# OCEAN DUMPING OF CHEMICAL MUNITIONS: ENVIRONMENTAL EFFECTS IN ARCTIC SEAS

MAY 1997

MEDEA

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The interactions between environment and national security are often not well articulated. In some cases, the coupling is apparent. For example, release of hazardous materials under specific circumstances can have a serious and quantifiably adverse effect on ecosystems with both direct and indirect consequences for the integrity of the environment and for human health. In other cases, associated, for example, with subtle consequences of genetic engineering or with active acoustic sensing of the ocean and atmosphere, we are just beginning to learn about the issues. Our understanding of relevant basic science may be rudimentary and further work must be done if we are to provide responsible guidance for policy.

This report, investigating potential environmental consequences of Cold War disposal of chemical munitions in the Russian Arctic, was produced by a subgroup of MEDEA scientists at the direction of the National Intelligence Council. It provides an excellent example of where well-founded conclusions on an important issue can be drawn from careful analysis despite gaps in data and less than perfect knowledge of detail; it may be viewed as a prototypical case for understanding a relationship between environment and national security. The study points up the need for broadly based disciplinary expertise in addressing the complex linkages that characterize such issues. It offers a clear example of the important and complementary roles academic and government scientists can bring to bear on a topic of mutual interest.

The report identifies several longer term studies which would lead to improved understanding of the potential impact on oceanic ecosystems of the disposal of munitions and toxic chemicals at sea. Such studies would be of interest for a broad range of disposal sites, not simply limited to the Arctic. It is my hope that the scientific conclusions reached here, when viewed by others, will lead to enlightened management of munitions disposed in the ocean.

I am indebted to the dedicated scientists both inside and outside government who generously contributed their time and talent to this important effort. MEDEA was pleased to contribute its expertise and guidance to the study. We look forward to working with government agencies in the future to address similar such topics of national and international interest at the intersection of concerns for environmental integrity and national security.

On behalf of MEDEA, I would like to acknowledge the extraordinary efforts and leadership provided by Otis Brown, who chaired the study, and by Ken Hawker. Without them, this project could not have been carried to its successful conclusion.

Dr. Michael McElroy
Chairman, MEDEA

MEDEA carried out this assessment of the potential for significant adverse impact on the arctic environment arising from past dumping of chemical warfare munitions in arctic seas at the request of the National Intelligence Council. The assessment primarily was concerned with determining the potential for environmental effects of sufficient magnitude as to pose some concern to a broadly defined U.S. national security.

The present report describes the study that was carried out and the findings and recommendations which were developed.

The study was carried out through a collaboration between an ocean science subgroup of MEDEA and a number of collaborators who brought specialized scientific and technical knowledge to the process.

The views reflected herein are those of MEDEA and specifically the following members who participated in this study:

Dr. Mark R. Abbott	Oregon State University
Dr. Peter G. Brewer	Monterey Bay Aquarium Research Institute
Dr. Otis B. Brown, Chair	University of Miami
Dr. Kenneth E. Hawker	The MITRE Corporation
Dr. Robert A. Holman	Oregon State University
Dr. Walter H. Munk	Scripps Institution of Oceanography
Dr. John Orcutt	Scripps Institution of Oceanography
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Dr. Norbert Untersteiner	University of Washington
Dr. Karl K. Turekian	Yale University
Dr. Wilford F. Weeks	University of Alaska/Consultant

In the course of their collaboration, a significant amount of effort was provided by the following individuals who researched much of the information and contributed in major ways to drafting sections of this report:

Dr. George O. Bizzigotti	Mitretek Systems
Dr. Robert Edson	Office of Naval Research
Mr. Robert E. Gerstein	Mitretek Systems
Dr. Jackie Grebmeier	University of Tennessee
Dr. Richard D. Mavis	Mitretek Systems
Dr. Thomas E. McEntee, Jr.	Mitretek Systems
Dr. Wade H. Smith	Mitretek Systems
Dr. Fred Tannis	Environmental Research Institute of Michigan
Dr. Barron L. Weand	Mitretek Systems

ACKNOWLEDGMENTS

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PROBLEM STATEMENT

The objective of this study was to develop a quantitative assessment of the potential for *significant* adverse impact on the arctic environment arising from the dumping of chemical warfare (CW) munitions in arctic seas by the USSR during the Cold War.

The task included estimating the potential for significant effects on the arctic ecosystem and related human factors. It did not include conducting an assessment of the compliance of ocean dumping of CW munitions with U.S. law or international convention, nor did it compare the risks associated with various possible disposal methods.

This study was primarily concerned with determining the potential for a significant environmental effect, that is, one large enough to be of some concern to U.S. national security, possibly through impact on economically important arctic fish stocks or on human health and safety.

RANGE OF POSSIBLE EFFECTS

Before beginning a discussion of the specific problem posed by USSR dumping in arctic seas, it will be useful to set the stage by reviewing the variety of possible environmental effects. In general CW agents have the potential to affect the ocean environment in various ways, some relatively benign, some very serious.

- Some agents are basically immobile and relatively non-toxic in seawater once released from munitions;

- Other agents have very short persistence in seawater and, therefore, presumably pose a limited threat to the environment;

- Some agents or their chemical reaction products may have the potential for biomagnification, resulting in increasing concentration within organisms as they pass upward through the food chain;

- The toxicity of some CW agents is so high that one cannot exclude, *a priori*, their causing effects over very large areas, as ocean circulation acts to transport toxic plumes across the arctic seas;

- CW agents can add to an existing burden of anthropogenic contamination of the seas caused by a wide variety of toxic compounds, *e.g.*, from industrial wastes, and thus can contribute to a cumulative effect;

Schematic Illustration of Ocean Dump Sites
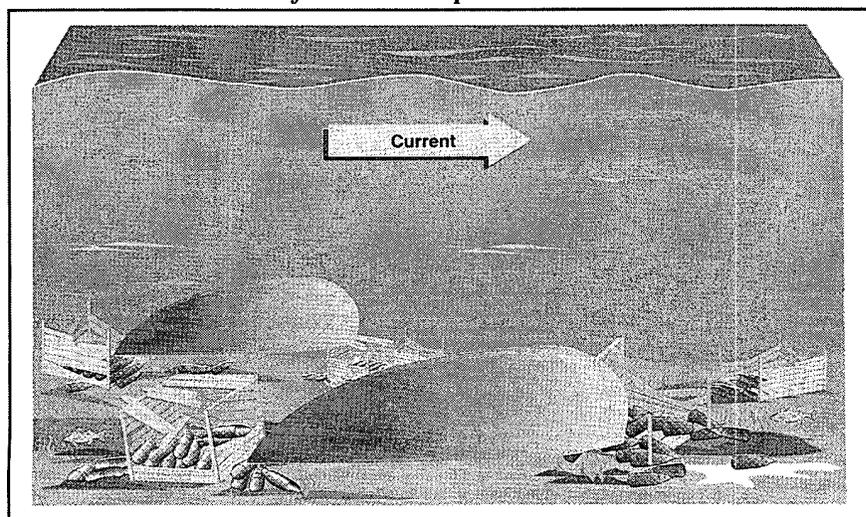
• Still other agents may remain contained in dumped munitions on the ocean floor with their casings as yet uncorroded and their agents unreleased.

Once CW agents are released into the sea, accounting for the resulting environmental effects is complicated by their complex and poorly understood toxicity to marine organisms and by their transport by ocean currents while the complex processes of chemical reaction and dilution, through turbulent mixing, take place.

No comprehensive scientific study of the entire chain of physical, chemical, toxicological, and biological processes is known to have been conducted. Nevertheless, several reports, primarily those concerned with the Baltic Sea, have concluded that these compounds pose little or no environmental threat, largely because of the chemical degradation of CW agents in seawater. The exception frequently noted is the threat to fishermen who may come into direct contact with agents inadvertently collected in their trawls.

The logical flow of the present assessment is shown in the figure below.

APPROACH

Most of what is known about arctic dumping of chemical munitions comes from anecdotal open sources. The present assessment is based on a synthesis of the best available estimates. The resultant picture of CW dumping is combined with results of a detailed analysis of the seawater chemistry and the toxicity of CW agents in computations of the spatial extent of toxic concentrations produced by the actions of ocean currents and turbulent mixing. Once the extent of toxicity governed by physical ocean processes is estimated, the resulting impact on the arctic marine environment is assessed.

Flow of the Study

HISTORICAL CONTEXT OF OCEAN DUMPING

Beginning before World War II and continuing through the Cold War, ocean dumping of chemical weapons was a fairly common international practice. Many nations, including the United States, other Western countries, and the USSR used this method of disposal of CW stocks.

In the years immediately following the war, there was extensive ocean dumping by the Allied powers in the Baltic Sea and in Japanese waters. Large ammunition depots were discovered in Germany, containing mustard gas grenades and mustard gas, sneezing gas, and tear gas bombs.

During 1946 and 1947, an estimated 50,000-150,000 tons of chemical munitions including mustard gas, sneezing gas, and tear gas, were dumped in the Baltic Sea, fifteen miles off the Danish island of Bornholm, at a depth of approximately 100 m. Approximately 2,000 tons of chemical munitions, predominantly mustard gas, were dumped in the Gotland basins off the coast of Sweden and possibly in other areas of the Baltic. Numerous reports and papers in medical journals have appeared providing statistics on accidents to fishermen engaged in trawling in the areas of the Baltic dump sites. Studies of the Baltic Sea CW problem continue to be conducted by the Helsinki Commission.

Details of dumping operations in Japanese waters were not widely known until 1972 when, as a result of numerous accidents with disposed CW reported in the 1960s and 1970s, the Japanese Prime Minister commissioned a national inquiry to investigate the status of the chemical weapons disposed of in the 1940s.

Surviving records of U.S. Army post-World War II dumping track the movements of CW agents, identify the ports of departure for ocean dumping and, in some cases, specify the location of the dump sites. The quantities dumped are given, in most cases, as a number of barge loads or by the name of the ship. It appears that most or all U.S. dumping involved CW munitions that had been sealed in concrete and steel vaults. A history of the transport of chemical weapons compiled by the U.S. Army in 1987 showed 314 movements beginning on 1 March 1946 and ending on 23 May 1974.

In the late 1960s, an *ad hoc* committee of the National Academy of Sciences (NAS) was appointed in response to an Army request to evaluate the hazards involved in the planned ocean disposal of surplus chemical warfare stocks. The committee began its report by noting that "continuing inaction will not reduce the hazards of eventual disposal of the chemicals and munitions intended for disposal in the 1969 Operation CHASE and, in some instances, will increase them."

The committee made several specific recommendations concerning the surplus chemical warfare munitions:

- For cluster bombs containing the agent Sarin (GB), disassembly at their storage site and chemical destruction of the withdrawn Sarin.

- For bulk containers of agent Mustard (H), incineration.

- For concrete and steel "coffins" containing Sarin-filled rockets, further study by a technical group including experts on demolition to consider whether there was a practically feasible way to dispose of the coffins on an Army establishment. In the event that the proposed study provided no feasible alternative method, the NAS committee recommended ocean dumping of the coffins. This is in fact what occurred.

This NAS study also noted that the effects on the ocean environment from ocean dumping of Sarin should be minimal because the agent would be dispersed only near the seafloor and hydrolysis would limit its active lifetime.

In 1984, another NAS Committee was asked to review methods for disposal of the U.S. Army's stockpile of CW agents. The Committee noted that ocean dumping was not consistent with current national and international law and "attempting either to modify the

laws or to seek an exception does not seem justified at this time." No detailed technical evaluation of the ocean dumping option was made.

In contrast to the well-characterized campaigns of chemical weapons dumping in the Baltic Sea, Japanese waters, and off the United States coasts, reports of such dumping by the USSR in the arctic seas have never been confirmed officially. The major source of information on Arctic dumping has been Lev Federov[1] who recently has written books on the subject of CW weapons and their disposal. Additionally, the open press has described alleged incidents in which obsolete Soviet chemical weapons, as well as captured World War-II-era German chemical munitions, were dumped in the northern and eastern seas surrounding Russia. Any study, including the present one, conducted in the absence of actual records of this dumping must contain substantial uncertainty, especially regarding site locations and total quantities dumped.

CW PRODUCTION AND INVENTORY

Mustard production by the Soviet Union between 1941 and 1945 was estimated to have approached 80,000 tons[2]. Production of low-purity mustard began prior to 1930 and, while reliable estimates of this phase of mustard production are not available, it is likely that up to 15,000 tons were produced. Lewisite (L) production during World War II slightly exceeded 20,000 tons. Consequently, combined production of mustard and Lewisite may have reached 115,000 tons by 1945.

There are descriptions of the capture of German production facilities for Tabun (GA) by the Soviet Army at the end of World War II. Allied data indicated that the German facility had produced 12,000 tons of Tabun. For purposes of this assessment, it has been assumed that no more than 30,000 tons of Tabun were dumped in arctic seas. This estimate is possibly too high, if one considers the German production only.

Sarin was apparently not produced successfully by the Soviets until the late 1950s. A German Sarin production facility was under construction at the end of World War II and the Soviet Army captured the equipment for its production, including pilot quantities and transported everything to the Soviet Union. It is not known if stocks of German Sarin weapons were captured by the Soviet Army. For the present study, the assumption was made that no more than 2,000 tons of Sarin was dumped in the arctic seas.

This assessment does not require precise dates of the dumping since our primary concern is to estimate environmental effects once an agent was released, not to predict when that release would, or did, occur. Based on Federov's analysis, we assume that the dumping of mustard and Lewisite took place in the 1940s and 1950s; the Tabun was also dumped in the 1950s; and that in the 1980s, Sarin as well as additional Tabun was dumped.

CW DUMPS IN ARCTIC SEAS

Identification of dump sites for this assessment was based upon delineation of restricted or hazardous areas on Soviet and later Russian-navigation maps for the arctic seas of interest. Based on this, and other, information, it is highly probable that dumping of munitions containing the CW agents Tabun, Sarin, mustard, and Lewisite were dumped in thousand metric ton quantities in the White, Kara, and Barents Seas.

The five sites identified in this assessment are shown on the map below.

Restricted Areas Associated with Potential CW Dumping Activities

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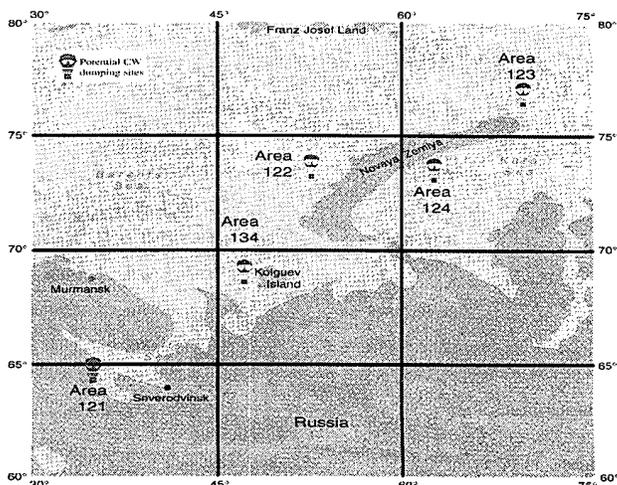
[1] A member of the Russian Academy of Science.
[2] Unless otherwise stated, tons will mean metric tons, *i.e.*, 1,000 kg, and refer to agents not munitions.

It is estimated that a *maximum* of approximately 40,000 tons of mustard and Lewisite were dumped into the White Sea and a *maximum* of 75,000 tons were dumped into the Barents and Kara Seas combined. A *maximum* of 30,000 tons of Tabun and 2,000 tons of Sarin was estimated to have been dumped in the White, Barents, and Kara Seas. These quantities refer to CW agents only and not the weaponized quantities, which would be approximately ten times greater.

CW AGENT RELEASE

A compilation of medical records and incident reports involving fishermen who recovered CW munitions in the Baltic Sea and Japanese waters since the end of World War II indicates that CW munitions dumped in the sea will remain intact for long periods if left undisturbed. The Baltic experience shows clearly that if fishing, especially bottom trawling, occurs at the dump sites, munitions on the seafloor can be disturbed, leading to harm and sometimes death. From 1946 to 1984, there were a total of 197 patients suffering from mustard gas exposure in the Baltic Sea. A total of 171 were treated as ambulatory patients and 26 were admitted to the hospital. In both 1947 and 1948, there

were two reported deaths resulting from a mustard disposal mishap. As recently as 1990, 101 incidents of fishermen finding CW munitions or agents were reported. Reports to the Helsinki Commission on Dumped Chemical Munitions state that, as recently as 1994, an examination of Baltic dump sites showed the presence of both intact and completely corroded munitions remaining on the seafloor.

Unlike the Baltic, there are no reports of fishermen encountering chemical weapons from arctic seas. This difference could be because the "Hazardous Dump Site" warnings on Russian charts has limited the scope of trawling activities at these sites, leaving the munitions to lie undisturbed on the seafloor for decades. Another contributing factor is that, with the exception of the Barents Sea, the arctic areas have historically been less heavily fished because the presence of pack ice limits access during most of the year.

Also, even when there has been widespread and continued disturbance of dump sites, as in the Baltic, it appears that large numbers of munitions continue to remain intact. If this were not the case, CW agents, primarily lumps of mustard, would not continue to be

Human Encounters with Dumped Chemical Weapons
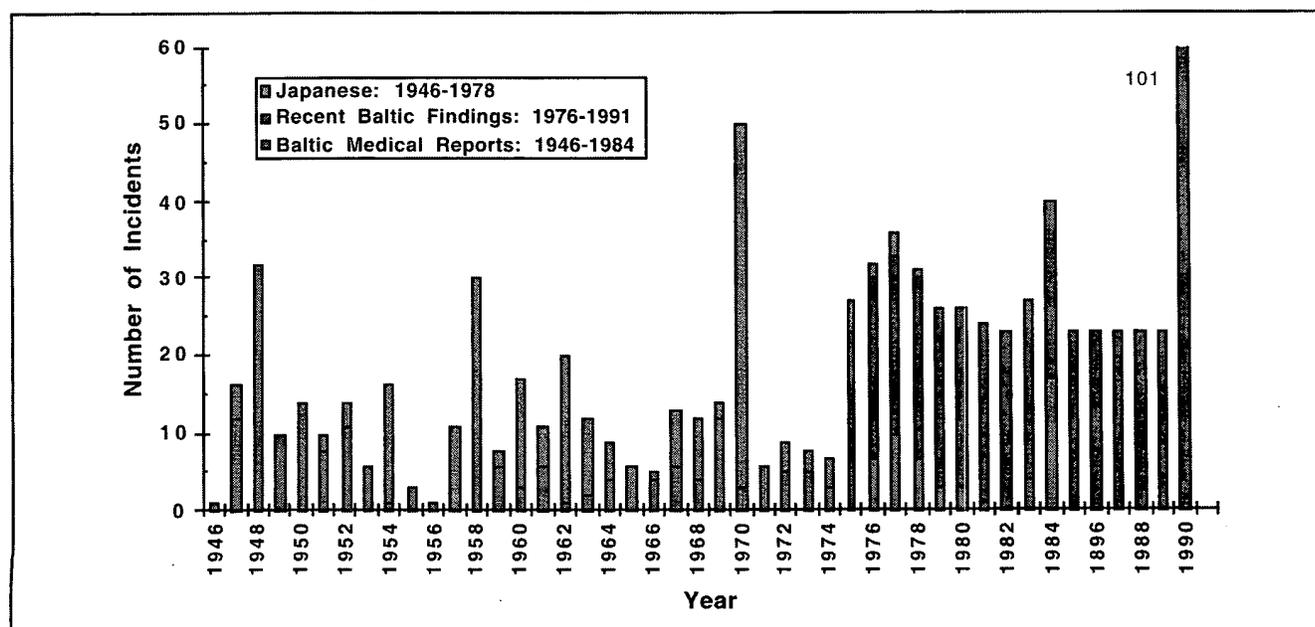
recovered decades later, because the agent would have dissolved.[3]

Lacking detailed information of the condition of the dump sites, it is possible to construct a plausible hypothetical picture based on what is known about other dump sites, shipwrecks, and the physics of ocean systems. The first step, following dumping, will be a slow corrosion of the steel containers, e.g., artillery shell or bomb casings. This is likely to produce a porous mass, or sludge, of iron oxides, until finally, the integrity of the casing is breached and the agent is released into the sea. At this point, conversion of the CW agent along various chemical pathways will begin, as will transport in the local ocean current and dilution through mixing, in the near-bottom turbulent boundary layer generated by the current.

CHEMISTRY OF CW AGENTS IN SEAWATER

Chemical transformations that the CW agents Tabun, Sarin, mustard, and Lewisite are likely to undergo in the marine environment are critical issues along the path to assessing their impact on the environment.

The chemistry of CW agents in the marine environment is dominated by hydrolysis, the reaction of the agents with water. For each toxic agent, hydrolysis results in characteristic reaction products. Some of these are basically inert biologically and others are as toxic as the original agent. These products are described below.

Tabun is fairly soluble in water and hydrolyzes over a period of days with a half life of forty hours. The principal toxic breakdown product is a stable cyanide compound, HCN.

Sarin is miscible, that is, it mixes in all proportions with water. It also hydrolyzes over a period of days, with a half-life of sixteen hours. Hydrolysis products are all very much less toxic than Sarin and can be assumed to be essentially inert.

Dissolved mustard hydrolyzes relatively rapidly, with a half life of five hours. However, the appearance of mustard in the marine environment is controlled by the rate at which it dissolves, which is much slower than

the rate of hydrolysis. The expected lifetimes of mustard lumps corresponding to typical munitions quantities are eight months for a 1 kg lump, e.g., in an artillery shell, eighteen months for a 10 kg lump, and thirty-nine months for a 100 kg lump, e.g., in a bomb.

Lewisite is soluble in water and hydrolyzes very rapidly, in seconds. The initial hydrolysis products of Lewisite are as toxic as Lewisite and persist in seawater for months or longer. The major toxic Lewisite reaction products are (2-chloroethenyl) arsonous acid and inorganic forms of arsenic. Their long persistence will result in redistribution by transport and mixing.

TOXICITY TO MARINE SPECIES

There are few measurements on the toxicity of CW agents to marine species. However, there is a great deal of information on toxicity to other organisms. The synthesis of this information provides an entry into the estimations of effects on marine organisms. The results show that, of the short-lived compounds, agents, or hydrolysis products, Tabun and Sarin are the most toxic. Of the long-lived compounds, organic arsenic, a hydrolysis product of Lewisite, is the most toxic.

The primary source of aquatic information used in this study was the AQUIRE database [Aquatic Toxicity Information Retrieval], which is supported by the U.S. Environmental Protection Agency. The AQUIRE toxicological data summary is designed for use as a stand-alone reference database or as a high-quality data source for risk assessment tools. Test organisms are limited to those that are exclusively aquatic. The system presently contains data on more than 2,700 species, 5,700 chemicals, over 9,300 references and approximately sixty effects from 130,000 toxicity tests.

Where available, measured LC_{50} values (the concentration of the agent in water, which resulted in the death of 50 percent of the exposed marine organisms during the specified time interval) were the most useful measure in assessing the toxic effects. Where LC_{50} values were unavailable, reported LD_{50} values (the lethal dose of the agent, which resulted in the death of 50 percent of the exposed organisms during the specified time interval) were used.

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[3]Dissolution of mustard and other CW agents is addressed quantitatively in this study.

For the purpose of estimating a toxic threshold for the chemicals of concern, the lowest reported LC_{50} was identified and one-tenth of this value was chosen as a concentration at which marine organisms would not experience acute toxicity. This value is identified as the Estimated No Effects Concentration (ENEC). The ENEC multiplied by ten (*i.e.*, the LC_{50} level) was established as the Estimated Probable Effects Concentrations (EPEC). The ENEC multiplied by one hundred was established as the Estimated Lethal Effects Concentrations (ELEC).

For simplicity, and because data does not exist to support a more fine grained analysis, *these levels (ENEC, etc.) are taken to apply equally to all marine species.* Data to support a more fine-grained analysis does not exist and this assumption consititutes one major source of uncertainty in this study.

EXTENT OF CONTAMINATION: SINGLE MUNITIONS

For the four types of CW agents considered, estimates were computed showing that the contamination by a leaking, *single* CW munition will be a local one, that is, confined to small ocean areas having dimensions on the order of hundreds of meters or less. This conclusion is valid at all concentrations of environmental concern. There is essentially no possibility of dispersing toxic levels of these agents throughout the entire arctic via ocean circulation.

The most plausible form of release of agents, other than mustard, is through pinholes in the casings formed

Schematic Appearance of Toxic Plume
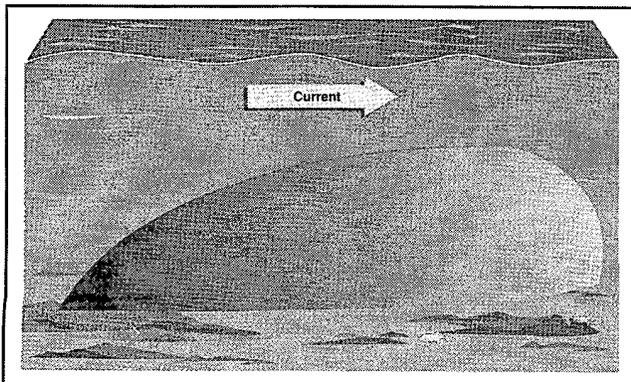
by corrosion. It is expected that once pinholes develop, agents will leak into the sea. This process may last days, even weeks or months. Once released, the agents will cause toxic plumes that have their maximum extent on the seafloor.

For release from single munitions, these plumes at ENEC will have dimensions on the order of a few hundred meters or less along the current, a few tens of meters across the current, and a few meters thick above the seafloor. Plume dimensions at higher concentrations, *e.g.*, EPEC will be much smaller. The volume of seawater contaminated at ENEC that is contained in such a plume will be no greater than a few thousand cubic meters and may be much less.

Plumes will persist while the CW agent is releasing from the munition, the slower the release, the longer the period. However, it also follows that the slower the release rate, the smaller the plume. The maximum volumes of contamination can occur only for release rates that would empty a typical artillery shell in a day or less.

Because of its high viscosity and low solubility, the dispersal of mustard occurs differently. Following an abrupt and complete disintegration of a munition casing by corrosion, the appearance of dissolved mustard agent in the sea is determined primarily by the exposed surface area (*i.e.*, the shape of the lump of mustard). After the last of the mustard is dissolved, the remaining agent in solution hydrolyzes rapidly and within twenty-five to fifty hours can be regarded as being completely eliminated from the environment. However, dissolution is a slow process, with estimates indicating that 1 kg lumps remain for months and 100 kg lumps for several years.

Moreover, mustard, once it is released from the munition and dissolved, can generate concentrations at toxic levels only in the *immediate* vicinity of the disintegrated munition, generating a plume only tens of centimeters in length and several centimeters thick. *This is an upper bound.* Thus, any adverse environmental effect can result only from direct contact with mustard exposed on the seafloor.

Maximum Extent of Contamination of the Seafloor[1]
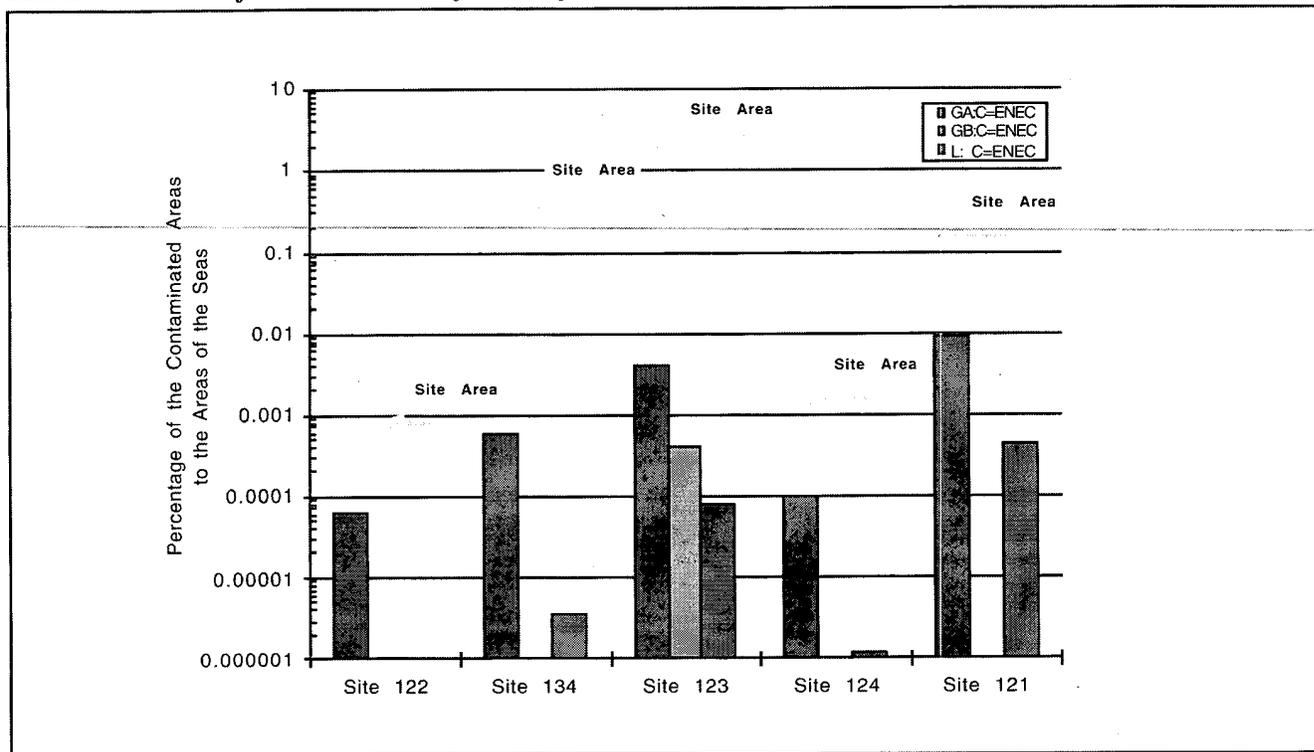
EXTENT OF CONTAMINATION: ENTIRE DUMP SITES

The extent of toxic waters at any given time at the dump sites were found to be limited to a small fraction of the area of the dump site itself and to heights of a few meters above the seafloor. In the worst case scenario, the entire area of the dump site would be contaminated to levels of EPEC and would remain so for years.

At the shallow dump site, Site 134, in the southern Barents Sea, there may be sufficient munitions to extend arsenic contamination upward throughout the water column. At the deeper sites toxic levels cannot extend upward toward the surface and into regions where increased light levels would support more biological activity.

The figure above shows an estimate of the fractional area of the seafloor that could be contaminated to an ENEC level at the various sites. The area fraction is referenced to the seafloor area of the regional sea in which the site is located. In this worst case estimate, it was assumed that all of the munitions release their CW agent over five years, an unrealistically short period, as the Baltic experience shows. It is seen that in all cases, the contaminated areas are less than the areas of the dump sites and are very small fractions of the total areas of the seas in which the dump sites are located. The fractional areas of the various sites are indicated for reference.

Because of the small sizes of the toxic plumes generated by individual munitions and the remote locations of the dump sites, there is very little possibility that toxic concentrations could be transported to nearby shores where they might more directly affect human activities. There is even less likelihood of transport to distant shores that would pose international concerns.

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[1]Note logarithmic scale in this figure.

THE ARCTIC ENVIRONMENT

All of the dump sites are located in relatively shallow continental waters. The Barents Sea has several basins 200 to 400 m deep among shallow banks and a large shallow area less than 100 m deep called the Pechora Sea. Most of the Kara Sea is less than 100 m deep, with deeper areas adjacent to Novaya Zemlya and troughs on the northern portion of the shelf. The White Sea has a central basin with a depth of 200 to 300 m and is connected to the Barents Sea by a shallow inlet of 25 m.

A pelagic (within the water column) food web is dominant in the waters deeper than 150 to 200 m. A bentho-pelagic (seafloor and water column) food web is dominant in shallower waters. The benthic (seafloor) community is an important component of the food web of the bentho-pelagic system and is much less important in the pelagic system. The figure below depicts the major components of the bentho-pelagic food web.

Components of Food Web
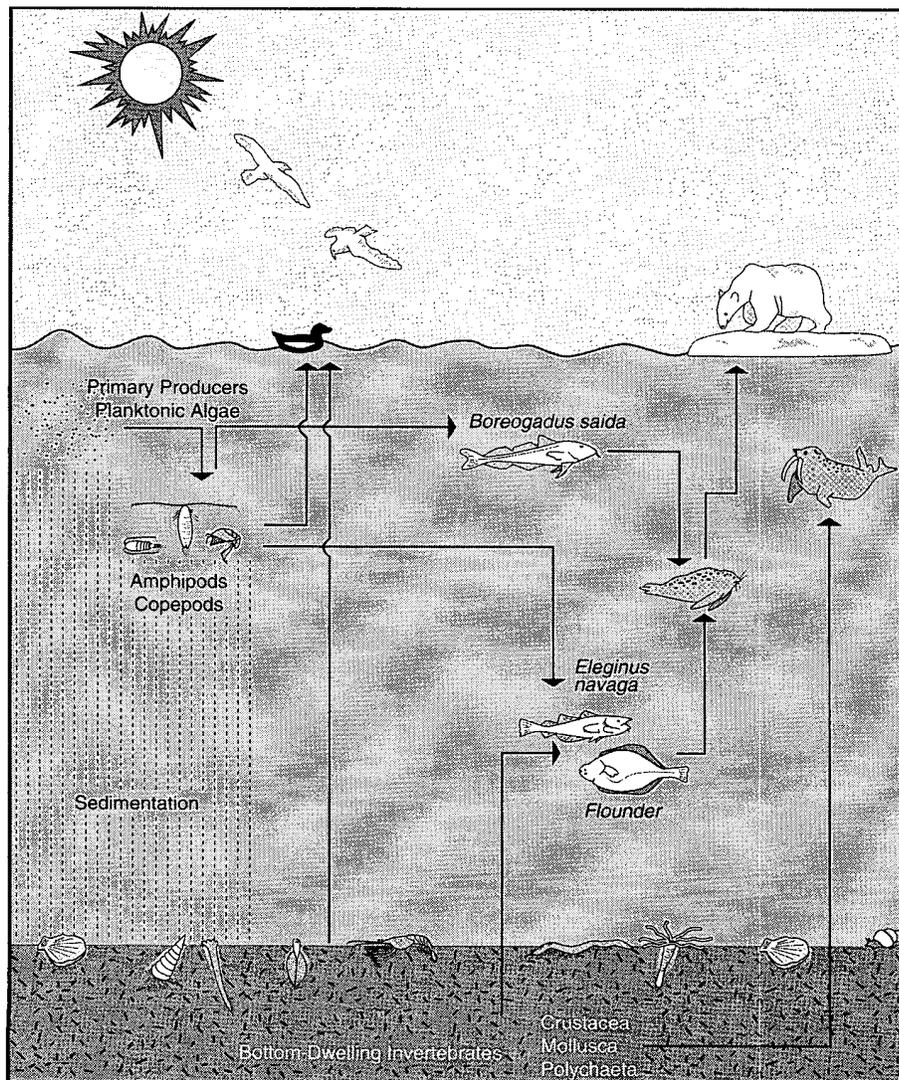
Barents Sea fish and shrimp populations are exploited by a large and important commercial fishery. Commercial fish landings from the Kara and White Seas are small in comparison. The Barents, White, and Kara Seas are areas of active exploration for oil and gas resources.

POTENTIAL THREATS TO THE ARCTIC ENVIRONMENT DUE TO PAST DUMPING

The regional marine systems can potentially be affected by a variety of activities past and present. These include the testing of nuclear weapons in the atmosphere on Novaya Zemlya, the disposal of solid and liquid radioactive material, the exploration and production of oil and gas resources, the over-exploitation of commercial fish stocks, and the disruption of benthic communities from using bottom trawls in the presence of dumped chemical weapons.

The main threats to marine ecosystems from the release of CW agents at the disposal sites are the direct toxicity of released agents and their breakdown products, bioaccumulation in the food web and long-term contamination of sediments from the arsenic contained in Lewisite.

Potential threats to human health and safety include the consumption of fish contaminated with arsenic, the capture of munitions and mustard lumps in trawl nets by the commercial fishery and the exposure of crews to agents during oil and gas resource exploration and development activities.

Potential economic threats are the loss of commercial fish markets because of arsenic contamination and increased costs of exploring for and developing offshore oil and gas resources.

Effects from chemical munitions would be cumulative with the adverse effects caused by other activities in the regional marine environments.

THE LIKELIHOOD OF A MAJOR ECOSYSTEM CATASTROPHE

This study found no evidence that the past dumping has led to a major catastrophe to the regional ecosystems or the arctic environment, as a whole, nor is there any evidence of a potential future threat of this magnitude.

The maximum area of the seafloor that could be affected by acutely toxic plumes would be no larger than the area of the disposal site and could be much less. In the absence of upwelling, toxic plumes would be present only within a few meters of the bottom. The worst-case effect would be the loss of benthic biomass and productivity in the disposal site area for up to a forty-year period.

The figure on the following page shows the distribution of benthic biomass in the Barents Sea in units of g m^{-2}. High values typically found in continental margins would be 300 g m^{-2} or greater. The dump sites are seen to be located in areas of relatively low biomass.

At the four deeper sites, the effect of losing this productivity on the ecosystem in the vicinity of the disposal site would be small because of the small contribution of the benthic community to the predominantly pelagic food web.

Effects on marine mammals would be small because the sites are too deep for walrus, which feed on benthic organisms, and are probably unattractive feeding areas for seals, because of the low benthic biomass present. Whale species that normally exploit mid-water food sources would not be likely to enter water very near the bottom.

It is unlikely that toxic levels at the shallow southern Barents disposal site, Site 134, would reach high enough levels to result in catastrophic effects. Effects on the size of the bird, walrus, and seal populations on

Distribution of Benthic Biomass in the Barents Sea

Units=g m^{-2}

up to 10	10-25	25-50	50-100	100-200	200-300	300-500	500-1000	over 1000
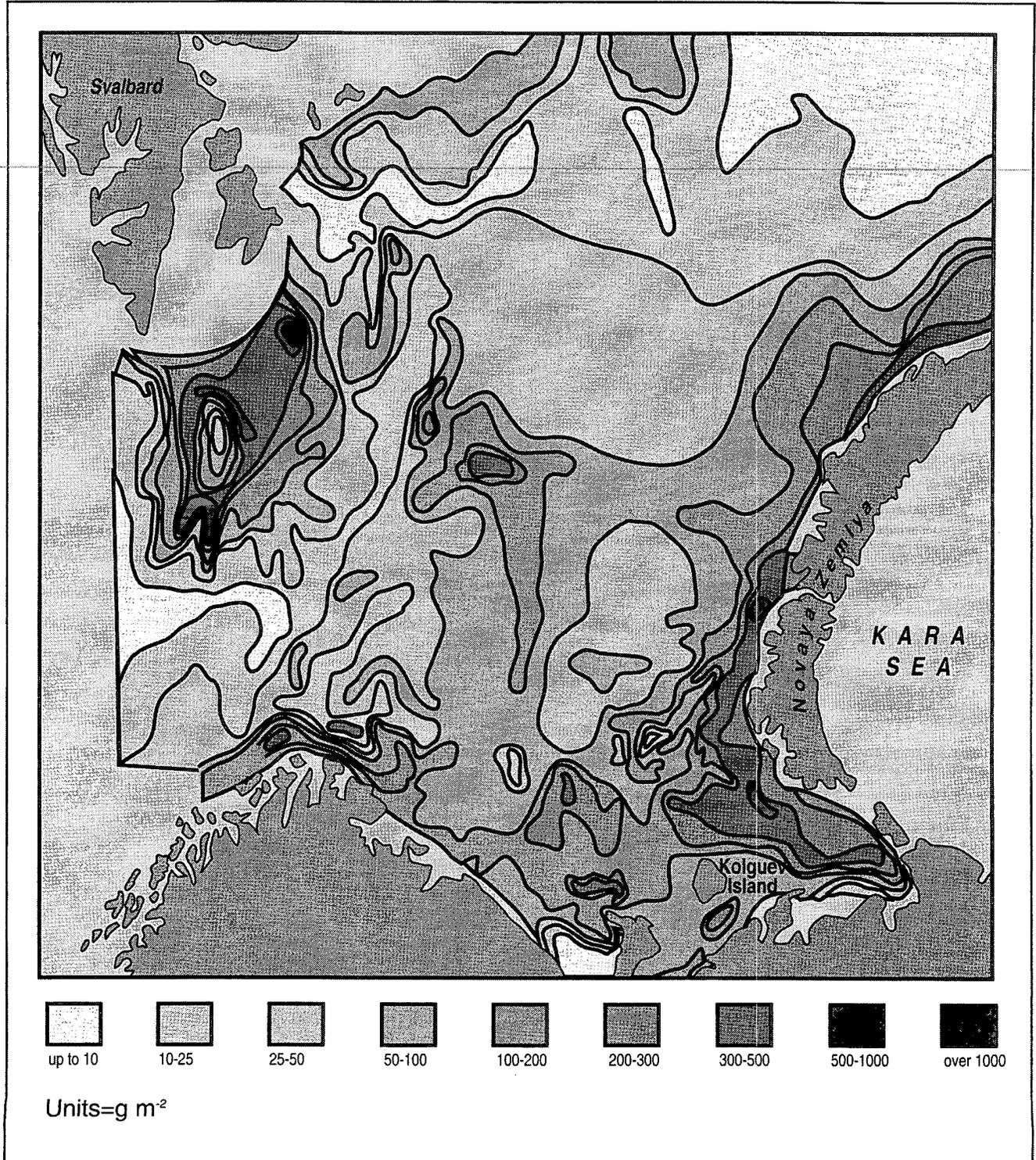
the northern and western shores of Kolguev Island could be moderate to large because the loss of the benthic productivity within the site area could significantly reduce the carrying capacity of the marine region supporting these populations. Effects on the larger Pechora Sea region would be small because the benthic area affected is small relative to the shallow production area within the 100 m isobath. The area of toxicity is also very small at this scale and could only affect a small portion of the stocks of pelagic organisms that are widely distributed in the region.

VIABILITY OF IMPORTANT MARINE SPECIES

It is improbable that any dominant regional species would be so significantly affected as to imperil its viability.

The major vertebrate and invertebrate populations are distributed over regions very much larger than the disposal sites. The contribution of benthic communities at deep disposal sites to pelagic stocks is small. The loss of carrying capacity at the shallow site is small compared to the very large regions that support the major stocks of invertebrates, fish, marine mammals, and birds.

While this study was conducted on the basis of the five identified CW disposal sites, there is sufficient diversity in their ocean environments to provide some confidence that the major results are relatively insensitive to details of site location. It is important to appreciate that while this assessment finds little possibility of major catastrophes to ecosystems or species, ocean dumping or highly toxic CW agents will certainly harm, even kill, numbers of individual organisms within the areas of the dump sites.

ECONOMIC EFFECTS

Any economic effects on the commercial fishery in the Barents, Kara, or White Seas are likely to be small to moderate. Effects of contamination on the size of commercial fish stocks would be very small, as discussed above. Bottom trawling is currently not a harvesting method extensively used at the deep disposal sites and fishing is currently strongly discouraged in all disposal sites.

Some fish in the vicinity of the shallow disposal site are likely to have increased body burdens of arsenic. Sale of fish harvested from this area could be banned in Finland and the United Kingdom if their arsenic concentration increases as the result of degradation of Lewisite. At present, these two European countries are the only countries that have standards for the maximum arsenic concentration allowed in commercial fish products. Sale of fish oils would probably not be affected because the refining process greatly reduces the content of contaminants.

HUMAN HEALTH AND SAFETY

Human health and safety concerns could potentially involve exposure of people engaged in off-shore activities, (fishing and oil/gas drilling), consumption of contaminated fish or shellfish, and the possibility of toxic concentrations being washed ashore by ocean currents.

It is highly unlikely that human health or safety could be impacted by toxic concentrations being carried ashore by ocean currents. Estimates of the extent of such concentrations show them to be limited to the immediate vicinity of the dump site.

Commercial fishing and offshore drilling and pipe laying crews could be directly exposed to chemical agents if these activities are carried out in the disposal sites.

Munitions still containing agents or solid lumps of mustard could be captured in trawl nets fished on the bottom. Boat crews would be at great risk of injury or death when the nets are brought on board, which has occurred for many years in the Baltic Sea and the Sea of Japan. Drilling crews could be exposed to a chemical agent that contaminates drilling mud or drill strings, which are materials and items that return to the drilling platform when drilling operations are carried out. Pipe laying crews could be exposed to agents brought to the surface and to agents on equipment used for pipeline construction. All of these are "point problems" specific to dump sites.

The region near Site 134 in the southern Barents Sea is an area of intense commercial fishing. Inorganic

arsenic is a proven carcinogen in humans. However, up to 99 percent of arsenic in fish tissue is in organic forms, which are not known to be carcinogenic. The discussion below assumes that the total arsenic is 99 percent in organic forms.

The increased risk to consumers eating fish quantities at the high end of the range, the 95th percentile, in the United States is likely to be small to modest. The increased risk from consuming fish contaminated with arsenic at 10 ppm of total arsenic (ten times the likely natural concentration) is in the range of one in 10,000 to one in 100,000. This is at the upper end of the range of increased risk usually acceptable to regulatory agencies concerned with human health. This estimate is conservative because it is based on the assumption that 50 to 100 percent of the fish consumed over a seventy-year lifetime is contaminated at 10 ppm.

The risk to indigenous peoples consuming large quantities of fish contaminated with arsenic at 10 ppm as a significant portion of their diet could be moderate. Given this level of consumption, the increased risk would be in the range of one in 1,000 to one in 10,000. The upper end of this range is a conservative estimate because it is based on consuming contaminated fish at all meals for a seventy-year lifetime.

CUMULATIVE EFFECTS

A variety of past and current activities in the Barents, Kara, and White Seas have adversely affected the marine environment. Any adverse environmental or economic effects resulting from the presence of chemical munitions would add to these effects.

The White Sea receives industrial and domestic wastewater effluents from human activities. The open press reported a 1990 spill of thousands of tons of rocket fuel into Dvina Bay from the Russian military base at Severodvinsk. This spill may have been the cause of an apparently large kill of invertebrates, fish, and seals in a large area of the Bay. Acid deposition, caused by atmospheric transport of emissions from the burning of fossil fuels in Europe, is occurring in the region. Acidification of regional soils may be a consequence of this deposition and may be causing the release of some metals from the soils into runoff

reaching the sea.

A variety of activities have affected the Barents Sea ecosystem. These include nuclear weapons testing in the atmosphere on Novaya Zemlya and in the offshore waters, disposal of liquid and solid radioactive materials, oil and gas exploration and production, and possible over-exploitation of the fishery. A very large proportion of the area of benthic habitat in the shallow central and southern areas of the Barents Sea may be damaged by bottom trawling. Although the magnitude of the damage is not known, the claim of damage has been disputed.

ENDANGERED SPECIES

The following animals are known to be or could be in the region and are considered threatened or endangered: the polar bear, the Atlantic walrus, the gray seal, the narwhal, the bowhead whale, the beluga whale, the harbor porpoise, and Dall's porpoise. These species are unlikely to be affected at the deep disposal sites. Data on the occurrence of these species at the shallow site was not found during our study, but there may be some risk to endangered species at this location.

The Atlantic walrus has the greatest potential to be affected at the shallow Southern Barents site. This species feeds predominantly on benthic organisms and could be exposed to toxic plumes and contaminated sediments. The site is in the historic range of this species, although no data on its existence at the site was found. The potential for effects on this species is likely to be small because the current occupied range of this species is large compared to the contaminated area.

BIOACCUMULATION AND LONG TERM EFFECTS

Most chemical agents and breakdown products would not bioaccumulate in the food web. Arsenic has a modest potential to bioaccumulate in the trophic levels most closely associated with arsenic-contaminated sediments. Some increase would occur in higher trophic levels. Biomagnification to high concentrations would not occur. Significant effects on the ecosystem

due to arsenic bioaccumulation are not likely. The potential exists, however, for economic effects on the commercial fishery, as discussed above.

Arsenic in Lewisite is released from munitions in organic forms. It is likely that these compounds would continue to undergo reactions to inorganic forms and enter the natural cycle of arsenic in the physical and biological environment of the region. The transport processes for arsenic in the marine environment are not well understood.

An area of sediment affected at 90 ppm was estimated for several quantities of Lewisite in order to bound the issue. This is the concentration that is likely to have significant effects on benthic organisms. For Lewisite quantities at Barents, and Kara Sea sites ranging from 7,500 tons to 75,000 tons, the area affected would be 240 - 2420 km^2. For Lewisite quantities at the White Sea site ranging from 4,000 to 40,000 tons, the area affected would be 130 - 1290 km^2. The likely effect of arsenic in sediments at 90 ppm would be to reduce benthic biomass and species diversity permanently.

Ecosystem effects at the deep disposal sites would be small because of the small coupling between the benthic community and the dominant pelagic community in the food web occurring in the deeper waters of the region.

Effects at the shallow disposal site would include a reduction in carrying capacity of the Kolguev Island region and some contamination of the food web by arsenic, as discussed above. The existing area is about 5,000 km^2 and is contaminated with arsenic in the Pechora Sea off the southern coast of Novaya Zemlya. If a large area is contaminated at the disposal site, the total contaminated area could be nearly 10 percent of the Pechora Sea region within the 100 m isobath. Permanent loss of some benthic productivity over a region of this size could have a modest effect on the carrying capacity of the Pechora Sea region.

SIGNIFICANT UNCERTAINTIES

While there are many uncertainties that could alter details of the analysis in this assessment, there are only a small number that could significantly alter the overall findings.

Total quantities of CW munitions dumped into arctic seas could be less, even significantly less, than indicated here, with correspondingly reduced likelihood for environmental impact.

All the evaluations of biological impact conducted in this study were based on applying the three benchmark concentrations uniformly to all marine species. This must remain as one of the most important sources of uncertainty, one that would be difficult to remove.

If bottom trawling does occur at the arctic CW dump sites, release of agents could be significantly accelerated and direct and acute harm to individuals and to fish catches is possible.

There are several additional uncertainties important to the analysis of environmental effects. These include the following: the rate of agent release from munitions, transport and fate of arsenic in Lewisite, the number and type of munitions present at each site, and knowledge of the physical and biological conditions at each site and its vicinity.

The rate of release of agents from a corroded munition is important to determining whether acute toxicity is an issue at a site. At slow but plausible release rates, essentially no toxic plume would be produced. In this situation, there would be no effects from acute toxicity. Additional analysis of corrosion processes could provide some additional insight as could observations of dump sites.

More detailed modeling of arsenic transport could provide some better definition of the area affected at each site. How far the arsenic in Lewisite and its breakdown products are transported before depositing in the sediments determines the concentration of arsenic contamination.

If third generation CW materials, such as V-gas, have been dumped into arctic seas, one could not easily exclude the possibility of environmental impact on a very much wider basis than found here. No anecdotal evidence of V-gas dumping in the Arctic has been found. However, the very long half-life (approximately five years) of V-gas, and its high toxicity suggest that a more careful examination of this question might be warranted.

CONCLUSIONS AND RECOMMENDATIONS

This study has found only a very small likelihood that the past dumping of chemical weapons in arctic seas would cause such a widespread impact on the arctic environment that it would be of concern to U.S. national security, however broadly that is interpreted. However, local adverse impacts may be present but the uncertainties in this dimension of the assessment are large.

