

SOUTHWEST RESEARCH INSTITUTE
6220 CULEBRA ROAD, P.O. DRAWER 28510
SAN ANTONIO, TEXAS 78228-0510

FIELD MANUAL ON ENVIRONMENTAL CHEMISTRY AND FATE OF CHEMICAL WARFARE AGENTS

FINAL REPORT

SwRI Project 01-5864

Prepared by

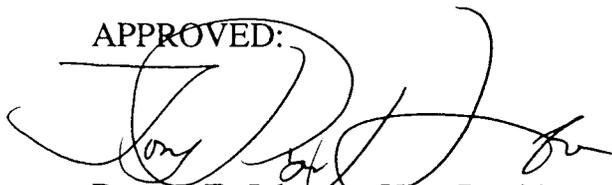
Dr. Michael G. MacNaughton
Joseph H. Brewer
Janet Ledbetter Ferrill

Prepared for

Department of the Army
Corps of Engineers, Huntsville Division

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APPROVED:



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

SOUTHWEST RESEARCH INSTITUTE

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MANUAL ORGANIZATION

This manual has been organized into 10 sections with references and an appendix. Section 1, the Introduction, is intended to briefly present the governmental program structure, purpose of the document, and background information. Sections 2 through 9 present the chemical, physical and degradation properties, human risk factors, and analytical techniques of the chemical agents categorized as organophosphorus agents, mustard agents, lewisite, phosgene, and phosgene oxime. Section 10 is the manual summary. A list of references is provided and an appendix has been included that contains definitions of risk factor abbreviations.

The field manual has been prepared from a parent report entitled "Environmental Chemistry and Fate of Chemical Warfare Agents," Southwest Research Institute, March 3, 1994. The report contains detailed information for each CWA, including chemical, fate, and degradation properties and mechanisms for hydrolysis reactions and half-lives. Additional sections discuss CWA decontaminant reactions, impacts on soil systems, biodegradation, environmental fate, analysis methods, and decomposition products of CWA. The appendix contains one page briefs summarizing each CWA chemical and physical properties, other topics discussed in the text, and human risk factors. A detailed list of references, pertinent also to this manual, is included in the report. The report should be used as back-up reference material for this field manual.

I. 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). 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 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). AEC is responsible for the evaluation and site characterizations of most active army installations.

The purpose of this document is for it to be used as a field manual at Department of Defense (DOD) installations containing CWA. Its intent is to present environmental chemistry and fate of the most prevalent CWA based on the available published research and literature. And to concisely present this information so that it may be used as a field reference for DOD personnel and their contractors as an aid in implementing the appropriate analytical, health and safety, and installation assessment and remediation programs. The manual has been prepared from primarily the perspective of the field engineer.

Background

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), Soman (GD), VX, hydrogen cyanide (AC), cyanogen chloride (CK) and phosgene (CG), phosgene oxime (CX), BZ, and CS (USACMDA, 1993).

These installations were identified in record searches as sites of CWA storage, shipping, munitions 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.

II. SULFUR MUSTARD (HD)

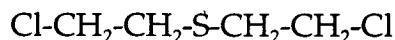
Chemical Name: Bis (2-chloroethyl) sulfide (CAS 505-60-2) (See Table 1).

Symbol: HD - Also other common sulphur mustard compounds denoted as H, T, HT, and HS.

Type: Blister agent

Molecular Formula: $C_4H_8Cl_2S$

Structure:



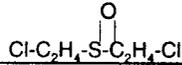
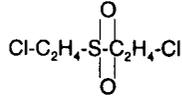
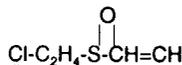
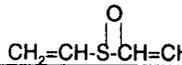
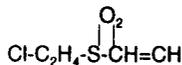
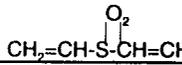
Description: Sulphur mustard (HD) is a strong blister agent (vesicant). Pure sulfur mustard is a colorless, odorless, oily liquid; however commercial products have a yellow/brown color with a sweet odor due to contaminants. Heating mustard to its boiling point results in thermal degradation and the formation 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.

Human Risk Factors: Commercial mustard (H) is normally a mixture of a large number of homologs which is more toxic than distilled mustard (HD). Mustards are extremely toxic to humans whether contact is through inhalation, ingestion, injection or absorbed through the skin. Mustards exist in both the liquid and gaseous phases. Unfortunately, the human sense of smell will not always detect the presence of mustard because it can be odorless, smell sweet, or even have a strong garlic and mustard odor. The following list presents human risk factors that have been established for exposure to mustards. An abbreviation legend is provided in the appendix.

LC _{t50} (inhalation)	- 1500 mg-min/m ³
IC _{t50} (skin)	- 2000 mg-min/m ³
IC _{t50} (eye)	- <200 mg-min/m ³
LD ₅₀ (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 ³ (worker TWA) - 0.0001 mg/m ³ (general public)

Hydrolysis and Degradation: Hydrolysis is the predominant mechanism of environmental degradation of mustards. Simply stated, hydrolysis is the decomposition of a chemical compound by reaction with water. Because of the low aqueous solubility of mustards, the rate of hydrolysis is determined by the amount of surface area exposed to the solvent, which is a function of particle size and turbulence. Experience has demonstrated that mustards can remain stable under water for years if there is little turbulence or mixing.

