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EASP 1200-12

SUMMARY REPORT ON A DATA BASE FOR PREDICTING CONSEQUENCES OF CHEMICAL DISPOSAL OPERATIONS

by

Joseph Epstein
David H. Rosenblatt
Physical Research Division
Chemical Laboratory
Edgewood Arsenal, MD

and

A. Gallacio
W. F. McTeague
Pitman-Dunn Laboratories
Frankford Arsenal, PA

January 1973

U S ARMY MUNITIONS COMMAND

DEPARTMENT OF THE ARMY
HEADQUARTERS, EDGEWOOD ARSENAL
EDGEWOOD ARSENAL, MARYLAND 21010

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DEPARTMENT OF THE ARMY
HEADQUARTERS, EDGEWOOD ARSENAL
EDGEWOOD ARSENAL, MARYLAND 21010

FOREWORD

The objective of this report is to provide data from which predictions of the hazards from a variety of past disposals of toxic chemical agents may be based.

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DIGEST

The objective of this report is to provide data from which predictions of the hazards from a variety of past disposals of toxic chemical agents may be based.

Literature searches were carried out (1) on the behavior of chemical agents in soil and (2) on the effects of corrosion on the stability of various containers when buried or when dumped in the ocean in order to obtain information needed for reasonably approximate estimation of residual hazards. Where sufficient information on factors affecting the hydrolysis rates of chemical agents in fresh water or in seawater had not been previously obtained, laboratory investigations were conducted on hydrolysis rates and on the toxicity of the hydrolysis products. Estimates are given of lengths of time the various chemical agents will remain hazardous after disposal by methods used in the past.

CONTENTS

SUMMARY REPORT ON A DATA BASE FOR PREDICTING CONSEQUENCES OF CHEMICAL DISPOSAL OPERATIONS

I. OBJECTIVE.

The objective of the present studies was to provide data on which predictions of the hazards from a variety of past toxic chemical disposals might be based.

II. SCOPE.

The scope of investigations needed to generate essential information is, of necessity, general. The behavior of chemical agents in soils is unpredictable because of several variables such as the gross characteristics of terrain and subsoil, the weather, the nature and distribution of agent, and the water content and type of soil. Because of the unpredictable behavior of chemicals in soils, a literature search rather than an experimental study was conducted. Experimental studies on corrosion would likewise have been difficult, and certainly far too time-consuming to be completed in short order. Thus, a literature search, along with an appropriate interpretation of information, was all that was needed for reasonably approximate answers. For those agents of particular interest, laboratory investigations were centered on hydrolysis and toxicity. The following discussion treats those agents that were initially considered important and explains why the experimental study was limited to only four of those agents (GA, H, HN-1, and L).

1. GA (Cyanodimethylamine ethoxyphosphine oxide).

This was the first German agent uncovered by US troops in 1945 when munitions charged with GA were captured. A total of 10,000 to 12,000 tons of GA were produced by the Germans; both 100-mm shell and 250-kg bombs were charged with this agent. German GA munitions were disposed of at sea by several nations. The United States has never made this agent in bulk nor filled munitions with it. There is unclassified information in the literature on hydrolysis rates and products of GA in fresh water, but there is no mention of hydrolysis rates and products of GA in seawater. The United States has never disposed of the agent by burial; and no information is available as to whether or not other nations have disposed of GA in this way. Most of the munitions captured by the United States were used in field tests in 1951 to determine decontamination procedures and downwind safety distances. Small amounts of GA were also distributed for laboratory studies on detection and decontamination methods and similar investigations. The United States must maintain an interest in the defensive aspects (that is, in decontamination and detection of, and protection against) of GA.

2. GB (Isopropyl methylphosphonofluoridate).

This is a United States agent. There is adequate information on hydrolysis rates in fresh water and in seawater and on the toxicity of the end products.

3. GD (Pinacolyl methylphosphonofluoridate).

GD has been an experimental agent in the United States; although it was made in Germany during World War II, no German munitions containing GD were ever found. The United States never made GD in bulk nor filled munitions with it. Thus, the United States never dumped it in the ocean or on the land. No information on its disposal by other nations is available.

4. VX (β-Diisopropylaminoethylmercapto-O-ethylmethylphosphonothioate).

This is a United States agent; therefore, sufficient data on hydrolysis in seawater and in fresh water, as well as data on the toxicity of the end products, are on hand.

5. H [Bis-(β-chloroethyl)sulfide].

This is a standard agent in many countries, dating back to World War I. Information on fresh-water hydrolysis rates and end products are well known, but seawater information is scanty. Two types of mustard have been synthesized:

a. HD, a pure bis-(β-chloroethyl)sulfide

b. Levenstein H (or simply H), which contains bis-(β-chloroethyl)sulfide plus polysulfides of varying composition in varying amounts and some colloidal sulfur.

The principal difference between HD and Levenstein H is that distilled H has a melting point of 14°C as compared to about 8°C for Levenstein H, whose melting point varies with the types and amounts of impurities present. Hydrolysis rates of the toxic component of either type of mustard and the end products of hydrolysis are the same.

6. HN Series.

These agents were made in the United States, but only HN-1 [Ethyl bis(β-chloroethyl)amine] was ever disposed of. It was disposed of by water, never by land burial. Fresh-water hydrolysis data exist, but there is no information on seawater chemistry. The hydrolytic decomposition products are not considered hazardous.

