the leaching action of the annual precipitation (Small 1984). Demek and Epstein (1959) postulated that in soils DDP would be formed from the reaction of EMPA and (DES)<sub>2</sub> systems.

Kaaijk and Frijlink (1977) followed the degradation of <sup>32</sup>P- and <sup>35</sup>S-labelled VX in humic sand. Using different extraction techniques, they were able to identify the decrease in VX and the formation of phosphorus and sulfur containing byproducts. In 8 days, VX was almost completely degraded, with the major sulfur containing byproduct being bis(2-diisopropylaminoethyl)disulfide (DES<sub>2</sub>). Approximately 50% of the phosphorous was found in water extracts and 40% in alkaline methanol extracts. Compared with humic sand in which 70% of the <sup>35</sup>S could be extracted, for humic loams and clay peat only 35% and 23% could be extracted, respectively. It was hypothesized that DES<sub>2</sub> was the compound that was strongly bound to the soil humic material. DES could not be ruled out as a decomposition product, however, since DES was rapidly oxidized to DES<sub>2</sub> either in soil or

during the extraction process. The 91-93% degradation of VX in 192 hours gives a half-life of approximately 54 hours, substantially less than that found in aqueous systems, except at pHs higher than 10. Although no data was provided on soil pH, humics are generally acid soils rather than alkaline soils.

Small (1984) summarized the results of "Project Little Seven" reported by Epstein et al., (1959) and Demek (1959), in which VX was added to a fine silty loam with a pH of 6.5. After 14 days in closed flasks, 2.5 to 7.5% of the VX was remaining. Varying the moisture between 4.5% and 50% did not effect the degradation rate. After 119 days, 53 to 66% of the theoretically possible DES<sub>2</sub> or DESH was found in the soil. Demek (1959) postulated that the degradation in excess of that predicted from hydrolysis was due to catalysis by the soil components and reaction of the residual VX with ethyl methylphosphonic acid.

HD - No studies were located which addressed the decomposition rate of HD in soil. The majority of studies involving the fate of HD in soil systems were focused on tactical issues concerned with persistence (Penski 1990a; Penski 1990b; Puzderliski 1980). At the soil surface, the predominate mechanism controlling the persistence of HD is evaporation, which it is expected to be minimal for subsurface contamination or for agents inside partially ruptured munitions. The role of vaporization as a mechanism of migration through soils is unknown; however, it has been observed that clays are unsuccessful as a barrier to HD vapor (Rosenblatt et al., 1975). Although HD dissolved in water readily hydrolyzes, numerous instances of spilled or buried HD remaining intact over many tens of years have been reported (Small 1984). As noted earlier, unless there is adequate mixing, TDG, HD polymers and/or other TDG-sulfonium salts would concentrate at the surface of HD and inhibit the dissolution of HD and subsequent hydrolysis. Particularly in soil systems where water slowly diffuses through the soil matrix, hydrolysis of bulk HD would be expected to be reduced. For situations where the HD is not in droplets, but dispersed or absorbed by the soil, hydrolysis would be expected to proceed if there is sufficient water present.

The intermediates and byproducts of HD hydrolysis are water soluble and, therefore, would be expected to migrate away from the initial site of contamination. Since many of the intermediates such as CH hydrolyze at a faster rate than HD, their presence at a site would indicate the presence of HD (Small 1984).

L - Lewisite would be expected to convert to the lewisite oxide even in arid region, since it reacts so readily with moisture. Lewisite applied to soil was more persistent than HD, which may be explained by the slow oxidation to the inorganic arsenic (Rosenblatt 1975).

CG and CX - No data was found on the interaction of CG or CX with soils. The fate of CG in soil systems will be dominated by its high volatility and rapid hydrolysis to CO<sub>2</sub> and HCl. CX would also be expected to be water soluble and decompose to CO<sub>2</sub>, HCl and hydroxyl amine hydrochloride.

## 9 BIODEGRADATION

Bacterial degradation of organic compounds is one of the most important mechanisms for the natural attenuation of pollutants in soil and aquatic systems. Microbial metabolism of pesticides is well documented, including those pesticides such as parathion which have structures similar to the organophosphorus agents (Khan 1980).

Actual data on the microbial degradation of CWA is limited (Trapp 1985). Mustards are cell poisons and would, therefore, be expected to inhibit bacterial growth. If bacterial degradation or oxidation did occur through exoenzymes, it would be a minor factor compared to other oxidative and/or hydrolytic reactions.

Organophosphonates have been shown to undergo complete metabolisms to alcohol, alkane and phosphate (Daughton, Cook and Alexander, 1979). *P. testosteroni* degraded O-alkyl alkylphosphonates, such as sarin and soman, by first cleaving the alkoxy group to yield the alcohol and divalent alkylphosphonate. The latter is further degraded to yield the alkane and inorganic orthophosphate. This degradation occurred under aerobic conditions only when the agents were the sole and limiting phosphorous source. This was the first report of microbial cleavage of the C-P bond, and the same organism could not break other carbon-heteroatoms such as arsenates, sulfonates and mercurials. In addition, the organism was not able to degrade an alkylphosphonothioate such as VX.

In another study, Cook et al., (1978) evaluated the ability of *Pseudomonas*, isolated from soils and sewage, to degrade phosphonates. They found that multiple strains of *Pseudomonas* could use 13 ionic alkylphosphonates or o,o dialkylphosphonates, including MPA and the sodium salt of IMPA as a phosphorous source, but only 2-aminoethylphosphonic could be used as a carbon source.

Daughton et al., (1979) investigated the microbial degradation and soil retention of MPA and other O-alkylmethylphosphonic acid esters. The soils of interest were a Spodosol (pH 3.9, 35% organic) a silty loam (pH 6.5, 5.5% organic) and three clays. As would be expected from the high organic content, the Spodosol retained 95.4% of the MPA in solution, 42% of IMPA and 32% of PMPA. The silty-loam only retained 11% of MPA in solution. The other alkylphosphonates and thiophosphates were not bound to the Spodosol. The observed retention of MPA is higher than would be expected from simple adsorption to the organic matter in the soil based on the  $K_{oc}$  of 1.4 (Small 1984).

When Spodosol was added to cultures of *P. Testosteroni* it inhibited its ability to use inorganic phosphorous and MPA as P sources. It did not effect the degradation of IMPA, however. This inhibition reflected the ability of the soil to strongly bind inorganic phosphate and MPA, but not IMPA, and make them unaccessible for microbial growth. It was observed that these products of organophosphorus hydrolysis would normally be accessible to microbial degradation, since they are water soluble. Since the phosphorous in phosphonates is only used if other more readily available P is not available, if inorganic phosphate is prevalent, little degradation would be predicted. However, where P is limiting, nutrient degradation of phosphonates may occur through bacterial action.