TABLE 1. 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	$\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-Cl}$ 	5819-08-9	Oxidation of HD
HO ₂	Mustard sulfone	$\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-Cl}$ 	471-03-4	Oxidation of HD
CVSO	2-Chloroethyl vinyl sulfoxide	$\text{Cl-C}_2\text{H}_4\text{-S-CH=CH}_2$ 	40709-82-8	Dechlorination of HD
DVSO	Divinyl sulfoxide	$\text{CH}_2=\text{CH-S-CH=CH}_2$ 	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 ₂	2-Chloroethyl vinyl sulfone	$\text{Cl-C}_2\text{H}_4\text{-S-CH=CH}_2$ 	7327-58-4	Dechlorination of HO ₂
DVSO ₂	Divinyl sulfone	$\text{CH}_2=\text{CH-S-CH=CH}_2$ 	77-77-0	Dechlorination of HO ₂
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	$\text{S-C}_2\text{H}_4\text{-S}^+(\text{C}_2\text{H}_4\text{OH})_2\text{-C}_2\text{H}_4\text{-S}^+(\text{C}_2\text{H}_4\text{OH})_2$	64036-79-9	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		15980-15-1	Dechlorination of CH
HDLP	HD Linear polymer	$\text{Cl-C}_2\text{H}_4\text{-(S-C}_2\text{H}_4\text{)}_n\text{-S-C}_2\text{H}_4\text{Cl}$	--	

The hydrolysis of H is also 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. In the first stage, onium compounds are formed which are highly reactive, and their interaction with enzymes, DNA and proteins is the basis for the skin toxicity of mustards. In the second stage, the onium compound further reacts with water to form other intermediate products such as thiodiglycol (TDG).

Significant variation in the hydrolysis rates of mustard in aqueous solution have been reported. 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. Studies have indicated that as temperature increases the half-life of mustard decreases (time required for one half of the original mustard to be degraded). Figure 1 shows the half-life versus temperature as reported by Franke (1982).

The calculated hydrolysis rate in freshwater is 2.5 times faster than in seawater (Rosenblatt et al., 1975). This results from the inhibition of the first stage of hydrolysis by chloride. The relative amounts of water present also affect the distribution of the hydrolysis byproducts. In dilute aqueous solutions, 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.

Two other common products that have been identified on surfaces and in groundwater at Rocky Mountain Arsenal are 1,4 dithiane (DT) and 1,4 oxathiane (OT) (Sanches 1993). These are formed by the de-chlorination of mustard and the half-mustard. DT is a thermal degradation product, and OT is a principal contaminant found on concrete contaminated with H. The half-life for OT is reported to be 1,747 hours (Sanches 1993). Decomposition products which may be found include the following:

- 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)

Decontaminant Reactions: 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. Decontaminants used for mustard agents include hypochlorite, which has been used extensively, DS2, and thermal destruction. Possible byproducts resulting from reactions with these decontamination processes are listed below:

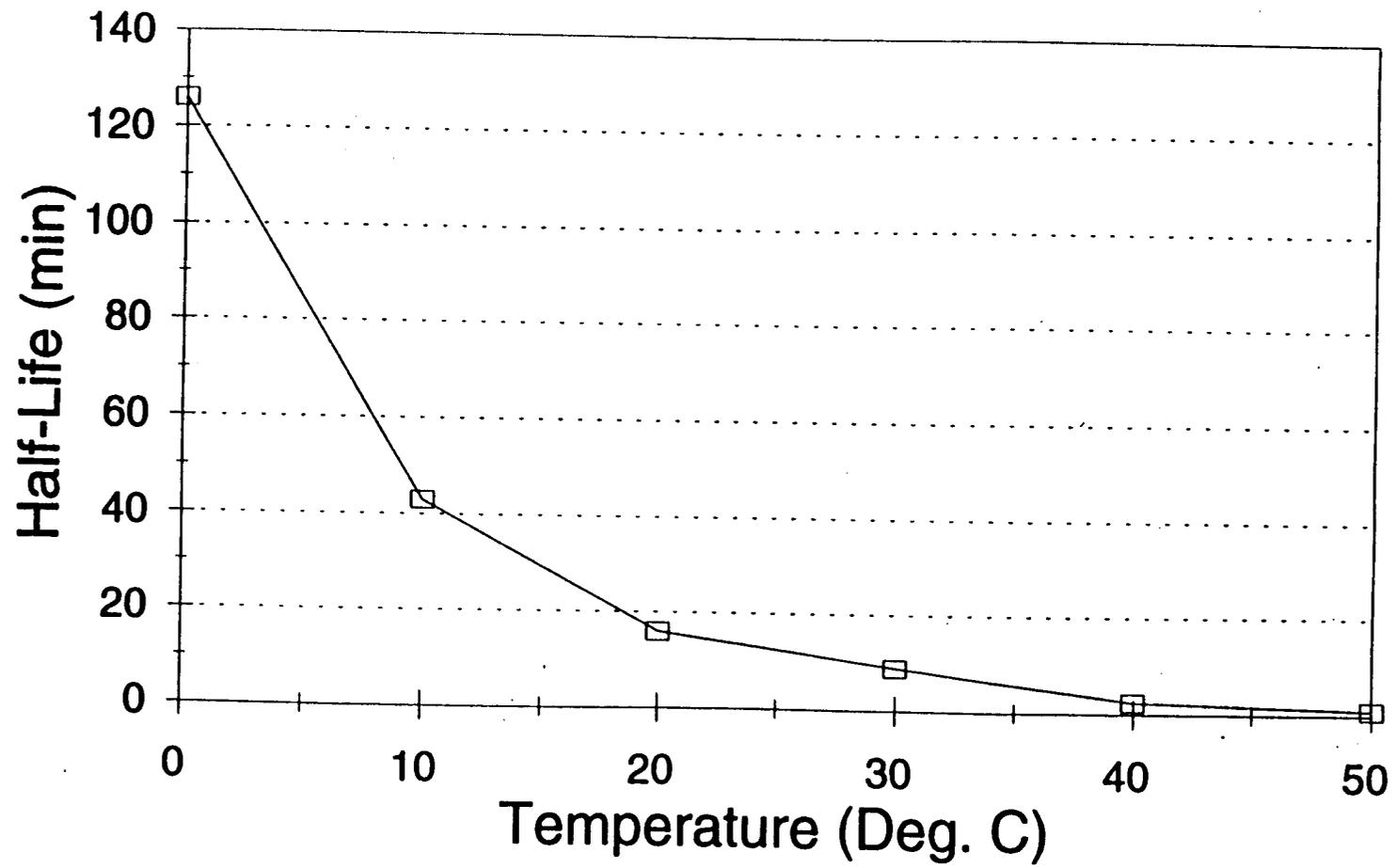


Figure 1. Effect of Temperature on HD Half-Life.

