

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

July 2007



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Abstract

313 references were reviewed to obtain data relevant to the fate, transport, and environmental impacts of chemical agents in marine environments. The review covers the chemical agents phosgene, cyanogen chloride, hydrogen cyanide, sulfur mustard, Lewisite, nitrogen mustard (HN1), Tabun, Sarin, and VX. Parameters covered in the review are boiling point, melting point, density, vapor pressure, solubility, Henry's Law constant, partition coefficients, dissociation constants, and hydrolysis rate constants and products. Recent ecotoxicity data are also discussed. Data gaps for these parameters and agents are identified and prioritized. In addition to the specific data gaps, the authors have identified several general issues that extend beyond single compounds or types of 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. 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. The data gaps identified in this work appear to cause a significantly smaller level of uncertainty.

KEYWORDS: marine environment, phosgene, cyanogen chloride, hydrogen cyanide, sulfur mustard, Lewisite, nitrogen mustard, Tabun, Sarin, VX, boiling point, melting point, density, vapor pressure, solubility, Henry's Law constant, partition coefficients, dissociation constants, hydrolysis rate constants and products.

Executive Summary

Between 1918 and 1970, disposing of excess, obsolete, and unserviceable chemical munitions and chemical agents (collectively referred to as chemical warfare materials) into ocean waters was an internationally accepted practice. During this period, the United States (US) disposed of large quantities of chemical warfare materials in several locations off its Atlantic and Pacific coasts as well as in Alaskan and Hawaiian waters. Recently, this topic has received renewed attention. In 2004, three bomb disposal technicians from Dover Air Force Base were injured and one was hospitalized as a result of exposure to mustard agent when a clam trawler brought up a 75 mm artillery shell that had been disposed at sea. In response to renewed public attention to sea disposal, Congress passed section 312(c) of the John Warner National Defense Authorization Act for Fiscal Year 2007 (P.L. 109-364), requiring the Department of Defense to conduct research on the effects of chemical munitions disposed of in United States ocean waters. This research will require the use of a number of physical, chemical, and toxicological parameters for the evaluation of the fate, transport, and environmental impacts of chemical warfare agents in marine environments.

This report is a critical review of the physical and chemical parameters required to evaluate the effects of chemical agents in ocean waters on the marine environment. Mammalian toxicological parameters used for assessing potential human exposures have been reviewed thoroughly elsewhere and are therefore not included in this review. This review covers data relevant to the chemical agents phosgene (CG), cyanogen chloride (CK), hydrogen cyanide (AC), sulfur mustard (HS), Lewisite (L), nitrogen mustard (HN1), GA (Tabun), GB (Sarin), and VX, which have been identified by the Department of Defense as the agents disposed of in United States ocean waters.

There are numerous published values for the boiling point and melting point of phosgene. Expressions for the density, vapor pressure, Henry's Law constant, and hydrolysis rate constant as functions of temperature are derived for phosgene from literature data. 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 dissociate in water.

There are numerous published values for the boiling point and several published values for the melting point of cyanogen chloride. Expressions for the density, vapor pressure, and hydrolysis rate constant as functions of temperature are derived for cyanogen chloride from literature data. The solubility of cyanogen chloride at 30 °C in aqueous sodium chloride solution as a function of chloride concentration is given. A value for the log of the partition coefficient between water and olive oil is reported. No data on Henry's Law constant were

found. Based on the relatively short hydrolytic half-life of cyanogen chloride, it appears that hydrolysis would dominate the fate of cyanogen chloride in the deep ocean, i.e., at depths where circulation to the surface would be slow. Cyanogen chloride does not dissociate in water.

There are numerous published values for the boiling point and melting point of hydrogen cyanide. Expressions for the density, vapor pressure, Henry's Law constant, and dissociation constant as functions of temperature are derived for hydrogen cyanide from literature data. Data on water solubility, partition coefficient, and hydrolysis are reviewed; hydrolysis would not be expected to be significant under environmental conditions. 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.

There are several published values for the boiling point and melting point of sulfur mustard. Expressions for the density, vapor pressure, and hydrolysis rate constant as functions of temperature are derived for sulfur mustard from literature data. The rate of hydrolysis in sea water at several temperatures and data on the rate at which sulfur mustard dissolves in water are also reviewed. Partition coefficients for ether-water and xylene-water systems have been published, and literature values for the octanol-water partition coefficient were determined to be estimates. Henry's Law constant values are discussed. Sulfur mustard does not dissociate in water. The formation of mustard "heel" in old munitions is also discussed.

There are several published values for the boiling point, melting point, and density of Lewisite. Expressions for the vapor pressure of Lewisite as a function of temperature are derived from literature data. Limited data indicate that the hydrolysis of Lewisite is extremely rapid. Lewisite does not dissociate in water.

There is a value in the literature for the melting point of nitrogen mustard; at ambient pressure, *N,N*-bis(2-chloroethyl)-*N*-ethylamine will polymerize before it boils. Expressions for the vapor pressure and density of nitrogen mustard as a function of temperature were found in the literature. Values for water solubility and the dissociation constant were found, and data on hydrolysis rates are reviewed. Conversion of nitrogen mustard to a dimer form in old munitions is also discussed.

There are values in the literature for the boiling point and the melting point of Tabun. Expressions for the density and vapor pressure as functions of temperature are derived for Tabun from literature data. Hydrolysis rate constants at various temperatures in pure water

and sea water are reviewed. Values for water solubility, Henry's Law Constant, and partition coefficient are also presented.

There are several values in the literature for the boiling point and the melting point of Sarin. Expressions for the density, vapor pressure, and hydrolysis rate constants as functions of temperature are derived for Sarin from literature data. Data on water solubility, Henry's Law constant, and partition coefficients are also reviewed.

There are values in the literature for the boiling point and melting point, of VX. Expressions for the vapor pressure, density, and hydrolysis rate constants in sea water as functions of temperature are derived for VX from literature data. Data on dissociation constant, water solubility, Henry's Law constant, and partition coefficient are also reviewed.

A recent review of ecotoxicity parameters for the chemical warfare agents and their breakdown products was updated.

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 the identified data gaps, the most useful data would be the following:

- Nitrogen mustard – data on the temperature dependence of the rate of hydrolysis of *N,N*-bis(2-chloroethyl)-*N*-ethylamine in sea water and on the partition coefficient, and ecotoxicity of the *N,N'*-diethyl-*N,N'*-di(2-chloroethyl)piperazinium dichloride dimer.
- Sulfur mustard – Ecotoxicity of the mustard heel material (or the primary constituent, *S*-(2-chloroethyl)-1,4-dithianium chloride)
- VX – bioconcentration measured at pH 8 (VX could 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 significantly increase the uncertainty of the result.

Other data gaps that appear to be less critical to fate and transport assessments include the following:

- 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.
- 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.

- Lewisite – data on hydrolysis and oxidation rates of intermediates such as chlorovinylarsonous acid are approximate at best, but there is extensive data on arsenic, the ultimate environmental product.
- 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 significant contribution for environmental fate assessments.

In addition to these specific data gaps, the authors have identified several general issues that extend beyond single compounds or types of data. These issues include the effect of pressure at deep ocean sites on hydrolysis rate constants, toxicity data for salt water species at low temperatures, more data on the environmental effects of slow-reacting components, and the fate of hydrogen cyanide in the deep sea environment.

In conclusion, there appears to be sufficient data in the literature on the chemical and physical parameters of the chemical warfare agents phosgene, hydrogen cyanide, cyanogen chloride, sulfur mustard, nitrogen mustard (HN1), Lewisite, Tabun, Sarin, and VX for evaluation of effects in marine environments. 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 and bulk containers 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 have identified several interesting areas for potential research, such research is not required for current government programs.

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Section 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 can be found before the mid-1940s. At the end of World War II, large chemical munitions stores were discovered in Germany and Japan. From 1946-1947, 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 the 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 in the Pacific Ocean and Japanese coastal waters.⁴ Most of these reports concern fishermen who had inadvertently snared plastic lumps of mustard gas in their nets. The US sea disposed a total of approximately 30,000 tons of chemical agent in several locations off its Atlantic and Pacific coasts as well as in Alaskan and Hawaiian waters.⁵ In 1972, Congress enacted the Marine Protection, Research, and Sanctuaries Act, which explicitly prohibited the disposal of chemical agents in ocean waters.⁶ This practice was also prohibited by the 1972 London Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter.⁷ The last ocean disposal of US chemical warfare materials occurred on 18 August 1970, and the issue of ocean disposal soon receded from public consciousness.

Recently, this topic has received renewed attention. In 2004, three bomb disposal technicians from Dover Air Force Base, Delaware were injured and one was hospitalized as a result of exposure to mustard agent when a clam trawler brought up a 75 mm artillery shell that had been disposed at sea. This incident brought renewed attention to the practice of sea disposal.^{8,9} In response to this renewed public attention, Congress passed section 312(c) of the John Warner National Defense Authorization Act for Fiscal Year 2007,¹⁰ requiring the Department of Defense to conduct research on the effects of chemical munitions disposed of in US ocean waters. This research will require the use of a number of physical, chemical, and toxicological parameters for the evaluation of the fate, transport, and environmental impacts of chemical warfare agents in marine environments.

The authors have undertaken a critical review of the physical and chemical parameters required to evaluate the effects of chemical munitions in ocean waters on the marine environment. Mammalian toxicological parameters used for assessing potential human exposures have been reviewed thoroughly elsewhere^{11,12} and are therefore not included in this review. Ecotoxicological parameters used for assessing potential ecological effects have also been reviewed elsewhere,¹¹ although the authors have found several additional studies not covered in that review, which will be discussed below. This review covers data relevant

to the chemical warfare agents phosgene (CG), cyanogen chloride (CK), hydrogen cyanide (AC), sulfur mustard (HS), Lewisite (L), nitrogen mustard (HN1), GA (Tabun), GB (Sarin), and VX, which have been identified by the US Army⁵ as the agents disposed of in US ocean waters. The structures of these agents are depicted in Figure 1-1.

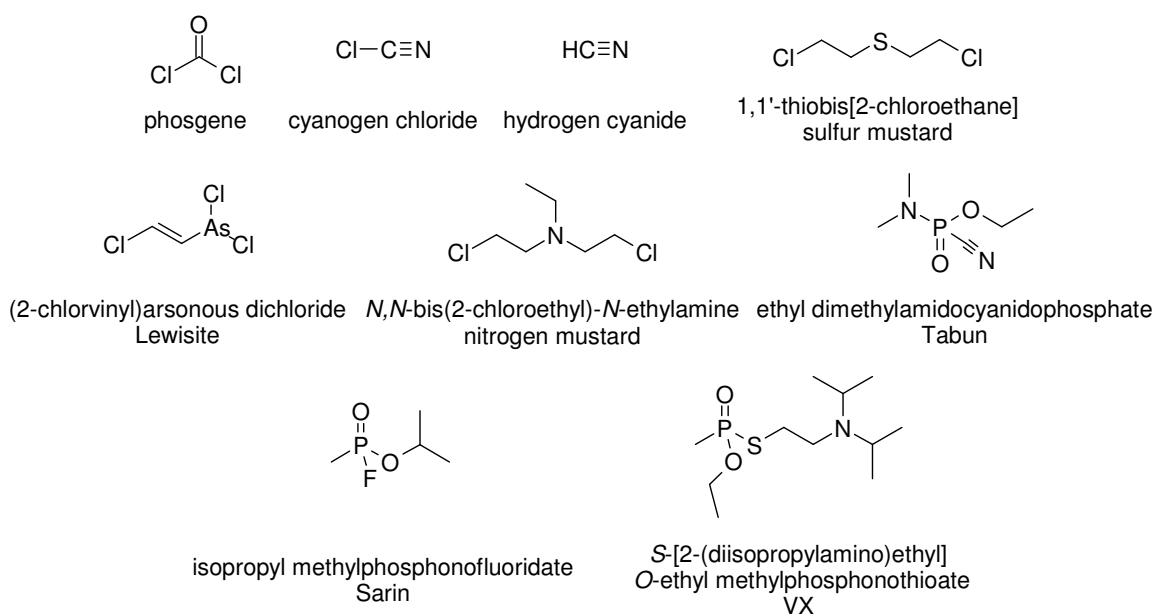


Figure 1-1. Chemical Agents

Section 2

Physical and Chemical Parameters

This study reviewed the available 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 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 the agent exists in the sea. Finally, hydrolysis rate constants (k) and products, where applicable, are key parameters to determining the fate of the agent. For many parameters, data from multiple studies were reviewed and determined to be mutually validating. Available data for these parameters are reviewed for each agent below.

US 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 as warm as 27 degrees Centigrade (°C) in Hawaiian waters in summer¹³ to 0-4 °C in Alaskan waters in winter.¹⁴ In contrast, at deep disposal sites, i.e., below the thermocline, temperatures approach 0 °C. Salinity in US oceanic waters is about 35 parts per thousand, with 90 percent 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;¹⁵ surface pH is typically 8.0 to 8.3, and declines to 7.4 to 8.0 in deep waters. Whenever available, this review presents data on the temperature-, pH-, and sodium chloride concentration-dependence of the parameter to allow for adjustment to give values relevant to the temperature and salinity specific to the disposal site under consideration.