7. L (β-chlorovinyl dichloroarsine).

This agent was made by the United States before World War II. Fresh-water information is on hand; but none has been generated with seawater. However, the compound is so easily decomposed by hydrolysis that, for all practical purposes, its behavior should be the same in both media. The chief problem is the toxicity and the fate of L-oxide.

8. CK and CG.

Because these compounds are so volatile and decompose so rapidly to products that are known to be nontoxic, the work to predict long-term effects of sea or land disposal was not considered necessary.

III. CORROSION OF CONTAINERS.

The corrosion of metallic materials of dumped chemical munitions relates importantly to the problem of toxic hazards from released chemical agents. Attention was directed to metal members of selected munitions that were well represented in earlier disposals and to environments approximating those reported for the disposal areas involved.

An exact rate of deterioration of metals subjected to prolonged exposure to natural conditions (namely, air, sea, or soil) is virtually impossible to attain. The many individual factors and conditions (some of which are not well defined) must be taken into account. So must the interplay of these with the materials which continually undergo change because of the interactions. Chemical and physical variations involving electrolyte composition, dissolved gases, pH, electrical resistivity, flow or change of the environment, and pressure must be integrated. Influences of dissimilar metal contacts, imposed or residual stresses in the material, or electrochemical cell action must be recognized if these are involved. On the other hand, delaying of corrosion because of naturally formed surface films or by previous application of a barrier coating (e.g., paint) also are to be considered.

Environmental considerations for the deep ocean include salinity, oxygen content, carbon dioxide content, temperature, hydrostatic pressure, current, geographic location, and sediments. Environmental considerations for soil include composition, pH, texture, moisture, electrical resistance, and temperature.

Reasonable and useful estimates may be projected from known data acquired in limited but actual tests in the environments.

Items selected for this study include shells, bombs, mines, rockets of various types, and 1-ton containers.

Generally, metal corrosion proceeds to a maximum rate near the beginning of exposure to an environment, after which it decreases until it reaches a lower and virtually uniform rate.

Although this also holds to some extent for penetration by pitting, pitting may also accelerate with time under certain conditions. However, the attack of ordinary steels in deep areas is quite uniform; overall pitting does not occur to any extent.

Soil burial invariably results in localized attack of metals in addition to general surface attack. Local effects may appear as severe as pitting; sometimes cracking or failure occur because of applied external stresses.

Carbon or wrought steels, the aluminum (6061), and brass alloys (of which the munitions are fabricated) are not sensitive to cracking failure in the environments of disposal. Crevice corrosion does occur when surfaces are partly masked. Steel embedded in ocean bottom silts corrodes at a slower rate than in areas not so covered. Aluminum alloys of the 6000 series, such as used for the M55 rocket, are quite variable in type and rate of corrosion even in the same environment. If aluminum is embedded in ocean floor silt, the corrosion of the masked portion accelerates roughly by a factor of 2, and pitting becomes pronounced. Brass and gilding metal are more resistant to corrosion in deep ocean environments than are the carbon steels.

When leaking containers are dumped into the sea or are buried, or when damage occurs as a result of impact with the ocean floor causing agent leakage of munitions, the rate of corrosion is not important. Concrete vaults in which excess munitions have been encased in recent years are subject to impact and hydrostatic pressure and may rupture when dropped into the sea if the impact and/or hydrostatic pressures are sufficiently high.

This report is primarily directed to intact munitions which will eventually deteriorate in the ocean or in the soil, and after natural corrosion, without any forewarning, will release the toxic agent.

Steel bodied munitions containers [such as shell – 4.2 inch, 75- 105- 155-mm; bombs M70, German (250 and 500 kg); mines – 1 gal. and M123 (2 gal.)] are indicated to remain intact for periods of 46 years to 749 years at ocean bottoms at about 5000 feet (1525 meters). The different time periods are related to wall thickness. Estimates for failure times of items buried in soil are from 4 years to 70 years (see table A-I, appendix).*

Because of susceptibility to rapid pitting of aluminum in deep seawater and in soils, aluminum bodied items (e.g., rocket M55) have a shorter time to failure than have steel items. Relatively thin-walled rocket bodies were indicated to be breached by corrosion in soils in approximately 10 years, and in deep ocean environment, they will fail in 2 years.

IV. BEHAVIOR OF AGENTS IN SEAWATER.

In the discussion which follows, it is assumed that the agent contained in shell or in ton cylinders will find its way into seawater either immediately (a short time after disposal of the container) or after a long residence time at the bottom of the ocean. In connection with the last mentioned possibility, the depth of the seawater will be of importance inasmuch as the temperature of the seawater varies with depth; for example, at depths greater than 200 meters, the temperature is below 10°C, at depths greater than 1000 meters, the temperature is below 5°C, and at depths greater than 3000 meters, the temperature is 0°C or slightly lower. If the residence time were sufficiently long and the temperature sufficiently low, mustard (HD or H) would probably have solidified.

A. Mustard.

When any amount of bulk mustard is introduced into water, three distinct regions are observed, as discussed below.

1. Surface Film.

A small amount of mustard will remain on the surface of the water as an iridescent film, similar to that produced by oil on water. Although the actual amount of mustard is slight, it will produce vesicant action if it comes in contact with the skin. This surface film is gradually

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* Tables A-I through A-V are in the appendix.

destroyed by hydrolysis, and to some extent by vaporization into the air. If the water surface is disturbed by wind action or by mechanical agitation, most of the surface film will form droplets which sink to the bottom, and hydrolysis of the remaining surface mustard will be greatly accelerated. In perfectly quiet water, the surface film may last for several days, but with any appreciable degree of agitation, the film will disappear within 24 to 48 hours.

