Parameters for Evaluation of the Fate, Transport, and Environmental Impacts of Chemical Agents in Marine Environments

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Contents

1. Introduction

Between 1918 and 1970, disposing of excess, obsolete, and unserviceable chemical munitions and chemical agents into ocean waters was an internationally accepted practice. Although there is some evidence of sea disposal in the aftermath of World War I, little documentation of this practice before the mid-1940s can be found. At the end of World War II, large chemical munitions stores were discovered in Germany and Japan. From 1946 to 1947, an estimated 50 000−150 000 tons of captured enemy chemical munitions were disposed in the Baltic Sea, and chemical munitions were also disposed in the Pacific Ocean and Sea of Japan after World War II. Accidents due to ocean disposal of chemical munitions have been reported in the Baltic Sea,[1,2] the Adriatic,[3] and the Pacific Ocean and Japanese coastal waters.[4] Most of these reports concern fishermen who inadvertently snared plastic lumps of the agent sulfur mustard in their nets. The United States disposed of a total of approximately 30 000 tons of chemical agent in several locations off its Atlantic[5,6] and Pacific coasts[5,7] as well as in Alaskan and Hawaiian waters.[5,8] In 1972, Congress enacted the Marine Protection, Research, and Sanctuaries Act, which explicitly prohibited disposal of chemical agents in ocean waters.[9] This practice was also prohibited by the 1972 London Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter.[10] The last ocean disposal of U.S. chemical warfare materials occurred on August 18, 1970, and the issue of ocean disposal soon receded from public consciousness.

Recently, the presence of disposed chemical weapons in U.S. coastal waters has received renewed attention. In 2004, three bomb disposal technicians from Dover Air Force Base, DE, were injured and one was hospitalized as a result of exposure to mustard agent when a clam trawler brought up a 75 mm chemical artillery shell that had been disposed at sea. This incident brought renewed attention to the practice of sea disposal both in the popular press[11,12] and in the technical literature.[6,7] Many of the chemical munitions that were disposed of 40−80 years ago have not yet ruptured or leaked; a large proportion of the discarded 30 000 tons remains on the sea floor. In response to this renewed public attention, Congress passed section 314(c) of the John Warner National Defense Authorization Act for Fiscal Year 2007,[13] requiring the Department of Defense to conduct research on the effects of chemical munitions disposed of in U.S. ocean waters. This research and future assessments of the risk these munitions pose to human health and the environment will require use of a number of physical, chemical, and toxicological parameters for evaluation of the fate, transport, and environmental impacts of chemical warfare agents in marine environments. As more information on disposal sites comes to light,[7] more assessments using these parameters will be performed.

Many of these physical and chemical parameters were measured long ago and have been compiled many times subsequently. A number of recent reviews cover several of the relevant parameters,[14−19] often citing previous compilations.[20−24] Many of these in turn cite earlier generations of data compilations,[25,26] making it difficult to determine the original source of the data. In addition, many of these compilations do not address all of the chemical agents disposed in U.S. coastal waters or address only a subset of the parameters required to assess environmental impacts. In a number of cases, qualifications, notably of estimated values, have been lost in translation and certain errors have been repeated. In view of the renewed interest in sea disposal of chemical weapons and the need for accurate and traceable values for use by risk assessors, the authors attempted to critically re-examine this entire data set, tracing as many values for these parameters as possible back to the original data sources.[27] In many cases, fusion of multiple independent data sets for a particular parameter show the degree to which the data are mutually validating and thus provide increased confidence in the data both to scientists using them directly as well as to laypersons interested in the issue of sea disposal. This review covers a wide time period; some of the agents covered first appeared in the literature more than two

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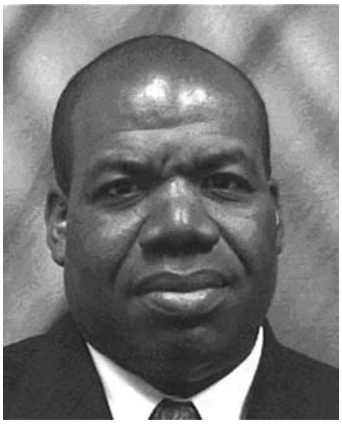

Harry Castelly earned his B.A. and M.S. degrees in Chemistry, both from George Mason University. He completed the requirements for both degrees while serving on active duty with the U.S. Army. He is currently pursuing his Ph.D. degree in Environmental Science and Policy at George Mason University and doing research on alternative fuels. He is now a research chemist with L-3 Communications.

centuries ago, and the most recent measurements appeared within a year of this review.

This review covers data relevant to the chemical warfare agents phosgene (military designation CG, **1**), cyanogen chloride (CK, **2**), hydrogen cyanide (AC, **3**), sulfur mustard (HS/H/HD, **4**), Lewisite (L, **5**), nitrogen mustard (HN1, **6**), GA (Tabun, **7**), GB (Sarin, **8**), and VX (**9**), which have been identified by the U.S. Army[5] as the agents disposed of in U.S. ocean waters. The structures of these agents are depicted in Figure 1. Physical and chemical parameters are covered in section 2. Section 3 presents a short assessment of the extent of data available for parameters used for assessing potential ecological effects. These ecotoxicological parameters have been reviewed recently elsewhere[17] and will be discussed here only briefly. Mammalian toxicological parameters used for assessing potential human exposures have been reviewed thoroughly by others[17,28] and are therefore not included in this review. Data gaps are identified in section 4.

Ahmed M. Hafez received his undergraduate degree in Chemistry from the College of William and Mary in Virginia, graduating with his B.S. degree in 1997. He did his graduate studies in Chemistry at Johns Hopkins University, obtaining his Ph.D. degree in 2003. He accepted a position at GEOMET Technologies, where he worked within their chemical surety laboratory conducting analyses of environmental and waste samples identifying the presence of chemical warfare agents, toxic industrial chemicals, and their respective precursors and degradation products. He then moved to Noblis, where he is presently a Lead Chemist at their Center for National Security and Intelligence. He currently assists several U.S. Army chemical demilitarization programs by providing a wide variety of independent technical, programmatic, safety, environmental, and operational evaluations for destruction of chemical warfare material.

Wade Smith is a Principal Scientist with Noblis. He earned his B.A. degree in Biology from Emory University in 1966, M.S. degree in Ecology from the University of North Carolina in 1971, and Ph.D. degree in Systems Ecology from the University of Florida in 1976. In 1975, he joined The MITRE Corp, part of which became Noblis in 1996. He analyzed the environmental transport, fate, and effects of chemical warfare agents in Russian arctic marine waters and participated on a team that assessed the potential risk to military personnel of chemical, biological, and radioactive agents released into marine systems. He has more than 30 years of experience with environmental impact analysis for many federal government clients.

2. Physical and Chemical Parameters

This study covered the available unclassified literature for several physical and chemical parameters used to determine the fate and transport of chemical warfare agents in marine environments. Boiling point and melting point are used to determine the initial physical state of an agent released to the marine environment. Density (D) determines whether undissolved agent rises or sinks in the water column. Vapor pressure (p), solubility, Henry's Law constant (K_H), and partition coefficients (P, K_{ow}) are important parameters for determining the phases and matrices in which the agent resides and is transported. Partition coefficients also allow

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risk assessors to determine whether or not the agents bioaccumulate in the food chain. Dissociation constants (K_a), where applicable, determine the form in which those agents which have acidic or basic groups exist in the sea. Finally, hydrolysis rate constants (k) and products, where applicable, are key parameters to determining the fate of the agent in the ocean. Available data for these parameters are reviewed below for each of the agents disposed of in U.S. coastal waters.

This review includes fusion of independent data sets for some of the parameters. These analyses involved combining the individual data values from the relevant data sets and performing a linear regression analysis on the data or on an appropriate linear form. For all data fusion regressions, the r^2 value for the regression indicated significant correlation at the 99.9% confidence level; coefficients for the resulting equation are given with ±standard error. We report regression results for the Clausius−Clapeyron equation for vapor pressures; because the regressions fit this form at the 99.9% confidence level, use of the Antoine vapor pressure equation was not deemed necessary.

Whenever available, this review presents data on the temperature, pH, and sodium chloride concentration dependence of these parameters. U.S. ocean disposal of chemical weapons occurred in areas with depths ranging from several hundred feet up to 16 000 feet.[5] Temperatures at shallower sites may be close to surface temperatures, which depend on latitude and could range from warmer values of 27 °C in Hawaiian waters in summer[29] to cooler values of 0−4 °C in Alaskan waters in winter.[30] In contrast, at deep disposal sites below the thermocline, temperatures approach 0 °C. Salinity in U.S. oceanic waters is about 35 parts per thousand, with 90% of the salt present as sodium chloride (NaCl) with the remainder including other salts such as magnesium. This corresponds to [NaCl] = 0.5 M. Oceanic pH values typically range from 7.7 to 8.2;[31] surface pH is typically 8.0−8.3 and declines to 7.4−8.0 in deep waters. Whenever possible, this review presents data that will allow users to adjust values for the temperature, pH, and salinity specific to the disposal site under consideration; there dependencies may also prove useful as assessments of fate are extended to sediments and associated pore waters.[7]

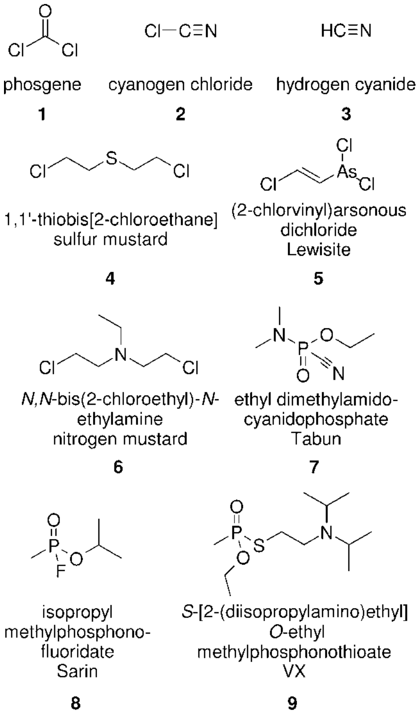


Figure 1. Chemical agents.

2.1. Phosgene (CG)

Phosgene (Chemical Abstracts Service [CAS] index name, carbonic dichloride; International Union of Pure and Applied Chemistry [IUPAC] name, carbonyl dichloride; CAS registry no. 75-44-5) was first obtained and identified in 1812 by Davy[32] and employed for the first time as a war gas at Nieltje in Flanders on December 19, 1915.[33] Phosgene is also a major chemical intermediate mainly used to produce polyurethane and polycarbonate plastics with annual worldwide production recently estimated as several million tons.[34,35] Additionally, phosgene is formed from the photoinduced oxidation as well as thermal degradation of chlorinated hydrocarbons in the atmosphere.[36] The United States produced approximately 1400 tons of phosgene during World War I[33,37] and 20 000 tons of phosgene during World War II, much of it for military applications.[38] Phosgene was loaded into a variety of American chemical munitions.[39] Approximately 29 tons of phosgene was disposed in U.S. coastal waters.[5] There is a considerable body of literature on the physical and chemical properties of phosgene because of its long history, wide use in the chemical industry, and trace occurrence in the atmosphere.

At ambient temperatures phosgene is a colorless gas with a characteristic odor described as "hay-like",[40] although many secondary references describe the odor as reminiscent of moldy hay.[24,26] The molecular formula of phosgene is CCl_2O, corresponding to a molecular weight of 98.92. There are numerous published values for the boiling point of phosgene;[41−48] these values agree quite well, giving a mean boiling point value of 8.0 ± 0.3 °C. The melting behavior of phosgene is reported to have multiple phase transitions.[49] The reported melting temperatures are −133.96 and −131.06 °C for the first two transitions; another paper reports a melting transition at −132.78 °C,[42] which appears to be intermediate between the first two transitions. Multiple papers report a third transition;[41,43,49,50] the mean melting point value from these studies is −128 ± 1 °C. This third phase transition is the one typically reported as the "melting point" in data

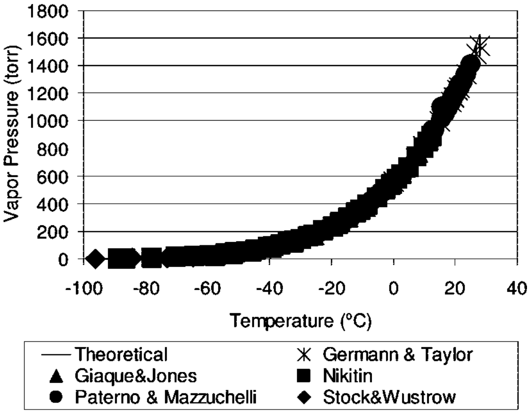


Figure 2. Vapor pressure values for phosgene ($r^2 = 0.992$, $n = 163$).