2.1 Phosgene (CG)

Phosgene was first obtained and identified in 1812 by Davy,¹⁶ and was employed for the first time as a war gas in December 1915. 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.^{17,18} Additionally, phosgene is formed from the photoinduced oxidation as well as thermal degradation of chlorinated hydrocarbons in the atmosphere.¹⁹ The US produced approximately 1,400 tons of phosgene during World War I^{20,21} and 20,000 tons of phosgene during World War II, much of it for military applications.²² Phosgene was loaded into a variety of American chemical munitions.²³

Approximately 29 tons of phosgene was disposed in US 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,”²⁴ although many secondary references describe the odor as reminiscent of moldy hay. The molecular formula of phosgene is COCl_2 , corresponding to a molecular weight of 98.92. There are numerous published values for the boiling point of phosgene;²⁵⁻³² the mean boiling point value from these studies is 8.0 ± 0.3 °C. The melting behavior of phosgene is reported to have multiple phase transitions.³³ The reported melting temperatures are -133.96 °C and -131.06 °C for the first two transitions; another paper reports a melting transition at -132.78 °C,²⁶ which appears to be intermediate between the first two transitions. Multiple papers report a third transition;^{25,27,33,34} the mean melting point value from these studies is -128 ± 1 °C. This phase transition is the one typically reported as the melting point in data compilations. Finally, there is a report of a melting point of -118 °C,³⁵ which may represent a measurement using impure material. The vapor pressure of phosgene has been studied by several groups as a function of temperature,^{25,27,28,31,36} the combined 163 data points from these studies fit the following expression over the temperature range -96.3 – 27.9 °C:

$$\log p(\text{torr}) = 7.77 (\pm 0.04) - \frac{1373 (\pm 10)}{T(\text{K})}$$

This expression is plotted with the data in Figure 2-1.

Density values for phosgene from multiple studies^{29,30,32,34,36-38} at temperatures ranging from -104 to 60.2 °C can be fit to the following expression:

$$D (\text{g/mL}) = 1.4226 (\pm 0.0007) - 0.00243 T (\pm 0.00003, \text{ °C})$$

This expression is plotted with the data in Figure 2-2.

Henry’s Law constant values for phosgene are provided in Table 2-1.

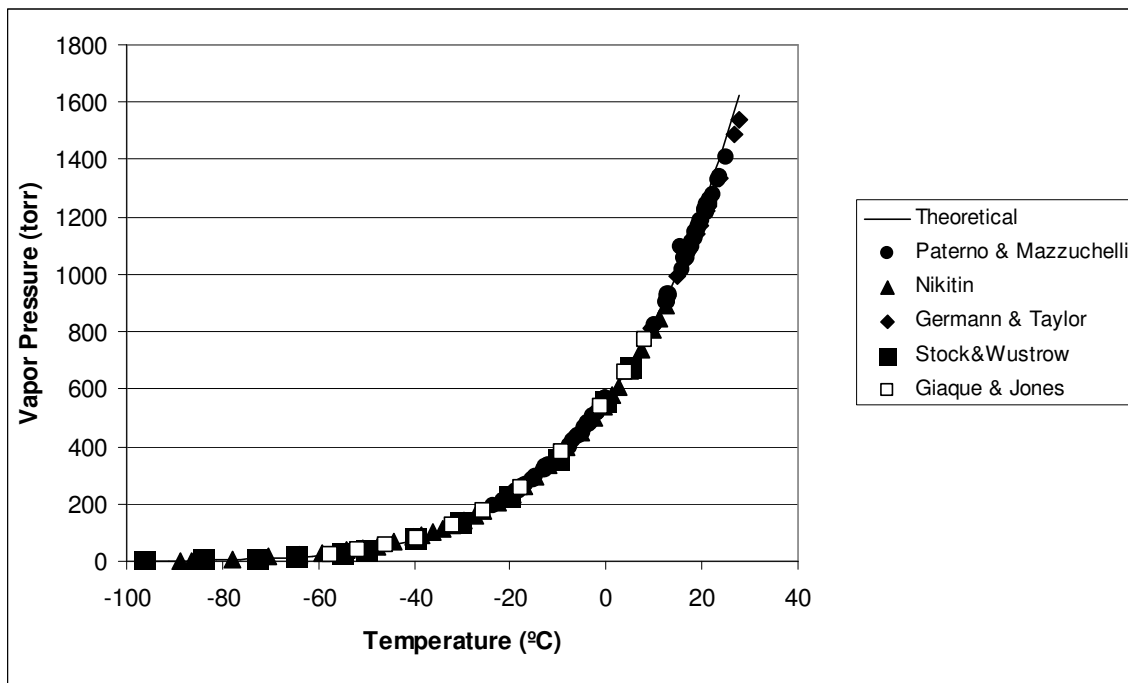


Figure 2-1. Vapor Pressure Values for Phosgene

Table 2-1. Henry's Law Constants for Phosgene

K_H (mole L ⁻¹ atm ⁻¹)	Temperature (°C)	Reference
0.25	0	19
0.15	5	39
0.2	20 (in sea water)	40
0.06	25	39

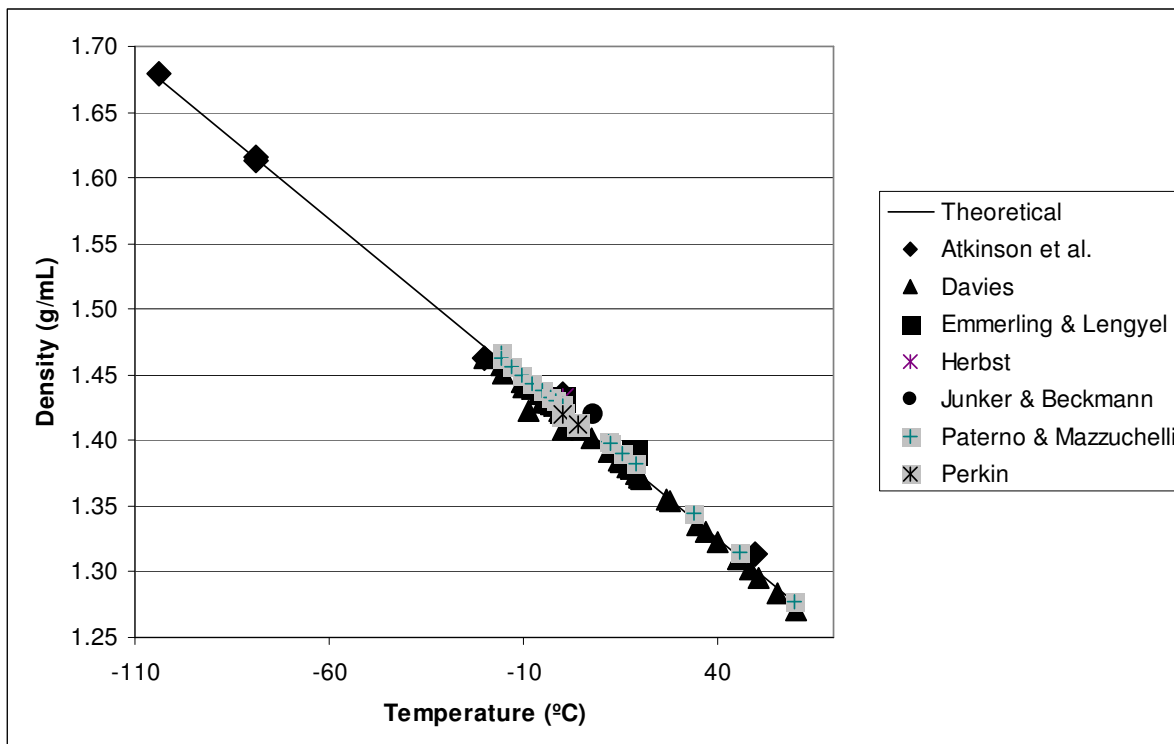


Figure 2-2. Density Values for Phosgene

An analysis of Henry's Law constant as a function of temperature¹⁹ using data from several literature sources^{41,42,43} gives the following expression:

$$\log K_H \left(\text{mole L}^{-1} \text{ atm}^{-1} \right) = \frac{1823.3}{T(\text{K})} - 7.283$$

This expression agrees with the fresh water values in Table 2-1, and suggests that the value in sea water 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.^{39,40,43} Several studies have examined rate constants as a function of temperature. One study presents the Arrhenius parameters for hydrolysis as $A = 1.4 \times 10^{10} \text{ sec}^{-1}$ and $E_a = 53 \text{ kJ mole}^{-1}$ over a range of 13-59 °C.⁴⁴ An analysis of rate constants from several other studies^{40,42-44} gives similar parameters, $A = 1.9 \times 10^{11} \text{ sec}^{-1}$ and $E_a = 57 \text{ kJ mole}^{-1}$ over a range of 15-45 °C. There are also two studies that give values of $4.6 \times 10^3 \text{ L mole}^{-1} \text{ sec}^{-1}$ and $4.6 \times 10^3 \text{ L mole}^{-1} \text{ sec}^{-1}$ for the rate

of the hydroxide-phosgene reaction at 25 °C.^{39,44} At pH 8 (approximately the pH of sea water), the hydroxide-phosgene reaction is significantly slower than the water-phosgene reaction and can therefore be neglected. The Arrhenius parameters yield a half-life for phosgene in water of 0.4-1 sec at 2 °C and 0.1-0.2 sec at 25 °C.

There is one study that indicates that phosgene is sorbed to soil, although the data do not appear to allow the calculation of an absorption coefficient.⁴⁵ 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 dissociate in water.

2.2 Cyanogen Chloride (CK)

Cyanogen chloride was prepared for the first time in 1789 by Berthollet,⁴⁶ and was subsequently characterized by Gay-Lussac.⁴⁷ 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 the production of triazine herbicides, optical brighteners, dyestuffs, and synthetic rubber.⁴⁸ Additionally, cyanogen chloride is formed from the chlorination of drinking water containing aromatic compounds and ammonium ion.^{49,50} The US produced roughly 12,500 tons of cyanogen chloride during World War II,²² and the compound has been loaded into several American chemical munitions.⁵¹ An estimated 205 tons of cyanogen chloride was disposed in US 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 with a highly irritating odor. The molecular formula of cyanogen chloride is CCIN, corresponding to a molecular weight of 89.53. There are numerous published values for the boiling point of cyanogen chloride;^{30,52-60} the mean boiling point value from these studies is 13 ± 1 °C. Similarly, there are several published values for the melting point of cyanogen chloride;^{52,57,58,61,62} the mean melting point value from these studies is -6.6 ± 1.0 °C. The vapor pressure of cyanogen chloride has been studied by several groups as a function of temperature;^{57,62,63} the combined 33 data points from these studies fit the following expression over the temperature range -12 – 17.82 °C:

$$\log p(\text{torr}) = 7.98 (\pm 0.06) - \frac{1456 (\pm 16)}{T(K)}$$

This expression is plotted with the data in Figure 2-3.

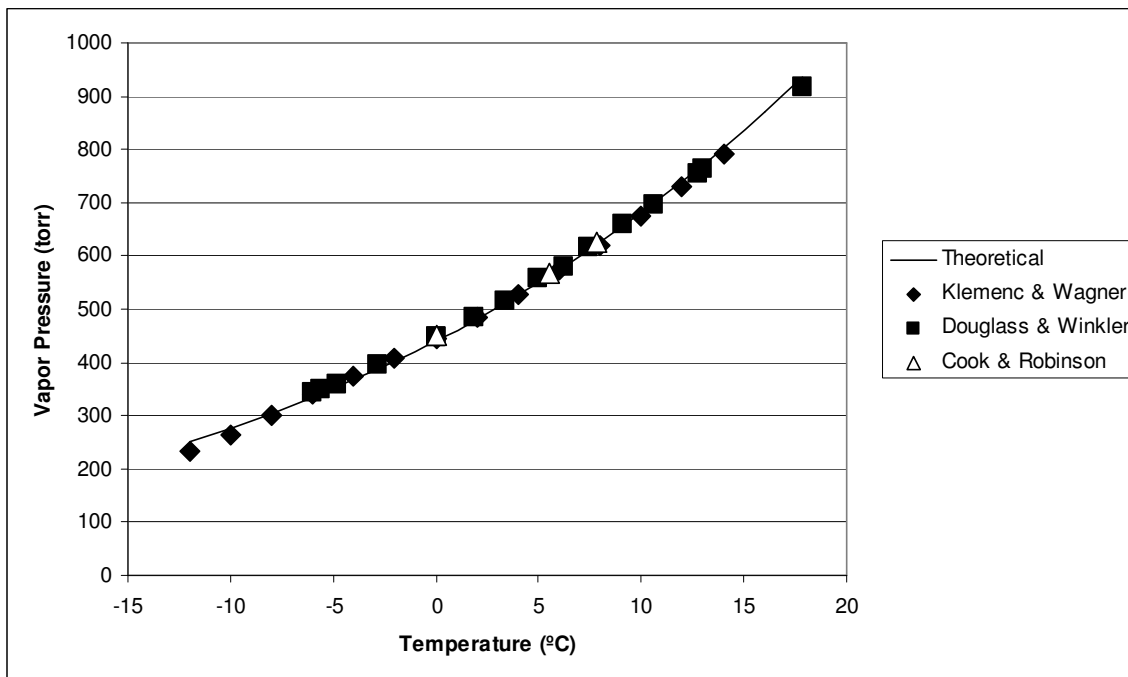


Figure 2-3. Vapor Pressure Values for Cyanogen Chloride

Density values for cyanogen chloride from multiple studies^{52,58,60,63,64} at temperatures ranging from -5.8 to 14 °C can be fit to the following expression:

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

This expression is plotted with the data in Figure 2-4.

This corresponds to a coefficient of expansion of 0.00173, which agrees reasonably well with Maugin and Simon,⁵² 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 study⁵⁷ reports a density value 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.