The most important information gaps involve the location and condition of the dump sites, the types and amounts of munitions dumped, and when they were dumped. In addition, no reports similar to the various European studies of the Baltic tracking reports of fishermen encountering CW munitions were found.

It is our recommendation that the U.S. Government not approach this information gap solely as a conventional intelligence problem. Rather, it should be viewed largely as a *scientific problem*, one where the intelligence and the scientific communities could collaborate.

Russian cooperation should be solicited to share information regarding past ocean dumping in both U.S. and Russian waters. Both countries could carry out an oceanographic survey of one of the dump sites considered in this assessment, including collection of water, sediment, biological samples, and underwater photography of the condition of the munitions. In addition, a low-level ongoing effort might be put in place to monitor local fishing conditions and, especially, to collect any information regarding encounters with chemical weapons debris in fish catches. These efforts should draw heavily upon the Baltic experience beginning with a comprehensive review of existing studies and site surveys of the various Baltic CW dump sites.

Advantage should be taken of any serendipitous opportunity that arises in connection with a planned oceanographic cruise in order to collect sediment, water samples, and even underwater photographs from one of the dump sites.

1.1 PROBLEM STATEMENT

The objective of this study was to develop a quantitative assessment of the potential for significant adverse environmental impact on arctic ecosystems arising from chemical warfare (CW) munitions dumped in arctic seas. While there have been several assessments of environmental impact associated with CW ocean dumping, there has been no quantitative evaluation of the amounts of CW agents that could be released into the sea, the level and duration of produced toxins, the effects on specific marine species, human health and safety, or economic factors.

It is important to appreciate that what was intended here was to understand the magnitude of any effects on arctic ecosystems and related human factors. It was not to conduct an assessment of compliance with U.S. law or international convention of ocean dumping of CW munitions. Further, to the extent that a full understanding cannot be reached because of unknown factors, the test to be applied will be that of "significant effect." For this study, this was taken to mean an effect large enough to have national security significance, perhaps through economic impact on the commercial fish market or to human health and safety. The four toxic agents (TA) examined in this study are Tabun (GA), Sarin (GB), mustard (H), and Lewisite (L).[1]

1.2 HISTORICAL CONTEXT

Immediately after World War II, Allied Forces needed to dispose of German and Japanese chemical weapon stockpiles. It was decided then that the simplest and safest method for disposal was to dump the captured stocks into marked disposal areas in the marine environment referred to as *dumping grounds*. Because official records either no longer exist or never existed, details on the dumping locations, quantities, and types of chemical munitions are often sketchy.

Accidents, mostly involving fisherman snaring chemical weapons with nets, have raised concerns regarding these dumping grounds (see Figure 1-1). These accidents have resulted in a variety of injuries and provide insight to life spans of the chemical agents dumped in seawater.

Figure 1-1: Schematic Illustration of Ocean Dump Sites

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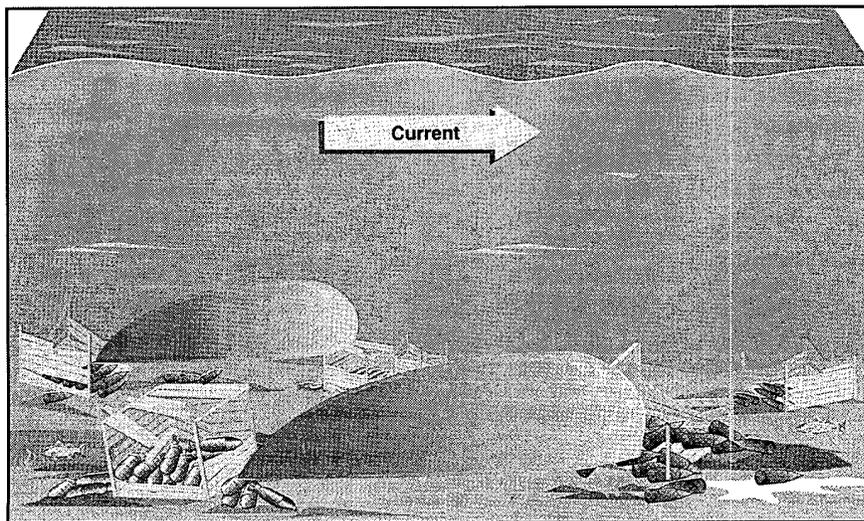
[1]Throughout this study, the German names, common names, and U.S. military designations of toxic agents were used interchangeably. Generally, the German names and common names were used in the narrative and the military designations were used in tables, equations and discussions thereof.

1.2.1 Chemical Munitions Dump Sites in the Baltic Sea

At the end of World War II, large ammunition depots were discovered in Germany containing mustard gas grenades and mustard gas, irritants (Clark I, Clark II, and Adamsite), and tear gas bombs. From 1946 to 1947, an estimated 50,000-150,000 tons of chemical munitions were dumped at a depth of approximately 100 meters in the Bornholm basin, fifteen miles off the Danish Island of Bornholm. Figure 1-2 details the official dumping grounds in the Bornholm Basin. Approximately 2,000 tons of chemical munitions, predominantly mustard gas and irritants, were dumped in the Gotland basins off the coast of Sweden.

Unofficial dumping took place as well, according to eyewitnesses who reported dumping activities north of the Gotland basins.[2,3] Table 1-1 is a compilation of what is known to have been dumped officially and unofficially in the Baltic Sea.

Figure 1-2: Official Dumping Grounds in the Baltic Sea[4]

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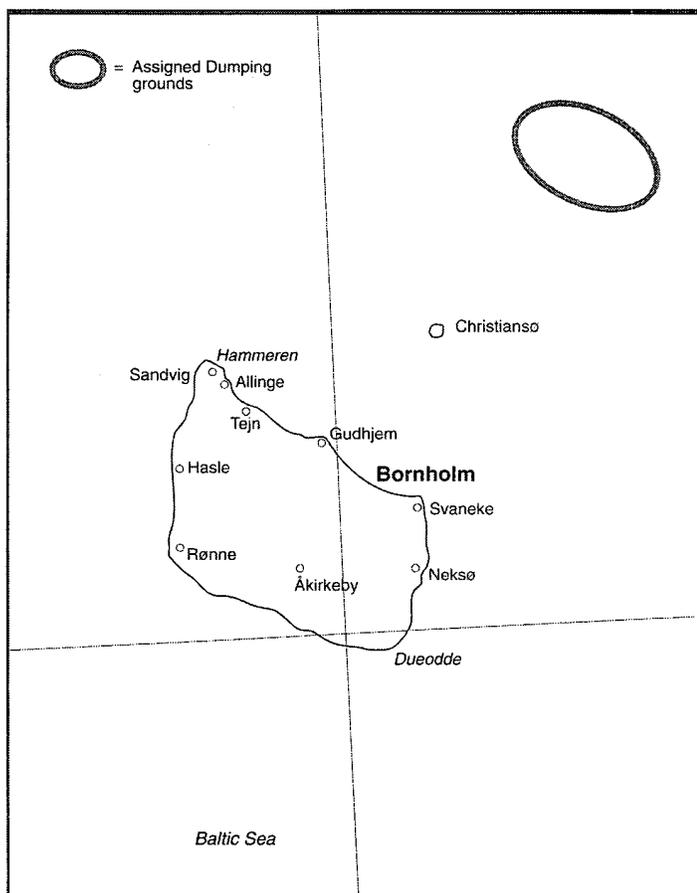
[2]Jorgensen, B.S., B. Olesen. and O. Bernsten, "Mustard Gas Accidents on Bornholm." *Danish Medical Weekly,* 8 July 1985, Vol. 147, No. 28. Published by the Danish Medical Society.

[3]Theobald, N. and N. Ruhl, "Chemical Warfare Agent Munitions in the Baltic Sea." *German Journal of Hydrography,* 1994, 46. 121-131, Current problems of the sea environment. Account of the Third International Scientific Symposium, held 4-5 May 1993, Hamburg.

[4]Reference 2.

Table 1-1: CW Dumping in the Baltic Sea[5]

Locations	Munitions Quantities	Chemical Agent Quantities	Chemical Agent Type
Bornholm Basin	35,300 to 43,300 tons	5,300 to 6,500 tons	Mustard, viscous mustard, Clark I, Clark II, Adamsite, chloroacetophenone, Phosgene, nitrogen mustards, Tabun
Sea area southwest of Bornholm	Up to 15,000 tons	2,250 tons	Unknown
Gotland Basin	2,000 tons	300 tons	Unknown
Little Belt	5,000 tons	750 tons	Tabun, phosgene

1.2.2 Chemical Munitions Dumping in Japanese Waters

Details of dumping operations in Japanese waters were not widely known until 1972 when the Japanese Prime Minister commissioned a national inquiry to investigate the status of the chemical weapons disposed of in the 1940s. Numerous accidents in the 1960s and 1970s prompted the inquiry and some details are now known.[6]

After the war, the elimination of chemical weapons was conducted by the U.S. occupation forces. As with the German weapons, it was determined that the safest method was to dump them in the sea in officially marked areas (see Figure 1-3). The U.S. mandated that the dumping areas be at least ten nautical miles from the Japanese shore and at depths of at least 1,000 m. The dumping operations were carried out by Japanese workers in chartered disposal ships. It is believed that

prior to the close of the war, the Japanese Imperial Army buried chemical munitions on land and dumped chemical weapons into the sea in unmarked disposal sites. Although no records of official burial sites were noted, there were reports of numerous accidents occurring away from the official dumping sites.[7]

1.2.3 Ocean Dumping of CW Agents by the United States

The United States used ocean dumping as a method for disposal of CW agents until August 1970, when the practice was discontinued. Table 1-2 summarizes ocean dumping for which records are available.

It appears unlikely that a completely accurate record of United States dumping activities can be reconstructed. In 1987, William R. Brankowitz of the U.S. Army Office of the Program Manager for Chemical Munitions (Demilitarization and Binary) (Provisional)

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[5]Reference 3.
[6]Kurata, H., The Joint Staff College of Defense Agency, Tokyo, Japan, *Lessons Learned from the Destruction of the Chemical Weapons of the Japanese Imperial Forces.*
[7]Reference 6.

Figure 1-3: CW Dumping Grounds in Japanese Waters[8]
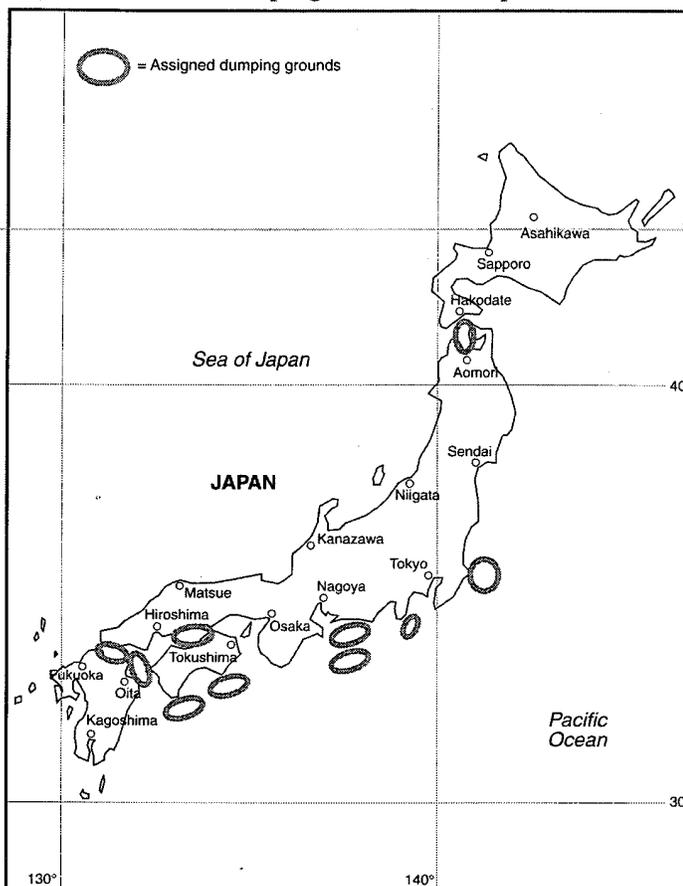
compiled a history of U.S. chemical weapons movements between 1946 and 1986.[9] Mr. Brankowitz stated that "had all of [the Army records] been preserved, [they] would have made for a complete record of all operations. Unfortunately, this was apparently not the case." In testimony before a Congressional subcommittee, the Department of State testified that the Department of Defense had not been able to provide records as to where it had dumped chemical munitions.[10] The United States Government is doubtful that it would be able to account completely for all of CW agent dumping following World War II.

In addition, there do not appear to be any surviving records concerning pre-war activities.

Those records that do survive identify the ports of departure for ocean dumping; however, locating exactly where the actual dumping occurred is sometimes difficult. The quantities dumped are given in many cases as a number of barge loads, or the name of the ship. In several cases, the movements of CW agents into the port prior to dumping can be found; however, the quantities are given as the number of rail cars. Such records do not account for material loaded

[8]Reference 6.

[9]Brankowitz, W. R., *Chemical Weapons Movement. History Compilation*, Office of the Program Manager for Chemical Munitions (Demilitarization and Binary) (Provisional), Aberdeen Proving Ground, MD, SAPEO-CDE-IS-87001, 12 June 1987, AD-A193348.

[10]*Ocean Disposal of Unserviceable Chemical Munitions*, hearings before the Subcommittee on Oceanography of the Committee on Merchant Marine and Fisheries, House of Representatives, Ninety first Congress, 3-7 August 1970, Serial no. 91-31, p. 102.

Table 1-2: *Summary Table of U. S. Dumping of Chemical Warfare Agents at Sea*

Agent	Loading Point/Destination (if known)	Date	Munition	Estimated Quantity
Phosgene	New Orleans Port of Entry, Braithwaite, LA	May 1946	Bombs	Less than 1 ton
	San Jacinto Ordnance Depot, Houston, TX			
	Charleston, SC/Site "Baker"	Aug 1946	Bombs, Mines, Bulk	Portions of 3 barge loads
Cyanogen Chloride	Edgewood Arsenal, MD/38°30'N 71°06'W	2-7 Aug 1964	Bulk, Projectiles	Less than 1 ton
GA	Charleston, SC/Site "Baker"	8-22 Aug 1946	Bombs, Mines	Portions of 2 barge loads
GB	Colts Neck Naval Pier, Earle, NJ/39°39'N 70°57'W	15 Jun 1967	Bulk, Rockets	39 tons
	Colts Neck Naval Pier, Earle, NJ/39°33'N 71°02'W	19 Jun 1968	Bulk, Rockets	266 tons (total GB and VX)
	Sunny Point, NC/29°21'N 76°0'W	18 Aug 1970	Rockets (vaults)	67 tons
H	Attu and Adak, Alaska/12 miles off Chichagoff	1947	Bulk	Unspecified
	Charleston, SC/Site "Baker"	Aug-Oct 1946	Bombs, Projectiles, Mines. Bulk	Over 7 tons
	Colts Neck Naval Pier, Earle, NJ/39°39'N 70°57'W	15 Jun 1967	Rockets, Bulk	3.890 tons
	Colts Neck Naval Pier, Earle, NJ/39°33'N 71°02'W	7 Aug 1968	Contaminated water	2,975 tons
	Edgewood Arsenal, MD/38°30'N 72°10'W	18 Jun 1962	Projectiles, Bulk	3 tons
	Edgewood Arsenal, MD/38°30'N 71°06'W	6-7 Aug 1964	Bulk, Projectiles	65 tons
	Naval Mine Depot, Yorktown, VA/Site "Baker"	21-25 Mar 1946	Projectiles	13 tons
	New Orleans Port of Entry, Braithwaite, LA	1-7 Mar 1946	Projectiles	207 tons
	NWS Concord, CA/37°40'N 125°0'W	8-19 Apr 1958	Bulk	9,030 tons
	Theodore Naval Magazine, Mobile, AL	13 Jul 1946	Bombs (German)	7 tons
Nitrogen mustard	Sunny Point, NC/"off South Carolina"	20-27 Mar 1958	Bulk	54 tons
	NWS Concord, CA/37°40'N 125°0'W	25 May 1958	Bulk	9 tons
L	Attu and Adak, Alaska/12 miles off Chichagoff	1947	Bulk	Unspecified
	Charleston, SC/Site "Baker"	Aug-Oct 1946	Bombs, Bulk. Projectiles. Mines	1,222 tons
	Charleston, SC/"300 miles off Florida"	15-20 Dec 1948	Bulk	3,154 tons
	Colts Neck Naval Pier, Earle, NJ/37°50'N 70°37'W	13-14 Nov 1957	Bulk	41 tons
	Edgewood Arsenal, MD/38°30'N 72°06'W	6-17 Jun 1960	Projectiles, Bulk	2 tons
	Edgewood Arsenal. MD/38°30'N 71°10'W	11-18 Jun 1962	Projectiles, Bulk	1 ton
	NWS Concord, CA/37°40'N 125°0'W	8-19 Apr 1958	Bulk, Bombs	1,257 tons
		25 May 1958	Bulk	285 tons
	Sunny Point, NC/"off South Carolina"	20-27 Mar 1958	Bulk	1,281 tons
Unspecified	Theodore Naval Magazine, Mobile, AL	Jan-Feb 1955	Unspecified	Barges (1 or 2)
VX	Colts Neck Naval Pier, Earle, NJ/39°33'N 71°02'W	19 Jun 1968	Bulk, Rockets	266 tons (total GB and VX)

at CW agent storage depots, *e.g,.* taken by barge from Edgewood Arsenal.

The United States dumped Lewisite between 1946 and 1962. Lewisite was loaded on ships and barges at Attu and Adak, Alaska; Concord, CA; Colts Neck, NJ; Edgewood Arsenal, MD; Sunny Point, NC; and Charleston, SC. Of particular significance were the following events:

- In late 1946, an estimated 1,222 tons[11] of Lewisite and 7 tons of mustard were shipped to Charleston, where there remained some mustard, phosgene, and Tabun that had arrived by ship from Europe. This material was dumped loose from barges.

- In December, 1948, the Army conducted Operation Geranium, during which 3,154 tons of Lewisite[12] were loaded aboard the S. S. Joshua Alexander, a World War II merchant hulk, in Charleston.

- In March, 1958, 1,281 tons of Lewisite and 54 tons of mustard[13] were dumped from barges loaded at Sunny Point.

- In April, 1958, the S. S. William Ralston was loaded in Concord with 1,257 tons of Lewisite and 301,000 M70 bombs containing mustard,[14] and scuttled at sea. In addition, 285 tons of Lewisite and 9 tons of mustard[15] were loaded onto a barge in Concord for dumping in May, 1958.

The available documents were not always precise in identifying where these dumps occurred. For example, "Atlantic Ocean, Dump Site 'Baker'" was the destination of the 1946 dumping campaign. However, in a number of cases there are strong indications as to specific dumping locations. The material loaded at Sunny Point in 1958 was dumped in the "Atlantic Ocean Off South Carolina." Records from the Naval operation CHASE in the mid-1960s indicated that a ship of surplus ammunition, loaded in Charleston, was sunk approximately 235 statute miles southeast of Charleston.[16] The Operation Geranium ship was scuttled "300 miles off Florida"; a site located 282 statute miles east, northeast of Cape Canaveral, Florida was used for ocean dumping of CW agents loaded at Sunny Point in 1970.[17] In contrast, records indicate that the S.S. William Ralston and the barge loaded at Concord were sunk at 37°40'N 125°0'W, approximately 55 statute miles west of San Francisco. Further investigation of Naval records might provide more precise locations for all the Lewisite dumping events described above.

Although ocean dumping had been widely used for the disposal of CW agents and munitions for many years, American public attention focused on the issue in the late 1960s. An *ad hoc* committee of the National Academy of Sciences (NAS) was appointed in response to an Army request to evaluate the hazards involved in the execution of planned ocean disposal of surplus CW stocks in 1969. The committee began its report by noting that "continuing inaction will not reduce the hazards of eventual disposal of the chemicals and munitions intended for disposal in the 1969 Operation CHASE, and in some instances will increase them." The committee then made several specific recommendations concerning the surplus chemical warfare munitions:

- For cluster bombs containing agent Sarin, disassembly at their storage site and chemical destruction of the withdrawn Sarin.

- For bulk containers of agent mustard, incineration.

- For concrete and steel "coffins" containing Sarin-filled rockets, further study by a technical group including experts on demolition to consider whether there was a practically feasible way to dispose of the coffins on an Army establishment. In the event that the proposed study could provide no feasible alternative method, the NAS committee

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[11]These are estimates of the actual weight of CW agents, based on the number of rail cars of munitions shipped to the port, a capacity of 20 tons of munitions per rail car, and typical fill weights for U.S. munitions (17% mustard by weight in projectiles, 30% agent by weight in bombs, and 53% agent by weight in bulk containers).
[12]Actual weight of CW agents calculated from counting dumped containers and munitions; Brankowitz, W. R., personal communication.
[13]Reference 12.
[14]Reference 12.
[15]Reference 12.
[16]SS Monahan, CHASE 9, 30 April 1967, at 31°40'N., 75°59'W. Reference 10, p. 99.
[17]SS LeBaron Russell Briggs, CHASE 10, 18 August 1970, at 29°21'N., 76°00'W, Reference 9 and Reference 10, p. 33.

recommended ocean dumping of the coffins. This is in fact what occurred.

The committee concluded with a suggestion outside its terms of reference that "the Department of Defense adopt basically the same approach to CW agents and munitions that the Atomic Energy Commission has adopted toward radioactive waste products from nuclear reactors. It should be assumed that all such agents and munitions will require eventual disposal and that dumping at sea should be avoided."

In 1972, the United States signed the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, which explicitly prohibits the dumping of materials "produced for biological or chemical warfare." Other signatories of the convention include nations such as France, Italy, Japan, the Union of Soviet Socialist Republics, and the United Kingdom which formerly or currently stockpile chemical weapons. Also in 1972, the Marine Protection, Research, and Sanctuaries Act was enacted, which prohibits the ocean dumping of chemical warfare agents from the United States.

In 1984, another NAS Committee was asked to review methods for disposal of the U.S. Army's stockpile of CW agents. The Committee noted that ocean dumping was not consistent with current national and international law and "attempting either to modify the laws or to seek an exception does not seem justified at this time;" no detailed technical evaluation of the ocean dumping option was made.

1.2.4 Accidents Related to CW Ocean Dump Sites

Accidents have been reported in both the Baltic Sea and along the coast of Japan. No reported accidents due to CW dumping were found in references on U.S. disposal activities other than accidents reported during the dumping operations in the late 1940s. Most reports in Germany and Japan were from fishermen who inadvertently had snared chemical weapons casings with their nets. In many instances, the fishermen were unaware of the danger of the chemical agents and severe injuries resulted. Accidents were also reported during the CW disposal process and during the decontamination of exposed vessels.

It is to be noted that because Denmark pays fishermen for the discovery of contaminated catches, there is extensive statistical data on the findings of chemical agents in the Baltic Sea by Danish fisherman.[18] The statistical data exists from 1976 to 1991. In the time between 1976 to 1990, the annual reported incidents range from five to forty-eight. In 1991, there was an increase to 101 discoveries. The reasons for this increase are not entirely clear although shifts in fishing grounds and heightened awareness of the problem among Danish fishermen are probable causes. German fishermen receive no incentive to report findings of chemical agents and therefore, there are fewer reports about finds by German fishermen in the Baltic Sea.

Most accidents have involved the dredging up of mustard gas, which over time typically forms an outer crust with a volatile, viscous liquid core. In liquid form, mustard gas penetrates ordinary textiles and leather in a few minutes, although oilskins, rubber and plastic offer limited protection.[19]

General injuries resulting from contact with chemical weapons include lesions accompanied by rashes, blistering and, in extreme cases, pathological death of tissue. Eyes are also commonly affected through the development of lesions, increased tear flow, sensitivity to light and swelling of the tissues.[20]

1.2.4.1 Baltic Sea Accidents

Figure 1-4 shows the distribution of mustard gas injuries by year in the Baltic Sea. From 1946 to 1984, there were a total of 197 patients reported suffering from mustard gas exposure in the Baltic Sea. A total of 171 were treated as ambulatory patients and 26 were admitted to the hospital. In both 1947 and 1948, there were two reported deaths resulting from a mustard disposal mishap. The study ran only through 1984.[21]

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[18]Reference 3.
[19]Reference 2.
[20]Reference 2.
[21]Reference 2.

Figure 1-4: Baltic Sea Accidents[22]
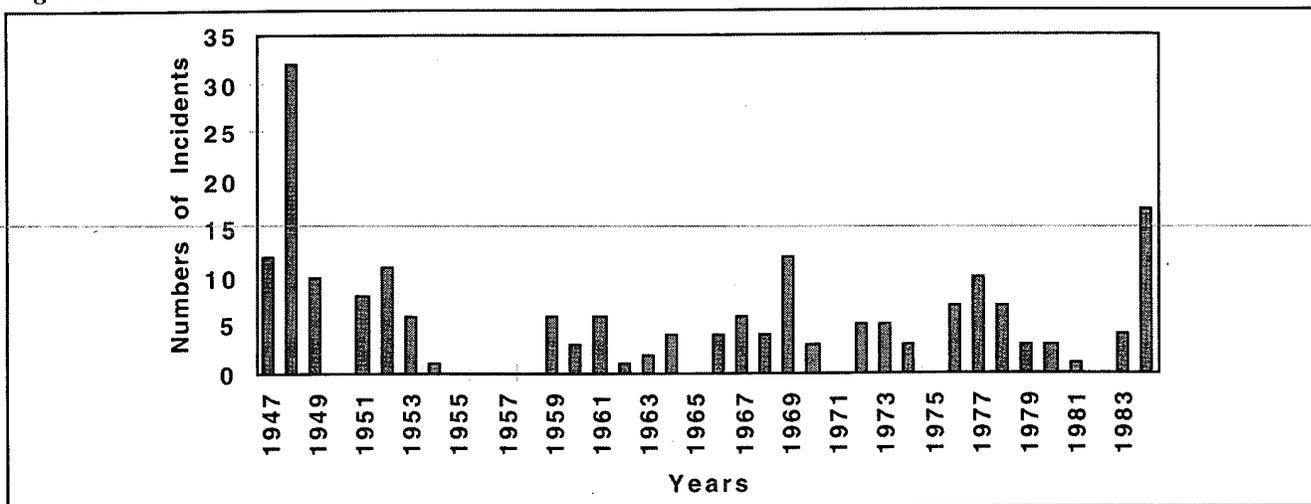
1.2.4.2 Japanese Accidents

In Japan, there were 102 reported incidents, resulting in 123 injuries and 20 casualties (see Figure 1-5).[23] These incidents include accidents attributed to both unofficial land and sea disposal as well as official sea disposal.

There was no distinction made in the reported accident statistics between land and sea incidents. It was noted that many of the accident sites have occurred on land and are attributed to unofficial disposal of chemical weapons by the Japanese Imperial Army, probably during the later stages of World War II.

Figure 1-5: Japanese Waters Accidents[24]
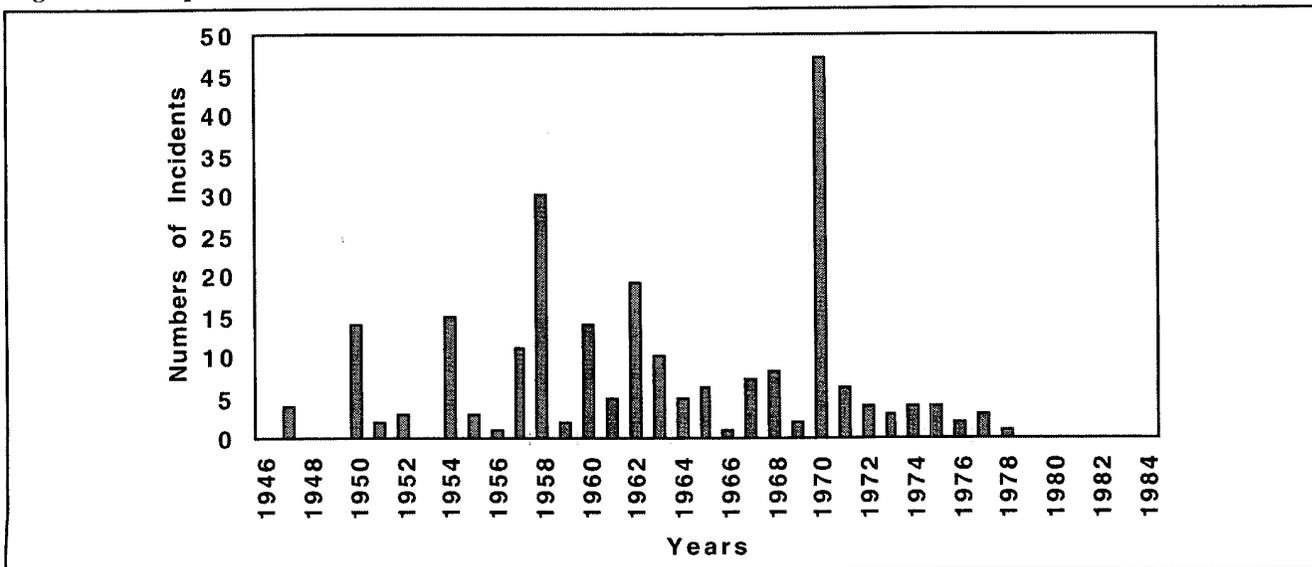
[22]Reference 2.
[23]Reference 6.
[24]Reference 6.

1.3 APPROACH

This study estimates the environmental impact of chemical munitions disposed in the Russian arctic. As such, there are many imponderables, not the least of which concerns the quality and diversity of information. Most of what is known comes from anecdotal sources. This study is based on the best estimates, which were synthesized from all sources concerning such disposal and then modulated by the total quantities known to have been in stockpiles pursuant to the 1972 International Convention on Chemical Munitions.

The toxic agents challenge the environment in varying ways:

• Some agents are basically immobile and relatively non-toxic in seawater once released from munitions;

• Other agents have very short persistence in seawater and, therefore, are of limited concern;

• Some compounds may have the potential for bio-magnification, resulting in their concentrations increasing as they pass upward through the food chain;

• Toxic levels for some CW agents are so low that one cannot exclude, *a priori*, their effects over very large scales, such as the entire arctic, as ocean currents transport toxic plumes;

• CW agents add to an already existing burden of anthropogenic contamination of the seas by a wide variety of toxic compounds (*e.g.*, from industrial wastes) and contribute to a cumulative effect at the ecosystem level not obvious when considering only direct toxicity on individual species;

• Finally, other agents may still be contained in dumped munitions and could pose future environmental or health risks as their casings corrode and agents are released into the environment.

Each agent released into the sea is transported by ocean currents and, possibly, by general ocean circulation, while the processes of chemical reaction and dilution take place. The processes of transport, dilution, and chemical persistence were evaluated in light of the biological toxicity of each agent. Once the volumetric and aerial extent of toxicity is estimated, the ecosystem impact is evaluated over this domain. It is at this point that we provide estimates of environmental impact for agent disposal.

1.4 THE ARCTIC RADIOACTIVE PROBLEM

It should be noted that this study is complementary to work done for the Arctic Nuclear Waste Program (ANWAP) in which the transport of radioactive materials in the arctic is studied.[25,26] Knowledge of basic arctic processes, circulation, and transport mechanisms, population dynamics and dietary habits of local inhabitants can be applied from ANWAP to this investigation. However, chemical contaminants differ significantly from radionuclide contaminants making direct application of ANWAP results meaningless with respect to the chemical munitions assessment. Differences between chemical and radionuclide contaminants include different half-lives, *i.e.*, days to years versus years to millenniums; different physical characteristics, *e.g.*, particle reactivity and solubility; and different toxicity affects; *i.e.*, acute versus chronic.

The ANWAP was initiated in 1993 as a result of Congressional concern over the disposal of nuclear materials by the former Soviet Union into the arctic marine environment. The program is part of the larger DoD Cooperative Threat Reduction (CTR) Program. Specific management of ANWAP is conducted by the Ocean, Atmosphere and Space Modeling and Prediction Division of the Office of Naval Research.

ANWAP is specifically aimed at addressing the following questions:

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[25]*Nuclear Pollution in Arctic Seas Preliminary Report to Congress*, Department of Defense, 1 Dec 93.
[26]*Department of Defense Arctic Nuclear Waste Assessment Program FY93-94*; Office of Naval Research 322-95-5; Editors: Julie Morgan and Louis Codispoti.

- What is the magnitude and location of the radioactive waste that has entered into the arctic marine environment;

- How is radioactive contamination transported about the arctic basin and what are the present levels in areas away from the various contamination sources;

- What is the risk to the environment and to human health as a result of this radioactive contamination.

The program is comprised of approximately eighty different projects conducting various types of research: field surveys, laboratory experiments, modeling studies, and archival data analysis. The investigators include contractors, academic institutions, government laboratories and agencies, and foreign institutions. Of particular emphasis is an attempt to include Russian institutions in this research program. To date approximately ten percent of the funds have gone to Russian institutions for research or logistical support. Additionally, ANWAP has strong linkages and collaborations with both national and international organizations concerned with arctic environmental contamination. These collaborations include the International Arctic Seas Assessment (IASA) Program and the Arctic Environmental Protection Strategy - Arctic Monitoring and Assessment Program.

The major conclusion from the research to date is that the largest signals for region-wide radionuclide contamination in the arctic marine environment appear to arise from the following:

- Atmospheric testing of nuclear weapons, a practice that has been discontinued;

- Nuclear fuel re-processing wastes carried into the arctic from re-processing facilities in Western Europe; and

- Accidents such as Chernobyl.

The order listed above represents the relative magnitude of the contribution to the contamination from each source. Because the signals from one and two have decreased with time, region-wide concentrations of radionuclides in the water column and in surface sediments appear to have decreased significantly from their peak levels. Overall, levels of radionuclide activity in the Arctic and Pacific regions are low. The Yenisey and Ob Rivers appear to have had only a modest impact on radionuclide levels in the Kara Sea and the Arctic Ocean region. However, local sites of elevated radionuclide concentration arising from dumping and weapons testing have been identified in the Kara Sea region.

While initial results are encouraging, there remain significant scientific issues specific to the arctic that must be addressed. They include sediment and sea ice processes affecting contaminant transport, data from winter periods, and watershed and river transport of contaminants. Additionally, quantification of the terrestrial source term and its impact on the marine environment is just beginning. The final result of this research will be in the form of a formal, integrated risk assessment. This assessment is scheduled for completion in the summer of 1997.

1.5   STEPS IN THE ANALYSIS

The steps taken in this study (see Figure 1-6) and described fully in subsequent chapters trace CW agents from their entry into the sea through to an assessment of their biological impact.

1-10

Figure 1-6: Analysis Flow
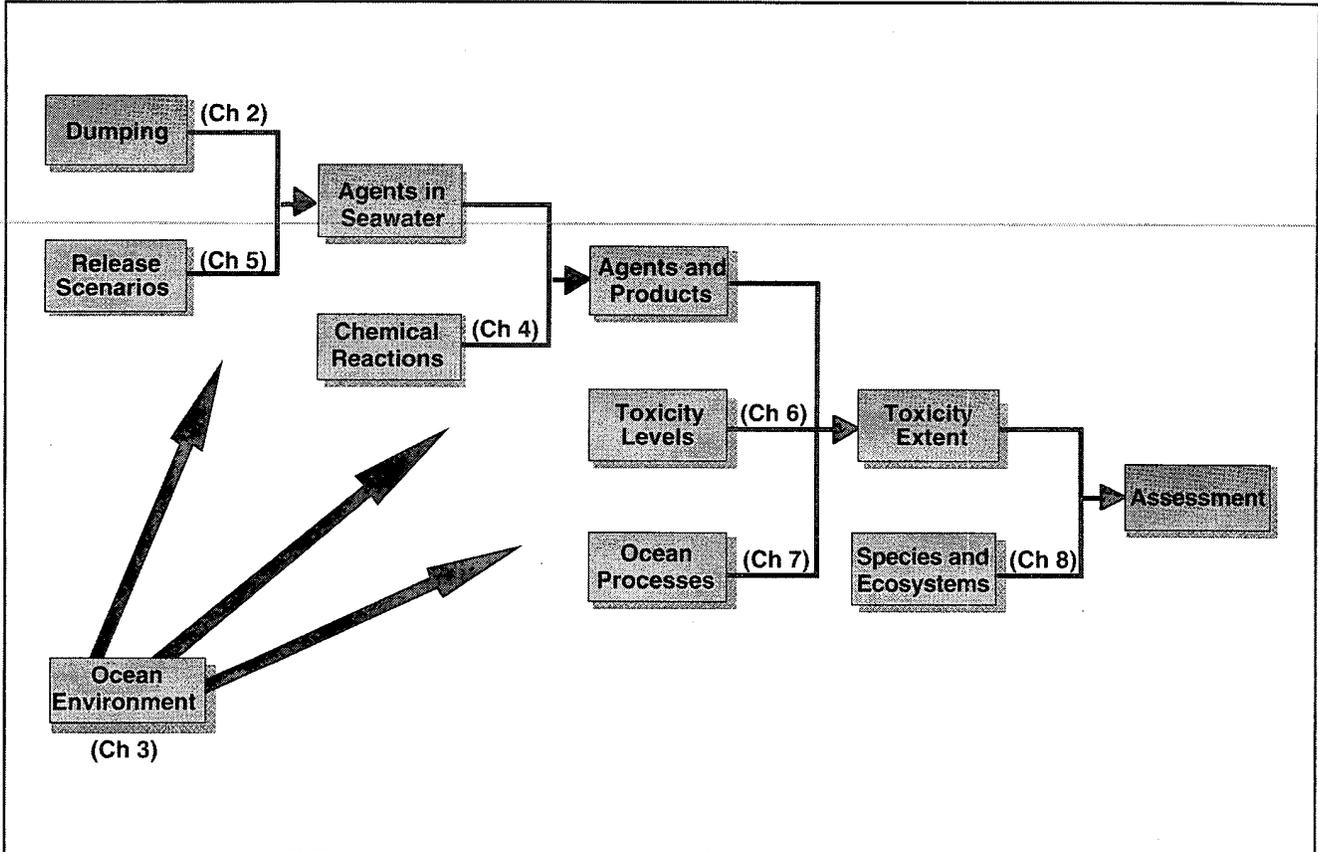
The Chapters in this report are organized as follows:

Chapter	Title	Content
2	CW Dumping in the Arctic Sea	Develops information on the types, amounts, locations, packaging, and disposal dates of CW materials dumped at sea. Identifies the five major dump sites to be evaluated in this study. Where specific data does not exist, bounds are provided.
3	Environmental Description	Summarizes the relevant aspects of the ocean environment in and around the dump sites, and the overall biological picture including estimated total biomass and major species.
4	Seawater Chemistry	Determines the chemical behavior of the various agents in seawater, accounting for arctic conditions. Identifies all the important reaction products, their persistence in seawater, and their significant characteristics (*e.g.*, density, solubility, etc.).
5	Release Scenarios	Develops chemical agent release scenarios describing the manner in which the agents are introduced into the sea, at what rates, and for how long. Because of the uncertainties surrounding dumped quantities and integrity of munitions casings, release scenarios are developed using bounds.
6	Toxicity Assessment	Determines the concentrations of each agent and important reaction products having significant biological activity. Identifies quantitatively three toxicity levels to be used in this study: no-effects, probable effects, and lethal effects. These three levels are used in Chapter 7 to develop the spatial extent of toxicity, and in Chapter 8, to assess the impact on arctic ecosystems.
7	Physical Processes	Determines the spatial and temporal time scales governing the behavior of CW agents once released into the sea. Estimates the extent of contamination when individual munitions leak. Extrapolates these results to the entire quantity of munitions at each dump site and arrives at total water volumes and seafloor areas reaching specific levels of toxicity for time periods that are also estimated.
8	Impact on Ecosystems	Determines the biological impact in the area of each dump site, and the probable impact on the local ecosystems. Develops an assessment of the probable impact on human health and safety and estimates the potential for economic impact.
9	Extensions	Addresses conclusions, V-gas and munitional burial.
10	Findings and Recommendations	Provides findings and recommendations concerning the assessment and the current state of knowledge on agent disposal in the arctic.

BACKGROUND

- To assess the environmental impact of Soviet CW dumping, estimates of chemical agents, their dumping locations, and quantities were chosen using a compilation of all available sources. Sources include Russian navigation charts, maps prepared by the Murmansk Marine Biological Institute, the Defense Mapping Agency, and the writings of Lev Federov.

CONCLUSIONS

- Based on Federov's estimates of Russian CW possession, the following toxic agents were chosen: mustard (H), Lewisite (L), Tabun (GA), and Sarin (GB). Representative dumping locations and quantities were selected for each of the toxic agents. An estimate of 40,000 tons of mustard and Lewisite were dumped into the White Sea and a total of 75,000 tons were dumped into the Barents and Kara Seas. A total of 30,000 tons of Tabun and 2,000 tons of Sarin are the estimates used for dumping in the White, Barents, and Kara Seas.

- The analysis does not require precise dates of the dumping. Using Federov's assumptions, the dumping of mustard and Lewisite took place in the 1940s and 1950s. Tabun was also dumped in the 1950s. In the 1980s, additional Tabun was dumped with Sarin.

2.1   INTRODUCTION

This chapter addresses the problem of establishing the quantities and types of toxic agents or CW munitions that may have been dumped in arctic seas by the USSR during the Cold War years. The estimates presented here, along with dates of the dumping and locations of dump sites are based on a compilation of all the material available. It is not possible to state confidence limits on these estimates, but they are believed to represent total quantities.

Reporting on occurrences of dumping of chemical agents and weapons in the Russian arctic seas is ambiguous and incomplete. In contrast to fairly well-documented campaigns of chemical weapons dumping

in the Baltic Sea by the Allies in the 1940s following the end of World War II, reports of such dumping in the arctic regions have never been confirmed officially. The open press has described alleged incidents in which obsolete Soviet chemical weapons and World War II-era German chemical munitions were dumped in the northern and far eastern seas surrounding Russia.

For the purpose of assessing the environmental impact of chemical agents and munitions in the arctic regions, the agents, dumping locations, and quantities listed in Table 2-1 have been selected.

Table 2-1: Chemical Agent Quantities Dumped in Russian Arctic Seas (in tons)

Location	Tabun (GA)	Sarin (GB)	Mustard (H)	Lewisite (L)
White Sea	30,000	2,000	40,000 H + L	
Barents Sea	total in	total in	75,000 H + L	
Kara Sea	all seas	all seas	total both seas	

2.2 TOTAL QUANTITIES

Reports in the open press on the dumping of Tabun in the arctic seas are scarce and only anecdotal. The Soviet Army captured the German production facilities for Tabun at the end of World War II. Allied data indicated that the German facility had produced 12,000 tons of Tabun.[1] For purposes of the study, it is assumed that no more than 30,000 tons of Tabun were dumped in arctic seas. This estimate is possibly too high, if only Germany is responsible for all Tabun produced.

Sarin was not produced successfully by the Soviets until the late 1950s. It is generally accepted that a German Sarin production facility was under construction at the end of World War II.[2] German equipment for its production, including pilot quantities, was captured by the Soviet Army and transported to the Soviet Union after World War II. It is not known if stocks of German Sarin weapons were captured by the Soviet Army. For the present study, the assumption will be made that no more than 2,000 tons of Sarin were dumped in the Russian arctic seas.

Mustard production by the Soviet Union during 1941 and 1945 has been estimated by Federov to have approached 80,000 tons.[3] Beginning before 1930, the Soviets produced low-purity mustard and, while reliable estimates of this phase of mustard production are not available, it is reasonable to assume that up to 15,000 tons were produced. Lewisite production during World War II slightly exceeded 20,000 tons. Thus, combined production of mustard and Lewisite may have reached 115,000 tons by 1945. These quantities all refer to the CW agents, not weaponized quantities.

A 1995 open-press report from Moscow indicated that 40,000 tons of mustard and Lewisite were dumped in

the White Sea during the 1950s and 1960s.[4] Lacking any other quantitative reporting, this value has been selected to represent the level of dumping in the White Sea in the present study. The balance, 75,000 tons of mustard and Lewisite, remains as the total quantity dumped in either or both the Barents and Kara Seas.

There are allegations that Soviets also dumped their chemical weapons agents in the seas adjoining its former boundaries, including the Baltic Sea, the Black Sea, the Sea of Okhotsk and the Sea of Japan.[5] These areas are outside the scope of the present study and will not be considered. Finally, there is no evidence or even suggestions that any quantities of the later generation chemical agents, Soman (GD) or VX, have been dumped into the Russian arctic seas.

2.3 OCEAN DUMP SITES IN ARCTIC WATERS

Although there are no confirmed ocean dumping sites for Russian or Soviet CW munitions apart from the Baltic Sea, there is, pervasive anecdotal evidence that extensive dumping of CW munitions in arctic seas did occur. The identification of specific sites for the present study is based upon the restricted areas on Russian navigation maps for the arctic seas of interest; dumping areas shown on maps prepared by Genady G. Matishov of the Murmansk Marine Biological Institute (MMBI) of the Russian Academy of Sciences (in cooperation with the Norwegian Polar Research Institute and the Institute of Oceanology of the Polish Academy of Sciences);[6,7] and the writings of Lev Federov.[8] These selected sites are representative of the types of oceanographic scenarios that comprise the Russian arctic seas. Locations selected for the present study are shown in Figure 2-1.

[1]Federov, L.A., *The Undeclared Chemical War in Russia: Politics Versus Ecology, 1995*, Translated from Russian by Foreign Broadcast Information Service.
[2]Franke, S., *Manual of Military Chemistry, Volume 1. Chemistry of Chemical Warfare Agents*, Deutscher Militärverlag: Berlin (East), 1967. Translated from German by U.S. Department of Commerce, National Bureau of Standards, Institute for Applied Technology. NTIS no. AD-849 866. pp. 247, 252.
[3]Reference 1.
[4]Moscow Interfax, 12 December 1995, 2052 GMT.
[5]Reference 1, §IV.3 and §IV.5.
[6]*Barents Sea: Biological Resources and Human Impact*, (map), Norwegian Polar Research Institute, Oslo, 1991; adapted from Russian original prepared by Genady G. Matishov, Murmansk Marine Biological Institute, Academy of Sciences of USSR.
[7]*Ecology of Novaya Zemlya Region*, (map), Institute of Oceanology, Polish Academy of Sciences, Sopot; Murmansk Marine Biological Institute, Russian Academy of Sciences, Murmansk; adapted from Russian original prepared by Genady G. Matishov.
[8]Lev Federov has a Ph.D. in physical chemistry and has published extensively on the former Soviet CW program. Although he never worked on the CW program, he is well-connected within the Soviet (former)/Russian scientific community. His writings offer a credible view of the past practices within the Soviet CW program.

Figure 2-1: Restricted Areas Associated with Potential CW Dumping Activities
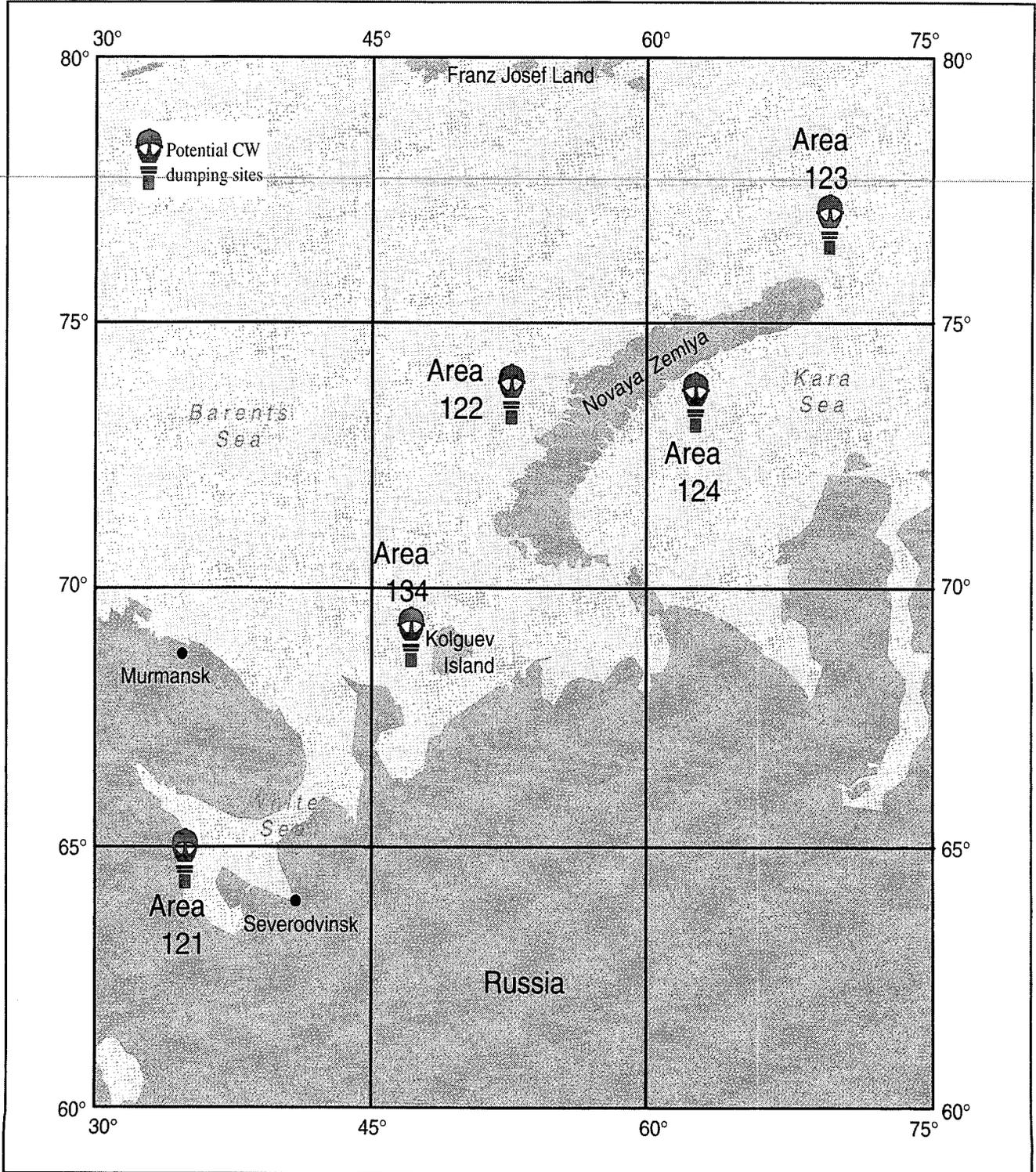
Federov provides numerous indications of organized dumping activities. The following are representative samples:[9]

> [P]er USSR Marshal R, Malinovsky's decree on 16 December 1949, a survey of storage facilities with captured munitions of German, Italian, Romanian, and Japanese armies was conducted. Munitions consisted primarily of air bombs, artillery shells, land-mines, and toxic agents (TA) in containers.[...] Several thousand shells were found which did not meet safety standards. In 30 days a decision was made to submerge these supplies in the sea. Marshal Malinovsky suggested three areas for submerging: areas of the White, Barents, and Baltic Seas.

> Destruction of chemical weapons, including burying and submerging, has been carried out during all times throughout the existence of the Soviet Army.