## 10 ENVIRONMENTAL FATE

Prediction of the environmental fate of buried CWA is complicated by a general lack of knowledge on if, or how, the agents were decontaminated, the configuration of the agent/munitions and the site-specific subsurface geology and hydrogeology. Although it is not possible to make definitive predictions of the form and migration of buried agents without detailed information on past activities and site specific information there are numerous chemical and physical properties and calculated parameters which are useful in predicting the relative behavior of chemical compounds in the environment. These properties and parameters can be used with other data gathered during preliminary assessments in planning remedial investigations and prioritizing sites for remediation. The key properties associated with predicting the chemical fate of organic chemicals include water solubility, vapor pressure, octanol-water partition coefficient, and half-life.

### Compound Properties

- Water Solubility ( $C_{sol}$ ): Solubility in water is the maximum capacity of a dissolved chemical in the aqueous phase at a specific temperature (T). Can be calculated from antilog ( $4.184 - 0.922 \log K_{ow}$ ). Units mg/L:
- Vapor Pressure ( $P_v$ ): Equivalent to the "solubility" in the air phase. Maximum capacity of the chemical in air at a specific temperature (T) and pressure (P). Units mm Hg.
- Octanol-Water Partition Coefficient ( $K_{ow}$ ): Provides a direct estimate of the hydrophobicity or partition tendency from water to organics such as natural humic material. Can be used to estimate the organic carbon-water participation coefficient ( $K_{oc} = \text{antilog}(1.377 + 0.544 \log K_{ow})$ ) and fishwater bioconcentration ( $K_b = \text{antilog}(0.845 \log K_{ow} - 0.586)$ ) (Lyman et al., 1981; Mabey and Mill 1978).
- Half-Life ( $t_{1/2}$ ): Time required for one half of the original mass to disappear from a medium due to evaporation, photodegradation, hydrolysis, biodegradation. Half-life depends on many factors and, therefore, literature values must be with caution.  $t_{1/2} = 0.693/k$  where k is the first order rate constant (hours<sup>-1</sup>). Unit hours.
- Henry's Law Constant (H): Ratio of the vapor pressure to the water solubility. Essentially the air-water partition coefficient  $H = (MW \times P_v) / (C_{sol} \times 760)$ . Units atm m<sup>3</sup>/mol.

### Calculated Environmental Transport Parameters

- Retardation Factor (R): A relative measure of the time required for a compound to traverse a certain distance in groundwater, compared to a highly water soluble compound. Calculated from the soil properties and  $K_{oc}$ .  $R = 1 + \rho/\theta(K_{oc} \times f_{oc})$ , where  $f_{oc}$  is an attribute of the specific soil  $\approx 0.02$ ,  $\rho$  is the soil density ( $\approx 1.4$ ), and  $\theta$  is the soil porosity ( $\approx 0.4$ ).
- Leaching Index (LI): Number of leachings required to reduce the soil concentration to one tenth of the original concentration assuming for each leaching one Kg of soil is in equilibrium with one L of water.  $f_{oc}$  is the fraction of the soil mass which is organic carbon.

$$\left[ 1 - \frac{1}{1 + 1 f_{(oc)} \times K_{(oc)}} \right]^{(LT)} = 0.1$$

- Volatility Potential (VP): The slope of the vapor pressure vs concentration of the compound in soil organics. Units mm Hg/mg/kg in soil.

$$VP = \frac{P_o}{C_{soil} \times K_{oc}}$$

- Air-Soil Partition Coefficient ( $R_o$ ): Concentration of a compound in air in contact with soil. Units mg/cm<sup>3</sup> for soil density of 1.4 g/cm<sup>3</sup>.

$$R_o \approx 3.85 \times 10^{-2} MW \times VP / f_{oc}$$

The chemical and physical properties of some of the agents and their decomposition products are shown in Table 7. The summary of these properties by Small (1984), which covered much of the data on GB, VX and HD, has been supplemented by adding other agents and their decomposition products. The calculated environmental transport properties are shown in Table 8, also modified from Small (1984). Although many of the physical properties and environmental transport indices are estimated from empirical substituent relationships from Hansch and Leo (1979) and Lyman et al., (1982), they can be used to assess the relative effects of environmental factors on the fate of the agents and their decomposition products at small burial sites. The use of these estimated factors is illustrated below. A computer search was made of numerous databases including Chemical Abstracts, Beilstein, and the National Library of Medicine Hazardous Substances Data Base. For most compounds, there was little or no data of environmental significance.

It is evident from a review of these tables that the hydrolysis of the agents in a soil system will markedly effect their environmental transport. Both GB and GD, with relatively high water solubility and medium log  $K_{ow}$  and  $K_{oc}$ , would not be leached by precipitation or transported by groundwater as would their degradation products IMPA and PMPA. The hydrolysis of GB would reduce the potential for vapor migration and/or evaporation as indicated by the lower volatility potential (VP) and air-soil partition coefficients ( $R_o$ ).

HD, for instance, has a log  $K_{ow}$  of 1.37 and  $K_{oc}$  of 133, indicating that it would be much more attracted to soil organics and clays than would the hydrolysis products which all have much lower  $K_{ow}$  and  $K_{oc}$  values. This is also reflected in the retardation factors. For example, HD would be expected to take over 6 times longer than TDG to migrate the same distance through soil. The opposite holds true for volatility. TDG has a significantly lower vapor pressure ( $P_o$ ) and volatility potential. In low moisture soils, such as found in arid regions, HD may migrate as vapor through the soil interstices.

This same increase in mobility is seen for most of the VX degradation products, except the  $(DE)_2S$  and  $(DES)_2$ . In the case of these final degradation products, their high  $\log K_{ow}$  of 4.47 and 3.48 reflects a strong affinity for organics and a low water solubility. This is also reflected in the high retardation factor which indicates that these compounds would be found much closer to the initial contamination site than VX and the other degradation products EMPA and EMPS. In samples taken from areas previously highly contaminated with VX at Dugway Proving Grounds (DPG), only MPA, a slow hydrolysis product of EMPA, could be found. The MPA was evenly distributed down to a depth of 102 cm, even though the DPG has an annual precipitation of less than 8 inches (Small 1984).

TABLE 7. CHEMICAL AND PHYSICAL PROPERTIES OF AGENTS AND AGENT DECOMPOSITION PRODUCTS  
(Modified From Small, 1984)