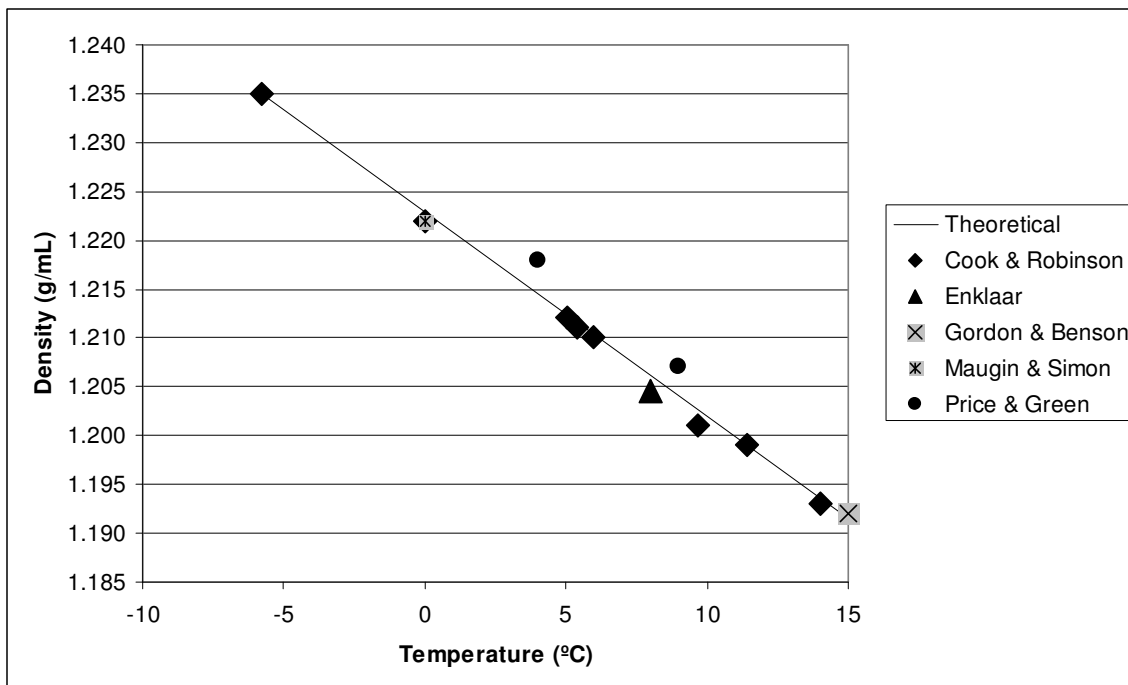


Figure 2-4. Density Values for Cyanogen Chloride

The solubility of cyanogen chloride in aqueous sodium chloride solution at 30 °C was found to obey the following expression:⁵⁹

$$[\text{ClCN}](\text{M, sat'd at } 30^\circ\text{C}) = 0.91(\pm 0.05) - 0.16(\pm 0.03)[\text{NaCl}](\text{M})$$

Another reference gives the water solubility at 8 °C as 7-8% (0.8-0.9 M).⁵⁸

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 the reaction of cyanogen chloride with water^{58,62,65} and with hydroxide ion.^{65,66} Analysis⁶⁵ shows that this data fit the following expression for an observed first order rate constant over the temperature range 5 – 45 °C:

$$k_{obs} (\text{sec}^{-1}) = 9.97 \times 10^8 e^{\frac{-87,180}{8.134T(\text{K})}} + 2.06 \times 10^{11} e^{\frac{-60,980}{8.134T(\text{K})}} [\text{OH}^-] (\text{mole L}^{-1})$$

At pH 8 (approximately the pH of sea water), 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.⁵⁸ There are other studies of cyanogen chloride hydrolysis that were conducted in buffer solutions that catalyze the hydrolysis;⁶⁷⁻⁶⁹ rate constants from these studies should not be used for assessments of the fate of cyanogens 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.”⁷⁰ Nevertheless, a value for the log of the partition coefficient between water and olive oil of 1.6 has been reported;⁷¹ this value suggests that the K_{ow} value is likely to be similarly low. However, based on 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 dissociate in water.

2.3 Hydrogen Cyanide (AC)

Hydrogen cyanide was one of the earliest compounds to be investigated in modern chemistry. Hydrogen cyanide was first obtained as hydrocyanic acid and its qualitative composition determined by Scheele in 1782.⁷² Water-free liquid hydrogen cyanide was first produced in 1811 by Gay Lussac, who first measured its properties.⁷³ Hydrogen cyanide and its salts are used in high volume in the steel, electroplating, mining, and chemical industries, with current annual US demand over 700,000 metric tons.⁷⁴ 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 major users of hydrogen cyanide during World War I, using less than 4,000 tons during the 1915-1918 period.⁷⁵ 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.⁷⁶ The US procured about 560 tons of hydrogen cyanide during World War II alone,²² and an estimated 10 tons of hydrogen cyanide was sea disposed in US coastal waters.⁵

Pure hydrogen cyanide is a clear colorless liquid with an odor described in standard sources as that of bitter almonds.⁷⁷ 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;^{73,78-89} the mean boiling point value from these studies is 25.9 ± 0.3 °C. Similarly, there are many published values for the melting point of pure hydrogen cyanide;^{80,82,83,90-96} the mean melting point value from these studies is -13.33 ± 0.05 °C. Several other reported melting points are significantly lower, suggesting that less pure material was used for those measurements.^{73,78,97-99} The vapor pressure of hydrogen cyanide has been studied by several groups as a function of temperature;^{78,80,84} the combined 36 data points from these studies fit the following expression over the temperature range -8.07 - 46.29 °C:

$$\log p(\text{torr}) = 7.746 (\pm 0.006) - \frac{1454 (\pm 2)}{T(\text{K})}$$

This expression is plotted with the data in Figure 2-5.

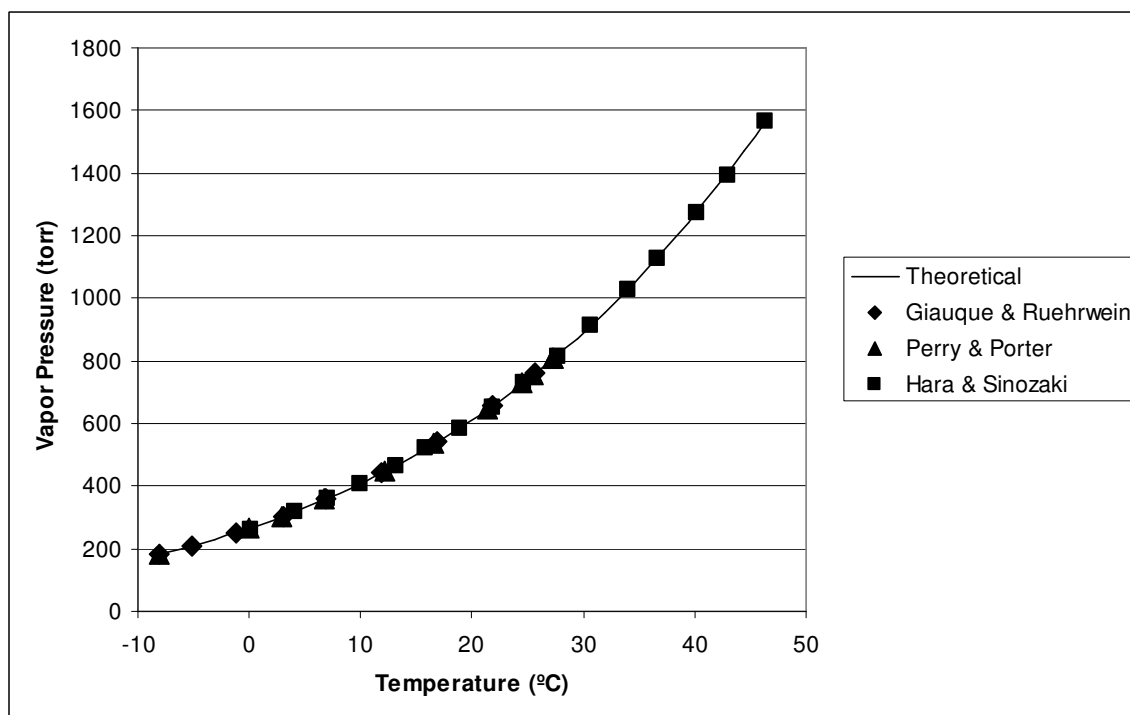


Figure 2-5. Vapor Pressure Values for Hydrogen Cyanide

Henry's Law constant has been measured as a function of temperature three times.¹⁰⁰⁻¹⁰² One of the studies¹⁰⁰ covered the temperature range from 0-100 °C and fits the data to the following expression:

$$\ln K_H (\text{kg} - \text{atm/mole}) = 9.585 - 0.03147 T (\text{K}) + 3.1704 \ln T - \frac{6302}{T}$$

The other studies were performed at higher temperature ranges; these two studies as well as two reports of K_H at 25 °C are available.^{103,104} All give K_H values that agree within a factor of 1.6.

The aqueous dissociation constant has been measured as a function of temperature twice.^{100,101} One of the studies¹⁰⁰ covers the temperature range from 0-150 °C and fits the data to the following expression:

$$\ln K_a = -12.1960 - 0.031482 T (\text{K}) + 3.7658 \ln T - \frac{6340.7}{T}$$

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.¹⁰⁵ 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,^{106,107,108} 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, it appears that at the pH of seawater, hydrogen cyanide will exist predominantly as the free acid.

Density values for hydrogen cyanide from multiple studies^{60,64,73,79,82,86,92-94,109} at temperatures ranging from -13.3 to 25.7 °C can be fit to the following expression:

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

This expression is plotted with the data in Figure 2-6.

Hydrogen cyanide is reported to be miscible with water at temperatures above -23.3 °C.⁹³ Hydrogen cyanide hydrolyzes slowly at low pH to form ammonium ion and formic acid,¹¹⁰ 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;¹¹¹⁻¹¹⁶ The Environmental Protection Agency has found no data to indicate that hydrogen cyanide bioconcentrates in aquatic organisms.^{110,117} The value for the log of the partition coefficient (log P) is reported as -0.25.¹¹⁸

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.”¹¹⁹ There is one study that indicates that hydrogen cyanide is sorbed to soil, although the data do not appear to allow the calculation of an absorption coefficient.⁴⁵

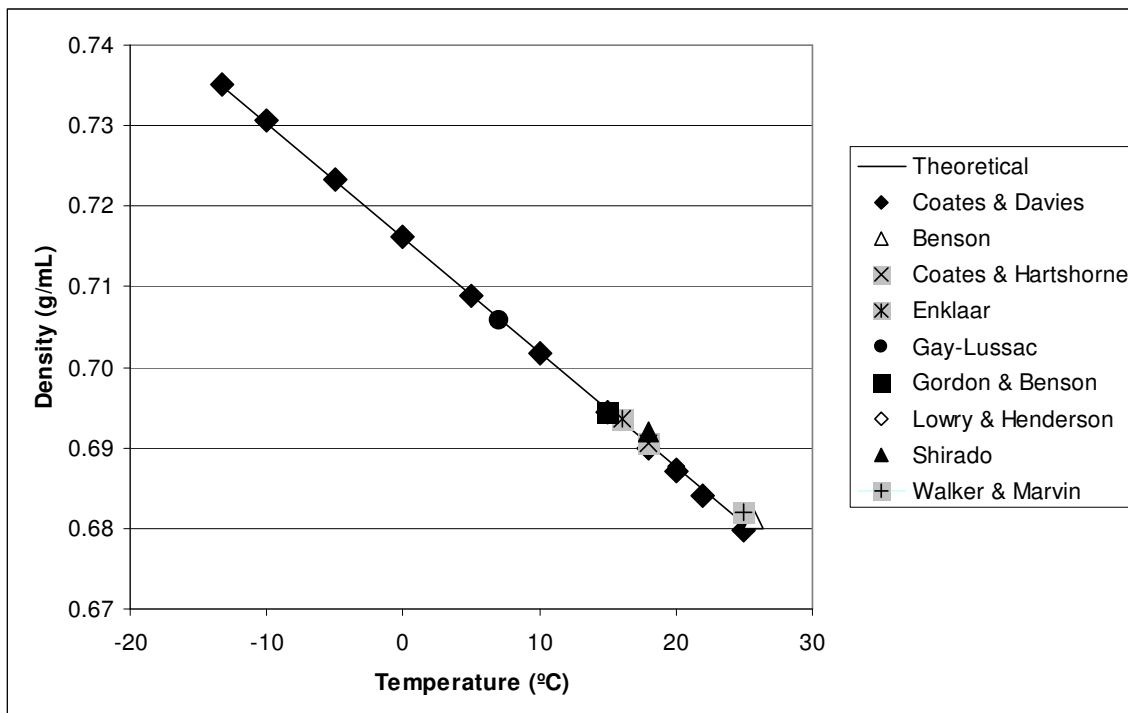


Figure 2-6. Density Values for Hydrogen Cyanide

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.

2.4 Sulfur Mustard (HS)

The principle active compound in sulfur mustard is 1,1'-thiobis[2-chloroethane]. This compound was probably first produced by Despretz¹²⁰ and then later by Riche,¹²¹ although neither isolated or identified the compound. The material was prepared in purer form by Niemann¹²² and independently by Guthrie,¹²³ both of whom noted the vesicant property of the material. Meyer¹²⁴ 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 12-13 July 1917 near Ypres in Flanders. The US produced 900 tons of mustard during World War I,^{20,21} and

over 87,000 tons of sulfur mustard during World War II.²² Sulfur mustard was loaded into many American chemical munitions,¹²⁵ and over 16,000 tons of mustard are estimated to have been sea disposed in US coastal waters.^{5,126} There is a considerable body of literature on 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,¹²³ or horseradish,¹²² although popular accounts also compare the odor to burning garlic and a “weak, sweet, agreeable odor.”¹²⁷ The crude material is straw-colored.¹²⁸ The molecular formula for 1,1'-thiobis[2-chloroethane] is C₄H₈Cl₂S, which corresponds to a molecular weight of 159.08. Five independent studies report that 1,1'-thiobis[2-chloroethane] boils with decomposition^{30,124,129-131,} at 216.9 ± 0.2 °C. Four studies of the melting point of pure 1,1'-thiobis[2-chloroethane]¹³²⁻¹³⁶ 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;^{128,131,137-139} lower and broader melting ranges are likely to 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.¹³⁹ Data from several studies^{128,132,135,137,140} show that the density of 1,1'-thiobis[2-chloroethane] obeys the following expression over the temperature range of 15 to 90 °C:

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

This expression is plotted with the data in Figure 2-7.