- Hypochlorite: sulfoxide (HO), sulfone (HO₂), and oxidation products of HD, HO₂, and HD-2TDG,
- DS2 decomposition products: divinyl chloride and 2-chloroethyl vinyl sulfide (CVS), and
- Thermal destruction: none when properly incinerated.

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 vesicant. Dechlorination of the sulfone produces divinyl sulfone which is highly toxic if injected and causes eye irritation and tearing.

Interaction with Soil Systems: No studies have been conducted which specifically address the decomposition rate of HD in soil. However, because of its chemical properties, mustard can be expected to generally react in soil like pesticides and other compounds of similar structure. 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, 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 not be expected to be degraded. 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.

Biodegradation: Actual data on the microbial degradation of HD 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.

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.

Analytical Techniques: For air matrixes mustard compounds H, HD, HT, and HS, are amenable to solid sorbent collection (EPA TO-1) and assay by gas chromatography (GC). These compounds are readily extracted from all other environmental media using hexane, chloroform, or dichloromethane. Products have been assayed using GC with flame photometric detector (FPD). USATHAMA Method LL04 is available for water assay of the H series degradation products.

Soil extraction methods for thiodiglycol analysis are available but tend to show high variability, as with USATHAMA Method LW 18. Other analytical methods for wet soil assay have been used but precision and accuracy techniques have not yet been established.

Assay of thiodiglycol in water systems is accomplished by concentration of the matrix and direct injection high pressure liquid chromatography (HPLC). Methods under development include solid phase extraction of analytes from water systems. Currently, application of USATHAMA Method LW 22 indicates sufficient sensitivity (low ppb); however, the method suffers significant variability.

III. VX

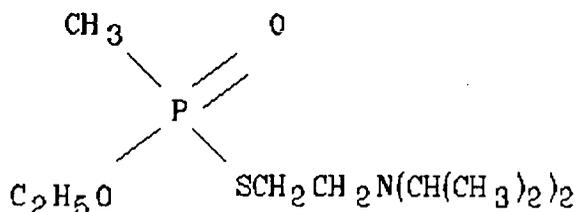
Chemical Name: O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (CAS 50782-69-9) (See Table 2).

Symbol: VX

Type: Organophosphorous nerve agent

Molecular Formula: $C_{11}H_{26}NO_2PS$

Structure: 16



Description: VX is either a colorless or amber, odorless liquid which is soluble in water and many organic solvents. VX is the least volatile of the organophosphorus agents with a vapor pressure of 0.0007 mm Hg (USA FM 3-9, 1975).

Human Risk Factors: VX is a lethal anticholinesterase agent which is hazardous through inhalation, ingestion, skin exposure and through contact with the eyes. The following list presents human risk factors that have been established for exposure to VX.

LCt ₅₀ (inhalation)	- 30 mg-min/m ³
LD ₅₀ (skin)	- 0.142 mg/kg
ICt ₅₀ (inhalation)	- 25 mg-min/m ³
Min Effect Dose (eye)	- 0.02 mg-min/m ³
Max. Permis. Conc. (water)	- 1.5 mg/L
Max. Permis. Conc. (air)	- 0.00001 mg/m ³ (worker TWA) - 0.000003 mg/m ³ (general public)
Max. Permis. Conc. (produce)	- 1.4 ug/Kg

Hydrolysis and Degradation: VX hydrolyzes very slowly except at very high pHs. In neutral aqueous solutions, the half-life ($t_{1/2}$) or the time to achieve 50% decomposition of the agent, for hydrolysis of VX is in excess of 2,300 hours at 25°C (Epstein et al., 1974). The reaction rate accelerates with increasing pH so that at pH 13, the $t_{1/2}$ was reported to be 16 minutes (USA FM 3-9, 1975). In contrast to other organophosphorus agents, the hydrolysis of VX is not accelerated at low

TABLE 2. ENVIRONMENTAL CHEMISTRY OF VX

Agent	Chemical Name	Structure	Reg #	Source
VX	O-ethyl S-(2-diisopropyl amino ethyl) methylphosphonothioate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{DIPAE-S-P-OC}_2\text{H}_5 \\ \\ \text{CH}_3 \end{array}$	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	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO-P-OC}_2\text{H}_5 \\ \\ \text{CH}_3 \end{array}$	1832-53-7	Hydrolysis of VX
EMPS	Ethyl methylphosphonothioic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HS-P-OC}_2\text{H}_5 \\ \\ \text{CH}_3 \end{array}$	18005-40-8	Hydrolysis of VX
DEOH	Diisopropylaminoethanol	DIPAE-OH	96-38-0	Hydrolysis of VX
DE ₂ S	Bis(2-diisopropylaminoethyl) sulfide	DIPAE-S-DIPAE	110501-56-9	Hydrolysis of VX
DES ₂	Bis(2-diisopropylaminoethyl) disulfide	$\begin{array}{c} \text{DIPAE-S} \\ \\ \text{DIPAE-S} \end{array}$	65332-44-7	Oxidation of DESH
DDP	Diethyl dimethylpyrophosphonate	$\begin{array}{c} \text{O} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O-P})_2\text{O} \\ \\ \text{CH}_3 \end{array}$	32288-17-8	Agent impurity
EA2191	S-(2-diisopropylaminoethyl) methylphosphonothioate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{DIPAE-S-P-OH} \\ \\ \text{CH}_3 \end{array}$	73207-98-4	Hydrolysis of VX
MPA	Methylphosphonic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO-P-OH} \\ \\ \text{CH}_3 \end{array}$	993-13-3	Hydrolysis of GB, GD, and VX
DPCA	N-Chlorodiisopropylamine	(iPr) ₂ -N-Cl	24948-81-0	Chlorination
IPCA	N-Chloroisopropylamine	iPr-N-H-Cl	26245-56-7	Chlorination
DIPAE	Diisopropylaminoethyl	(iPr) ₂ NCH ₂ CH ₂	--	--
DIPC	Diisopropylcarboimide	iPr-N=C-N-iPr	693-13-0	Stabilizer
DIPU	1,3 Diisopropylurea	$\begin{array}{c} \text{iPr-NH-C-NY-iPr} \\ \parallel \\ \text{O} \end{array}$	4128-37-4	Hydrolysis of DIPC

pHs. However, it is apparent there is a substantial base catalyzed increase in the reaction rate at higher pHs.