2. Bottom Deposit.

Most of the mustard will be found at the bottom of the water in the form of large oil-like masses. This mustard will remain in this condition, if undisturbed, for long periods (several months at least), and during this time it will be an active vesicant. Solution of mustard into water from this bottom deposit will take place continuously but at a very slow rate. However, the rate of destruction by hydrolysis is practically the same as the rate of solution, and as a result at no time will there be more than a few parts per million (ppm) of unhydrolyzed, vesicant mustard in the supernatant water. If the water and bottom deposit of mustard are agitated violently by mechanical means, solution of the mustard will be accelerated, and more unhydrolyzed (vesicant) mustard will be found in the water. However, as noted previously, at low temperatures such as exist at the bottom of the ocean below depths of about 2000 meters, H will presumably exist in solid form. The rate of solution is dependent upon the state of H, a higher rate of solution being found for the solid than for the liquid.

3. Intermediate Region.

Between the surface film and the large bottom deposit of mustard, the water will be practically free from the droplets of agent. After this initial period of settling, this intermediate region, although containing no droplets of mustard, will be contaminated with traces of the hydrolysis products which are not vesicant. As time passes and the hydrolysis of the surface film and bottom deposit of mustard takes place, the concentrations of these harmless hydrolysis products in the intermediate region will increase.

The rate of solution of mustard is dependent upon the temperature and the degree of agitation. The rate of solution of liquid H in seawater, under comparable stirring conditions, is only two-thirds of that in distilled water. On the bottom of the ocean, where the temperature is 2° to 4°C, H solidifies and remains as a solid material. One can assume that there will be a flow of water over the surface of the solid. The solution rate of solid mustard in seawater flowing at rates from 0.05 to 0.16 knots is up to four times that of the solution rate of liquid mustard.

Once the mustard is dissolved, it hydrolyzes rapidly. Table I shows the half life of H at various temperatures in seawater.

Table I. Half Life of H in Seawater
at Different Temperatures

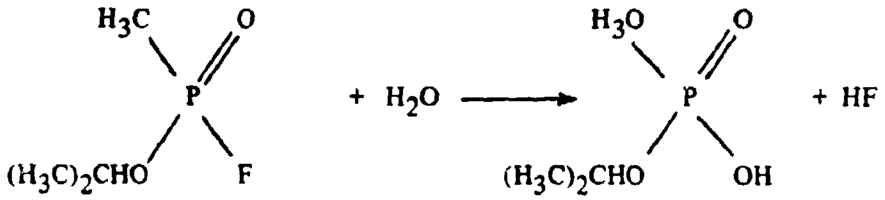
Temperature	$t_{1/2}$
°C	min
5	175
15	49
25	15

Thus, even at temperatures as low as 5°C, the mustard which dissolves has been reduced from its original concentration to 1/1000 of the value in about 30 hours (10 half lives), and to one millionth of its original concentration in about 12.5 days (20 half lives). The ultimate products of mustard hydrolysis (thiodiglycol and hydrochloric acid) are, as far as is known, nontoxic materials. However, an intermediate in the hydrolysis of mustard is β-chloroethyl, hydroxyethyl sulfide, which is almost as toxic as H itself, as measured by its effect on the rabbit eye. Its rate of hydrolysis is comparable to that of H; hence, its concentration will reach appreciable values (ca. 40% of the original concentration) during H hydrolysis. Since it possesses toxicity similar to that of H, the half life for destruction of total toxic materials is increased to approximately twice the times given in table I, and at temperatures of 5°C, it should be considered that reduction of the original quantity of toxic material to one-millionth of that quantity will require 25 to 30 days.

In summary, the life of mustard and its toxic hydrolysis product in seawater will probably be determined by the rate at which the mustard dissolves. This will be a function of temperature, degree of agitation, and/or velocity of currents. It is estimated that it would take about 5 years to dissolve 1 ton of frozen H (in the shape of a cylinder) at the bottom of the ocean. Once the mustard is dissolved, the hydrolysis proceeds rapidly to innocuous products. The concentration of hazardous materials in any area will be very small because of diffusion and/or ocean currents and their rapid rates of hydrolysis.

B. GB.

The hydrolysis of GB in water occurs as follows:



The products of hydrolysis are considered to be nontoxic. The rate of hydrolysis is pH-dependent in waters above pH = 6.5. In distilled water or in natural waters of low dissolved mineral content, the equation relating the half life of GB with hydroxide ion concentration is

$$\log t_{1/2} = \frac{5039}{T} - 8.035 - \text{pH} \qquad (1)$$

where $t_{1/2}$ is the half life in hours and T is in °K. Since the hydrolysis of GB produces two acidic materials (the pK_a of isopropyl methylphosphonic acid is 1.96, that of HF is 3.14), the rate of hydrolysis of GB in unbuffered or only slightly buffered dilute aqueous solutions of pH ≥ 7 changes with time as a result of the lowering of the pH of the water by the acidic hydrolysis products. If the concentration of GB is sufficiently low (10^{-4} to 10^{-5} M) so that a goodly percentage must be hydrolyzed before the pH of the water is lowered only slightly, then the hydrolysis rate of GB also decreases slightly. As hydrolysis continues, the rate decreases further until a pH is attained such that there is no further change in the rate of hydrolysis. At pH 6.5 the hydrolysis rate is at a minimum, and solutions of GB at this pH are relatively stable, the $t_{1/2}$ being approximately 150 hours at 25°C.