A number of workers have examined the vapor pressure of 1,1'-thiobis[2-chloroethane] as a function of temperature.^{135,141-144} Using those data along with boiling points at reduced pressure^{128,130-132, 145-148} indicates that the vapor pressure of 1,1'-thiobis[2-chloroethane] obeys the following expression over the temperature range of -10 to 122.5 °C

$$\log p(\text{torr}) = 8.9(\pm 0.2) - \frac{2930(\pm 60)}{T(\text{K})}$$

This expression is plotted with the data in Figure 2-8.

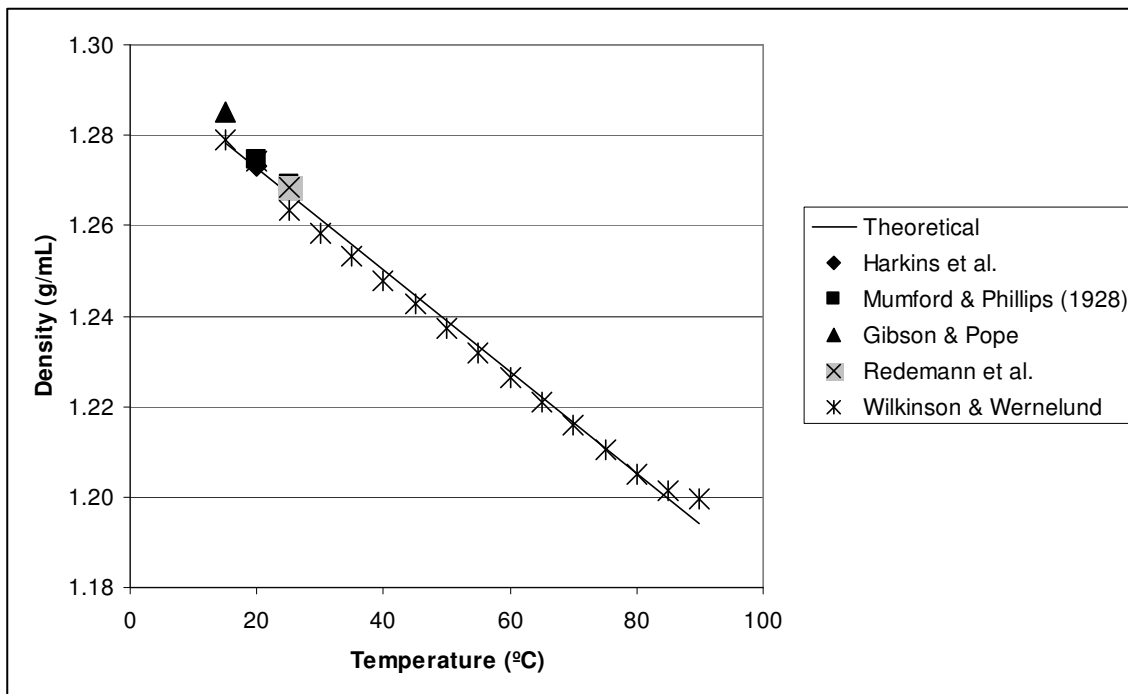


Figure 2-7. Density Values for Sulfur Mustard

The primary fate of 1,1'-thiobis[2-chloroethane] in water is hydrolysis, primarily to thiodiglycol and hydrogen chloride. Hydrolysis generally proceeds as shown in Figure 2-9; the degree to which the reaction proceeds through the sulfonium chloride intermediates H-TG, H-2TG, and CH-TG depends on the concentration of mustard in the aqueous solution.¹⁴⁹⁻¹⁵¹ The initial formation of H-TG in the aqueous phase requires the accumulation of the thiodiglycol (TG) reaction product and appears less significant in a marine environment where currents can remove the hydrolysis product.

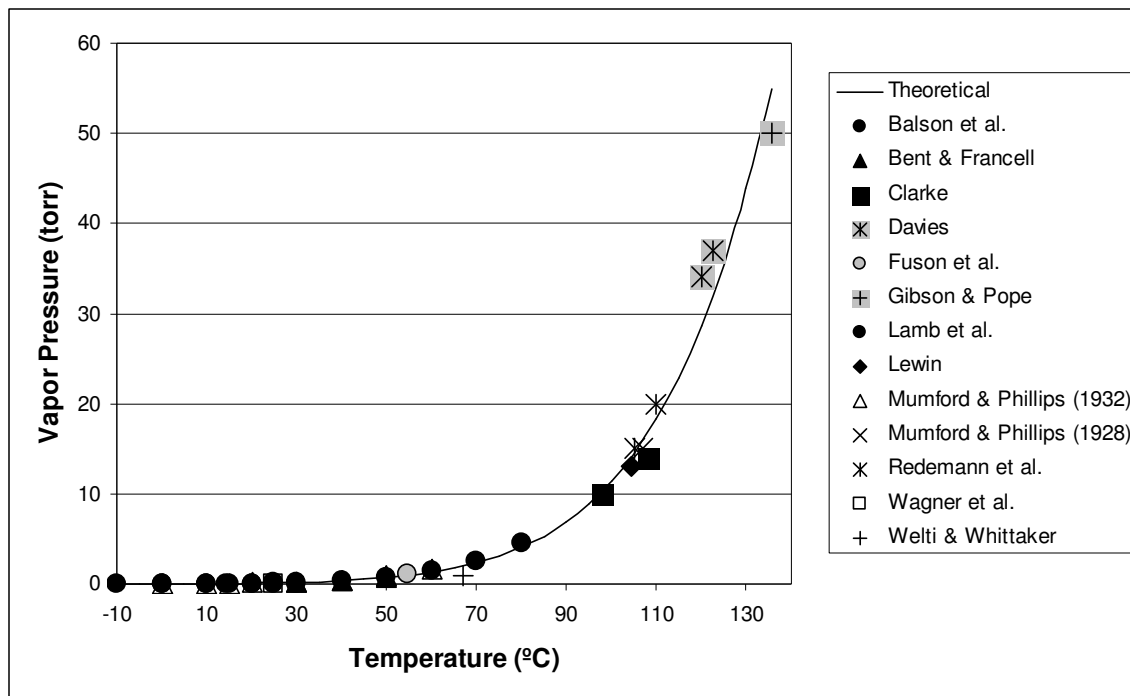


Figure 2-8. Vapor Pressure Values for Sulfur Mustard

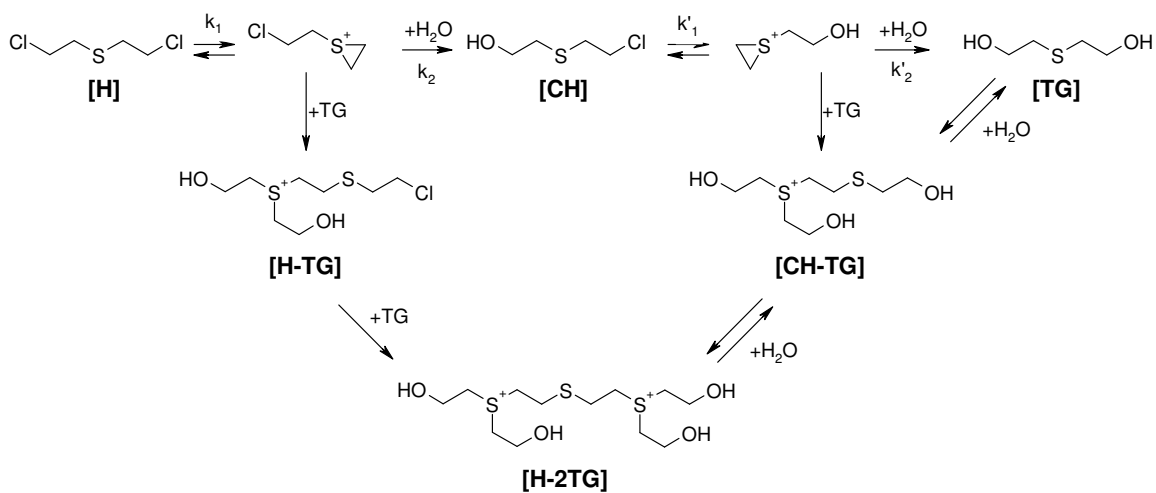


Figure 2-9. Hydrolysis of sulfur mustard

Numerous groups have measured rate constants for the reaction of 1,1'-thiobis[2-chloroethane] with water. Ogston, et al., measured values at 25 °C of $k_I = 0.174 \text{ min}^{-1}$ for 1,1'-thiobis[2-chloroethane] and $k'_I = 0.223 \text{ min}^{-1}$ for 2-([2-chloroethyl]thio)ethanol; k_2 and k'_2 are rapid compared to k_I and k'_I respectively.¹⁵² Independently, Bartlett and Swain established values at 25 °C of $k_I = 0.155 \text{ min}^{-1}$ and $k'_I = 0.260 \text{ min}^{-1}$.¹⁵³ 2-([2-chloroethyl]thio)ethanol is thus a relatively short-lived hydrolysis intermediate. Other groups have measured reaction rates for 1,1'-thiobis[2-chloroethane] from 0-50 °C,¹⁵⁴⁻¹⁵⁸ 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.¹⁵⁹ A recent study determined the activation energy of 18.5 kcal mole⁻¹ for 1,1'-thiobis[2-chloroethane] hydrolysis,¹⁶⁰ which allows the calculation of rate constants at different temperatures.

The rate of 1,1'-thiobis[2-chloroethane] hydrolysis in sea water 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 sea water at several different temperatures.¹⁶¹ These values are given in Table 2-2.

Table 2-2. Half-lives of 1,1'-Thiobis[2-chloroethane] in Sea Water

T (°C)	sea water $t_{1/2}$ (min)	k_I , calculated (min^{-1})
5	175	0.0040
15	49	0.0141
25	15	0.046

The corresponding rates are slower than the reaction rates in pure water because aqueous chloride ion affects the equilibrium between 1,1'-thiobis[2-chloroethane] and the intermediate episulfonium ion. The effect of chloride is to slow the observed rate of hydrolysis by a factor of 3.6, which is in close agreement with the value calculated using the Bronsted-Bjerrum rate equation to account for the effect of sea water'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.¹⁻⁴ 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,¹⁵⁶ 0.92 g/L¹⁶² and 0.68 g/L¹⁶³ at 25 °C, and 0.48 g/L in "cold water" at an unspecified temperature.¹⁶⁴ A compilation of solubility

values includes a listing of 0.678 g/L at 25 °C;¹⁶⁵ although the authors are unable to trace the source of the value; it may refer to the previous 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:¹⁶⁶

$$\sigma (\text{gm cm}^{-2} \text{sec}^{-1}) = 233.7 e^{-\left[\frac{12,350}{8.134 T (\text{K})} \right]}$$

More recently, Demek et al. measured the rate of sulfur mustard dissolution as $3.4 \times 10^{-7} \text{ gm cm}^{-2} \text{ sec}^{-1}$ at 4 °C in a 0.15 knot current.¹⁶⁷ Epstein et al. estimated that a one ton block of 1,1'-thiobis[2-chloroethane] would require 5 years to dissolve.¹⁶⁸ However, lumps of sulfur mustard have apparently persisted in the ocean for decades,²⁻⁴ suggesting that the above values overestimate the rate of dissolution. It has been suggested that the formation of a sulfonium salt-rich layer at the mustard water interface slows the dissolution of mustard.¹⁶⁹ If a cylinder of solid 1,1'-thiobis[2-chloroethane] with surface area of $4 \times 10^4 \text{ cm}^2$ is placed in a 0.15 knot current, the 1,1'-thiobis[2-chloroethane] concentration drops within 1 foot to 0.3 ppm.¹⁷⁰ Thus, in order to perform environmental fate assessments of 1,1'-thiobis[2-chloroethane], both the hydrolysis rate in sea water and dissolution rate must be considered.

The authors have been unable to find an original experimental value for the log of the octanol-water partition coefficient ($\log K_{ow}$). Several estimates are available. One report estimates a value of 1.37 at an unspecified temperature,¹⁶⁹ whereas subsequent compilations report the identical value without indicating that it is estimated.^{11,171} A higher value of 2.41 has also been reported in several data compilations, but this value also appears to be an estimate.¹⁷² The log of the ether-water partition coefficient at an unspecified temperature has been reported as 1.93,¹⁷³ and the xylene:water partition coefficient at 20 °C is reported to be greater than 200 ($\log K > 2.3$).¹⁷⁴ 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 sea water into other matrices should not be a significant fate.

Three values of Henry's Law constant at 25 °C, all derived from solubility and vapor pressure values,^{165,169,171} appear in the literature, giving a mean value of $2.6 \pm 0.6 \times 10^{-5} \text{ atm m}^3/\text{mol}$.

1,1'-Thiobis[2-chloroethane] does not dissociate in water.

Mustard "heel" 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,^{175,176} shown in Figure 2-10.