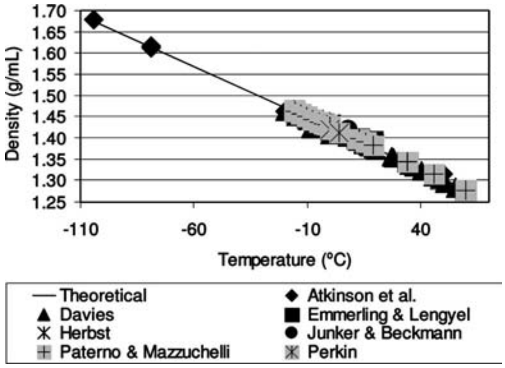


Figure 3. Density values for phosgene ($r^2 = 0.993$, $n = 71$).

Table 1. Henry's Law Constants for Phosgene

K_H (mol·L^{-1}·atm^{-1})	T (°C)	ref
0.25	0	36
0.15	5	58
0.2	20 (in seawater)	59
0.06	25	58

compilations. Finally, there is an earlier report of a melting point of −118 °C,[51] which disagrees with the other reported values and potentially represents a measurement using impure material. The vapor pressure of phosgene has been studied by several groups as a function of temperature;[41,43,44,47,52] the combined 163 data points from these studies fit eq 1 over the temperature range from −96.3 to 27.9 °C

$$\log p(\mathrm{Torr}) = 7.77(\pm 0.04) - \frac{1373(\pm 10)}{T(\mathrm{K})} \qquad (1)$$

This expression is plotted with the data in Figure 2; the data from these independent studies agree very well, giving a high degree of confidence in the derived expression.

Density values for phosgene from multiple studies[45,46,48,50,52−54] at temperatures ranging from −104 to 60.2 °C can be fit to eq 2

$$D(\mathrm{g/mL}) = 1.4226(\pm 0.0007) - 0.00243T(\pm 0.00003,\ ^\circ\mathrm{C}) \qquad (2)$$

This expression is plotted with the data in Figure 3, again showing excellent agreement between independent studies.

Henry's Law constant values for phosgene are provided in Table 1. An analysis of Henry's Law constant as a function of temperature[36] using data from several literature sources[55−57] gives eq 3

$$\log K_H(\mathrm{mol{\cdot}L^{-1}{\cdot}atm^{-1}}) = \frac{1823.3}{T(\mathrm{K})} - 70283 \qquad (3)$$

This expression agrees with the fresh water values in Table 1 and suggests that the value in seawater is nearly twice what would be expected for fresh water.

The primary fate of phosgene in water is hydrolysis to chloride and carbon dioxide. Rate constants have been measured for the reaction of phosgene with water.[57−59] Several studies have examined rate constants as a function of temperature. One study presents the Arrhenius parameters for hydrolysis as $A = 1.4 \times 10^{10}$ s^{-1} and $E_a = 53$ kJ mol^{-1} over a range of 13−59 °C.[60] An analysis of rate constants from several other studies[56,57,59,60] gives similar parameters, $A = 1.9 \times 10^{11}$ s^{-1} and $E_a = 57$ kJ mol^{-1} over a range of 15−45 °C. These expressions give rate constants that agree within a factor of about 2 over this temperature range. There are also two studies that give values of 4.6×10^3 [58] and 2.8×10^4 L mol^{-1} s^{-1} [60] for the rate of the hydroxide−-phosgene reaction at 25 °C. At pH 8 (approximately the pH of seawater), the hydroxide−phosgene reaction is significantly slower than the water−phosgene reaction and can therefore be neglected. The Arrhenius parameters for the water−phosgene reaction yield a half-life for phosgene in water of 0.4−1 s at 2 °C and 0.1−0.2 s at 25 °C.

There is one study that indicates that phosgene is sorbed to soil, although the data do not appear to allow calculation of an absorption coefficient.[61] There are no values available in the literature for phosgene solubility in water or partition coefficients, but these values are not required for environmental assessments because of the extremely short half-life of phosgene in water. Phosgene does not undergo acid−base dissociation in water.

2.2. Cyanogen Chloride (CK)

Cyanogen chloride (CAS index name, cyanogen chloride; IUPAC name, carbononitridic chloride; CAS registry no. 506-77-4) was prepared for the first time in 1789 by Berthollet[62] and subsequently characterized by Gay-Lussac.[63] It was used during World War I by the French both alone and mixed with arsenic trichloride. Other applications of cyanogen chloride include chemical synthesis, metal cleaning, ore refining, and production of triazine herbicides, optical brighteners, dyestuffs, and synthetic rubber.[64] Additionally, cyanogen chloride is formed from the chlorination of drinking water containing aromatic compounds and ammonium ion.[65,66] The United States produced roughly 12 500 tons of cyanogen chloride during World War II,[38] and the compound has been loaded into several American chemical munitions.[39] An estimated 205 tons of cyanogen chloride was disposed in U.S. coastal waters.[5] There is a considerable body of literature on the physical and chemical properties of cyanogen chloride because of its long history and occurrence in drinking water.

Pure cyanogen chloride is a clear colorless liquid or gas with a highly irritating odor. The molecular formula of cyanogen chloride is CClN, corresponding to a molecular weight of 61.47. There are numerous published values for the boiling point of cyanogen chloride,[46,67−75] all of which agree reasonably well; the mean boiling point value from these studies is 13 ± 1 °C. Similarly, there are several published values in agreement for the melting point of cyanogen chloride;[67,72,73,76,77] the mean melting point value from these studies is −6.6 ± 1.0 °C. The vapor pressure of

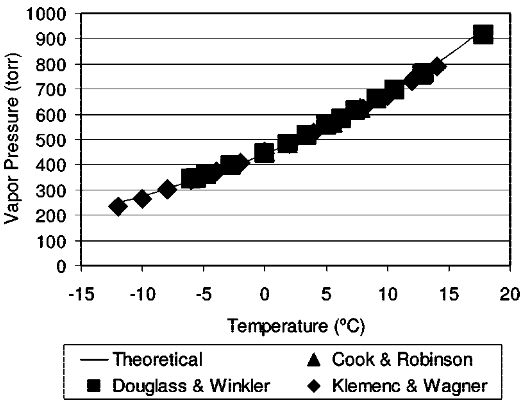


Figure 4. Vapor pressure values for cyanogen chloride ($r^2 = 0.996$, $n = 33$).

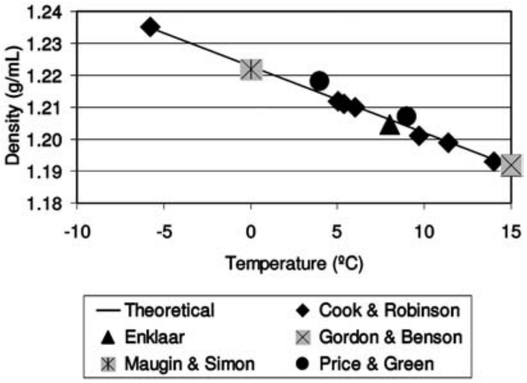


Figure 5. Density values for cyanogen chloride ($r^2 = 0.984$, $n = 13$).

cyanogen chloride has been studied by several groups as a function of temperature;[72,77,78] the combined 33 data points from these studies fit eq 4 over the temperature range from −12 to 17.82 °C

$$\log p(\mathrm{Torr}) = 10.562 - \frac{4068}{T(\mathrm{K})} \qquad (4)$$

This expression is plotted with the data in Figure 4, which shows the agreement between these independent data sets.

Density values for cyanogen chloride from multiple studies[67,73,75,78,79] at temperatures ranging from −5.8 to 14 °C can be fit to eq 5

$$D(\mathrm{g/mL}) = 1.2228(\pm 0.0007) - 0.00208T(\pm 0.00008, ^\circ\mathrm{C}) \qquad (5)$$

This expression is plotted with the data in Figure 5; these independent observations are in good agreement. The derived expression corresponds to a coefficient of expansion of 0.00173, which agrees reasonably well with Maugin and Simon,[67] who report a coefficient of expansion of 0.0015 for the temperature range of 0−45 °C, although they give the measured density only at 0 °C. One other study[72] reports a density value of 1.247 at 0 °C that differs significantly (by nearly 7 standard deviations) from the other studies; this value was determined to be an outlier and not included in the derivation of the density expression; the same study reports melting point and vapor pressure data that agree well with other studies but a molecular weight that is higher than the accepted value by roughly the same factor as the density is high, suggesting that there may have been an error in determining the weight.

The solubility of cyanogen chloride in aqueous sodium chloride solution at 30 °C was found to obey eq 6[74]

$$[\mathrm{ClCN}](\mathrm{M, satd\ at\ 30\ ^\circ C}) = 0.91(\pm 0.05) - 0.16(\pm 0.03)[\mathrm{NaCl}](\mathrm{M}) \qquad (6)$$

Another reference gives the water solubility at 8 °C as 7−8% (0.8−0.9 M).[73]

The primary fate of cyanogen chloride in water is hydrolysis to chloride and cyanate species; cyanic acid subsequently hydrolyzes to ammonia and carbon dioxide. Rate constants have been measured for reaction of cyanogen chloride with water[73,77,80] and hydroxide ion.[80,81] Analysis[80] shows that this data fit eq 7 for an observed first-order rate constant over the temperature range 5−45 °C

$$k_{\mathrm{obs}}(\mathrm{s}^{-1}) = 99.97 \times 10^{8}\ \mathrm{e}^{\frac{-87\,180}{8.134T(\mathrm{K})}} + 2.06 \times 10^{11}\ \mathrm{e}^{\frac{-60\,980}{8.134T(\mathrm{K})}}[\mathrm{OH}^-](\mathrm{mol{\cdot}L}^{-1}) \qquad (7)$$

At pH 8 (approximately the pH of seawater) this expression yields a half-life for cyanogen chloride of 19 days at 5 °C and 3 days at 25 °C. However, this expression does not account for a slight inhibition of cyanogen chloride hydrolysis in the presence of chloride ions.[73] There are other studies of cyanogen chloride hydrolysis that were conducted in buffer solutions that catalyze the hydrolysis;[82−84] rate constants from these studies should not be used for assessments of the fate of cyanogen chloride in the marine environment because they overestimate the hydrolysis rate under such conditions.

The Agency for Toxic Substances and Disease Registry (ATSDR) has stated and this review confirms that “no information could be found in the available literature on the transport and partitioning of cyanogen chloride in the environment or its partitioning coefficients (K_{oc}, K_{ow}) or Henry’s law constants”.[64] Nevertheless, a value for the log of the partition coefficient between water and olive oil of 1.6 has been reported;[85] this value suggests that the K_{ow} value is likely to be similarly low. However, on the basis of the relatively short hydrolytic half-life of cyanogen chloride it appears that hydrolysis would dominate the fate of cyanogen chloride in the deep ocean. Cyanogen chloride does not undergo acid−base dissociation in water.

2.3. Hydrogen Cyanide (AC)

Hydrogen cyanide (CAS index name, hydrocyanic acid; IUPAC name, formonitrile; CAS registry no. 74-90-8) was one of the earliest compounds to be investigated in modern chemistry. Hydrogen cyanide was first obtained as aqueous hydrocyanic acid, and its qualitative composition was determined by Scheele in 1782.[86] Water-free liquid hydrogen cyanide was produced in 1811 by Gay-Lussac, who first measured its properties.[87] Hydrogen cyanide and its salts are used in high volume in the steel, electroplating, mining, and chemical industries with current annual U.S. demand of more than 700 000 t.[64] There is an extensive body of literature on the physical and chemical properties of hydrogen cyanide because of its long history and extensive use.