> [Destruction or disposal techniques include] submerging of chemical munitions and containers with TA of Soviet production and captured foreign products in the Baltic, Barents, White, Kara, and Black Seas and in the Sea of Okhotsk and Japan; and probably in other seas. The total number of large ocean areas is estimated at twelve, although there are hundreds of smaller sites, including submerging of TA in rivers and swamps.

> Excerpts from a report by V. Danilov-Danilyan (Minister of Environmental Protection and Natural Resources of the Russian Federation): 'The Ministry is involved in collection, analysis and summarizing of data related to the problem of chemical weapons submerging in the territorial waters of Russia. We came to the conclusion that the Baltic, Barents, Kara, Okhotsk, Black, and Japan Seas have been subjected to this type of anthropogenic impact for more than 50 years.'

> Loading of this hazardous cargo was implemented at the following shipping centers: at Pechenga Station (Petsamo), destination Port Liinahamari (Murmanskaya Oblast') by truck for submerging in the Barents and Kara Seas, known dates: 1959-62; at Severodvinsk Navy Port (Arkhangel'skaya Oblast') for submerging in the White and Barents Seas; known dates: 1947-56[.]

2.3.1 Barents Sea

According to the maps prepared by Matishov, two sites in the Barents Sea were candidate locations for CW munitions dumping: one site is located off the west coast of Novaya Zemlya at 72°N50' 49°E00', the second is north of Kolguev Island at 69°N35' 47°E55'. These are shown on Russian navigation maps as Areas 122 and 134, respectively.[10,11]

Area 122 off Novaya Zemlya is depicted as a circle with a diameter of 7.4 km, this corresponds to an area of about 43 km^2. Water depths in this area range from 205 to 220 m.

Area 134 off Kolguev Island is also circular, having a diameter of 25.9 km and an area of about 528 km^2. Water depths are remarkably shallow, ranging from only 33 to 60 m.[12]

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[9]Reference 1, §IV.3 and §IV.5.
[10]*Barents and Kara Seas: Novaya Zemlya (1:1,000,000)*, Map No. 696, Directorate of Navigation and Oceanography of the Ministry of Defense of the USSR (1988).
[11]*Northern Arctic Ocean, Barents Sea: From Cape Orlov-Terskiy to Entrance of Kara Straits (1:750,000)*, Map No. 650, Directorate of Navigation and Oceanography of the Ministry of Defense of the USSR (ca. 1988).
[12]Reference 11.

Although there were eyewitness accounts of submersions of CW in an area near Spitsbergen, maps and navigation charts do not show any restrictions in this area. It seems doubtful that any organized dumping would have occurred, given that no dumped CW munitions have been revealed to date.

2.3.2 Kara Sea

In the Kara Sea, an explosives and military materials dumping area is shown in the Matishov maps. It is located at the northern end of Novaya Zemlya, off Cape Zhelanyia, in the region bounded by 77-78°N 68-70°E. It encompasses an area of roughly 17,150 km². This region is depicted on a Russian nautical map as Area 123.[13] Water depths in this area range from 220 to 620 m with the typical depth being 450 m. In a related map, this area is designated as a dumping location for explosives and military materials.[14] Chemical weapons were submerged "...on the border of the Barents and Kara Seas - an area near Novaya Zemlya close to Cape Zhelnie[.]"[15]

A second area, Area No. 124, is located at 73°N19' 58°E12' off the eastern coast of Novaya Zemlya. Area 124 is circular, having a diameter of 9.4 km which corresponds to an area of about 67 km². The depth of this area is approximately 270 m.

2.3.3 White Sea

In the White Sea, sites of submerging are well known. "They can be found on navigation maps where these sites are referred to as 'explosive materials dump.' Two sites of toxic agents submerging are indicated under this code on the White Sea navigation map to the North-East from Solovetsk Islands (so-called areas No. 120 and 121), while a total of 16 areas are indicated on this map as restricted for navigation[.]"[16]

Both sites were identified on a Defense Mapping Agency map.[17] Area 120 cautions that magnetic anomalies may be encountered. On the other hand, in Area 121, anchoring, bottom fishing, and submarine works are prohibited, which is more suggestive of hazards from dumped munitions and chemical weapons. Area 121 is located at 65°N25' 36°E40'. It is a 15.75 km by 18.52 km rectangle, having an area of approximately 292 km². Depths in this area range from 100 to 225 m.

There have been reports on official comments, provided by Gen. S. Petrov (Stanislav Veniaminovich), confirming "small burial sites" of chemical weapons in the White Sea.[18]

2.4   DATES OF DUMPING

Official acknowledgment of past Soviet practices of chemical weapons dumping is nonexistent. According to the provisions of the 1972 Convention on Chemical Weapons, the Soviets were not required to declare chemical weapons previously destroyed, that is, buried between 1946-77 or submerged between 1946-85.[19]

There were four major phases of Soviet chemical weapons destruction, as follows:[20]

- The first and most comprehensive phase of dumping was between 1946 and 1950. At that time, a large quantity of mustard gas from Far Eastern supplies was submerged in the Sea of Japan. The quantity was estimated to be 30,000 tons, although it is unclear if that quantity is the net weight of the mustard or the weight with the munitions included.

- The second phase of chemical weapons destruction was between 1956 and 1962. During this phase, the Soviets began dumping second generation weapons. Also at this time, the Soviets changed their military strategy and emptied Air Force warehouses of artillery, Zarine, and other toxic agents. These toxic agents, along with their munitions, were earmarked for dumping into the northern seas.

[13]Reference 10.
[14]E. Tikkanen, M. Varmola, T. Katermaa, Eds., *Symposium on the State of the Environment and Environmental Monitoring in the Northern Fennoscandia and the Kola Peninsula*, Arctic Centre, University of Lapland, Rovaniemi, 1992, p. 116.
[15]Reference 1, § IV.5.
[16]Reference 1, § IV.5, picture 14.
[17]*Russia: Beloye More (White Sea) Pulonga to Ostrov Zhizhginskiy*, Map No 42600, Defense Mapping Agency.
[18]Reference 1, §IV.5.
[19]Reference 1, §IV.5.
[20]Reference 1, §IV.3.

- The third phase, in the 1970s, saw the destruction, probably through submersion, of chemical munitions filled with first generation toxic agents. There were also reports of land burial sites.

- The fourth and final phase was in the 1980s. By this time, munitions with first generation toxic agents had almost disappeared. Supplies of persistent toxic agents were left at two Chemical Forces bases in Kambarka and Gorny, where they had been stored in containers for the past few decades.

It is not important for our purposes to identify dates with very much precision, but generally, the following general dates seem reasonable:

Late 1940s: Dumping of mustard and Lewisite;

Late 1950s: Dumping of additional mustard and Lewisite, as well as Tabun;

1980s: Dumping of Tabun and Sarin.

2.5   WEAPON TYPES

Mustard, Lewisite and their combinations were loaded in a variety of air bombs, artillery shells, rocket artillery shells, and mines.[21] There are anecdotal reports on the disposal at sea of air bombs, artillery shells, mines, and containers containing toxic agents without specifying quantities of specific weapons or agent type. In the case where a quantity was identified, there was no determination between agent weight and the gross weight of the filled munitions. For purposes of establishing quantities of CW agents contained in these munitions, the estimates in Table 2-2 can be used.

Table 2-2: Quantity of CW Agents in Individual Munitions*

Munition Type	Designation	Quantity of CW Agent (kg)
Air Bombs	KhAB-25	15
	KhAB-100	60
	KhAB-200	100
	KhAB-500	280
	OKhAB-250	50
Artillery Shells	AKhS-76	0.40
	AKhS-85	0.45
	AKhS-122	1.3 Mustard; 3.3 Lewisite
	AKhS-152	2.6 Mustard; 5.5 Lewisite
Rocket Shells	Mkh-13	3.0
	MS-14	3.0
Mines	M-82	?
	M-120	?

*Unless otherwise noted, the type of CW agent is undetermined.

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[21]Reference 1, §I.5.

BACKGROUND

- Most of the Barents Sea shelf is in several basins 200 to 400 m deep among shallow banks. The southeastern portion of the shelf, called the Pechora Sea, is 100 m or less in depth. The southern portion of the shelf is dominated by warm Atlantic water, which flows onto the shelf from the west. The northern portion is dominated by cold arctic water flowing in from the arctic basin to the north. The water masses meet and mix at the Polar Front. A pelagic community is dominant in the deeper parts of the Barents Sea. A bentho-pelagic community is dominant in the shallow areas. The benthic community is more important in the bentho-pelagic system than in the pelagic system. Barents Sea fish and shrimp populations are exploited by a large and important commercial fishery, which exists primarily in the waters south of the Polar Front.

- Most of the Kara Sea is less than 100 m deep. Deeper areas include a basin adjacent to Novaya Zemlya, which is 400 m deep, and troughs on the northern portion of the shelf, which are up to 600 m deep. Biological productivity in the Kara Sea is less than in the Barents Sea. Commercial fish landings are small compared to the Barents Sea fishery.

- The White Sea is a basin connected to the Barents Sea by a shallow inlet. The deep central basin is 200 to 300 m deep. The inlet connection to the Barents Sea is about 25 m deep. Three water layers exist. The deep layer occupies depths below 130 m and has little mixing with the intermediate and surface layers. Commercial fish landings are very small compared to the Barents Sea fishery.

- Four of the five designated disposal sites are located in water 200 m or deeper. The fifth site is in water 30-50 m deep. At all sites, bottom salinity is greater than 34 parts per thousand (ppt). Bottom water temperature is less than 0°C at the deep sites and about 3°C at the shallow site.

- The regional marine systems are affected by other activities past and ongoing. These include testing of nuclear weapons, disposal of solid and liquid radioactive material, and exploration and production of oil and gas resources.

CONCLUSIONS

- The Barents, Kara, and White Seas are arctic marine ecosystems each with distinct characteristics.

- The fish and shrimp populations in the Barents Sea support important commercial fisheries. Commercial fishing in the Kara and White Seas is less important.

3.1   INTRODUCTION

The arctic seas potentially affected by the dumping of chemical munitions are located in northern Scandinavia and northwestern Russia. They include the Barents Sea, Kara Sea, and White Sea. Each has distinct oceanographic and ecological characteristics. This chapter summarizes the important oceanographic and ecological features of each of these areas, with emphasis on the five dump sites identified in Chapter 2.

3.2   BARENTS SEA

The Barents Sea is a large, continental shelf system off the coast of northern Norway and northwest Russia (see Figure 3-1). The boundaries are the Norwegian Sea to the west, the Arctic Ocean to the north, and Novaya Zemlya and the Kara Sea to the east. The shallow southeastern portion of the Barents Sea is also known as the Pechora Sea.

Figure 3-1: Bathymetry of the Barents Sea Shelf [1]

Scale 1:6,000,000 at 75°N
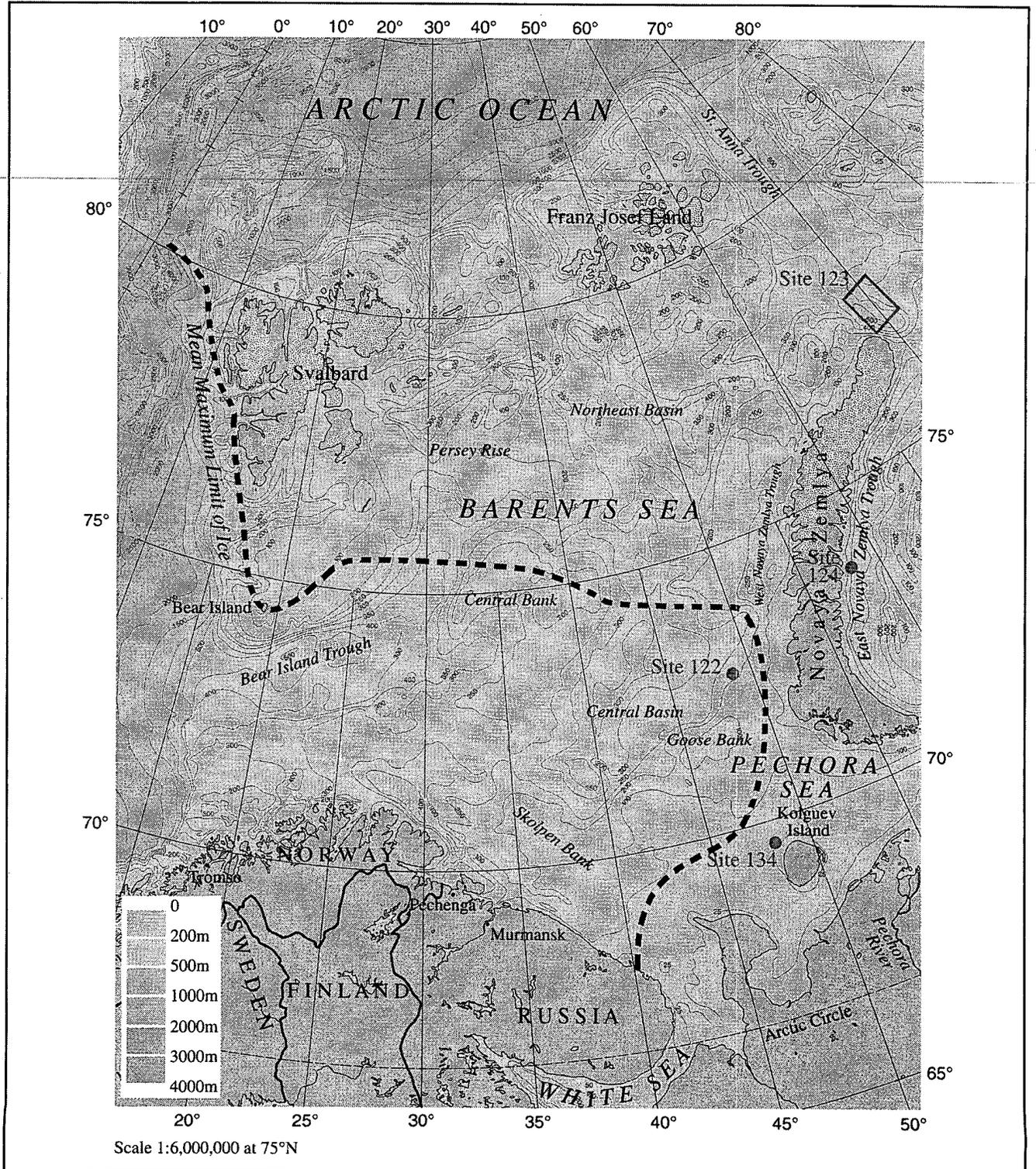
[1]Perry, R.K and H.S. Fleming, 1987. *Bathymetry of the Arctic Ocean.* The Geological Society of America, Boulder, CO.

3.2.1 Physical Characteristics

The bathymetry, the interaction of Atlantic and Arctic water masses, and the volume of inflow freshwater are important determinants for the physical characteristics of the Barents Sea. The volume of the Barents Sea is approximately 300,000 km³.[2]

3.2.1.1 Bathymetry

The majority of the Barents Sea shelf is 200 to 400 m deep. The bathymetry of this area is characterized by deep basins and shallow banks. The larger southeastern portion of the shelf is shallower with depths less than 100 m.[3]

3.2.1.2 Sediments

Sandy silts and muds cover most of the Barents Sea bottom in areas deeper than 200 m, with the muds occurring predominantly in the basins deeper than 200 m. The sediments of the shallow Pechora Sea and other shallow areas are primarily sand and sandy silt,[4,5] with many areas of rocky or stony bottoms.[6] Because of the small amount of freshwater inflow, the sedimentation rate is very low and is estimated to be 1-3 cm/1,000 years.[7]

Brown muds or a brown tint to the sediments is characteristic of the sediments of the northern portion of the shelf. This is due to ferric and manganic hydroxides, which exist as concretions and, in some places, as a thin pavement.[8,9]

3.2.1.3 Hydrography

The volume of freshwater flowing into the Barents Sea is small compared to the volume of shelf water. The main source is the Pechora River, which flows into the shallow Pechora Sea.

Because of the low volume of freshwater inflow, currents and water masses in the Barents Sea are determined mainly by inflow and mixing of Atlantic and coastal waters from the Norwegian Sea from the west with arctic water from the Arctic Ocean from the north (see Figure 3-2).[10] Atlantic and coastal waters from the Norwegian Sea flow onto the shelf between the Norwegian coast and Bear Island. This water, flowing from west to east, covers much of the southern part of the shelf. Water from the Arctic Ocean flows onto the shelf from the north and east. Currents in arctic water are westward or southwestward. The two water masses meet and mix at the Polar Front.

Vertical stability of the shelf water masses may vary during the year. Atlantic and Arctic water may be homogeneous in the winter (see Figure 3-3). In the summer, arctic water stratifies near the surface because salinity decreases due to ice melting and the temperature increases due to solar warming of the surface layer. Coastal and Atlantic waters, which are ice-free during the winter, also stratify near the surface in the warm period because of some freshwater input from Norwegian and Russian coastal streams and solar warming of the surface layer.

Formation of dense bottom water in the fall is important to the hydrographic structure of the shelf waters.[11,12] Formation of dense bottom water is a two-step process. First, water density increases as surface water cools in the fall. Cooling slows as the water temperature nears the freezing point. The second step begins with ice formation. Surface water density increases rapidly because of the increase in salinity resulting from rejection of brine to the water from the

[2]Loeng, H. 1991. "Features of the Physical Oceanographic Conditions of the Barents Sea." *Polar Research* 10(1):5-18.
[3]Cherkis, N.Z.; 1991. *Bathymetry of the Barents and Kara Seas. Map and chart series MCH047.* The Geological Society of America, Boulder, CO.
[4]Zenkevitch, L. et al. 1963. *Biology of the Seas of the USSR.* Interscience Publishers, New York, NY.
[5]Fairbridge, R.W. (ed.). 1966. *The Encyclopedia of Oceanography.* Reinhold Publishing Corporation. New York, NY.
[6]Demel, K. and S. Rutkowicz. 1966. *The Barents Sea (Morze Barentsa).* Translated from the Polish by the U.S. Department of the Interior and the National Science Foundation. Clearinghouse for Federal Scientific and Technical Information, Springfield, VA.
[7]Reference 5.
[8]Ingri. 1985. "Geochemistry of Ferromanganese Concretions in the Barents Sea." *Marine Geology 67:*101-119.
[9]Reference 4.
[10]Reference 2.
[11]Midttun, L. 1985. "Formation of Dense Bottom Water in the Barents Sea." *Deep-Sea Research 32*(10):1233-1241.
[12]Gawarkiewicz, G. and D.C. Chapman. 1995. "A Numerical Study of Dense Water Formation and Transport on a Shallow, Sloping Continental Shelf". *Journal of Geophysical Research* 100(C3):4489-4507.

Figure 3-2: General Surface Currents in the Barents Sea[13]
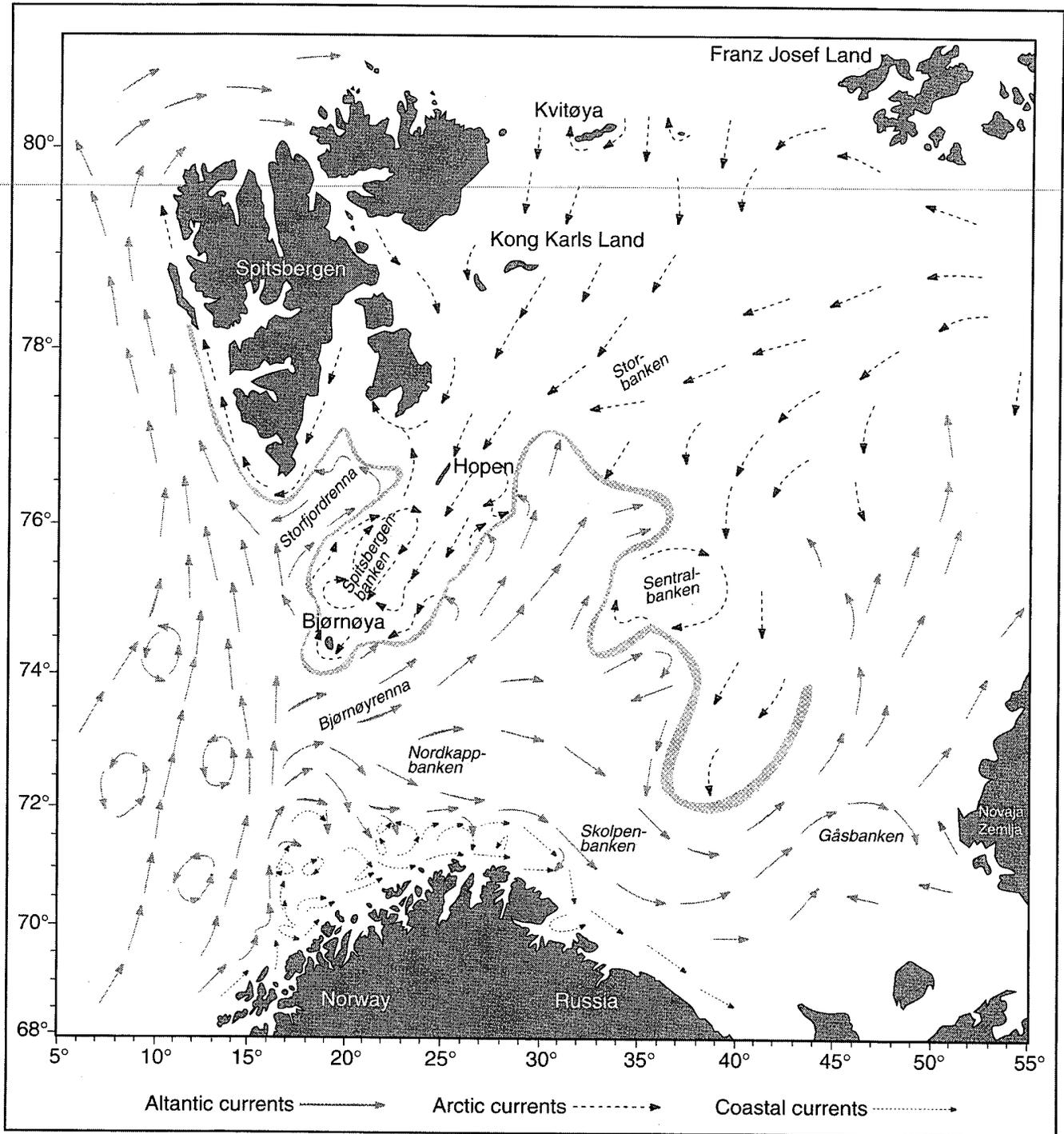
[13]Reference 2.

Figure 3-3: Vertical Profiles of Temperature, Salinity, and Density (as σ-t) in Arctic and Atlantic Water Masses in the Barents Sea[14]
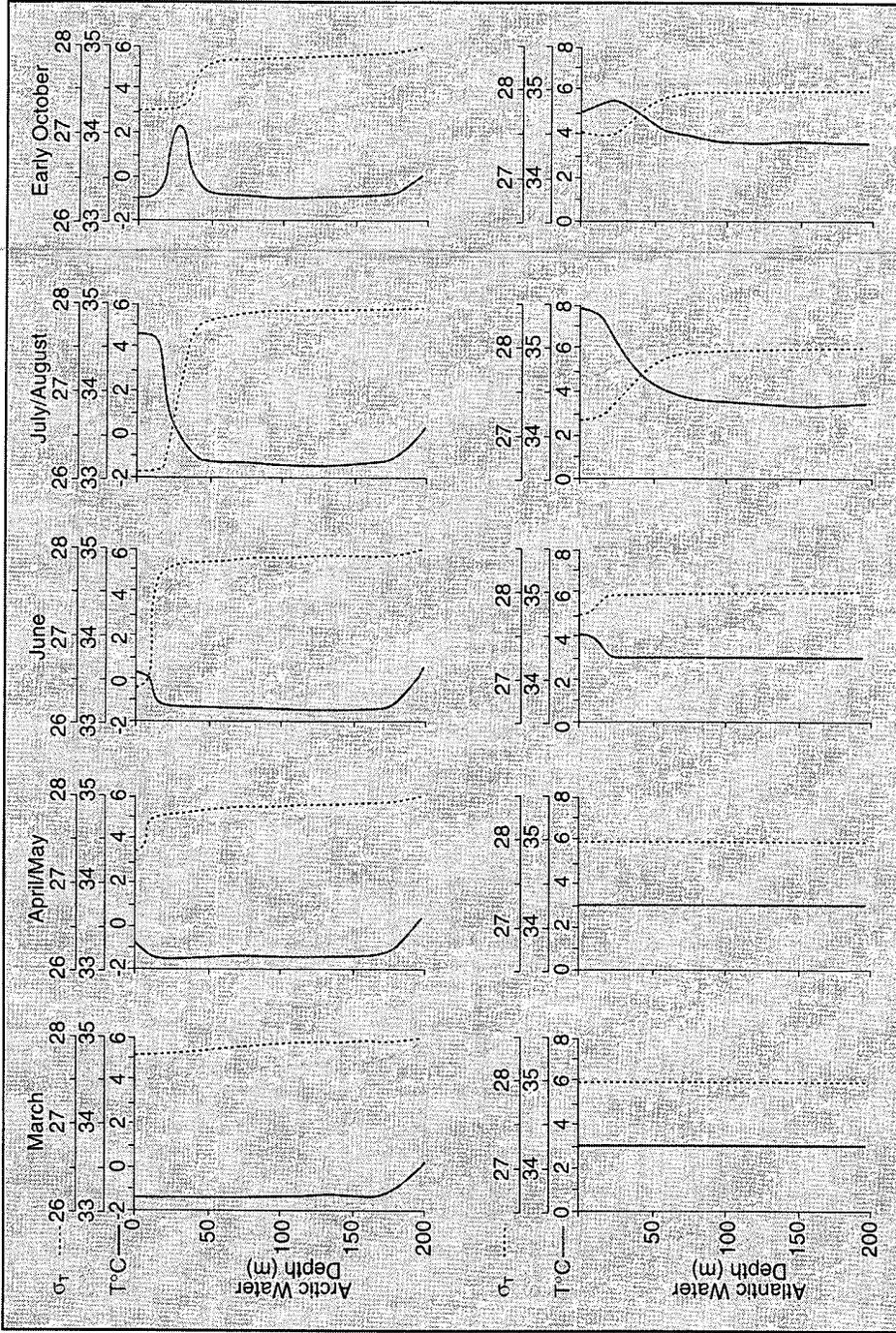
[14]Reference 2.

forming ice. This dense water then sinks to the bottom and flows along slopes and into depressions. In water less than about ten meters deep, formation of dense bottom water can cause convective mixing of the whole water column and resuspension of bottom sediments. The dense bottom water layer flowing away from the source may be only ten meters to a few tens of meters thick. Because of the density difference, there is little mixing of the bottom water layer and overlying water.

Formation of dense bottom water has been documented on the shallow bank adjacent to the west coast of Novaya Zemlya and may occur also in other shallow areas, such as the banks east of Svalbard.[15] The dense water formed over the shallow bank west of Novaya Zemlya sinks to the bottom and flows downslope along the bottom into the basins to the west and northwest. It also flows to the northeast along the bank slope and into the St. Anna Trough between Novaya Zemlya and Franz Josef Land.

3.2.1.4 Water Temperature and Salinity

The Atlantic and Arctic water masses have different salinity and temperature characteristics (see Figure 3-3). Arctic water has a temperature of -1.5°C and a salinity of about 34.5 ppt. Atlantic water has a temperature of about 3°C and a salinity of about 35 ppt. In the summer for each water mass, the top fifty meters have higher temperatures and lower salinity than the deeper water.

3.2.1.5 Ice Cover

The warm Atlantic water of the southwestern portion of the Barents Sea remains ice-free all year (see Figure 3-1). The maximum extent of ice cover in winter in the central and eastern Barents Sea can vary considerably from year to year. In most years, the entire shelf is free of ice in the summer.

3.2.2 Biological Characteristics

The Barents Sea is a biologically productive shelf ecosystem with two main types of ecological communities.[16] In the deep central and western parts of the sea, where depths are 200 to 400 m except on banks, the community is primarily a pelagic one. A bentho-pelagic community occurs in the areas less than 100 m deep. The sea is an important nursery and feeding ground for commercially important fish stocks, which are exploited by an international commercial fishery in the western area and a Russian fishery east of 30°E.

3.2.2.1 Pelagic Community

The pelagic community is a simple food web with a few dominant species at each trophic level (see Figure 3-4).[17,18] Most biological activity takes place in the water column. The benthic community is less important in the food web.

3.2.2.1.1 Plankton. The base of the food web is the phytoplankton, which produce organic matter by photosynthesis. Diatoms and colonial algae are the dominant phytoplankton types. Calanoid copepods (*Calanus finmarchicus* and *C. glacialis*) and krill (*Thysanoessa spp.*) are the dominant herbivores feeding on the phytoplankton.[19,20,21]

3.2.2.1.2 Planktivores. Capelin (*Mallotus villosus*), herring (*Clupea harengus*) and polar cod (*Boreogadus saida*) are the main planktivorous fish feeding on the zooplankton.

[15]Reference 2.

[16]Savinova, T.N., G.W. Gabrielsen and S. Falk-Petersen. 1995. *Chemical Pollution in the Arctic and Sub-Arctic Marine Ecosystems: An Overview of Current Knowledge.* NINA-fagrapport 1. 68 pp. Trondheim, Norway.

[17]Gjosaeter, H. 1995. "Pelagic Fish and the Ecological Impact of the Modern Fishing Industry in the Barents Sea." *Arctic* 48(3):267-278.

[18]Reference 16.

[19]Hansen, B., et al. 1990. "Post-bloom Grazing by *Calanus glacialis*, *C. finmarchicus* and *C. hyperboreus* in the Region of the Polar Front, Barents Sea." *Marine Biology* 104:5-14.

[20]Pedersen, G., K.S. Tande and E.M. Nilssen. 1995. "Temporal and Regional Variation in the Copepod Community in the Central Barents Sea During Spring and Early Summer 1988 and 1989." *Journal of Plankton Research* 17(2):263-282.

[21]Tande, K.S. and U. Bamstedt. 1985. "Grazing Rates of the Copepods *Calanus glacialis* and *C. finmarchicus* in the Arctic Waters of the Barents Sea." *Marine Biology* 87:251-258.

Figure 3-4: Main Components of the Pelagic Food Web in the Barents Sea[22]

Haptophyceae
Phaeocystis pouchetii

Phytoplankton production, April to September

Diatoms
Chaetoceros socialis
Nitzschia grunowii

Calanus finmarchicus

Metridia longa

Thysanoessa raschii

Dense krill layers

Thysanoessa inermis

Maganyctiphanes norvegica

Detritus

Phytoplankton origin   Animal origin

Sagitta elegans

Main Food Pathway   Important Food Pathway   Minor Food Pathway

Capelin

Deep-Sea Prawn

Cod

[22]Reference 16.

The entire life cycle of the capelin stock takes place in the Barents Sea.[23,24,25] Capelin adults are most abundant in the arctic water mass of the northern part of the shelf. Adults migrate in late winter to the spawning grounds in the shallow coastal waters on the southern shelf off Norway and Russia. Hatched larvae float east and north with the coastal and Atlantic water currents to the nursery areas of the central shelf.

The Barents Sea is the nursery area for the herring stock. Spawning occurs in the Norwegian Sea along the coast of northern Norway. Eggs and larvae are transported to the Barents Sea in the Norwegian Coastal Current. Herring remain primarily in the Atlantic water mass in the southern Barents Sea for two to four years before migrating to the spawning areas in the Norwegian Sea.[26]

The biology of the polar cod is not well known.[27] The species occurs throughout the Barents Sea but mainly in the eastern and northeastern part of the shelf. Spawning takes place in the Pechora Sea and, possibly, east of Svalbard during winter or early spring. Polar cod are found near the bottom, but apparently feed mainly on pelagic organisms.

3.2.2.1.3 Predators. The Arcto-Norwegian Cod (*Gadus morhua*), marine mammals and sea birds are important consumers of fish.[28,29] The life cycle of the Arcto-Norwegian cod is similar to the herring. The main spawning grounds are in the Norwegian Sea off northern Norway near Lofoton. Eggs and larvae are carried into the Barents Sea by the Norwegian coastal current and Atlantic current.[30] Larvae are pelagic for five to six months and then settle to the bottom for further development. Adults remain mostly in the Atlantic water of the shelf.[31]

Capelin and herring are an important source of food for fish-eating sea birds. In the spring during ice melt, thick-billed murres (*Uria lomvia*) are abundant along the ice edge and on pack ice.[32] In August and September, fulmars and kittiwakes constitute the vast majority of birds on the central and northern shelf. The distribution of these birds is generally correlated with the distribution of capelin and polar cod,[33] which remain mostly in the arctic water mass.

Marine mammals are important consumers of fish. Seals are found along the ice edge, on pack ice, and along the shore.[34] Harp seals can forage at depths as great as 300 m.[35]

3.2.2.1.4 Whales. The numbers and distribution of whales in the region are not well known. Minke and humpback whales as well as white-sided and white-beaked dolphins are known to be important.[36,37] Beluga whales are found in the Pechora Sea region as far west as the White Sea and along the west coast of Novaya Zemlya.[38] Additional species also are known to occur.[39]

[23]Giske. L., H.R. Skjoldal and D.L. Aksnes. 1992. "A conceptual model of distribution of capelin in the Barents Sea." *Sarsia* 77:147-156.
[24]Reference 17.
[25]Tjelmeland, S. and B. Bogstad. 1993. "The Barents Sea capelin stock collapse: a lesson to learn." pp. 127-139. *In* S.J. Smith, J.J. Hunt and D. Rivard (ed.). *Risk Evaluation and Biological Reference Points for Fisheries Management*. Canadian Special Publication in Fisheries and Aquatic Science 120.
[26]Reference 17.
[27]Reference 17.
[28]Reference 17.
[29]Reference 16.
[30]Helle. K. 1994. "Distribution of Early Juvenile Arcto-Norwegian Cod (*Gadus morhua L.*) in Relation to Food Abundance and Watermass Properties. *ICES Marine Sciences Symposium 198:*440-448.
[31]Reference 25.
[32]Hunt, G.L., Jr., V. Bakken and F. Mehlum. 1996. "Marine Birds in the Marginal Ice Zone of the Barents Sea in Late Winter and Spring." *Arctic* 49(1):53-61.
[33]Borkin, I.V., et al. 1992. "Results of aerial surveys of sea birds in the Barents Sea." pp. 205-216. *In* Bogstad. B. and S. Tjelmeland (eds.). *Interrelations Between Fish Populations in the Barents Sea. Proceedings of the Fifth PINRO-IMR Symposium*, Murmansk, 12-16 August 1991. Institute of Marine Research, Bergen, Norway.
[34]Reference 17.
[35]Lydersen, C., et al. 1991. "Feeding Habits of Northeast Harp Seals (*Phoca groenlandica*) Along the Summer Ice Edge of the Barents Sea." *Canadian Journal of Fisheries and Aquatic Sciences* 48:2180-2183.
[36]Reference 17.
[37]Schweder, T., et al. 1996. *Abundance of Northeastern MinkeWhales, Estimates for 1989 and 1995*. SC/48/NA1.
[38]Matishov, G.G. 1991. *Barents Sea: Biological Resources and Human Impact*. Map prepared in cooperation with Murmansk Marine Biological Institute of Academy of Sciences of the USSR, Norwegian Polar Research Institute, and Institute of Oceanology of the Polish Academy of Sciences. Apatity, Russia.
[39]Reference 6.

Both baleen and toothed whales are known to occur in the Barents Sea. Baleen whales filter large volumes of water to obtain plankton and small fish for food. Toothed whales exploit the regional fish and squid stocks.

3.2.2.2 Bentho-Pelagic Community

The bentho-pelagic community of the shallower areas of the Barents Sea is illustrated in Figure 3-5. Much of the organic matter produced in the phytoplankton sinks to the bottom without being consumed by zooplankton and is available to benthic organisms. Fish, sea birds and marine mammals are important components of the food web in this community. Birds feed on both fish and the benthic organisms. Walrus feed on benthic organisms. Polar bears feed on marine mammals.[40]

Walrus occur in the shallow Pechora Sea region, along the Novaya Zemlya coast and on Franz Josef Land and Svalbard.[41,42] Although walrus hunting is no longer allowed, populations are much reduced from prehunting numbers.

3.2.2.3 Benthic Community

The biomass of the benthic community varies greatly over the shelf area (see Figure 3-6).[43,44,45,46] Biomass in water deeper than 200 m is generally low, usually less than 100 g m^{-2}, with large areas less than 50 g m^{-2}. A much greater biomass of 200 to 500 g m^{-2} occurs in shallow areas, such as banks and the Pechora Sea region. Small areas of very high biomass greater than 500 g m^{-2} occur in the northern Pechora Sea and along the west coast of Novaya Zemlya.

3.2.3 Commercial Fishery

Capelin, herring, blue whiting, cod, haddock, and other finfish populations in the Barents Sea are exploited by a large fishery.[47,48] The most important species are capelin, herring, and blue whiting.[49] The size of the fish stocks vary greatly from year to year, depending on oceanographic and climatic conditions that affect the success of spawning and the survival of eggs, larvae, and juveniles of the various species.[50,51]

Most of the finfish harvest takes place in the warm water of the Atlantic water mass and in the vicinity of the Polar Front. Capelin are harvested using purse seines. Both midwater and bottom trawling are used extensively for other species. Polar cod are harvested primarily in the eastern Barents Sea and the shallow area of the Pechora Sea region.

The northern shrimp (*Pandalus borealis*) is also harvested commercially.[52]

3.3 KARA SEA

The Kara Sea is a shallow shelf system bounded by Novaya Zemlya and Franz Josef Land on the west, the Arctic Ocean on the north, and the Russian land mass and Severnaya Zemlya on the east (see Figure 3-7). The sea receives large freshwater inflows seasonally from the Ob and Yenisey Rivers, which are among the largest rivers in the world.

[40]Reference 16.
[41]Reference 38.
[42]*Atlas of the Arctic. 1985.* Lenin Arctic and Antarctic Scientific Research Institute. Moscow.
[43]Pfirman, S.L., J. Kogeler and B. Anselme. 1995. "Coastal Environments of the Western Kara and Eastern Barents Seas." *Deep-Sea Research 42*(6): 1391-1412.
[44]Pogrebov, V.B. 1994. "Assessment of the Ecological State of the West-Arctic Shelf by Benthos." *Proceedings of the Workshop on Arctic Contamination,* May 2-7, 1993, Anchorage, AK. Arctic Research of the United States 8:290-294.
[45]Zatsepin, V.I. 1970. "On the Significance of Various Ecological Groups of Animals in the Bottom Communities of the Greenland, Norwegian, and the Barents Sea." *In* J.H. Steele (ed.). *Marine Ecosystems.* Oliver & Boyd, Edinburgh. Reprint by Otto Koeltz, Antiquariat, Koenigstein-Ts./B.R.D.,1973.
[46]Reference 4.
[47]Reference 17.
[48]Klungsoyr, J., R. Saetre, L. Foyn, and H. Loeng. 1995. "Man's Impact on the Barents Sea." *Arctic 48*(3):279-296.
[49]Luka, G.I., A.I. Mukhin, and V.P. Ponomarenko. 1987. "Living Resources of the Arctic and Sub-Arctic Regions and Their Exploitation." Paper made available at the 1987 ICES Symposium.
[50]Reference 17.
[51]Oiestad, V. 1994. "Historic Changes in Cod Stocks and Cod Fisheries: Northeast Arctic Cod." *ICES Marine Sciences Symposium* 198:17-30.
[52]Reference 50.

Figure 3-5: Main Components of the Bentho-Pelagic Food Web in the Barents Sea[53]
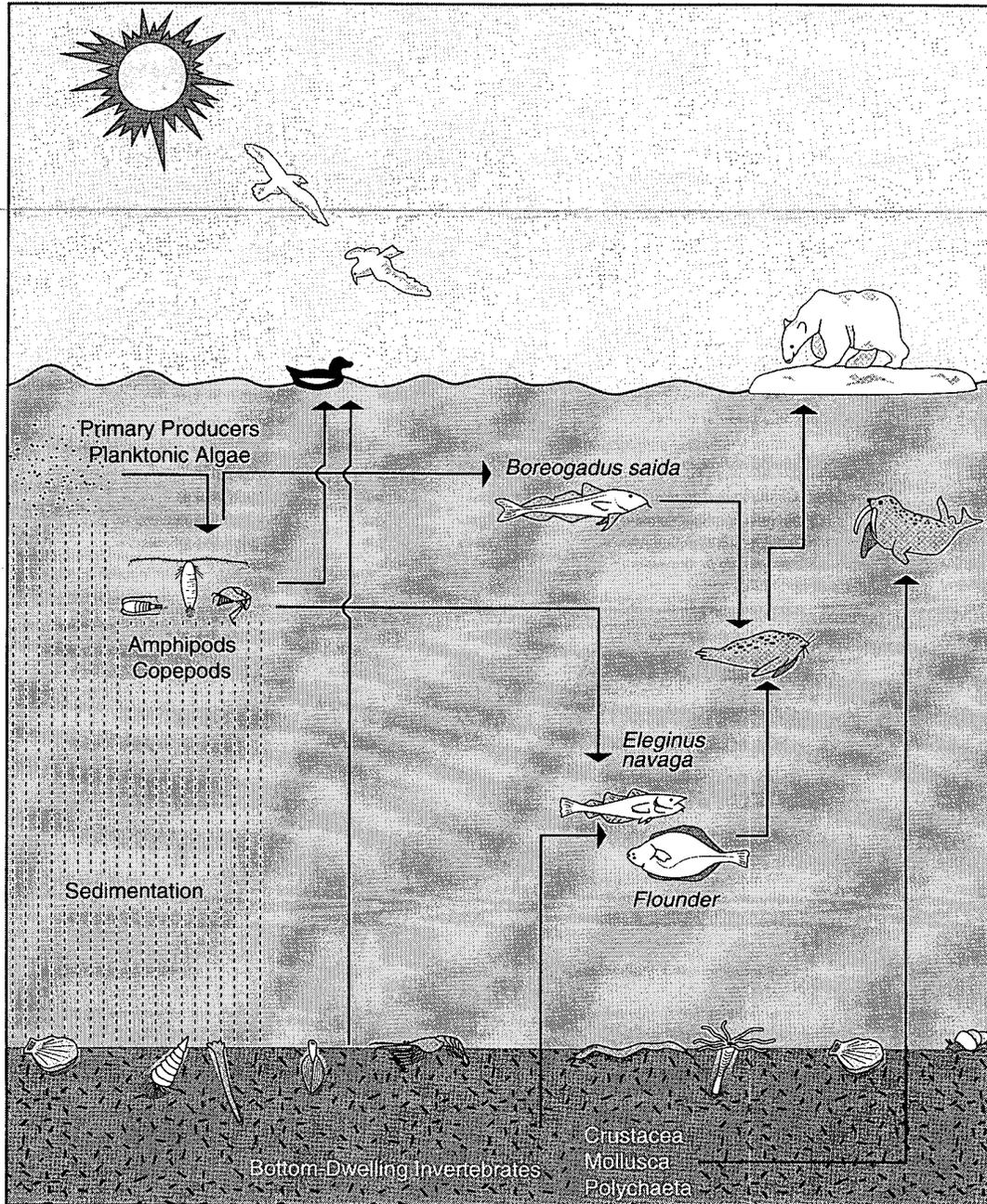
[53]Reference 16.

Figure 3-6: Distribution of Benthic Biomass in the Barents Sea[54]
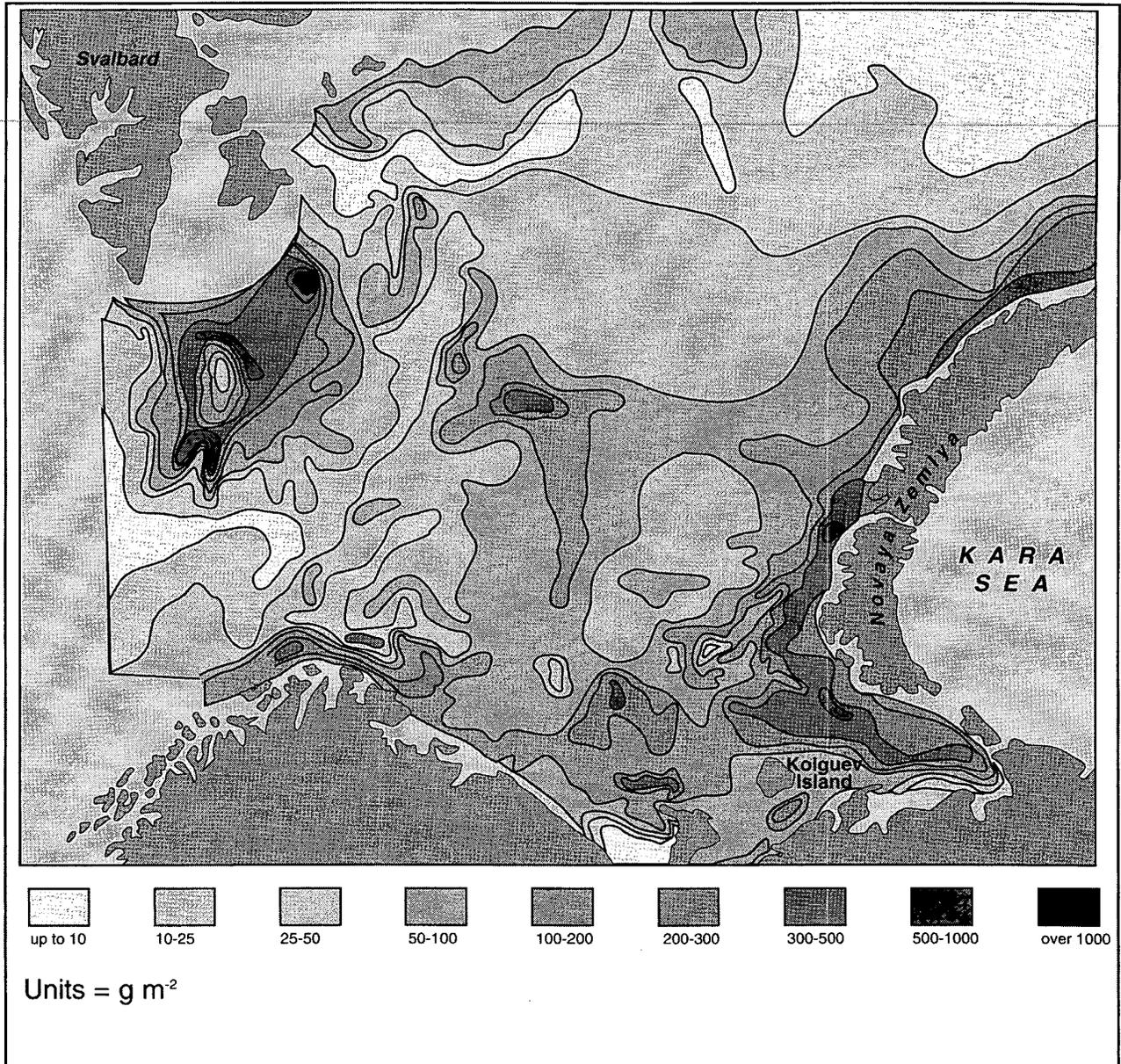
[54]Reference 45.

Figure 3-7: Bathymetry of the Kara Sea[55]
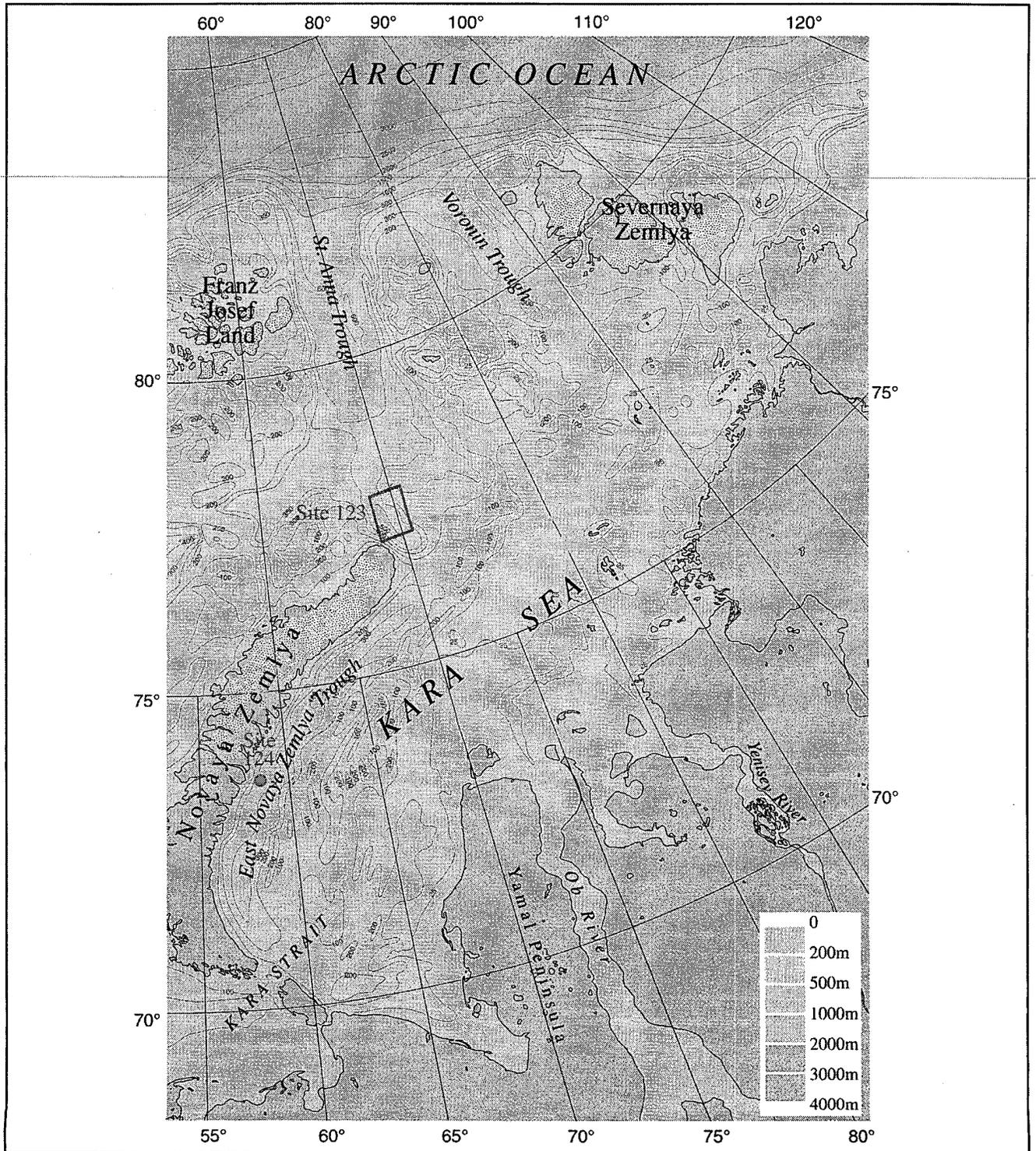
[55]Reference 1.