Different reactions predominate for the hydrolysis of VX at acid, neutral and alkaline pHs. Table 2 lists the potential reaction products of VX. 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. 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. The VX decomposition products that may be found are listed below.

- 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)

Decontaminant Reactions: Calcium hypochlorite has been used to decontaminate VX. The reaction is reported to have a half-life of 1.5 minutes and produce ethyl methyl phosphonate (Yurow 1982). Thermal destruction of VX produces methylfluorophosphoric acid and O-ethyl O-(2-diisopropylaminoethyl) methylphosphonate.

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. For example, 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.

Interaction with Soil Systems: 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.

Kaaijk and Frijlink (1977) followed the degradation of ³²P- and ³⁵S-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 (DES₂). Approximately 50% of the phosphorus was found in water extracts and 40% in alkaline methanol extracts. Compared with humic sand in which 70% of the ³⁵S could be extracted, for humic loams

and clay peat only 35% and 23% could be extracted, respectively. It was hypothesized that DES₂ 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 DES₂ 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 DES₂ 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.

Biodegradation: Organic soils such as Spodosol (pH 3.9, 35% organic) have been shown to retain greater percentages of organophosphonates than low organic content soils such as silty-loams (pH 6.5, 5.5% organic). Daughton et al., (1979) investigated the microbial degradation and soil retention of MPA and other O-alkylmethylphosphonic acid esters with Spodosol retaining 95.4% of the MPA in solution, 42% of IMPA and 32% of PMPA. The silty-loam only retained 11% of MPA in solution.

When Spodosol was added to cultures of *P. Testosteroni* it inhibited its ability to use inorganic phosphorous and MPA as phosphorous 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 phosphorous is not available, if inorganic phosphate is prevalent, little degradation would be predicted. However, where phosphorous is limiting, nutrient degradation of phosphonates may occur through bacterial action.

Environmental Transport: Most of the decomposition products are more water soluble; however, DE₂S and DES₂ have high octanol-water partition coefficients and, therefore, would be bound to soil organics.

Analytical Techniques: 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 using this AgF pad prior to introduction.

The assay of VX degradation products will follow those methods identified for the organophosphorus - 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 products of VX will extract and are amenable to GC assay. 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.

IV. SARIN (GB)

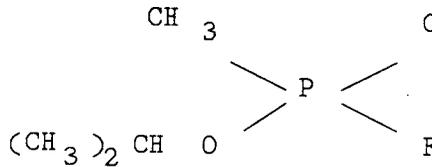
Chemical Name: Isopropyl methylphosphonofluoridate (CAS 107-44-8) (See Table 3).

Symbol: GB

Type: Organophosphorous nerve agent

Molecular Formula: C₄H₁₀PO₂F

Structure:



Description: Sarin (GB) is a colorless or amber, odorless liquid which is soluble in water and many organic solvents. GB is very volatile with a vapor pressure of 2.9 mm Hg at 25°C. 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.

Human Risk Factors: GB is a lethal anticholinesterase agent which is hazardous through inhalation, ingestion, skin exposure and through contact with the eyes. The human risk factors presented below represent established values for exposure to GB.

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

TABLE 3. ENVIRONMENTAL CHEMISTRY OF SARIN

Agent	Chemical Name	Structure	Reg #	Source
GB	Isopropyl methyl phosphonofluoridate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{iPr-O-P-F} \\ \\ \text{CH}_3 \end{array}$	107-44-8	Percent Agent
IMPA	Isopropyl methylphosphonic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{iPr-O-P-OH} \\ \\ \text{CH}_3 \end{array}$	1832-54-8	Hydrolysis of GB
iPr	Isopropyl	$\text{CH}_3\text{-CH-CH}_3$	--	--

Hydrolysis and Degradation: The hydrolysis of GB 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. 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.

The hydrolysis rates of GB are a function of the temperature and pH of the medium, with the rate being minimum between pH 4 and 6. 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 Ellin (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.

The other two important variables in the hydrolysis rate of GB are temperature and the type, and concentration of dissolved ionic species. Figure 2 illustrates the effect of temperature on GB half-life for solutions with a pH of 7.0. There is approximately a four-fold increase in the rate per 10° 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. 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).

Decomposition products which may be found include isopropyl methylphosphonic acid (CAS 1832-54-8) and methyl phosphonic acid (CAS 993-13-3).

Decontaminant Reactions: Hypochlorite has been used to decontaminate GB and is expected to produce isopropyl methylphosphonate as the hydrolytic reaction. Thermal destruction of GB produces methylfluorophosphoric acid and O-ethyl O-(2-diisopropylaminoethyl) methylphosphonate.