Compound Name or Abbreviation	log $K_{ow}$	$C_{sat}$ mg/L	$K_{ow}$	$P_v$ mm Hg	MW
GB	0.72	>>	59	2.9	140
IMPA	-0.54	$4.8 \times 10^4$	12	$3.4 \times 10^{-3}$	140
GD	1.8	$2 \times 10^4$	200	0.4	182.2
PMPA	0.54	$4.8 \times 10^3$	50		180
DMP	-3.35	$>1.8 \times 10^6$	0.4		94
DIPC				5.1	126
DIPU	1.38	$8.2 \times 10^2$	134	$9.2 \times 10^{-3}$	144
TBA	4.23	1.9	4800	$2.8 \times 10^{-1}$	185
GA	0.11	$1.2 \times 10^4$	25	$7.3 \times 10^{-2}$	162
EDPA	-0.26	$2.6 \times 10^4$	16		153
EPC	-1.12	$1.6 \times 10^3$	6		134
PC	-2.56	$>1.8 \times 10^6$	1		107
VX	2.09	$3.0 \times 10^4$	330	$3.0 \times 10^{-4}$	268
EMPA	-1.15	$1.8 \times 10^3$	5.6	$3.6 \times 10^{-4}$	124
EMPS	1.26	$1.1 \times 10^3$	115	$4.3 \times 10^{-2}$	140
DEOH	1.08	$1.5 \times 10^3$	92	1.8	145
(DE) <sub>2</sub> S	4.47	1.2	6400	$2.7 \times 10^{-7}$	288
(DES) <sub>2</sub>	3.48	0.5	1900	$5.9 \times 10^{-3}$	320
DDP	-2.12	$>1.0 \times 10^6$	1.7		154
EA2191	0.96		79		241
MPA	-2.28	$>1.0 \times 10^6$	1.4		98
DPCA	2.17	$1.5 \times 10^2$	360	2	145.5
IPCA	0.56	$4.7 \times 10^3$	48	6	93.5
PA	1.39	$2.9 \times 10^3$	136		125
DMPAC	1.02	$1.8 \times 10^3$	85		134
HD	1.37	$1.0 \times 10^3$	133	$1.0 \times 10^{-1}$	159
TDG	-0.77	$7.8 \times 10^4$	9.1	$1.9 \times 10^{-3}$	118
CVS	1.11	$1.4 \times 10^3$	96	5.8	122.5
DVS	0.85	$2.5 \times 10^3$	69	$6.0 \times 10^1$	86
HO	-0.85	$9.3 \times 10^4$	8.2	$6.5 \times 10^{-1}$	175
HO <sub>2</sub>	-0.51	$1.1 \times 10^4$	13	$9.6 \times 10^{-1}$	191
CVSO	-1.11	$1.6 \times 10^3$	5.9	$6.4 \times 10^{-2}$	138.5
DVSO	-1.37	$2.8 \times 10^3$	4.3	$9.2 \times 10^{-1}$	102
HVS	0.53	$5.0 \times 10^3$	46	3.8	102
CVSO <sub>2</sub>	-0.77	$7.8 \times 10^4$	9.1	$2.3 \times 10^{-2}$	154.5
DVSO <sub>2</sub>	-1.03	$1.4 \times 10^3$	6.6	$9.0 \times 10^{-2}$	118
HD-TDG	Unstable				
HD-2TDG	Unstable				
CH-TDG	Unstable				
DT	0.77	$3 \times 10^3$	63	$8.0 \times 10^{-1}$	120
OT	-0.26	$2.7 \times 10^4$	17		
L	0.5	$5 \times 10^3$	45	0.58	207.3
LOH					
LO	0.2	$1 \times 10^4$	31		
LO <sub>x</sub>					
LA					
CG	Unstable				
CX	Unstable				

TABLE 8. CALCULATED ENVIRONMENTAL TRANSPORT INDICES FOR AGENTS AND AGENT DECOMPOSITION PRODUCTS  
(Modified From Small, 1984)

Compound Name or Acronym	LI	VP	R	H	R <sub>e</sub>
GB	3.7	4.9 X 10 <sup>-8</sup>	5.1	5.4 X 10 <sup>-7</sup>	1.3 X 10 <sup>-5</sup>
IMPA	1.4	5.8 X 10 <sup>-9</sup>	1.8	1.3 X 10 <sup>-8</sup>	1.6 X 10 <sup>-6</sup>
GD	10.3	1 X 10 <sup>-7</sup>	15	14.8 X 10 <sup>-6</sup>	3.5 X 10 <sup>-5</sup>
PHPA	3.3		4.5		
DMP	0.5		1.0		
DIPC					
DIPU	7.3	8.4 X 10 <sup>-8</sup>	10	2.1 X 10 <sup>-6</sup>	2.3 X 10 <sup>-5</sup>
TBA	220	3.1 X 10 <sup>-5</sup>	330	3.5 X 10 <sup>-2</sup>	1.1 X 10 <sup>-2</sup>
GA	2	2.4 X 10 <sup>-7</sup>	2.8	1.3X10 <sup>-6</sup>	1X10 <sup>-4</sup>
EDPA	1.6		2.1		
EPC	1.0		1.4		
PC	0.6		1.1		
VX	16	3.0 X 10 <sup>-11</sup>	24	3.5 X 10 <sup>-9</sup>	1.5 X 10 <sup>-8</sup>
EMPA	1.0	3.6 X 10 <sup>-10</sup>	1.4	3.3 X 10 <sup>-10</sup>	8.6 X 10 <sup>-8</sup>
EMPS	6.4	3.5 X 10 <sup>-7</sup>	9.1	7.5 X 10 <sup>-6</sup>	9.4 X 10 <sup>-5</sup>
DEOH	5.3	1.3 X 10 <sup>-5</sup>	7.5	2.2 X 10 <sup>-4</sup>	3.6 X 10 <sup>-3</sup>
(DE) <sub>2</sub> S	300	3.6 X 10 <sup>-11</sup>	450	8.8 X 10 <sup>-8</sup>	2.0 X 10 <sup>-6</sup>
(DES) <sub>2</sub>	87	3.4 X 10 <sup>-13</sup>	130	2.6 X 10 <sup>-10</sup>	2.1 X 10 <sup>-10</sup>
DDP	0.67		1.1		
EA2191	4.7		6.6		
MPA	1.4		1.1		
DPCA	18	3.6 X 10 <sup>-5</sup>	26	2.5 X 10 <sup>-3</sup>	1.0 X 10 <sup>-2</sup>
IPCA	3.0	2.7 X 10 <sup>-5</sup>	4.4	1.6 X 10 <sup>-4</sup>	4.9 X 10 <sup>-3</sup>
HD	7.2	7.6 X 10 <sup>-7</sup>	10	2.1 X 10 <sup>-5</sup>	2.3 X 10 <sup>-4</sup>
TDG	1.2	2.1 X 10 <sup>-12</sup>	1.6	3.0 X 10 <sup>-12</sup>	4.8 X 10 <sup>-10</sup>
CVS	5.5	4.2 X 10 <sup>-5</sup>	7.7	6.5 X 10 <sup>-4</sup>	9.9 X 10 <sup>-3</sup>
DVS	4.2	3.5 X 10 <sup>-4</sup>	5.8	2.7 X 10 <sup>-3</sup>	5.8 X 10 <sup>-2</sup>
HO	1.2	8.5 X 10 <sup>-7</sup>	1.6	1.6 X 10 <sup>-6</sup>	2.9 X 10 <sup>-4</sup>
HO <sub>2</sub>	1.9	6.9 X 10 <sup>-6</sup>	1.9	2.2 X 10 <sup>-5</sup>	2.5 X 10 <sup>-3</sup>
CVSO	1	6.8 X 10 <sup>-8</sup>	1.4	7.3 X 10 <sup>-8</sup>	1.8 X 10 <sup>-5</sup>
DVSO	0.91	7.7 X 10 <sup>-7</sup>	1.3	1.0 X 10 <sup>-7</sup>	1.5 X 10 <sup>-4</sup>
HVS	3.1	1.7 X 10 <sup>-5</sup>	4.2	1.0 X 10 <sup>-4</sup>	3.3 X 10 <sup>-3</sup>
CVSO <sub>2</sub>	1.2	3.2 X 10 <sup>-8</sup>	1.6	6.0 X 10 <sup>-8</sup>	9.5 X 10 <sup>-6</sup>
DVSO <sub>2</sub>	1.1	9.7 X 10 <sup>-8</sup>	1.5	1.0 X 10 <sup>-7</sup>	2.2 X 10 <sup>-5</sup>
HD-TDG					
HD-2TDG					
CH-TDG					
DT	3.9	4.3 X 10 <sup>-6</sup>	5.4	4.2 X 10 <sup>-5</sup>	9.9 X 10 <sup>-4</sup>
OT					
L	3.1	2.6 X 10 <sup>-6</sup>	4.2	3.2 X 10 <sup>-5</sup>	1 X 10 <sup>-3</sup>
LOH					
LO	2.4		3.2		
LO <sub>2</sub>					
LA					
CG					
CX					