When the concentration of GB is high (>0.01 M), relatively large quantities of acid are produced with only a small percentage of GB decomposing, thus producing low pH levels (<4). Subsequent hydrolysis results in lower pH's and higher rates of decomposition. In this case, there is an autocatalysis of hydrolysis and the rates can far exceed that predicted from the pH of the initial solution.

The pH dependency of the rate of GB hydrolysis in seawater is qualitatively similar to that in distilled water, and seawater has only small buffering capacity. The quantity of acid produced by the total hydrolysis of a 10^{-4} M GB solution (∿15 ppm) is already sufficient to overwhelm the buffer content in the seawater. A constant pH (less than 0.1 unit pH change) is maintained if the solution is equal to or less than 10^{-5} M in GB. If the concentration is between 10^{-5} and 10^{-4} M, the rate of hydrolysis will decrease with time. Such solutions will be relatively more stable than more dilute solutions. If, however, the initial concentration of GB is $\geq 10^{-2}$ M, then one observes an autocatalysis of hydrolysis.

For waters of low solids content, or even for waters containing relatively large quantities of alkali metal salts of strong acids, the quantitative relationship shown in equation (1) provides a reasonable estimate of the half life of GB in low concentrations. But studies of the catalytic effect of metal ions on the rate of hydrolysis have shown that relatively small concentrations of metal ions can markedly accelerate the rate of GB decomposition in water. The ions present in seawater that might be expected to contribute to the hydrolysis rate are metal-hydroxo ions, hydroxide ions, and bicarbonate and carbonate anions. However, from studies of the effects of various salts on the hydrolytic stability of GB, it is expected that the primary ions present in seawater that would affect the hydrolysis rate are calcium and magnesium. The activities of these ions in seawater are: $A_{Mg^{2+}} = 0.0169$ and $A_{Ca^{2+}} = 0.00264$, respectively. Other metallic ions, although excellent catalysts for the hydrolysis of GB, are present in concentrations that are too low to be practically significant. Even hydroxide ion contributes very little to the overall hydrolysis rate, and the contributions of the bicarbonate and carbonate anions may be neglected.

The first-order rate of decomposition of GB in seawater, if we assume constant pH, can be estimated from the equation:

$$k_{obs} = k_2 \cdot \frac{K_a \cdot C_o}{[H^+] + K_a} + k_2' \cdot \frac{K_a' \cdot C_o'}{[H^+] + K_a'} + k_2'' \cdot \frac{K_w}{[H^+]}$$

where k_2 and k_2' are the bimolecular rate constants for the hydroxo complexes of magnesium and calcium, respectively, and k_2'' is the bimolecular rate constant for the reaction with the hydroxide ion; K_a and K_a' are the ionization constants for the two hydrated alkaline-earth ions at 25°C (pK_a of $Mg^{2+} = 11.4$ and pK_a of $Ca^{2+} = 12.7$), and C_o and C_o' are their activities in seawater. The values of k_2 and k_2' at 25°C, at unit activities, are 3.9×10^3 and 3.4×10^3 $M^{-1}min^{-1}$, respectively. For values of k_2, k_2', K_a and K_a', at lower temperatures, it was assumed that the temperature dependence of k_2 and k_2' is the same as that of k_2'' and that of K_a and K_a' is the same as that of K_w, the water constant.

A comparison of the predicted values with the experimentally determined values is shown in table II. The agreement between the calculated values and the experimental values at 15° and 25°C is very good; at 0.2°C the predicted value is too high by a factor of approximately 2, a result that is not too surprising in view of the assumptions and the long extrapolation.

Table II. Comparison of Predicted with
Experimentally Found Half Lives

Temperature	pH	$t_{1/2}$	
		Calculated values	Experimental values
°C			
25	7.6	61.2 min	58.1 ±0.3 min[a]
	7.9	30.7 min	25 ±3 min[b]
15	7.7	167 min	159 ±2 min[a]
0.2	7.7	28.8 hr	15.9 ±0.1 hr[a]

[a] Two determinations

[b] Four determinations

At a constant pH of 7.7, the half life ($t_{1/2}$) of GB at any temperature T between 0° and 25°C in seawater can be calculated from the equation:

$$\log t_{1/2} = \frac{4325}{T} - 12.84$$

There is good evidence to indicate that the organic hydrolysis product of GB has little or no toxicity. Rats fed water containing as much as 200 ppm of the hydrolysis products of GB for 3 weeks showed no ill effects. The fact that isopropyl methylphosphonic acid (one of the products of hydrolysis) does not possess activity similar to that of GB is consistent with expectations based on our knowledge of the mechanism of the toxicity of GB (and other phosphorus esters).

C. GA.

GA hydrolyzes in water along two independent paths, depending upon the pH of the water. In seawater, apparently one of these routes is preferred forming a phosphonic acid and cyanide ion.

The half lives in minutes of GA in seawater at three temperatures are shown in table III.

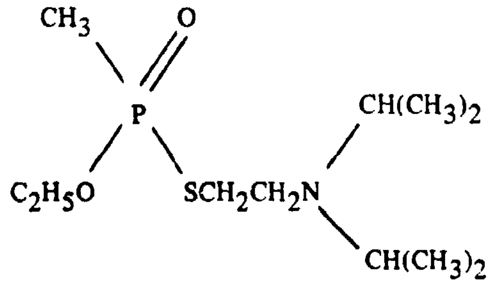
Table III. Half Life of GA in Seawater at Three Temperatures

Temperatures	$t_{1/2}$
°C	min
15	475
20	267
25	175

From this data, it is estimated that the half life at 4°C will be slightly more than 21 hours. Thus, one-thousandth of the original quantity would remain after less than 9 days at this temperature. The products of hydrolysis are considered to be nontoxic in the range of concentrations likely to be encountered due to GA contamination and hydrolysis. Unlike H, the solution of GA in water is rapid; hence, the controlling factor in the decomposition of GA is its hydrolysis.