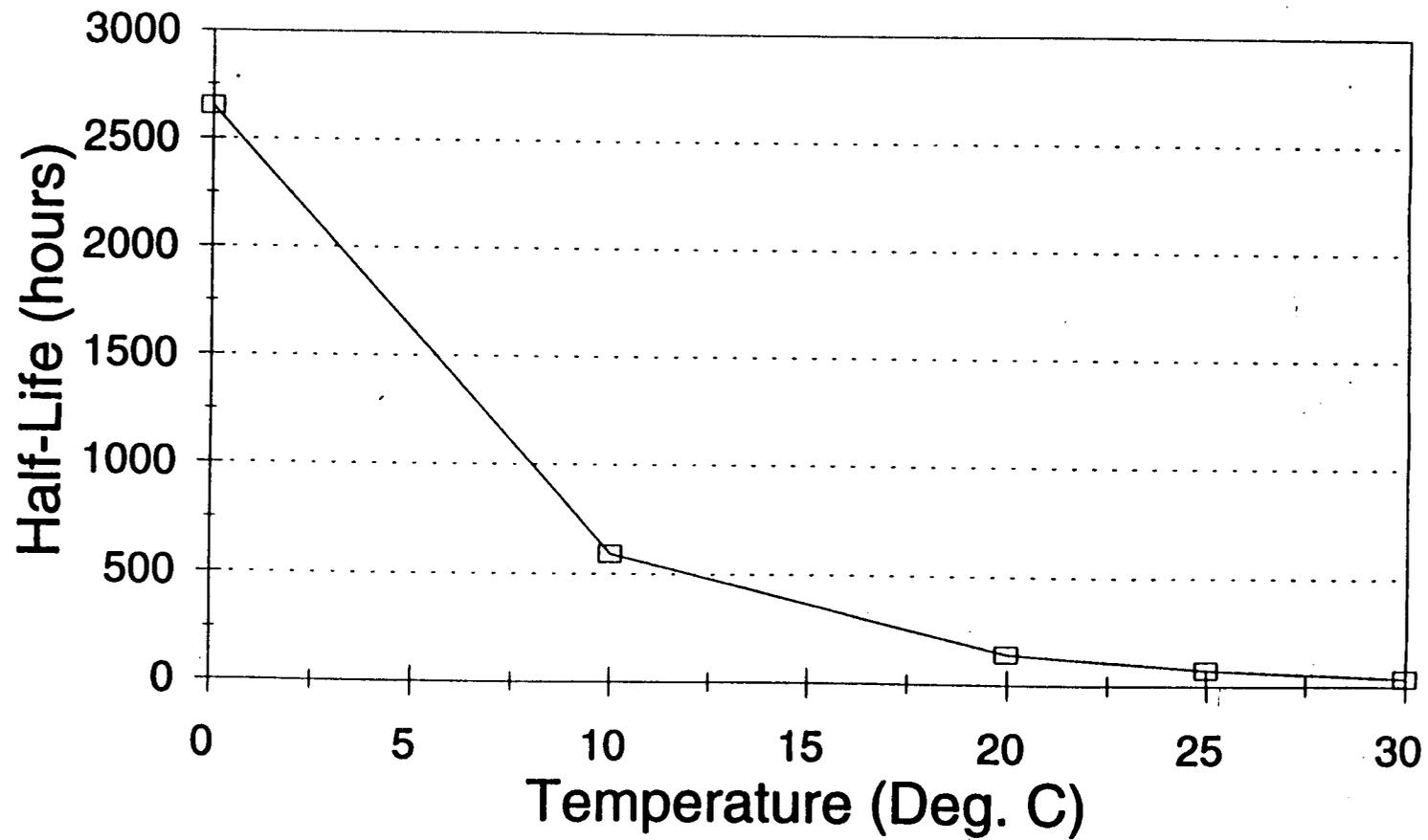


Figure 2. Effect of Temperature on GB Half-Life.

Risk of Decomposition Products: Decomposition products are considered nontoxic.

Interaction with Soil Systems: The decomposition of GB on γ -alumina were done by Kuiper et al., 1976. GB was strongly adsorbed to the γ -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).

Organic soils such as Spodosol (pH 3.9, 35% organic) have been shown to retain greater percentages of organophosphonates than low organic content soils such as silty-loams (pH 6.5, 5.5% organic). Daughton et al., (1979) investigated the microbial degradation and soil retention of MPA and other O-alkylmethylphosphonic acid esters with Spodosol retaining 95.4% of the MPA in solution, 42% of IMPA and 32% of PMPA. The silty-loam only retained 11% of MPA in solution.

Biodegradation: GB biodegrades similarly to other organophosphonates. 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 GB and GD, 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 reports 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.

When Spodosol was added to cultures of *P. Testosteroni* it inhibited its ability to use inorganic phosphorous and MPA as phosphorous 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 phosphorous is not available, if inorganic phosphate is prevalent, little degradation would be predicted. However, where phosphorous is limiting, nutrient degradation of phosphonates may occur through bacterial action.

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

Analytical Techniques: 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.

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 derivatized phosphonic acids is performed using GCMS.

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

V. SOMAN (GD)

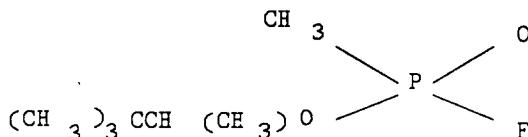
Chemical Name: O-pinacolyl methylphosphonofluoridate (CAS 96-64-0) (See Table 4).

Symbol: GD

Type: Organophosphorous nerve agent

Molecular Formula: C₇H₁₆PO₂F

Structure:



Description: Soman (GD) has a vapor pressure of 0.4 mm Hg, rendering it less volatile than GB. GD is a colorless or amber, odorless liquid which is soluble in water and many organic solvents.

Human Risk Factors: GD is a lethal anticholinesterase agent which is hazardous through inhalation, ingestion, skin exposure and through contact with the eyes. The following list presents human risk factors that have been established for exposure to GD.

LC _t ₅₀ (inhalation)	- 70 mg-min/m ³
LD ₅₀ (skin)	- 5 mg/kg
IC _t ₅₀ (inhalation)	- 35 mg-min/m ³
Min Effect Dose (eye)	- 0.2 mg-min/m ³
Max. Permis. Conc. (water)	- 2.8 mg/L
Max. Permis. Conc. (air)	- 0.00003 mg/m ³ (worker TWA) - 0.000003 mg/m ³ (general public)

Hydrolysis and Degradation: Because GD is a fluorophosphonate, hydrolysis is similar to GB, occurring 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. For more details about hydrolysis of GD, see section IV GB - Hydrolysis and Degradation.