# 11 ANALYSIS OF CHEMICAL WARFARE AGENTS AND THEIR DECOMPOSITION PRODUCTS

## 11.1 Analytical Techniques

The most comprehensive evaluation of analytical methods for the determination of agents in environmental media is presented in the Non-Stockpile Monitoring Concept Plan (USACMDS June 1993). Detection systems for all CWA in all media are presented. The most thorough presentation of techniques available includes field screening and health and safety monitoring methods. A summary presented in the plan is included as Tables 9 and 10.

Lacking in this document are procedures to characterize soils and water for the CWA degradation products. Although many are EPA listed compounds such as hydrogen chloride, others are unique to the CWA parents and are non-toxic. As a result, standard methods for their detection are unavailable. Techniques are needed to assay some of these products in environmental media to levels consistent with anticipated remediation goals (low ppb).

### 11.1.1 *Mustard as H, HD, HT, HS*

The compounds are amenable to solid sorbent collection (EPA TO-1) and assay by GC for air matrixes. These compounds are readily extracted from all other environmental media using hexane, chloroform, or dichloromethane. The extracts may then be assayed using GC/FPD systems.

Products have been assayed using GC with FPD detection. All except the polar glycol compounds are readily extracted from all media using the same solvent system used to assay the parent agent. Co-elution has been the major problem encountered, however, easily overcome with GC column selection. USATHAMA Method LL04 is available for water assay of the H series degradation products.

Thiodiglycol is extractable from dry soils with recoveries in the 70 to 100% range. Solvent systems must include, in significant portions, (>20 %) acetonitrile or acetone. Wet soils with moisture content above 20% must be ambient air dried until a moisture content of less than 5% is obtained. Heat may be applied, at a low level (100° F). This method for wet soil assay of thiodiglycol was utilized at Southwest Research Institute; however, precision and accuracy of the technique has not been established. USATHAMA Method LW 18 is also used, but suffers from high variability.

Assay of thiodiglycol in water systems is accomplished by concentration of the matrix and direct injection HPLC. Methods under development include solid phase extraction of analytes from water systems. Should this procedure show promise, soil leachates could also be prepared using aqueous solvents. Solid phase removal/concentration of the thiodiglycol in the leachate would then be used prior to GC/FPD assay. Currently, USATHAMA Method LW 22 employs a concentration step using XAD-7, which is similar to the C-18 resin used for solid phase extractions. Application indicates sufficient sensitivity (low ppb); however, the method suffers significant variability.

### **11.1.2 Nerve Agents GB, GA, GD**

These compounds are readily assayed from any environmental media using GC techniques. Solid sorbent collection of headspace or a purge of soils/water is used to concentrate the analyte prior to assay.

The phosphonates and amines are extractable and amenable to analysis by GC. Air samples should be collected on polyurethane/XAD resin systems, as these compounds will not reverse under thermal loading of the tenax or chromosorb used in the parent compound monitoring systems. After collection, elution of the resin using DCM or hexane is preferred over extraction, due to the relatively high volatility of these analytes.

Extractive techniques have been successful on water and soil systems for the phosphonates and phosphonic acids, provided the solvent concentration step is performed at a slow rate. DCM has indicated some improved recovery, as compared to other solvents used in extraction.

The phosphonates are amenable to assay by GC. The phosphonic acids must be derivatized before assay by GC. USATHAMA suggests using trimethylsiloxane; however, reduced interference has been seen using trifluoroacetic anhydride as a derivatizing agent. Assay of the derivitized phosphonic acids is performed using GCMS.

Assay of water samples has been demonstrated using direct injection ion chromatography; however, the method sensitivity is very high and selectivity is poor.

The acid gases in air can be collected on silica gel and assayed using ion chromatography. Water sample assay is performed by direct injection ion chromatography. Soils must undergo an aqueous leach step prior to direct assay by IC. Sensitivity is high and background concentrations of these compounds makes interpretation difficult.

### **11.1.3 Nerve Agent VX**

VX is assayed in air using a derivatization GC/FPD method (DAAMS with AgF filter). Water may be directly injected onto the AgF filter for assay. Water can be also be extracted with DCM after pH adjustment (slightly basic). Soils contaminated with VX can be assayed after extraction with a polar solvent such as acetone or ether, in addition to hexane or DCM.

All VX extracts must be injected onto a AgF pad (DAAMS) prior to GC assay. The parent compound is not amenable to GC, and must be converted prior to introduction.

The assay of VX degradation products will follow those methods identified for the G type agents. Most all of the compounds are readily extracted from environmental media. Air sample collection is performed using PUF/XAD collection media over the Tenax or chromosorb systems used for the parent CWA. Solvent elution over extraction preparation techniques are preferred for this air collection resin. The diisopropylamine and dimethylamine will extract and are amenable to GC assay. Conditions and column of the GC system must be appropriate. These compounds also require protection from light and oxygen. Amber collection vessels and a nitrogen purge of container

headspace is recommended for sample transport. Only the phosphonic acids must undergo a derivatization step prior to GC introduction.

The numerous alcohols and cyclic compounds presented as degradation products of VX may be assayed from air using Tenax collection, thermal desorption/GC assay. EPA methods such as TO 1 and TO 14 may be applied to these volatile compounds. In soil and water samples, the alcohols require derivatization just as performed for the phosphonic acids. The cyclic compounds should readily purge from water or soil media and be amenable to GC.

#### **11.1.4 Chemical Agents Phosgene (CG), Cyanogen Chloride (CK) and Hydrogen Cyanide (AC)**

Analytical methods for detection of these compounds in environmental media has been established. The detection of phosgene in air will follow procedures identified by EPA SW 846 methods for volatile organics (TO 1 and TO 14, specifically). The cyanogen and hydrogen cyanide agents are amenable to ion chromatography or colorimetric techniques.

#### **11.1.5 L-Lewisite**

Lewisite detected as the parent agent has not been performed as the compound is highly unstable. The primary degradation products (oxide or hydroxide) are detected using colorimetric techniques. The conversion of the product to arsenic or arsine allows detection using AA methodology.

Efforts are underway for methods to determine L in air on a continuous basis. There is some evidence that the DAAMS collection system may be utilized. There are also continuous tape monitoring systems (MDA) that employ calorimetric techniques specific to arsines. The tape systems show lack of specificity, and are susceptible to ambient moisture and temperature variations.