The French were the first to use hydrogen cyanide as a chemical warfare agent on July 1, 1916 during the Battle of the Somme.[33] The French were the only major users of hydrogen cyanide during World War I, using a bit less than 4000 tons during the 1915−1918 period.[26] Although its high vapor pressure and rapid diffusion are presumed to have limited its effectiveness as a chemical weapon, hydrogen cyanide was used in several American chemical munitions.[39] The United States procured about 560 tons of hydrogen

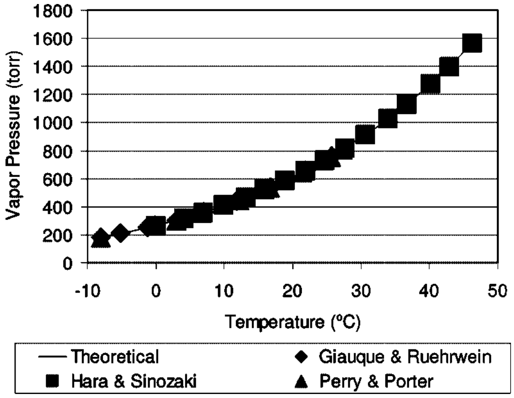


Figure 6. Vapor pressure values for hydrogen cyanide ($r^2 = 0.99996$, $n = 36$).

cyanide during World War II alone,[38] and an estimated 10 tons of hydrogen cyanide was sea disposed in U.S. coastal waters.[5]

Pure hydrogen cyanide is a clear colorless liquid with an odor described in standard sources as that of bitter almonds.[88] The molecular formula of hydrogen cyanide is CHN, corresponding to a molecular weight of 27.026. There are numerous published values for the boiling point of pure hydrogen cyanide,[87,89−100] all in excellent agreement; the mean boiling point value from these studies is 25.9 ± 0.3 °C. Similarly, there are many published values giving similar values for the melting point of pure hydrogen cyanide;[91,93,94,101−107] the mean melting point value from these studies is −13.33 ± 0.05 °C. Several others reported melting points that are significantly lower, suggesting that less pure material was used for those measurements.[87,89,108−110] The vapor pressure of hydrogen cyanide has been studied by several groups as a function of temperature;[89,91,95] the combined 36 data points from these studies fit eq 8 over the temperature range from −8.07 to 46.29 °C

$$\log p(\mathrm{Torr}) = 7.746(\pm 0.006) - \frac{1457(\pm 2)}{T(\mathrm{K})} \qquad (8)$$

This expression is plotted with the data in Figure 6; the data from these independent experiments are in very good agreement.

Henry's Law constant has been measured as a function of temperature three times.[111−113] One of the studies[111] covered the temperature range from 0 to 100 °C and fits the data to eq 9

$$\ln K_{\mathrm{H}}(\mathrm{kg \cdot atm/mol}) = 9.585 - 0.03147T(\mathrm{K}) + 3.1704 \ln T - \frac{6302}{T} \qquad (9)$$

The other studies were performed at higher temperature ranges; these two studies as well as two additional reports of K_{H} at 25 °C[114,115] provide values that agree within a factor of 1.6.

The aqueous dissociation constant of hydrogen cyanide has been measured as a function of temperature twice.[111,112] One of the studies[111] covers the temperature range from 0 to 150 °C and fits the data to eq 10

$$\ln K_{\mathrm{a}} = -12.1960 - 0.031482T(\mathrm{K}) + 3.7658 \ln T - \frac{6340.7}{T} \qquad (10)$$

The pK_{a} value calculated from this expression for 25 °C is 9.29, which is close to the preferred pK_{a} value of 9.21 ± 0.02 at 25 °C.[116] The other study gives similar K_{a} values but was performed at a higher temperature range. Several studies indicate that the pK_{a} value decreases somewhat at the ionic strength of seawater (approximately 0.7 M) to a value of 8.95 at 25 °C,[117−119] although there is disagreement about the behavior at higher ionic strength. Although the data may not allow a precise value to be calculated for marine conditions, all available data indicate that at the pH of seawater, hydrogen cyanide will exist predominantly as the free acid.

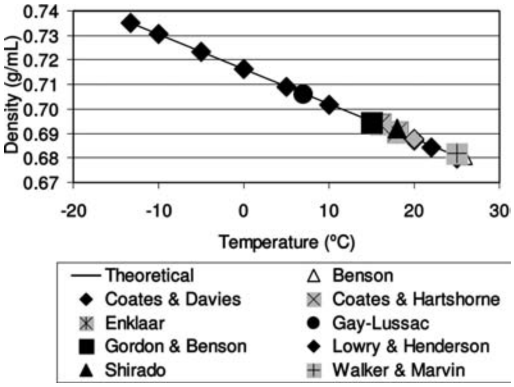


Figure 7. Density values for hydrogen cyanide ($r^2 = 0.998$, $n = 21$).

Density values for hydrogen cyanide from multiple studies[75,79,87,90,93,97,103−105,120] at temperatures ranging from −13.3 to 25.7 °C can be fit to eq 11

$$D(\mathrm{g/mL}) = 0.7161(\pm 0.0002) - 0.00142T(\pm 0.00001, {}^{\circ}\mathrm{C}) \qquad (11)$$

This expression is plotted with the data in Figure 7; the data from these independent studies agree very well.

Hydrogen cyanide is reported to be miscible with water at temperatures above −23.3 °C.[104] Hydrogen cyanide hydrolyzes slowly at low pH to form ammonium ion and formic acid,[121] although this reaction would not be expected to be significant under environmental conditions. In lieu of hydrolysis, biodegradation is likely to be a major fate of hydrogen cyanide; this process occurs in natural surface waters and is dependent on such factors as concentration, pH, temperature, availability of nutrients, and acclimation of microbes.[122−127] The Environmental Protection Agency has found no data to indicate that hydrogen cyanide bioconcentrates in aquatic organisms.[121,128] The value for the log of the partition coefficient (log P) is reported as −0.25.[129]

ATSDR stated that "except for soil partition (K_{oc}) coefficient, data for the physical and chemical properties of hydrogen cyanide are available to estimate its environmental fate".[64] There is one study that indicates that hydrogen cyanide is sorbed to soil, although the data do not appear to allow calculation of an absorption coefficient.[61]

Volatilization and biodegradation are considered to be the most significant processes for loss of hydrogen cyanide from surface water. However, there have been no studies focusing on hydrogen cyanide in deeper oceanic waters, from which volatilization is likely to be much slower. In deeper water, even weak sorption could become a significant process and information on nutrients and microbial populations is unlikely to be available; as a result, estimation of the lifetime of hydrogen cyanide in deeper ocean waters is likely to be difficult.

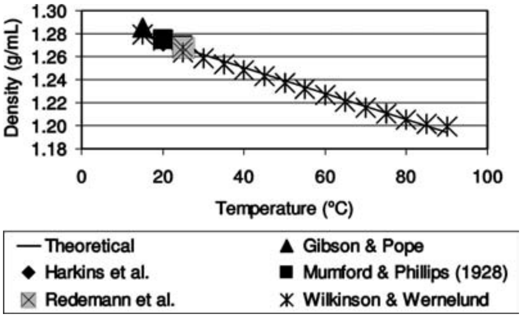


Figure 8. Density values for sulfur mustard ($r^2 = 0.991$, $n = 21$).

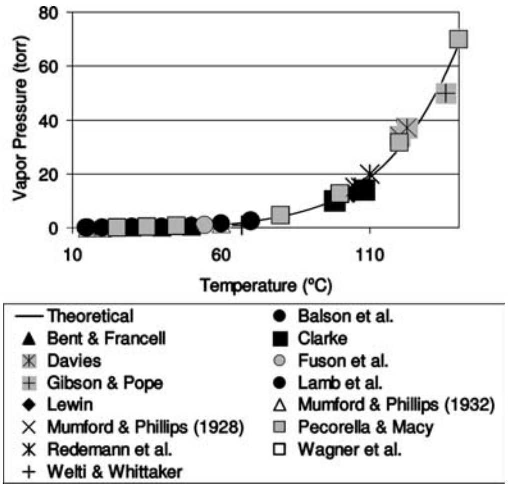


Figure 9. Vapor pressure values for sulfur mustard ($r^2 = 0.991$, $n = 48$).

2.4. Sulfur Mustard (HS/H/HD)

The principle active compound in sulfur mustard is 1,1′-thiobis[2-chloroethane] (CAS index name, 1,1′-thiobis[2-chloroethane]; IUPAC name, bis(2-chloroethyl) sulfide; CAS registry no. 505-60-2). This compound was probably first produced by Despretz[130] and then later by Riche,[131] although neither isolated nor identified the compound. The material was prepared in purer form by Niemann[132] and independently by Guthrie,[133] both of whom noted the vesicant property of the material. Meyer[134] subsequently prepared and established the structure of 1,1′-thiobis[2-chloroethane]. Chemical warfare has been the only significant use of sulfur mustard. Sulfur mustard was first used in chemical warfare by the Germans on the night of July 12−13, 1917 near Ypres in Flanders. The United States produced 900 tons of mustard during World War I[33,37] and more than 87 000 tons of sulfur mustard during World War II.[38] Sulfur mustard was loaded into many American chemical munitions,[39] and more than 16 000 tons of mustard are estimated to have been sea disposed in U.S. coastal waters.[5,8] Historically, sulfur mustard has been referred to using the designation HS, H, and HD, depending on the period and grade of the material. The current NATO designation is HD, for material that was distilled starting in the late 1940s. H is the designation for undistilled mustard, and HS was a historical designation used during World War I. There is a considerable body of academic literature on the chemical and physical properties of sulfur mustard, much of it published in the years immediately after each of the two World Wars.

Early workers indicated that 1,1′-thiobis[2-chloroethane] had a “not unpleasant” odor resembling oil of mustard[133] or horseradish,[132] although popular accounts also compare the odor to burning garlic and a “weak, sweet, agreeable odor”.[135] The crude material is straw colored.[136] The molecular formula for 1,1′-thiobis[2-chloroethane] is $C_4H_8Cl_2S$, which corresponds to a molecular weight of 159.08. Five independent studies report that 1,1′-thiobis[2-chloroethane] boils at atmospheric pressure with decomposition;[46,134,137−139] the mean boiling point is 216.9 ± 0.2 °C. Four studies of the melting point of pure 1,1′-thiobis[2-chloroethane][140−144] give a mean melting point value of 14.46 ± 0.04 °C. Several other studies report lower values, presumably because they used less pure material;[136,139,145−147] lower and broader melting ranges typically apply to weapons-grade material. One of the studies indicates that treating melting point as a function of pressure gives a slope of 74 megabars per degree.[147] Data from several studies[136,140,143,145,148] show that the density of 1,1′-thiobis[2-chloroethane] obeys eq 12 over the temperature range of 15−90 °C

$$D(\text{g/mL}) = 1.295(\pm 0.001) - 0.00112(\pm 0.00002)T(^\circ\text{C}) \qquad (12)$$

This expression is plotted with the data in Figure 8; although only one data set covered temperatures above 25 °C, the expression shows good agreement in the 15−25 °C temperature range covered by multiple data sets.

A number of workers examined the vapor pressure of 1,1′-thiobis[2-chloroethane] as a function of temperature.[143,149−153] Using those data along with boiling points at reduced pressure[136,138−140,154−157] indicates that the vapor pressure of 1,1′-thiobis[2-chloroethane] obeys eq 13 over the temperature range from 14 to 217 °C

$$\log p(\text{Torr}) = 9.1(\pm 0.1) - \frac{2990(\pm 40)}{T(\text{K})} \qquad (13)$$

This expression is plotted with the data in Figure 9; these independent data sets are in very good agreement. A similar analysis[158] of the data from several of the same studies[137,149,151,153] was fitted to the following Antoine equation (eq 14) for vapor pressure

$$\log P(\text{Torr}) = 7.47(\pm 0.03) - \frac{1941(\pm 6)}{(T(^\circ\text{C}) + 204.671)} \qquad (14)$$

The Antoine equation agrees within 90−124% of the Clausius−Clapeyron equation over the temperature range from the melting point to 140 °C. A recent study provided eq 15 for the vapor pressure of solid HD over the temperature range from −25 to 13 °C[159,160]

$$\log p(\text{Torr}) = 15.45(\pm 0.09) - \frac{4230(\pm 20)}{T(\text{K})} \qquad (15)$$

Note that this equation differs from the equation for liquid HD because the slope is related to the heat of sublimation (79 kJ/mol) rather than the heat of fusion (55 kJ/mol).