3.3.1 Physical Characteristics

The Kara Sea is characterized by shallow areas and deep troughs and by the large volume of freshwater inflow. Its volume is approximately 111,000 km³.[56]

3.3.1.1 Bathymetry

Most of the Kara Sea shelf is less than 100 m deep with large areas shallower than 50 m (see Figure 3-7). Deep areas are the East Novaya Zemlya Trough and the St. Anna and Voronin Troughs.[57] The St. Anna and Voronin Troughs reach a maximum depth of about 630 m and open into the arctic basin.[58]

3.3.1.2 Sediments

Silty clay or mud are the dominant sediments in the Kara Sea basin.[59,60,61] Terrigenous silt of glacial marine type is found in the deeper areas. In the southwestern portion of the sea, a cyclonic or counterclockwise surface circulation pattern favors the accumulation of mud at shallow depths. The sediments are brown in color indicating the presence of manganese and iron oxides. A large number of ferromanganese concretions are characteristic of the Kara Sea.[62]

Sands and silty sands predominate in the shallow shelf area near the mouths of the Ob and Yenisey Rivers in the southeastern portion of the basin. This portion of the basin is characterized by submerged terraces which trend northeast-southwest. The terraces mark the transgressive and regressive stages of multiple glaciations. Hard rock bottom is encountered in many places on the margins of these terraces. The absence of sedimentary cover is indicative of a generally slow rate of sedimentation, or scouring, by strong currents.

3.3.1.3 Hydrography

The Kara Sea is greatly influenced by the large seasonal inflow of freshwater from the Ob and Yenisey Rivers. Most discharge occurs between May and October with peak flow in June. Some flow also continues during the winter.[63] River water remains in the central and eastern portions of the shelf, although the pattern is variable from year to year.

The general surface circulation in the Kara Sea is shown in Figure 3-8.[64] The large seasonal freshwater inflow from the Ob and Yenisey Rivers flows to the northeast across the shallow portion of the shelf. This inflow creates a strongly stratified water column in the surface layer. Ocean water enters the Kara Sea through the straits at the south end of Novaya Zemlya and from the Barents Sea and Arctic Ocean on the north. A counterclockwise gyre is present in the western portion of the shelf over the East Novaya Zemlya Trough. A two-way water exchange takes place with the Barents Sea through the Kara Strait at the south end of Novaya Zemlya.

Two-directional flow occurs at depths in the St. Anna Trough.[65,66] Atlantic water flows southward onto the shelf along the western side of the trough while the water flow is northward into the arctic basin on the east side of the trough. Some of the southward flowing water enters the East Novaya Zemlya Trough.

3.3.1.4 Water Temperature and Salinity

In the East Novaya Zemlya Trough, water temperature in depths below 50 m is constant all year at about -1.8°C to -1.5°C. The surface temperature is warmer

[56]Andrew, J.A. and J.H. Kravitz. 1974. "Sediment Distribution in Deep Areas of the Northern Kara Sea." pp. 231-256. In Herman, Y. (ed.). Marine Geology and Oceanography of the Arctic Seas. Springer-Verlag, New York, NY.
[57]Reference 3.
[58]Reference 56.
[59]Reference 56.
[60]Reference 5.
[61]Reference 4.
[62]Reference 4.
[63]Reference 43.
[64]Pavlov, V.K. and S.L. Pfirman. 1995. "Hydrographic Structure and Variability of the Kara Sea: Implications for Pollutant Distribution." Deep-Sea Research II 42(6):1369-1390.
[65]Reference 56.
[66]Hanzlick, D. and K. Aagaard. 1980. "Freshwater and Atlantic Water in the Kara Sea." Journal of Geophysical Research 85(C9):4937-4942.

Figure 3-8: General Circulation of the Kara Sea[67]
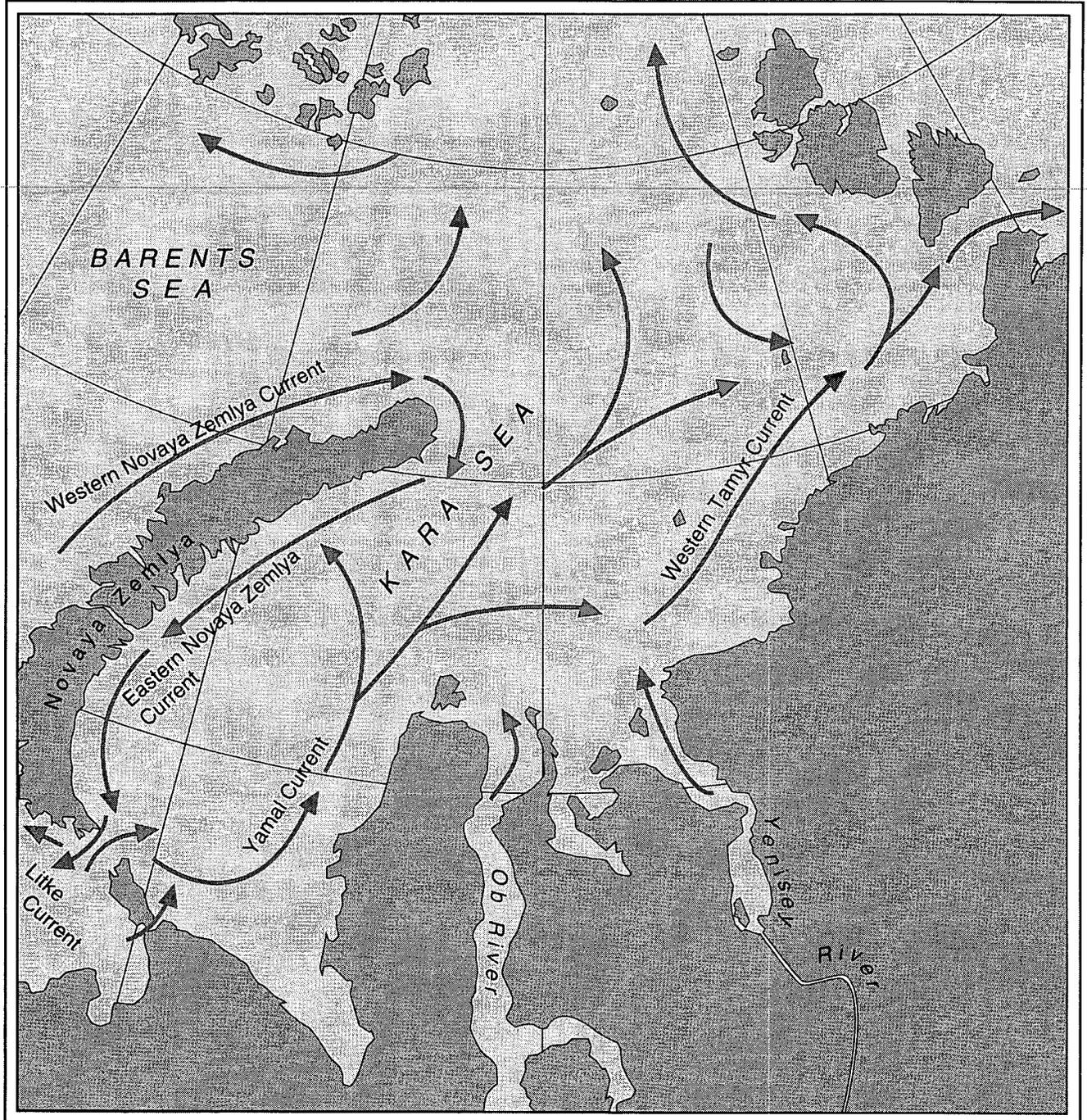
[67]Reference 64.

during the summer (see Figure 3-9).[68] Bottom water temperature in the St. Anna Trough is about -1.4°C.[69]

Surface salinities are low near the mouth of the Ob and Yenisey River and in the near shore region to the northeast in the direction of the current flow.[70] The East Novaya Zemlya Trough accumulates high salinity water of about 34.5 ppt (see Figure 3-9).[71] Rapid cooling and ice formation in the shallow water along the east coast of Novaya Zemlya creates brine that drains into the trough.[72]

The water column is strongly stratified in the top 50 m in warm weather periods due to solar warming and salinity reduction from freshwater inflow.

3.3.1.5 Ice Cover

The generalized sea ice characteristics of the Kara Sea are shown in Figure 3-10.[73] The entire sea is usually covered with ice in winter except for polynyas in the eastern portion of the sea that form over many years. Fast ice lasts into July in many areas. The entire sea is usually free of sea ice by early August. The persistent mass of ice off Novaya Zemlya, which sometimes lasts all summer, results from the cyclonic gyre in the surface water of this region. The icebergs sometimes observed along the east coast of Novaya Zemlya are thought to originate by calving from glaciers that terminate in bays on the northern portion of the island.

3.3.2 Biological Characteristics

Phytoplankton is dominated by diatoms and peridineans. The main zooplankton species is *Calanus finmarchicus*, which is less dominant in biomass than in the Barents Sea. Zooplankton biomass of 25-75 g m^{-3} is typical of the Russian arctic shelf seas to the east, but much less than the biomass of greater than 150 g m^{-3} in the Barents Sea.[74]

Benthic organism biomass is low in much of the Kara Sea (see Figure 3-11). Biomass in the areas of brown mud are generally less than 25 g m^{-2}. Biomass in the troughs is less than 5 g m^{-2}.[75] (Note: While pelagic biomass is normally given in units of mass per unit volume of seawater, benthic biomass is given in mass per unit area of the seabed.)

Fish biomass is much less than in the productive Barents Sea. Typical species are polar cod, navaga, eelpouts, polar dab and seapoachers.[76] Very small populations occur in the areas of brown muds.[77]

Beluga whales occur throughout the Kara Sea. Walrus occur only along the coast of Novaya Zemlya and in the southern portion of the sea between the Kara Straits and the Yamal Peninsula.[78] Polar bears occur on Novaya Zemlya.[79]

3.3.3 Commercial Fisheries

The commercial fishery is limited in the Kara Sea because of the small biomass of fish. The largest catch is polar cod by trawl and seine in the southern portion of the region.[80]

3.4 WHITE SEA

The White Sea is an enclosed, fjord-like marine system in northwestern Russia connected to the Barents Sea (see Figure 3-12).

3.4.1 Physical Characteristics

Important characteristics of the White Sea are the deep central basin and the three-layered structure of the water mass. Its volume is estimated to be 17,000 km^3.[81]

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[68]Reference 64.
[69]Reference 56.
[70]Reference 64.
[71]Reference 64.
[72]Pavlov, V.K., et al. 1996. "Hydrometeorological Regime of the Kara, Laptev, and East-Siberian Seas." Technical Memorandum APL-UW TM1-96. Applied Physics Laboratory. University of Washington, Seattle, WA.
[73]Reference 64.
[74]Reference 4.
[75]Reference 4.
[76]Reference 50.
[77]Reference 4.
[78]Reference 42.
[79]Reference 38.
[80]Reference 49.
[81]Reference 3.

Figure 3-9: Salinity and Temperature Profiles in the East Novaya Zemlya Trough in September (A) and the Following Winter (B)[82]
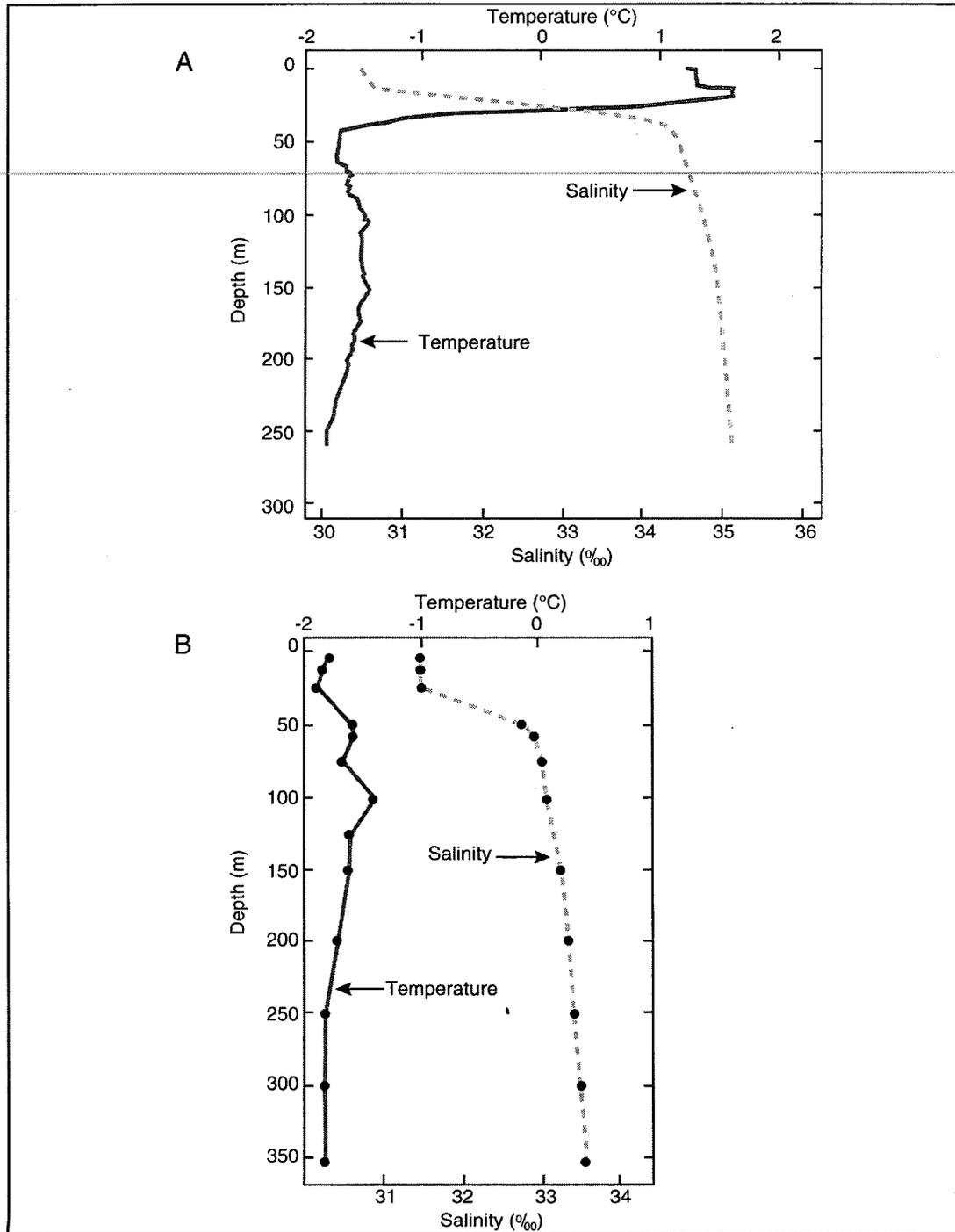
[82]Reference 64.

Figure 3-10: Generalized Ice Conditions in the Kara Sea[83]

Figure 3-11: Distribution of Benthic Biomass in the Kara Sea[84]

Units=g m⁻²

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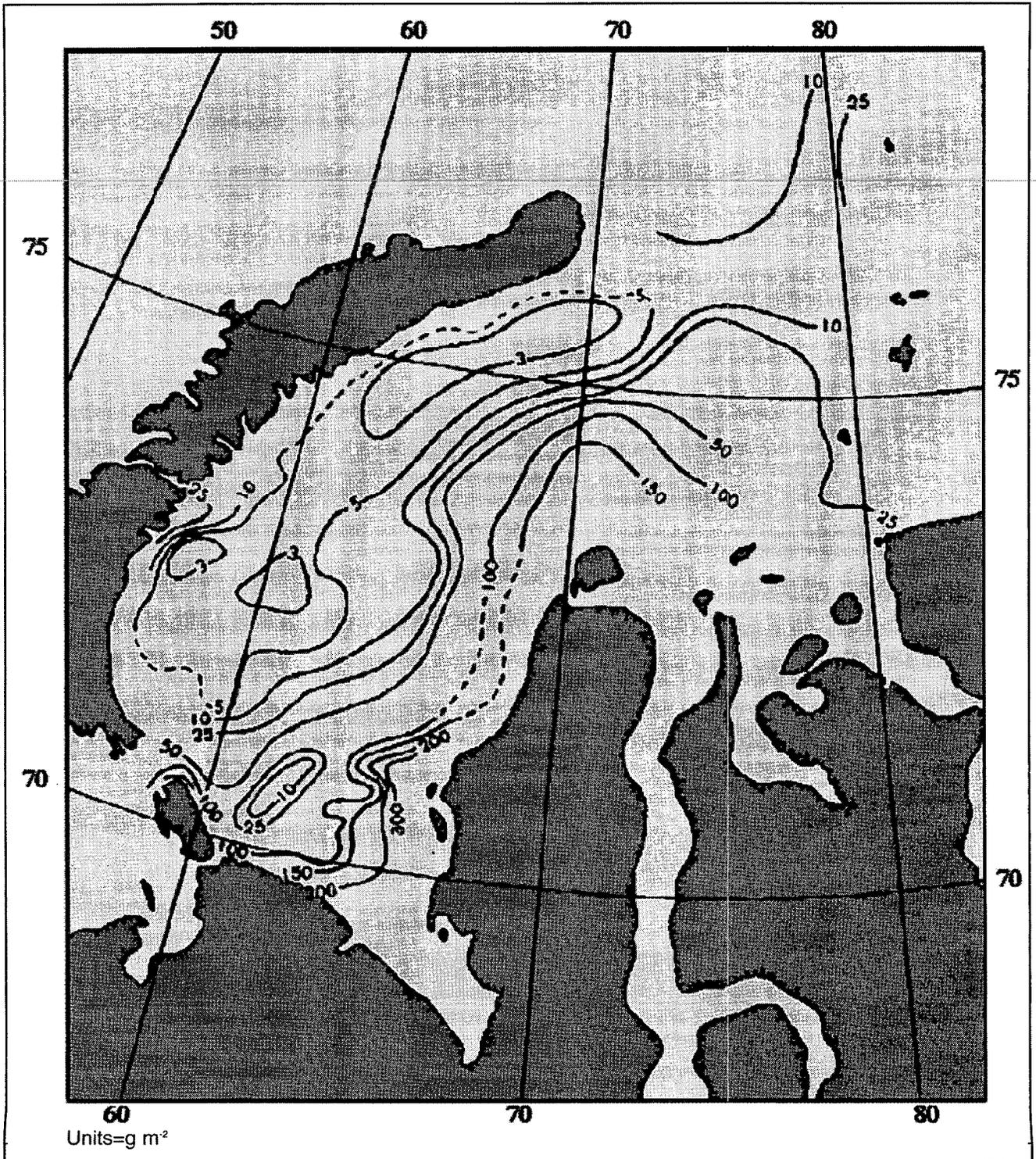
[84]Reference 4.

Figure 3-12: Bathymetry of the White Sea[85]
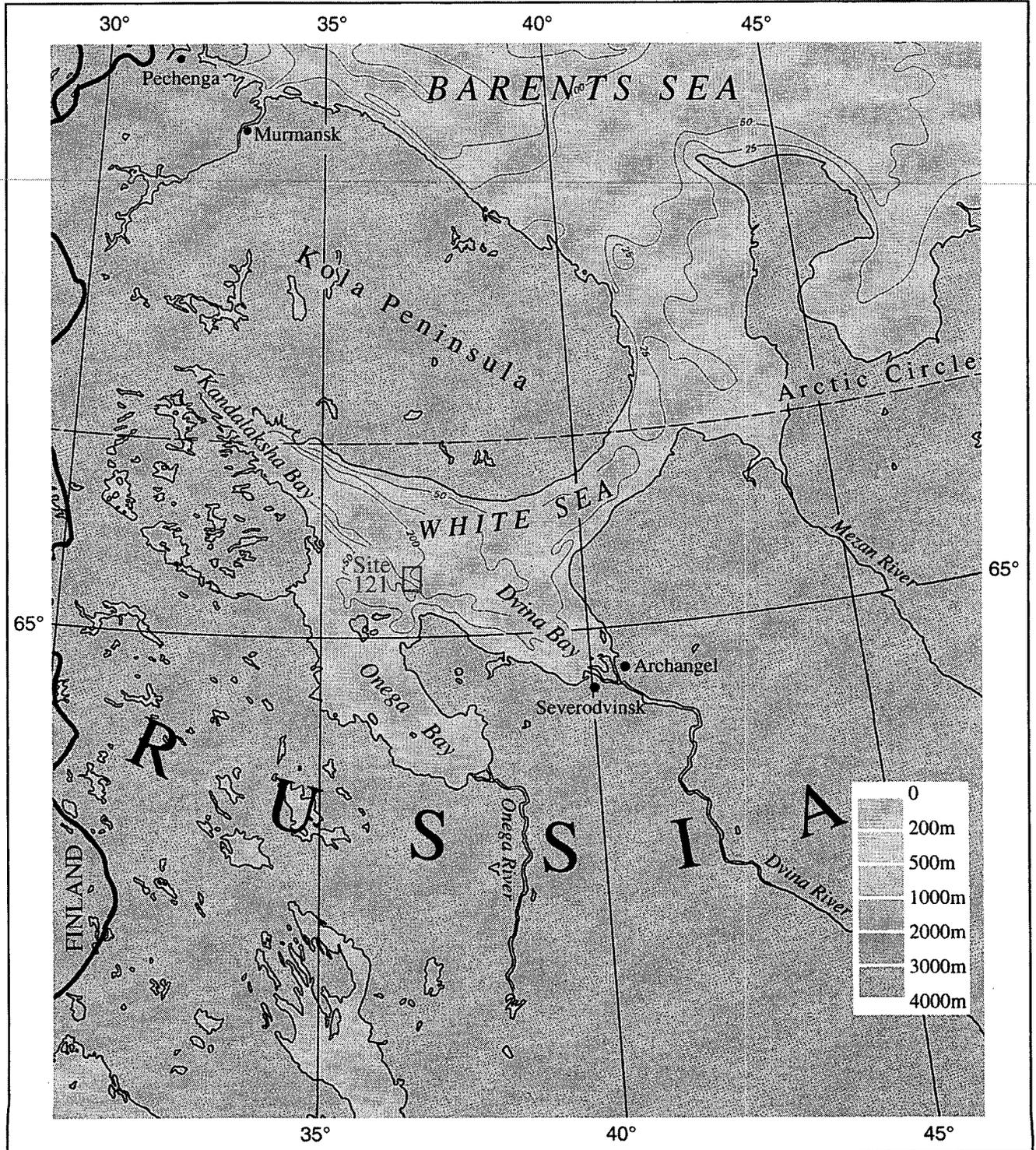
3.4.1.1 Bathymetry

The White Sea is a basin separated at its entrance to the Barents Sea by a sill at a depth of 25 m (see Figure 3-12).[86] The deep central basin has a maximum depth greater than 300 m. The shallow southern Onega Bay is less than 50 m deep. Dvina Bay slopes downward toward the central basin. Depths in this bay are mostly less than 100 m. The central basin occupies much of Kandalaksha Bay with shallow edges less than 100 m deep.

3.4.1.2 Sediments

Pebbles, gravel, and sand are the dominant sediments in the shallows along the coast and in Strait Gorlo, which is the passage between the White Sea and the Barents Sea. Fine-grained sediments (muddy sand, sand, and mud) occur on the slopes of the central basin of the White Sea. The central basin is covered by very fine-grained, brown clay-like mud.[87,88] The sedimentation rate for the central basin is about 2 cm per 1,000 years and about 30 cm per 1,000 years in the near-shore areas.[89]

3.4.1.3 Hydrography, Water Temperature, and Salinity

Three water masses exist in the White Sea.[90] A surface layer approximately 10 m deep forms in the summer as a result of ice melting, freshwater inflow, and surface heating from increased insolation. In this layer, the salinity is less than 26 ppt and the temperature is greater than 10° C. An intermediate layer also forms in the summer with salinity of 26 to 29 ppt and a temperature of -1° to +5°C. This layer occupies depths from 10 m to 60 m. A deep layer, which forms in the winter, has a salinity greater than 29 ppt and a temperature less than -1°C. This water occupies depths greater than 130 m. A transition layer often occurs between each of the three water layers. In the winter, the top two summer water masses are the only ones involved in convective mixing.

The main sources of freshwater enter the White Sea in Dvina Bay from the Dvina River and in Onega Bay from the Onega River.

3.4.1.4 Ice Cover

The White Sea is usually completely covered with ice in the winter and free of ice in the warm months.

3.4.2 Biological Characteristics

Phytoplankton are mainly diatoms and peridinea.[91] The diatoms include the genus *Chaeratoceros*. Peridineans include *Ceratium fusus* and *Peridinium conicum*.

The zooplankton community comprises two groups corresponding to the layered structure of the water mass.[92] One group, comprising boreal and cosmopolitan species, lives in the upper summer-formed layers, primarily in the upper 15 m. These species include *Evadne nordmanni*, *Fritillaria borealis* and *Acartia longiremis*. The other group, comprising arctic and arcto-boreal species, lives in the cold water of the deep layer, primarily below a depth of 60 m. The species include *Calanus glacialis*, *Oikopleura vanhofferi*, *Metridia longa* and *Clione limacina*.

Three distinct benthic communities have been identified that correspond roughly with the three-layered water mass structure of the sea. Types of organisms present are also influenced by sediment type.[93] The *Portlandia arctica* community is the dominant type on pelite silts in the cold water of the deep water layer.[94] Benthic organisms in the deep basin are primarily deposit feeders, while those in shallower waters are primarily suspension feeders.[95]

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[86]Reference 3.
[87]Reference 4.
[88]Reference 5.
[89]Reference 5.
[90]Beklemishev, K.V., N.L. Semenova and O.I. Malyutin. 1980. *Factors Determining the Biological Structure of the White Sea*.
[91]Reference 4.
[92]Kolosova, Ye.G. 1978. "Some Vertical Distribution Patterns of Zooplankton of the White Sea Determined by the Recurrent Group." *Oceanology* 18(2):210-213.
[93]Reference 90.
[94]Naumov, A.D. 1979. "Peculiarities of Composition and Distribution of Benthic Fauna in Lov Iinlet (White Sea)." pp. 128-136. *Ecology of the Sea Shelf Benthic Fauna and Flora*. P.P. Shirshov Institute of Oceanology, Academy of Sciences of the USSR, Moscow.
[95]Reference 90.

Fish species present include herring, navaga, smelt, White Sea cod, dab, and whitefish. Arctic cod and capelin also enter the White Sea at times.[96] Three populations of White Sea herring (*Clupea harengus marisalbi*) live in the White Sea.[97] This species feed intensively on large and small zooplankton.[98]

Seals are common in the White Sea. The Beluga whale also occurs.[99]

3.4.3 Commercial Fishery

Fish stocks of the White Sea are exploited by a small Russian commercial fishery. Navaga and White Sea herring account for most of the landings. Other species harvested include smelts, cod, and dab.[100]

3.5 PRIMARY PRODUCTION AND ENERGY TRANSFER THROUGH THE FOOD WEB

Arctic ecosystems must be adapted to survive in a cold environment that receives solar energy for only a portion of the year. Production of organic matter by phytoplankton (primary production) begins with the return of significant solar radiation in the spring. As the ice melts and moves northward during the spring and summer, an intense bloom of phytoplankton with high rates of primary production occurs in the vicinity of the ice edge. In the pelagic community, zooplankton graze on most of the bloom, leaving little to settle to the bottom as food for benthic organisms. In the shallower areas, much of the primary production sinks to the bottom without being grazed, becoming available to benthic organisms.

Because energy from the sun needed to produce organic matter by photosynthesis is available for only part of the year, the biological communities have evolved with mechanisms to capture the food produced

in the short period of primary production. The biological communities store the energy for later use during the period of low insolation. Much of the energy is stored in lipid compounds or fats.[101] Copepods grazing on phytoplankton grow continuously during the bloom period, increasing their lipid content during this time from 15 percent to 70 percent during the two to three month period of the spring bloom. Krill increase their lipid content over five months from 15 percent to 50 percent. The energy captured and stored by zooplankton is passed up the food web to capelin, which increases its lipid content from 10 percent to 50 percent.[102] The energy finally reaches the top carnivores, such as marine mammals, sea birds, and polar bears. Marine mammals and polar bears store much of the fat so that the energy is available during the long period of low light, cold temperatures, and ice cover when food is scarce. The transfer of energy stored in lipids from phytoplankton to capelin is shown in Figure 3-13. The dependence on energy storage in lipids makes arctic ecosystems particularly vulnerable to bioaccumulation of contaminants that are preferentially stored in fats, such as chlorinated hydrocarbons.

3.6 THREATENED AND ENDANGERED SPECIES

Many of the mammal species of the study region are threatened, endangered, or greatly reduced in numbers. Hunting of many of the species continued into the 1950s and 1960s.

The polar bear, Atlantic walrus, gray seal, narwhale, and bowhead whale are listed in the Red Book of Russia, which is the list of protected species in Russia.[103,104] The 1994 Red List of Threatened Animals of the International Union for the Conservation of Nature lists the following regional animals and their

[96]Reference 4.
[97]Naymark, Ye.B., 1993. "Analysis of the Population Dynamics of the White Sea Herring." *Journal of Ichthyology 33*(2):48-55.
[98]Slonova, S.A. 1978. *The Feeding of the White Sea Herring, Clupea harengus maris-albi.*
[99]Reference 42.
[100]Reference 49.
[101]Reference 16.
[102]Falk-Petersen, S., C.C.E. Hopkins and J.R. Sargent. 1990. "Trophic Relationships in the Pelagic, Arctic Food Web." pp. 315-333. *In* Barnes, M. and R.N. Gibson (eds.). *Trophic Relationships in the Marine Environment.* Aberdeen University Press, Scotland.
[103]Matishov, G.G. 1993. *Anthropogenous Destruction of the Ecosystems in the Barents and the Norwegian Seas.* Kola Scientific Center, Russian Academy of Sciences, Apatity.
[104]Russian Academy of Sciences. 1993. *Environment and Ecosystems of the Franz Josef Land (Archipelago and Shelf).* Kola Scientific Center, Russian Academy of Sciences Press, Apatity.

Figure 3-13: Transfer of Lipids from Phytoplankton to Capelin in the Barents Sea Ecosystem[105]
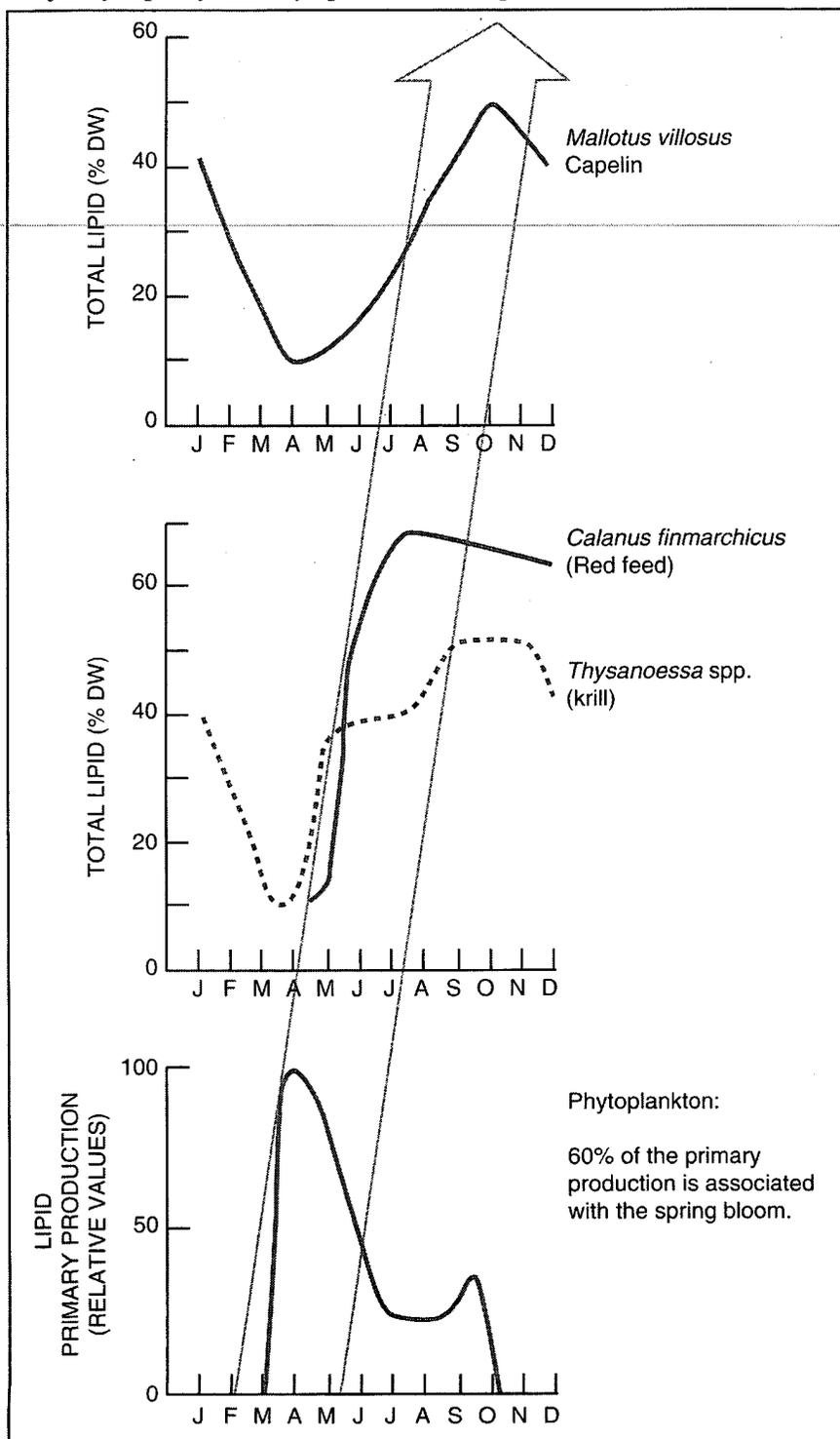
[105]Reference 16.

status for the Russian Federation: polar bear (vulnerable); beluga whale, narwhal, harbour porpoise, and Dall's porpoise (insufficiently known).

Whales are protected under the International Convention for the Regulation of Whaling. Regional species protected under the U.S. Endangered Species Act are the blue whale, bowhead whale, humpback whale, and sperm whale.

3.7 INDIGENOUS PEOPLES

Indigenous groups inhabit the study region and obtain a portion of their food from the marine waters that could be contaminated with arsenic. These groups are potentially at risk of exposure to arsenic-contaminated fish, shellfish, and marine mammals if these food sources are a substantial portion of their diet.

Two principal groups of indigenous people populate the study area. The Lapps, also known as the Sami, occupy the European section extending from northern Norway through the extreme northwestern section of the Russian Arctic into the Kola Peninsula. The Nenets and Khanty are found in the central and eastern portion of the study area on the land masses bordering the southern and eastern coasts of the Kara Sea.

The Sami are of four regional and cultural types. These include the forest, field (mountain, river), sea, and Kola Peninsula Sami. The sea Sami live along the arctic coast of Norway. In winter they hunt and in the summer they fish on the sea. The Sami of the Kola Peninsula are the original inhabitants of the region. Their population has remained roughly the same, slightly below 2,000. They live mostly by fishing and by herding reindeer.

The Nenets and Khanty were primarily nomadic reindeer herdsman who migrated up and down the Yamal Peninsula seeking seasonal pastures for their herds. In the early 1930s, these nomadic people were forced onto collective farms and the state established boarding schools for the children of both the nomadic families and the settled villagers. The children retained little knowledge of their parents' subsistence economy.

When the collective farms of the 1930s were transformed into the Soviet farms of the 1960s, the Nenets and the Khanty became hired workers in the state-run reindeer breeding enterprises. More recently, the economy of the region has begun to stabilize and sustainable fishing and hunting enterprises were established alongside the reindeer breeding industry. However, the discovery of huge gas deposits on the Yamal Peninsula and the impending development of these resources are new factors affecting the Nenets and Khanty peoples.

The breakup of the former Soviet Union has been accompanied by increased liberalization in political life, growing independence among scholars and the press, and the advent of new social movements. This shift has fostered the creation of special social and political organizations of native peoples. These organizations are helping to curb the threats to their culture and their traditional means of earning a livelihood.[106]

3.8 OTHER ACTIVITIES IN THE STUDY REGION

Other past and ongoing activities affect the marine ecosystems of the study region. These include disposal of nuclear wastes, testing of nuclear weapons and exploration and production of oil and gas resources.

3.8.1 Nuclear Waste Disposal

Both liquid low level nuclear wastes and high level wastes (including reactor vessels with spent nuclear fuel) have been dumped in Eurasian arctic waters.[107,108] Dumping has taken place since 1959 with the latest known dumping to have occurred in 1991.

Liquid waste with the highest radioactive concentration has been dumped in three dumping fields in the central portion of the Barents Sea. The first dumping field is off the west coast of Novaya Zemlya in an area ranging from about 73° to 77° north latitude and 48° to 52° east longitude. Further to the west, the second area extends from 72° to 78° north and ranges between 41° and 45° east. The third high level waste

[106]Krupnik, I.I. 1993. *Arctic Adaptations: Native Whalers and Reindeer Herders of Northern Eurasia.* University Press of New England, Hanover, NH. Translated by Marcia Levenson.
[107]Reference 48.
[108]Sjoeblom, K.L. and G.S. Linsley. 1995. "The International Arctic Seas Assessment Project: Progress Report." *IAEA Bulletin* 37(2).

disposal area is a 1° by 2° area centered on 73° north and 35° east.

Disposal of low level nuclear wastes has occurred in dumping areas off the Barents Sea coast of the Kola Peninsula.

Solid radioactive waste has been dumped in several locations throughout the Barents and Kara Seas. Solid wastes include containers, reactor parts, generators, cooling pumps, tools, and equipment. In some instances the material was stored on ships or barges that were sunk. Aside from the known disposal areas in the Barents Sea, several dumping areas have been identified in the Kara Sea.

Both the Northern Fleet and the civil fleet of nuclear icebreakers have dumped material in eight different bays on the east coast of Novaya Zemlya and in the Kara Sea, in both the Novaya Zemlya and St. Anna's Troughs. Sinkings are known to have occurred in Techeniya Bay and in the southeast Barents Sea near Kolguev Island. An accidental sinking occurred in 1989 as a result of a fire aboard the nuclear-powered submarine Komsomolets. The submarine sank at the western entrance to the Barents Sea about halfway between Svalbard and Bear Island.

3.8.2 Testing of Nuclear Weapons

Several hundred nuclear tests, both above and below ground, are known to have occurred on Novaya Zemlya. The principal testing areas were located along the central west coast of the island. Also, nuclear devices were tested near Guba Chernaya, in Point Cernyi, in the extreme southwest portion of the island.[109] Atmospheric fallout, runoff and river borne contaminants, in addition to direct release into the oceans, have contributed radioactive pollutants to the northern ocean areas.

3.8.3 Oil and Gas Resource Exploration and Exploitation

Exploration and exploitation programs for petroleum resources are currently underway in both the Barents and Kara Seas.[110] Geophysical investigations in the Norwegian sector of the Barents Sea began in 1969. Acreage was offered and awarded to several companies in the Norwegian fifth round of concessions in 1980. By 1993, fourteen concession rounds have resulted in steady growth in the leased acreage. Drilling activity has been maintained at a low but stable level with fifty wildcat wells having been drilled over the period. There have been several important discoveries of natural gas but only minor oil discoveries. The Hammerfest Basin lies between 71° 10′ and 71° 40′ north and 20° to 22° east and is the principal area of interest in the Norwegian sector of the Barents Sea.

The Russian sector of the Barents Sea and the Kara Sea has been explored more extensively, first by Russian oil interests and then by these same interests in partnership with foreign entities. The onshore oil and gas fields of the Timan-Pechora basin border the Pechora Sea. Investigations in the Pechora Sea carried out during the 1960s established the probability that a major sedimentary basin lay offshore. Numerous offshore prospects have been identified. Some of these are either ready for drilling or have been the object of some initial drilling. The Prirazlomnoya oil field is a recent significant discovery in this region.

Exploration surveys in the Russian sector of the Barents Sea in the 1970s identified about twenty-five prospective structures. About twenty-five wells have been drilled and some very significant finds, primarily of gas, have been made. These extend in a band from the west coast of Novaya Zemlya southwestward toward the city of Murmansk on the Kola Peninsula.

[109]Reference 1.
[110]Dore, A.G. 1995. "Barents Sea Geology, Petroleum Resources, Commercial Potential." *Arctic* 48(3):207-222.

The Russian sector of the Barents Sea may be divided into two hydrocarbon provinces. The southeast region is characterized by promising shows of oil, whereas the central and southwestern portions of the region appear to contain significant gas reserves.

Natural gas deposits beneath the eastern portion of the Kara Sea are considered to be the seaward extension of the gas province on the Yamal Peninsula.

3.9   MUNITIONS DISPOSAL SITES

As described in Chapter 2, five munitions disposal sites have been identified. Two sites are in the Barents Sea, two are in the Kara Sea and one is in the White Sea. Four of the sites are located in water deeper than 200 m. The site near Kolguev Island in the Pechora Sea region is located in shallow water.

Characteristics of the disposal sites are given in Table 3-1. Bathymetry of each site is shown in Figures 3-1, 3-7, and 3-12. No data that had been gathered from within sites 121, 122, 124, and 134 was found. Characteristics of these sites are inferred from information in Sections 3.1 through 3.8. Sediment and bottom water temperature data are available for disposal site 123 in the St. Anna Trough.[1]

Table 3-1: Characteristics of Explosives Disposal Sites in the Study Region

Site	Site No.	Location (lat., long.)	Area (km²)	Water Depth (m)	Sediment Type	Benthic Biomass (g m⁻²)	Ecosystem Type
Barents Sea	122	72N50 49E00	43	about 220	silty sand or sandy silt	50 to 200	pelagic
	134	69N35 47E55	528	30-50	sand or silty sand	50 to 200	bentho-pelagic
Kara Sea	123	77-78N 68-70E	17,150	mostly 450-550	sandy mud, mud	less than 10	pelagic
	124	73N29 58E12	67	200-250	silt	less than 10	pelagic
White Sea	121	65N20-30 36E30-50	292	200-250, some 100-200	mud	low	pelagic

BACKGROUND

- This chapter describes the chemical transformations that CW agents Tabun, Sarin, mustard and Lewisite are likely to undergo in the marine environment.

- Temperature, pH, ion concentrations, and pressure are characteristics of the marine environment that potentially affect the persistence of CW agents.

- The chemistry of CW agents in the marine environment is dominated by hydrolysis, the reaction of the agents with water. Major products of the hydrolysis reactions are identified.

- All agents and their hydrolysis products have estimated log K_{ow} values of less than three.

- Some of the important characteristics of these agents are:

CW Agent	Solubility, g L^{-1}	$k_{hydrolysis}$, hr^{-1}	$t_{1/2}$
Tabun (GA)	72	0.017	40 hr
Sarin (GB)	miscible	0.044	15.9 hr
Mustard (H)	0.3	0.132	5.3 hr
Lewisite (L)	0.5	> 20	< 2.1 min

CONCLUSIONS

- The key features of the chemistry of the CW agents in the marine environment are as follows:

  - Tabun is fairly soluble in water and hydrolyzes over a period of days;

  - Sarin is miscible (mixes in all proportions) with water and also hydrolyzes over a period of days;

  - Dissolved mustard hydrolyzes relatively rapidly. However, the persistence of mustard in the marine environment is controlled by the rate at which it dissolves;

  - Lewisite is soluble in water and hydrolyzes very rapidly. The initial hydrolysis products of Lewisite are also very toxic and persist in seawater for months or longer. Ultimately, the Lewisite hydrolysis products are converted to arsenic.

4.1 INTRODUCTION

This chapter describes the chemical transformations that CW agents are likely to undergo in the marine environment. Chemical structures of the four CW agents covered in this study are provided in Table 4-1, along with their common names, Chemical Abstracts Service (CAS) names, molecular formulas, molecular weights, and CAS registry numbers.

The key questions addressed in this chapter are summarized in Table 4-2, followed by a compilation of

those characteristics of the marine environment that affect the persistence of CW agents. Information will be provided for each of these agents on the following:

- Manufacture of the agent;
- Hydrolysis reactions and rates;
- Oxidation reactions;
- Photolysis reactions; and
- Thermolysis reactions.

After the individual agents (Tabun, Sarin, mustard and Lewisite) are considered, a brief survey of the

Table 4-1: Chemical Structures of CW Agents

Common Name(s)	Chemical Abstracts Service (CAS) Name	Molecular Formula	Molecular Weight	CAS Registry Number	Chemical Structure
GA, Tabun	Dimethylphosphoramidocyanidic acid, ethyl ester	$C_5H_{11}N_2O_2P$	162.12	77-81-6	$CH_3CH_2O-P(=O)-N(CH_3)(CH_3)$, CN
GB, Sarin	Methylphosphonofluoridic acid, (1-methylethyl) ester	$C_4H_{10}FO_2P$	140.09	107-44-8	$F-P(=O)-O-CH_3$, $CH_3 CH_3$
H, Mustard gas, yperite, sulfur mustard, Kampfstoff Lost	1,1'-thiobis[2-chloroethane]	$C_4H_8Cl_2S$	159.08	505-60-2	$Cl-CH_2 CH_2-S-CH_2 CH_2-Cl$
L, Lewisite	(2-chloroethenyl)arsonous dichloride	$C_2H_2AsCl_3$	207.32	541-25-3	Cl ... $AsCl_2$

4-2

Table 4-2: Key Questions Related to CW Agent Chemistry

1	How soluble is the agent and how fast will it dissolve in seawater at 0°C?
2	How rapidly will the agent react with seawater?
3	What substances are produced by that reaction?
4	What other chemical reactions will occur?
5	What are the physical properties of the agent and the reaction products that will affect environmental fate and transport?

chemistry of arsenic in the environment follows and a discussion of the effects of pressure on hydrolysis rates concludes this chapter.

4.2 CHARACTERISTICS OF THE MARINE ENVIRONMENT AFFECTING PERSISTENCE OF CHEMICAL WARFARE AGENTS

The chemistry related to the environmental fate and transport of chemical warfare agents at the floor of the ocean is an important component of this study. However, few measurements of chemical properties and reaction rates of the compounds of interest for this study are made under the conditions found at the ocean floor in the study area. Nevertheless, existing measurements have been extrapolated to those conditions according to well-established chemical principles. The characteristics of the ocean environment that potentially affect the rates at which reactions occur include the following:

- Temperature. In the areas where CW munitions were dumped, the temperatures at the bottom of the sea range from 3°C in parts of the Barents Sea to -1.8°C at the bottom of the East Novaya Zemlya Trough. All reaction rates have been adjusted to 0°C as representative of the conditions in the various study areas.

- pH. The rates of hydrolysis reactions by hydroxide anion are dependent on the hydroxide concentration, and thus on pH. All reaction rates were adjusted to pH 8.1.

- Concentration of metal ions. Magnesium and calcium ions and their complexes are known to catalyze the hydrolysis of Sarin. The range of salinity found in the study area (see Chapter 3) indicate that the ionic concentrations should be typical of seawater, *i.e.*, $[Mg^{+2}] = 0.05357$ mole L^{-1} and $[Ca^{+2}] = 0.01024$ mole L^{-1}.

- Concentration of chloride ion. Chloride inhibits the hydrolysis of mustard. In seawater, $[Cl^-] = 0.55$ mole L^{-1}.

- Ionic strength (μ). The dependence of the inhibition of mustard hydrolysis by chloride also depends on ionic strength. In seawater, $\mu = 0.70$.

- Pressure. In the study area, munitions were dumped at depths ranging from 33 to 620 m. The pressures at such depths range from approximately 3 to 62 atmospheres.

4.3 CHEMISTRY OF TABUN

4.3.1 General Information

Tabun was discovered in 1936 by G. Shrader of IG Farben in Germany[1] and was first manufactured in 1942.[2] Tabun was used by the Iraqis during the Iran-Iraq war.[3] Pure Tabun or GA is a colorless liquid with a fruity odor.[4] The industrial product has a brownish color and an odor reminiscent of bitter almonds from the formation of hydrogen cyanide. The industrial product generally contains 5-20% chlorobenzene (*vide infra*) as a solvent and stabilizer. The physical properties of Tabun are given in Table 4-3. In the absence of a measured solubility value at 0°C or information on the temperature dependence of solubility, the value of 72 g L⁻¹ will be used for the solubility of Tabun at 0°C.

Table 4-3: Physical Properties of Tabun (GA)[5]

Melting point	-50°C
Boiling point	246°C
Vapor pressure (20°C)	0.07 mm Hg
Density (20°C)	1.077 g cm^{-3}
Aqueous solubility (no temperature provided)	0.5 g L^{-1}
Aqueous solubility (20°C)[6]	72 g L^{-1}
Estimated log K_{OW}[7]	-1.44

4.3.2 Manufacturing Processes

The manufacturing processes for Tabun generally involve the reaction of phosphorous oxychloride with dimethylamine, sodium cyanide, and ethanol, as in the original Schrader process:[8]

$$POCl_3 + (CH_3)_2NH \rightarrow \begin{array}{c} CH_3 \\ \diagdown \\ N\text{-}P\text{-}C \\ \diagup \quad | \\ CH_3 \quad Cl \end{array} + NaCN/CH_3CH_2OH \rightarrow \begin{array}{c} CH_3 \\ \diagdown \\ N\text{-}P\text{-}O\text{-}CH_2CH_3 \\ \diagup \quad | \\ CH_3 \quad CN \end{array}$$
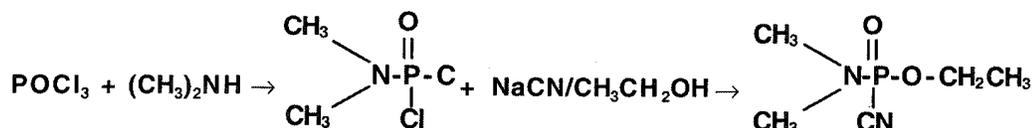
The order of addition is not critical. One variant of the process adds ethanol followed by dimethylamine followed by cyanide. Another adds dimethylamine first, then sodium cyanide and ethanol separately in that order. A third variant reaction uses phosphorous trichloride as the starting material and cyanogen chloride rather than cyanide:

$$PCl_3 + CH_3CH_2OH \rightarrow (CH_3CH_2O)_2PCl + (CH_3)_2NH \rightarrow \begin{array}{c} CH_3 \\ \diagdown \\ N\text{-}P\text{-}O\text{-}CH_2CH_3 \\ \diagup \quad | \\ CH_3 \quad O\text{-}CH_2CH_3 \end{array} + Cl\text{-}CN \rightarrow$$

$$\begin{array}{c} CH_3 \\ \diagdown \\ N\text{-}P\text{-}O\text{-}CH_2CH_3 \\ \diagup \quad | \\ CH_3 \quad CN \end{array}$$
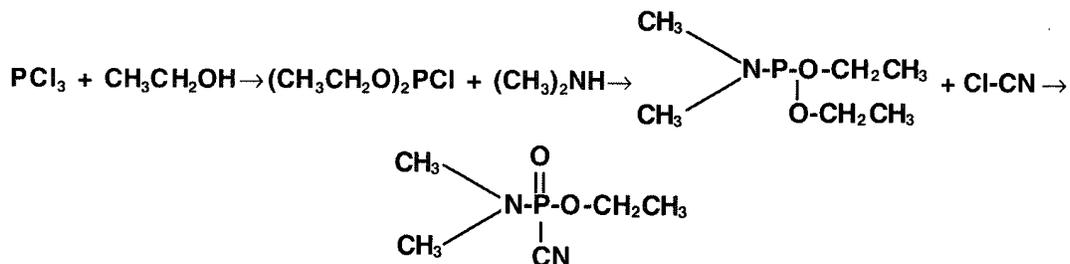
[1]Antonov, N., *Chemical Weapons at the Turn of the Century*, LN 72-96, p. 30.