The hydrolysis rate of GD is a function of the temperature and pH of the medium, with the rate being minimum between pH 4 and 6. 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. GD thickened with poly (methyl methacrylate) to increase the viscosity and reduce the volatility had a

TABLE 4. ENVIRONMENTAL CHEMISTRY OF SOMAN

Agent	Chemical Name	Structure	Reg #	Source
GD	O-pinacolyl methylphosphonofluoridate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{PIN-O-P-F} \\ \\ \text{CH}_3 \end{array}$	96-64-0 50642-24-5	Percent Agent
PMPA	O-pinacolyl methylphosphonic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{PIN-O-P-OH} \\ \\ \text{CH}_3 \end{array}$	616-52-4	Hydrolysis
DMP	Disodium methylphosphonate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-P-ONa} \\ \\ \text{ONa} \end{array}$	16002-10-1	Hydrolysis
PIN	Pinacolyl	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)\text{C-C} \\ \\ \text{H} \end{array}$	--	--

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.

Decomposition products which may be found include pinacolyl methylphosphonic acid (CAS 616-52-4) and methyl phosphonic acid (CAS 993-13-3).

Decontaminant Reactions: No specific data found in the literature for GD decontaminant reactions, although it is expected to react similarly to GB. For GB, decontamination has been performed using hypochlorite, which produces isopropyl methylphosphonate, and thermal destruction which produces methylfluorophosphoric acid and O-ethyl-(2-diisopropylaminoethyl).

Risk of Decomposition Products: Decomposition products are considered nontoxic.

Interaction with Soil Systems: No specific soil data in the literature, however, the decomposition of GD would be expected to be similar to GB. See section IV GB - Interaction with Soil Systems.

Biodegradation: GD biodegrades similarly to GB and other organophosphonates. For additional information see section IV GB - Biodegradation. Organophosphonates have been shown to undergo complete metabolisms to alcohol, alkane and phosphate (Daughton, Cook and Alexander, 1979). It has been observed that the products of organophosphorus hydrolysis would normally be accessible to microbial degradation, since they are water soluble. Organic soils such as Spodosol (pH 3.9, 35% organic) have been shown to retain greater percentages of organophosphonates than low organic content soils such as silty-loams (pH 6.5, 5.5% organic).

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

Analytical Techniques: Analytical techniques for GD are the same as those presented for GB in section IV GB - Analytical Techniques.

VI. TABUN (GA)

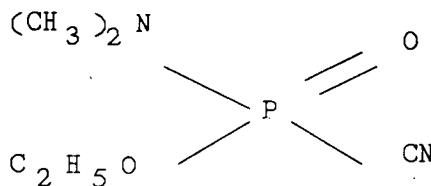
Chemical Name: Ethyl n,n-dimethylphosphoramidocyanidate (CAS 77-81-6) (See Table 5).

Symbol: GA

Type: Organophosphorous nerve agent

Molecular Formula: $C_3H_{11}N_2PO_2$

Structure:



Description: Tabun (GA) is less volatile than GB with a vapor pressure of 0.07 mm Hg. GA is a colorless or amber, odorless liquid which is soluble in water and many organic solvents.

Human Risk Factors: 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. The following list presents human risk factors that have been established for exposure to GA.

LC _{t50} (inhalation)	- 135 mg-min/m ³
LD ₅₀ (skin)	- 14-21 mg/kg
IC _{t50} (skin)	- 20,000 mg-min/m ³
Min Effect Dose (eye)	- ~0.2 mg-min/m ³
Max. Permis. Conc. (water)	- 2.8 mg/L
Max. Permis. Conc. (air)	- 0.0001 mg/m ³ (worker TWA) - 0.000001mg/m ³ (general public)
Max. Permis. Conc. (produce)	- 2.6-3.5 µg/Kg

Hydrolysis and Degradation: GA is unstable in neutral aqueous solutions with attacks occurring at both the P-N and P-CN bonds. 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⁻ 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). 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 half-life of GA tends to decrease

TABLE 5. ENVIRONMENTAL CHEMISTRY OF TABUN

GA	Ethyl n,n-dimethylphosphor aminocyanidate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{CN} \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	77-81-6	Percent Agent
EDPA	o-ethyl n,n-dimethylphosphoramidate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{OH} \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	Not found	Hydrolysis of GA
EPC	o-ethyl phosphorocyanidate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{CN} \\ \\ \text{OH} \end{array}$	117529-17-6	Hydrolysis of GA
PC	Phosphorocyanidate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{CN} \\ \\ \text{OH} \end{array}$	23852-43-9	Hydrolysis of GA
PA	Dimethylphosphoramidate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	33876-51-6	Hydrolysis of GA
DMPAC	Dimethylphosphoramidocyanidate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{CN} \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	63917-41-9	Hydrolysis of GA

as the pH increases with a significant drop in half-life above pH 9. Decomposition products which may be found include the following:

hydrogen cyanide (74-90-8)
o-ethyl n,n-dimethylphosphoramidate
o-ethyl phosphorocyanidate (CAS 23852-43-9)
dimethylphosphoramidate (CAS 33876-51-6)
dimethyl phosphoramidocyanidate (CAS 63917-41-9)

Decontaminant Reactions: No specific literature data found for GA decontaminant reactions, although it is expected to react similarly to GB. Bleach, dilute alkaline solutions or DS_2 are recommended (USA FM 3-9, 1975).

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.

Interaction with Soil Systems: No specific soil data in the literature, however, the decomposition of GA would be expected to be similar to GB. See section IV GB - Interaction with Soil Systems for more information.

Biodegradation: GA would be expected to biodegrade similarly to GB and other organophosphonates. For additional information see section IV GB - Biodegradation.

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

Analytical Techniques: Analytical techniques for GA are the same as those presented for GB. Total cyanide may also be assayed. Atomic absorption flame assay or inductively coupled argon plasma specific to cyanide could be considered for soil and water systems. Background cyanide levels will preclude low level detection.