All L degradation product assay in water and soil should employ traditional EPA sanctioned AA techniques. Sensitivity is satisfactory for remediation verification and the methods are applicable to all environmental media.

### **11.2 Analytical Summary**

It is important to realize that methods for the evaluation of degradation products have not been evaluated to Class I status. With the exception of the sulfur related USATHAMA referenced methods, all of the mentioned have supporting results, with minimal rigorous test data in support of performance. Most of the techniques have been applied with regard to treaty verification tasks here at SwRI and other research organizations.

Table 11 summarizes techniques applied with success to some of the degradation compounds in environmental media. Most of the referenced GC approaches were performed using GC/MS or high resolution GC/MS. Detection methods are best left to the specific application as interferant compounds are site specific. Where mass spec is specified it should be employed. All of the techniques mentioned have indicated detection ability in the low ppb range.

TABLE 9. AVAILABLE METHODS FOR GENERIC MONITORING (USACMDA, 1993)

Agent	NRT Alarm	Confirmation/Historical	High-level Screen (at site) <sup>b</sup>	Laboratory <sup>c</sup>	Recovered Material <sup>d</sup>
<b>Chemical Agents</b>					
GA	ACAMS /MINICAMS	DAAMS	Enzyme ticket or red band tube	Extr. then GC/FPD	ACAMS /MINICAMS
GB	ACAMS /MINICAMS	DAAMS	Enzyme ticket or red band tube	Extr. then GC/FPD	ACAMS /MINICAMS
GD	ACAMS /MINICAMS	DAAMS	Enzyme ticket or red band tube	Extr. then GC/FPD	ACAMS /MINICAMS
VX	ACAMS /MINICAMS	DAAMS	Enzyme ticket or red band tube	Extr. then GC/FPD	ACAMS /MINICAMS
L	ACAMS /MINICAMS	Bubbler	Double yellow band tube	Extr. then IC <sup>e</sup>	Double yellow band tube
HD	ACAMS /MINICAMS	DAAMS	Blue band tube	Extr. then GC/FPD	ACAMS /MINICAMS
HN (1-3)	Blue band tube	bubbler	Blue band tube	Extr. then GC/MS	Blue band tube
AC	TGM55	bubbler	Blue band tube	Extr. or pyrolysis then GC/MS	Blue band tube
CK	TGM55	bubbler	Blue band tube	Extr. then GC/MS	Blue band tube
CG	TGM55	bubbler	Blue band tube	Extr. then GC/MS <sup>f</sup>	Blue band tube
BZ	g	g		Extr. then GC/MS	
H:HD	ACAMS /MINICAMS	DAAMS	Blue band tube	Extr. then GC/FPD	ACAMS /MINICAMS
HT:HD	ACAMS /MINICAMS	DAAMS	Blue band tube	Extr. then GC/FPD	ACAMS /MINICAMS
HL:HD HL:L	ACAMS /MINICAMS	DAAMS bubbler	Blue band tube Double yellow band tube	Extr. then GC/FPD Extr. then IC	ACAMS /MINICAMS Double yellow band tube
CX			Blue band tube		
<b>Military Chemical Compounds</b>					
DM				Extr. then HPLC	Colorimetric
CA or BBC	OVA/PID				
CN, CNS, CNB	OVA/PID	NIOSH 291	Blue band tube	Extr. then GC/MS	Blue band tube
WP	h	h		Extr. then GC/FPD	
PS	OVA/PID			Extr. then GC/MS	

a Includes water, sediment, and soil samples, and liquid and solid wastes.

b Field screening method

c Laboratory analysis method

d Identification of agent will be confirmed by dilution and laboratory analysis.

e L is rapidly hydrolyzed to CVAA and is not expected to be found in aqueous samples; however, CVAA can be analyzed by IC.

f CG rapidly hydrolyzed and is not expected to be found in aqueous samples, but may be present in soils and solid samples.

g Insufficient information is available to recommend a NRT alarm for TWA monitoring. BZ ASC levels can be monitored with BezeTrog and the LEAP can be used to sample ambient concentration and provide historical documentation.

h Method not required.

TABLE 10. PERFORMANCE CHARACTERISTICS OF NEAR-REAL-TIME MONITORS AND KITS (USACMDA, 1993)

Values Are mg/m<sup>3</sup> Unless Noted

	Response Time (min)	GA	GB	GD	VX	HD	L	HN	CX	H <sup>1</sup>	HL <sup>1</sup>	HT <sup>1</sup>	AC	CL	CG	BZ	DM	CA	CM (CNS, CNG)	WP	PS
NRT Monitor																					
ACAMS <sup>2</sup>	3 to 5	0.0001 <sup>3</sup>	0.0001	0.00003 <sup>3</sup>	0.00001	0.003				0.003	0.003	0.003									
MINICAMS <sup>2</sup>	5 to 12	0.0001	0.0001	0.00003	0.00001	0.003	0.003 <sup>4</sup>	NYT		0.003	0.003	0.003									
OVA		und	und	und	und	und	und	und		und	und	und									
MM-1/ EM-640	und	und	und	und	und	und		NYT		und	und	und									
SpectraTrek 520	DA	DA	DA	DA	DA	DA		NYT		DA	DA	DA									
RAID-1	0.06 to 2	0.005	0.005	0.005	0.005	0.02	0.02	NYT	NYT	0.02	0.02	0.02	0.01	und	und						
DAM	1	0.03	0.03	0.03	0.03	0.03		0.03		0.03	0.03	0.03		und <sup>6</sup>							
ICAM		EXP	EXP	EXP	EXP	EXP	EXP			EXP	EXP	EXP									
ACADA		EXP	EXP	EXP	EXP	EXP	EXP			EXP	EXP	EXP									
AVM		NYT	NYT	NYT	NYT	NYT				NYT	NYT	NYT									
EVM	>0.25	EXP	EXP	EXP	EXP	EXP		EXP		EXP	EXP	EXP									
Microtip	0.05	NYT	NYT	NYT	NYT	NYT	NYT	NYT		NYT	NYT	NYT									
ICAD	2	0.2-0.5	0.2-0.5	0.2-0.5	ND	10	10			≥10	≥10	≥10	≥50	≥50	≥50						
TG-300/800	0.5												0.02		0.02						
M8/M43 <sup>5</sup>	3	und	und	und	und																
M8A1/ M43A1	0.5	0.1	0.1	0.1	0.1																
MIRAN 1BX	0.05 to 1														0.4						
SPINCON/ IC	15						0.0003 <sup>4</sup>														
TGM-555	8.5 to 10												0.002	0.005	0.02						

TABLE 10. (Continued)  
 PERFORMANCE CHARACTERISTICS OF NEAR-REAL-TIME MONITORS AND KITS (USACMDA, 1993)  
 Values Are mg/m<sup>3</sup> Unless Noted