[2]Franke. S., *Manual of Military Chemistry, Volume 1. Chemistry of Chemical Warfare Agents*, Deutscher Militärverlag: Berlin (East), 1967. Translated from German by U.S. Department of Commerce, National Bureau of Standards, Institute for Applied Technology, NTIS no. AD-849 866, pp. 240-241, unless otherwise noted.

[3]Perera, J., *New Scientist*, 4 April 1985, 107, 8.

[4]*The Merck Index*, 11 ed., Budavari, S.: OíNiel. M. J.; Amith, A.; Heckelmanm P. E., Eds., Merck & Co.: Rahway, NJ. 1989, p. 1427, compound no. 9001.

[5]Reference 2.

[6]*Chemical Agent Data Sheets*, Vol. I, EO-SR-74001, Edgewood Arsenal, 1974.

[7]Estimated using Syracuse Research Corporation, LOGKOW version 1.50; see Meylan, W. M.; Howard, P. H., "Atom/Fragment Contribution Method for Estimating Octanol-Water Partition Coefficients," *J. Pharm. Sci.* 1995, 84(1): 83-92.

[8]Wyant, R. E. et al. *Final Report on Chemical Lists for Analyte Selection*, Battelle, 1993, Contract No. 92 H363340-000, Table 2.

4.3.3 Hydrolysis

At pH ≥ 7, Tabun is hydrolyzed by hydroxide anion, producing cyanide anion and monoethyl dimethylphosphoramidate as initial products:

$$CH_3\text{-}N\text{-}P\text{-}O\text{-}CH_2CH_3 + OH^- \rightarrow CN^- + CH_3\text{-}N\text{-}P\text{-}O\text{-}CH_2CH_3$$
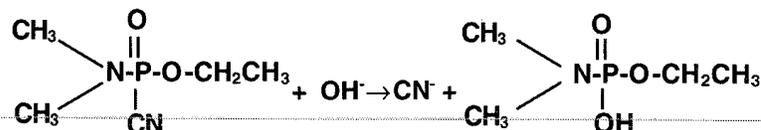
At pH < 9 and > 3, Tabun is hydrolyzed by water, producing the same initial products:

$$CH_3\text{-}N\text{-}P\text{-}O\text{-}CH_2CH_3 + H_2O \rightarrow HCN + CH_3\text{-}N\text{-}P\text{-}O\text{-}CH_2CH_3$$
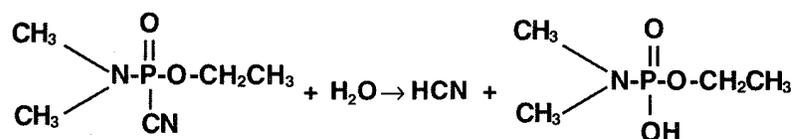
At pH ≤ 5, Tabun is hydrolyzed by acid. The acidic reaction produces protonated dimethylamine and monoethyl phosphorocyanate:

$$CH_3\text{-}N\text{-}P\text{-}O\text{-}CH_2CH_3 + H_3O^+ \rightarrow CH_3\text{-}NH_2^+ + HO\text{-}P\text{-}O\text{-}CH_2CH_3$$
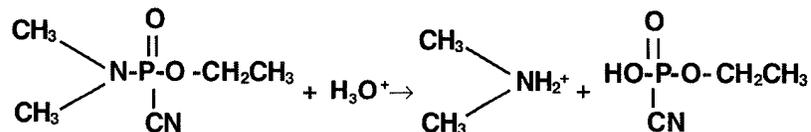
Under the conditions found in the ocean (pH 8.1), both the neutral and basic reactions occur, producing cyanide as the first hydrolysis product. The monoethyl dimethylphosphoramidate subsequently hydrolyzes to ethanol and dimethylphosphoramidic acid, which in turn slowly hydrolyzes to dimethylamine and phosphoric acid:

$$CH_3\text{-}N\text{-}P\text{-}O\text{-}CH_2CH_3 \rightarrow CH_3CH_2OH + CH_3\text{-}N\text{-}P\text{-}OH \rightarrow H_3PO_4 + (CH_3)_2NH$$
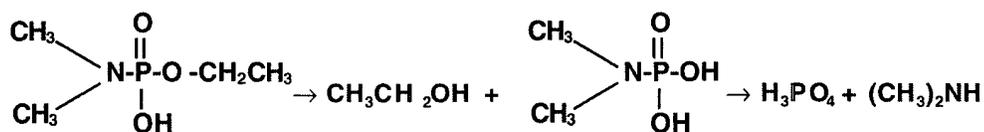
The compounds produced during the hydrolysis reaction in the marine environment are listed in Table 4-4. Of these products, cyanide and dimethylamine are known to have significant toxicity (see Chapter 6).

4-5

Table 4-4: Tabun (GA) Hydrolysis Products

Compound	MW	Solubility, g L^{-1}	Estimated log K_{ow}[7]	Product Produced from 1 kg GA, g
Cyanide (as HCN)	27.03	miscible[9]	-0.69	167
Dimethylphosphoramidic acid, monoethyl ester	153.12	–	-0.04	944
Dimethylphosphoramidic acid	125.06	–	-0.59	771
Ethanol	46.07	miscible[10]	-0.14	284
Dimethylamine	45.08	911[11]	-0.17	278
Phosphoric Acid	98.00	5480[11]	–	604

The rate constant for the hydrolysis of Tabun has been measured at a variety of pH and temperatures; these values are reported in Table 4-5. From this data, an activation energy, E_a, of 10.1 kcal mole^{-1} was calculated for the basic hydrolysis of Tabun.[12] Thus, at pH 8.1 and 0°C, the rate constant for the basic process is calculated using the Arrhenius expression[13] as $k_{OH} = 1.35 \times 10^{-3}$hr^{-1}. No E_a is available for the neutral Tabun hydrolysis reaction. A group of U.S. Army researchers has also measured the half-life of Tabun in seawater at several different temperatures; these values are reported in Table 4-6 along with the corresponding rate constants.

Table 4-5: Tabun (GA) Hydrolysis Rate Constants

T (°C)	pH	k_{obsd} (hr^{-1})	Reference
25	5.00	0.39	[14]
20	5.10	0.07	[15]
20	7.20	0.17	[15]
20	8.60	0.28	[15]
25	8.50	0.26	[12]
25	8.75	0.33	[12]
25	9.00	0.50	[12]
25	9.00	0.42	[16]
25	9.50	1.26	[12]
35	9.00	1.44	[12]
35	9.50	4.21	[12]

Table 4-6: Tabun (GA) Hydrolysis Half-lives in Seawater[17]

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

[9]Reference 4, p. 760, compound no. 4722.
[10]Reference 4, p. 594, compound no. 3716.
[11]EPA ASTER data base.
[12]Larsson, L., *The alkaline hydrolysis of two sarin analogues and of Tabun*, Acta Chim. Scand., 1958, 12, 783-785.
[13] $k = Ae^{-\frac{E_a}{RT}}$. For two temperatures T_1 and T_2, $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.
[14]Larsson. L., *The Hydrolysis of Dimethylamido-Ethoxy-Phosphoryl Cyanide (Tabun)*, Acta Chim. Scand., 1953, 7, 306-314.15
[15]Holmstedt, B., Synthesis and pharmacology of dimethyl-amidoethoxy-phosphoryl cyanide (Tabun) together with a description of some allied antichloinesterase compounds containing the N-P bond, Acta Physiol. Scand., 1951, 25, Suppl. No. 90, Stockholm, half-lives taken from figure 2, p. 35.
[16]Desire, B. and S. Saint-Andre, "Interaction of Soman With (-cyclodextrin," *Fundam. Appl. Toxicol.*, 1986, 7(4), 646-657.
[17]Epstein, J. *et al.*, "Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations," *EASP 1200-12*, January 1973, AD-B955399 (distribution limited to U.S. Government).

Two approaches were used to estimate the rate of the neutral reaction under seafloor conditions. Using a "normal" solution, ion-dipole reaction E_a equal to approximately 20 kcal mole[-1],[18] one can calculate a rate constant $k_w = 0.018$ hr[-1] from the value of 0.39 hr^{-1} (measured at 25°C and pH 5.0), or $k_w = 0.014$ hr[-1] from the value of 0.17 hr^{-1} (measured at 20°C and pH 7.2). These two rate constants should reflect the pH-independent rate of the neutral reaction. Based on this calculation, it is apparent that at pH 8.1 and 0°C the neutral reaction will dominate the observed rate of reaction, and that Tabun hydrolysis should occur with a rate constant $k_{observed} = k_{OH} + k_w = 0.015 - 0.019$ hr[-1]. Alternatively, one can use the Arrhenius expression to extrapolate the seawater data to 0°C, giving $k_{observed} = 0.017$ hr[-1], equivalent to a half life, $t_{1/2} = 40$ hours. The latter value will be used as the hydrolysis rate constant for Tabun in seawater at 0°C. No information is available on the rate at which Tabun dissolves in water. Therefore, given the fairly high solubility of Tabun, it will be assumed for purposes of this study that the rate of dissolution is limited only by the physical mixing of Tabun with water.

4.3.4 Photolysis

Tabun and its hydrolysis products exhibit no significant phototransformations in sunlight.[19]

4.3.5 Thermolysis

Tabun and its hydrolysis products are thermally stable at temperatures less than 49°C.[20]

4.3.6 Properties of Chlorobenzene

Tabun, as an industrial product, generally contains five to twenty percent chlorobenzene (CAS registry no. 108-90-7) as a solvent and a stabilizer. It is a colorless liquid with a not unpleasant odor used as a chemical intermediate and solvent. Chlorobenzene is unreactive toward water and decomposes only at high temperatures. The physical properties of chlorobenzene are given in Table 4-7.

Table 4-7: Physical Properties of Chlorobenzene[21]

Melting point	-45°C
Boiling point	131-132°C
Density (20°C)	1.107 g cm^{-3}
Log k_{ow}[22]	2.84
Aqueous solubility[23]	11.9 g L^{-1}

4.4 CHEMISTRY OF SARIN

4.4.1 General Information

Sarin or GB was discovered in Germany in 1939 by G. Shrader. Thirty tons of it were produced in pilot plants beginning in July 1944.[24] Two large industrial plants for full scale Sarin production were under construction at the conclusion of World War II. Sarin is a colorless and odorless liquid. The rate of dissolution of Sarin is limited only by the physical mixing with water because water and Sarin are miscible. The physical properties of Sarin are given in Table 4-8.

[18]Hammes, G. G., *Principles of Chemical Kinetics*, Academic Press: New York, 1978, p. 170.
[19]Reference 8, Table 1.
[20]Reference 19.
[21]Reference 4, p. 327, compound no. 2122 unless otherwise noted.
[22]Sangster, J., LOGKOW DATABANK, Sangster Research Laboratories, Montreal, Quebec, Canada, 1994.
[23]*The Kirk-Othmer Encyclopedia of Science and Technology*, 4 ed., Vol. 6, p. 94.
[24]Reference 2, pp. 247, 252.

Table 4-8: Physical Properties of Sarin (GB)[25]

Melting point	-57°C
Boiling point	147°C
Vapor pressure (20°C)	1.48 mm Hg
Density (20°C)	1.11 g cm⁻³
Aqueous solubility	miscible
Estimated log K_{ow}[7]	0.24
Log $K_{benzene-water}$[26]	0.31

4.4.2 Manufacturing Processes[27]

The key intermediate in the manufacture of Sarin is methylphosphonyl dichloride (dichlor). There are several manufacturing routes to dichlor. The "DMPH" process proceeds from phosphorous trichloride and methanol through several intermediates:

$$PCl_3 + CH_3OH \rightarrow (CH_3O)_3P + HCl \rightarrow$$
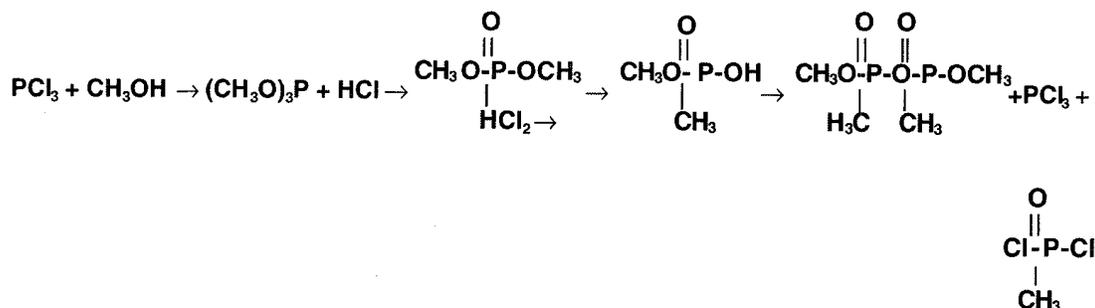
The high temperature methane (HTM) reaction involves catalytic oxidation:
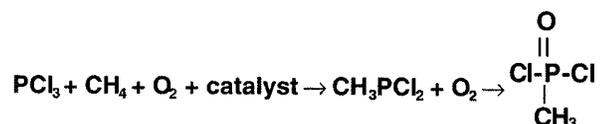
The HTM Pyro reaction is a hybrid of the two previous reactions:
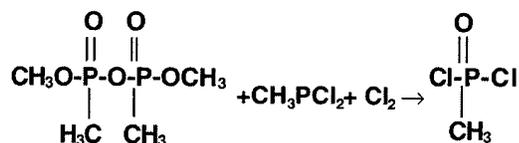
There are a number of similar reaction schemes that have been used to manufacture dichlor. Dichlor is converted to methylphosphonyldifluoride (difluor) using either hydrofluoric acid or sodium fluoride:

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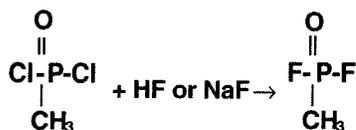
[25]Reference 2, pp. 247, 252 unless otherwise noted.
[26]Rosenthal, R. W., R. Proper and J. Epstein, "The Distribution of Some Phosphonofluoridates Between Organic Solvents and Water," *J. Phys. Chem.*, 1956; 60, 1596-1598.
[27]Reference 8, Table 3.

Finally, difluor reacts with 2-propanol to give Sarin. This is the same reaction that occurs during delivery of Sarin binary munitions:

$$\begin{array}{c} O \\ \parallel \\ F\text{-}P\text{-}F \\ | \\ CH_3 \end{array} + (CH_3)_2CHOH \rightarrow \begin{array}{c} O \\ \parallel \\ F\text{-}P\text{-}O\text{-}CHCH_3 \\ | \quad | \\ CH_3 CH_3 \end{array} + HF$$
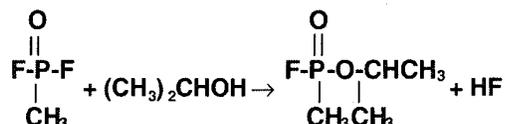
The HF byproduct can be used to convert dichlor to difluor *in situ*; typically, a 1:1 mixture of dichlor and difluor is mixed with 2-propanol in the manufacturing process.

4.4.3 Hydrolysis

Sarin undergoes hydrolysis by acidic, neutral, and basic mechanisms, all of which produce fluoride and isopropyl methylphosphonate as the initial products. Under the conditions found in the ocean (pH 8.1), both the neutral and basic reactions will occur. The neutral reaction is as follows:

$$\begin{array}{c} O \\ \parallel \\ F\text{-}P\text{-}O\text{-}CHCH_3 \\ | \quad | \\ CH_3 CH_3 \end{array} + H_2O \rightarrow HF + \begin{array}{c} O \\ \parallel \\ HO\text{-}P\text{-}O\text{-}CHCH_3 \\ | \quad | \\ CH_3 CH_3 \end{array} \rightarrow \begin{array}{c} O \\ \parallel \\ HO\text{-}P\text{-}OH \\ | \\ CH_3 \end{array} + (CH_3)_2CHOH$$
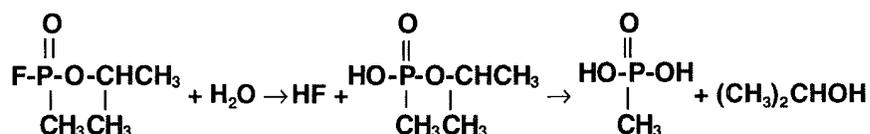
The basic reaction produces the same products by way of a different mechanism. The compounds produced during the basic hydrolysis reaction are given in Table 4-9. Of these products, only fluoride is known to have significant toxicity, as discussed in Chapter 6. Hydrolysis reaction rate constants for Sarin for the basic (k_{OH}) and the neutral (k_W) reactions, as a function of temperature, are listed in Table 4-10.

Table 4-9: Sarin (GB) Hydrolysis Products

Compound	MW	Solubility, g L^{-1}	Estimated log K_{ow}[7]	Product Produced from 1 kg GB, g
Fluoride (as HF)	20.01	"very"[28]	–	143
Methylphosphonic acid, 1-methylethyl ester	138.10	–	0.27	986
2-Propanol	60.10	miscible[29]	0.28	429
Methylphosphonic acid	96.02	"very"[30]	-0.70	685

[28]Reference 4, p. 760, compound no. 4723.
[29]Reference 4, p. 820, compound no. 5093
[30]Weast, R.C., Ed., *Handbook of Chemistry and Physics,* 56th ed., CRC Press, 1976.

Table 4-10: Sarin (GB) 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}	[31]
25	23.7	5×10^{-5}	[31]
25	25.80	—	[32]
35	42.40	—	[31]
42.5	63.7	5×10^{-5}	[31]

The $\bar{E}_a$ values of 10.6 kcal mole^{-1} [33] and 9.1 kcal mole^{-1} [34] were calculated from the basic rate constants. Other observed rate constants for Sarin hydrolysis at various temperature and pH values are given in Table 4-11.

Table 4-11: Observed Sarin (GB) Hydrolysis Rate Constants

T	pH	k_{obsd} (hr^{-1})	Reference
23	4.5-5.0	0.00334	[35]
25	7.4	0.0324	[16]
25	9	0.84	[16]
25	9	1.2	[36]

In seawater, at a reported constant pH of 7.7, the half-life of Sarin at any temperature between 0 and 25°C can be estimated using the following expression:[37]

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

In seawater, Ca^{+2} and Mg^{+2} significantly catalyze Sarin hydrolysis. At 0.2°C in seawater, the measured half-life of Sarin is 15.9 hours,[38,39] corresponding to a rate constant for hydrolysis of 0.044 hr^{-1}. Finally, if the initial concentration of Sarin is ≥ 0.01 mole L^{-1} (1.4 g L^{-1}), the quantity of acidic reaction products will be sufficient to overwhelm the buffering capacity of seawater[40] and autocatalysis will occur, increasing the rate of hydrolysis.

[31] Gustafson, R.L.; A.E. Martell, "A Kinetic Study of the Copper(II) Chelate-catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate (Sarin)." *J. Am. Chem. Soc.*, 1962, 84, 2309-2316.

[32] Larsson, L., *The Alkaline Hydrolysis of Isopropoxy-Methyl-Phosophoryl Fluoride (Sarin) and Some Analogues, Acta Chem. Scand.*, 1957, 11, 1131-1142.

[33] Reference 31.

[34] Reference 32.

[35] Ellin, R.I., W.A. Groff, and A. Kaminskis, "The Stability of Sarin and Soman in Dilute Aqueous Solutions and the Catalytic Effect of Acetate Ion," *J. Environ. Sci. Health, Part B*, 1981, *B16(6)*, 713-717.

[36] van Hooidonk, C. and J.C.A.E. Breebaart-Hansen, "Stereospecific reaction of isopropyl methylphosphonofluoridate (Sarin) with α-cyclodextrin: a model for enzyme inhibition," *Rec. Trav. Chim. Pays Bas*, 1970, 89, 289-299.

[37] Epstein, J., "Rate of Decomposition of Sarin in Seawater," *Science*, 1970, 170, 1936-1938.

[38] Reference 37.

[39] Demek, M. M. et al., "Behavior of Chemical Agents in Seawater," *EATR* 4417, August 1970, AD-873242.

[40] Reference 38.

4.4.4   Photolysis

Sarin and its hydrolysis products exhibit no significant phototransformations in sunlight.[41]

4.4.5   Thermolysis

Sarin and its hydrolysis products are thermally stable at temperatures less than 49°C.[42]

4.5   CHEMISTRY OF MUSTARD

4.5.1   General Information

Mustard or H was first used on the night of 12-13 July 1917 by the Germans against the British near Ypres in Belgium.[43] Subsequent documented uses of mustard include use by the Italians during the invasion of Ethiopia in 1935[44] and by both sides in the Iran-Iraq war.[45] Large quantities were prepared by both the Allies and the Axis during World War II, although no CW agents are known to have been used in combat.[46] When pure, mustard is a colorless and odorless liquid. Agent grade material is typically yellow to dark brown with a sweet odor reminiscent of freshly cut hay and it is a strong vesicant.[47,48] Physical properties of mustard are given in Table 4-12.

Table 4-12: Physical Properties of Mustard (H)[49]

Melting point	13-14°C
Boiling point	215-217°C
Vapor pressure (20°C)	0.11 mm Hg
Density (20°C)	1.27 g cm^{-3}
Aqueous solubility (20°C)	0.8 g L^{-1}
Aqueous solubility (10°C)[50]	0.7 g L^{-1}
Aqueous solubility (0°C)[51]	0.3 g L^{-1}
Estimated log K_{oc}[52]	2.12
Estimated log K_{ow}[52]	1.37
Estimated log K_{ow}[7]	2.41

4.5.2   Manufacturing Processes

There are several methods used to manufacture mustard. The original preparation of mustard involved the intermediate thiodiglycol (TDG, 2,2'-thiobis[ethanol]) prepared from sodium sulfide and ethylene oxide (which is in turn prepared from ethylene):

[41]Reference 19.
[42]Reference 19.
[43]Reference 2, pp. 114, 115.
[44]Reference 2, pp. 114, 115.
[45]Reference 3.
[46]Reference 2, pp. 114, 115.
[47]Reference 4, p. 995, compound no. 6225.
[48]The Kirk-Othmer *Encyclopedia of Science and Technology,* 4 ed., Vol. 5, pp. 795-802.
[49]Reference 3, pp. 247, 252 unless otherwise indicated.
[50]Hopkins, E. F., "On Dichlorethylsulphide (Mustard Gas). III. Solubility and Hydrolysis of Dichlorethylsulphide With a New Method for Estimating Small Amounts of the Same," J. *Pharmacol.,* 1919, 12, 393-403.
[51]Reference 2, p. 120.
[52]Lyman, W. J., W. F. Reehl, D.H. Rosenblatt, eds., *Handbook of Chemical Property Estimation Methods,* McGraw-Hill Book Company: New York, NY, 1981.

$$\text{Na}_2\text{S} + 2 \;\; \overset{\text{O}}{\underset{\text{CH}_2\text{---}\text{CH}_2}{\triangle}} \;\; \rightarrow \text{neutralize} \rightarrow \text{HO-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-OH}$$

TDG then reacts with hydrogen chloride or other chlorinating agents:

$$\text{HO-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-OH} + 2\text{ HCl} \rightarrow \text{Cl-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-Cl}$$

This preparation is more complicated and time-consuming in comparison with direct methods. Direct synthesis is the fastest, most economical method of production. There are two direct synthesis methods, the Guthrie method:

$$\text{CH}_2\text{=CH}_2 + \text{SCl}_2 \rightarrow \text{Cl-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-Cl}$$

and the Levinstein method:

$$\text{CH}_2\text{=CH}_2 + \text{S}_2\text{Cl}_2 \rightarrow \text{Cl-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-Cl} + \text{S}$$

The Levinstein method also produces the CW agent Q and other higher analogues of mustard.

The former Soviet Union used a variation on the Levinstein process developed by V. S. Zaykov. In the Zaykov process, propylene was used to replace all or part of the ethylene, giving a mixture of mustard, 1,1'-thiobis[2-chloropropane], and various mixed analogues which have a lower freezing temperature than pure mustard.[53] The reactivity of Zaykov mustard should be entirely analogous to the reactivity of mustard.

4.5.3   Hydrolysis

The first step in the hydrolysis of mustard is a nucleophilic attack of the sulfide S neighboring group on the β-carbon to form an intermediate sulfonium ion: [54]
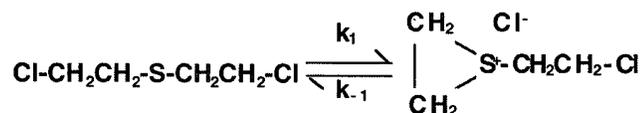
This is considered to be an S_N1 reaction with anchimeric ("neighboring group") assistance. The reactant and the ion pair are in equilibrium, so that the observed reaction rate will decrease with increasing chloride concentration. Water attacks the sulfonium ion at one of the ring carbons, opening the ring to give hemimustard and hydrogen chloride:
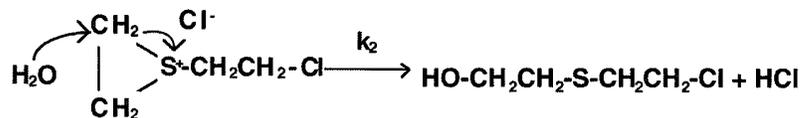
[53]Fedorov, L. A., *Chemical Weapons in Russia: History, Ecology, Politics, Center of Ecological Policy of Russia: Moscow,* 1994, pp. 4-12, 18. Translated from Russian by Foreign Broadcast Information Service.

[54]Bartlett, P. D., C. G. Swain, "Kinetics of Hydrolysis and Displacement Reactions of ß, ß'-Dichlorodiethyl Sulfide (Mustard Gas) and of ß-Chloro-ß-hydroxydiethyl Sulfide (Mustard Chlorohydrin)," *J. Am. Chem. Soc.* 1949, 71, 1406-1415.

Hemimustard is also a vesicant. It then reacts in a similar fashion with water to give thiodiglycol and an additional molecule of hydrogen chloride:
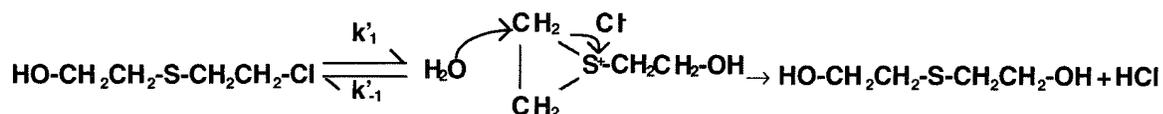
The cyclic intermediate formed from hemimustard also reacts via an internal displacement to give 1,4-thioxane and an additional molecule of hydrogen chloride:
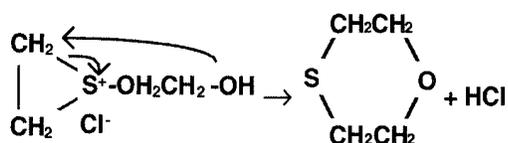
The hemimustard hydrolysis reaction produces a ratio of thiodiglycol to thioxane roughly 4:1.[55] The amounts of TDG and thioxane produced by mustard hydrolysis are given in Table 4-13.

Table 4-13: Mustard (H) Hydrolysis Products

Compound	FW	Solubility,[11] g L^{-1}	Estimated log K$_{ow}$[7]	Product Produced from 1 kg H, g
TDG	122.19	6900	-0.62	648
1,4-Thioxane	104.17	286	0.53	120

A rate constant at 25°C of k_1 = 0.155 min^{-1} for mustard has been established and, for hemimustard k'_1=0.260 min^{-1}.[56] Hemimustard is a relatively short-lived hydrolysis intermediate. The kinetics of hydrolysis have been determined at different temperatures and are presented in Table 4-14.[57] The activation enthalpy, $\Delta H^{\ddagger}$ = 18.5 kcal mole^{-1}, has been determined for mustard hydrolysis.[58]

Another consideration is that aqueous chloride ions affect the equilibrium between mustard and the intermediate sulfonium ion. One approach to calculating the magnitude of this effect is to use the experimental value for the reaction rate at 0°C and correct for the chloride ion present in seawater. The effect of chloride is to slow the observed rate of mustard hydrolysis by a factor equal to:

$$\frac{k_{Cl^-}}{k_{H_2O}} = \frac{1}{1 + F_{Cl^-}^{\mu}\left[Cl^-\right]}$$

[55]D'Agostino, P. A., and L. R. Provost, "The Identification of Compounds in Mustard Hydrolysate (U)," *DRES Suffield Report 412,* Ralston, Alberta, Canada, 1985, available through DTIC AD-A156381, Table III. This report also identifies 1,4-dithiane and 2-(vinylthio)ethanol as products in the aqueous phase from hydrolysis at high concentrations of H (> 2 mole L^{-1}) at high temperature (100(C). These substances likely arise from the high concentration and temperature used by the Canadians and are likely to represent minor pathways under the conditions at the sea floor of the study area.
[56]Reference 54.
[57]Recently, investigators have questioned the validity of the rate constants in References 60, 62 and 63 because they were calculated assuming a single first-order reaction rather than consecutive first-order reactions. See Ward, J.r.; Seiders, R.P., *On the activation energy for the hydrolysis of bis (2-chloroethyl) sulfide, Thermochim.* Acta, 1984, 81, 343-348. However, using accepted values for $\Delta H^{\ddagger}$=(18.5 kcal mole^{-1}) and the observed rate constant at 25°C (0.155 min^{-1}) gives a calculated value of k_1 = 0.0089 min^{-1} at 0°C, which is in reasonable accord with the experimental value of 0.0068 min^{-1}.
[58]Yang, Y. C., et al. "On the activation energy for the hydrolysis of bis(2-chloroethyl) sulfide. II", *Thermochim. Acta,* 1987, 114, 313-317.

where F varies with the ionic strength according to the Bronsted-Bjerrum rate equation with a limiting value of $F^0_{Cl^-} = 32.2$ L mole^{-1} at zero ionic strength:[59]

$$\log_{10} F^\mu_{Cl^-} = \log_{10} F^0_{Cl^-} + 2Az_{R_3S^+}z_{Cl^-}\mu^{1/2}$$

which uses the constant from the Debye-Hückel equation:[60]

$$A = \left[\frac{(2\pi N_0)^{1/2}}{2.303} \left(\frac{e^2}{10\varepsilon\ kT} \right)^{3/2} \right]$$

At 0°C, the value of the Debye-Hückel A term is calculated as 0.55. The charges (z_{R_3S} and z_{Cl^-}) are +1 and -1, and the ionic strength of seawater, ($\mu = 0.70$, which gives a value of $F^\mu_{Cl^-} = 3.8$ for seawater at 0°C. If the hydrolysis rate constant in freshwater is 0.0068 min^{-1} at 0°C and [Cl$^-$] = 0.55 mole L^{-1} this gives a hydrolysis rate constant k_1 = 0.0022 min^{-1} in seawater.[61]

Table 4-14: Hydrolysis Rate Constants of Mustard (H) at Various Temperatures

T (°C)	k_1, min^{-1}	Reference
0	0.0068	62
0.6	[0.0044][63]	50
5	0.0124	62
10	0.0224	62
10	[0.0131][63]	50
12.5	0.0215	64
14.5	0.028	65
15	0.0390	62
20	0.0696	62
20	0.044	64
20	[0.046][63]	50
24.6	0.097	65
25	0.118	62
30	0.188	64
30	[0.20][63]	50
36.8	0.385	65
37.5	[0.28][63]	50
40	0.0.924	50
40	0.261	64
50	0.646	64

[59]Reference 54.

[60]Castellan, G. W., *Physical Chemistry, 2nd ed.*, Addison-Wesley: Reading, Massachusetts, 1971, p. 375.

[61]Note however, that the ionic strength of seawater is above the level at which deviations from the Debye-Hückel law are typically observed. The true value of the rate constant may be somewhat higher due to such deviations.

[62]Brookfield, K. J., F. N. Woodward, and R. Owens, "The Kinetics of Hydrolysis of Vesicants. Part II. 2,2 Dichlorodiethylsulphide (H)," *Sutton Oak Report 576.* Great Britain, 3 March 1942.

[63]The accuracy of the rate constants in reference 45 have been questioned because of the experimental technique used by Hopkins: Doering, W. E.; Linstead, R. P. "Reactions of the Chlorine Atoms of Mustard Gas in Aqueous Media," *OSRD Report 1094*, December 1942.

[64]Mohler, H., J. Hartnagel, *Chemische Kampfstoffe XXIII. Hydrolyse von β,β-Dichlor-diäthyl-sulfid, Helv. Chim. Acta*, 1941, 24, 564-570.

[65]Peters, R. A., E. Walker, "Rate of liberation of Acid by ß, ß-'-Dichlorodiethyl Sulfide and its Analogous and its Relation to the "Acid" Theory of Skin Vesication, *Biochem. J.,* 1923, 17, 260-276.

A group of U.S. Army researchers has also measured the half-life of mustard in seawater at several different temperatures; these values are reported in Table 4-15 along with the corresponding rate constants. An alternative approach to calculating the magnitude of the chloride effect is to use the experimental value for the reaction rate in seawater and extrapolate that rate to 0°C. The extrapolated reaction rate, $k_1 = 0.0020$ min^{-1}, is in agreement with the value previously calculated. The rate constant of 0.0022 min^{-1} will be used as the mustard hydrolysis rate in subsequent chapters of this study.

Table 4-15: Half-lives of Mustard (H) in Seawater[66]

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

Despite the relative rapidity of the hydrolysis reaction, mustard has been found to persist in soil or even in water for periods of decades.[67,68] In such incidents of long-term persistence, the common thread is the presence of bulk mustard. While the hydrolysis of *dissolved* mustard is relatively fast, the dissolution of mustard does not occur rapidly. A likely sequence for the fate of bulk mustard introduced into quiescent water would be the following:

- Mustard that initially dissolves from the droplet is hydrolyzed to TDG.

- At the interface where little water is present, the intermediate sulfonium ion forms and then reacts with another molecule of mustard (rather than with water) to form 1,2-bis[(2-chloroethyl)thio]ethane (Q) and 1,2-dichloroethane:

$$Cl\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}Cl + Cl\text{-}CH_2CH_2\text{-}Cl$$
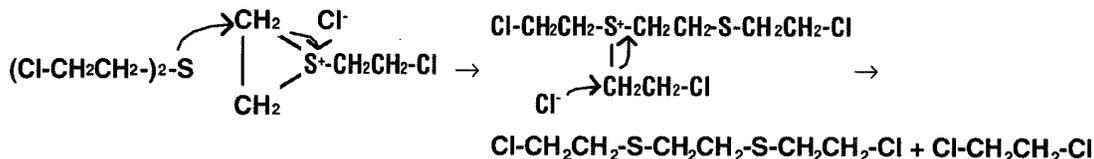
In addition, Q is a byproduct of several methods of mustard agent manufacturing, including the Levinstein process used by the United States. Thus, under long term storage conditions of mustard, significant additional amounts of Q can accumulate in the container.

Note that the presence of a certain level of Q was considered desirable because it is a powerful vesicant in its own right and depresses the freezing point of mustard. The solubility of Q is 0.3 g L^{-1}.[69]

[66]Reference 17.

[67]Munitions disposed of in the Baltic Sea after World War II have released mustard that has been brought to the surface, where it has injured fishermen as recently as 1984: Jorgensen, B. S., B. Olesen, O. Berntsen, *Mustard gas accidents on Bornholm, Ugeskr. Laeger*, 1985, 147(28), 2251-2254.

[68]Munitions disposed of in the Pacific Ocean and Japanese coastal waters after World War II have released mustard that has been brought to the surface, where it has injured people as recently as 1978: Kurata, H., *Lessons learned from the destruction of the chemical weapons of the Japanese Imperial Forces, in Chemical Weapons: Destruction and Conversion*, Stockholm International Peace Research Institute. Taylor and Francis: London, 1980, pp. 77-93.

[69]Reference 2, p. 135

- Due to lack of appreciable motion, a concentrated TDG layer builds up at the mustard droplet water interface. The TDG at the interface also reacts with the intermediate sulfonium ion to form stable sulfonium salts of the type:[70]

$$(HO\text{-}CH_2CH_2\text{-})_2\text{-}S \quad + \quad \underset{CH_2}{\overset{CH_2}{\overset{\displaystyle \diagup}{\underset{\diagdown}{|}}}} S^+\text{-}CH_2CH_2\text{-}Cl \quad Cl^- \;\rightarrow\; \underset{CH_2CH_2\text{-}OH}{\overset{HO\text{-}CH_2CH_2\text{-}S^+\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}Cl}{|}} \quad +$$

$$HO\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}OH \;\rightarrow\; \underset{CH_2CH_2\text{-}OH}{\overset{HO\text{-}CH_2CH_2\text{-}S^+\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}S^+\text{-}CH_2CH_2\text{-}OH}{|}} \qquad \underset{CH_2CH_2\text{-}OH}{\overset{}{|}}$$

- In time, non-reactive sulfonium salts such as these and higher homologues (*e.g.*, from the analogous reactions of Q) build up at the interface between the mustard droplet and the bulk aqueous phase. The sulfonium salts create a thicker boundary layer.

- Dissolution of mustard slows because the driving force for diffusion of mustard into the bulk aqueous phase decreases. Similarly, diffusion of water into the mustard droplet slows, which lowers the observed rate of hydrolysis. However, if the water is subject to disturbance, such as a heavy rain, or is rapidly flowing, it is less likely that mustard droplets would persist for significant periods.

Brookfield, et al. first established the rate (σ) at which mustard dissolves in quiescent water as a function of temperature:[71]
More recently, Demek et al. measured the rate of mustard dissolution as $\sigma = 3.4 \times 10^{-7}$ gm cm^{-2} sec^{-1} at 4°C, 0.15 knot current.[72] Epstein, et al. estimated that a one ton block of mustard would require five years to dissolve.[73] If a cylinder of solid mustard with surface area of 4×10^4 cm^2 is placed in a 0.15 knot current, mustard concentration

$$\sigma\,(gm\,cm^{-2}\,sec^{-1}) = 233.7e^{-\left(\frac{12{,}350}{RT}\right)}$$

drops within one foot to 0.3 ppm.[74] Thus, in order to perform environmental fate assessments of mustard, both the hydrolysis and dissolution rate must be considered.

4.5.4   Photolysis

Mustard and its hydrolysis products exhibit no significant phototransformations in sunlight.[75]

4.5.5   Thermolysis

Mustard and its hydrolysis products are thermally stable at temperatures less than 49°C.[76]

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[70]Yang, Y. C., et al. "Kinetics and Mechanism of the Hydrolysis of 2 Chloroethyl Sulfides," *J. Org. Chem.*, 1988, 53(14), 3293-3297.
[71]Brookfield, K. J., E. A. Moelwyn-Hughes, J. W. C. Phillips, "The Rate of Dissolution of 2,2'-dichlorodiethylsulphide (H) in Distilled and Natural Waters," *Sutton Oak Report 615,* Great Britain, 26 November 1942.[72]Reference 39.
[72]Reference 39.
[73]Reference 17.
[74]Brumfield, J. L., et al. Appendix D *Results of the Chemical Survey at DWD Area A in 1972,* in Wilkniss, P. E., *Environmental Condition Report for Deep Water Dump Area A,* NRL Report 7553, Naval Research Laboratory, Washington, DC, 1 March 1973, p. 43.
[75]Reference 19.
[76]Reference 19.

4.5.6 Oxidative Degradation

Mustard and a number of its hydrolysis products are oxidized in air at significant rates, giving the sulfoxide and sulfone analogs. These reactions occur more readily under alkaline conditions.[77] The sulfoxide and sulfone analogs of mustard are toxic, but undergo hydrolysis to less toxic products. It is unlikely, however, that the oxidation reactions will compete with hydrolysis to any significant extent in the marine environment. Therefore, these oxidation products will not be considered in subsequent chapters of this study.

4.6 CHEMISTRY OF LEWISITE

4.6.1 General Information

Lewisite was first prepared by Americans toward the end of World War I, but was never used because of the armistice. During World War II, both the American and German armies had considerable stocks of Lewisite available.[78] It may have been used by the Iraqis in addition to mustard agent.[79] Industrially-produced Lewisite has a strong penetrating geranium odor; the pure compound is odorless. Physical properties of Lewisite are given in Table 4-16.

Table 4-16: Physical Properties of Lewisite (L)[80]

Melting point	-18°C
Boiling point	190°C
Vapor pressure (20°C)	0.35 mm Hg
Density (20°C)	1.89 g cm^{-3}
Aqueous solubility	0.5 g L^{-1}
Estimated log K_{ow}[81]	2-3
Estimated log K_d for arsenic[82]	2.30

4.6.2 Manufacturing Processes

Lewisite is manufactured from acetylene and arsenic trichloride using cuprous chloride as catalyst:
This procedure gives a mixture of *cis-* and *trans-* isomers of Lewisite, plus small amounts of bis(2-

$$HC \equiv CH + AsCl_3 \rightarrow Cl\text{-}CH=CH\text{-}AsCl_2$$
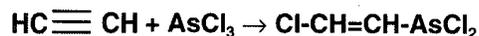
chlorovinyl)chloroarsine, tris(2-chlorovinyl)arsine, and arsenic trichloride. These minor constituents are less toxic than Lewisite and produce analogous products when they react. Therefore, they will not be considered in subsequent chapters of this study.

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[77]Reference 19.
[78]Reference 2. pp. 157-8.
[79]Reference 3.
[80]Reference 2, pp. 247, 252 unless otherwise noted.
[81]ClCH=CHPCl$_2$ has an estimated value of 2.51 using reference 7: no fragment descriptions were available for arsenic.
[82]Baes, C. F.,et al.,1984. *A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides Through Agriculture,* Oak Ridge National Laboratory report ORNL-5786, p.58: The estimate of arsenic soil-water distribution coefficient is based on a soil-to-plant elemental transfer coefficient for vegetative portions of food crops and feedplants (B_{iv}) of 0.040.

4.6.3 Hydrolysis

The hydrolysis of Lewisite proceeds according to the following scheme:

$$Cl\text{-}CH\text{=}CH\text{-}AsCl_2 + 2\ H_2O \quad \rightarrow \quad Cl\text{-}CH\text{=}CH\text{-}As(OH)_2 + 2HCl \qquad \text{fast}$$
$$\text{2-chlorovinylarsonous acid}$$

$$Cl\text{-}CH\text{=}CH\text{-}As(OH)_2 \quad \rightleftharpoons \quad Cl\text{-}CH\text{=}CH\text{-}As\text{=}O + H_2O \qquad \text{slow}$$
$$\text{Lewisite oxide}$$

$$Cl\text{-}CH\text{=}CH\text{-}As\text{=}O \quad \rightleftharpoons \quad \text{polymer} \qquad \text{slow}$$
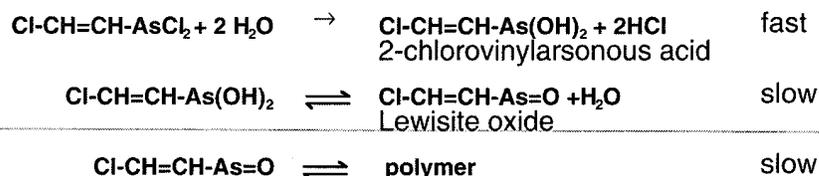
The hydrolysis product mixture has a reported log $K_{\text{benzene-water}} \leq 0.15$.[83] The initial hydrolysis reaction is rapid relative to formation of the 2 chloro-vinylarsenous acid/Lewisite oxide equilibrium mixture. Lewisite is more rapidly hydrolyzed than mustard.[84] The literature contains a report that states that "complete hydrolysis of the chlorine attached to the arsenic occurs within a few minutes at 20°C," whereas at 5°C, "90 percent hydrolyzes rapidly, the rest more slowly."[85] If 90 percent of Lewisite hydrolyzes within two minutes, the rate is at least fifty times the rate for mustard at 5°C. If we take the rate of hydrolysis of mustard at 0°C as 0.0068 min^{-1}, then the rate of Lewisite at 0°C ought to be at least 0.34 min^{-1} based on the literature report; the reaction rate is likely more rapid.

The immediate hydrolysis products, 2 chloro-vinylarsenous acid and Lewisite oxide, are also vesicants.[86] There is no appreciable difference in toxicity between Lewisite and the 2-chlorovinyl-arsenous acid/Lewisite oxide equilibrium mixture. Given the rapidity of hydrolysis it is possible that these species are responsible *in vivo* for the effects of Lewisite. The vesicant properties of the mixture are reported to remain unchanged after storage for ten weeks in seawater.[87]

Over time, the hydrolysis products will be transformed into both other organic and inorganic forms of arsenic. Waters and Williams observed that cold alkali decomposes 2 chlorovinylarsonous acid into arsonous acid, acetylene, and chloride:[88]

$$Cl\text{-}CH\text{=}CH\text{-}As(OH)_2 + OH^- \rightarrow Cl^- + HC\equiv CH + As(OH)_3$$
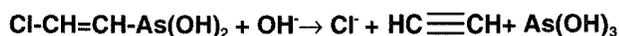
At 17°C, this reaction shows no detectable acetylene product after 24 hours at pH 8.5, a slight amount of product after twenty-four hours at pH 9.5 and substantial amounts of product after two hours at pH 10.5. An approximate extrapolation to 0°C and pH 8.1 indicates that the reaction should occur on a time scale of months in seawater. This time scale is roughly consistent with the observation in reference 17 of continued vesicant properties after ten weeks. The arsenous acid produced will subsequently undergo the expected transformations of arsenic in the environment (*vide infra*). The products of Lewisite hydrolysis are given in Table 4-17.

[83]Waters, W. A., J. H. Williams, "Hydrolyses and Derivatives of Some Vesicant Arsenicals," *J. Chem. Soc.* 1950, 18-22.
[84]Reference 83.
[85]*Chemical Abstracts* 20:2552, Abstract of Rovida, G., *Sperimentale*, 1926, 80, 5-24.
[86]Reference 83.
[87]Reference 17.
[88]Reference 83.

Table 4-17: Hydrolysis Product from Lewisite (L)

Compound	FW	Solubility, $g L^{-1}$	Estimated log K_{ow}	Product Produced from 1 kg L, g
2-chlorovinylarsonous acid	170.43	≈ 20[89]	1.4-2.4[90]	822
Lewisite oxide	152.41	≈ 20[89]	-1.4 to -0.4[91]	735
Arsenic	74.92	—	—	361

No information is available on the rate at which Lewisite dissolves in water. A U.S. Army scientist has indicated that like mustard, the hydrolysis of Lewisite is limited by the rate of dissolution.[92] However, given that Lewisite hydrolyzes much more rapidly than mustard, it is unclear whether of not the rate of dissolution will affect the release of Lewisite. Therefore, it will be assumed for purposes of this study that the rate of dissolution is limited only by the physical mixing of Lewisite with water.

4.6.4 Oxidation

Lewisite does not oxidize significantly. However, the oxide produced by hydrolysis can be slowly oxidized to 2-chlorovinylarsonic acid:

$$Cl\text{-}CH\text{=}CH\text{---}As\text{=}O \xrightarrow{[O]} \overset{\overset{\displaystyle O}{\displaystyle \|}}{Cl\text{-}CH\text{=}CH\text{-}\underset{\underset{\displaystyle OH}{\displaystyle |}}{As}\text{-}OH}$$
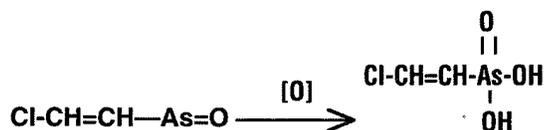
4.6.5 Photolysis

Lewisite and its hydrolysis products exhibit no significant phototransformations in sunlight.[93]

4.6.6 Thermolysis

Lewisite and its hydrolysis products are thermally stable at temperatures less than 49°C.[94]

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[89]The hydrolysis mixture has a solubility greater than two percent in seawater; see reference 17.
[90]ClCH=CHP(OH)₂ has an estimated value of 1.94 using reference 7; no fragment descriptions were available for arsenic.
[91]ClCH=CHP=O has an estimated value of -0.94 using reference 7; no fragment descriptions were available for arsenic.
[92]Dr. Y. C. Yang, Edgewood Research, Development, and Engineering Center, personal communication to the author.
[93]Reference 19.
[94]Reference 19.

4.7   THE CHEMISTRY OF ARSENIC IN THE ENVIRONMENT

The arsenic from Lewisite is hydrolyzed and converted to arsonous acid, as discussed above. Once this occurs, the arsenic from Lewisite will be indistinguishable from and undergo the characteristic environmental reactions of ubiquitous environmental arsenic acid. The arsenous acid (H_3AsO_3) in the +3 oxidation state will be oxidized to arsenate ($HAsO_4^{-2}$ and $H_2AsO_4^-$) in the +5 oxidation date according to the reduction potential of the environment. The ionization of arsenate ions is controlled by the pH of the water. In natural waters, the predominant species are $H_2AsO_4^-$, $HAsO_4^{-2}$ and H_3AsO_3; in sediment, $HAsO_4^{-2}$ and H_3AsO_3 predominate.[95]

Dissolved arsenic enters the biological arsenic cycle and is transformed into less toxic methylated derivatives or into volatile arsines. Dimethylarsine is produced in *methanobacterium* species via an anaerobic biomethylation pathway:[96]
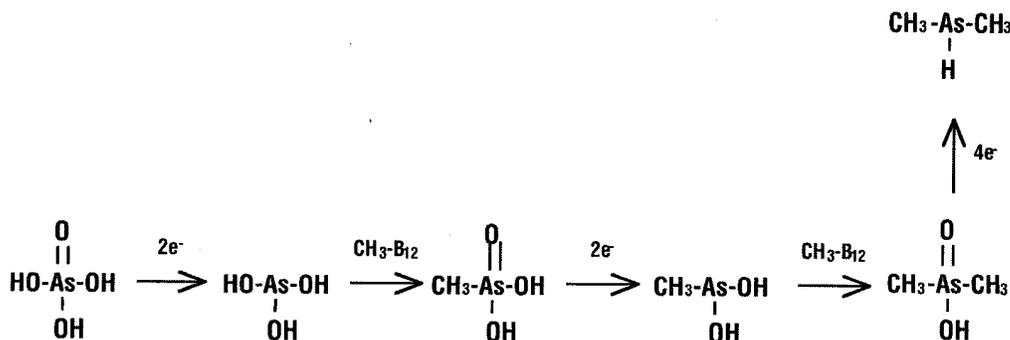
Under aerobic conditions, the biomethylation pathway continues to trimethyl arsine:
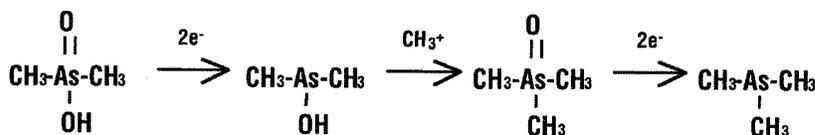
The methylated arsines are then excreted from the organism. Marine algae, marine invertebrates, and fish retain a portion of the arsenate within the cells as complex organic compounds including dimethylarsenosugars, arseno-lipids, and arsenobetaine.[97]
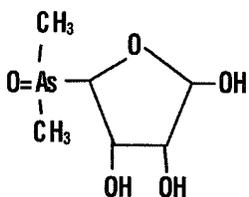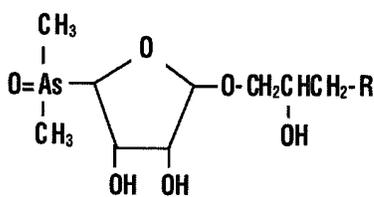
Arsenosugar　　　　Arsenolipid　　　　Arsenobetaine
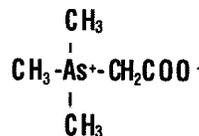
[95]Lemmo. N. V., et al. "Assessment of the Chemical and Biological Significance of Arsenical Compounds in a Heavily Contaminated Watershed. Part I. The Fate and Speciation of Arsenical Compounds in Aquatic Environments-A Literature Review," *J. Environ. Sci. Health, Part A,* 1983, A18, 335-387.