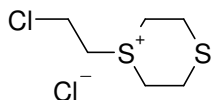


Figure 2-10. S-(2-Chloroethyl)-1,4-Dithianium Chloride Component of Mustard Heel

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.¹⁷⁷

2.5 Lewisite (L)

2-Chlorovinylarsonous dichloride 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, after reviewing Nieuwland's thesis, isolated 2-chlorovinylarsonous dichloride in somewhat purer form, which they called Lewisite.¹⁷⁸ There is some evidence that German scientists also studied Lewisite during World War I.¹⁷⁹ Lewisite is the first of the major chemical warfare agents that was produced for such use before it was described in the open literature.¹⁸⁰ The US produced an estimated 150 tons of Lewisite during World War I, and approximately 20,000 tons of Lewisite was produced during World War II.²² Lewisite was loaded into many American chemical munitions,¹⁸¹ and 11,141 tons of Lewisite are estimated to have been sea disposed in US ocean waters.⁵ There is a moderate body of literature on the constituents of Lewisite, most of it published in the 1920s and late 1940s.

The chemical warfare agent Lewisite is a mixture of *cis*- and *trans*-2-chlorovinylarsonous dichloride, isomers of bis(2-chlorovinyl)arsinous chloride, and isomers of tris(2-chlorovinyl)arsine. The vesicant and the largest component in most Lewisite is 2-chlorovinylarsonous dichloride. Industrially-produced Lewisite is reported to have a strong penetrating geranium odor;¹⁸² pure 2-chlorovinylarsonous dichloride is odorless. 2-Chlorovinylarsonous dichloride has a molecular weight of 207.32 and a molecular formula of C₂H₂AsCl₃. The boiling point for 2-chlorovinylarsonous dichloride at ambient pressure has been reported as 196.6 °C¹⁸³ and ca. 203 °C.³⁰ The melting point for 2-chlorovinylarsonous dichloride has variously been reported as 0.1 °C,¹⁸⁴ -1.2 °C,¹⁸³ and -2.5 °C;¹⁸⁵ differences may be due to different levels of *cis*- and *trans*- isomers in the tested material. Lewisite is expected to remain liquid at substantially lower temperatures because of the presence of the other chlorovinylarsines.

The density of 2-chlorovinylarsonous dichloride is reported as 1.888 g/mL at 20 °C,¹⁸⁶ and 1.8799 g/mL¹⁸⁷ and 1.8793 g/mL at 25 °C;¹⁸³ 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 the following expression over the temperature range of 0 to 60 °C:¹⁸⁷

$$\log p(\text{torr}) = 9.1000 - \frac{2786.6}{T(\text{K})}$$

This study does not report individual data points. Using vapor pressure and reduced boiling point data from several other studies^{183,184,187-190} gives the following expression for the temperature range of 25 to 200 °C:

$$\log p(\text{torr}) = 7.9(\pm 0.5) - \frac{2400(\pm 200)}{T(\text{K})}$$

This expression is plotted with the data in Figure 2-11. The two expressions agree to within a factor of 1.5 or better between 25 and 60 °C, where the two data sets overlap.

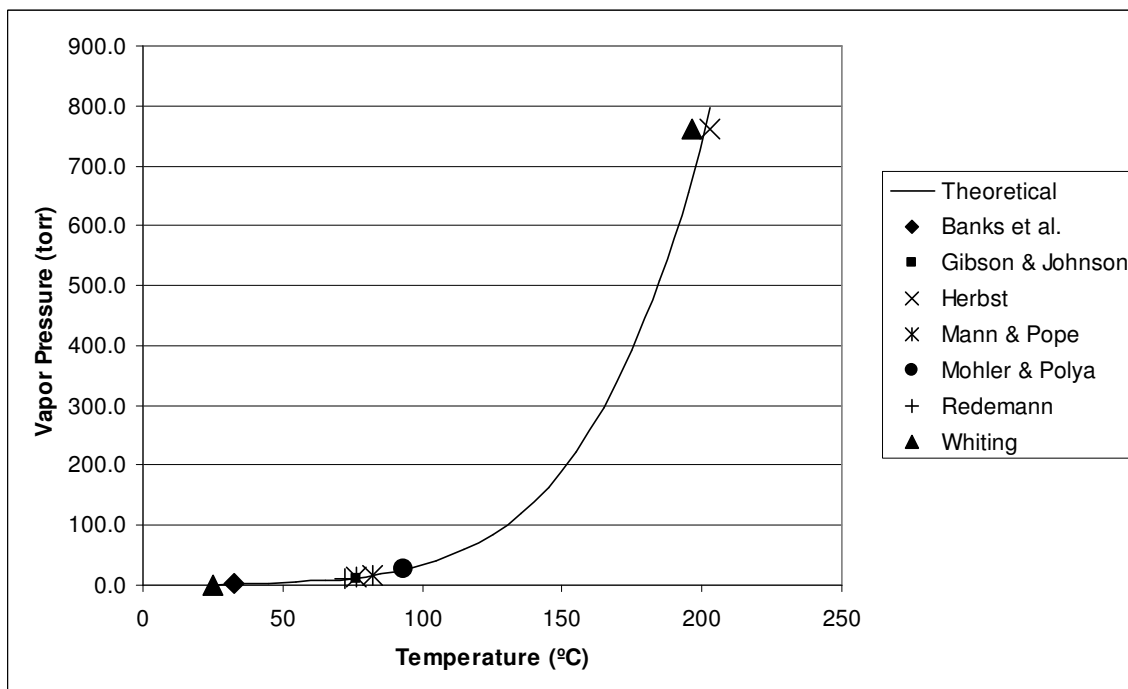


Figure 2-11. Vapor Pressure Values for Lewisite

Note that 2-chlorovinylarsonous dichloride is the most volatile component in Lewisite.

The hydrolysis of 2-chlorovinylarsonous dichloride proceeds as shown in Figure 2-12. The initial 2-chlorovinylarsonous dichloride hydrolysis reaction is rapid relative to formation of the 2-chlorovinylarsonous acid/Lewisite oxide equilibrium mixture.¹⁹¹ The literature indicates that production of two equivalents of chloride occurs within three minutes at 20 °C. At 5 °C, 90% reaction occurs within 2 minutes; the completion of the reaction requires several hours.¹⁹² The titration methodology used in this study does not allow the determination of precise rate constants, because over 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.

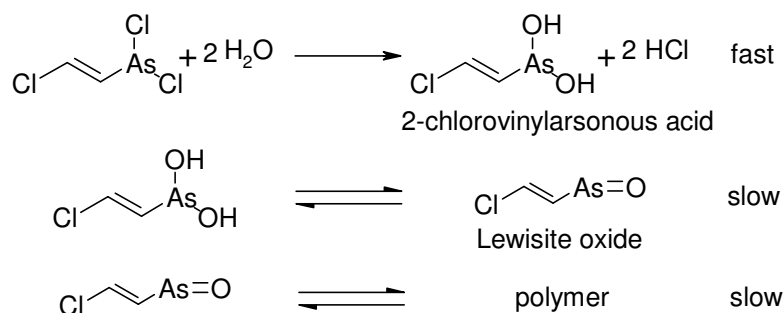


Figure 2-12. Hydrolysis of 2-Chlorovinylarsonous Dichloride

The immediate hydrolysis products 2-chlorovinylarsonous acid and Lewisite oxide are also vesicants.¹⁹¹ 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.¹¹ The vesicant properties of the mixture are reported to remain unchanged after storage for 10 weeks in sea water.¹⁶⁸ The hydrolysis product mixture has a reported log $K_{\text{benzene-water}}$ of 0.15.¹⁹¹

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 hours at pH 8.5, shows a slight amount of product after 24 hours at pH 9.5, and shows substantial amounts of product after 2 hours at pH 10.5. This is roughly consistent with the observation of continued vesicant properties after 10 weeks at 0 °C in sea water. 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,¹⁹³ and several data compilations report values for Henry's Law constant (0.00032 atm m³/mol)¹¹ and log of the partition coefficient (2.56)¹⁹⁴ 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. Lewisite does not dissociate 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.^{195,196} 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 was studied extensively prior to and during World War II, but the compound was first described in the open literature in 1946.¹⁹⁷ 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,²² although it is unclear whether it was ever loaded as a standard fill into any munition.¹⁹⁸ 57 tons of HN1 are estimated to have been disposed in the ocean.¹⁹⁹ This review found only limited information on *N,N*-bis(2-chloroethyl)-*N*-ethylamine, presumably because it is a more recent development than the previous agents, has no significant industrial use, and was a less important chemical warfare agent.

The molecular weight of *N,N*-bis(2-chloroethyl)-*N*-ethylamine is 170.08 and the molecular formula is C₆H₁₃Cl₂N. The melting point of this compound was measured as -34.2 °C.²⁰⁰ 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 torr²⁰¹ and 85.5 °C at 12 torr.²⁰² One study indicates that the *N,N*-bis(2-chloroethyl)-*N*-ethylamine vapor pressure fits the following expression over the temperature range 0-60 °C:²⁰²

$$\log p \text{ (torr)} = 9.01892 - \frac{2868.9}{T(\text{K})}$$

The density of *N,N*-bis(2-chloroethyl)-*N*-ethylamine^{200,202} obeys the following expression over the temperature range of 10 to 35 °C:

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

This expression is plotted with the data in Figure 2-13.

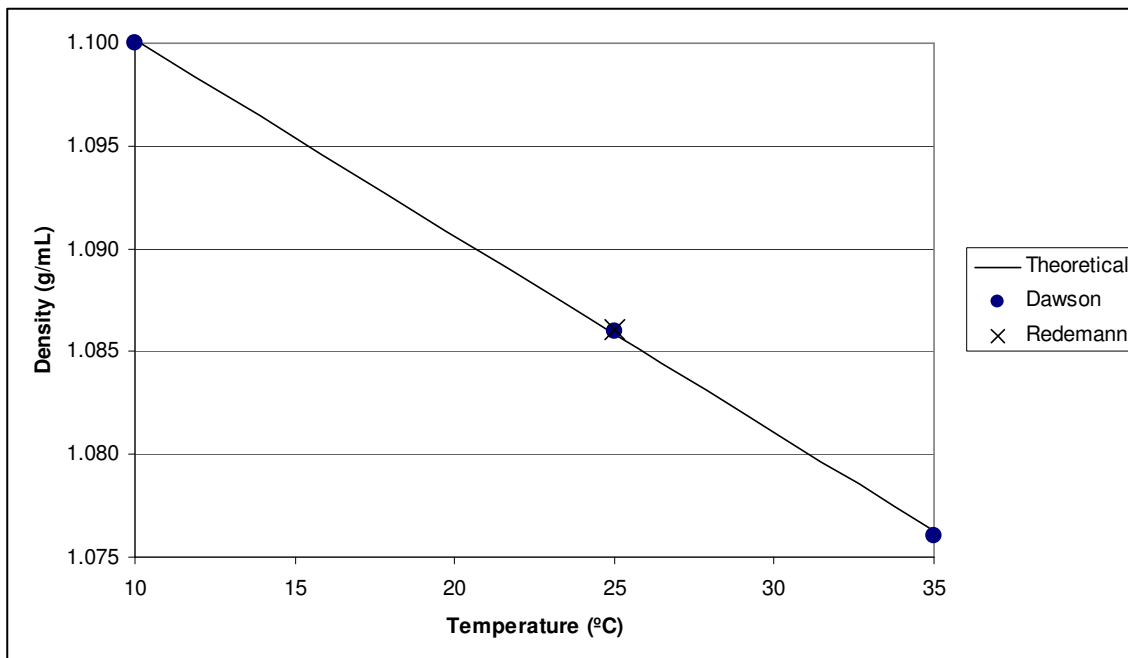


Figure 2-13. Density Values for Nitrogen Mustard

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.²⁰³ Another source gives a value of 6.3 at an unspecified temperature.²⁰¹ These values indicate that the free base will be the predominant species at the pH of sea water. Hydrolysis proceeds as shown in Figure 2-14.

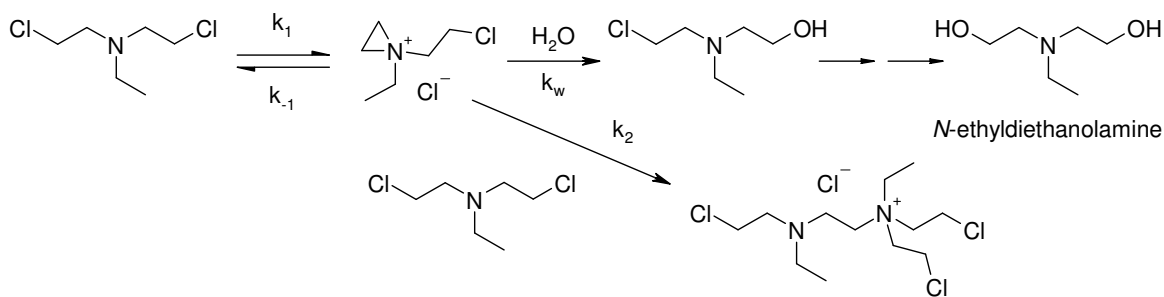


Figure 2-14. Hydrolysis of Nitrogen Mustard

Although the reaction mechanisms are qualitatively similar, the hydrolysis of nitrogen mustard is more complicated than the hydrolysis of sulfur mustard for two reasons:

- Nitrogen mustards can form dimers in aqueous solution
- The ethyleniminium ion is more stable than the ethylenesulfonium ion

A 1% aqueous solution of *N,N*-bis(2-chloroethyl)-*N*-ethylamine at 25 °C forms the ethyleniminium ion with $k_1 = 0.049 \text{ hr}^{-1}$.²⁰⁴ A more detailed examination of the mechanism was conducted in aqueous acetone, giving the rate constants in Table 2-3.²⁰⁵

Table 2-3. 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 hr^{-1}	0.24 hr^{-1}
k_{-1}	$1.5\text{-}7.0 \text{ hr}^{-1}$, with strong negative dependence on ionic strength	Not given
k_2	$0.074\text{-}0.090 \text{ hr}^{-1}$	0.0023 hr^{-1}
k_w	$0.0050\text{-}0.0063 \text{ hr}^{-1}$	$0.0013\text{-}0.0017 \text{ hr}^{-1}$

In the first study, after 70 hours approximately 28% of *N,N*-bis(2-chloroethyl)-*N*-ethylamine remained, with 5% of the ethyleniminium salt, 35% of the *N*-(2-chloroethyl)-*N*-ethylethanolamine, 28% of *N*-ethyldiethanolamine, and 4% of the piperazinium dimer.²⁰⁴ In other studies, 0.34% aqueous *N,N*-bis(2-chloroethyl)-*N*-ethylamine is completely converted to ethyldiethanolamine in 24 hours at pH 8 and 25 °C; at higher agent concentrations quaternary ammonium dimers were also formed.¹⁹⁷ Finally, 0.8% *N,N*-bis(2-chloroethyl)-*N*-ethylamine in water was converted quantitatively to *N*-ethyldiethanolamine in 13 days at room temperature.²⁰⁶ No measurements of the temperature dependence of nitrogen mustard hydrolysis rates were found.