VII. LEWISITE (L)

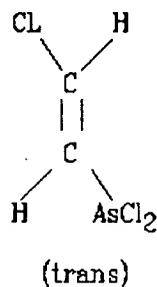
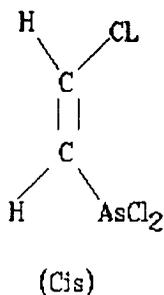
Chemical Name: Dichloro (2-chlorovinyl) arsine (CAS 541-25-3) (See Table 6).

Symbol: L

Type: Blister agent

Molecular Formula: $C_2H_2AsCl_3$

Structure:



Description: Lewisite (L). L is an organic arsenic compound 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 (Sanches 1993).

The vapor pressure of L (0.58-1.6 mm Hg) is slightly higher than GD, 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).

Human Risk Factors: Lewisite (L) is a strong blister agent (vesicant) which also causes pulmonary edema, diarrhea, and low blood pressure. L is absorbed rapidly through the skin and causes injury immediately upon contact (Franke 1982). Methyl and ethyl dichloroarsines cause both skin necrosis and a general toxic effect due to the trivalent arsenic. The contact hazards of L 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 following list presents human risk factors that have been established for exposure to L.

TABLE 6. ENVIRONMENTAL CHEMISTRY OF LEWSITE

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	$\text{C}_2\text{H}_4\text{ClO}_2\text{As}$	85090-33-1	1st Hydrolysis product
LO	2-Chlorovinyl Arsenicoxide	$\text{ClCH}=\text{CH}-\text{AsO}$	123089-28-1	2nd Hydrolysis product
LO _n	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

LCt ₅₀ (inhalation)	-1200 mg-min/m ³
LCt ₅₀ (skin)	->1500 mg-min/m ³
ICt ₅₀ (eye)	-<300 mg-min/m ³
Max. Permis. Conc. (water)	-2 mg/L
Max. Permis. Conc. (air)	-0.003 mg/m ³ (worker TWA)
	-0.003 mg/m ³ (general public)

Hydrolysis and Degradation: The hydrolysis of L 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 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 (As₂S₃) is formed. Above pH 10 the *trans* isomer hydrolysis reaction should be complete in a day (Waters and Williams 1950).

The dichloroarsine group, -AsCl₂, 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. L quickly volatilizes or is usually converted to lewisite oxide. Decomposition products which may be found include the following:

- 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)

Decontaminant Reactions: No specific data found in the literature for L decontaminant reactions. Supertropical bleach (STB), DS₂ or alkaline solutions are recommended decontaminants (USA FM 3-9, 1975). However, hypochlorite and thermal destruction are also conventional methods of decontamination.

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

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

Biodegradation: Actual data on the microbial degradation of CWAs is limited (Trapp 1985). Because of their similarity in structure to pesticides, it is expected that L would undergo similar microbial metabolism to the 2-chlorovinyl arsonic acid.

Environmental Transport: L in soil either vaporizes or is quickly converted to the oxide in the presence of moisture. Lewisite oxide is water soluble and may be microbially oxidized. Both would be transported by groundwater or leached by precipitation.

Analytical Techniques: Detection of L as the parent agent has not been accomplished as the compound is highly unstable. The primary degradation products (oxide or hydroxide) are detected using bubbler collection and colorimetric assay techniques. The conversion of the product to arsenic or arsine will allow detection using atomic absorption (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. The assay of L in air using DAAMS techniques shows very high sensitivity. Interfacing compounds and more importantly, residual derivatization reagents, preclude adequate detection of organo-arsenicals. There are also continuous tape monitoring systems (MDA) that employ colorimetric 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 soil and water should employ traditional EPA sanctioned AA techniques. Sensitivity is satisfactory for remediation verification and the methods are applicable to all environmental media. Sufficient background samples must be available to establish the site baseline of natural arsenic.

VIII. PHOSGENE (CG)

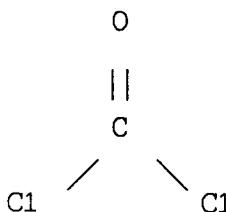
Chemical Name: Carbonyl chloride (CAS 75-44-5)

Symbol: CG

Type: Choking agent

Molecular Formula: OCCl_2

Structure:



Description: Phosgene (CG) is a colorless gas which condenses at 8.2°C. The vapors have an odor of "rotting fruit" (Franke 1982). The vapor pressure of CG at 25°C is 1,379 mm Hg.

Human Risk Factors: CG 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. The following list presents human risk factors that have been established for exposure to CG.

LCL ₀ (inhalation)	- 202 mg-min/m ³ in 5 minutes
LC ₅₀ (inhalation)	- 3200 mg/m ³
TCL ₀ (inhalation)	- 101 mg/m ³
Max. Permis. Conc. (air)	- 0.04 mg/m ³ (worker TWA)

Hydrolysis and Degradation: 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°C, 10 grams/liter of CG is completely hydrolyzed in 20 seconds, forming CO₂ and HCl (Franke 1982). In air CG is relatively stable, decreasing noticeably only after several hours. For example in 22 hours, 24% of a 12.5 ppm vapor remained unhydrolyzed (Franke 1982). Hydrolysis is promoted by bases with the formation of NaCO₃ and NaCl.

Decontaminant Reactions: No data in literature for specific CG decontaminant reactions. Since CG is a gas, aeration of closed spaces will reduce the hazard.

Risk of Decomposition Products: CG completely decomposes to CO₂ and HCl. These decomposition products are considered nontoxic.

Interaction with Soil Systems: No data was found on the interaction of CG with soils. The fate of CG in soil systems will be dominated by its high volatility and rapid hydrolysis to CO₂ and HCl.

Biodegradation: Since CG is a gas, volatilization will dominate and microbial degradation is not expected to be important.

Environmental Transport: With its high vapor pressure, vaporization will dominate the environmental chemistry of CG. In the vapor phase, CG is relatively stable.

Analytical Techniques: Analytical methods for detection of CG in environmental media have been established. Samples are extracted and then analyzed using GC and MS instrumentation. Because CG rapidly hydrolyzes it is not expected to be found in aqueous samples, although it may be adsorbed to dry soils and solid samples. The detection of CG in air will follow procedures identified by EPA SW 846 methods for volatile organics (TO 1 and TO 14, specifically).