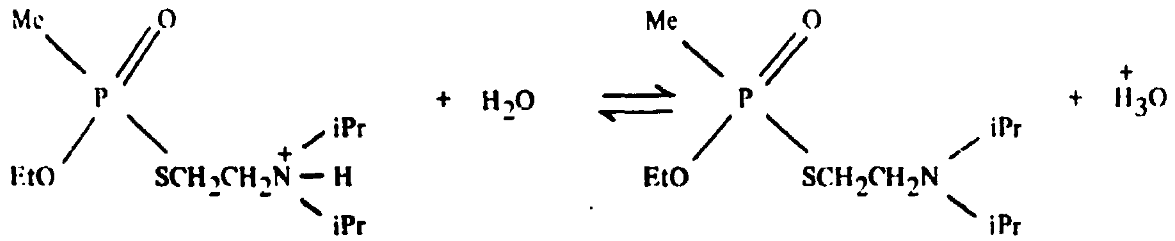
D. VX.

VX is β-diisopropylaminoethylmercapto-O-ethyl methylphosphonothioate.



VX

In aqueous solution, especially at neutral and slightly alkaline pH levels, it exists in two forms, the protonated species (A) and the free base form (B).



(A) (B)

The ionization constant (K_a) for the protonated species (A) at 25°C is 7.6×10^{-10}. The ratio of the forms A:B at any pH can be calculated readily from the relationship:

$$\frac{A}{B} = \frac{[H^+]}{K_a}$$

In seawater, then, where the $[H^+]$ ranges between 10^{-9} and 10^{-7} M, the protonated species will be the dominant one.

The distinction between these forms is not trivial, because they react qualitatively and quantitatively differently with water molecules and hydroxide ions and have vastly different effects on fish.

The hydrolysis of VX in neutral and slightly alkaline solution is complex; at least five products have been isolated from a hydrolyzed solution of VX. One of the products of hydrolysis of VX is highly toxic, approaching the activity of VX itself, and is even more stable to hydrolysis than is VX. It is estimated from theoretical considerations that the hydrolysis rate of the toxic hydrolysis product is 1/100 that of VX. Although the toxicity of this product to marine species has not been determined, it is estimated that the neutral to slightly alkaline medium hydrolysate of VX would be one-tenth as toxic as the original VX. At t = 5°C (T = 278°K), the half life of VX is approximately 230 days (about 2/3 year) with 6.5 years (10 half lives) being required to destroy 99.9% of the original material. The reduction of the toxicity of a solution of VX to 1 /1000 of its original toxicity requires not only the destruction of VX but also the destruction of its hydrolysis product. The hydrolysis product is formed to the amount of one-third the initial VX concentration; its toxicity is about 1/10 that of VX. A further hydrolysis of approximately 99% of hydrolysis product must be effected after the VX has hydrolyzed to meet the requirements of the solution being 1/1000 the original toxicity. Using a rate value of the hydrolysis product of 1/100 that of VX, it is estimated that approximately 400 years would be required to reduce the toxicity of a VX solution to 1/1000 of its original toxicity were hydrolysis the only factor. However, in the real-life situation, diffusion and dilution and their effects upon the toxicity must be considered. Needless to say, VX (or any chemical agent) deposited in a large body of water would spread in all directions with the rate of spreading and diffusion varying with temperature, velocity of ocean currents, etc. In the case of VX or other agents where the hydrolysis rate is very low, the diffusion and dilution phenomena will be the important factors in determining the toxic hazard (which would probably not be longer than several weeks, for example, for 10 pounds of VX) in seawater due to contamination by VX.

It has been shown that values of the Lt50 (time for 50% of the test species to die) for fish can be correlated with the concentration of the B form of a V-agent; thus, the agent toxicity (to fish) must be attributed entirely to this form. The agreement between the observed Lt50 values and those predicted on this assumption is remarkably good, and provides the basis for selection of a contamination level hazardous to marine life. In this connection, it has been shown that fish can survive for longer periods of time at lower temperatures when exposed to the same concentration of the nerve agent GB. It is expected that the differences in the LCt50's (concentration × time for 50% of the test species to die) of fish at two temperatures will be greater when the contaminant is VX than when it is GB, since the dissociation constant of VX decreases with decreasing temperature and the quantity of the B form of VX at a given pH will, therefore, be less at the lower temperatures.

F. HN-1.

HN-1, a nitrogen mustard, has a higher solubility than has H in water (about 3000 to 5200 ppm as compared to 700 to 900 ppm for H). Also, being a tertiary amine, HN-1 may be expected to increase in solubility with decreasing temperatures, whereas that of H decreases with decreasing temperature. Thus, at the bottom of the ocean where temperatures may be as low as 4°C, there may be a wide difference in solubilities of the two mustards. Also HN-1 (which freezes at -34°C) will remain as a liquid, whereas H(F.P. = 14°C) will solidify. Although HN-1 has satisfactory storage stability for consideration as a chemical warfare agent, it does, nevertheless, decompose with the formation of piperazium salts. The piperazium salts are probably much less toxic than is the parent compound. These facts make it likely that any HN-1 which reaches the bottom of the ocean in intact shells or cylinders will (1) spontaneously decompose to a large extent while stored in the munition, and (2) dissolve readily when the stored components finally contact the seawater. The undecomposed HN-1 will then undergo hydrolysis.