The value of the water solubility is the subject of some confusion. One data compilation reports the water solubility of *N,N*-bis(2-chloroethyl)-*N*-ethylamine as 4 g/L,²⁰⁷ although the authors could not trace the source of that value to its origin. The hydrolysis studies suggest that the solubility may be as high as 0.8% (8 g/L).²⁰⁶ A recent compilation¹¹ 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)²⁰⁴ as applying to HN1. Later in the text, the NH3 solubility of 0.16 g/L²⁰⁸ is reported because Franke states that “the ethyl compound behaves approximately like” HN3. A Henry’s law constant of $3.5 \times 10^{-4} \text{ atm}\cdot\text{m}^3/\text{mole}$ is given in some data compilations,²⁰⁹ which indicate it

has been calculated from 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-m³/mole. 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.²⁰⁹

One final qualitative observation is that *N,N*-bis(2-chloroethyl)-*N*-ethylamine is unstable, forming the *N,N'*-diethyl-*N,N'*-di(2-chloroethyl)piperazinium dichloride dimer at room temperature.²⁰¹ Although no rates are available, it is likely that a significant amount of nitrogen mustard in munitions, most if not all of which were sea disposed by 1958,¹⁹⁹ 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 (ethyl dimethylamidocyanidophosphate), the first organophosphate nerve agent, was initially prepared on 23 December 1936 in Dr. Gerhard Schrader's laboratory at I. G. Farbenindustrie in Leverkusen. 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 1951.²¹⁰ 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.²¹¹ Tabun was later loaded into some American chemical munitions.²¹² One ton of Tabun is documented as being disposed in US 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;²¹³ weapons grade material is reported in many compilations to have a fruity odor.²⁰⁸ It has a molecular formula of C₅H₁₁N₂O₂P and a formula weight of 162.13. The boiling point at ambient pressure is reported as 246 °C,²¹⁴ and the melting point is reported to be -50 °C.²¹⁵ Data for the boiling point at reduced pressure and for vapor pressure^{213,214-217} can be fit to the following expression over the range of 25 to 246 °C:

$$\log p \text{ (torr)} = 8.6 (\pm 0.2) - \frac{2900 (\pm 60)}{T \text{ (K)}}$$

This expression is plotted with the data in Figure 2-15 (the ambient boiling point is not shown in the figure).

The density from several studies over the range of 9.8 to 35 °C²¹⁴⁻²¹⁶ can be fit to the following expression:

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

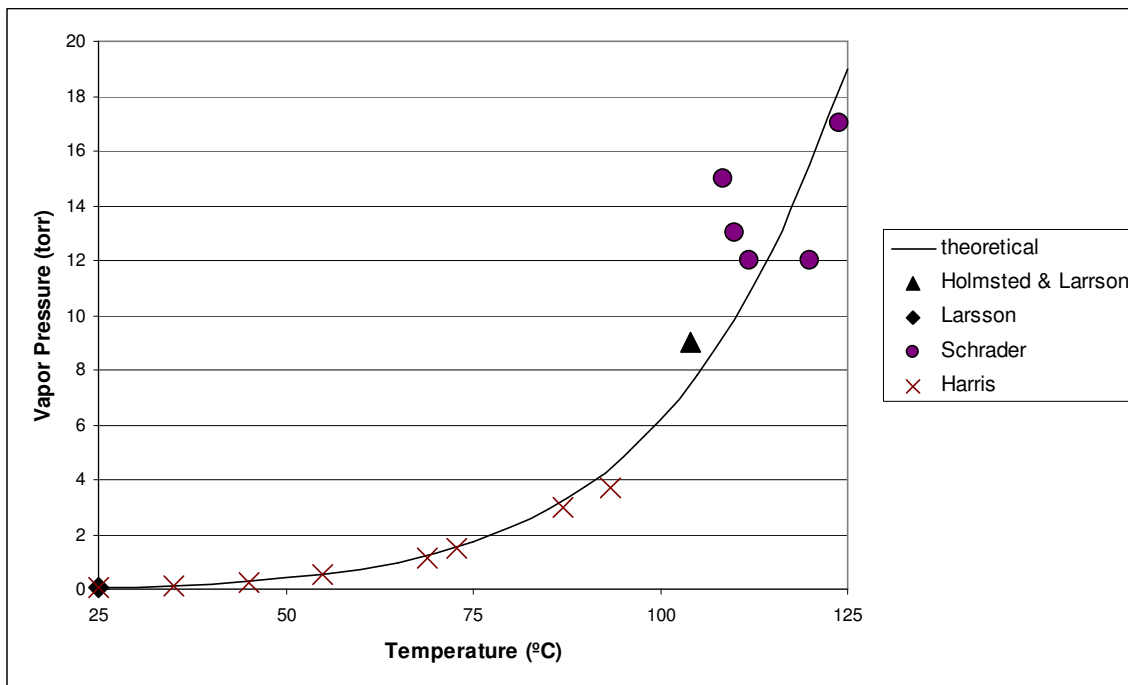


Figure 2-15. Vapor Pressure Values for Tabun

This expression is plotted with the data in Figure 2-16.

At $\text{pH} > 7$, Tabun is hydrolyzed by hydroxide anion, producing cyanide anion and monoethyl dimethylphosphoramidate as shown in Figure 2-17.

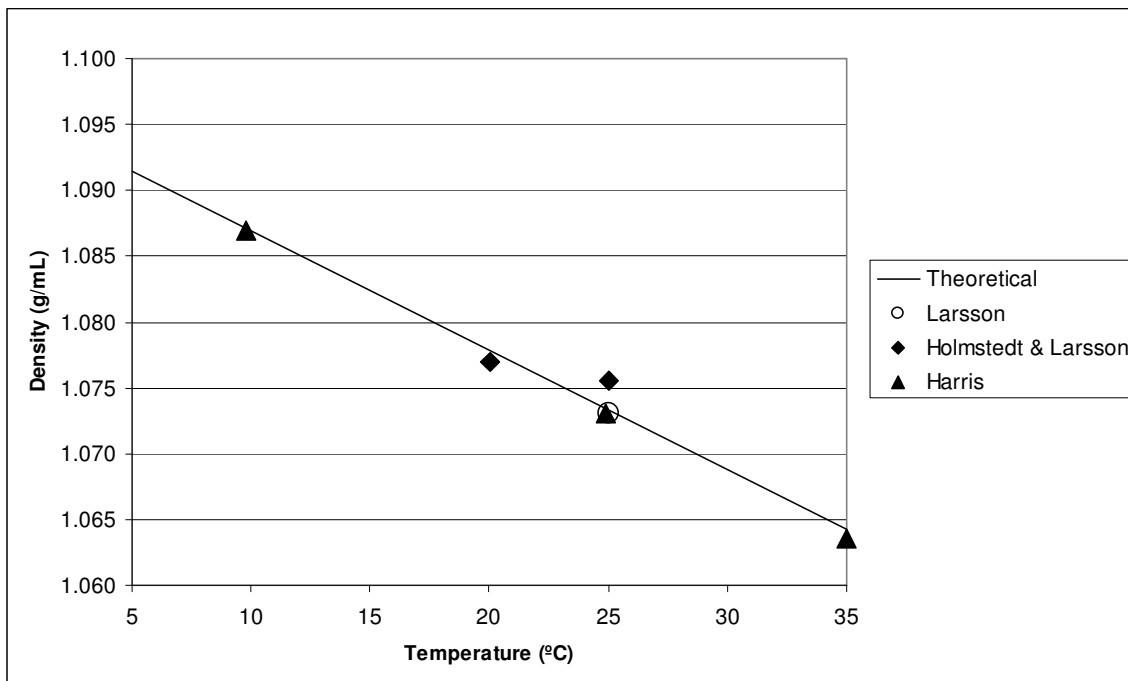


Figure 2-16. Density Values for Tabun

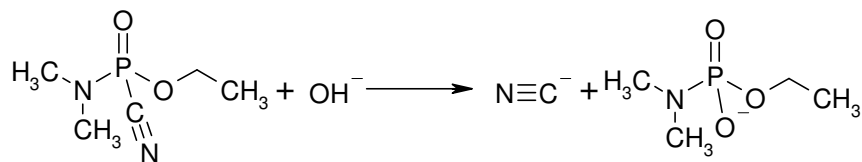


Figure 2-17. Hydrolysis of Tabun

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 towards hydrolysis under basic conditions,²¹⁸ whereas a previous investigation of ethyl diethylphosphoramidate and homologues indicated that the N-P bond was the more reactive.²¹⁹

Rate constants for the hydrolysis of Tabun has been measured at a variety of pH and temperature values; these measurements are given in Table 2-4 along with references to the experimental literature. From these data, an activation energy, E_a , of 10.1 kcal mole⁻¹ was calculated for the basic hydrolysis of Tabun.²²⁰

Table 2-4. Tabun Hydrolysis Rate Constants

T (°C)	pH	k_{obsd} (hr ⁻¹)	Reference
25	5.00	0.39	218
20	5.10	0.07	210
20	7.20	0.17	210
20	8.60	0.28	210
25	8.50	0.26	220
25	8.75	0.33	220
25	9.00	0.50	220
25	9.00	0.42	221
35	9.00	1.44	220
25	9.50	1.26	220
35	9.50	4.21	220

A group of US Army researchers has also measured the half-life of GA in sea water at several different temperatures;¹⁶⁸ these values are given along with the corresponding rate constants in Table 2-5.

Table 2-5. Tabun Hydrolysis Half-lives in Sea Water

T (°C)	sea water $t_{1/2}$ (min)	k_{obsd} , calculated (hr ⁻¹)
15	475	0.088
20	267	0.156
25	175	0.238

The calculated rate constants are roughly consistent with comparable values in Table 2-4, suggesting that the effects of the ionic strength and composition of sea water on the hydrolysis rate is minor.

The water solubility of Tabun is 98 g/L at 0 °C and 72 g/L at 20 °C.^{207,222} Several recent compilations^{11,223} 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 m³/mol at 25 °C,¹¹ which is calculated from the vapor pressure²¹⁶ and the erroneous water solubility. One can calculate a

Henry's Law Constant of 1.40×10^{-7} atm m³/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 measured as 0.384 ± 0.033 at room temperature.²²⁴

2.8 Sarin (GB)

In 1938, a second potent organophosphate nerve agent named Sarin (isopropyl methylphosphonofluoridate, GB) was discovered. Sarin was produced in pilot-scale quantities by the Germans just before the end of World War II,²¹¹ and was later a mainstay of Soviet and American chemical arsenals. Sarin has been loaded into a wide variety of American chemical munitions,²²⁵ and an estimated 239 tons of Sarin were disposed in US waters.⁵ There is a moderate amount of data on Sarin available in the open literature.

Isopropyl methylphosphonofluoridate is an odorless liquid under ambient conditions, and has a molecular formula of C₄H₁₀FO₂P and a formula weight of 140.10. The boiling point at ambient pressure is reported in various data compilations as 147 °C²²⁶ and 158 °C,¹¹ and the melting point is reported to be -56.3 °C.²²⁷ One study reports that the vapor pressure of isopropyl methylphosphonofluoridate obeys the following expression over the temperature range of 0 to 60 °C:²²⁸

$$\log p(\text{torr}) = 9.8990 - \frac{2850.9}{T(\text{K})}$$

This study does not report individual data points. Using vapor pressure and reduced boiling point data from several other studies^{226,228-234} gives the following expression for the temperature range of 0 to 147 °C:

$$\log p(\text{torr}) = 9.4 (\pm 0.1) - \frac{2700(\pm 40)}{T(\text{K})}$$

This expression is plotted with the data in Figure 2-18 (the ambient boiling point is not shown in the figure). The two expressions agree to within 10 percent between 0 and 60 °C, where the two data sets overlap.