[96]McBride, B. C., et al. "Anaerobic and Aerobic Alkylation of Arsenic," in Brinkman, F. E. and J. M. Bellama, Eds., *Organometals and Organometalloids, ACS Symp. Ser.* 1978, 82, 94 115.

[97]Tamaki, S. and W. T. Frankenberger, "Environmental Biochemistry of Arsenic," *Rev. Environ. Cont. Toxicol.,* 1992, 124, 79-110.

4.8 EFFECTS OF PRESSURE ON HYDROLYSIS RATES

Munitions disposed of at depths of 33 to 620 m in water will experience roughly 3 to 62 atmospheres of pressure. High pressure can influence the rates of chemical reactions according to the expression:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{\Delta V^{\ddagger}}{RT}, \text{ or } \ln k = \ln k_0 + \frac{P \Delta V^{\ddagger}}{RT}$$

where k is the rate constant, P is pressure, $\Delta V^{\ddagger}$ is the volume of activation for the reaction, R is the gas constant, and T is absolute temperature.[98] In the absence of any measurements of volumes of activation for the hydrolysis reactions described above, estimates of the contributions of bond formation (+10 mL mole^{-1}) and cleavage (-10 mL mole^{-1}) and ionization (-20 mL mole^{-1}) will be used.[99] The rate determining step of Sarin hydrolysis has been reported to be breakdown of the pentacoordinate reaction intermediate resulting from addition of water or hydroxide to the Sarin phosphorus atom,[100] a volume of activation of 10 mL mole^{-1} can be assumed. For other phosphonate hydrolyses, formation of the P-O bond is rate determining.[101] Thus, for the hydrolysis of Tabun, a volume of activation of +10 mL mole^{-1} can be assumed. For mustard hydrolysis, bond cleavage plus ionization occur in the rate determining step, giving a volume of activation of 10 mL mole^{-1}. At 62 atm pressure, volumes of activation of +10 mL mole^{-1} and -10 mL mole^{-1} give k/k₀ values of 1.03 and 0.97, respectively. The range of activation volumes for reactions in aqueous solvents runs from +17.7 mL mole^{-1} to -50 mL mole^{-1}.[102] These values give k/k_0 values from 1.05 to 0.87. These calculations indicate that it is likely that pressures at depths up to 620 m will affect the rates of hydrolysis by 3 percent or less; it is very unlikely that the effect will exceed 13 percent. The effect of pressure on reaction rates is small compared to the uncertainties involved in extrapolating rate constants to low temperatures, as well as to seawater ionic strength and pH. Thus, pressure effects can be safely ignored in subsequent analyses of this report.

4.9 UNCERTAINTIES

The environmental fate of the CW agents and breakdown products covered by this study depends on the rates of the chemical transformations described previously in this chapter. Uncertainties in the rates of chemical and physical processes result in uncertainties in the environmental fate and, consequently, in uncertainties in the environmental effects of ocean dumping. Quantitative data from the peer-reviewed literature are available for only some of the chemical and physical processes discussed in this chapter. The remaining values are estimated, adding uncertainty to this assessment.

The available data in the literature for the following rates are either qualitative or semi-quantitative:

- Hydrolysis rate of Lewisite;
- Dissolution rate of Lewisite at 0°C;
- Hydrolysis rates of 2-chlorovinylarsonous acid, 2-chlorovinylarsonous oxide, and Lewisite polymer;
- Rates at which 2-chlorovinylarsonous acid forms 2-chlorovinylarsonous oxide and Lewisite polymer and the rates of the reverse reactions; and
- Oxidation rate of 2-chlorovinylarsonous acid.

This study is limited by using only rough estimates of these parameters. Quantitative measurements would allow a more precise estimate of the fate of Lewisite in the marine environment. In addition, no information is available in the literature for the dissolution rate of Tabun at 0°C. However, this study uses a plausible assumption for this parameter; it appears unlikely that a quantitative measurement would improve the estimate of the environmental fate of Tabun.

[98]Evans, M. G. and M. Polanyi. *Some Applications of the Transition State Method to the Calculation of Reaction Velocities, Especially in Solution, Trans. Faraday Soc.*, 1935, 31, 875.
[99]Asano, T. and W. J. LeNoble, "Activation and Reaction Volumes in Solution," *Chem. Rev.*, 1978, 78, 407.
[100]Reference 31.
[101]Kovach, I. M. et al. "Nucleophilic and Protolytic Catalysis of Phosphonate Hydrolysis: Isotope Effects and Activation Parameters," *J. Am. Chem. Soc.*, 1993, 115(12), 5138-5144.
[102]Reference 99.

There are no quantitative measurements for the following:

- Hydrolysis rate of Tabun at 0°C in seawater; or

- Hydrolysis rate of mustard at 0°C in seawater.

For these parameters, available information allows extrapolation from reported conditions to conditions in the study area according to well-established chemical principles. Furthermore, these extrapolations are confirmed using independent data from limited circulation, non-peer reviewed documents. Again, it appears unlikely that quantitative measurements of these parameters would improve the estimates of the environmental fate of Tabun and mustard.

Finally, there are several parameters for which only estimates are available. These include log K_{ow} for all compounds (except chlorobenzene) covered in this study and the aqueous solubilities of the following substances:

- monoethyl ester of dimethylphosphoramidic acid;

- dimethylphosphoramidic acid; and

- 1-methylethyl ester of methylphosphonic acid.

Estimating the environmental fate of the compounds covered by this study does not require very precise values of these parameters. The available estimates for log K_{ow} and aqueous solubility are sufficiently reliable for purposes of this study.

4.10 SUMMARY OF SIGNIFICANT CHEMICAL PROPERTIES

The chemistry of CW agents in the marine environment is dominated by hydrolysis, the reaction of the agents with water. The key features of the chemistry of the CW agents in the marine environment are:

- Tabun is fairly soluble in water and hydrolyzes over a period of days.

- Sarin is miscible (mixes in all proportions) with water and also hydrolyzes over a period of days.

- Dissolved mustard hydrolyzes relatively rapidly. However, the persistence of mustard in the marine environment is controlled by the rate at which it dissolves; dissolution is much slower than hydrolysis, requiring months for kilogram sized quantities.

- Lewisite is soluble in water and hydrolyzes very rapidly. The initial hydrolysis products of Lewisite are also very toxic and persist in seawater for months or longer. Ultimately, the Lewisite hydrolysis products are converted to arsenic.

The following key physical properties of agents and hydrolysis products that relate to their environmental fate and transport are summarized in Tables 4-18 through 4-21.

- Aqueous solubility is used in calculating the amount of an agent that is released from dumped munitions and in determining the environmental fate of a substance.

- Hydrolysis rate constant ($k_{hydrolysis}$) determines the rate at which an agent reacts with and thus is removed from water.

- Half-life ($t_{1/2}$) of an agent in seawater is the time required for the concentration of the agent to decrease by 50 percent; this is another measure of the rate at which the agent is removed from water and is calculated directly from $k_{hydrolysis}$.

- Estimated log of the octanol-water partition coefficient (K_{ow}) is a measure of how a substance partitions between water and octanol. Octanol is a surrogate for animal fat; log K_{ow} is used in the analysis of the accumulation of the substance in tissues of living organisms.

- The rate of dissolution (σ), which governs the persistence of mustard in the environment.

Table 4-18: Summary of Tabun (GA) Chemistry in Seawater

Tabun; Dimethylphosphoramidocyanidic acid, ethyl ester
77-81-6
$C_5H_{11}N_2O_2P$, MW 162.12

Solubility, g L⁻¹	$k_{hydrolysis}$ hr⁻¹	$t_{1/2}$	log K_{ow} (estimate)
72	0.017	40 hr	-1.44

Common Name(s) of Hydrolysis Product	Chemical Abstracts Service (CAS) Name of Hydrolysis Product	Molecular Formula	Molecular Weight	CAS Registry Number	Chemical Structure	Solubility, g L⁻¹	Estimated log K_{ow}
Hydrogen cyanide	Hydrocyanic acid	HCN	27.03	57-12-5	HCN	miscible	-0.69
—	Dimethylphosphoramidic acid, monoethyl ester	$C_4H_{12}NO_3P$	153.12	2632-86-2		—	-0.04
grain alcohol	Ethanol	C_2H_6O	46.07	64.17-5	CH_3CH_2OH	miscible	-0.14
—	Dimethylphosphoramidic acid	$C_2H_8NO_3P$	125.06	33876-51-6		—	-0.59
Dimethylamine	N-Methylmethanamine	C_2H_7N	45.08	124-40-3	CH_3NHCH_3	911	-0.17
orthophosphoric acid	Phosphoric acid	H_3O_4P	98.00	7664-38-2	H_3PO_4	5480	—
—	Chlorobenzene*	C_6H_5Cl	112.56	108-90-7		11.9	2.84
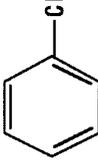
* Chlorobenzene is not a hydrolysis product, but is present at 5-20 percent in German-produced GA.

Table 4-19: Summary of Sarin (GB) Chemistry in Seawater

Sarin; Methylphosphonofluoridic acid, (1-methylethyl) ester
107-44-8
$C_4H_{10}FO_2P$, MW 140.09

Solubility, g L^{-1}	$k_{hydrolysis}$, hr^{-1}	$t_{1/2}$	log K_{ow} (estimate)
miscible	0.044	15.8 hr	0.31

Common Name(s) of Hydrolysis Product	Chemical Abstracts Service (CAS) Name of Hydrolysis Product	Molecular Formula	Molecular Weight	CAS Registry Number	Chemical Structure	Solubility, g L^{-1}	Estimated log K_{ow}
Hydrogen Fluoride	Hydrofluoric acid	HF	20.01	7664-39-3	HF	"very"	—
IPMA	Methylphosphonic acid, mono(1-methylethyl) ester	$C_4H_{11}O_3P$	138.10	1832-54-8		—	0.27
Isopropyl Alcohol	2-Propanol	C_3H_8O	60.10	67-63-0		miscible	0.28
MPA	Methylphosphonic acid	CH_5O_3P	96.02	993-13-5		"very"	-0.70

Table 4-20: Summary of Mustard (H) Chemistry in Seawater

Mustard gas; yperite; sulfur mustard; Kampfstoff Lost; 1,1'-thiobis[2-chloroethane]   **Cl-CH₂CH₂-S-CH₂CH₂-Cl**
505-60-2
C₄H₈Cl₂S, MW 159.08

Solubility, gL⁻¹	k_hydrolysis, hr⁻¹	t₁/₂	logK_ow (estimate)	σ, g cm⁻²sec⁻¹
0.3	0.132	5.3 hr	1.4-2.4	3.4×10⁻⁷

Common Name(s) of Hydrolysis Product	Chemical Abstracts Service (CAS) Name of Hydrolysis Product	Molecular Formula	Molecular Weight	CAS Registry Number	Chemical Structure	gm of product produced from 1 kg H	Solubility, g L⁻¹	Estimated log K_ow
Thiodiglycol	2,2'-thiobis[ethanol]	C₄H₁₀O₂S	122.19	111-48-8	**HO-CH₂CH₂-S-CH₂CH₂-OH**	648	6900	-0.62
1,4-Thioxane	1,4-oxathiane	C₄H₈OS	104.17	15980-15-1		120	286	0.53
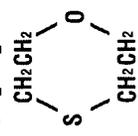
Table 4-21: Summary of Lewisite (L) Chemistry in Seawater

Lewisite; (2-chlorovinyl)dichloroarsine; (2-chloroethenyl)arsonous dichloride
541-25-3
$C_2H_2AsCl_3$, MW 207.32

Solubility, g L^{-1}	$k_{hydrolysis}$, hr^{-1}	$t_{1/2}$	log K$_{ow}$ (estimate)
0.5	> 20	< 2.1 min	2-3

Common Name(s) of Hydrolysis Product	Chemical Abstracts Service (CAS) Name of Hydrolysis Product	Molecular Formula	Molecular Weight	CAS Registry Number	Chemical Structure	Solubility, g L^{-1}	Estimated log K$_{ow}$
2-Chlorovinylarsonous acid	(2-chloroethenyl)arsonous acid	$C_2H_4AsClO_2$	170.43	85090-33-1		≈ 20	1.4 - 2.4
Lewisite oxide	(2-chloroethenyl)oxoarsine	C_2H_2AsClO	152.41	123089-28-1		≈ 20	-1.4 - -0.4
2-Chlorovinylarsonic acid	(2-chloroethenyl)arsonic acid	$C_2H_4AsClO_3$	186.43	64038-44-4		—	—
—	Arsenic	As	74.92	7440-38-2	As	—	—
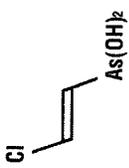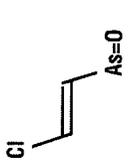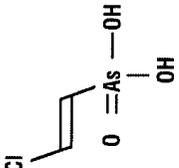
BACKGROUND

- Release of agents from individual munitions containing Tabun, Sarin, or Lewisite was modeled as either of the following two types:
  - Impulsive release of the entire charge (over a matter of minutes);
  - Steady state release with rates in the range one of 0.001 to one kg day^{-1}.

- Release of Mustard (H) will be modeled as immediate release of viscous third followed by slow dissolution over many weeks. Rates of production of dissolved mustard from a typical artillery shell are estimated to be on the order of 0.01 kg per day for one hundred days.

- It is assumed that less than five percent of all munitions dumped will begin to release agents immediately following dumping.

- After dumping and for a very long period it is possible that only a small number of very thin walled bombs will release CW agent and that artillery shells may take many decades to corrode sufficiently to *begin* release.

- CW munitions were disposed of at sea in five areas whose sizes range from 43 km^2 to 17,150 km^2.

- The highest density of munitions is expected to be in the White Sea where there are as many as 68,000 munitions per km^2.

- The primary release periods that are times over which all the munitions at any site could be expected to undergo corrosive disintegration are assumed to be in the range of five to fifty years, and this was treated parametrically.

- Estimates of the number of munitions per square kilometer range from approximately 100 to 100,000 with separations between munitions that are leaking ranging from hundreds of meters to a few kilometers. Tens of meters is possible in a few cases.

CONCLUSIONS

- For each primary release period and each site, four release scenarios were developed, as follows:
  - Two scenarios governing the release of Tabun, Sarin, and Lewisite:
    - One using a steady state model and
    - One using an impulsive model;
  - One scenario for mustard using the calculations of dissolution; and
  - One scenario governing the five percent of munitions expected to release immediately upon dumping.

- While there are significant uncertainties, these release scenarios and associated models are consistent with known facts. It is not expected that deviations from these scenarios and models will lead to significantly different environmental assessments.

5.1   INTRODUCTION

This chapter address the problem of determining how CW agents are released into the sea. The departure point is established by the results of Chapter 2, which identified the dump sites, the CW agents dumped, and the total quantities; and by Chapter 4, which established the physical properties of the agents and their seawater chemistry. The general picture that we have of the dumped munitions is shown schematically in Figure 5-1.

The challenge in this chapter is to use the little information available and attempt to bound some of the important characteristics of these dump sites. The key questions to be addressed in this Chapter are summarized in Table 5-1.

Table 5-1: Key Questions Related to Release Scenarios

Q #	Question
1	At what rate is each CW agent released into the sea?
2	For how long a period does this release continue?
3	What is the spatial distribution of released agent?
4	To what extent are leaking munitions likely to be sufficiently separated to that the extent of contamination can be determined independently?
5	What are the major uncertainties and what can they affect?
6	What is the simplest mathematical model that reasonably describes these conclusions?

Figure 5-1: Schematic Illustration of Ocean Dump Sites
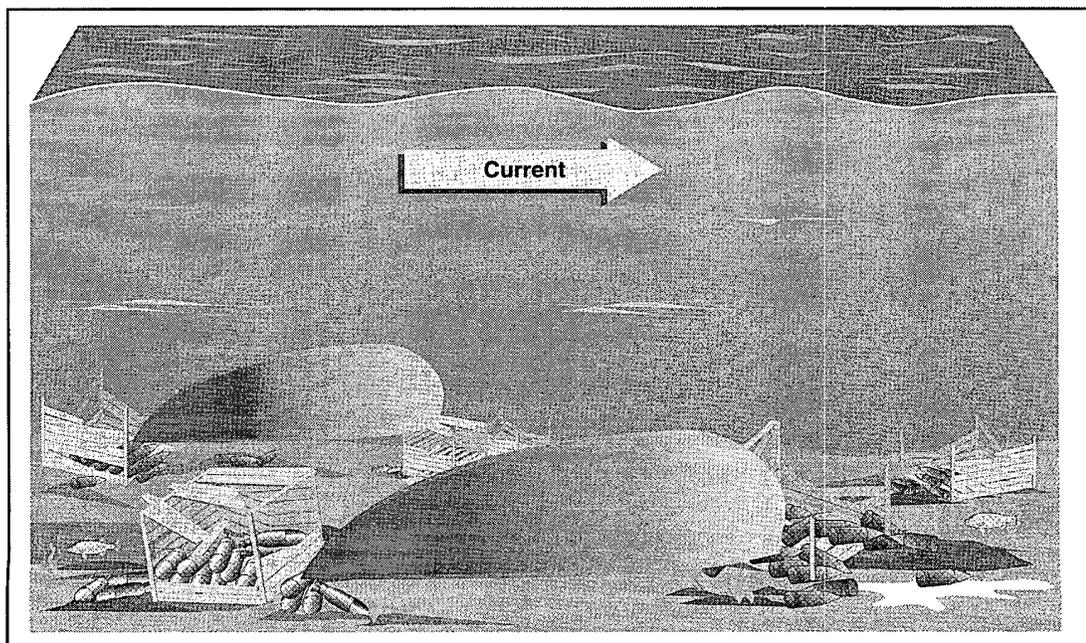
In principle, these questions could be answered if one knew the probability distribution for release of an agent at rate Q from a single, given munition and the distribution of types of munitions that were dumped at each site. In practice we know neither quantity, nor type of munition.

Even if full knowledge of the materials used in the manufacture of each munition type were available, the authors have little confidence that a limited investigation of corrosion processes would lead to a quantitative picture of agent release in which one had any reasonable confidence. However, while very little is known with certainty about how chemical munitions behave on the seafloor, we hypothesize the following scenario: Immediately after dumping there is, presumably, a transient period when munitions with cracks and other defects immediately begin to leak CW agents. Subsequently there could be some protracted period, governed by corrosion processes, over which little or no release is seen. Finally, with pinholes developing followed by corrosive disintegration, CW agents are introduced into the local environment.

All of this is assuming that the munitions are undisturbed. As the Baltic experience shows however, when trawling occurs over the dump sites, even the viscous mustard, which is probably solid, will be released from munitions. Presumably, this happens because battering and scraping by the trawl removes the thin parts of a badly corroded casing.

The other key distribution is the spatial distribution of munitions on the seafloor. In principle spatial distribution is ascertainable since one might hope to do a survey with unmanned vehicles and combine this with deck log records from the ships that did the supposed dumping. However, there have been no such surveys, and to our knowledge no deck logs exist.

Given this degree of ignorance about both distributions, the only recourse was to use existing clues and to bound the problem in some manner that allows useful conclusions to be drawn.

Lest it be imagined that release scenarios could somehow turn out to be irrelevant, it is worthwhile to calibrate one's intuition by examining the total volumes of seawater that could be contaminated by the total quantities of CW agents thought to have been dumped (see Chapter 2). Using the maximum concentrations at which no biological effects are expected (ENEC) and the total quantities, Table 5-2 shows the maximum volumes of water that it would be possible to contaminate (in the unrealistic case in which all the agent is instantaneously released and dispersed over these volumes before hydrolysis can act).

These volumes are very large indeed, the largest, 30,000 km³, represents approximately 25 percent of the total volume of the Kara Sea. It is the release scenario, distributing the release over time, that will reduce the volume of water that can be contaminated at a given toxic level.

Table 5-2: Maximum Contaminated Volumes in Hypothetical Release

Agent	Total Quantity (kg)	Maximum Non-toxic Concentration (mg L^{-1})	Maximum Volume of Contaminated Water (km³)
GA (Tabun)	3×10^7	0.001	3×10^4
GB (Sarin)	2×10^6	0.001	2×10^3
L (Lewisite*)	12×10^7	0.02	6×10^3

*Table 2-1 gives 115 KT for H+L; here we use this for L alone solely as an illustration.

5.2 AGENT RELEASE FROM INDIVIDUAL MUNITIONS

5.2.1 Dump Sites and Total Release Times

If release of CW agents from sealed munitions occurs as a result of corrosive processes attacking the casing walls, as opposed to the seals on the filling port, and assuming that materials are the same, then artillery shells would take approximately five, and perhaps ten times as long to corrode to the point of agent release. It is our impression that artillery shells could be made of a more corrosion-resistant steel than bombs, but it may also be that corrosion around the seals is the primary mechanism of release.

Despite the uncertainties, it is intuitive to expect artillery shells to remain intact much longer than thinner walled bombs. It is our view that the Baltic experience, could be almost entirely the result of leakage from bombs and that there could be very large quantities of intact artillery shells *in situ*.

Figure 5-2 combines the available information from the Baltic and the Japanese experiences onto a single graph (see references in Chapter 1).

The Baltic data for the 1976-1991 period are reports by Danish fishermen of "findings" and do not necessarily indicate any medical problems. It can be presumed that such "findings" occurred in previous years as well although the only reports that we found were those indicating enough harm to have been entered as medical reports.

While drawing any solid conclusions from this data is somewhat risky, we can construct some relatively clear consistent hypotheses.

- There may be a "small" initial release immediately following dumping, possibly due to munitions having material defects or munitions damaged by the dumping.

Figure 5-2: CW Munitions Related Incidents
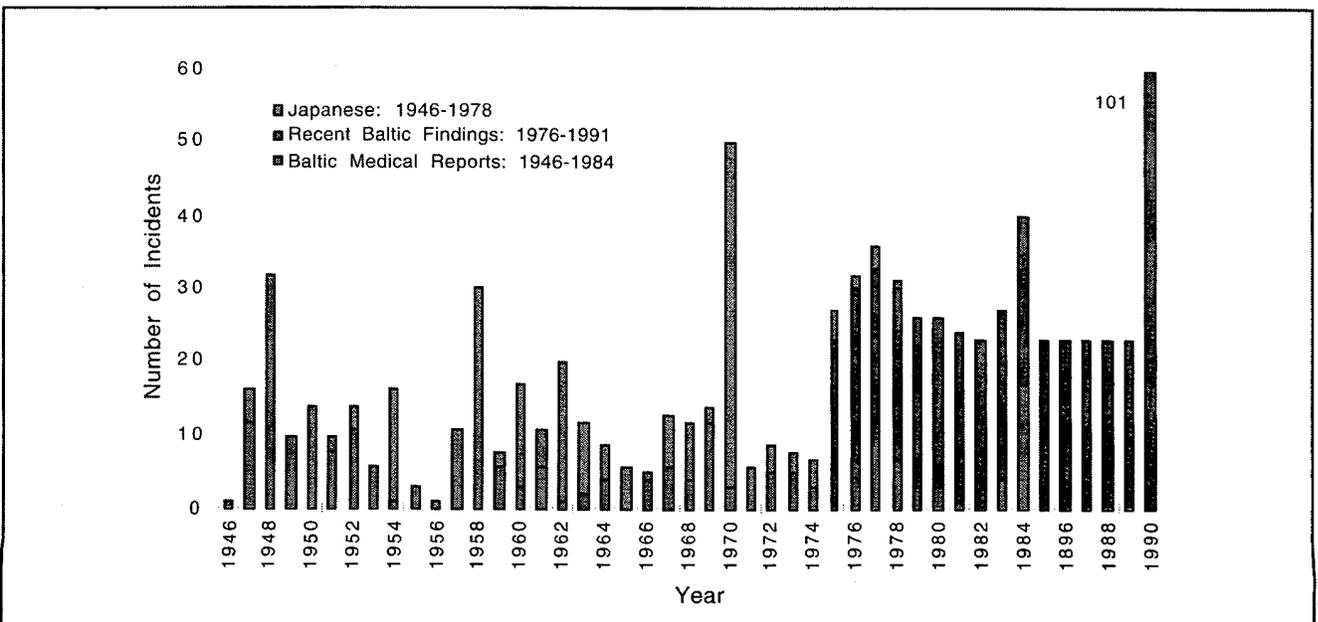
- There may be a period following this post-dumping release during which very few munitions are opened; presumably, this is when corrosion is acting on the casing.

- Trawling can be expected to batter the munitions sufficiently to open them and release agents.

- The corrosive disintegration of munitions appears to take place over decades, perhaps many decades. There is no data strongly indicating that extensive corrosive disintegration, especially of artillery shells, has occurred as yet.

- Mustard, when released, stays relatively intact on the seafloor for weeks or months. This is evident from the recovery of mustard lumps.

This data, primarily involving the near-solid mustard, does not shed any light on the possibility of corrosion causing pinholes in the casing through which the CW agent leaks at very low rates. One must expect that this process does occur and may be the primary means for release of highly soluble agents. We are led to hypothesize, then, that the distribution of release events could be as shown schematically in Figure 5-3.

The distribution contains three periods, the initial transient, the extended period during which corrosion attacks the casings, and the primary release period during which agents are released from munitions as they develop pinholes. Release from a *single* munition may take days, weeks or even months, but the period T is thought of as lasting years, perhaps a few decades. Of course, we do not expect that this "boxcar" distribution best represents reality, which probably would be modeled better as a Rayleigh distribution. It is reasonable to expect that after time T_1, in which corrosion decays casings and which lasts decades, there will be a primary release extending for T years during which there will be a somewhat constant rate of individual munitions beginning to release agents. This is summarized in Table 5-3.

Although there is no reason to suppose that forty years represents the maximum release period, we will take it as such, simply for lack of evidence to the contrary and because doing so will provide an upper bound on

Figure 5-3: Schematic Illustration of the Distribution of Release Events
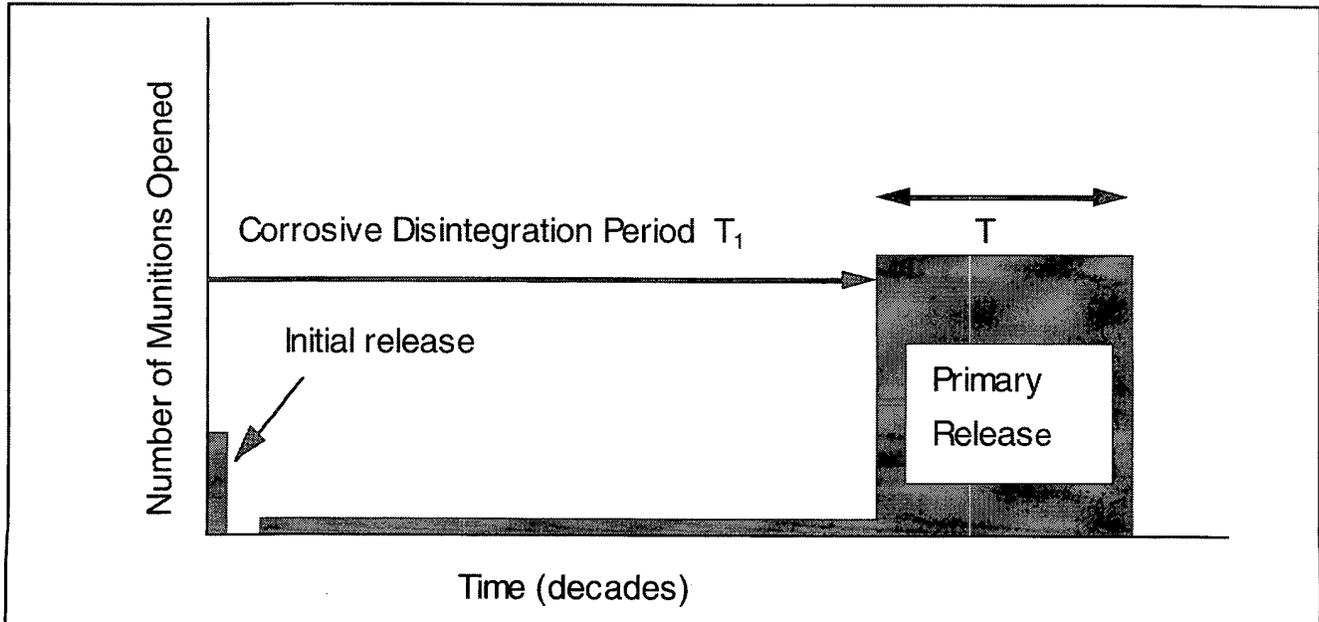
Table 5-3: Assumed Distribution of Release Events

Period	Duration	Quantity
Initial release	Duration may be days to months	<5% of munitions release in this period
Corrosive period t<T_1	$T_1 \approx$ 50-100 years	Very few munitions will release if left undisturbed; assumed to be zero
Primary release period	T ≈ 10-50+ years	>95% of munitions released at a uniform rate over period T

possible harm to the environment since spreading releases out over longer periods leads to lower agent concentrations and reduced toxicity.

5.2.2 Release from Individual Munitions

One point to be considered is the total quantity of agent that could have been in a given individual munition. Table 2-2 contains the best information available to the authors at the time of writing. As stated above, artillery shell casings are expected to be thicker than the bomb casings. More specifically, bomb casings are expected to be 5 to 10 mm in thickness while artillery shells are expected to be 25 to 50 mm in thickness. Consequently, bomb casings are expected to undergo corrosive disintegration much more rapidly than the shells. As stated in Chapter 2, the bulk of CW agents thought to have been released were in the form of artillery shells, followed by bombs. Not listed above are bulk storage canisters, thought to have been an insignificant factor in this problem since almost all the captured or manufactured CW agent is thought to have been "weaponized." The agents dumped at any particular site are unknown mixtures of these types, but mixtures certainly dominated by artillery shells.

We assume that the release of mustard from a single munition, because of its high viscosity and low dissolution rate, is abrupt. That is, the effect of pinhole leaks is negligible and nothing of interest happens until the casing is essentially completely corroded. This is at least consistent with reports from the Baltic describing lumps of mustard, with no mention of fragments of casing.

The question of pinhole leaks needs to be discussed briefly in order to argue that there are two bounds that constrain this problem. On the one hand, if the release rate is so slow that dilution and hydrolysis effectively reduce agent concentrations to harmless levels essentially as fast as it is released, then that rate, or any slower rate, will produce no biological harm. Later we will quantify this. On the other hand, if the release is so rapid that it happens over a time short compared to all the other time scales in the problem, see Chapter 7, then it might just as well be an instantaneous release. In any case, the release can proceed only as long as the agent remains in the munition. In this way, while we know no more about the growth of pinhole leaks than before, some useful bounds may be possible.

Figure 5-4 shows a simple calculation of released mass as a function of time for various release rates Q.

Artillery shells could support a release rate of as great as 1 kg per day for tens of hours, a time much greater than the time required to reach a steady state condition. However, much greater rates, say 10 kg day⁻¹, could only be supported for times that become comparable with the time required to establish a steady state and thus need to be addressed differently.

Because Tabun and Sarin are highly soluble in water and Lewisite may have a high dissolution rate, the wide variety of the rates and times illustrated in Figure 5-3 are applicable to these agents.

Mustard however, is a very different story. It is very viscous at 0°C. In fact, it is not solid because it was mixed with other compounds in order to lower its

Figure 5-4: Illustration of Agents Released at Various Rates
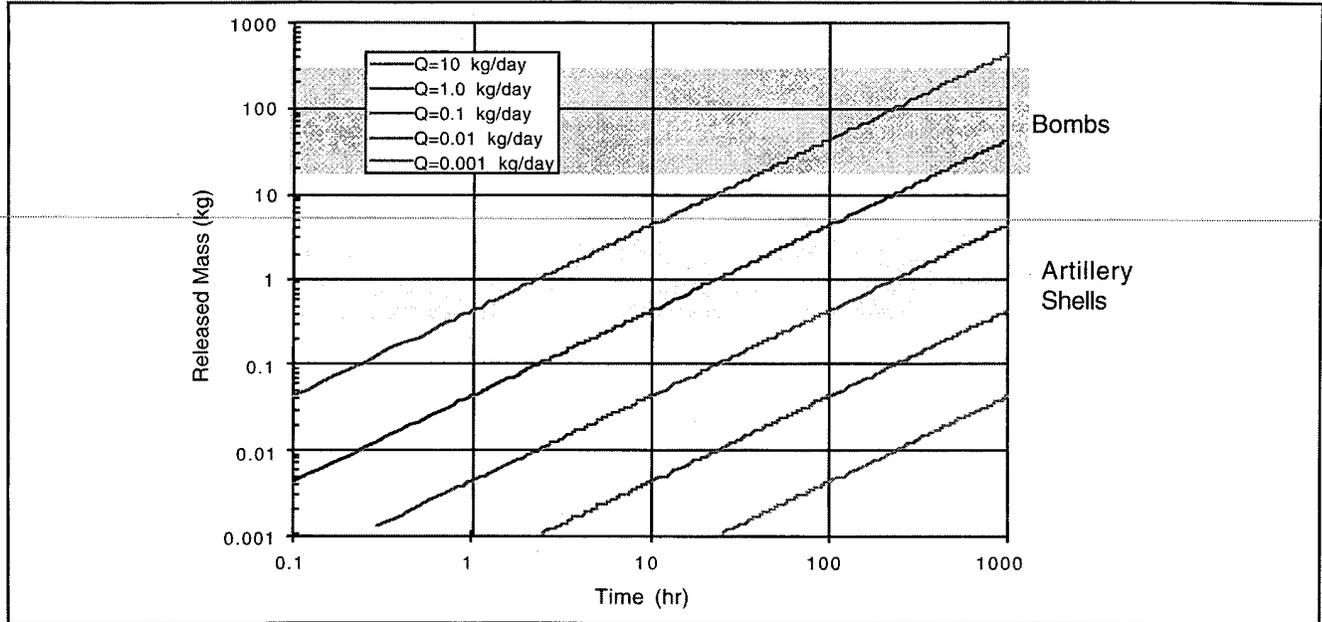
freezing point so that it could be used in cold weather military operations. In addition, the dissolution rate ($\approx 3 \times 10^{-7}$ gcm^{-2} s^{-1}) is so low that this process might well dominate all others.

Mustard releases into one of two scenarios: dissolution of a sphere, and dissolution of a thin cylinder or a "pancake." The rate of production of dissolved mustard for a sphere immersed in seawater, having a dissolution rate of Σ and an initial radius of R_o, is given by Equation 5-1,

$$Q = (3M_0/t_M)(1 - t/t_M)^2 \qquad (5-1)$$

where the lifetime of the sphere, is given by

$$t_M^s = \rho R_0 \Sigma^{-1} \qquad (5-2)$$

The fraction of mass remaining in the dissolving sphere is given by Equation 5-3:

$$1 - M/M_0 = (1 - t/t_M)^3 \qquad (5-3)$$

For the pancake the radius R_O and height εR_O q is still given by Equation 5-1 but with the maximum lifetime defined by Equation 5-4.

$$t_M^p = 3\rho R_0 (\varepsilon/(1 + 2\varepsilon)) \Sigma^{-1} \qquad (5-4)$$

In the second case, it is assumed that dissolution occurs at the top and sides of the pancake but not on the bottom, where it rests on the seafloor.[1]

Table 5-4 provides expected lifetimes for several masses of mustard for these two models.

It is not difficult to believe that many, if not all, of the mustard globs found by fishermen in the Baltic could have come from bombs, not only because their casings are thinner and corrode faster than artillery shells, but because the life of the mustard once released is much longer, making it more likely for them to be found. The fraction of mass remaining intact for a 1 kg mass is shown in Figure 5-5, which

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[1]Presumably while wet, the lack of flow beneath would quickly lead to saturation and no further dissolution.

Table 5-4: Expected Maximum Lifetimes of Mustard (H) in Seawater

Mass of H	1 kg	10 kg	100 kg
Lifetime (hrs) Spherical Model	5900	13,000	28,000 (≈ 3.2 yr)
Lifetime (hrs) Thin Pancake Model	3500	7600	16,000 (≈ 1.9 yr)

also graphs Equation 5-3, using a 1 kg mass of mustard in two shapes. The sphere has a radius of 5.73 cm and the pancake has a radius of 13.58 cm as well as a very small height of 1.36 cm.

Since a sphere is the solid having the minimum surface area for given volume and the pancake shown is very thin, we regard these estimates as bounding the realistic dissolution of mustard released from a disintegrating munition. Figure 5-6 shows this quantity, Q, for the two shapes.

Several conclusions can be made:

- Mustard released from munitions in kilogram quantities will be introduced into the sea as dissolved agent at very low rates, on the order of 10^{-6} kg day^{-1};

- This rate will remain approximately constant over long periods, perhaps as long as several thousand hours;

Figure 5-5: Fraction of a 1 kg Mass of Mustard Remaining Intact
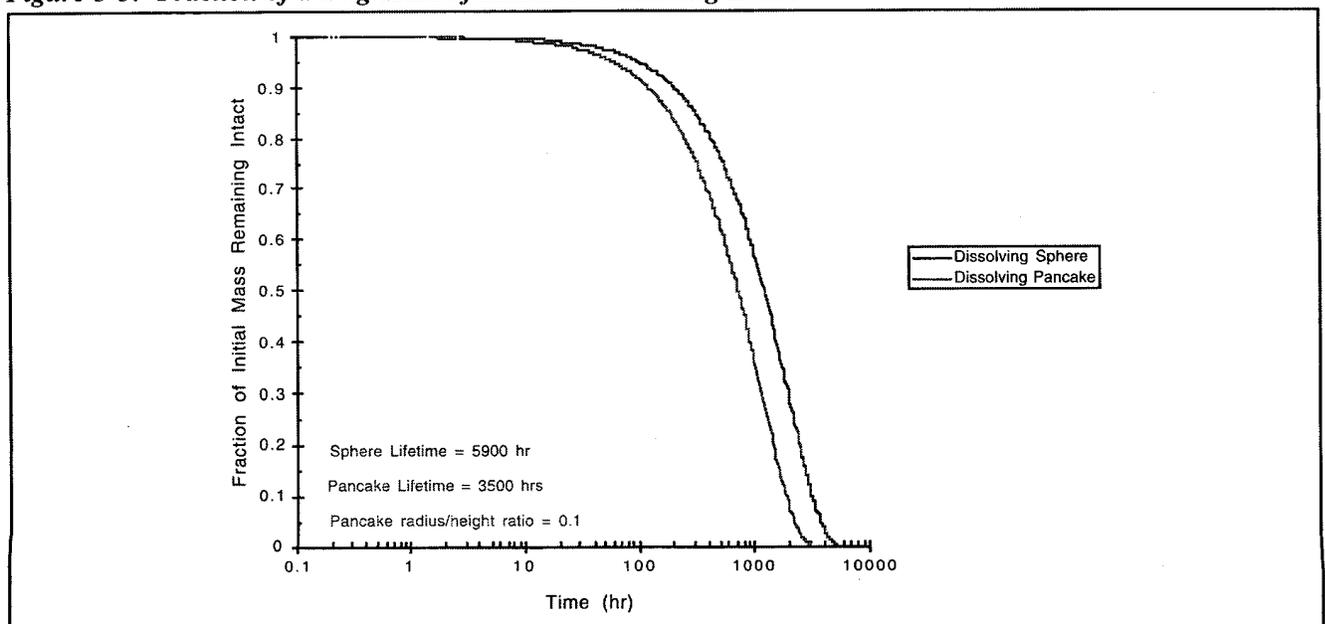
Figure 5-6: Production Rate of Dissolved Mustard from Two Shapes
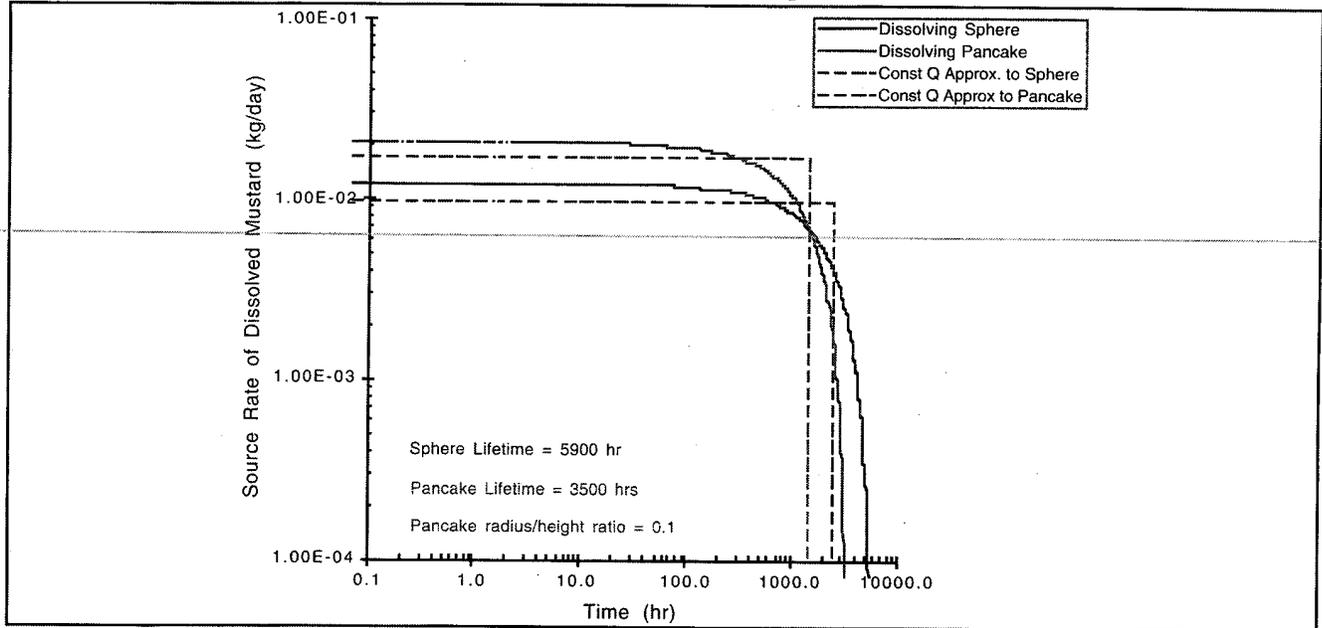
- A simple approximation to what happens is a constant effective Q over a period equal to two "half-lives" with an effective rate of $Q \approx M_0/2t_{1/2}$. In the cases of the sphere and the pancake, as seen in Figure 5-5, $t_{1/2}$ is equal to 1,225 and 720 hours respectively. For the sphere, this makes Q approximately equal to 0.0098 kg per day for 102 days and for the pancake, Q is approximately equal to 9.917 kg per day for 60 days. These approximations are shown as dotted lines in Figure 5-5.

With the approximations discussed above it becomes plausible to consider that one release model is applicable to all four agents, a constant rate of release Q for some time t. Another release model that needs to be considered, if only to bound the eventual estimation of toxicity extent, is a single, sudden release or an impulsive release of all the agent in the munition. This model will not be applicable to mustard. We will be able to model only the temporal behavior of a release of the CW agents shown in Table 5-5.

5.3   SPATIAL DISTRIBUTIONS AT DUMP SITES

Since there is no hard information about how munitions were dumped or about conditions at the sites, it will be necessary to make some assumptions that are consistent with what little is known, which is largely the Baltic experience. We reasonably suppose that dumping of munitions from a ship in arctic seas at some time in the 1950s to 1980s would result in the following:

- The intention to remain within the area designated;

- Dumping pallets or crates of munitions while drifting with the current in calm seas or at low speed, with occasional corrections to remain within the site;

- Multiple ship loads to each dump site;

Table 5-5: Temporal Release Models to be Adopted

Model	Lifetime	Release Rate (single munition)
Initial Release ≤5% of munitions at site	<1 month	Instantaneous
Distributed Constant Release >All agents >95% of all munitions at site=N	T=up to 50 years Rate of opening is uniform, R=N/T	Rate $Q=M/t$ M=mass/munition t=1-100 days Q-0.001-1 kg day^{-1} for a 1 kg mass of agent
Distributed Impulsive Release >GA/GB/L >95% of munitions at site, N	T=up to 50 years Rate of opening is uniform, R=N/T	Injected mass = 1 kg

- Navigation errors, *e.g.,* star sights, LORAN (-C in later years), and DR of approximately 5 to 10 km; and

- Human factors.

One might expect there to be a somewhat random scattering of munitions across the dump site and even outside of it, possibly with a greater concentration toward the center.

We also plausibly assume that the larger dump sites are large for a reason, namely the intention to dump more munitions there. That is, lacking any other information, the physical area of the dump site is significant as an indication of the quantities dumped. However, in order to avoid the results being dominated by the uncertain area of the very large Site 123 in the Kara Sea, a few adjustments will be made to increase the quantities assigned to the smaller sites. Taking the results of Table 2-1 and the foregoing, we assumed the prescription in Table 5-6.

In Table 5-6, the total quantities given by Table 2-1 for H+L have been equally divided between H and L. The third column, giving the density of agent per square kilometer, is numerically equal to the number of munitions per square kilometer if the typical munition

is assumed to contain 1 kg of agent. These same spatial density values are shown graphically in Figure 5-7.

5.4 AGENT RELEASE MODELS

In Section 5.2.1, we argued that it was plausible to assume that however long the period from dumping to the beginning of significant release, T_1, the primary release period T would last years, perhaps decades and that, lacking other guidance, we would assume that the occurrence of leaking munitions would be uniformly distributed over this period. Given these assumptions, and the estimates in Table 5-6, it is possible to estimate the number of leaking munitions at a site. This will be done for T equaling five, ten, twenty, and forty years.

In Chapter 7, we argue that the plumes created by leaking munitions could be separate from one another, thus allowing the contaminated seafloor areas and water volumes to be computed simply by multiplication of the number by the area or volume contaminated by a single munition. The mean spacing between all of the munitions (again assuming 1 kg munitions) is simply the reciprocal of the square root of the number per unit area. Similarly, with an estimate of the total number of leaking munitions, it is

Table 5-6: Quantities of Agents and Densities at Each Dump Site

Total Quantity in Ocean Area (from Ch 2)	Estimated Quantity of Agent at Site (KT)	Agent Density kg km^{-2}	Mean Spacing between munitions m
Barents Sea • H+L≈5 KT • GA≈5 KT • GB≈0 KT	**Site 122** • H≈0.25 • L≈0.25 • GA≈0.5 • GB≈0	**Site 122 (43 km^2)** • H≈5.8x10^3 • L≈5.8x10^3 • GA≈1.1x10^4 • GB≈0	**Site 122** • H≈13 • L≈13 • GA≈10 • GB≈0
	Site 134 • H≈2.25 • L≈2.25 • GA≈4.5 • GB≈0	**Site 134 (528 km^2)** • H≈4.3x10^3 • L≈4.3x10^3 • GA≈8.5x10^3 • GB≈0	**Site 134** • H≈15 • L≈15 • GA≈11 • GB≈0
Kara Sea • H+L≈70 KT • GA≈20 KT • GB≈2 KT	**Site 123** • H≈34.5 • L≈34.5 • GA≈19.5 • GB≈2 KT	**Site 123 (17,150 km^2)** • H≈2x10^3 • L≈2x10^3 • GA≈1.1x10^3 • GB≈1.2x10^2	**Site 123** • H≈22 • L≈22 • GA≈30 • GB≈91
	Site 124 • H≈0.5 • L≈0.5 • GA≈0.5 • GB≈0	**Site 124 (62 km^2)** • H≈8.1x10^3 • L≈8.1x10^3 • GA≈8.1x10^3 • GB≈0	**Site 124** • H≈11 • L≈11 • GA≈11 • GB≈0
White Sea • H+L≈40 KT • GA≈5 KT • GB≈0 KT	**Site 121** • H≈20 • L≈20 • GA≈5 • GB≈0	**Site 121 (292 km^2)** • H≈6.8x10^4 • L≈6.8x10^4 • GA≈1.7x10^4 • GB≈0	**Site 121** • H≈4 • L≈4 • GA≈8 • GB≈0

Figure 5-7: Estimated Spatial Density of Agents at the Dump Sites
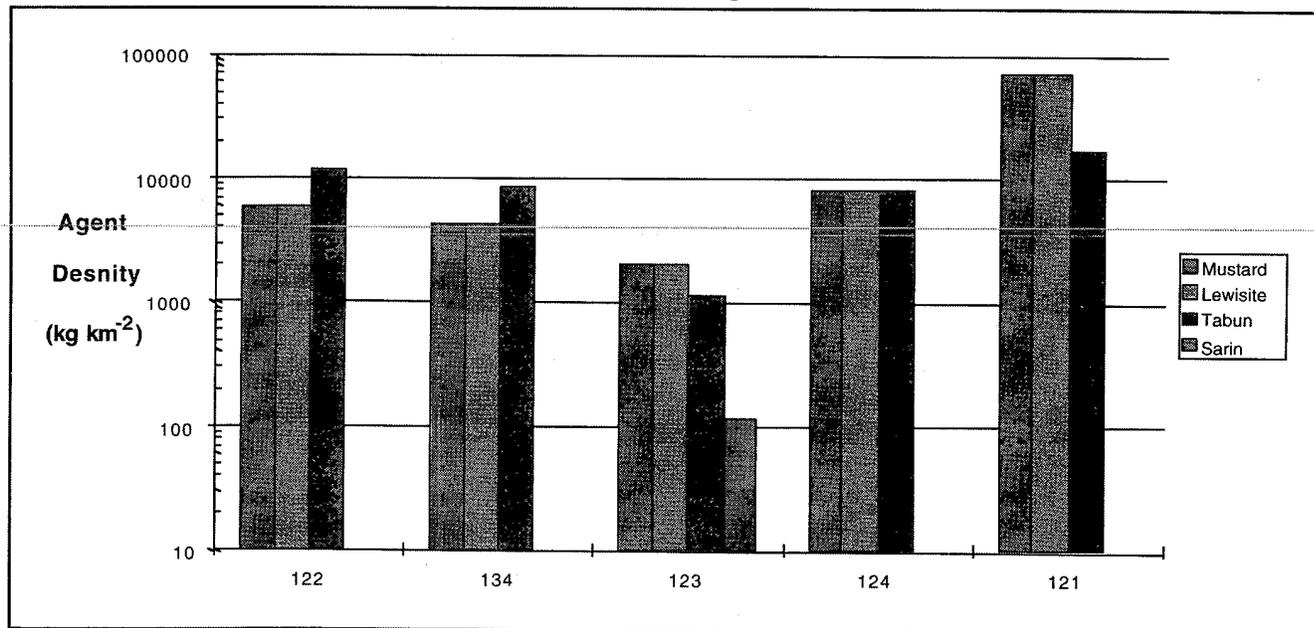
possible to estimate their number per unit area and then their mean separation.