The hydrolysis process of HN-1 is similar to that of H. The final hydrolysis product is the nontoxic bis-β hydroxyethyl amine. Since the intermediate chlorohydrin possesses toxic properties similar to those of the parent HN-1, a half time of hydrolysis of all toxic materials has been calculated from available basic data to be about 12.5 days at 5°C. It has been shown experimentally that the observed rate of the cyclization step of HN-1 in seawater agrees with that calculated from the data for the cyclization of HN-1 in fresh water. These investigations also point out that the rates of spontaneous decomposition and hydrolysis will be similar for seawater and for fresh water and that estimates of the hydrolysis rates of HN-1 in the two types of water can be made rather easily.

F. Lewisite.

The stored material designated Lewisite actually consists of a mixture of several arsenic compounds: (1) Lewisite I (L-I), β chlorovinyl dichloroarsine, (2) Lewisite II (L-II), bis-β chlorovinyl chloroarsine, and (3) arsenic trichloride. The last mentioned compound hydrolyzes instantaneously in seawater to form arsenious and hydrochloric acids. The trivalent arsenic of arsenious acid is gradually oxidized to the pentavalent state to produce the less toxic arsenic acid. Considering the amount of arsenic trichloride in the stored material, the rate of hydrolysis, and the toxicity of the products, it is considered that arsenic trichloride presents no hazard if disposed of in seawater.

L-I immediately hydrolyzes to form the hydrated Lewisite oxide which then converts to the corresponding Lewisite oxide (LI-O).

The oxide is fairly soluble in seawater, i.e., over 20,000 ppm, and the hydrated oxide, being a weak acid, is also quite soluble in seawater at pH 8. Thus, it may be expected that the converted L-I will be found in solution, although some possibility exists that LI-O will polymerize to less soluble and less readily dissolved materials in seawater.

According to intravenous mouse toxicity and rabbit dye damage tests, there is no appreciable difference in the intravenous toxicity between L-I and LI-O; furthermore, LI-O is only slightly less damaging to the rabbit eye than is L-I. From toxicity and rabbit eye damage tests, there is no appreciable decrease in local reactions in the eye following topical application of LI-O after storage in seawater for at least 10 weeks. Moreover, aeration of seawater solutions of LI-O for 20 hours failed to change the local ocular effectiveness of LI-O. It appears from these studies that L-I produces a highly stable and toxic material when dispersed in water. We do not know how long the LI-O retains its effectiveness.

L-II hydrolyzes more slowly than does L-I. Its rate of hydrolysis has not been determined. Its solubility in seawater is low. It appears to be about one-fourth as toxic to mice by intravenous administration but equally as effective as L-I or LI-O in producing irritation to the rabbit eye. For all compounds, about 1 μg in the eye is the "threshold" quantity for irritation; about 1 mg will produce permanent damage. The probability of exposure to 1 mg of any compound which has been dumped into the ocean is remote.

G. Summary.

It is impossible to make even a rough prediction of the dissemination pattern for toxic agents released from munitions lying on the ocean bottom. Nevertheless, one may list the following considerations, to be applied in specific instances:

1. If a container is open or becomes open to the surroundings (i.e., it is a leaker or it corrodes) with very small apertures, it is possible that seawater will penetrate as the void space in the munition diminishes due to pressure. Detoxification of the agent, especially GA or GB (and to a lesser degree HN-1 and VX), will take place within the munition.

2. When a water-immiscible agent is opened to the sea, its rate of solution will depend to a great degree on the ocean currents sweeping past. This would be especially important for HD, a solid below about 14°C. Solution of all agents into the ocean will be very slow unless a large surface is exposed.

3. The rate of travel of dissolved agent to the surface is governed largely by diffusion; as the agent rises toward the surface it undergoes dilution. Ocean currents, except in a few isolated spots, would effect only lateral transfer, with attendant dilution.

4. The rates of hydrolysis of HD, GA, GB, and HN-1 are important relative to the time needed for them to diffuse. The hydrolysis rates of VX and L would be of little or no importance, since the toxicity would change so slowly.

5. A comparison of the hydrolysis of agents in seawater versus fresh water reveals that the rates for VX, GA, and HN-1 are not appreciably different in the two media. GB hydrolyzes more rapidly in seawater and HD more slowly.

V. BEHAVIOR OF AGENTS IN SOIL.

A. Mustard (H).

Studies have been made on the vaporization of mustard at 70° to 78°F and 27% to 35% relative humidity after experimental application to calcareous soils and on the effect of added moisture to several types of soil under controlled conditions. Recoveries from the calcareous soils varied from 7% to 32% when sampled for about 6 hours; when sampling was continued until no more H vaporized (15 to 55 hours), the percentages of the initial contamination recovered increased, varying from 12% to 66%. Both the rate of vapor generation and the percent of mustard recovered in the vapor state depended on the pH, moisture content, and physical constituents of the soils. Finer soils gave a lower return of vapor than did coarse, sandy soils. Considering the effects of particulate size in a soil irrespective of the chemical components, particulates above 1 mm in diameter would play very little part in the adsorption, and thus in the retention of an agent such as H. Below 1-mm-diameter sizes, as the particle size decreases, the surface area greatly increases, therby increasing the adsorbing power of the soil. Plots of vapor return versus moisture content go through a maximum which varies with the type of soil. The state of the unrecovered agent remaining in the soil was not determined.