	Response Time (min)	GA	GB	GD	VX	HD	L	HN	CX	H'	HL'	HT'	AC	CL	CG	BZ	DM	CA	CM (CNS, CNG)	WP	PS
Draeger Tubes	Various					1.0		1.0		1.0	1.0	1.0	2.5		0.09						
KITS																					
M18A2	1 to 5	0.1-1.0	0.1-1.0	0.1-1.0	0.5	10	und	und	0.5	und	und	8	und	12							
M272 (mg/l)	20	0.02	0.02	0.02	0.02	2	2	und		2	und	und	20	und				und			
M9/M9	immediate	Gross	Gross	Gross	Gross	Gross				Gross											
M256	13 to 15	0.05	0.05	0.05	0.15	3.0	14	und	und	und	und	und	und	und							
M256A1	13 to 16	0.005	0.005	0.005	0.02	3.0	14	und	5	und	und	und	11	10							

Gross: Large concentrations over the HLE. Generally refers to liquid contamination.  
 und: Procedure is known to detect this agent but concentrations is not defined.  
 EXP: Monitor still in development or production phase and has not been fielded. These are the assumed agents that it will monitor.  
 FID: During manufacture's field testing the instrument failed to detect the presence of agent.  
 NYT: Unit should respond to this agent but has not yet been tested.  
 DA: Agent data is available from the vendor through nondisclosure agreement.  
 Detection levels based on measuring mixture as HD.  
 Values listed are for TWA. The ACAMS and MINICAMS may also be used to monitor ASC and HLE hazard levels.  
 The ACAMS has not been certified for this agent but the monitor should be capable of monitoring this agent.  
 This is an experimental method that has not been field tested.  
 This is an obsolete high-level alarm which is no longer supported.  
 Unit will respond to this agent but is not in the standard programming.  
 Microtip detects generic organic vapors at approximately 0.7 mg/m<sup>3</sup> (benzene equivalent), but has not been tested for agent.

TABLE 11. FOR LABORATORY ASSAY OF CWA DEGRADATION PRODUCTS				
Compound	Environmental Matrix			
	Soil	Water	Air	Comment
<b>H Agents</b>				
dithiane	ExGC	ExGC	TDGC	
thiodiglycol	LSPED	SPED	NA	dry-ExDGC
oxathiane	ExGC	ExGC	TDGC	
sulfoxide	ExGC	ExGC	TDGC	
sulfone	ExGC	ExGC	TDGC	
<b>G Agents</b>				
methyl phosphonates	ExGC	ExGC	XEGC	
phosphonic acids	ExDGC	ExDGC	NA	
pinacolyl alcohol	ExDGC	ExDGC	NA	
<b>VX</b>				
methyl phosphonates	ExGC	ExGC	XEGC	
phosphonic acids	ExDGC	ExDGC	NA	
pinacolyl alcohol	ExDGC	ExDGC	NA	
dimethylamine	PGC	PGC	TDGC	
diisopropylamine	ExGC	ExGC	TDGC	
<b>CG, CK, AC Agents</b>				
none applicable				
<b>L</b>				
CVAA	ExIC	NA	ExGC	
arsenic	ExAA	IC	ExGC	

- ExGC extraction followed by gas chromatography  
 TDGC tenax collection; thermal desorption from collection resin into gas chromatograph  
 SPED solid phase extraction of liquid using C-18; extraction and derivatization prior to gas chromatographic assay  
 LSPED aqueous leach; solid phase extraction of liquid leach using C-18; elution and derivatization prior to gas chromatographic assay  
 XEGC XAD/PUF collection followed by elution with solvent; gas chromatography/mass spec assay  
 XEDGC XAD/PUF collection followed by elution with solvent; derivative and assay by mass spec.  
 ExDGC extraction followed by derivatization; assay by gas chromatography  
 PGC purge from matrix into tenax trap; thermal desorption to mass spec for assay  
 ExIC extraction followed by ion chromatography  
 ExAA extraction followed by atomic adsorption assay

## 12 SUMMARY

The significant potential for chemical warfare agent contamination at FUDS, and on active DOD installations, makes it important that USA professionals involved with site assessment and remediation be aware of the environmental chemistry of the chemical agents and their degradation products. This report summarizes data on the fate and transport of these compounds from the professional chemistry and environmental literature, USA technical reports, and some foreign documents. This report was written for use by non-chemists in the planning and executing the cleanup of these contaminated sites. Those environmental characteristics of a site which may affect the level or the extent of contamination were analyzed for the agents of interest. Trends are displayed in graphs for ease of use, since trends and relative rates are more relevant in extrapolating laboratory data to real field situations. The reader is referred to the original reference for more detailed information. Other summaries which were useful in compiling this report were Small (1984), Trapp (1985), Britton (1986), Sanches (1993), and Franke (1982). The extensive eight volume series by the Finish Ministry of Foreign Affairs, Methodology and Instrumentation for Sampling and Analysis in the Verification of Chemical Disarmament, also provides detailed information on sampling and analytical methods for many of the agents.

There are many gaps in the chemical and environmental data, particularly for decomposition products. Especially lacking is field data from actual contaminated sites. As the USA non-stockpile chemical material program generates such data, it should be incorporated into this document. A concise summary of the environmental chemistry of each agent is included in the Appendix. These data sheets contain much of the relevant information and can be removed for easy use in the field.

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**APPENDIX**  
**CHEMICAL AGENT SUMMARY**

## SULFUR MUSTARD (HD)

**Chemical Name:** Bis(2-chloroethyl)sulfide (CAS 505-60-2)

**Molecular Formula:**  $C_4H_8Cl_2S$

**Structure:**



**Description:** HD is a strong blister agent (vesicant).

<b>Human Risk Factors:</b>	LC <sub>50</sub> (inhalation)	- 1500 mg-min/m <sup>3</sup>
	IC <sub>50</sub> (skin)	- 2000 mg-min/m <sup>3</sup>
	IC <sub>50</sub> (eye)	- <200 mg-min/m <sup>3</sup>
	LD <sub>50</sub> (skin)	- 100 mg/Kg
	Max. Permis. Conc. (water)	- 0.23 ug/L (adult)
		- 0.0022 ug/L (infant)
	Max. Permis. Conc. (air)	- 0.003 mg/m <sup>3</sup> (worker TWA)
		- 0.0001 mg/m <sup>3</sup> (general public)

**Representative Half-Lives:** 4-13 minutes (25 C)

**Decomposition Products:** hemi mustard (CAS 693-30-1)  
thiodiglycol (CAS 111-48-8)  
2-chloroethyl vinyl sulfide (CAS 81142-02-1)  
mustard sulfoxide (CAS 5819-08-9)  
mustard sulfone (CAS 471-03-4)  
2-chloroethyl vinyl sulfoxide (40709-82-8)  
divinyl sulfoxide (1115-15-7)  
Bis (2-hydroxyethyl)-2-(2-chloroethylthio) ethyl sulfonium (CAS 64036-91-5)  
Bis-2(bis(2-hydroxyethyl)-sulfonium ethyl) sulfide (CAS 64036-79-9)  
1,4 dithiane (CAS 505-29-3)  
1,4 oxathiane (CAS 15980-15-1)

**Risk of Decomposition Products:** A number of the short-lived hydrolysis and dechlorination products of HD can still produce toxic effects. Thiodiglycol appears to produce signs of toxicity similar to glycols. The sulfone and sulfoxide oxidation products of thiodiglycol are considered non-toxic but are vesicant. Dechlorination of the sulfone produces divinyl sulfone which is highly toxic if injected and causes eye irritation and tearing.