The primary fate of 1,1′-thiobis[2-chloroethane] in water is hydrolysis, primarily to thiodiglycol (TDG, CAS registry no. 111-48-8) and hydrogen chloride. Hydrolysis generally proceeds as shown in Scheme 1; the degree to which the reaction proceeds through the sulfonium chloride intermediates H-TG (CAS registry no. 45088-63-9), H-2TG (CAS registry no. 64036-80-2), and CH-TG (CAS registry no. 107327-27-5) depends on the concentration of mustard in the aqueous solution.[161−163] The initial formation of H-TG in the aqueous phase requires accumulation of the TDG

Scheme 1. Hydrolysis of Sulfur Mustard

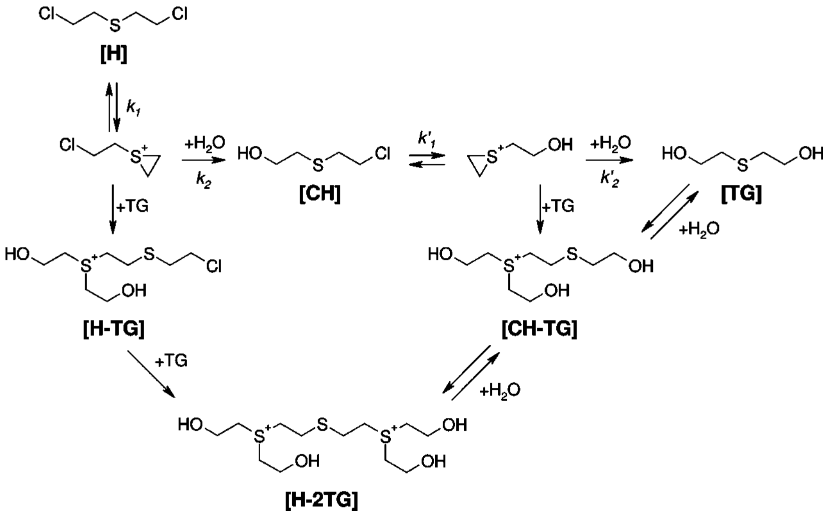


Table 2. Half-Lives of 1,1′-Thiobis[2-chloroethane] in Seawater

T (°C)	seawater $t_{1/2}$ (min)	k_1, calcd (min^{-1})
5	175	0.0040
15	49	0.0141
25	15	0.046

reaction product and appears less significant in a marine environment where currents can remove the hydrolysis product.

Numerous groups have measured rate constants for reaction of 1,1′-thiobis[2-chloroethane] with water. Ogston et al. measured values at 25 °C of $k_1 = 0.174$ min^{-1} for 1,1′-thiobis[2-chloroethane] and $k'_1 = 0.223$ min^{-1} for 2-([2-chloroethyl]thio)ethanol (CH, CAS registry no. 693-30-1); k_2 and k'_2 are rapid compared to k_1 and k'_1, respectively.[164] Independently, Bartlett and Swain reported values at 25 °C of $k_1 = 0.155$ min^{-1} and $k'_1 = 0.260$ min^{-1}.[165] CH is thus a relatively short-lived hydrolysis intermediate. Other groups have measured reaction rates for 1,1′-thiobis[2-chloroethane] from 0 to 50 °C,[166−170] although the validity of these rate constants has been questioned because some were calculated assuming a single first-order reaction rather than consecutive first-order reactions.[171] A recent study determined the activation energy of 18.5 kcal mol^{-1} for 1,1′-thiobis[2-chloroethane] hydrolysis,[172] which allows calculation of rate constants at different temperatures. The rate of 1,1′-thiobis[2-chloroethane] hydrolysis in seawater is, however, considerably slower than the rate of hydrolysis in pure water. A group of U.S. Army researchers has measured the half-life of 1,1′-thiobis[2-chloroethane] in seawater at several different temperatures.[173] These values are given in Table 2. The rates in seawater are slower than the corresponding reaction rates in pure water because aqueous chloride ion displaces the equilibrium between 1,1′-thiobis[2-chloroethane] and the intermediate episulfonium chloride toward the reactants. The effect of chloride is to slow the observed rate of hydrolysis by a factor of 3.8 at 25 °C, which is in close agreement with a value of 3.5 calculated for 0.55 M chloride ion (a typical level of seawater salinity) using the Brønsted−Bjerrum law to correct for the effect of seawater's ionic strength on the chloride ion activity.

Despite the relative rapidity of the hydrolysis reaction, 1,1′-thiobis[2-chloroethane] has been found to persist in soil or even under water for periods of decades.[1,2,4,174] This is believed to be due to the low solubility of sulfur mustard in water and the slow rate at which mustard dissolves in water. 1,1′-Thiobis[2-chloroethane] is only sparingly soluble in water. Literature values for water solubility include 0.7 g/L at 10 °C,[168] 0.92[175] and 0.68 g/L[176] at 25 °C, and 0.48 g/L in "cold water" at an unspecified temperature.[177] A compilation of solubility values includes a listing of 0.678 g/L at 25 °C;[178] although the authors are unable to trace the source of the value, it may refer to the previously cited 0.68 g/L measurement.

However, the saturation water solubility is likely to be less important to the fate of 1,1′-thiobis[2-chloroethane] released to the marine environment than the rate at which it dissolves. Brookfield et al. first established the rate at which 1,1′-thiobis[2-chloroethane] dissolves in quiescent water as a function of temperature, which follows eq 16[179]

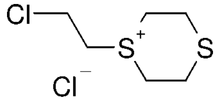
$$\sigma(\mathrm{g{\cdot}cm^{-2}{\cdot}s^{-1}}) = 233.7e^{-\left[\frac{12,350}{1987T(\mathrm{K})}\right]} \qquad (16)$$

More recently, Demek et al. measured the rate of sulfur mustard dissolution as 3.4×10^{-7} gm cm^{-2} s^{-1} at 4 °C in a 0.15 knot current.[23] Epstein et al. estimated that a one ton block of 1,1′-thiobis[2-chloroethane] would require 5 years to dissolve.[173] However, lumps of sulfur mustard have apparently persisted in the ocean for decades,[2,4,174] suggesting that the above values overestimate the rate of dissolution. It has been suggested that formation of a sulfonium salt-rich layer at the mustard water interface slows the dissolution of mustard.[21] Thus, in order to perform environmental fate assessments of 1,1′-thiobis[2-chloroethane], both the hydrolysis rate in seawater and dissolution rate must be considered. The result is that for a cylinder of solid 1,1′-thiobis[2-chloroethane] with surface area of 4×10^4 cm^2 placed in a 0.15 knot current the 1,1′-thiobis[2-chloroethane] concentration drops within 1 foot to 0.3 ppm.[180]

The authors were unable to find an original experimental value for the log of the octanol−water partition coefficient (log K_{ow}). Several estimates are available for this parameter. One report estimates a value of 1.37 at an unspecified temperature,[21] whereas subsequent compilations report the identical value without indicating that it is estimated.[17,19] A higher value of 2.41 has also been reported in several data compilations, but this value also appears to be an estimate.[181] The log of the ether−water partition coefficient at an unspecified temperature has been measured as 1.93,[182] and the xylene:water partition coefficient at 20 °C is reported to be greater than 200 (log $K > 2.3$).[183] These values suggest that the estimates of log K_{ow} are reasonably accurate. In addition, the relative rapidity of hydrolysis suggests that partitioning of mustard from seawater into other matrices should not be a significant environmental fate.

Three values of Henry's Law constant at 25 °C, all derived from solubility and vapor pressure values, appear in the literature,[19,21,178] giving a mean value of $2.6 \pm 0.6 \times 10^{-5}$ atm m^3/mol. 1,1′-Thiobis[2-chloroethane] does not undergo acid−base dissociation in water.

Finally, evaluation of mustard-containing munitions disposed in the ocean may also consider mustard "heel", which is a solid material that forms in mustard munitions upon prolonged storage. It is composed of occluded liquid mustard in a mixture of iron salts and *S*-(2-chloroethyl)-1,4-dithianium chloride (**10**, CAS registry no. 30843-67-5).[184,185] Mustard heel is water soluble, but the authors have been unable to locate any quantitative data on the fate of mustard heel once it dissolves in water. It would be expected to be relatively nonvolatile, and it has been shown to react with water within several hours.[186]



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2.5. Lewisite (L)

2-Chlorovinylarsonous dichloride (CAS index name, arsonous dichloride, As-(2-chloroethenyl)-; IUPAC name, (2-chloroethenyl)arsonous dichloride; CAS registry no. 541-25-3) may have been first prepared by Julius Nieuwland as part of his doctoral research at Catholic University in 1903. A team of Americans headed by Capt. W. Lee Lewis working at Catholic University in 1918 reviewed Nieuwland's thesis and then isolated 2-chlorovinylarsonous dichloride in somewhat purer form, which they called Lewisite.[187] There is some evidence that German scientists also studied Lewisite during World War I.[188] Lewisite is the first major chemical warfare agent that was produced for such use before it was described in the open literature.[189] The United States produced an estimated 150 tons of Lewisite during World War I, and approximately 20 000 tons of Lewisite was produced during World War II.[38] Lewisite was loaded into many American chemical munitions,[39] and 11 141 tons of Lewisite are estimated to have been sea disposed in U.S. ocean waters.[5] There is a moderate body of literature on the constituents of Lewisite, much of it published in the 1920s and late 1940s.

The chemical warfare agent Lewisite is a mixture of *cis*- and *trans*-2-chlorovinylarsonous dichloride (referred to as L1), isomers of bis(2-chlorovinyl)arsinous chloride (L2, CAS registry no. 40334-69-8), and isomers of tris(2-chlorovinyl)arsine (L3, CAS registry no. 40334-70-1). The vesicant and main component in most Lewisite is 2-chlorovinylarsonous dichloride. Industrially produced Lewisite is reported to have a strong penetrating geranium odor,[187] although pure 2-chlorovinylarsonous dichloride is odorless. 2-Chlorovinylarsonous dichloride has a molecular weight of 207.32 and molecular formula of $C_2H_2AsCl_3$. The boiling point for 2-chlorovinylarsonous dichloride at ambient pressure has been reported as 196.6[190] and ca. 203 °C.[46] The melting point for 2-chlorovinylarsonous dichloride has variously been reported as 0.1,[191] −1.2,[190] and −2.5 °C;[192] differences are likely due to different levels of cis and trans isomers in the tested material. Weapons-grade Lewisite is expected to remain liquid at substantially lower temperatures because of the presence of the L2 and L3 chlorovinylarsines.

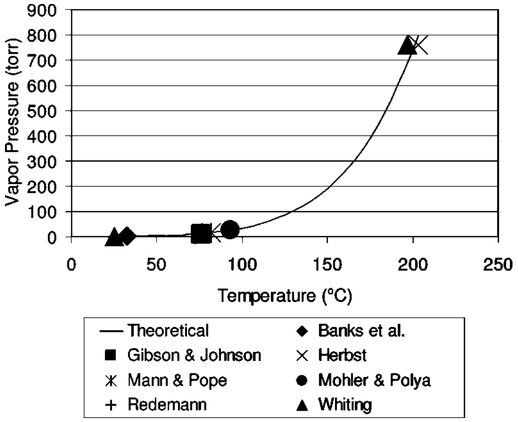
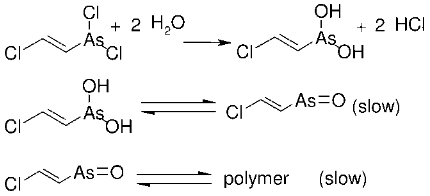


Figure 10. Vapor pressure values for Lewisite ($r^2 = 0.960$, $n = 7$).

Scheme 2. Hydrolysis of 2-Chlorovinylarsonous Dichloride



The density of 2-chlorovinylarsonous dichloride is reported as 1.888 g/mL at 20 °C[193] and 1.8799[194] and 1.8793 g/mL at 25 °C.[190] These data are insufficient to allow precise extrapolation to higher or lower temperatures, although it is virtually certain that Lewisite will have a density significantly greater than that of water at any temperature encountered in the marine environment.

One study reports that the vapor pressure of 2-chlorovinylarsonous dichloride obeys eq 17 over the temperature range from 0 to 60 °C[194]

$$\log p(\mathrm{Torr}) = 9.1000 - \frac{2786.6}{T(\mathrm{K})} \tag{17}$$

This study does not report individual data points and cannot be combined with other data sets. Using vapor pressure and reduced boiling point data from several other studies[190,191,194−197] gives eq 18 for the temperature range from 25 to 200 °C

$$\log p(\mathrm{Torr}) = 7.9(\pm 0.5) - \frac{2400(\pm 200)}{T(\mathrm{K})} \tag{18}$$

This expression is plotted with the data in Figure 10; these independent data sets correlate well. Moreover, the two independently derived expressions agree to within a factor of 1.5 or better between 25 and 60 °C, where the two data sets overlap. Note that 2-chlorovinylarsonous dichloride is the most volatile component in Lewisite and the predominant constituent. Thus, the vapor pressure of Lewisite is determined in large part by the 2-chlorovinylarsonous dichloride vapor pressure.