IX. PHOSGENE OXIME (CX)

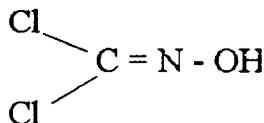
Chemical Name: Dichloroformoxime

Symbol: CX

Type: Irritant agent

Molecular Formula: CCl₂NOH

Structure:



Description: Phosgene oxime (CX) is a low melting-point solid or a yellowish brown liquid. The melting point is in the range of 39° to 40°C, the boiling point is 129°C, and the saturation vapor pressure is 20-25 mg/l (Franke 1982).

Human Risk Factors: CX is a powerful irritant which produces an immediate effect upon contact (USA FM 3-9, 1975). CX is a severe irritant to the eyes, mucus membranes, and skin.

LCt (eye irritation)	- 25 mg/m ³
LC ₅₀ (inhalation)	- 3200 mg/m ³
TCL ₀ (inhalation)	- 101 mg/m ³
Max. Permis. Conc. (air)	- 0.04 mg/m ³ (worker TWA)

Hydrolysis and Degradation: CX readily absorbs moisture and tends to polymerize in the presence of water and light. No hydrolysis rate data was in the literature; however, it is reported to dissolve slowly but readily in water, forming CO₂, HCl, and hydroxylamine hydrochloride (NH₃OHCl). 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). CX decomposition products that may be found are:

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

Decontaminant Reactions: Ammonium hydroxide and other alkalies react readily with CX to form nontoxic byproducts.

Risk of Decomposition Products: Decomposition products are considered nontoxic.

Interaction with Soil Systems: No data was found on the interaction of CX with soils. The fate of CX in soil systems would be expected to be water soluble and decompose to CO₂, HCl, and hydroxylamine hydrochloride.

Biodegradation: No biodegradation data found in the literature.

Environmental Transport: CX gas decomposes to CO₂ and HCl in the presence of moisture.

Analytical Techniques: Assay for CX is identical to that of CG.

X. SUMMARY

The significant potential for CWA 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 and interaction in soil systems. Data on the interaction of CWA in soil systems is limited. 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, it would not be expected to play a predominant role in degradation.

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.

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APPENDIX

HUMAN RISK FACTOR ABBREVIATIONS

The following paragraphs explain the abbreviations used for chemical agent human risk factors.

LCt₅₀ = Median Lethal Dosage

The median lethal dosage of a chemical agent that is inhaled as a vapor or aerosol is generally expressed as the LCt₅₀. The LCt₅₀ of a chemical agent is the dosage (vapor concentration of the agent multiplied by the time of exposure) that is lethal to 50 percent of exposed unprotected people at some given breathing rate. For skin, the dosage is equal to the time of exposure in minutes of an individual's unprotected skin multiplied by the concentration of the agent cloud. It varies with the degree of protection provided by masks and clothing worn by personnel and by the breathing rate. The unit used to express LCt₅₀ is milligram-minutes per cubic meter (mg-min/m³) (USA FM 3-9, 1975). Lethal Concentration 50 (LC₅₀) is equivalent to LCt₅₀ except that the unit used to express it is mg/m³.

LD₅₀ = Lethal Dosage

The lethal dosage of a chemical substance is the calculated dose of a substance which is expected to cause the death of 50 percent of a defined experimental animal population, as determined from the exposure to the substance, by any route other than inhalation (ingestion, or absorbed through the skin or eyes) (Fundamentals of Industrial Hygiene, 1979). The LD₅₀ of a chemical agent is the dosage that is lethal to 50 percent of exposed unprotected people. It varies with the degree of protection provided by masks and clothing worn by personnel. The unit used to express LD₅₀ is milligrams per kilogram (mg/Kg).

ICt₅₀ = Median Incapacitating Dosage

The incapacitating dosage of a chemical agent is generally expressed as the median incapacitating dosage - the amount of inhaled or absorbed vapor that is sufficient to disable 50 percent of exposed unprotected people. Incapacitating dosages vary in accordance with the protection provided by masks and clothing worn by people and by the breathing rate. The unit used to express ICt₅₀ is mg-min/m³ (USA FM 3-9, 1975).

Max. Permis. Conc. = Maximum Permissible Concentration

Maximum permissible concentrations (MPC) are based on federal regulations for exposure routes through ingestion, skin and eye absorption, and inhalation. Foremost, MPCs were established to regulate worker exposures. MPCs are recommended maximum average concentrations of radionuclides or chemical substances to which a worker may be exposed, assuming that he works 8 hours a day, 5 days a week, and 50 weeks a year (Fundamentals of Industrial Hygiene, 1979). The units used to express MPCs are in micrograms per liter (µg/L) for water, micrograms per kilogram (µg/Kg) for produce, and in mg/m³ for air.

Min. Effect Dose = Minimum Effect Dose

The minimum effect dose for a chemical agent is the minimum amount of a chemical agent that is employed to produce recognizable effects on people. The unit used to express the minimum effect dose for the eyes is $\text{mg}\cdot\text{min}/\text{m}^3$.

LCL₀ = Lethal Concentration Low

The lethal concentration low is the lowest concentration of a substance in air, other than LC₅₀, which has been reported to have caused death in humans or animals. The reported concentrations may be entered for periods of exposure which are less than 24 hours (acute) or greater than 24 hours (subacute and chronic) (Registry of Toxic Effects of Chemical Substances, Volume 1, 1980). The unit to express LCL₀ is $\text{mg}\cdot\text{min}/\text{m}^3$.

TCL₀ = Threshold Concentration Limit

The threshold concentration limit is the smallest amount by which a warfare agent or toxic substance can produce the first recognizable injuries (Textbook of Military Chemistry, Volume I, 1977). This concentration is expressed in mg/m^3 . Concentrations below these threshold values are not dangerous and do not cause any clear injuries, unless constantly exposed over time.