Mustard sprayed on the surface of soil remains vesicant for only about 2 weeks, decomposing under the influence of natural environmental conditions. Mustard that leaks to some depth into soil will remain vesicant at least 3 years after contamination. Mustard in containers is stable for long periods. It may be concluded that deep contamination of soil by mustard, where the agent cannot vaporize or undergo weathering, may persist for many years; for instance, mustard which had been dumped at Edgewood Arsenal ("O" field) in 1941 was still present in trace amounts until it was decontaminated in 1971.

Liquid mustard was found to kill vegetation, but the vapor did not.

B. GB.

Stabilized GB in munitions withstands prolonged storage.

Because GB is infinitely miscible with water and easily hydrolyzed, it should not last for a long time in the soil. It

> *"can be detected in Dugway surface soil for only a short period... The major contributors to the degradation of (this compound) are an increase in soil moisture and ambient temperature. If the soil is oven-dry or if the temperature is below freezing, the (agent) decomposes very slowly. Little agent is lost from the soil through vaporization."**

The lifetimes of GB were examined at 0°, 25°, and 37°C and loadings of 2.0- and 8.0-oz per square yard in sand, sandy loam, and high-humus loam in a 2-mph wind. Persistency was defined as the volatilization time for 99% of that part of the agent that evaporated off, and was recovered from, the vapor state. As might be expected, the agent was more persistent at the higher loading. There was only a slight difference in persistency at the different temperatures and in the different soils. The total amounts volatilized were generally greatest at the higher temperatures and with the coarser soils (soils > sandy loam > high-humus loam). These amounts ranged from 21.5% to 94.0%. It may be assumed that agent not recovered had decomposed. Although the decomposition rate would increase with temperature, volatility would increase to a greater degree. The times for 99% removal of GB ranged from 2.5 to 24 hours.

Excluding slow-leaking buried munitions, there does not appear to be a long-term hazard from GB leaks into the soil, except, perhaps, in very dry or cold areas.

C. Lewisite.

Lewisite (L) is quite stable with respect to storage in munitions. When L was placed on soil at 125°F, 20% evaporated in the first hour and none thereafter. Even less evaporated under higher humidities. This behavior is consistent with the extremely facile hydrolysis of L to the relatively nonvolatile Lewisite oxide (LO). Higher calcareous (calcium carbonate-containing) or alkaline soils tie up relatively higher proportions of the Lewisite applied; but in any event, an appreciable proportion fails to volatilize. Soil that has been contaminated with Lewisite continues to retain its vesicant behavior for a long time. This is perfectly understandable, since LO is nearly as toxic as Lewisite itself, though not volatile.

Lewisite, like many other trivalent arsenicals, is a potent herbicide. In the pentavalent state, both the herbicidal activities and the mammalian toxicities of most arsenicals are markedly lower than in the trivalent state. Present studies indicate this to be true of LO mammalian toxicity also. The tendency towards oxidation to the pentavelent state or reduction to the trivalent form will probably depend on soil conditions.

D. VX.

Stabilized VX munitions can last for several years without serious deterioration, especially at low or moderate temperatures.

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* Personal communication. M. A. Rothenberg.

The lifetime of VX in soil is somewhat variable, depending on the temperature, the organic matter content, and perhaps moisture.

> *"If the soil is ven-dry or if the temperature is below freezing, the (agent decomposes) very slowly. Little agent is lost from the soil through evaporation. Low concentrations of VX are tightly bound as agent by dry Dugway soil... However, VX is released or decomposed as the moisture content increases. The recovery of agent and associated decomposition products from soil is only 30 to 50% with current methods."**

Another source, concerned with a different soil, minimized the effect of moisture. The moisture content (0.045%, 20% and 50%) had an initially negligible effect on the lifetime of VX at 25°C and 1% loading in Carroll Island soil; $t_{0.5}$ was 2 days and $t_{0.05}$ was 10 days in each case. Thereafter, the loss rate was less in the dry soils than in the moist ones. The loss rates of VX at 0.01% loading in various fairly dry soils were investigated; after 1 week, in most cases, the VX content had decreased to 10% of the initial value (range about 3% to 30%).

When VX decomposes in soil, other toxic cholinesterase inhibitors can form from the decomposition products, notably, a pyrophosphonate ester. These compounds persist in the soil for a long time. For example, compounds possessing anticholinesterase activity were extracted from Carroll Island soil as late as 3 months after application of VX to the soil.

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* Personal communication, M. A. Rothenberg.

APPENDIX

TABLES

Table A-I. Estimated Time to Penetration by Corrosion of Munition Containers[a]

Munition item	Time to penetration	
	Deep ocean 5600 ft West Pacific Coast US location	Soil – South Eastern US location[b]
	years	years
4.2-inch Shell	151	15
75-mm Shell	319	29
105-mm Shell	483	44
155-mm Shell	749	69
Bomb, M70 (115 lb)	252	7
Bomb, German (500 lb)	125	12
Bomb, German (1000 lb)	125	12
Rocket, M55	2[c,d]	10
Mine, 1 gal.	46[e,f]	4
Mine, M23 (2 gal.)	47[e,f]	4
Ton container	539	49

[a] Penetration of thinnest section.

[b] Gravelly Clay or Susquehanna Clay.