Hydrolysis of 2-chlorovinylarsonous dichloride proceeds as shown in Scheme 2. The initial 2-chlorovinylarsonous dichloride hydrolysis reaction is rapid relative to formation of the 2-chlorovinylarsonous acid (CAS registry no. 85090-

33-1)/Lewisite oxide (CAS registry no. 3088-37-7) equilibrium mixture.[198] The literature indicates that production of two equivalents of chloride occurs within 3 min at 20 °C. At 5 °C, 90% reaction occurs within 2 min; completion of the reaction requires several hours.[199] The titration methodology used in this study does not allow determination of precise rate constants because more than 80% of the reaction occurs before the first measurement can be obtained. Nevertheless, these data indicate that the hydrolysis rate constant at 20 °C is on the order of 1 min^{-1}. The immediate hydrolysis products 2-chlorovinylarsonous acid and Lewisite oxide are also vesicants.[198] The toxicity of the 2-chlorovinylarsonous acid/Lewisite oxide equilibrium mixture is quite high; given the rapidity of hydrolysis it is possible that 2-chlorovinylarsonous acid and Lewisite oxide are responsible in vivo for many of the systemic effects of Lewisite.[17] The vesicant properties of the mixture are reported to remain unchanged after storage for 10 weeks in seawater.[173] The hydrolysis product mixture has a reported log $K_{\text{benzene-water}}$ of 0.15.[198]

Over time the hydrolysis products will be transformed into both organic and inorganic forms of arsenic. Waters and Williams observed that cold alkali decomposes 2-chlorovinylarsonous acid into arsonous acid, acetylene, and chloride. At 17 °C, this reaction shows no detectable acetylene product after 24 h at pH 8.5, a slight amount of product after 24 h at pH 9.5, and substantial amounts of product after 2 h at pH 10.5.[198] This is roughly consistent with the observation of continued vesicant properties after 10 weeks at 0 °C in seawater. The arsonous acid produced by this reaction will subsequently undergo the expected transformations of inorganic arsenic in the environment.

The water solubility of Lewisite is reported to be 0.5 g/L,[200] and several data compilations report values for Henry's Law constant (0.00032 atm m^3/mol)[17] and log of the partition coefficient (2.56)[201] for Lewisite. However, given the extremely short lifetime of dissolved 2-chlorovinylarsonous dichloride the validity of these values is questionable. Nevertheless, the fate of 2-chlorovinylarsonous dichloride in water is primarily hydrolysis, so accurate values for these three parameters are less critical to assessing the environmental impacts of Lewisite in the marine environment. Lewisite does not undergo acid−base dissociation in water.

2.6. Nitrogen Mustard (HN1)

In 1935, Kyle Ward, Jr. published an article describing the first of the nitrogen mustards, a vesicant agent now known as HN3.[202,203] The U.S. Army eventually standardized on *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine (HN1) as its nitrogen mustard agent. This agent will be covered in this review. *N*,*N*-Bis(2-chloroethyl)-*N*-ethylamine (CAS index name, ethanamine, 2-chloro-*N*-(2-chloroethyl)-*N*-ethylethanamine; IUPAC name, 2-chloro-*N*-(2-chloroethyl)-*N*-ethyl-ethanamine; CAS registry no. 538-07-8) was studied extensively prior to and during World War II, but the compound was first described in the open literature in 1946.[204] Chemical warfare has been the only significant use of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine, although there do not appear to be any reports of its use in combat by any nation. About 100 tons of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine was produced during World War II,[38] although it is unclear whether it was ever loaded as a standard fill into any munition.[39] Fifty seven tons of HN1 are estimated to have been disposed in the ocean.[8] This review found only limited information on *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine, presumably because it is a more recent development than the agents covered in previous sections, has no significant industrial use, and was a less important chemical warfare agent.

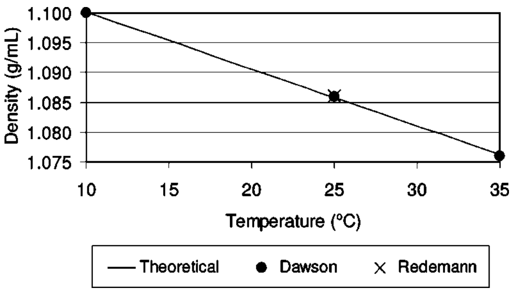


Figure 11. Density values for nitrogen mustard ($r^2 = 0.999$, $n = 4$).

The molecular weight of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine is 170.08, and the molecular formula is $C_6H_{13}Cl_2N$. The compound is reported to possess a faint fishy or soapy odor.[205] The melting point of this compound was measured as −34.2 °C.[206] At ambient pressure, *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine will polymerize before it boils. The boiling point at reduced pressure has been reported as 73 °C at 4.5 Torr[207] and 85.5 °C at 12 Torr.[208] One study indicates that the *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine vapor pressure fits eq 19 over the temperature range 0−60 °C[208]

$$\log p(\text{Torr}) = 9.0182 - \frac{2868.9}{T(\text{K})} \qquad (19)$$

The density of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine[206,208] obeys eq 20 over the temperature range from 10 to 35 °C

$$D(\text{g/mL}) = 1.1097(\pm 0.0005) - 0.00096(\pm 0.00002)T(°\text{C}) \qquad (20)$$

This expression is plotted with the data in Figure 11; the two data sets are consistent.

One source reports the pK_a value of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine as 6.78 at 0 °C and 6.57 at 25 °C.[209] Another source gives a value of 6.3 at an unspecified temperature.[207] These values indicate that the free amine will be the predominant species at the pH of seawater. Hydrolysis proceeds as shown in Scheme 3. Although the reaction mechanisms are qualitatively similar, hydrolysis of nitrogen mustard is more complicated than hydrolysis of sulfur mustard for two reasons: nitrogen mustards can more easily form dimers in aqueous solution and the ethyleniminium ion (CAS registry no. 36086-29-0) has a considerably longer lifetime in water than the analogous episulfonium ion.

A 1% aqueous solution of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine at 25 °C forms the ethyleniminium ion with $k_1 = 0.049\ \text{h}^{-1}$.[210] A more detailed examination of the mechanism was conducted in aqueous acetone, giving the rate constants in Table 3.[211] In the first study, after 70 h approximately 28% of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine remained with 5% of the ethyleniminium salt, 35% of *N*-(2-chloroethyl)-*N*-ethylethanolamine (CAS registry no. 4669-20-9), 28% of *N*-ethyldiethanolamine (CAS registry no. 139-87-7), and 4% of the piperazinium dimer (CAS registry no. 63884-24-2).[210] In other studies, 0.34% aqueous *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine is completely converted to ethyldiethanolamine in 24 h at pH 8 and 25 °C; at higher agent concentrations quaternary ammonium dimers were also formed.[204] Finally, 0.8% *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine in water was converted quantitatively to *N*-ethyldi-

Scheme 3. Hydrolysis of Nitrogen Mustard

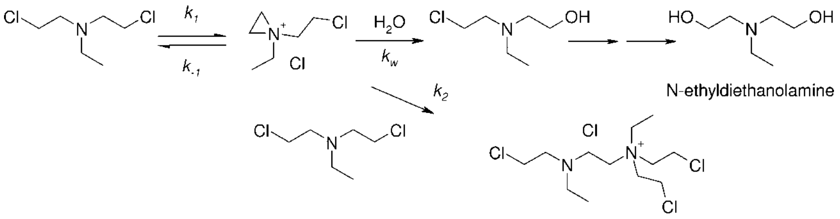


Table 3. Nitrogen Mustard Hydrolysis Rate Constants in Aqueous Acetone at 25 °C

rate constant	2:1 acetone:water	1:3 acetone:water
k_1	0.085 h^{-1}	0.24 h^{-1}
k_{-1}	1.5−7.0 h^{-1}, with strong negative dependence on ionic strength	not given
k_2	0.074−0.090 h^{-1}	0.0023 h^{-1}
k_w	0.0050−0.0063 h^{-1}	0.0013−0.0017 h^{-1}

ethanolamine in 13 days at room temperature.[212] No measurements of the temperature dependence of nitrogen mustard hydrolysis rates were found. One early compilation gave an approximate half-life in water at 25 °C of 1.3 min;[205] this value has been repeated in subsequent compilations.[16,213] However, this value corresponds to a first-order rate constant of 32 h^{-1}, which is much faster than the values reported in ref 210 or suggested by ref 211 in the peer-reviewed literature. Because of this conflict and the lack of experimental data to support the 1.3 min half-life value, the authors would caution against its uncritical use.

The value of the water solubility of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine is the subject of some confusion. The earliest report of water solubility for HN1 is 4 g/L,[16,205] although this summary report does not give the source of the measurement. The hydrolysis studies suggest that the solubility may be as high as 0.8% (8 g/L).[212] A recent review[17] reports two different values; both appear to be erroneous. Table 1 in the reference appears to be a typographical error, reporting the 12 g/L solubility of the methyl analogue (HN2)[210] as applying to HN1. Later in the text the NH3 solubility of 0.16 g/L is reported, citing Franke,[22] who apparently uses the solubility of HN3 for HN1 because "the ethyl compound behaves approximately like" HN3.

A Henry's law constant of 3.5×10^{-4} atm-m^3/mol is given in some data compilations,[214] which indicates it has been calculated from the 0.16 g/L water solubility value and the vapor pressure value; using the 4 g/L solubility value would result in a Henry's law constant estimate of 1.4×10^{-5} atm-m^3/mol. There does not appear to be a measured octanol−water partition coefficient for *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine, although some compilations list a value of 2.02 estimated from fragment constants.[214]

One final qualitative observation is that *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine is somewhat unstable, forming the *N*,*N*′-diethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride dimer at room temperature.[207] Although no rate constants are available, one-sixth of the material was converted to a solid thought to be dimer after storage at 50 °C for 5 months.[215] Thus, it seems likely that a significant amount of nitrogen mustard in undersea munitions, most if not all of which was disposed by 1958,[8] has by now been converted to the dimer form. This reaction would correspondingly lower the amount of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine available to be released from those munitions.

2.7. Tabun (GA)

Tabun (GA, CAS index name, phosphoramidocyanidic acid, *N*,*N*-dimethyl-, ethyl ester; IUPAC name, ethyl dimethylamidocyanidophosphate; CAS registry no. 77-81-6), the first organophosphate nerve agent, was initially prepared on Dec 23, 1936 in Dr. Gerhard Schrader's laboratory at I. G. Farbenindustrie in Leverkusen.[216] The identity of the compound was kept secret at least through 1943, and the first report of Tabun in the open literature appears to be in 1951.[217] The compound was first produced industrially in 1942 at Dyhernfurth-am-Oder in Silesia, with an estimated 12 000 tons produced by the end of the war.[218] Tabun was later loaded into some American chemical munitions.[39] One ton of Tabun is documented as being disposed in U.S. waters.[5] There is a moderate amount of data available on Tabun in the open literature.

Pure Tabun is a colorless liquid with a sweetish smell;[216] weapons-grade material is reported in many compilations to have a fruity odor.[16,22] It has a molecular formula of $C_5H_{11}N_2O_2P$ and formula weight of 162.13. The boiling point at ambient pressure is reported as 246 °C,[219] and the melting point is reported to be −50 °C.[220] Data for the boiling point at reduced pressure and for vapor pressure[216,219−222] can be fit to eq 21 over the range of 25−246 °C

$$\log p(\mathrm{Torr}) = 8.6(\pm 0.2) - \frac{2900(\pm 60)}{T(\mathrm{K})} \tag{21}$$

This expression is plotted with the data in Figure 12, which shows the agreement among the data from various sources. Note that the ambient boiling point is not shown in the figure but was included in the analysis.

The density from several studies over the range from 9.8 to 35 °C[219−221] can be fit to eq 22

$$D(\mathrm{g/mL}) = 1.096(\pm 0.002) - 0.00090(\pm 0.00007)T(°\mathrm{C}) \tag{22}$$

This expression is plotted with the data in Figure 13, showing the agreement between the various data sources.