Table 5-7 gives estimates of the mean spacing of all munitions and the density of leaking munitions per day. That is, if X is the km^2 per day of leaking munitions and we later decide to consider a time of five days for a single munition to empty itself, thus giving a leakage rate of Q, then the mean number of munitions leaking per km^2 in any five day interval is 5X.

The largest number in this table is 38 munitions $km^{-2}day^{-1}$. The fact that it is so small means that even for a total release period of five years, there will be *less* than 760 (38x20) leaking munitions per square kilometer even if the release time of a single munition is, say, twenty days. This would give a mean spacing *greater* than 28 m between leaking munitions. If, by contrast, the release period is fifty years, the mean spacing between leaking munitions, again emptying in twenty days, would become approximately 300 m.

We have learned something about the constraints imposed by the expected length of the primary release

period of a site of munitions and by the size of the dump sites. The major conclusions of this section are as follows:

- The munitions have a mean density on the seafloor at the sites ranging from a few hundred to tens of thousands per square kilometer with the maximum still being less than one munition per 15 m^2.

- This assumes all munitions hold 1 kg of CW agent and since many munitions, like the bombs, hold a great deal more, the actual density will be smaller.

- If the primary release period for a site is in the range of five to forty years, and the time for a single 1 kg munition to release all of its agent is 1/Q days, then the mean number of leaking munitions per square kilometer at the site is given by D/Q where D is the appropriate number in Table 5-7. This number, D/Q, is expected to be on the order of several hundred or less.

- The large quantity of CW munitions thought to have been dumped in the White Sea, coupled with the relatively small area of that dump site (121), lead to

Table 5-7: Estimated Density of Leaking Munitions

Site/ (#/km²) Total (Table 5-5)	(#/km²day⁻¹) Leaking T=5 yr	(#/km²day⁻¹) Leaking T=10 yr	(#/km²day⁻¹) Leaking T=20 yr	(#/km²day⁻¹) Leaking T=40 yr
Barents Sea Site 122 (43 km²)				
• H≈5.8x10³	3.19	1.59	0.8	0.4
• L≈5.8x10³	3.19	1.59	0.8	0.4
• GA≈1.1x10⁴	6.37	3.19	1.6	0.8
• GB≈0	0.00	0.00	0.00	0.00
Barents Sea Site 134 (528 km²)				
• H≈4.3x10³	2.34	1.17	0.58	0.29
• L≈4.3x10³	2.34	1.17	0.58	0.29
• GA≈8.5x10³	4.670	2.335	1.17	0.58
• GB≈0	0.00	0.00	0.00	0.00
Kara Sea Site 123 (17,150 km²)				
• H≈2x10³	1.10	0.55	0.28	0.14
• L≈2x10³	1.10	0.55	0.28	0.14
• GA≈1.1x10³	0.62	0.31	0.16	0.078
• GB≈1.2x10²	0.06	0.03	0.016	0.008
Kara Sea Site 124 (62 km²)				
• H≈8.1x10³	4.42	2.21	1.11	0.55
• L≈8.1x10³	4.42	2.21	1.11	0.55
• GA≈8.1x10³	4.42	2.21	1.11	0.55
• GB≈0	0.00	0.00	0.00	0.00
White Sea Site 121 (292 km²)				
• H≈6.8x10⁴	37.5	18.77	9.38	4.69
• L≈6.8x10⁴	37.5	18.77	9.38	4.69
• GA≈1.7x10⁴	9.38	4.69	2.35	1.17
• GB≈0	0.00	0.00	0.00	0.00

the conclusion that the mean density of munitions at this site must be greater than at any other site.

- The most important uncertainty concerns the partitioning of the total quantities of munitions across the dump sites in the Barents and Kara Seas. If, for example, a large quantity of munitions were dumped at a small shallow site in the Barents Sea, then its small size would necessarily lead to a high density of munitions. We have taken this small size as an indicator that this did not occur, but this is a shaky assumption.

5.5   CW AGENT RELEASE MODELS

Based on the foregoing we have developed three release models, each of which contains a quantity of munitions, a release rate for a single munition and the primary release period over which the entire site releases all of its agent.

Scenario 1: Tabun, Sarin and Lewisite Constant Release

- The munitions in quantities given in Table 5-6 are distributed uniformly over the dump sites;

- The time to initial release from 95 percent of the individual munitions is uniformly distributed in time over T which is treated parametrically as being in the range of five to fifty years.

- For these values of T, the densities of munitions leaking per km^2 day^{-1} are as given in Table 5-6.

- The release of the agent from an individual munition happens at a constant rate Q over a period which will be taken to be approximately one to one hundred days which gives for 1 kg munitions, Q=10 kg day^{-1} - 0.001 kg day^{-1}.

Scenario 2: Tabun, Sarin and Lewisite Instantaneous Release

- The munitions in Table 5-6 are uniformly distributed over the entire dump site;

- The time delay to release from 95 percent of the individual munitions is uniformly distributed in time over T which is treated parametrically as being in the range of five to fifty years.

- The spatial density of munitions which have disintegrated and begun to dissolve at the site is given by Table 5-6.

- Release of dissolved agent from an individual munition can be neglected until complete disintegration of the casing when mustard is deposited on the seafloor. Dissolution results in mustard agent being introduced into the sea at a rate of x 0.01 kg day^{-1} for a time on the order of 100 days.

Scenario 3: Immediate Release (5%) of All Agents

- The munitions are uniformly distributed over the entire dump site;

- Five percent of the individual munitions are released immediately.

5.6   UNCERTAINTIES

In view of the quantitative results contained in the previous section, and the shaky foundation of fact on which they were based, it is important to review what has been accounted for in these release scenarios, what has not, and how much the latter could affect the results.

What has been accounted for?

- Total quantities of agents thought to have been dumped (Table 2-1);

- The types of agents dumped;

- The locations of the dump sites;

- Large dump sites are large for a reason, namely that more munitions were dumped there;

- Empirical data showing that munitions remain on the seafloor in relatively intact form for long periods, with corrosive disintegration happening over decades; and

- The physical properties *i.e.*, impulsive release or slow dissolution, of the various agents.

What has not been accounted for and how much does it matter?

- Even if the total quantities of agent in Table 2-1 are correct, the breakdown by site is highly uncertain and was guided roughly by the areas of the sites;

- An accurate accounting for corrosion, except to the extent that it exists;

- The actual distribution of munitions on the seafloor at the dump sites;

- The "waiting period" T_1 for the release to begin was not addressed in this chapter, but it has been in Chapter 7 when it is necessary to draw conclusions about ecosystem impact; and

- The temporal distribution of release, especially the total time T.

It is possible to view these uncertainties as implying that so little is known that there is no objective way to proceed. However, we do place some credibility in the total quantities of dumped munitions and in the identification of the dump sites. In addition, there can be little doubt that the munitions were scattered across large areas of the seafloor when dumped, if only because of navigational errors. Finally, the Baltic experience certainly suggests that munitions on the seafloor will remain intact for long periods; otherwise, even the slow dissolution rate of mustard would have caused all the agent to have disappeared by now. The bounds developed here, falling back on a parametric treatment of a few unknown quantities, would seem to credibly bound the problem of release scenarios.

BACKGROUND

- All available toxicity data regarding the chemical warfare agents of primary concern and the expected degradation products in the marine environment were gathered and summarized.

- This information was used to compare the toxicities of the different agents and their degradation products and to decide which chemicals may represent a toxic threat to the environment.

- For each of those chemicals that are potentially toxic, an *estimated no effects concentration* [ENEC] was derived, usually as one-tenth of the lowest LC_{50} value for marine organisms.

- In addition, to define areas affected by these chemicals, *estimated probable effects concentrations* [EPEC], and *estimated lethal effects concentrations* [ELEC] were designated as ten and one hundred times the ENEC concentrations, respectively.

- Because of the sparseness of studies of long-term, non-lethal effects at low concentration, the bi-levels established here are considered more reliable at ELEC and EPEC levels than ENEC.

- For simplicity and because data does not exist for those agents to support a more true ground analysis, these levels [ENEC, etc.] are taken to apply equally to all marine species.

CONCLUSIONS

- Tabun (GA) and Sarin (GB) are of approximately equal toxicity. They were both assigned an ENEC of 1 µg l^{-1}. Mustard (H) is orders of magnitude less toxic with an ENEC of 200 µg l^{-1}. Lewisite has intermediate toxicity with an ENEC of 20 µg l^{-1}.

- Cyanide is a breakdown product of Tabun and was assigned an ENEC of 7 µg l^{-1}. Dimethylamine is also a breakdown product of Tabun with an ENEC of 115 µg l^{-1}. Chlorobenzene is a component of the Tabun formulation, present up to twenty percent. Chlorobenzene was assigned an ENEC of 1,000 µg l^{-1}.

- Most of the breakdown products of Sarin have toxicities six orders of magnitude less than Sarin. Fluoride is the only exception to this and it was assigned an ENEC of 200 µg l^{-1}.

- Mustard breakdown products are thiodyglycol, with an ENEC of 1,470,000 µg l^{-1} and 1,4-thioxane with an ENEC of 26,000 µg l^{-1}.

- Lewisite hydrolyzes to 2-chlorovinylarsonous acid, which was assigned an ENEC of 20 µg l^{-1}, the same as the parent compound Lewisite. Inorganic arsenic is the ultimate degradation product of Lewisite, with an ENEC of 90 µg l^{-1}.

6.1   OBJECTIVES

This chapter addresses the problem of determining the toxicity in the marine environment. The available toxicity information was used to compare the toxicities of the different agents and their degradation products and to decide which chemicals may represent a toxic threat to the environment. For each of those chemicals that are potentially toxic, an *estimated no effects concentration* [ENEC] was derived, as described below, to be used in the interpretation of the results of modeling their transport and breakdown. Table 6-1 presents the ENEC values derived in this chapter.

Table 6-1: Estimated Concentration Thresholds for Toxic Effects

Chemical	ENEC μg l⁻¹	EPEC μg l⁻¹	ELEC μg l⁻¹
GA	1	10	100
Chlorobenzene (contaminant with GA)	1,000	10,000	100,000
Cyanide (GA degradation product)	7	70	700
Dimethylamine	115	1,150	11,500
GB	1	10	100
Fluoride	200	2,000	20,000
H	200	2,000	20,000
Thiodiglycol	1,470,000	14,700,000	147,000,000
1,4-thioxane	26,000	260,000	2,600,000
L	20	200	2,000
Arsenic (inorganic)	90	900	9,000
2-chlorovinylarsonous acid	20	200	2,000

ENEC = Estimated No Effects Concentration
EPEC = Estimated Probable Effects Concentration
ELEC = Estimated Likely Effects Concentration

Also discussed below are dose-response experiments for acute toxicity that represent the most commonly available information. This type of experiment provides the range of the amounts of chemical intake per kg body weight (dose) or the amounts of chemical per volume of water (concentration) that result in the death of the animal. The data from this type of experiment on laboratory animals and aquatic species is the basis for the assessment of the toxicities of each chemical of concern.

6.2 DATA SOURCES

Toxicity information on chemical warfare agent hydrolysis products was retrieved by searching the CAS database, which covers the literature since 1967. This was supplemented with other conventional reference materials. Toxicity information for the agents themselves was obtained from conventional reference materials. The primary source of aquatic information used in this report was the AQUIRE

database [Aquatic Toxicity Information Retrieval], which is supported by the U.S. Environmental Protection Agency (EPA). The AQUIRE toxicological data summary is designed for use as a stand-alone reference database or as a high-quality data source for risk assessment tools. The majority of reported test results post-date 1970 and current publications are continually and systematically acquired and reviewed. Test organisms are limited to those that are exclusively aquatic. The system presently contains data on more than 2,700 species, 5,700 chemicals, 9,300 references, and approximately 60 effects from 130,000 toxicity tests.

6.3 APPROACH

There are many variables in a toxicity study that affect the relevance of the results to the assessment being made. In particular, the species used in the study, the endpoint of the study, and the length of time of exposure are important considerations. The general

approach used to apply available toxicity information to the assessment of toxic effects in the marine environment was as follows.

Focus on acute toxicity. The assessment of potential environmental effects of chemical release would be based ideally on studies of all possible effects of the chemicals of concern on all of the specific species found in the affected ecosystem. The reality of the available information, however, is that studies of non-lethal, long-term (chronic) endpoints in species other than laboratory animals are rare or non-existent. Available information on the chemicals of concern in this analysis is limited to studies of laboratory animals and selected aquatic species with acute toxicity, *i.e.*, death, as the endpoint. For many of the chemicals of concern, especially the chemical agents themselves, acute toxicity *is* the primary concern, since they are acutely toxic, degrade over the course of hours, and would not be expected to produce chronic effects in either the laboratory or the environment.

The reported LC_{50} values[1] were the most useful measure in assessing the toxic effects of these chemicals in seawater. The reported LD_{50} values[2] for aquatic and laboratory species were also considered in order to compare toxicities where LC_{50} values were limited or not available. The values of LC_{50} vary with the organism tested, reflecting the variation in sensitivity of different species to different chemicals. They also vary inversely with the length of exposure, with longer exposure times resulting in lower LC_{50} values. For the purpose of estimating a toxic threshold for chemicals of concern, generally the lowest reported LC_{50} was identified and one-tenth of this value was chosen as a concentration at which marine organisms would not experience acute toxicity. This value is identified as the *estimated no effects concentration* [ENEC]. For the purpose of defining volumes of sea that would experience toxic effects of these chemicals, the ENEC was multiplied by ten to yield *estimated probable effects concentrations* [EPEC] and by one hundred to yield *estimated lethal effects*

concentrations [ELEC]. Values of EPEC and ELEC are shown in Table 6-1 along with the ENEC values.

Use data from marine species. No data was found for arctic species or for the temperature of the study region. Toxicity data from marine organisms was used preferentially, when available. However, for many chemicals of concern, information was only available for freshwater organisms.

Identify substances with little potential for acute marine toxicity. The maximum amounts of the degradation products per kilogram of the chemical agents were calculated from the stoichiometric relationships in Chapter 4. From these amounts and assumed release scenarios for the agents, maximum concentrations can be calculated. Actual concentrations will be substantially less than those calculated in this way because the breakdown reactions are not instantaneous and because the primary breakdown products are subject to further degradation and dilution. However, if the maximum potential concentration of a substance based on the assumed release scenario for the agent can be shown to be significantly less than its ENEC value, then the substance can be assumed to be of no concern with respect to acute marine toxicity.

6.4 TOXICITY OF TABUN AND ITS BREAKDOWN PRODUCTS

Tabun is a potent inhibitor of cholinesterase, which is the mechanism of its toxicity. The LD_{50} values for various laboratory animals are shown in Table 6-2. It is similar to Sarin in its toxicity to mice, with an LD_{50} for intraperitoneal injection of 0.6 mg kg^{-1} compared to 0.42 mg kg^{-1} for Sarin. Tabun is about one-third as toxic as Sarin in guinea pigs, with a subcutaneous LD_{50} of 0.12 µg kg^{-1} vs. 0.039 µg kg^{-1} for Sarin. A drinking water criteria for Tabun has been established at 1.5 µg l^{-1}, compared to 0.73 µg l^{-1} for Sarin.[3]

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[1] Lethal concentration 50, the concentration of the substance that resulted in the death of 50 percent of the exposed organisms during the specified time interval.
[2] Lethal dose 50, the dose of the substance that resulted in the death of 50 percent of the exposed organisms during the specified time interval.
[3] U.S. Army, 1996. "Interim Chronic Toxicological Criteria for Chemical Warfare Compounds." Memorandum MCHB-DC-C, U.S. Army Center for Health and Preventive Medicine.

Table 6-2: LD_{50} Values for Tabun (GA) in Laboratory Animals[4]

Substance	Species	LD_{50}	Comment
GA	Mice	0.6 mg kg^{-1}	intraperitoneal injection Holmstedt (1959)
	Guinea Pigs	0.12 mg kg^{-1}	subcutaneous injection Gordon and Leadbeater (1977)
	Rabbits	960 mgmin/m^3	LC_{50} in air Chemical Agent Data Sheets

No information on the aquatic toxicity of Tabun is available in the AQUIRE database. Because the toxicity of Tabun, as shown by the above LD_{50} values and drinking water criteria, is similar to that of Sarin, the ENEC for Sarin, 1 µg l^{-1}, which is derived below on the basis of aquatic toxicity measures, was adopted for Tabun.

No toxicity information is available for the monoethyl ester of dimethylphosphoramidic acid or dimethylphosphoramidic acid, which are the primary hydrolysis products of Tabun. The lack of the cyanide-phosphate bond in these hydrolysis products renders them much less reactive, however and, thus, they are significantly less toxic than Tabun. Larsson demonstrated a first-order loss of toxicity of Tabun

during its hydrolysis, with no apparent indication of toxicity due to the buildup of the hydrolysis products.[5] The absence of toxicity data for these hydrolysis products indicates they will not exert marine toxicity.

Dimethylamine, which is the hydrolysis product of dimethylphosphoramidic acid, has a low toxicity compared to the ENEC of Tabun. LC_{50} values for daphnia and rainbow trout are shown in Table 6-3. The LC_{50} values range from 1,150 µg l^{-1} to 118,000 µg l^{-1}, which is three to five orders of magnitude less toxic than the ENEC of Tabun. Applying a multiplier of 0.1 to the lowest LC_{50} (1,150 µg l^{-1}) to estimate the concentration at which acute marine toxicity will be negligible, yields an ENEC value of 115 µg l^{-1} for dimethylamine.

Table 6-3: LC_{50} Values for Dimethylamine[6]

Substance	Species	LC_{50}/EC_{50} (µg l^{-1})	Comment
Dimethylamine	Water flea - Daphnia magna	50,000	2 days Ref. 11455
	Rainbow trout - Oncorhynchus mykiss	1,150	50 days Ref. 871
	Rainbow trout - Oncorhynchus mykiss	10,000	30 days Ref. 871
	Rainbow trout - Oncorhynchus mykiss	17,000 - 118,000	4 days Ref. 5089

[4]Holmstedt, B. 1959. "Pharmacology of Organophosphate Cholinesterase Inhibitors." *Pharmacology Review* 11: 567-688; Gordon, J.J., and L. Leadbeater. 1977. "The Prophylactic Use of 1-Methyl, 2 Hydroxyiminomethyl-pyridinium Methanesulfonate (P2S) in the Treatment of Organophosphate Poisoning." *Toxicology and Applied Pharmacology 40*: 109-114; Chemical Agent Data Sheets, Vol. I EO-SR-74001, Edgewood Arsenal, 1974.
[5]Larsson, L. 1953. " The Hydrolysis of Dimethylamido-Ethoxy-Phosphoryl Cyanide (Tabun)." *Acta Chemica Scandinavica* 7: 306-314.
[6]AQUIRE [Aquatic Toxicity Information Retrieval], U.S. Environmental Protection Agency.

Cyanide is also a hydrolysis product of Tabun. LC_{50} values for cyanide for several aquatic species are shown in Table 6-4. It is more toxic than the other hydrolysis products of Tabun, yet less toxic than Tabun by two orders of magnitude. Because of its relatively higher toxicity compared to other hydrolysis products, and its persistence, an ENEC was derived to be 7 μg l^{-1}, one-tenth of the lowest reported LC_{50}.

Chlorobenzene is a component of Tabun that can be present in the mixture at five to twenty percent. Its toxicity is much lower than Tabun as shown by the LC_{50} values in Table 6-5. The most sensitive saltwater species is the sheepshead minnow and an ENEC of 1,000 μg l^{-1} was derived as one-tenth of the LC_{50} for this species.

Table 6-4: LC_{50} Values for Cyanide[7]

Substance	Species	LC_{50}/EC50 (μg l^{-1})	Comment
Cyanide	Opossum shrimp - Mysidopsis bahia	113	4 days Ref. 11331
		70	29 - 51 days max. accept. tox. conc. -mortality
Hydrogen Cyanide	Pinfish - Lagodon rhomboides	69	1 day Ref. 933
Sodium Cyanide	Three spine stickleback - Gasterosteus aculeatus	154 - 225	14 - 45 days Ref. 8778
	Aholehole - Kuhlia sanvicensis	1,000 - 20,000	0.001 day Ref. 10010
	Golden mullet - Mugil auratus	300	1 day
	Archiannelid - Dinophilus gyrociliatus	5,937 - 11,446	1 - 4 days Ref. 11940

[7]Reference 6.

Table 6-5: LC$_{50}$ Values for Chlorobenzene[8]

Substance	Species	FW/SW	LC$_{50}$/EC50 (μg l^{-1})	Comment
Chlorobenzene	Goldfish - Carassius auratus	FW	51,620	
	Goldfish- Carassius auratus (embryo-larval)	FW	880 - 1,040	8 days
	Fathead Minnow - Pimephales promelas	FW	29,120 - 33,930	
	Guppy - Poecilia reticulata	FW	45,530	
	Bluegill - Lepomis macrochirus	FW	15,900 - 24,000	
	Opossum Shrimp - Mysidopsis bahia	SW	16,400	
	Sheepshead Minnow - Cyprinodon variegatus	SW	10,500	
	Rainbow Trout embryo - Oncorhynchus mykiss	FW	90 (100% mortality)	16 days
	Largemouth Bass (embryo-larval) Micropterus salmoides	FW	50 - 60	7.5 days

6.5 TOXICITY OF SARIN AND ITS BREAKDOWN PRODUCTS

Sarin is a potent inhibitor of cholinesterase, which is the mechanism of its toxicity. The LD$_{50}$ values for various laboratory animals are shown in Table 6-6. It is similar to Tabun in its toxicity to mice, with an LD$_{50}$ for intraperitoneal injection of 0.42 mg kg^{-1} compared to 0.60 mg kg^{-1} for Tabun. Sarin is about three times as toxic as Tabun in guinea pigs, with a subcutaneous LD$_{50}$ of 0.039 μg kg^{-1} vs. 0.12 μg kg^{-1} for Tabun. A drinking water criteria for Sarin has been established at 0.73 μg l^{-1}.[9]

[8]U.S. EPA. 1980. *Ambient Water Quality Criteria for Chlorinated Benzenes.* EPA-440/5-80-028, Criteria and Standards Division, Office of Water Regulations and Standards, Washington, D.C.
[9]Reference 3.

Table 6-6: LD$_{50}$ Values for Sarin (GB) in Laboratory Animals[10]

Substance	Species	LD$_{50}$	Comment
GB	Mice	0.42mg/kg	intraperitoneal injection Holmstedt (1959)
	Guinea Pigs	0.0358mg/kg	subcutaneous injection Gordon and Leadbeater (1977)
	Rabbits	0.030	subcutaneous injection Gordon and Leadbeter (1977)

The aquatic toxicity of Sarin has been studied in three freshwater species: fathead minnows, sunfish and goldfish.[11] Time-to-death of 50 percent of the test species at several concentrations was measured as shown in Table 6-7. At 0.01 ppm (10 μg l^{-1}), the lowest concentration studied, 50 percent of the test groups died after 1.2, 1.7, and 6.9 days for minnows, sunfish and goldfish, respectively, at 12°C. Extrapolation of the concentration data to lower concentrations suggests that 50 percent of the most sensitive species, the fathead minnow, would survive for 28 days at 0.001 ppm (1 μg l^{-1}), which is one-tenth the lowest concentration studied. Since the half-life of Sarin in seawater is estimated to be about 16 hours, (see Chapter 5) a concentration of 1 μg l^{-1} would persist for only a small fraction of the 28 day survival time. Thus 1 μg l^{-1} was chosen as the ENEC for Sarin.

An earlier report by Weiss[12] calculated LC$_{50}$ values from data at only 24°C for both Tabun and Sarin for sunfish, fathead minnows, and goldfish. These calculations showed the toxicity of these two compounds to be within the same order of magnitude, with Sarin being the more toxic. No data were given for lower temperatures approaching that of seawater in the study region. Thus, the data from the later report[13] at 12°C were used to derive the ENEC values for both Sarin and Tabun.

[10]Holmstedt, B. 1959. "Pharmacology of Organophosphate Cholinesterase Inhibitors." *Pharmacology Review 11:* 567-688; Gordon. J.J., and L. Leadbeater. 1977. "The Prophylactic Use of 1-Methyl, 2-Hydroxyiminomethyl-Pyridinium Methanesulfonate (P2S) in the Treatment of Organophosphate Poisoning." *Toxicology and Applied Pharmacology* 40: 109-114.
[11]Weiss, C.M. and J.L. Botts. 1957. "The Response of Some Freshwater Fish to Isopropyl Methylphosphonofluoridate (Sarin) in Water." *Limnology and Oceanography 2:363-370.*
[12]Weiss, C.M., 1955. "The Response of Some Freshwater Fish to G Agents in Water." Medical Laboratories Research Report No. 358. Army Chemical Center, Aberdeen, MD.
[13]Reference 11.

Table 6-7: Time to Death of Aquatic Species at Various Concentrations of Sarin (GB)[14]

Species	GB Concentration ppm	Time (minutes) to Death at 24° C	Time (minutes) to Death at 12° C
Minnow	50.0	0.80	1.3
	10.0	1.25	2.7
	1.0	3.25	11.0
	0.1	26	80
	0.01	360	1,700
Sunfish	50.0	0.95	1.55
	10.0	1.65	3.4
	1.0	5.8	14
	0.1	35	120
	0.01	320	2,400
Goldfish	50.0	1.5	2.3
	10.0	2.2	4.2
	1.0	7.5	19
	0.1	52	170
	0.01	2,000	10,000

The hydrolysis products of Sarin are less toxic than the parent compound by orders of magnitude. No aquatic toxicity data was found for methylphosphonic acid, mono, (1-methylethyl) ester. This primary hydrolysis product of Sarin has oral LC_{50} values in drinking water of rats and mice, as shown in Table 6-8, in the range of 5.6 to 7.7 gm l^{-1} and a no effects concentration of 3 gm l^{-1} for rats.[15] For methylphosphonic acid, LC_{50} values are available for aquatic species and are shown in Table 6-9. They are in the range of 0.58 gm l^{-1} for freshwater protozoa, 4.4 gm l^{-1} for daphnids, 10.6 to 13.6 gm l^{-1} for minnows and sunfish, and 17.8 gm l^{-1} for algae. Isopropanol is also only toxic in the concentration range of grams per liter. While no aquatic toxicity data are available, the oral LD_{50} in rats is 5.8 gm kg^{-1} and 1.4 gm kg^{-1} is fatal in humans. From these values, compared to the toxicity of Sarin, it can be readily concluded that these hydrolysis products will present less of a toxicity threat to the environment than Sarin by six orders of magnitude and that their areas of influence will be less than that of Sarin by a similar factor.

[14]Reference 11.
[15]Mecler, F.J. 1981. *Mammalian Toxicological Evaluation of DIMP and DCPD (Phase III-IMPA)*. Litton Bionetics, AD-A107574, 277p.

Table 6-8: LD$_{50}$ Values for Methylphosphonic Acid, mono, (1-methylethyl) ester[16]

Substance	Species	Sex	LC$_{50}$ (mg l^{-1}) in Drinking Water	Comment
Methyl-phosphonic Acid, mono, (1-methylethyl) ester	Mice	Male	5,620	
	Mice	Female	6,550	
	Rat	Male	7,650	No Effects at 3,000mg/l
	Rat	Female	6,070	

Table 6-9: LD$_{50}$ Values for Methylphosphonic Acid[17]

Substance	Species	FW/SW	LC$_{50}$ (μg l^{-1})	Comment
Methyl-phosphonic Acid	Daphnids	FW	4,443,000	24 hr.
	Fathead minnow - Pimephales promelas	FW	13,549,000	24 hr.
	Fathead minnow - Pimephales promelas	FW	10,733,000	48 hr.
	Fathead minnow - Pimephales promelas	FW	10,617,000	96 hr.
	Bluegill - Lepomis macrochirus	FW	11,087,000	96 hr.
	Protozoa	SW	581,000	7 day
	Algae Selenastrum capricornutum	SW	17,806,000	14 day

The toxicity of fluoride is also several orders of magnitude less than that of Sarin. Table 6-10 shows LC$_{50}$ values for several aquatic species. The most sensitive species, Scud, shows a range of LC$_{50}$ values from 1.95 to 6.90 mg l^{-1}. Because of the persistence of fluoride in the environment, an ENEC was chosen as 0.2 mg l^{-1}, one-tenth of the lowest LC$_{50}$ reported for this most sensitive species.

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[16]Reference 15.

[17]Williams, R.T., W.R. Miller, and A.R. MacGillivray. 1987. "Environmental Fate and Effects of Tributyl Phosphate and Methyl Phosphonic Acid." *CRDEC-CR-87103* 144p.

Table 6-10: Toxicity of Fluoride to Aquatic Species[18]

Substance	Species	LC_{50} (μg l^{-1})	Comment
Sodium Fluoride	Scud-Grandidierella sp.	1,950 - 6,900	90 day test Ref. 15590
	Oyster - Ostrea angasi	30,000	21 day test Ref. 13222
	Brown mussel - Perna perna	1,400 - 26,500	5 day test Ref. 2653
	Rock oyster - Saccostrea commercialus	30,000	21 day test Ref. 13222
	Mud crab - Tylodiplax blephariskios	52,000	72 day test Ref. 2653
	Tigerfish Therapon jarbua	100,000	4 day test Ref. 2653
	Striped mullet Mugil cephalus	100,000	4 day test Ref. 2653

6.6 TOXICITY OF MUSTARD AND ITS BREAKDOWN PRODUCTS

Mustard is a vesicant and alkylating agent, producing cytotoxic action on the hematopoietic tissues, which are especially sensitive. The rate of detoxification in the human body is very slow and repeated exposures produce a cumulative effect. Mustard has been found to be a human carcinogen by the International Agency for Research on Cancer. The oral LD_{50} for man is 0.7 mg kg^{-1}. A drinking water criteria for mustard has been established as 0.26 μg l^{-1}.[19] Mustard is lipid soluble and can be absorbed into all organs. Skin penetration is rapid without skin irritation. Swelling and reddening of the skin occurs after a latency period of 4-24 hours. Although the dissolution of mustard into water is slow, dissolved mustard hydrolyzes with a maximum half-life of 5.25 hours. Hydrolysis products include thiodiglycol and 1,4-Thioxane.

No information was found in the AQUIRE database for mustard. However, a study by Buswell et al. (1944)[20] of time-to-death for bluegill sunfish found a very large increase in toxicity with increasing concentration. No deaths were observed at a concentration of 1 mg l^{-1} during thirty days of exposure. At 2 mg l^{-1}, twenty-two out of thirty sunfish died during a thirty-day test. At 5 mg l^{-1}, all individuals died in about thirteen days. Similar results were found for red-eared sunfish and black bullheads. While these data are not amenable to a conventional LC_{50} calculation, the intermediate dose of 2 mg l^{-1} can be taken as an approximation of an LC_{50}. Using a multiplier of 0.1, to estimate the concentration at which acute aquatic toxicity will be negligible, yields a value of 200 μg l^{-1} for the mustard ENEC.

[18]Reference 6.
[19]Reference 3.
[20]Buswell, A.M. et al. 1944. *The Effect of Certain Chemical Warfare Agents in Water on Aquatic Organisms.* Report OSRD No. 3589, Division 9 of the National Defense Research Committee, Office of Scientific Research and Development.

Thiodiglycol (TDG), a hydrolysis product of mustard, is several orders of magnitude less toxic than mustard. TDG was the subject of study with three freshwater species in the AQUIRE database. The LC_{50} values estimated for the water flea, the fathead minnow and the channel catfish were all very high, ranging from approximately 15 to 40 gm l^{-1}. The most sensitive species, the water flea, had an LC_{50} of 14,700,000 μg l^{-1}. Using a multiplier of 0.1 to estimate the concentration at which acute marine toxicity will be negligible yields a value of 1,470,000 μg l^{-1} for an ENEC for TDG. The solubility of mustard is 0.3 g l^{-1} at 0°C, or 300,000 μg l^{-1}. If this concentration of mustard were stoichiometrically converted to TDG, the result would be a concentration of 194,000 μg l^{-1}. Because this maximum possible concentration of TDG is an order of magnitude less than the water flea LC_{50}, the marine toxicity of TDG, as a product of hydrolysis of released mustard, will not be of concern.

No data on the environmental effects of 1,4-thioxane, a hydrolysis product of mustard, was found. However, this compound has a preliminary remediation goal value for drinking water, set by Region 9 of the U.S. EPA, of 26 mg l^{-1}. Because this concentration is intended to be protective of human health, it may be also assumed to be the ENEC for this compound. Assuming that mustard was released at its maximum solubility of 0.3 g l^{-1} at 0°C, stoichiometric hydrolysis would yield a concentration of 36 mg l^{-1} of 1,4-thioxane which is only slightly higher than the preliminary remediation goal.

6.7 TOXICITY OF LEWISITE AND ITS BREAKDOWN PRODUCTS

Lewisite is a vesicant which rapidly hydrolyzes in the aquatic environment. A drinking water criteria for Lewisite has been established as 3.7 μg l^{-1}.[21] The immediate hydrolysis products, (2 chlorovinyl)arsonous acid and (2-chlorovinyl)arsonous oxide, are also vesicants. Ultimately the degradation of one mass unit of Lewisite can result in the production of 0.361 units of inorganic arsenic. In addition to Lewisite itself, toxicity concerns have focused on these three products.

No information was found in the AQUIRE database for Lewisite. However, others[22] reported on the effects of Lewisite on several freshwater fish species, as shown in Table 6-11. The golden shiner was found to be the most sensitive of the species tested, with two out of five (40 percent) of the test organisms dead at a Lewisite concentration of 0.2 mg l^{-1}. One-tenth of this value, 20 μg l^{-1}, is chosen as the ENEC. The solubility of Lewisite, 500 mg l^{-1} at 20°C, is three orders of magnitude greater than the ENEC value.

Table 6-11: Toxicity of Lewisite (L) to Freshwater Fish[23]

Species	Lowest Toxic Concentration (mg l^{-1})
Golden Shiner	0.2
Bluegill	0.5
Bass	<2
Sunfish	no deaths during 24 hr. exposure at 6.5 mg l^{-1}

[21]Reference 3.
[22]Rosenblatt, David H. et al., editors. 1975. *Problem Definition Studies on Potential Environmental Pollutants II Physical, Chemical, Toxicological, and Biological Properties of 16 Substances.* Technical Report 7509. U.S. Army Medical Bioengineering Research and Development Laboratory.
[23]Reference 22.

No information was found on the aquatic toxicity of the hydrolysis products, (2-chlorovinyl)arsonous acid and (2-chlorovinyl)arsonous oxide. These compounds have been reported to show intravenous and ocular toxicity similar to Lewisite.[24] The rapid hydrolysis of Lewisite and the similar toxicity of these hydrolysis products makes it likely that the hydrolysis products are the active form of Lewisite. An ENEC equal to that of Lewisite was assigned to 2-chlorvinylarsonous acid.

The toxicity of inorganic arsenic toward several aquatic species is shown in Table 6-12. The lowest LC_{50} value is for the marine Calanoid copepod *Acartia clausi*. A four day exposure indicated an LC_{50} of 907 μg l^{-1}. Using a multiplier of 0.1, to estimate the concentration at which direct aquatic toxicity will be negligible, yields a value of 90 μg l^{-1} for the inorganic arsenic ENEC. Note that evaluation of this limit should consider that one mass unit of Lewisite can ultimately result in only 0.361 units of arsenic.

Table 6-12: LC_{50} Values for Arsenic in Aquatic Species[25]

Substance	Species	LC_{50}/EC_{50} (μg l^{-1})	Comment
Arsenic	Opossum shrimp - Mysidopsis bahia	1,740 - 2,319	4 days Ref. 11331
	Water flea - Daphnia magna	1,900 - 3,800	2 days Ref. 11181
	Bluegill - Lepomis macrochirus	5,000	mortality, 183 days Ref. 2143
	Water flea - Simocephalis vetalus	1,700	2 days Ref. 11181
	Water flea - Ceriodaphnia reticulata	1,800	2 days Ref. 11181
	Calanoid copepod Acartia clausi	907	4 days Ref. 3746

[24]Epstein J. et al. 1973. *Summary Report on a Data Base for Predicting Consequences for Chemical Disposal Operations.* Edgewood Arsenal Special Report 1200-12.
[25]Reference 6.

BACKGROUND

- A methodology was developed to quantify the effects of advection, mixing or dilution, and hydrolysis on CW agents that have been released into the sea from single munitions and to extrapolate this in order to estimate the extent of toxicity at typical arctic dump sites.

- For the four types of CW agents considered, convincing results were reached showing that the contamination of the sea by a *single* leaking CW munition will be a *local one*; that is, one confined to an area with dimensions on the order of a kilometer or less.

- Release of Agents from Single Munitions Results
Released agents will be confined to volumes on the order of $L_H \times L_H \times L_V$ where L_H and L_V are the horizontal and vertical mixing distances measured on a hydrolysis time scale. These dimensions will be on the order of tens of meters.

Mustard, however it is released, can lead to, at most, concentrations at or above minimum toxic levels only in the immediate vicinity of the disintegrated munition, generating a plume only centimeters in length and several centimeters thick. *This is an upper bound.* However, the slow dissolution rate, which limits the physical extent, also results in this small region of toxicity persisting for long periods.

Agents released very rapidly in 1 kg quantities, *i.e.*, fractured munitions, will produce toxic concentrations over water volumes and seafloor areas as follows:

	Volumes (m^3)	Areas (m^2)	Duration (hr)
Tabun	2.3×10^5	1.4×10^4	11
Sarin	2.4×10^5	1.4×10^4	11
Lewisite	2.4×10^2	8.3×10^1	0.4

The agents released slowly form plumes that will have dimensions on the order of a few hundred meters along the current, a few tens of meters across the current, and less than ten meters thick above the seafloor. These sizes are upper bounds and could be much less.

Plume sizes generated by a slow release are typified by a release of Tabun at 1 kg/day, which produces a plume at a concentration of "no biological effects" having a volume of less than 10^4 m^3 and an area on the seafloor of less than 10^3 m^2.

CONCLUSIONS

The extent of toxic contamination at the dump sites is limited to a fraction of the area of the dump site itself and to heights above the seafloor of a few tens of meters although probably much less. Sufficient munitions were probably dumped to extend the overall duration of the contamination for decades once significant release begins, which may itself take many decades.

As an example of the low end of toxic extent, the largest dump, Site 123 (Kara Sea), may have had as much as 30,000 tons of mustard dumped. This quantity of agent, if it were released over a ten year period, would lead to contamination of a very large number of small areas within the site totaling less than 1 km^2 in area, with each individual plume lasting approximately three to four months. This is an upper bound since the total period over which release occurs is probably approximately thirty to fifty years not ten.

However, the more toxic and soluble agents, also probably dumped in kiloton quantities, could produce much more extensive contamination at the dump sites, though still confined to the site area. For example, the quantity of agents possibly dumped at Site 123 could contaminate 1,000 km^2 at ENEC if released uniformly over a period of five years. Similarly, the toxic contamination at the shallow Barents Sea site, 134, could approach fifty percent of the site area for a five year primary release period. However, the Baltic Sea experience suggests rather strongly that corrosion of munitions takes place over long periods, some munitions releasing agent very soon after dumping and some remaining intact after fifty years.

7.1 INTRODUCTION

This chapter addresses the problem of determining the spatial and temporal changes in the concentration of CW agents once they are released into the sea. *It is important to appreciate that* it is necessary to obtain numerical estimates of the spatial extent of contamination at specific concentrations in order to evaluate ecosystem effects. These effects will hinge on bounding the spatial extent of toxic levels and their duration. However, the overriding driver in this entire study is that CW agents appear to have been disposed of in arctic seas in quantities of 10^6 to 10^7 kg. Thus, in the absence of quantitative estimates of the extent of toxic concentration, there would be no confidence that ecosystem effects could be usefully bounded. The primary objective of this chapter is to estimate the volume of seawater and the associated seafloor areas that could be contaminated at the benchmark ENEC and EPEC concentrations for each CW agent.

The job of this chapter primarily will involve determining the spatial and temporal scales governing the processes shown in Table 7-1 and in determining which of them dominate in given circumstances.

At a minimum, the important physical effects include the hydrolysis of agents into toxic and non-toxic products (see Chapter 4); the transport of agents and the hydrolysis products by ocean currents; and the dilution, as a result of mixing by eddy diffusion in the benthic boundary layer. Effects for possible future consideration include the scavenging of agents by particulates or scavenging at the seafloor.

In this approach, the first step was to develop estimates of the extent of contamination produced by a single munition, *e.g.*, the dimensions of toxic plumes, and then to combine these estimates with the results provided in Chapter 5 on release scenarios. Having done that, the overall extent of contamination produced by the five dump sites emerged. This data was used to answer the seven key questions, listed in Table 7-2. These answers were used to assess the impact on arctic ecosystems (see Chapter 8).

Answering Question 1, establishes the fundamental limits on the time scales of the problem. Answering Questions 2 through 5 establishes space and time boundaries which limit the extent of the toxic levels. This concept is illustrated schematically in Figure 7-1, where "space" denotes the contaminated volume of the plume or the associated area of the contaminated seafloor, and time the period over which the plume persists.

The departure point for investigations into the effects of physical processes is defined by the conclusions of Chapters 2, 4, and 5. The environmental descriptions provided in Chapter 3 supply the basic framework for the modeling to be carried out here, while the toxic levels provided in Chapter 6 establishes the bounds on the concentrations that are relevant to considerations of an ecosystem impact in Chapter 8.

Table 7-1: The Fundamental Local Physical Processes

Physical Process	Symbol/ Units	Meaning
Dissolution	Σ $g\ cm^{-2}s^{-1}$	The rate at which the CW agent dissolves in seawater, it is governed by corrosion rates of munitions casings.
Hydrolysis	k s^{-1}	The rate at which the dissolved agent reacts chemically with water to form byproducts.
Advection	v $m\ s^{-1}$	The transport of dissolved agent in an ocean current that has speed v and is moving in the direction v, possibly due to long term mean circulation or to tides or other processes.
Eddy Diffusion	K m^2s^{-1}	The rate at which dissolved agent is diluted by turbulent mixing.

Table 7-2: *Key Questions Related to Physical Processes*

Q#	Questions
1	Following release from a single munition, how does the quantity of CW agent change with time due to chemical reactions?
2	Following a sudden release of CW agents, what is the spatial extent of toxic contamination and how does it change with time?
3	What is the spatial extent of the toxic plume that is expected to form if a CW agent is slowly released into the ocean over a long period of time?
4	To what degree are the answers to Questions 1 through 3 sensitive to details of the local ocean environment?
5	What is the potential for the transport of toxic concentrations by ocean currents over great distances?
6	What is the total extent, including water volumes and affected areas of the seafloor, of toxic concentrations produced at a dump site?
7	What is the sensitivity of the answer to Question 6 to uncertainties in the analysis?

Figure 7-1: *Schematic Illustration of the "Size" of the Problem*
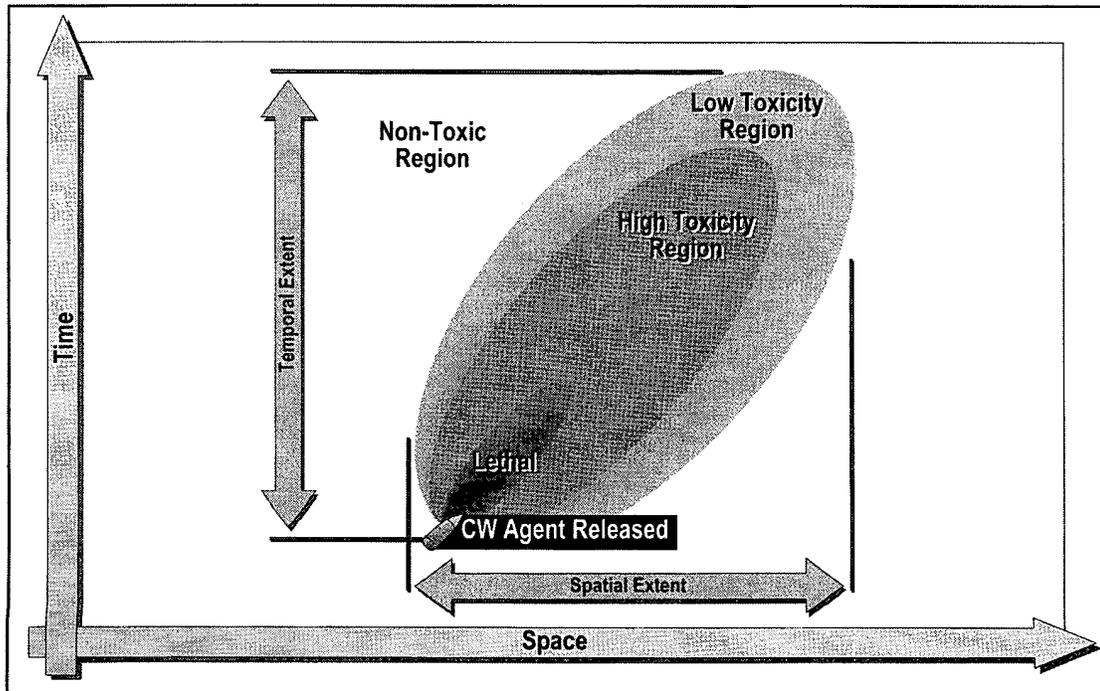
For the reader's convenience, Table 7-3 provides a guide to the remainder of the material in this chapter.

7.2 THE CONCEPTUAL MODEL

The key to the utility of this chapter will reside in capturing the essential elements of the real problem in a model that is tractable and in obtaining answers that are illuminating. The most important area in which considerable approximation will be necessary concerns the treatment of mixing where a simple eddy diffusion model will be used to parameterize the process. In addition, the chemical model will assume independence of hydrolysis from the process of eddy diffusion, an approximation which requires that the time scales of hydrolysis are much slower than those of turbulent mixing in the benthic boundary layer. In the case of CW agents having hydrolysis half-lives of many hours (see Chapter 4) this is a very good approximation since it can be expected that mixing through small scale eddy diffusion in the benthic boundary layer is a process in which spatial scales are centimeters with time scales in seconds.

Recalling Chapter 4, the hydrolysis of the agents Tabun, Sarin and dissolved mustard was modeled as simple reactions producing non-toxic products that are of no further concern here. On the other hand, the model for Lewisite showed it hydrolyzing into a variety of toxic arsenical compounds with subsequent reactions simply redistributing arsenic into stable, inorganic, toxic compounds. For purposes of this chapter, the chemical model will be assumed to be one of the following three types:

Table 7-3: Reader's Guide to Chapter 7 Material

Section	Title	Purpose
7.2	The Conceptual Model	Establishes the mathematical models of agent release, hydrolysis, and ocean physical processes to be expected.
7.3	Agent Release and Hydrolysis	Determines the total quantities of CW agents that remain as a function of time following a release, including release rate considerations.
7.4	Spatial and Temporal Scales	Establishes bounds on dilution and transport of spatially averaged quantities for impulsive (acute) and steady state (chronic) agent release events.
7.5	Toxic Levels from an Impulsive (Acute) Release	Determines the manner in which toxic levels of a pulse of contaminated seawater are transported by an ocean current while mixing and hydrolysis continue to decrease toxic levels.
7.6	Steady State (Chronic) Release of CW Agents	Considers a steady release event and establishes the spatial extent of the toxic plume.
7.7	Toxic Levels at the Dump Sites	Discusses the effect of a large number of munitions spread across an extended region of the seafloor.
7.8	Potential for Accumulation of Contaminants in the Sediments	Discusses the potential for several hydrolysis products to accumulate in seafloor sediments over long periods of time.
7.9	Summary of Results	Summarizes the primary results obtained in this chapter for Tabun, Sarin, mustard, and Lewisite.

(A) CWA $\xrightarrow{k}$ SNTP

(B) CWA $\xrightarrow{k}$ $(1-\varepsilon)$ SNTP $+ \varepsilon$ STP

CWA $\xrightarrow{k_1}$ $(1-e_1)$ SNTP $+ e_1$ USTP

(C) USTP $\xrightarrow{k_2}$ $(1-e_2)$ SNTP $+ e_2$ STP
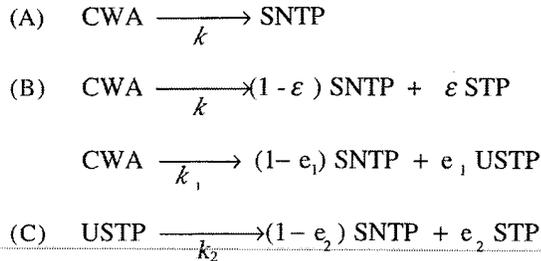
where ε is the mass fraction determined by the stoichiometry of the reaction and k is the hydrolysis rate constant. The abbreviations stand for Chemical Warfare Agent (CWA), Stable Toxic Products (STP), Unstable Toxic Products (USTP) and Stable Non-Toxic Products (SNTP). Reaction (A) applies to Sarin and mustard. Reaction (B) applies to Tabun with STP being hydrocynanic acid (HCN). Reaction (C) applies to Lewisite where the products are organic and inorganic arsenicals.

The coupled equations governing the quantities of agent M_A and product M_P in reaction (A) 1 are $dM_A/dt = -k\,M_A$ and $dM_P/dt = k\,M_A$, with modifications

to account for two products in reaction B. Figure 7-2 illustrates the behavior of the second reaction for a *hypothetical* hydrolysis rate, where $k = 0.0000192$/s (half-life of 10 hr) and $\varepsilon = 0.25$.

7.2.1 CW Agent Injection Model

If the physical processes of hydrolysis, mixing, and advection are slow compared to the rate of agent release, the appropriate model is the impulsive (*i.e.*, acute), while if the physical processes are rapid compared to the release, then the appropriate model is a steady state one (*i.e.*, constant release rate). The relevant physics obtained from these two events bound the problem. The degree to which either situation fits the actual release process depends on two time scales, the duration of a significant release of CW agent, and the time for physical processes to produce dispersal and hydrolysis of the agent.

The two types of behavior expected from agents released into water are depicted schematically in Figure 7-3, along with their simplest mathematical models.