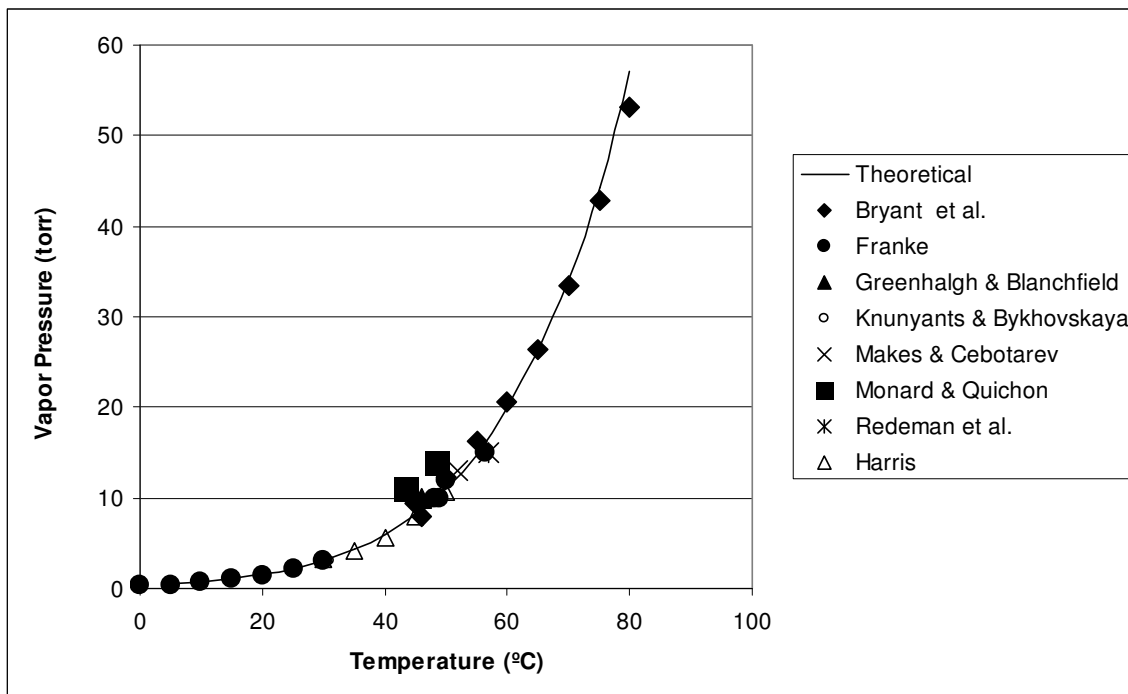


Figure 2-18. Vapor Pressure Values for Sarin

Values for density from multiple studies^{226,228-230,233-235} over the range of 10 to 69 °C can be fit to the following expression:

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

This expression is plotted with the data in Figure 2-19.

The water solubility of isopropyl methylphosphonofluoridate increases as temperature decreases. GB is miscible with water in all proportions at both 0.0 °C and 25 °C.²³⁶ One compilation reports a Henry's Law constant of 5.4×10^{-7} atm m³/mole at 25 °C;¹¹ 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).²³⁶

The log K_{ow} value for isopropyl methylphosphonofluoridate was measured as 0.299 ± 0.016 at room temperature.²²⁴ Partition coefficients for isopropyl methylphosphonofluoridate between water and other organic solvents have 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.²³⁷

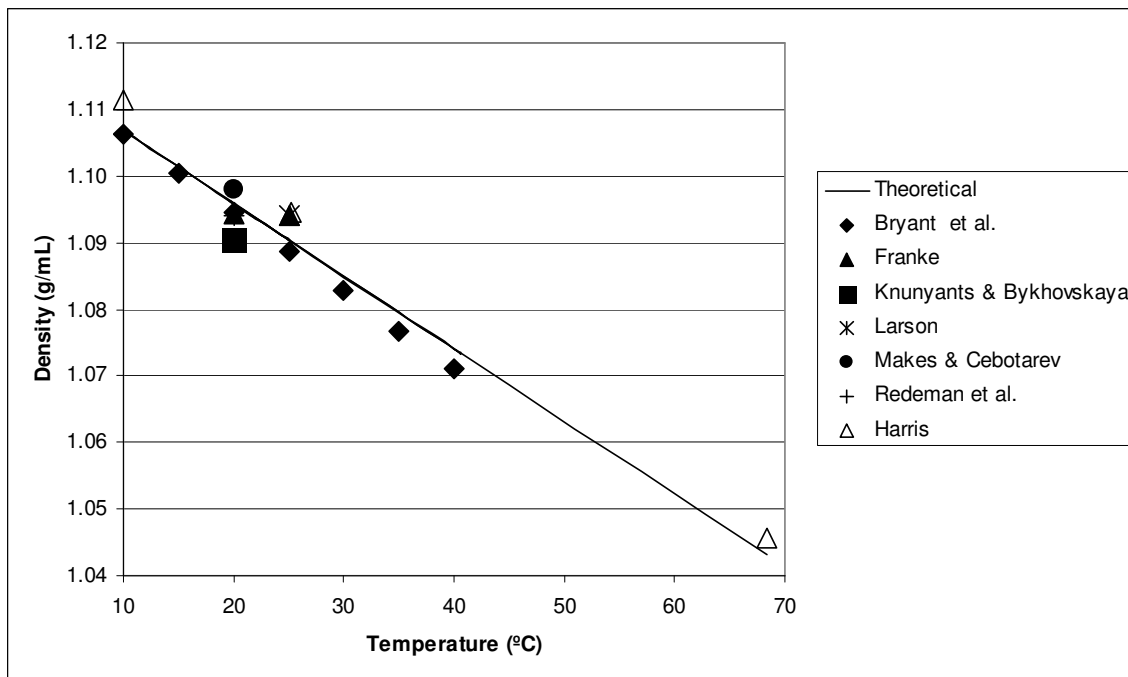


Figure 2-19. Density Values for Sarin

Isopropyl methylphosphonofluoridate undergoes hydrolysis by acidic, neutral, and basic mechanisms, all of which give fluoride and isopropyl methylphosphonate (IMPA) as the initial products. IMPA is slowly converted to methylphosphonic acid (MPA) and isopropyl alcohol in the environment. The neutral reaction is shown in Figure 2-20.

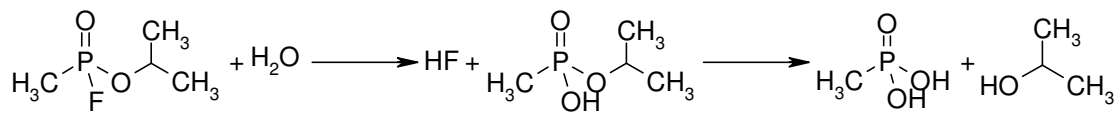


Figure 2-20. Hydrolysis of isopropyl methylphosphonate.

Rate constants for isopropyl methylphosphonofluoridate hydrolysis rates are given in Table 2-6. E_a values of $10.6 \text{ kcal mole}^{-1}$ ²³⁸ and $9.1 \text{ kcal mole}^{-1}$ ²³⁵ were calculated from the rate constants for basic hydrolysis.

Table 2-6. Isopropyl Methylphosphonofluoridate Hydrolysis Rate Constants*

T (°C)	k_{OH} (L mole ⁻¹ sec ⁻¹)	k_w (sec ⁻¹)	Reference
0.3	4.67	1.7×10^{-5}	238
25	23.7	5×10^{-5}	238
25	25.80	NA	235
35	42.40	NA	235
42.5	63.7	5×10^{-5}	238

*NA= not available

Several other studies have presented observed rate constants for isopropyl methylphosphonofluoridate hydrolysis at various pH values at room temperature.^{221,239,240} These studies are generally consistent with the values in Table 2-6.

In sea water, 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 the following expression:²⁴¹

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

Epstein reports that Ca⁺² and Mg⁺² in sea water significantly catalyze isopropyl methylphosphonofluoridate hydrolysis. At 0.2 °C in sea water, the measured half-life of GB is 15.9 hours,^{167,241} corresponding to a rate constant for hydrolysis of 7.3×10^{-4} sec⁻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 mole/L (1.4 g/L), the quantity of acidic reaction products will be sufficient to overwhelm the buffering capacity of sea water,²⁴¹ 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 sea water, the carbodiimide should be converted to the analogous urea by hydrolysis.

2.9 VX

The use of VX as a chemical warfare agent resulted from work in 1952 and 1953 by several groups working independently who discovered the high toxicity of organophosphate esters of substituted 2-aminoethanethiols.^{242,243} The British chemical weapons laboratory at Porton began investigating this class of compounds, and notified the US chemical weapons

laboratory at Edgewood, which began a systematic investigation of the entire class. In 1958, the US selected VX (*S*-(2-[diisopropylamino]ethyl)-*O*-ethyl methylphosphonothioate) for manufacture. Construction of the production plant began in 1959; production ran from 1961 through 1968. US government classified the chemical structure of VX as secret until the early 1970s.²⁴⁴ VX has been loaded into several American chemical munitions,²⁴⁵ and an estimated 124 tons of VX was disposed in US coastal waters.⁵ This review found only limited information on VX, presumably because the chemical identity of VX was classified for so long and experiments with VX should only be conducted by specially trained personnel in a limited number of laboratories.

VX is an odorless liquid under ambient conditions, and has a molecular formula of C₁₁H₂₆NO₂PS and a molecular weight of 267.37. Many secondary sources list the boiling point of VX at ambient pressure as 298 °C with decomposition.¹¹ However, it appears that the ambient pressure boiling point is not experimental, but was calculated based on the extrapolation of vapor pressure measurement.^{246,247} A good melting point of VX has never been obtained; the value is below -60 °C.^{248,249} Values for density²⁴⁸ over the range of 25 to 50 °C can be fit to the following expression:

$$D(\text{g/mL}) = 1.029(\pm 0.003) - 0.00082(\pm 0.00007)T(^{\circ}\text{C})$$

This expression is plotted with the data in Figure 2-21.

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 °C²⁵⁰ and results in the following expression:

$$\log p(\text{torr}) = 13.9(\pm 0.7) - \frac{5200(\pm 200)}{T(\text{K})}$$

The second study covers the temperature range between -12 and 103 °C²⁵¹ and provides the following expression, although individual data points are not recorded:

$$\log p(\text{torr}) = 10.562 - \frac{4068}{T(\text{K})}$$

The data points in Buchanan et al.²⁴⁷ 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.

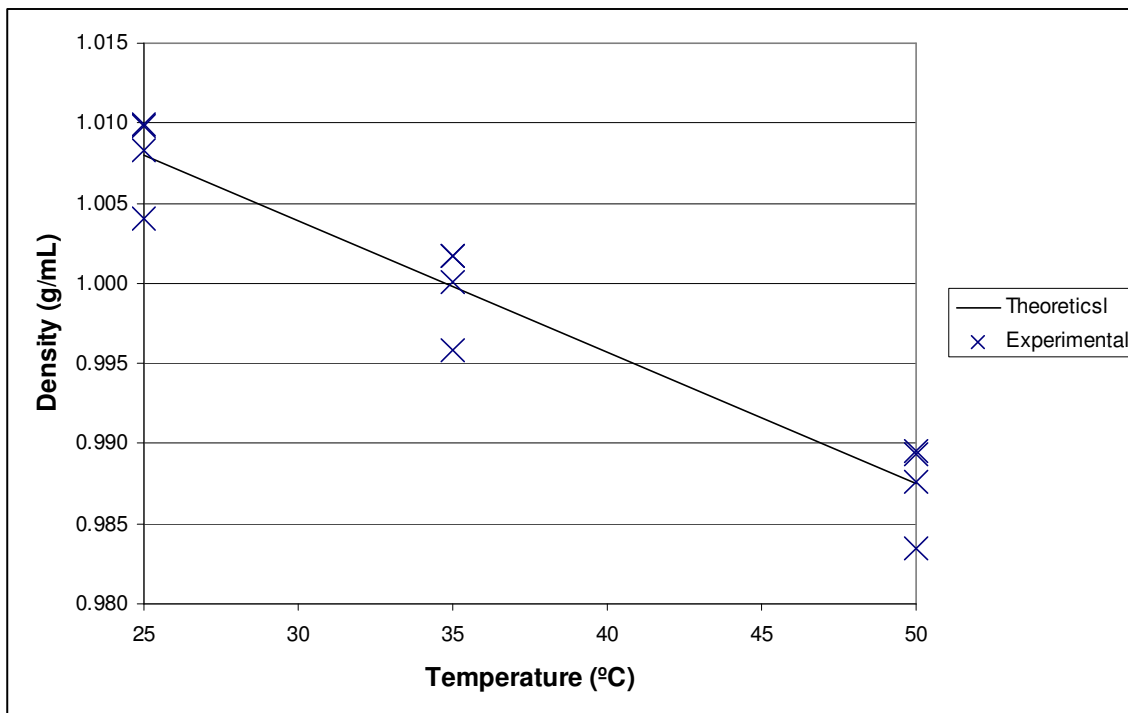


Figure 2-21. Density Values for VX

The negative log of the dissociation constant (pK_a) of VX is variously given as 8.6²⁵² and 9.12 at 25 °C.¹⁶⁸ This indicates that the amino group of VX will be predominantly protonated at the pH of sea water. VX has a lower consolute temperature of 9.4 °C in pure water;²⁴⁸ this is often reported as miscibility.²⁵³ At higher temperatures, VX is soluble in water to 75 g/L at 15 °C and 30 g/L at 25 °C, whereas water is soluble in VX to 220 g/L VX at 15 °C and 160 g/L at 25 °C.²⁴⁸ The solubility of VX in water decreases significantly as pH increases.²⁵⁴ A recent compilation of data lists the Henry's Law constant as 3.5×10^{-9} atm m³/mole at pH 6;¹¹ the solubility value and the vapor pressure at 25 °C using the expression above give a similar value of 2.6×10^{-9} atm m³/mole. The log K_{ow} of VX was measured as 0.675 ± 0.070 at room temperature,²²⁴ although a significantly different estimated value of 2.09 is given in some data compilations.¹¹

Hydrolysis of VX, along with other aspects of detoxification, was recently reviewed.²⁵⁵ A summary of key hydrolysis pathways is shown in Figure 2-22.