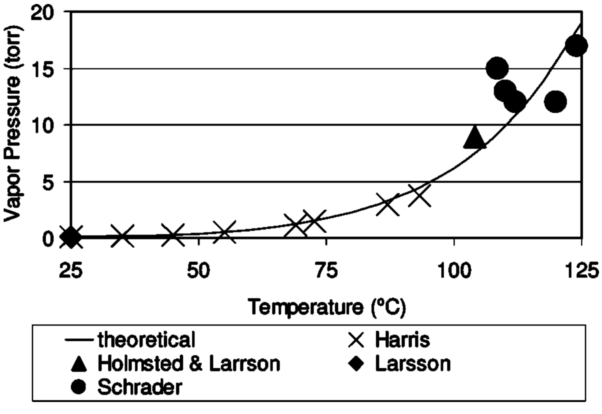


Figure 12. Vapor pressure values for Tabun (r^2 = 0.994, n = 16).

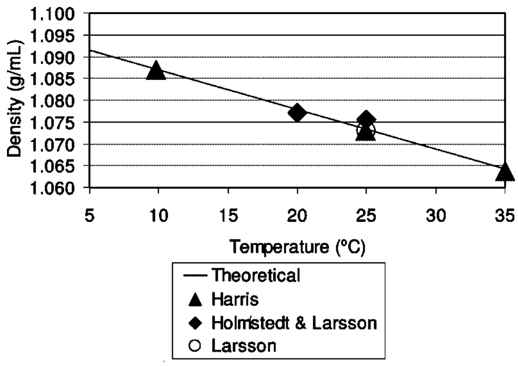


Figure 13. Density values for Tabun ($r^2 = 0.977$, $n = 6$).

Scheme 4. Hydrolysis of Tabun

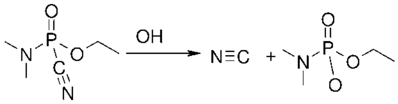


Table 4. Tabun Hydrolysis Rate Constants

T (°C)	pH	k_{obsd} (h^{-1})	ref
25	5.00	0.39	224
20	5.10	0.07	217
20	7.20	0.17	217
20	8.60	0.28	217
25	8.50	0.26	223
25	8.75	0.33	223
25	9.00	0.50	223
25	9.00	0.42	248
35	9.00	1.44	223
25	9.50	1.26	223
35	9.50	4.21	223

Table 5. Tabun Hydrolysis Half-Lives in Seawater

T (°C)	seawater $t_{1/2}$ (min)	k_{obsd}, calcd (h^{-1})
15	475	0.088
20	267	0.156
25	175	0.238

At pH > 7 Tabun is hydrolyzed by hydroxide anion, producing cyanide anion and monoethyl dimethylphosphoramidate (CAS registry no. 2632-86-2) as shown in Scheme 4. Rate constants for hydrolysis of Tabun have been measured at a variety of pH and temperature values; these measurements are given in Table 4 along with references to the experimental literature. From these data an activation energy, E_a, of 10.1 kcal mol^{-1} was calculated for the basic hydrolysis of Tabun.[223] A group of U.S. Army researchers has also measured the half-life of GA in seawater at several different temperatures;[173] these values are given along with the corresponding rate constants in Table 5. The calculated rate constants are roughly consistent with comparable values in Table 4, suggesting that the effects of the ionic strength and composition of seawater on the hydrolysis rate is minor. Reports of the subsequent reactivity of monoethyl dimethylphosphoramidate conflict. One study reported that the P−O bond is more reactive than the N−P bond toward hydrolysis under basic conditions,[224] whereas a previous investigation of ethyl diethylphosphoramidate and homologues indicated that the N−P bond was the more reactive.[225]

The water solubility of Tabun is 98 g/L at 0 °C and 72 g/L at 20 °C.[16,226] Several recent compilations[17,227] report the 98 g/L value at 25 °C, which appears to be an error. One of the compilations lists a Henry's Law constant of 1.52 × 10^{-7} atm m^3/mol at 25 °C,[17] which is calculated from the vapor pressure[221] and the erroneous water solubility. One can calculate a Henry's Law constant of 1.40 × 10^{-7} atm m^3/mol at 20 °C using the solubility at that temperature and a vapor pressure extrapolated from the equation given previously in this section. Finally, the log K_{ow} value for Tabun was recently measured as 0.384 ± 0.033 at room temperature.[228,229]

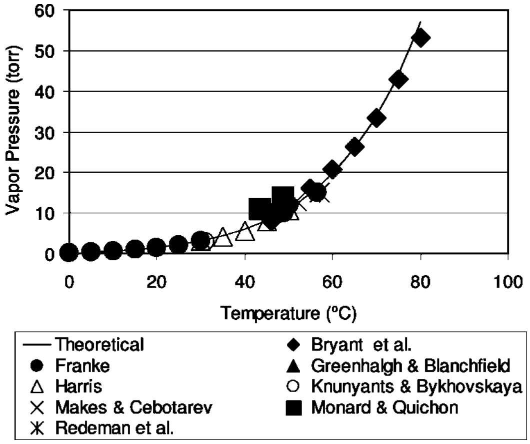


Figure 14. Vapor pressure values for Sarin ($r^2 = 0.993$, $n = 32$).

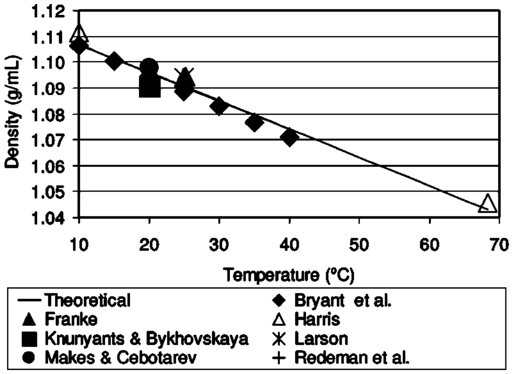


Figure 15. Density values for Sarin ($r^2 = 0.961$, $n = 16$).

2.8. Sarin (GB)

In 1938, a second potent organophosphate nerve agent named Sarin (GB, CAS index name, phosphonofluoridic acid, *P*-methyl-, 1-methylethyl ester; IUPAC name, isopropyl methylphosphonofluoridate; CAS registry no. 107-44-8) was discovered. Sarin was produced in pilot-scale quantities by the Germans just before the end of World War II[218] and later became a mainstay of Soviet and American chemical arsenals. Sarin has been loaded into a wide variety of American chemical munitions,[39] and an estimated 239 tons of Sarin were disposed in U.S. waters.[5] There is a moderate amount of data on Sarin available in the open literature.

Pure isopropyl methylphosphonofluoridate is an odorless liquid under ambient conditions and has a molecular formula of $C_4H_{10}FO_2P$ and a formula weight of 140.10. Weapons-grade GB is reported to have an acidic odor, reminiscent of hydrogen chloride.[230] The boiling point at ambient pressure is reported in various data compilations as 147[24] and 158 °C,[17] and the melting point is reported to be −56.3 °C.[231] One study reports that the vapor pressure of isopropyl methylphosphonofluoridate obeys eq 23 over the temperature range from 0 to 60 °C[232]

$$\log p(\mathrm{Torr}) = 9.8990 - \frac{2850.9}{T(\mathrm{K})} \quad (23)$$

This study does not report individual data points. Using vapor pressure and reduced boiling point data from several other studies[24,232−238] gives eq 24 for the temperature range from 0 to 147 °C

$$\log p(\mathrm{Torr}) = 9.4(\pm 0.1) - \frac{2700(\pm 40)}{T(\mathrm{K})} \quad (24)$$

This expression is plotted with the data in Figure 14, showing good agreement between the various data sources. Note that the ambient boiling point is not shown in the figure but was included in the analysis. The two expressions agree to within 10% between 0 and 60 °C, where the two data sets overlap.

Values for density from multiple studies[24,232−234,237−239] over the range from 10 to 69 °C can be fit to eq 25

$$D(\mathrm{g/mL}) = 1.118(\pm 0.002) - 0.00109(\pm 0.00006)T(°\mathrm{C}) \quad (25)$$

This expression is plotted with the data in Figure 15, showing the good agreement between the individual data sources.

The water solubility of isopropyl methylphosphonofluoridate increases as temperature decreases. GB is miscible with water in all proportions at both 0.0 and 25 °C.[240] One compilation reports a Henry's Law constant of 5.4×10^{-7} atm m^3/mol at 25 °C,[17] which appears to be calculated from the vapor pressure and a solubility value of 100%. However, the vapor pressure of GB over water shows a strong positive deviation from Henry's Law with an activity coefficient exceeding 5 at low agent mole fractions (<0.1).[240]

Isopropyl methylphosphonofluoridate undergoes hydrolysis by acidic, neutral, and basic mechanisms, all of which give fluoride and isopropyl methylphosphonate (IMPA, CAS registry no. 1832-54-8) as the initial products. IMPA is slowly converted to methylphosphonic acid (MPA, CAS registry no. 993-13-5) and isopropyl alcohol in the environment, most likely via biodegradation[241−244] as abiotic processes are orders of magnitude slower.[245,246] The neutral reaction is shown in Scheme 5. Rate constants for isopropyl methylphosphonofluoridate hydrolysis rates are given in Table 6. E_a values of 10.6[247] and 9.1 kcal mol^{-1}[239] were calculated from the rate constants for basic hydrolysis.

Scheme 5. Hydrolysis of Sarin

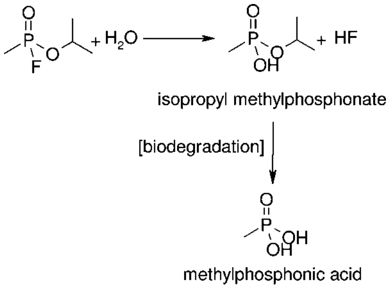


Table 6. Isopropyl Methylphosphonofluoridate Hydrolysis Rate Constants

T (°C)	k_{OH} (L mol^{-1} s^{-1})	k_w (s^{-1})	ref
0.3	4.67	1.7×10^{-5}	247
25	23.7	5×10^{-5}	247
25	25.80	NA[a]	239
35	42.40	NA[a]	239
42.5	63.7	5×10^{-5}	247

[a] NA= not available.

Several other studies have presented observed rate constants for isopropyl methylphosphonofluoridate hydrolysis at various pH values at room temperature.[248−250] These studies are generally consistent with the values in Table 6. In seawater, at a reported constant pH of 7.7, the half-life of isopropyl methylphosphonofluoridate at any temperature between 0 and 25 °C can be estimated using eq 26[251]

$$\log t_{1/2}(\mathrm{min}) = \frac{4325}{T(\mathrm{K})} - 12.84 \quad (26)$$

Epstein reports that Ca^{2+} and Mg^{2+} in seawater significantly catalyze isopropyl methylphosphonofluoridate hydrolysis. At 0.2 °C in seawater the measured half-life of GB is 15.9 h,[23,251] corresponding to a rate constant for hydrolysis of 7.3×10^{-4} s^{-1}, which is 38 times the expected rate constant for the same conditions in fresh water. Finally, if the initial concentration of isopropyl methylphosphonofluoridate exceeds 0.01 mol/L (1.4 g/L), the quantity of acidic reaction products will be sufficient to overwhelm the buffering capacity of seawater[251] and autocatalysis will occur, increasing the rate of hydrolysis. One additional factor that could complicate the analysis of the effect of GB on the marine environment is the presence of carbodiimide stabilizers in some GB. At the pH of seawater the carbodiimide should be converted to the analogous urea by hydrolysis.

The log K_{ow} value for isopropyl methylphosphonofluoridate was measured as 0.299 ± 0.016 at room temperature.[228,229] Partition coefficients for isopropyl methylphosphonofluoridate between water and other organic solvents have also been measured with log P values ranging from 31.2 for chloroform/water to 0.20 for *n*-heptane/water at temperatures between 25 and 29 °C.[252]

2.9. VX

Use of VX as a chemical warfare agent resulted from work in 1952 and 1953 by several groups working independently that discovered the high toxicity of organophosphate esters of substituted 2-aminoethanethiols.[253−255] The British chemical weapons laboratory at Porton began investigating this class of compounds and notified the U.S. chemical weapons laboratory at Edgewood, which began a systematic investigation of the entire class. In 1958, the United States selected VX (CAS index name, phosphonothioic acid, *P*-methyl-, *S*-[2-[bis(1-methylethyl)amino]ethyl] *O*-ethyl ester; IUPAC name, *S*-[2-(diisopropylamino)ethyl] *O*-ethyl methylphosphonothioate; CAS registry no. 50782-69-9) for manufacture. Construction of the production plant began in 1959; production ran from 1961 to 1968. The U.S. government classified the chemical structure of VX as secret until the early 1970s.[256] VX has been loaded into several American chemical munitions,[39] and an estimated 124 tons of VX was disposed in U.S. coastal waters.[5] This review found only limited information on VX, presumably because it was the last of the agents covered in this review to be prepared, the chemical identity of VX was classified for so long, and the material poses such a hazard that experiments with VX should only be conducted by specially trained personnel in a limited number of laboratories.