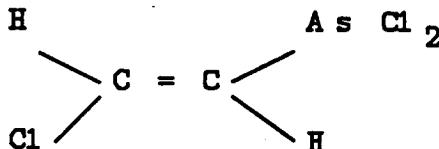
**Environmental Transport:** The hydrolysis products such as thiodiglycol are all more water soluble than HD and would tend to migrate at a higher rate than the parent compound. The formation of polymers at the surface of mustard in quiescent conditions and the concentration of thiodiglycol in the surface/water interface significantly retards solvation of mustard and pockets of pure mustard have been found even under water.

## LEWISITE (L)

**Chemical Name:** dichloro (2-chlorovinyl) arsine (CAS 541-25-3)

**Molecular Formula:**  $C_2H_2AsCl_3$

**Structure:**



**Description:** L is a strong blister agent (vesicant) which also causes pulmonary edema, diarrhea, and low blood pressure.

<b>Human Risk Factors:</b>	LC <sub>50</sub> (inhalation)	- 1200 mg-min/m <sup>3</sup>
	LC <sub>50</sub> (skin)	- > 1500 mg-min/m <sup>3</sup>
	IC <sub>50</sub> (eye)	- <300 mg-min/m <sup>3</sup>
	Max. Permis. Conc. (water)	- 2 mg/L
	Max. Permis. Conc. (air)	- 0.003 mg/m <sup>3</sup> (worker TWA) - 0.003 mg/m <sup>3</sup> (general public)

**Representative Half-Lives:** Quickly volatilizes or is converted to lewisite oxide.

**Decomposition Products:** dihydroxy-2-chlorovinylarsine (CAS 85090-33-1)  
2-chlorovinyl arsenic oxide (lewisite oxide) (CAS 123089-28-1)  
2-chlorovinyl arsonic acid (CAS 64038-44-4)  
sodium arsinite (CAS 11137-68-1)

**Risk of Decomposition Products:** Lewisite oxide damages skin and is absorbed into the bloodstream where it produces systemic effect typical of arsenical compounds. The oxidation product of lewisite oxide, 2-chlorovinyl arsonic acid, has markedly reduced toxicity.

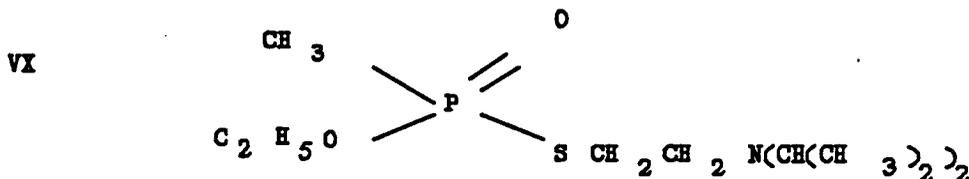
**Environmental Transport:** Lewisite in soil either vaporizes or is quickly converted to the oxide in the presence of moisture. Lewisite oxide is water soluble and maybe microbially oxidized to the 2-chlorovinyl arsonic acid. Both would be transported by groundwater or leached by precipitation.

(VX)

**Chemical Name:** o-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (CAS 50782-69-9)

**Molecular Formula:** C<sub>11</sub>H<sub>26</sub>NO<sub>2</sub>PS

**Structure:**



**Description:** VX is a lethal anticholinesterase agent which is hazardous through inhalation, ingestion, skin exposure and through contact with the eyes.

<b>Human Risk Factors:</b>	LC <sub>50</sub> (inhalation)	- 30 mg-min/m <sup>3</sup>
	LD <sub>50</sub> (skin)	- 0.142 mg/kg
	IC <sub>50</sub> (inhalation)	- 25 mg-min/m <sup>3</sup>
	Min Effect Dose (eye)	- 0.02 mg-min/m <sup>3</sup>
	Max. Permis. Conc. (water)	- 1.5 mg/L
	Max. Permis. Conc. (air)	- 0.00001 mg/m <sup>3</sup> (worker TWA)
		- 0.000003 mg/m <sup>3</sup> (general public)
	Max. Permis. Conc. (produce)	- 1.4 ug/Kg

<b>Representative Half-Lives:</b>	Acidic (pH 4)	- 2257 hours
	Neutral (pH 7)	- 995 hours
	Alkaline (pH 10)	- 40.5 hours

**Decomposition Products:** diisopropylaminoethyl mercaptan (CAS 5482-07-9)  
methyl phosphonic acid (CAS 993-13-3)  
ethyl methylphosphonothioic acid (CAS 18005-40-8)  
Bis(2-diisopropylaminoethyl) sulfide (CAS 110501-56-9)  
Bis((2-diisopropylaminoethyl) disulfide (CAS 65332-44-7)  
S-(diisopropylaminoethyl) methylphosphonothioate (CAS 73207-98-4)  
diisopropylaminoethanol (CAS 96-80-0)  
diisopropylaminoethyl methylphosphonic acid (CAS 73207-98-4)

**Risk of Decomposition Products:** The anticholinesterase inhibition of VX decreases slower than the disappearance of VX indicating that some of the decomposition products still exhibit a toxic effect.

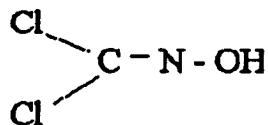
**Environmental Transport:** Most of the decomposition products are more water soluble; however, DE<sub>2</sub>S and DES<sub>2</sub> have high log Kow and, therefore, would be bound to soil organics.

## PHOSGENE OXIME (CX)

**Chemical Name:**

**Molecular Formula:**  $\text{CCl}_2\text{NOH}$

**Structure:**



**Description:** Phosgene oxime is a severe irritant to the eyes, mucus membranes, and skin.

<b>Human Risk Factors:</b>	LCt(eye irritation)	- 25 mg/m <sup>3</sup>
	LC <sub>50</sub> (inhalation)	- 3200 mg/m <sup>3</sup>
	TCL <sub>0</sub> (inhalation)	- 101 mg/m <sup>3</sup>
	Max. Permis. Conc. (air)	- 0.04 mg/m <sup>3</sup> (worker TWA)

**Representative Half-Lives:** Rate data is not available; however, CX is reported to dissolve in water and hydrolyze.

**Decomposition Products:** hydroxylamine hydrochloride (CAS 5470-11-1)  
carbon dioxide (CAS 124-38-9)  
hydrogen chloride (CAS 7647-01-0)

**Risk of Decomposition Products:** Decomposition products are considered nontoxic.

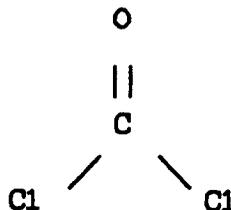
**Environmental Transport:** Gas decomposes in the presence of moisture.