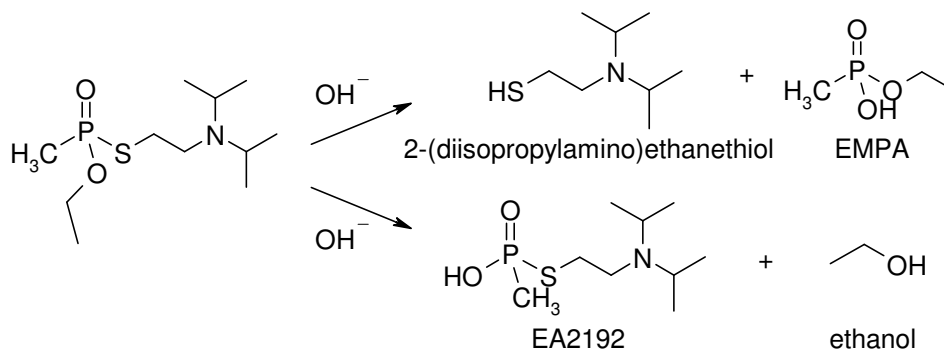


Figure 2-22. Hydrolysis of VX.

One reference gives hydrolysis rate constants for VX as $8.4 \times 10^{-3} \text{ hr}^{-1}$ ($[\text{VX}]_0 = 2$ percent) and $12.1 \times 10^{-3} \text{ hr}^{-1}$ ($[\text{VX}]_0 = 0.5$ percent) in distilled water at 21°C .²⁵⁶ Rate constants of 0.130 hr^{-1} at pH 8 and 0.281 hr^{-1} at pH 9 have also been measured at 55.6°C .²⁵² One reference fits the rate constants for the hydrolysis of VX at 25°C as well as rate constants for the diethylamino- analog to the equation:²⁵²

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

Cu^{+2} and Ca^{+2} are known to catalyze the hydrolysis of both methylphosphonofluoridates (see above) and of thiophosphoric esters.²⁵⁷ However, there is a report that Cu^{+2} does not catalyze VX hydrolysis to any significant degree,²⁵⁸ and a recent review notes that “no transition metals or complexes have yet been reported to catalyze the hydrolysis of VX.”²⁵⁵ Rate constants have been measured at pH 7.7 in a synthetic sea water solution at several temperatures between 15°C and 45°C ; $k_{\text{obs}} = 4 \times 10^{-3} \text{ hr}^{-1}$ at 25°C ; this corresponds to a half life of 170 hr. The rate constant at pH 7.7 as a function of temperature obeyed the following expression:¹⁶⁷

$$\log k_{\text{obs}} (\text{hr}^{-1}) = 24.286 - \frac{7954}{T (\text{K})}$$

Extrapolating to 2°C , this expression gives a rate constant of $k_{\text{obs}} = 2 \times 10^{-5} \text{ hr}^{-1}$, corresponding to a half-life of over 3 yr. 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 and its hydrolysis products.

As shown in Figure 2-22, the hydrolysis of VX can follow two pathways. One pathway produces 2-(diisopropylamino)ethanethiol and the ethyl ester of methylphosphonic acid (EMPA), which are significantly lower in toxicity than the starting VX.¹¹ However, a second pathway produces ethanol and (*S*-[2-[diisopropylamino]ethyl]-methylphosphonothiolate), also known as EA2192. EA2192 is approximately as toxic as the starting VX.¹¹ 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 EA2192.²⁵² Under acidic conditions, EA2192 hydrolyzes faster than VX,²⁵⁹ and under strongly basic conditions, EA2192 undergoes hydrolysis over roughly four orders of magnitude more slowly than VX,²⁶⁰ but the authors cannot locate any data for the rate of hydrolysis of EA2192 at the pH of sea water. 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 sea water, 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, the reaction of EA2192 is expected under all conditions to be slower than the reaction of VX,²⁶⁰ and so it is likely that EA2192 will persist in sea water 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.^{11,170} 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 sea water as a zwitterion with a molecular weight of 239.32, and 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 the hydrolysis of VX in sea water 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.

Section 3

Ecotoxicity Parameters

Munro et al.¹¹ have recently reviewed the literature on the toxicity to aquatic organisms for the agents and breakdown products in this current study except phosgene and hydrogen cyanide. The current study has identified several additional studies published since that review or not covered in that review. This additional information is presented below.

3.1 Phosgene

Phosgene was not included in the review by Munro et al. As part of the current study, 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 of chloride ions and carbon dioxide would not be toxic at the concentrations that would result in the marine environment from the breakdown of phosgene released from disposed munitions.

3.2 Cyanogen Chloride

Munro et al. cite three sources of data on cyanogen chloride, which were for freshwater fish and invertebrates.²⁶¹⁻²⁶³ They found no information on the breakdown product cyanic acid. In this 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; median lethal concentration (LC₅₀) values reviewed by Munro et al. were 120 to 150 µg/L.¹¹

3.3 Hydrogen Cyanide

The highly toxic effects of hydrogen cyanide have been extensively studied because of its use in the mining industry and in other industrial processes.²⁶⁴⁻²⁶⁷ The U.S. EPA Ecotox data base lists 24 published papers about the effects on freshwater invertebrates and fish.

At seawater pH of about 8.3, hydrogen cyanide will be present mostly as the unionized acid, which is very toxic to freshwater organisms. LC₅₀ values reported in the Ecotox data base range from 10 to several hundred µg/L. Lower water temperatures increased toxicity in freshwater fish.

3.4 Sulfur Mustard

Munro et al. cites two sources of data on sulfur mustard.^{223, 268} The current study identified several other studies. Murabi²⁶⁹ reported an acute toxicity test of sulfur mustard to

the water flea (*Daphnia magna*). Organisms were exposed to mustard at 0.3 mg/L and 0.5 mg/L at 19 °C for 24, 48, and 72 hours. Greater mustard concentrations were not used because of the hazard to the researchers. There was no mortality in any of the tests. These results are consistent with data from another study,²⁶⁸ which report threshold effect concentrations for five freshwater fish species, crayfish, and the bullfrog of 2-10 ppm. However, another test²⁷⁰ by another researcher (reported in Murabi) found that 33.3 percent of *Daphnia sp.* died after 72 hours of exposure to 0.033 mg/L of mustard in fresh water.

Murabi²⁶⁹ also provides data from several references on the effect of mustard on species of saltwater phytoplankton, crustaceans, mollusks, and fish.^{271,272} 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 reviewed by Munro et al.

Munro et al. reported on one study of the breakdown product thiodiglycol.²⁷³ The Organization for Economic Cooperation and Development (OECD) has published an assessment of thiodiglycol.²⁷⁴ Data are presented in Table 3-1 for toxicity to aquatic species from unpublished studies conducted by BASF AG.²⁷⁵⁻²⁷⁹ 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 Munro et al.

Table 3-1. Acute Toxicity of Thiodiglycol to Aquatic Organisms

Organism	Effect	Notes	Ref.
<i>Leuciscus idus</i> (fish)	LC ₅₀ (96 h), 10,000 mg/L	Static test. No mortality at concentrations up to 10,000 mg/L.	275
<i>Daphnia magna</i> (water flea)	EC ₅₀ (48 h),* 500 mg/L	No immobilization at 500 mg/L.	276
<i>Desmodesmus subspicatus</i> (algae)	EC _{10,50,90} (72 h),* 500 mg/L	Effect on growth.	277
Activated sludge	EC ₂₀ (30 min),* 1000 mg/L	Inhibition of oxygen consumption rate	278
<i>Pseudomonas putida</i> (microorganism)	EC ₂₀ (17 h),* 10,000 mg/L	Inhibition of cell multiplication	279

*EC_{nn} = Effective concentration affecting nn% of the test population

One group measured the inhibition of methane production of an anaerobic sludge blanket reactor for thiodiglycol concentrations of 0.5 to 10.0 g/L. An EC₅₀ (24 h) was estimated to be 4.2 g/L.²⁸⁰ This is consistent with the values reported in Table 3-1.

Another study determined an acute 24 hour EC₅₀ value for 1,4-dithiane, a substance present as an impurity in mustard, for the water flea *Daphnia magna* as 23.2 mg/L.²⁸¹ 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.¹¹

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. No data were found on the toxicity of *S*-(2-chloroethyl)-1,4-dithianium chloride to aquatic organisms.

3.5 Lewisite

Munro cite three sources of data on Lewisite and its hydrolysis products.^{268,282,283} Test organisms were freshwater species of fish, tadpole, phytoplankton, and aquatic plants. 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.²⁸⁴ 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,²⁸⁵ 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. Some recent review articles are provided in the references.²⁸⁶⁻²⁹⁸

3.6 Nitrogen Mustard (HN1)

Munro et al. cite one source of data on nitrogen mustard,²⁶⁸ 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. cite an LC₅₀ 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.²⁹⁹

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. As discussed above, it is likely that most or all 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 LD₅₀ in mice for the close analogue (methyl vs. ethyl) *N,N'*-dimethyl-*N,N'*-di(2-chloroethyl)piperazinium dichloride.³⁰⁰ The LD₅₀ 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.

3.7 Tabun

Munro et al. cite one source of data on Tabun,³⁰¹ which found high toxicity to several species of freshwater fish (LC₅₀ of 0.7 to 1.3 mg/L). One source of data on the breakdown product dimethylamine was cited,³⁰² 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.

3.8 Sarin

Munro et al. cite one source of data on Sarin,³⁰¹ which found high toxicity (LC₅₀ 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. LC₅₀ 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 3-2.³⁰³ Test water temperature was 24 °C for eggs and 23 °C for fry. The LC₅₀ 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 LC₅₀ 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.¹¹ Munro et al. did not report any data for IMPA.

Table 3-2. Median Lethal Concentration (LC₅₀) of IMPA

Organism	LC ₅₀ (mg/L)	Time (hours)
Golden shiner eggs	66.6	72
Golden shiner 15-dph fry	93.9	96
Channel catfish eggs	167.5	168
Channel catfish 15-dph fry	144.1	96

dph = day posthatch

MPA is produced very slowly as a breakdown product of IMPA. Munro et al. cited one study of MPA.³⁰⁴ 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 to 10,000 mg/L.²⁸⁰ The results are consistent with data presented in Munro et al. for LC₅₀ and EC₅₀ values for freshwater algae, protozoan communities, invertebrates, and fish.

Munro et al. cited four studies of the Sarin impurity DIMP on toxicity to freshwater aquatic organisms.³⁰⁵⁻³⁰⁸ The bluegill sunfish was reported as the most sensitive species tested with an LC₅₀ 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.³⁰⁹

3.9 VX

Munro et al. cite one study for the toxicity of VX to the salt water species blue crab, white perch, and striped bass.³¹⁰ The concentration needed to kill 50 percent of the fish tested was 0.1 ppm or less. The concentration needed to kill 50 percent 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,¹¹ EA2192 may be approximately as toxic to marine organisms as VX. Ethanol would not be toxic at concentrations likely to occur in the marine environment if VX is released from disposed munitions.

Section 4

Data Summary

The adequacy of the reviewed data for conducting fate and transport evaluations for chemical warfare agents in the marine environment is summarized in Table 4-1. Each type of data is rated as fully adequate, adequate under most circumstances, or adequate under some circumstances. Data that do not apply or do not significantly affect the evaluation are indicated as not required.

Table 4-1. Summary of Data Adequacy for Conducting Fate and Transport Evaluations*

Agent	Boiling Point	Melting Point	Density	Vapor Pressure	Water Solubility	Henry's Law Constant	Partition Coefficients	Dissociation Constants	Hydrolysis Rate Constant(s)	Ecotoxicity
phosgene	●	●	●	●	■	●	■	■	●	■
cyanogen chloride	●	●	●	●	●	●	●	■	●	●
hydrogen cyanide	●	●	●	●	●	●	●	●	■	●
sulfur mustard	●	●	●	●	●	●	◆	■	●	○
Lewisite	●	●	●	●	●	■	■	■	◆	●
nitrogen, mustard (HN1)	●	●	◆	●	●	◆	○	●	○	○
Tabun	●	●	●	●	●	●	●	■	●	●
Sarin	●	●	●	●	●	●	●	■	●	●
VX	●	●	●	●	●	●	●	●	●	●

*● = fully adequate, ◆ = adequate under most circumstances, ○ = adequate under some circumstances, ■ = not required

Section 5

Data Gap Analysis

One result of this review has been to identify areas where additional data would be desirable. The authors have prioritized the data gaps identified in this study based on 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. 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:

- Nitrogen mustard – data on the temperature dependence of the rate of hydrolysis of *N,N*-bis(2-chloroethyl)-*N*-ethylamine in sea water and on the partition coefficient, and ecotoxicity of the *N,N'*-diethyl-*N,N'*-di(2-chloroethyl)piperazinium dichloride dimer.
- Sulfur mustard – Ecotoxicity of the mustard heel material (or the primary constituent, *S*-(2-chloroethyl)-1,4-dithianium chloride)
- VX – bioconcentration measured at pH 8 (VX could 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 significantly increase the uncertainty of the result.

Other data gaps that appear to be less critical to fate and transport assessments include the following:

- 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.
- 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.
- Lewisite – data on hydrolysis and oxidation rates of intermediates such as chlorovinylarsonous acid are approximate at best, but there is extensive data on arsenic, the ultimate environmental product.

- 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 significant contribution for environmental fate assessments.

In addition to these specific data gaps, the authors have 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 sea water at relevant temperature. However, no measurements appear to be available for hydrolysis rates at the pressures experienced in deep water. 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 8,000 ft depth.³¹¹ This suggests that pressure effects are unlikely to significantly affect environmental fate assessments, although determination of activation volumes for sulfur mustard and one nerve agent to confirm that agent hydrolysis reactions are within this modest range could be useful.

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.

Section 6

Conclusions

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. 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 many assessments.^{312,313} 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 have identified several interesting areas for potential research, such research is not required for current government programs

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