Pure VX is an odorless liquid under ambient conditions and has a molecular formula of $C_{11}H_{26}NO_2PS$ and molecular weight of 267.37. Weapons-grade VX has a pronounced thiol odor.[230] Many secondary sources list the boiling point of VX at ambient pressure as 298 °C with decomposition.[17] However, it appears that the ambient pressure boiling point

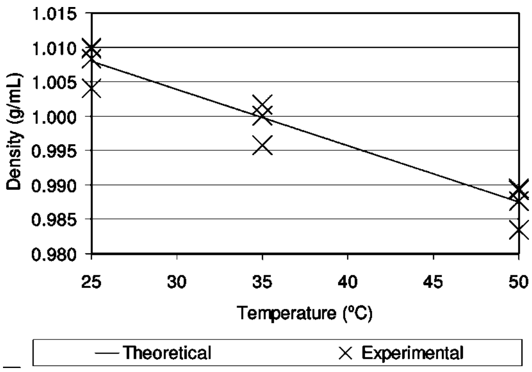


Figure 16. Density values for VX ($r^2 = 0.924$, $n = 12$).

is not experimental but was calculated on the basis of the extrapolation of vapor pressure measurement.[257,258] A good melting point of VX has never been obtained; the best interpretation is that the value is below −60 °C.[259] A number of secondary references report the value of the VX melting point as −39 °C; this appears to have originated in a misunderstanding of the results reported in ref 259.

Values for density[259] over the range from 25 to 50 °C can be fit to eq 27

$$D(\mathrm{g/mL}) = 1.029(\pm 0.003) - 0.00082(\pm 0.00007)T(°\mathrm{C}) \tag{27}$$

This expression is plotted with the data in Figure 16.

Two studies of VX vapor pressure as a function of temperature have been published. One covers the temperature range between 7.5 and 42.4 °C[260] and results in eq 28

$$\log p(\mathrm{Torr}) = 13.9(\pm 0.7) - \frac{5200(\pm 200)}{T(\mathrm{K})} \tag{28}$$

The second study covers the temperature range between −12 and 103 °C[261] and provides eq 29, although individual data points are not recorded

$$\log p(\mathrm{Torr}) = 10.562 - \frac{4068}{T(\mathrm{K})} \tag{29}$$

The data points in Buchanan et al.[258] appear to fit the second equation more closely. The two expressions give vapor pressures that agree to within an order of magnitude or better between 7.5 and 42.4 °C, where the two data sets overlap.

The pK_a value of VX is variously given as 8.6[262] and 9.12 at 25 °C.[173] This indicates that the amino group of VX will be predominantly protonated at the pH of seawater. VX has a lower consolute temperature of 9.4 °C in pure water;[259] this is often reported as miscibility below that temperature.[263] At higher temperatures VX is soluble in water at levels of 75 g/L at 15 °C and 30 g/L at 25 °C, whereas water is soluble in VX at 220 g/L at 15 °C and 160 g/L at 25 °C.[259] The solubility of VX in water decreases significantly as pH increases.[264] A recent compilation of data lists the Henry's Law constant as 3.5×10^{-9} atm m^3/mol at pH 6;[17] the solubility value and the vapor pressure at 25 °C using the expression above give a similar value of 2.6×10^{-9} atm m^3/mol. The log K_{ow} of VX was measured as 0.675 ± 0.070 at room temperature,[228,229] although a significantly different estimated value of 2.09 is given in some data compilations.[17]

Hydrolysis of VX, along with other aspects of detoxification, was recently reviewed.[265] A summary of key hydrolysis pathways is shown in Scheme 6. One reference gives hydrolysis rate constants for VX as 8.4×10^{-3} h^{-1} ($[\mathrm{VX}]_0 = 2\%$) and 12.1×10^{-3} h^{-1} ($[\mathrm{VX}]_0 = 0.5\%$) in distilled water at 21 °C.[266] Rate constants of 0.130 h^{-1} at pH 8 and 0.281 h^{-1} at pH 9 have also been measured at 55.6 °C.[262] One reference fits the rate constants for hydrolysis of VX at 25 °C as well as rate constants for the diethylamino analog to eq 30[262]

$$k_{\mathrm{obsd}} = 2.9 \times 10^{-4}\frac{[\mathrm{H}^+]}{2.5 \times 10^{-9} + [\mathrm{H}^+]} + 1.5 \times 10^{-2}\frac{2.5 \times 10^{-9}}{2.5 \times 10^{-9} + [\mathrm{H}^+]} + 30[\mathrm{OH}^-]\frac{2.5 \times 10^{-9}}{2.5 \times 10^{-9} + [\mathrm{H}^+]} \tag{30}$$

Cu^{2+} and Ca^{2+} are known to catalyze hydrolysis of both methylphosphonofluoridates (see above) and thiophosphoric esters.[267] However, there is a report that Cu^{2+} does not catalyze VX hydrolysis to any significant degree,[268] and a recent review notes that "no transition metals or complexes have yet been reported to catalyze the hydrolysis of VX".[265] Rate constants have been measured at pH 7.7 in a synthetic seawater solution at several temperatures between 15 and 45 °C; $k_{\mathrm{obs}} = 4 \times 10^{-3}$ h^{-1} at 25 °C; this corresponds to a half-life of 170 h. The rate constant in seawater at pH 7.7 as a function of temperature obeyed eq 31[23]

$$\log k_{\mathrm{obs}}(\mathrm{h}^{-1}) = 24.286 - \frac{7954}{T(\mathrm{K})} \tag{31}$$

Extrapolating to 2 °C, this expression gives a rate constant of $k_{\mathrm{obs}} = 2 \times 10^{-5}$ h^{-1}, corresponding to a half-life in deep water of more than 3 years. VX is thus expected to be longer lived in the marine environment than most other chemical warfare agents. VX also contains carbodiimide stabilizers, but their presence is less likely to complicate the analysis of VX in the marine environment because VX has a much longer half-life than does GB. Thus, the relatively larger extent of hydrolysis of the carbodiimide to the analogous urea and dilution as the plume disperses will diminish the effect of carbodiimides on VX in the marine environment and its hydrolysis products.

As shown in Scheme 6, hydrolysis of VX can follow two pathways. One pathway produces 2-(diisopropylamino)ethanethiol (CAS registry no. 5842-07-9) and the ethyl ester of methylphosphonic acid (EMPA, CAS registry no. 1832-53-7), which are significantly lower in toxicity than the starting VX.[17] However, a second pathway produces ethanol

Scheme 6. Hydrolysis of VX Structure 10: *S*-(2-chloroethyl)-1,4-dithianium Chloride

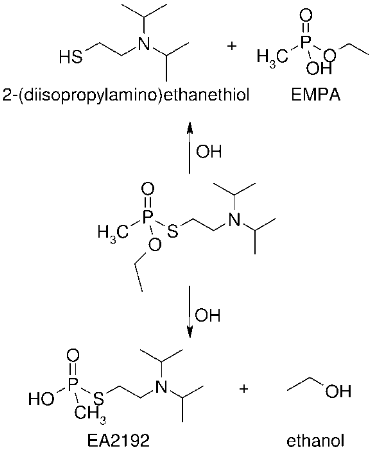


Table 7. Acute Toxicity of Thiodiglycol to Aquatic Organisms

organism	effect	notes	ref
Leuciscus idus (fish)	LC_{50} (96 h), 10 000 mg/L	static test; no mortality at concentrations up to 10 000 mg/L	283
Daphnia magna (water flea)	EC_{50} (48 h),[a] 500 mg/L	no immobilization at 500 mg/L	284
Desmodesmus subspicatus (algae)	$EC_{10,50,90}$ (72 h),[a] 500 mg/L	effect on growth	285
activated sludge	EC_{20} (30 min),[a] 1000 mg/L	inhibition of oxygen consumption rate	286
Pseudomonas putida(microorganism)	EC_{20} (17 h),[a] 10 000 mg/L	inhibition of cell multiplication	287

[a] EC_{nn} = Effective concentration affecting nn% of the test population.

and *S*-(2-[diisopropylamino]ethyl) methylphosphonothiolate (CAS registry no. 73207-98-4), also known as EA2192, which is approximately as toxic as the starting VX when administered intravenously.[17] Measurements at pH 8 and 25 °C indicate that 34% of the diethyl analogue of VX is converted to the corresponding EA2192 analogue; at 55.6 °C, 35% of VX is converted to EA2192.[262] Under acidic conditions EA2192 hydrolyzes faster than VX,[262] and under strongly basic conditions EA2192 undergoes hydrolysis roughly 4 orders of magnitude more slowly than VX,[269] but the authors cannot locate any data for the rate of hydrolysis of EA2192 at the pH of seawater. It has been suggested that the relatively slow hydrolysis at high pH was due at least in part to electrostatic repulsion between hydroxide and anionic EA2192. At the pH of seawater, EA2192 is likely to be predominantly zwitterionic, so the reactivity at high and low pH relative to VX provides little indication of the likely behavior. However, reaction of EA2192 is expected under all conditions to be slower than reaction of VX,[269] and so it is likely that EA2192 will persist in seawater even longer than VX. Thus, the environmental effects of EA2192 may be more significant than the effects of the original VX.

The authors can find no measurements of physical properties for EA2192, although estimated values have been published in several sources.[17,180] Some of the properties covered in this review (boiling and melting points, bulk density, and bulk solubility) are not relevant for EA2192 because it is produced in aqueous solution rather than being released as a bulk material. However, volatility and partitioning parameters for EA2192 remain of interest. Although quantitative data are unavailable, EA2192 is expected to be relatively nonvolatile because it is likely present at the pH of seawater as a zwitterion with a molecular weight of 239.32. It is also expected to partition preferentially into the aqueous phase rather than into organic materials for the same reason. Moreover, the properties of EA2192 are not considered critical data gaps because hydrolysis of VX in seawater is so slow. Dilution to well below detectable levels will have occurred long before the hydrolysis process that generates EA2192 proceeds to a significant degree.

3. Ecotoxicity Parameters

The literature on the toxicity to aquatic organisms for the agents and breakdown products has been reviewed recently[14,17] except for phosgene and hydrogen cyanide. Therefore, the current review does not attempt to critically evaluate the ecotoxicity values. However, as part of this review the authors evaluated areas where additional research may be required, so the relevant ecotoxicity studies are briefly considered for that purpose.

No data were found on the toxicity of phosgene to aquatic organisms. However, the extremely rapid hydrolysis of phosgene in water makes it unlikely that marine organisms would be directly exposed to phosgene if released from munitions disposed in the ocean. The phosgene hydrolysis products—chloride ions and carbon dioxide—are unlikely to be toxic at concentrations that would result in the marine environment from the breakdown of phosgene released from disposed munitions.

The highly toxic effects of hydrogen cyanide have been extensively studied because of its use in the mining industry and other industrial processes.[270−273] At the time of this review, the U.S. Environmental Protection Agency's Ecotox database listed 24 published papers about the effects on freshwater invertebrates and fish. At seawater pH of about 8.3 hydrogen cyanide will be present predominantly as the unionized acid, which is very toxic to freshwater organisms. Median lethal concentration (LC_{50}) values reported in the Ecotox database range from 10 to several hundred μg/L. Lower water temperatures increased toxicity in freshwater fish.

Previous reviews[14,17] cite three sources of data on cyanogen chloride, which were for freshwater fish and invertebrates.[274−276] These reviews found no information on the breakdown product cyanic acid. In the current study no additional toxicity data were identified for cyanogen chloride. Cyanogen chloride is very toxic to aquatic invertebrates and fish and is similar to that of hydrogen cyanide; LC_{50} values were 120−150 μg/L.