## PHOSGENE (CG)

**Chemical Name:** carbonyl chloride (CAS 75-44-5)

**Molecular Formula:**  $\text{OCCl}_2$

**Structure:**



**Description:** Phosgene is a severe eye and skin irritant and is highly toxic by inhalation. Acute exposure results in respiratory and circulatory failure. Chronic exposure can also cause emphysema and dermatitis.

<b>Human Risk Factors:</b>	$\text{LCL}_{50}$ (inhalation)	- 202 mg-min/m <sup>3</sup> in 5 minutes
	$\text{LC}_{50}$ (inhalation)	- 3200 mg/m <sup>3</sup>
	$\text{TCL}_{50}$ (inhalation)	- 101 mg/m <sup>3</sup>
	Max. Permis. Conc. (air)	- 0.04 mg/m <sup>3</sup> (worker TWA)

**Representative Half-Lives:** CG rapidly hydrolyzes in water. Even at 0°C, 10 g/L of CG is hydrolyzed in 20 seconds. In air CG is more stable. In 22 hours, 24% of a 12.5 ppm vapor remained.

**Decomposition Products:** Completely decomposes to  $\text{CO}_2$  and HCl.

**Risk of Decomposition Products:** Decomposition products are considered nontoxic.

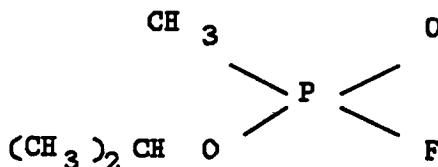
**Environmental Transport:** With a high vapor pressure (1379 mm Hg @ 25°C) vaporization will dominate the environmental chemistry of CG. In the vapor phase, CG is relatively stable.

## SARIN (GB)

**Chemical Name:** isopropyl methylphosphonofluoridate (CAS 107-44-8)

**Molecular Formula:**  $C_4H_{10}PO_2F$

**Structure:**



**Description:** GB is a lethal anticholinesterase agent which is hazardous through inhalation, ingestion, skin exposure and through contact with the eyes.

<b>Human Risk Factors:</b>	LC <sub>50</sub> (inhalation)	- 70 mg-min/m <sup>3</sup>
	LD <sub>50</sub> (skin)	- 24 mg/kg
	IC <sub>50</sub> (skin)	- 35 mg-min/m <sup>3</sup>
	Min Effect Dose (eye)	- 0.2 mg-min/m <sup>3</sup>
	Max. Permis. Conc. (water)	- 2.8 mg/L
	Max. Permis. Conc. (air)	- 0.0001 mg/m <sup>3</sup> (worker TWA)
		- 0.000001 mg/m <sup>3</sup> (general public)
	Max. Permis. Conc. (produce)	- 2.6-3.5 µg/Kg

<b>Representative Half-Lives:</b>	Acidic (pH 4.25)	- 0.95 hours
	Neutral (pH 6.5)	- 237 hours
	Alkaline (pH 9)	- 0.6 hours

**Decomposition Products:** isopropyl methylphosphonic acid (CAS 1832-54-8)  
methyl phosphonic acid (CAS 993-13-3)

**Risk of Decomposition Products:** Decomposition products are considered nontoxic.

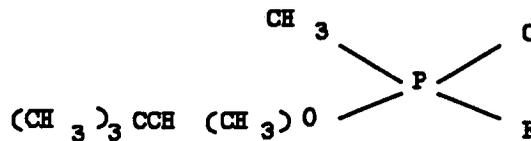
**Environmental Transport:** Decomposition products are more water soluble and have a lower affinity for organics than GB. GB has a high vapor pressure and would volatilize if exposed to the atmosphere. Vapor would also migrate through the soil in hot, dry conditions.

## SOMAN (GD)

**Chemical Name:** o-pinacolyl methylphosphonofluoridate (CAS 96-64-0)

**Molecular Formula:**  $C_7H_{16}PO_2F$

**Structure:**



**Description:** GD is a lethal anticholinesterase agent which is hazardous through inhalation, ingestion, skin exposure and through contact with the eyes.

<b>Human Risk Factors:</b>	LC <sub>50</sub> (inhalation)	- 70 mg-min/m <sup>3</sup>
	LD <sub>50</sub> (skin)	- 5 mg/kg
	IC <sub>50</sub> (inhalation)	- 35 mg-min/m <sup>3</sup>
	Min Effect Dose (eye)	- 0.2 mg-min/m <sup>3</sup>
	Max. Permis. Conc. (water)	- 2.8 mg/L
	Max. Permis. Conc. (air)	- 0.00003 mg/m <sup>3</sup> (worker TWA)
		- 0.000003 mg/m <sup>3</sup> (general public)

<b>Representative Half-Lives:</b>	Acidic (pH 5)	- 41 hours
	Neutral (pH 7.6)	- 21.7 hours
	Alkaline (pH 10)	- 0.6 hours

**Decomposition Products:** pinacolyl methylphosphonic acid (CAS 616-52-4) methyl phosphonic acid (CAS 993-13-3)

**Risk of Decomposition Products:** Decomposition products are considered nontoxic.

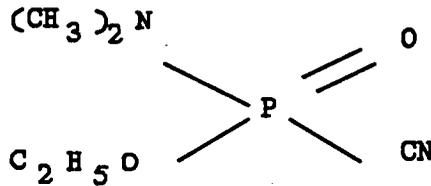
**Environmental Transport:** Decomposition products are more water soluble and have lower affinity for organics than GD.

## TABUN (GA)

**Chemical Name:** ethyl n,n-dimethylphosphoramidocyanidate (CAS 77-81-6)

**Molecular Formula:**  $C_3H_{11}N_2PO$

**Structure:**



**Description:** GA is a lethal anticholinesterase agent which is approximately half as toxic as GB. GA has a more irritating effect on the eyes than GB.

<b>Human Risk Factors:</b>	LC <sub>50</sub> (inhalation)	- 135 mg-min/m <sup>3</sup>
	LD <sub>50</sub> (skin)	- 14-21 mg/kg
	IC <sub>50</sub> (skin)	- 20,000 mg-min/m <sup>3</sup>
	Min Effect Dose (eye)	- ~0.2 mg-min/m <sup>3</sup>
	Max. Permis. Conc. (water)	- 2.8 mg/L
	Max. Permis. Conc. (air)	- 0.0001 mg/m <sup>3</sup> (worker TWA) - 0.000001 mg/m <sup>3</sup> (general public)
	Max. Permis. Conc. (produce)	- 2.6-3.5 µg/Kg

<b>Representative Half-Lives:</b>	Acidic (pH 3)	- 14 hours
	Neutral (pH 5)	- 2.5 hours
	Alkaline (pH 9)	- 2 hours

**Decomposition Products:**  
o-ethyl n,n-dimethylphosphoramidate  
o-ethyl phosphorocyanidate (CAS 23852-43-9)  
dimethylphosphoramidate (CAS 33876-51-6)  
dimethyl phosphoramidocyanidate (CAS 63917-41-9)

**Risk of Decomposition Products:** Most decomposition products exhibit low toxicity; however, cyanide may be generated in basic solutions. This could pose a serious health hazard.

**Environmental Transport:** Decomposition products are slightly more soluble than GA, and would be expected to be leached by precipitation and groundwater.