[c] Indicated rupture at time of dumping - probably initiating at hydrostatic pressures of ca. 3500 psi.

[d] Penetration by pitting corrosion of aluminum portion of rocket container.

[e] Probable rupture of container by hydrostatic pressure; compare note "c" above.

[f] Penetration by normal corrosion of steel container.

Table A-II. Decomposition Time[a] for GB in Various Media at Different Temperatures

Temperature		Medium		
		Water[b]	Seawater	Soil[c]
°C	(°F)	hours	hours	hours
5	(41)	12500-125	90	2.5 to 24
15	(59)	3000-30	25	
25	(77)	750-7.5	8	

[a] The decomposition time is given as the time required for 99.9% decomposition of the agent. In water, if the original concentration were 1 ppm, the concentration remaining would be 1 ppb after the decomposition time.

[b] A range of times is given for decomposition in natural waters because the rate is dependent upon the pH of the water, and the pH of natural waters will vary. For a discussion of the effect of pH on the hydrolysis rate of GB, see the written portion of this report. The ranges given in the table refer to waters of pH 7.0 to 9.0, with the higher pH waters having the smaller decomposition times.

[c] Time for 99% removal of GB. GB is lost by both volatilization and hydrolysis. If GB is on the soil, most is lost by volatilization; if in the soil, most by hydrolysis. The major contributors to rate of degradation and volatilization are soil moisture and ambient temperature.

Table A-III. Decomposition Time[a] for H in Various Media at Different Temperatures

Temperature		Medium		
		Water	Seawater	Soil[b]
°C	(°F)	hours	hours	hours
5	(41)	15	29	2 weeks to > 3 years
15	(59)	3.8	8.2	
25	(77)	1	2.5	

[a] The decomposition time is given as the time required for 99.9% decomposition of the agent. In water, if the original concentration were 1 ppm, the concentration remaining would be 1 ppb after the decomposition time; decomposition time is after H dissolves. Also, one of the decomposition products is approximately as toxic and as stable as H itself.

[b] Rate and amount of H vaporized from soil depends upon type of soil, pH, and moisture content. Mustard sprayed on the surface of soil remains vesicant for about 2 weeks; H that had leaked to some depth into soil was still vesicant at least 3 years after contamination.

Table A-IV. Decomposition Time[a] for GA in Various Media at Different Temperatures

Temperature		Medium		
		Water	Seawater	Soil
°C	(°F)	hours	hours	hours
5	(41)	b-140	213	N/A[c]
15	(59)	b-42	79	
20	(68)	b-22	45	
25	(77)	48-14	29	

[a] The decomposition time is given as the time required for 99.9% decomposition of the agent. In water, if the original concentration were 1 ppm, the concentration remaining would be 1 ppb after the decomposition time.

[b] No reliable data available at pH ca. 7 and temperatures < 25°C.

[c] GA never disposed of by land burial.

Table A-V. Decomposition Time[a] for VX in Various Media at Different Temperatures

Temperature		Medium		
		Water[b]	Seawater	Soil
°C	(°F)	years	years	days
5	(41)	20-1[c]	3.3[c]	10[d]
15	(59)	4-0.26[c]	0.8[c]	
25	(77)	1.1-ca. 1 mo.	0.2	

[a] The decomposition time is given as the time required for 99.9% decomposition of the agent. In water, if the original concentration were 1 ppm, the concentration remaining would be 1 ppb after the decomposition time. Also, one of the decomposition products is toxic and even more stable than VX. The decomposition time to 99.9% destruction of the toxicity will be considerably longer (but inestimable from present data) than that given in the table.

[b] The range of pH of the water is from 7 to 9; the decomposition times are lowest at the highest pH values.

[c] Decomposition time at lower temperatures are extrapolated from data at 25° and 55°C [Epstein, J., and Bauer, V. E., Army Science Conference Proceedings. 14-17 June 1966. Volume III (U). pp 135-147. Callahan, J. J., and Scott, R. U. CWLR 2356. Hydrolysis of VM and VX in Dilute Aqueous Solutions (U). January 1960. CONFIDENTIAL Report. See also Epstein, J., Bauer, V. E., and Chasanov, M. CWLR 2125. Kinetics and Mechanisms of the Hydrolysis of EA 1517 in Dilute Aqueous Solution (U). May 1957. CONFIDENTIAL Report].

[d] Decomposition time is dependent upon amount of agent, type of soil, pH, water content, organic matter, and temperature. Also, other toxic cholinesterase inhibitors can form from the decomposition products and persist in the soil for a long time. The estimate given is time for 95% decomposition at 25°C at 1% agent loading. VX is very persistent in dry soil (e.g., Dugway soil) or at low temperature.

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11. SUPPLEMENTARY NOTES

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US Army Munitions Command

13. ABSTRACT

The objective of this report is to provide data from which predictions of the hazards from a variety of past disposals of toxic chemical agents may be based. Literature searches were carried out on the behavior of chemical agents in soil and on the effects of corrosion on stability of various containers when buried or when dumped in the ocean in order to obtain information needed for reasonably approximate estimation of residual hazards. When sufficient information on factors affecting the hydrolysis rates of chemical agents in fresh or seawater had not been obtained previously, laboratory investigations were conducted on hydrolysis rates and on the toxicity of the hydrolysis products. Estimates are given of lengths of time the various chemical agents will remain hazardous after disposal by methods used in the past.

14. KEYWORDS

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L
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GB
GD
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Solution rates
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