The recent reviews[14,17] cite three sources of data on sulfur mustard.[227,277,278] These reported data in the effects of sulfur mustard on the water flea (*Daphnia magna*) and five freshwater fish species, crayfish, and the bullfrog. One of the cited reports[278] also provides data from several additional references on the effect of mustard on species of saltwater phytoplankton, crustaceans, mollusks, and fish.[279,280] These studies were conducted at concentrations ranging from ppb (μg/L) to a few ppm (mg/L). Results were consistent with the findings of the studies in the reviews.

These reviews reported on one study of the mustard breakdown product thiodiglycol.[281] The Organization for Economic Cooperation and Development (OECD) has published a recent assessment of thiodiglycol.[282] Data are presented in Table 7 for toxicity to aquatic species from unpublished studies conducted by BASF.[283−287] These data are consistent with previously reported data that thiodiglycol has very low or no toxicity to aquatic organisms. OECD states that thiodiglycol is of low toxicity to the aquatic environment based on short-term tests from three trophic levels, which is consistent with data reported in recent reviews.[14,17] One group measured inhibition of methane production of an anaerobic sludge blanket reactor for thiodiglycol concentrations of 0.5−10.0 g/L. A 24 h median effective concentration (EC_{50}) was estimated to be 4.2 g/L.[288] This is consistent with the values reported in Table 7. Another study determined an acute 24 h EC_{50} value for 1,4-dithiane, a substance present as an impurity in mustard, for the water flea *D. magna* as 23.2 mg/L.[289] This value is about an order of magnitude greater (less toxic) than the acute toxicity value for sulfur mustard to freshwater fish of 2 mg/L reported in the Munro et al. review.[17]

As discussed previously, sulfur mustard may also undergo reaction in its container to form a heel material, composed primarily of *S*-(2-chloroethyl)-1,4-dithianium chloride, **10**. No data were found on the toxicity of *S*-(2-chloroethyl)-1,4-dithianium chloride to aquatic organisms.

The recent reviews[14,17] cite three sources of data on Lewisite and its hydrolysis products.[277,290,291] Test organisms were freshwater species of fish, tadpole, phytoplankton, and aquatic plants. In addition, the current study found a dietary exposure study for Lewisite at two dose levels in the food of the three-spined stickleback (*Gasterosteus aculeatus* L.), a marine species.[292] No significant differences were observed between the dosed and control groups for mortality, liver function (EROD activity), and presence of cellular degenerations. A review of Lewisite chemistry and toxicology has been published[293] but does not contain data on toxicity to aquatic organisms. Arsenic is an ultimate degradation product from Lewisite. The transport, transformation, fate, and effects of arsenic in the marine environment have been studied extensively and will not be summarized here.[294−306]

Recent reviews[14,17] cite one source of data on nitrogen mustard[277] which may have tested hydrolysis products because it was a 30-day test. The current study found no additional information on aquatic toxicity. Munro et al.[17] cite an LC_{50} value of 160−200 mg/L for the breakdown product *N*-ethyldiethanolamine for the creek chub (*Semolitus atromaculatus*), a freshwater fish, but do not provide a reference. The value is identical to that reported by Gillette et al.[307]

As discussed in the section on the chemical and physical properties, *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine is unstable and slowly turns into the *N*,*N*′-diethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride dimer in the container. It is likely that much of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine disposed in the marine environment may now be in the dimer form, which is what would be released to the environment. No data were found on the toxicity of the *N*,*N*′-diethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride to aquatic organisms. Data were found for the subcutaneous median lethal dose (LD_{50}) in mice for the close analogue (methyl vs ethyl) *N*,*N*′-dimethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride.[308] The LD_{50} in mice for *N*,*N*′-dimethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride is approximately 200 times greater (less toxic) than *N*,*N*-bis(2-chloroethyl)-*N*-methylamine. Since the compounds are such close analogues, *N*,*N*′-diethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride may be similarly less toxic than *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine.

Recent reviews[14,17] cite one source of data on Tabun,[309] which found high toxicity to several species of freshwater fish (LC_{50} of 0.7−1.3 mg/L). One source of data on the breakdown product dimethylamine was cited[310] which found moderate toxicity to the water flea (freshwater invertebrate) and rainbow trout. The current study found no additional aquatic toxicity data for Tabun or its breakdown products.

Recent reviews[14,17] cite one source of data on Sarin,[309] which found high toxicity (LC_{50} less than 1 mg/L) for freshwater fish species. The current study did not find any additional studies of the direct toxicity of Sarin to aquatic organisms.

IMPA is the immediate hydrolysis breakdown product for Sarin. LC_{50} values have been measured in a bioassay for the freshwater fish golden shiner and channel catfish eggs and 15-day posthatch fry; these data are presented in Table 8.[311] Test water temperature was 24 °C for eggs and 23 °C for fry. The LC_{50} value for eggs was the concentration at which one-half the eggs failed to hatch. Golden shiner eggs and fry were more sensitive than channel catfish eggs and fry. These LC_{50} values are 5−6 orders of magnitude greater (less toxic) than those for the direct toxicity of Sarin to freshwater fish, which were 1−2 μg/L.[17] Munro et al. did not report any data for IMPA.[17]

Table 8. Median Lethal Concentration (LC_{50}) of IMPA

organism	LC_{50} (mg/L)	time (h)
golden shiner eggs	66.6	72
golden shiner 15-day post hatch fry	93.9	96
channel catfish eggs	167.5	168
channel catfish 15-day post hatch fry	144.1	96

MPA is produced very slowly as a breakdown product of IMPA. The recent reviews[14,17] cited one study of MPA.[312] MPA was determined to have almost no toxic effect on the methane production activity of an anaerobic sludge blanket reactor for MPA concentrations of 500−10 000 mg/L.[288] The results are consistent with data presented in Munro et al.[17] for LC_{50} and EC_{50} values for freshwater algae, protozoan communities, invertebrates, and fish.

Recent reviews[14,17] cited four studies of the Sarin impurity DIMP on toxicity to freshwater aquatic organisms.[313−316] The bluegill sunfish was reported as the most sensitive species tested with an LC_{50} of 257 mg/L. The current study did not find any additional aquatic toxicity data for DIMP. A toxicological profile has been published for potential human health effects but does not contain data on aquatic organisms.[317]

Recent reviews[14,17] cite one study for the toxicity of VX to the salt water species blue crab, white perch, and striped bass.[318] The concentration needed to kill 50% of the fish tested was 0.1 ppm or less. The concentration needed to kill 50% of the blue crabs was 215 ppm. The current study did not find any additional aquatic toxicity data for VX.

EA2192, EMPA, 2-(diisopropylamino)ethanethiol, and ethanol would be the significant VX breakdown products in the marine environment. No aquatic toxicity data were found for EA2192, EMPA, or 2-(diisopropylamino)ethanethiol. However, based on mammalian toxicity data,[17] EA2192 may be approximately as toxic to marine organisms as VX. Ethanol would not be considered toxic at concentrations likely to occur in the marine environment if VX is released from disposed munitions.

4. Conclusions

One result of this review has been to identify areas where additional data would be desirable. The authors prioritized the data gaps identified in this study on the basis of our experience in conducting fate and transport evaluations for chemical warfare agents in the marine environment and our consideration of the available data. Given the available data and what they suggest will be the dominant fate and transport mechanisms, there are no data gaps that leave one unable to conduct a reasonable assessment for any agent of potential effects on the marine environment. For this reason, we have not rated any data gaps as critical to fill. Of the identified data gaps, the most useful data would be the following. (1) Nitrogen mustard: data on the temperature dependence of the rate of hydrolysis of *N*,*N*-bis(2-chloroethyl)-*N*-ethylamine in seawater and on the partition coefficient, and ecotoxicity of the *N*,*N*′-diethyl-*N*,*N*′-di(2-chloroethyl)piperazinium dichloride dimer. (2) Sulfur mustard: ecotoxicity of the mustard heel material (or the primary constituent, *S*-(2-chloroethyl)-1,4-dithianium chloride). (3) VX: bioconcentration measured at pH 8 (VX could potentially accumulate in lower organisms in the marine environment); EA2192 ecotoxicity. Under some combinations of environmental conditions, these data might affect the accuracy of the assessment but appear unlikely to decrease the uncertainty of the result significantly.

Other data gaps that appear to be less critical to fate and transport assessments include the following. (1) Nitrogen mustard: there are data giving the Henry's law constant at a single temperature only, but these values suggest that the parameter is less important to fate assessments. (2) Sulfur mustard: there appears to be no experimental value for the standard octanol−water partition coefficient; various sources list estimates that differ by an order of magnitude. However, the environmental fate of 1,1′-thiobis[2-chloroethane] is dominated by dissolution and hydrolysis, so obtaining an experimental partition coefficient is unlikely to significantly affect fate and transport assessments. (3) Lewisite: data on hydrolysis and oxidation rates of intermediates such as chlorovinylarsonous acid are approximate at best. (4) Effect of carbodiimide stabilizers on Sarin fate and transport. Such data would be useful under some circumstances but are less useful for assessment of release scenarios where the agent and stabilizer are quickly dispersed and diluted. Our judgment is that these data gaps would minimally affect the accuracy of the assessment or the uncertainty of the result.

It is possible that some data that would fill these data gaps have been collected by one or more governmental laboratories but have never been published in the open literature; a review by such organizations of internal archives and publication of such data if located would be a useful contribution for environmental fate assessments.

In addition to these specific data gaps, the authors identified several general issues that extend beyond single compounds or types of data. In general, there are sufficient data on hydrolysis rate constants to allow for sound extrapolation to obtain values for seawater at relevant temperature. However, no measurements appear to be available for hydrolysis rates at the pressures experienced in deep water, where many U.S. munitions were disposed. One literature review of activation volumes provides a range of known effects that correspond to rate constants changing by a factor of 0.6−1.2 at 8000 ft depth.[319] This suggests that pressure effects are unlikely to affect environmental fate assessments significantly, although it could be useful to determine activation volumes for sulfur mustard and one nerve agent to confirm that the pressure dependence of agent hydrolysis reactions falls within this modest range.

Toxicity data for salt water species at low temperatures would also be useful. The literature on aquatic toxicity tests or bioassays for agents and their breakdown products are modest, and most of those tests were conducted on freshwater species. In addition, few tests have been conducted at the temperatures typically found in deeper marine environments. Nonetheless, there is sufficient data to give a general understanding of likely toxicities, so additional testing is not considered critical.

More data on the environmental effects of slow-reacting components would be useful. Many of the chemical agents are hydrolyzed relatively quickly to much less toxic materials. However, VX, EA2192 (from VX), and the methylphosphonate esters EMPA (from VX) and IMPA (from Sarin) are expected to be long lived in ocean waters. Because of this, the effect of these materials on aquatic organisms will be determined by transport and fate phenomena when released into ocean waters.

Finally, it would be desirable to have additional information on the fate of hydrogen cyanide in the deep sea environment. There is extensive data for fate assessments in shallow water, where volatilization to the atmosphere is a main fate but transport from deeper sites to the surface can be very slow. Other processes may dominate the fate of hydrogen cyanide in deep water, so a more detailed and integrated investigation into the fate of hydrogen cyanide in deep ocean waters may be useful.

This study has compiled a significant body of the physical and chemical data needed to allow for evaluation of the fate, transport, and environmental impacts of these agents in the marine environment with a reasonable degree of accuracy. The authors and sponsors of this work believe that this compilation will be of considerable use to those conducting such assessments. We conclude that there appears to be sufficient data in the literature on the chemical and physical parameters of the chemical agents phosgene, hydrogen cyanide, cyanogen chloride, sulfur mustard, nitrogen mustard (HN1), Lewisite, Tabun, Sarin, and VX for this purpose. Although some data gaps have been identified, these data gaps are not considered critical to such evaluations. The primary source of uncertainty in the evaluation of the fate, transport, and environmental impacts of these agents remains the rate at which they are released into the environment, which was not addressed in this review. The rate at which sea disposed munitions will leak their contents has to date been assumed in most assessments.[320,321] Actual leakage rates could be orders of magnitude smaller, which introduces a significant degree of uncertainty because the environmental effects in general scale linearly with the source term. The rate at which munitions will leak their contents is the subject of ongoing research. The data gaps identified in this work appear to cause a significantly smaller level of uncertainty. Thus, although the authors identified several interesting areas for potential research, such research is not required to support risk assessments required for current government programs.

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