Figure 7-2: Illustration of Chemical Reaction Quantities
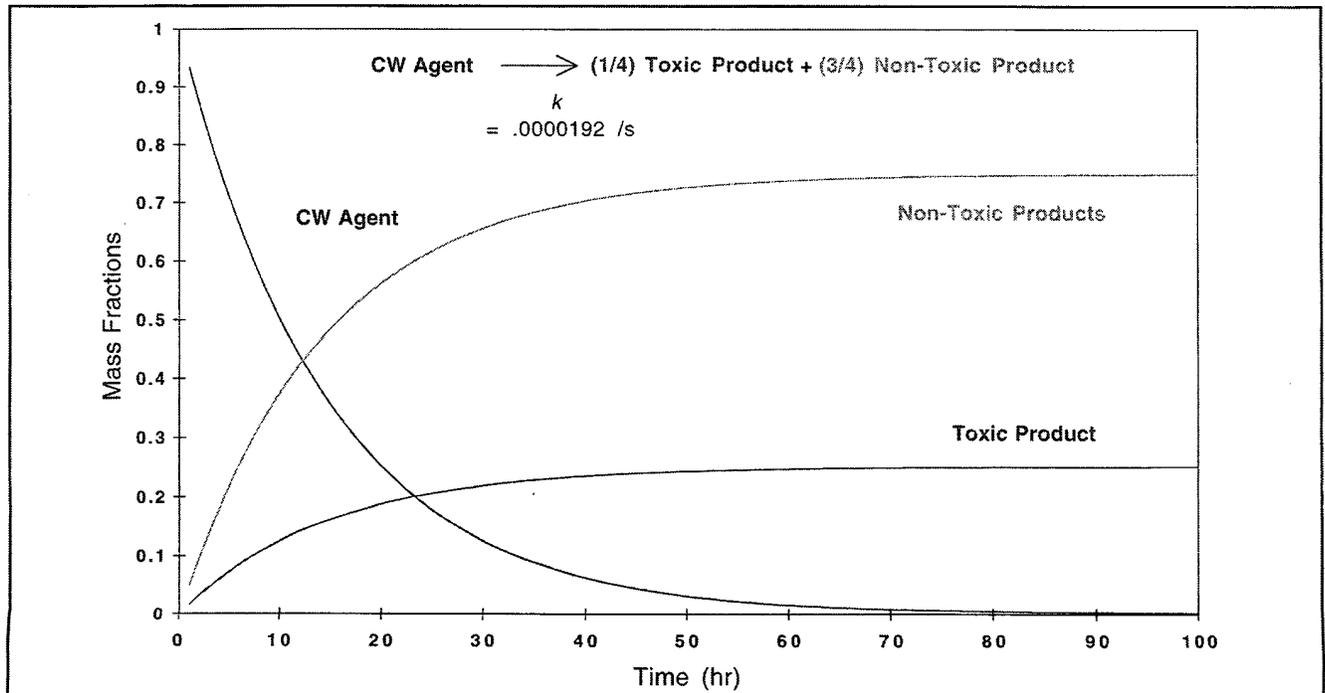
Figure 7-3: *Illustration of Agent Release Models*
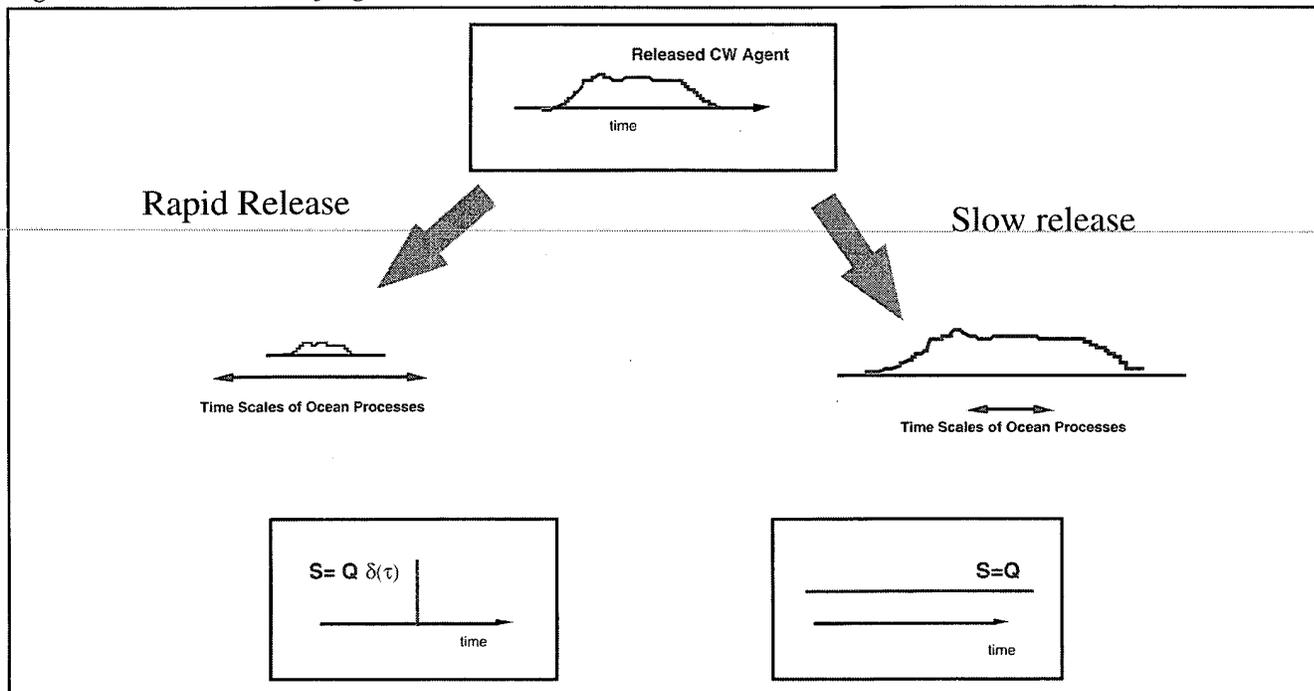
As seen in Chapter 5, the situation for mustard is somewhat special and must be considered separately to get a useful picture. It will be argued later that a useful model is one with a constant injection of dissolved mustard for an extended life, followed by a "switching off" when the lump of mustard is completely dissolved.

7.2.2 Physical Model

A wide variety of physical processes act to redistribute in space and time the CW agents that are released into the sea. At a sufficiently detailed level, a model of this redistribution should account for changes in momentum, density, temperature, and chemical composition at spatial scales corresponding to those of mixing in the benthic boundary layer, *i.e.*, centimeters. In addition to this variety of small-scale processes, various circulation processes act to redistribute momentum and density over larger scales. Development of a model accounting for the coupled hydrodynamical and chemical processes governing the evolution of CW agents and their reaction products in

the benthic boundary layer and *having the necessary spatial resolution* lies well beyond the scope of this study.

A full treatment of the problem at hand might begin with the flow fields defined throughout the water column over the region of interest; and hydrodynamic equations, incorporating the effects of stress at the seafloor interface. This stress leads to turbulence in a benthic boundary layer and to mixing. Of course, in order to know the flow fields one must begin either with assumptions about the size of the ocean region that is relevant and introduce the flow fields from the outside (*e.g.*, North Atlantic current flowing into the Barents, tidal flows, etc.), or with a general circulation model including wind driven and tidal effects. Even with the flow fields identified, the closure problem must be addressed since turbulence is normally treated statistically.

Even if one wanted to proceed with the latter approach, one would be faced with the problem that mixing in the benthic boundary layer is empirically thought to be a

process whose spatial scales are on the order of centimeters and a full numerical solution of ocean circulation at centimeter resolution remains impractical. In fact, even a regional model of circulation in the Barents Sea taking the flow fields as input from the outside, would have resolutions far too coarse to address our problem.

Another plausible approach is to rely on the averaging of turbulent effects over sufficiently large spatial scales to allow a description in terms of eddy diffusion, analogous to Fick's law for molecular diffusion, yet not averaging over scales so large that they are comparable with those of hydrolysis or advective processes. The separation of scales necessary to justify such a model would seem to be plausible in the CW problem so long as we do not ask detailed questions about the fine grained behavior of agents within the benthic boundary layer. In addition, as will be seen later, this approach produces only a parameterization which requires that the flow and the eddy diffusivity be introduced by relying on experiment and physical intuition and does not provide a self-consistent description of the governing physics.

The need for a simple model suggests that we must first attempt to determine if a *local* description will suffice, that is, requiring treatment of ocean scales only on the order of a few tens of kilometers and times on the order of hundreds of hours or less. If so, we would be done; if not, then large scale circulation, and possibly other effects, would need to be considered.

At a minimum, we should account for the process already identified, hydrolysis, as well as for the local ocean current and the turbulent mixing of agents (*i.e.*, dilution). Since the time scales of hydrolysis are exponentially shorter than the half-life of radioactive decay of even the most "worrisome" isotopes, the CW agent problem may not require the full treatment of arctic circulation and may turn out to be a local problem.

Before proceeding to deal with some level of complexity it will be worthwhile to summarize the expected behavior of agents released into the sea.

- From Chapter 5, we expect that Tabun, Sarin, and Lewisite can be released either at very slow rates for

times on the order of many hydrolysis half-lives or very abruptly in kilogram quantities.

- From Chapter 4, we expect agents Tabun, Sarin, and mustard, with half-lives measured at 40, 15.9, and 5.3 hours respectively, to effectively vanish from the ocean over a time scale on the order of a few tens of half-lives.

- From Chapter 6 which summarized levels of toxicity, one concludes that 1 kg of agent when diluted could contaminate, *at most*, the volumes of water listed in Table 7-4. These quantities could not actually be realized in practice since they would require near-instantaneous release throughout the volume.

- Based on common experience with mixing, it might be expected that dilution of a kilogram of agent to one hundred cubic meters, a factor of approximately 10^5, could take place in less than several hours and perhaps in minutes. This would be a time comparable to, or less than, the hydrolysis half-life of the agents being studied and indicates that both hydrolysis and dilution could be important factors.

- During the processes of dilution and hydrolysis, there will be transport in the prevailing current. With a current of 0.1 knot (or approximately 5 cm s^{-1}) and an effective lifetime of one hundred hours, the maximum distance that an agent could be transported before it reached a safe level would be approximately 18 km.

Table 7-4: Volumes to Specific Concentrations of 1 kg of Agent

Agent	Volume at (est) No-effects Level m³	Volume at (est) Probable Effects Level m³
GA	1 x 10⁶	1 x10⁵
GB	1 x 10⁶	1 x10⁵
H	5 x 10⁶	5 x10³
L		
Agent	5 x 10⁴	5 x10³
Arsenic	1 x 10⁴	1 x10³

By these simple arguments we are led to expect that the problem *may be local*, and that "local" will mean times shorter than a few hundred hours and distances less than a hundred kilometers. This is already important as a working hypothesis, although it will be more comforting to see it emerge from a detailed analysis so that the interplay of the processes can be understood.

The coordinate system and general depiction of the local environment to be used is shown schematically in Figure 7-4.

With the coarse-grained view of the parameterization articulated at the beginning of this subsection, the effects of mixing are described by a diffusion-like process containing as a proportionality constant, the eddy diffusivity, which must be prescribed based on empirical knowledge. With this assumption, the rate of change of concentration (coarse grained over suitable spatial scales) is given by the usual advective-diffusion equation.

$$\partial C / \partial t = S(x,y,z,t) - k\, C - \underline{v} \cdot \nabla_H C + K_H \nabla^2 C + K_v \nabla_v{}^2 C,$$

$$(7\text{-}1)$$

where the diffusivities in the horizontal and vertical directions are K_H and K_v respectively, and the current $\underline{v}$ is assumed to be in the x-y (horizontal) plane. $S(\underline{r},t)$ is the source function developed in Chapter 5 and summarized in Section 7.2.2.

It is important to appreciate that while mathematically the current, v, and the eddy diffusivity, K, appear to be independent parameters, they are connected by the underlying physics of turbulent mixing. However, since the flows are not known in our problem the diffusivities cannot be estimated and both must be treated parametrically, guided by an empirical knowledge of the upper limits on ocean currents due to circulation or tides, and by measurements of diffusivity.

This can produce no understanding of the physics of turbulent mixing, but it can produce an estimate of mean concentration as a function of space and time, which is the objective. It is not intended that calculations based on this equation should be regarded as an analysis of ocean circulation or of benthic boundary layers, only that solutions, with suitable values of the parameters, adequately describe the

Figure 7-4: Local Ocean Environment and Coordinate System

7-8
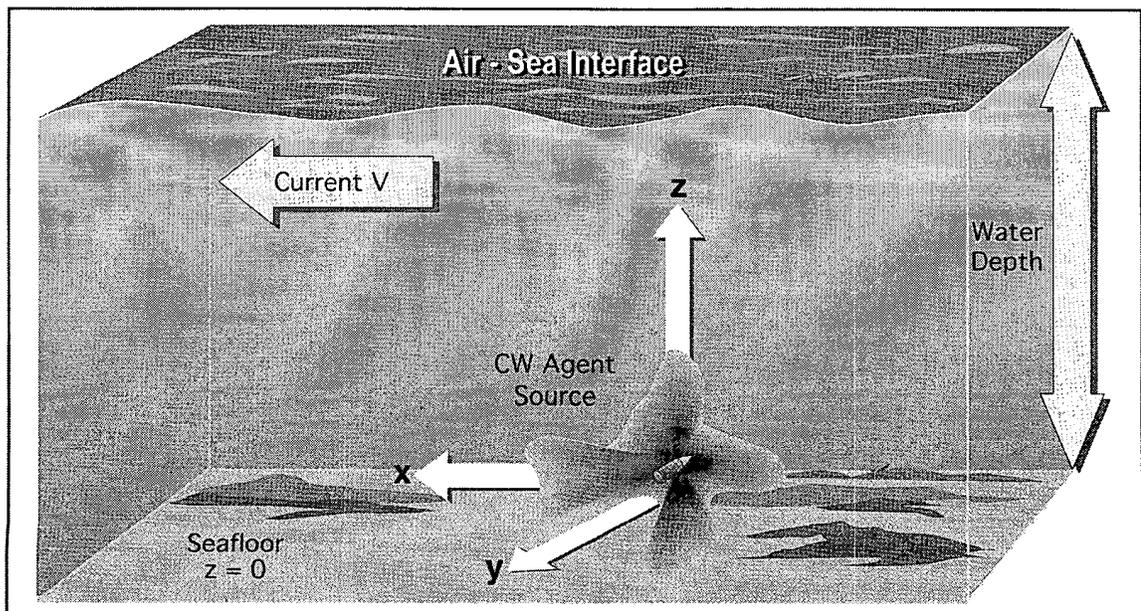
averaged behavior of the concentration of CW agents. Discussion of the use of "diffusion" models of turbulent mixing are given in references one through five.[1,2,3,4,5]

In addition to this equation, we must address what happens at the boundaries, *i.e.*, the seafloor and the sea surface. Consistent with our intention to first address the local problem, both boundaries will be taken as plane, as suggested by Figure 7-3. In the local environment changes in bathymetry will be ignored, accounting only for the mean water depth at the dump sites. Moreover, at least initially, it will be assumed that there is no flux across either boundary, that is,

$$\frac{\partial C}{\partial z} = 0 , \quad z = \{ 0 , H \} . \tag{7-2}$$

Later it may turn out to be important to address volume or boundary scavenging. This would be needed in the case of the stable arsenical reaction products for example. In the case of boundary scavenging the condition on the normal gradient at the seafloor would be modified to give $(-v_b/K_H)$ on the right side of Equation 7-2, where v_b is a speed associated with deposition (note, v_b would be negative indicating deposition into the seafloor).

7.3 AGENT RELEASE AND HYDROLYSIS

This section discusses the evolution of total mass of agent in the ocean and the concentration averaged over large plane surfaces. The reason for this initial focus is pragmatic. By dealing with these integrated quantities, Equation 7-1 will need to be solved in one or two dimensions only, thus extracting useful results with minimum complexity.

7.3.1 Total Mass of CW Agent in the Ocean

The total mass of agent in the ocean, M, is given by

$$M(t) = \int_{ocean} C(x, y, z, t) \ d^3 r. \tag{7-3}$$

Integrating Equation 7-1 over the volume using Green's theorem to obtain surface integrals from integrating the diffusivity terms and applying the boundary condition of vanishing flux across the boundaries, one obtains,

$$\frac{dM}{dt} = -k M + \int_{ocean} S(x, y, z, t) \ d^3 r = -k M + S_0(t) \tag{7-4}$$

where S_0 is the volume integral of the source function,

$$S_o(t) = \int_{ocean} S(x, y, z, t) \ d^3 r \tag{7-5}$$

The modifications to include the chemical reactions discussed in Section 7.2.1 are straightforward.

7.3.1.1 Results for Tabun and Sarin

Using the hydrolysis rates from Chapter 4 with modifications to account for HCN and using an impulsive source in Equation 7-4 results in the solutions illustrated in Figure 7-5.

A sudden release of 1 kg of Tabun would result in a decrease by six orders of magnitude, to 1 mg, in approximately 800 hours and for Sarin approximately 300 hours. Of course, over such a period of time, turbulent mixing would be expected to dominate the behavior of the concentration. We have therefore learned that for the non-persistent agents, Tabun and Sarin in particular, there is an outer bound on the direct toxicity problem of some hundreds of hours. Moreover, this bound does *not* depend on any knowledge of ocean parameters such as diffusivities, or processes such as upwelling, tidal currents, and large scale circulation. However, such a bound does *not* apply to stable toxic reaction products, such as HCN, as can be seen in Figure 7-5.

There is no reason why corrosion of the munitions could not cause highly soluble agents like Tabun and Sarin to be leaked into the sea at very slow rates as

[1] International Atomic Energy Agency, 1983, *An Oceanographic Model for the Dispersion of Wastes Disposed of in the Deep Sea*, Report No. 19.
[2] Monin, A.S. and A.M. Yaglom, 1971, *Statistical Fluid Mechanics*, Vol 1. Cambridge, MA, MIT Press.
[3] Csanady, G.T., 1973, *Turbulent Diffusion in the Environment*, D. Reidel Publishing Company, Boston, MA, Ch 5.
[4] McComb, W.D., 1990, *The Physics of Fluid Turbulence*, Oxford University Press, New York, Ch 12.
[5] Hunt, J.C.R., "Turbulent Diffusion from Sources in Complex Flows," *Ann. Rev. Fluid. Mech., 1985*, Ch 12, pp 447-485.

Figure 7-5: Hydrolysis of Tabun (GA) and Sarin (GB)
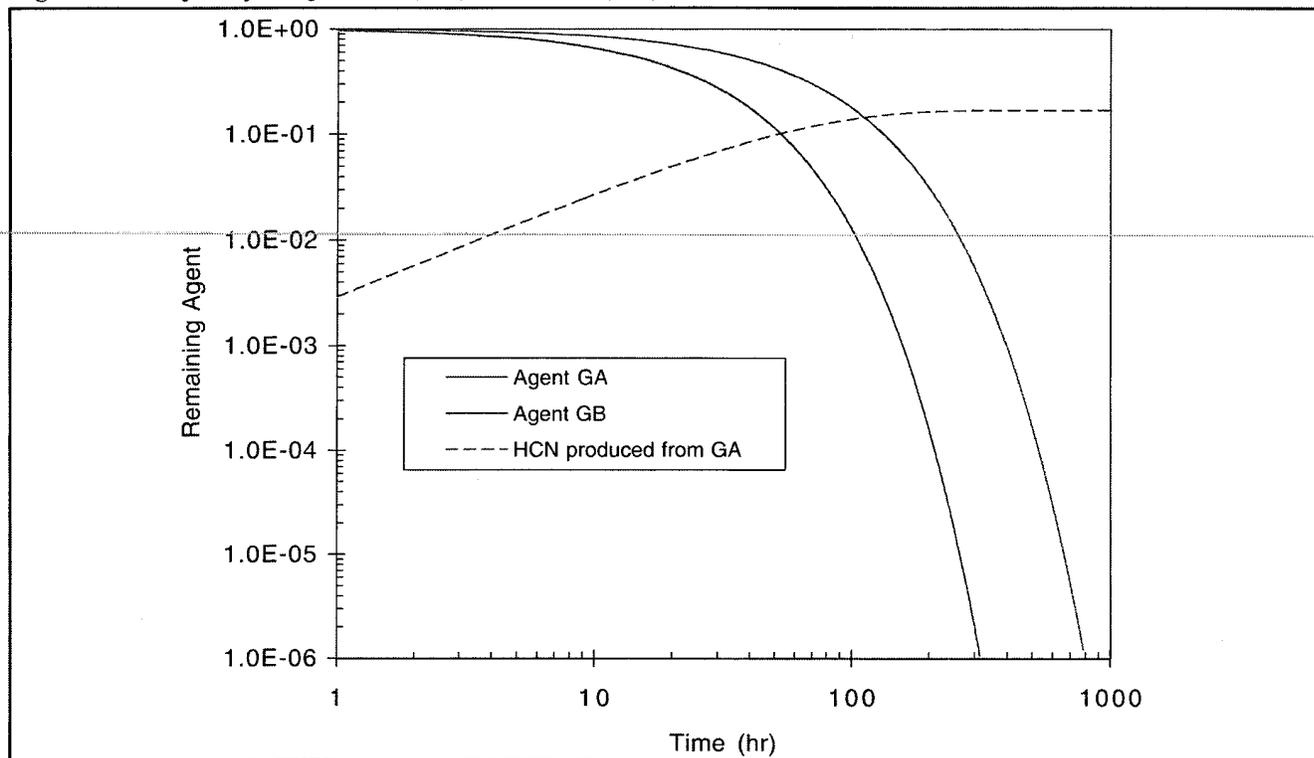
pinholes develop. Since we lacked detailed knowledge of the complex corrosion process, a parametric analysis was necessary to determine what would occur. The simplest model for such a process is a steady release with an abrupt start and cessation. That is, for time, T, S = Q/T for 0<t<T and S = 0 otherwise. The results of using this model for the cases of Tabun and Sarin are shown in Figure 7-6 for two durations, 24 hours (1 kg day⁻¹) and 240 hours (0.1 kg day⁻¹).

In all four cases, the total quantity of agent is 1 kg. The time at which the release ends, 24 and 240 hours respectively, are clearly seen as the points at which there is no further increase of agent in the water. The total mass of agent Tabun is reduced to one gram in less than 500 hours. For Sarin, the time to one gram remaining is less than 300 hours. For perspective, we note that it will be shown later that a rate appreciably less than approximately 0.1 kg day⁻¹ will result in plumes of essentially negligible dimensions.

SUMMARY OF RESULTS FOR TABUN AND SARIN

- Regardless of transport and mixing processes, an impulsive or acute release of Tabun will hydrolyze kilogram quantities down to gram quantities in less than approximately 600 hours. This time period represents the upper bound on the temporal scale of toxicity of Tabun following a sudden release into cold seawater and not one that is sensitive to other uncertainties.

- The situation for Sarin is similar except the upper bound is approximately 300 hours.

- Either agent could be released at very slow rates through pinhole leaks in munitions casings. The time scale of such a release would be governed by the release time constant.

Figure 7-6: Tabun (GA)/Sarin (GB) Hydrolysis for Various Release Rates
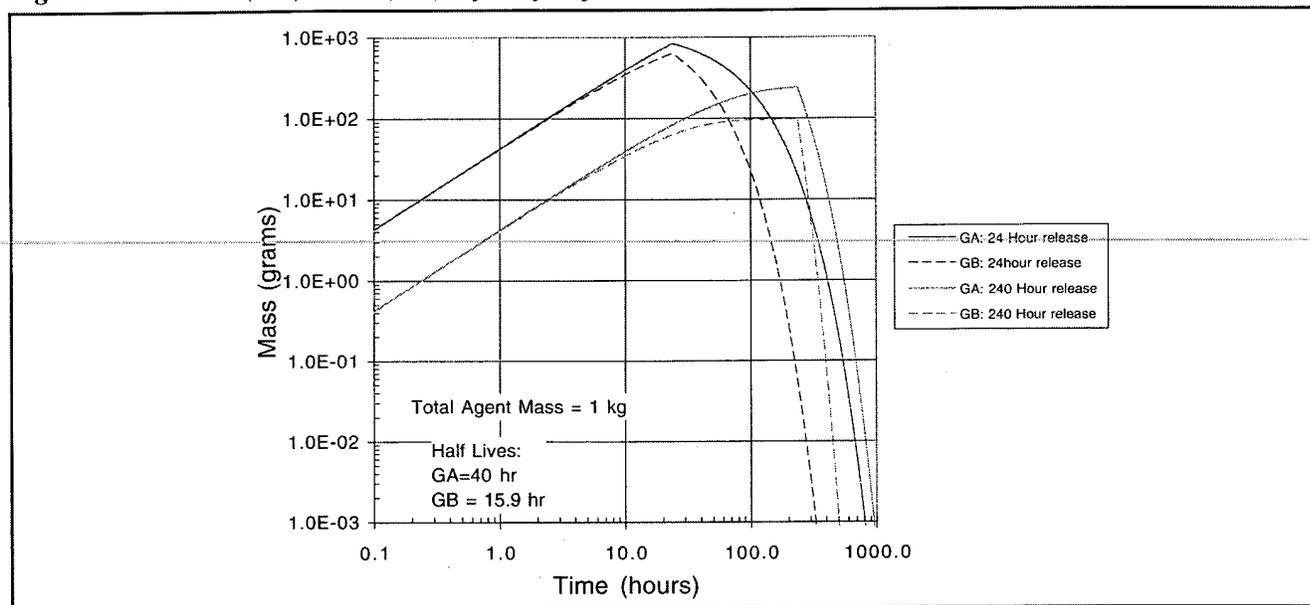
7.3.1.2 Results for Lewisite

Since the reaction products of Lewisite hydrolysis include stable and nearly stable toxic compounds, we cannot expect to find so convenient an upper bound on the time scale of the problem, at least not until we include the effects of mixing. For present purposes it will suffice to examine the hydrolysis of Lewisite and confirm what is to be expected, *i.e.*, rapid conversion into arsenicals.

In Chapter 4, it was shown that the hydrolysis of Lewisite takes place in two stages. The first stage is a very rapid reaction resulting in the quasi-stable (2-chloroethenyl)arsonous acid, proceeding on a time scale of seconds and producing approximately 822 grams per 1 kg of Lewisite. The second reaction, resulting in inorganic arsenic, takes place on a time scale of months and produces 361 grams of arsenic per 1 kg of Lewisite. As argued in Chapter 6, (2-chloroethenyl)arsonous acid is at least four times more toxic than inorganic arsenic and with its long half-life is a very serious environmental concern.

Figure 7-7 shows the results of this model with Lewisite being released at a constant rate of 1 kg day⁻¹ for a period

of twenty-four hours a total mass of 1 kg. The half-life of (2-chloroethenyl)arsonous acid is estimated to be two months for purposes of this illustration. The most important conclusion is that over the period encompassing the times of interest in our modeling, the predominant toxic agent present is (2-chloroethenyl)arsonous acid, not Lewisite and not inorganic arsenic.

Although there is nothing very significant about twenty-four hours, such a release rate is probably much higher than corrosive disintegration of a shell casing would produce. On the other hand, the basic conclusions would be unchanged as long as the release occurred on a short time scale compared to the second stage reaction of two months. This is illustrated in Figure 7-8, which shows the same calculations as in Figure 7-7 except that its release rate has been reduced by a factor of ten and the duration extended by the same factor.

Over the time scales in which we expect to be interested (minutes to tens of hours) it will be (2-chloroethenyl)arsonous acid that will be present in quantity, not Lewisite.

7-11

Figure 7-7: Hydrolysis of 1 kg of Lewisite (L) Released at 1 kg day⁻¹
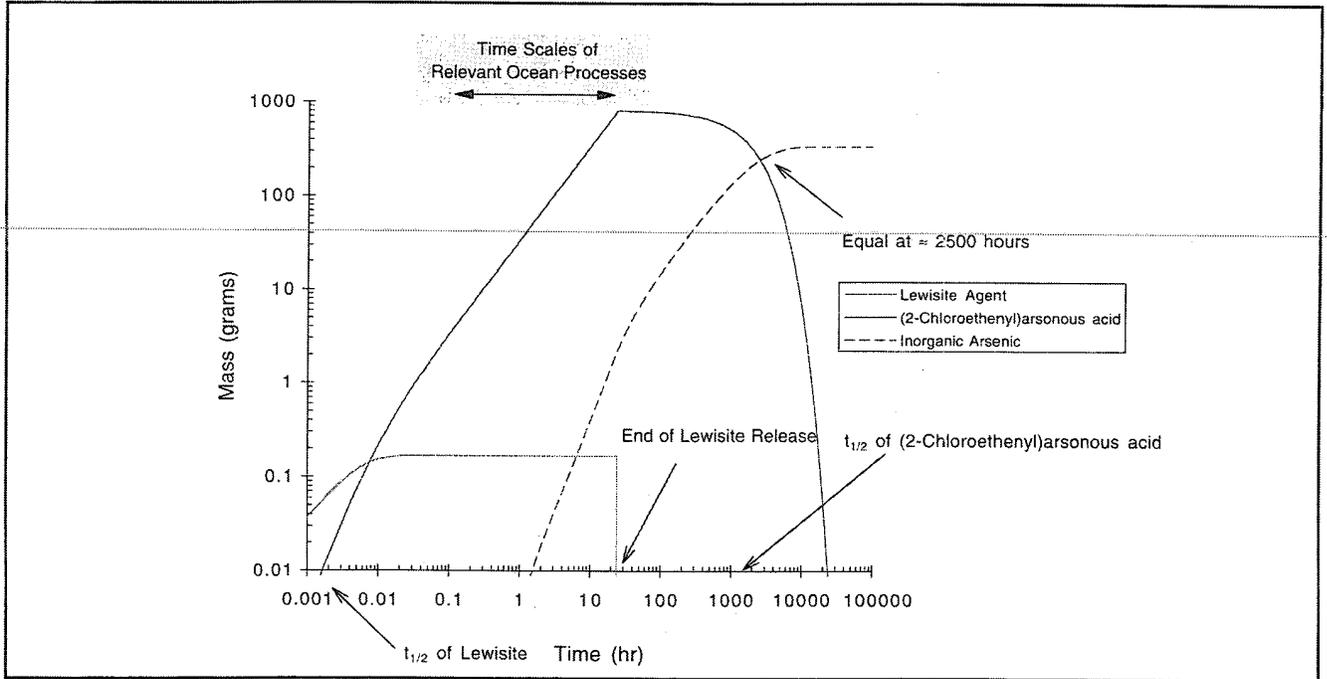
Figure 7-8: Hydrolysis of 1 kg of Lewisite (L) Released at 0.1 kg Day⁻¹
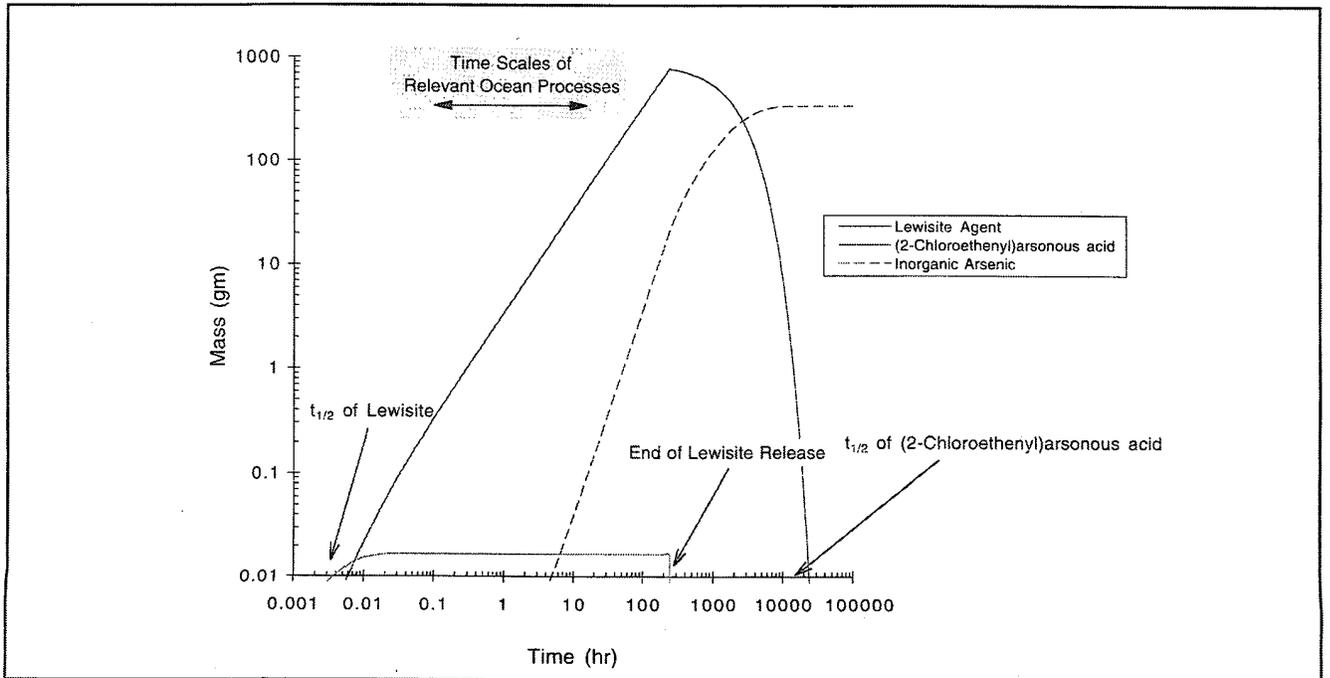
SUMMARY OF RESULTS FOR LEWISITE

- Once released, hydrolysis will rapidly convert Lewisite agent to highly toxic quasi stable (2-chloroethenyl)arsonous acid.

- For purposes of this assessment, the direct effects of Lewisite can be ignored since it will exist in the environment for mere seconds, a time scale much shorter than those associated with advection and mixing much less biological processes. This, in turn, means that the agent will exist only in the immediate vicinity of leaking munitions.

- The major toxic reaction products, (2-chloroethenyl)arsonous acid and inorganic arsenic, appear in respective quantities of approximately eighty percent and thirty percent of the mass of Lewisite. They persist in the environment for long periods and are redistributed by advection and mixing.

- For the time scales of interest in the ocean problem, the predominant toxic substance will be (2-chloroethenyl)arsonous acid, which will persist for several months before it is converted to inorganic arsenic, which has lower toxicity.

- Should corrosive disintegration of the munition result in release through small pinholes, release of Lewisite into the ocean could occur on time scales of days, even weeks or months. In such a case, conversion to (2-chloroethenyl)arsonous acid and then to inorganic arsenic would occur at a rate determined by the release rate. The total quantities present at any time would be determined by both hydrolysis of organic arsenic and the release rates.

7.3.1.3 Results for Mustard

Because of its very slow dissolution rate and its low solubility, the appearance of mustard agent in seawater is governed by its dissolution rate, while its disappearance is governed by its hydrolysis rate.

Since dissolution depends upon the surface area exposed to seawater and also to its shape, there cannot be a single definitive answer to the fate of a given amount of mustard once it has been released from its casing by corrosion. However, as we saw in Chapter 5, we can bound the problem by considering two plausible situations, a spherical clump and a thin pancake. The former is an upper bound since a sphere is the shape having least surface area for a given volume. As the Baltic experience shows, mustard not specifically modified for cold weather operations tends to solidify in cold seawater. However, since there are reasons to believe that the Soviet military requirements included consideration of cold weather operations, it is likely that the mustard dumped in the arctic seas might well resemble highly viscous fluids. Therefore, it seems reasonable and informative to continue to consider dissolution of both spherical and pancake shapes.

Figure 7-9 shows the results of both shapes for the initial release of 1 kg of mustard. The lifetimes of the shapes are 5,900 hours for the sphere and 3,500 hours for the pancake. For contrast with the sphere and to work toward what seemed physically plausible as a minimum bound, this model has the pancake spread very thin, being 27 cm in diameter and only 1.4 cm thick.

The sphere dissolves more slowly than the pancake, and has a longer lifetime. Since it has the same initial mass, a lower level of dissolved mustard is injected into the sea until times near the end of the life of the pancake. Mustard in solution, as represented by the dotted curves rises steadily from 0 initially, to peak near the respective lifetimes. Although it cannot be seen on this figure because of the scale, mustard persists for a short period after mustard has dissolved until hydrolysis can eliminate it. This can be seen more readily in Figure 7-10 which shows the same calculations on an expanded scale.

Figure 7-9: Dissolution and Hydrolysis of 1 kg of Mustard (H)
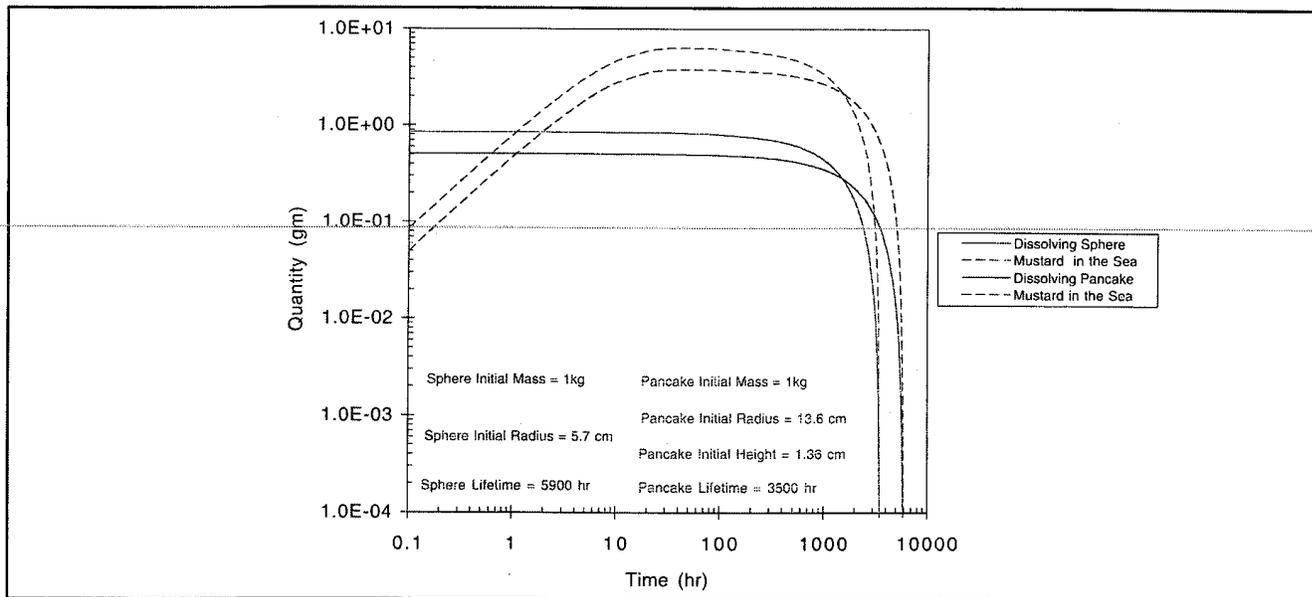
Figure 7-10: Dissolution and Hydrolysis Near the End of Life
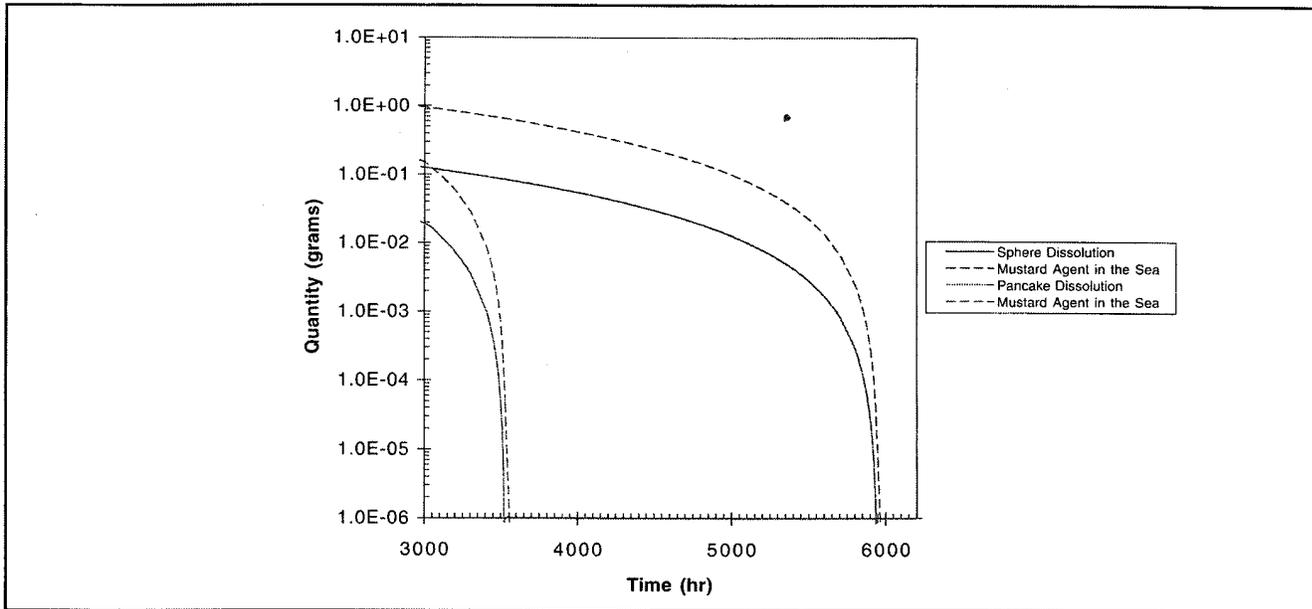
It can be seen that in accord with expectations, small amounts of dissolved mustard persist for several half-lives once the last of the liquid/solid clump has disappeared.

The most important conclusions that can be drawn from these calculations are as follows:

7-14

SUMMARY OF RESULTS FOR MUSTARD

- Following abrupt and complete disintegration of a munition casing by corrosion, the appearance of dissolved mustard agent in the sea is determined primarily by the shape of the clump of mustard, with the total lifetime for a 1 kg quantity being approximately 150 to 250 days.

- Mustard clumps originating in bombs containing on the order of 100 kg could persist for periods up to several years before being completely dissolved (see Chapter 5). The rate of introduction of dissolved mustard into the sea would be larger for such large clumps according to the ratio of surface areas, which is approximately equal to mass$^{2/3}$.

- After the last of the mustard charge is dissolved, the remaining agent in solution hydrolyzes rapidly and within five to ten hydrolysis lifetimes that is, approximately twenty-five to fifty hours and can be regarded as completely eliminated from the environment.

- Because of the relatively slow dissolution rate and rapid hydrolysis rate, the amount of mustard agent in the water is very low, with the maximum being less than ten grams from the notional 1 kg quantity.

7.4 SPATIAL AND TEMPORAL SCALES

This section addresses the physical processes of advection and mixing. In order to extract the important results easily, we will examine a one-dimensional problem. However, rather than artificially abstracting the three-dimensional problem to a single dimension, spatial integrations will be introduced obtaining "averaged" concentrations which obey a transport equation having one spatial dimension. This approach will not allow us to obtain estimates for the spatial and temporal changes in concentration or for boundaries on toxic levels. It will allow us to obtain estimates of the major spatial and temporal scales governing the problem.

Specifically, by integrating over two spatial dimensions and then examining the concentration in one spatial and one time dimension, it will be possible to understand the general character of more general four-dimensional solutions. The quantity of most interest is obtained by integrating over x and y,

$$C_{xy}(z, t) = \iint_A C(x, y, z, t) \, dx \, dy \qquad (7\text{-}6)$$

where the integrals are taken over the entire plane. For convenience, we will refer to quantities as "averaged" concentration, although the factor of inverse area required to produce an average is missing and the units are mass/length. In fact, this quantity is mass density, the mass of agent per unit length in the vertical direction. When integrated over the remaining spatial coordinate this quantity yields the total mass treated in Section 7.3.

When introduced in Equation 7-1, and using Green's theorem to rewrite the area integral of a divergence, one obtains for the following C_{xy}:

$$\partial C_{xy}/\partial t = S_1(z, t) + K_V \, \partial^2 C_{xy}/\partial^2 z - k\, C_{xy} - \oint dl \cdot \left[\underline{v}\, C + K_H \underline{\nabla} \right] \qquad (7\text{-}7)$$

where the line integral is around the boundaries of the x-y plane and therefore vanishes. The result becomes:

$$\partial C_{xy}/\partial t = S_1(z, t) + K_V \, \partial^2 C_{xy}/\partial z^2 - k\, C_{xy} \qquad (7\text{-}8)$$

The function S_1 is the integral of S over x-y. The quantity C_{xy} obeys the spatial boundary conditions associated with those of the concentration, *i.e.*, normal flux vanishes at the boundaries. In the remainder of this section, Equation 7-8 will be solved for two cases, a steady state event and an impulsive event.

7.4.1 Steady State Events

Using $S = Q \, \delta(x) \, \delta(y) \, \delta(z)$ and setting $\partial C/\partial t = 0$ in any of these equations, the equation for a steady state event will be obtained.

The equation for vertical mass density, together with the boundary conditions of $\partial C_{xy}/\partial z = 0$ at $z = \{o, H\}$ is:

$$K_v \frac{\partial^2 C_{xy}}{\partial z^2} - k C_{xy} = Q \, \delta(z) \qquad (7\text{-}9)$$

and can be solved by first moving the source from z=0 to $z=z_0$ and later letting $z_0=0$. The solution for $z > z_0$, denoted $C_{xy}^{>}$ is found to be:

$$C^{>}_{xy}(z) = [QL_v / K_v]\partial \Delta^{-1} \cosh [(z - H)/L_v]\cosh [z_0/L_v] \qquad (7\text{-}10)$$

where,

$$\Delta = \cosh [(z_0 - H)/L_v] \sinh[z/L_{v_0}] - \sinh[(z_0 - H)/L_v] \cosh [z_0/L_v]$$

and $L_v = \sqrt{K_v / k}$. The parameter L_v has the dimensions of length and represents the vertical mixing distance, which is the square of the vertical diffussivity measured on a hydrolysis time scale.

The solution for $z < z_0$, denoted $C_{xy}^{<}$, is found to be:

$$C^{<}_{xy} = [QL_v / K_v]\partial \Delta^{-1} \cosh [z /L_v] \cosh [(z_0 - H)/L_v] \qquad (7\text{-}11)$$

Now setting $z_0 = 0$, we have (only the first solution $C_{xy}^{>}$ is interesting now),

$$C_{xy}(z) = \left[Q /\sqrt{kK_v}\right] \cosh [(z\text{-}H)/L_v] /\sinh [H/L_v] \qquad (7\text{-}12)$$

The most interesting result that is immediately obtainable from Equation 7-12 is the ratio of the concentration at the sea surface, z=H and the seafloor, z=0. This is found to be:

$$R = C_{xy} (\text{seafloor}) / C_{xy} (\text{surface}) = \cosh (H/L_v) \qquad (7\text{-}13)$$

The values of R in relation to several values of K_H are shown in Table 7-5. The water depth of 30 m is the shallowest depth at any of the dump sites. Provided that $K_v < 0.001$ m^2 s^{-1}, there will be effectively no agent present at or near the sea surface, in water depths greater than or equal to 30 m. In other words, the CW agent extends above the seafloor in appreciable quantities only to a height of a few vertical mixing lengths. Moreover, in such circumstances one may ignore the sea surface boundary condition and treat the problem as a half-space, thus simplifying future results.

Vertical diffusivities are not very well-established, however, there are some relevant published values cited as high as 3×10^{-4} on the Yermak Plateau.[6] Consequently, 0.001 m^{2}s^{-1} may be taken as an upper bound for our purposes.

In any case, it is clear from Table 7-5 that unless Kv is greater than 0.001 m^{2}s^{-1}, there will not be appreciable quantities near the sea surface. This is illustrated in Figure 7-11 which depicts C_{xy} (z) as a function of

Table 7-5: Ratios of Seafloor/Sea Surface Concentrations C_{xy}

Vertical Diffusivity K_v (m^{2}s^{-1})	R for GA	R for GB	R for H
0.0001	3.4×10^2	1.6×10^4	2.3×10^7
0.001	4.0	1.4×10^1	1.5×10^2
0.01	0.7	1.6	3.1
Vertical Mixing Length m (L_v=0.001)	14.5	9.1	5.3

[6]L. Padman. "Small Scale Physical Processes in the Arctic Ocean," in *Arctic Oceanography: Marginal Ice Zones and Continental Shelves*, AGU, 1995.

Figure 7-11: Dependence of C_{xy} (z) on Height Above the Seafloor
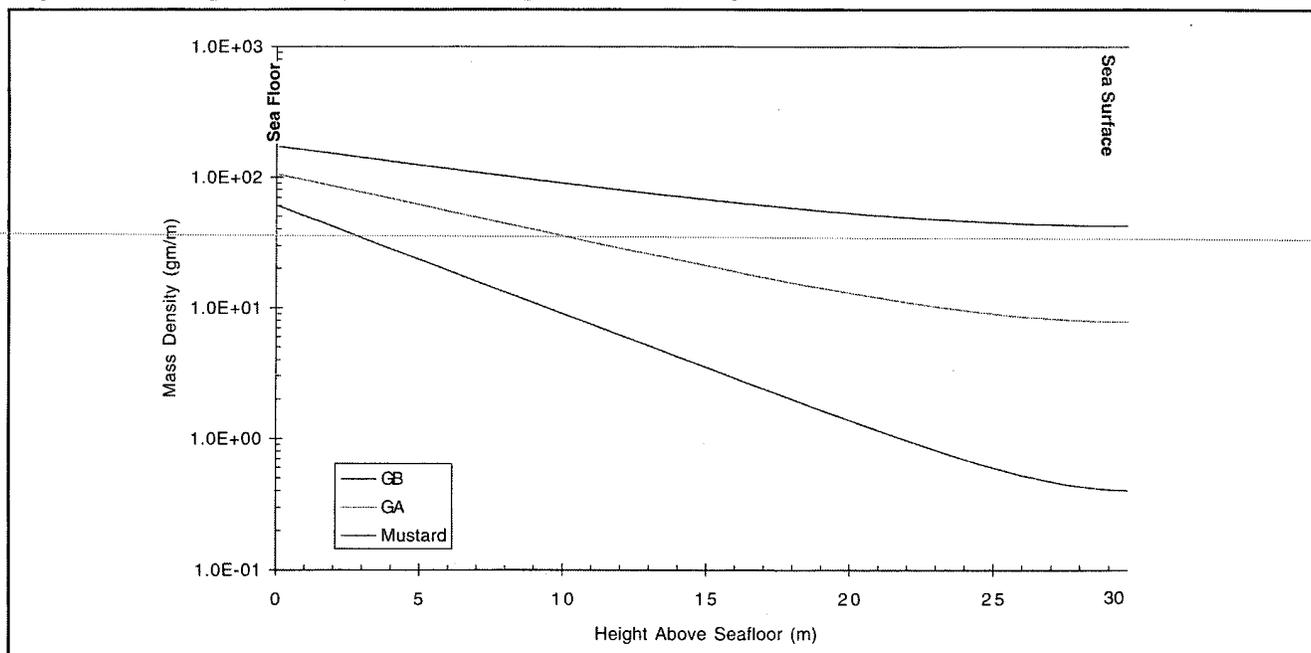
height above the seafloor for a steady injection of 0.01157 gram second^{-1} (1 kg day^{-1}) in the minimum water depth of 30 m.

The situation for Lewisite is quite different. The hydrolysis rate for the agent itself is so rapid that there could be no appreciable vertical mixing. Of course, a steady state solution itself would make no sense for the Lewisite agent. On the other hand, the principal reaction product, (2 chloroethenyl)arsonous acid, having a half-life of approximately two months, certainly could establish a steady state if slowly released. Since for this compound L_V equals approximately 87 m, it would mix upward through the entire water column even at significant water depths. Long before mixing could occur in the vertical over several factors of L_V, we expect to find that mixing in the horizontal would have resulted in quantities diminished to well below safety thresholds.

In this section we have considered the linear mass density produced by integrating over the x-y plane. If one were to consider the corresponding integration over the other pairs of spatial coordinates, (x,z) and (y,z), equations analogous to Equation 7-8 would be obtained and solutions would contain the horizontal counterpart to the vertical mixing length, $L_H = \sqrt{K_H / k}$. As before, the parameter L_H has the dimension of length and represents the horizontal mixing distance, which is the square of the horizontal diffussivity measured on a hydrolysis time scale.

There are several important conclusions that can be drawn even from this simple analysis as follows:

SUMMARY

- For a steady state source, the linear mass densities over a horizontal plane are characterized by the following three exponential decreases:

  (a) Above the seafloor with a length scale of $L_v = \sqrt{K_v / k}$;

  (b) Across the ocean current with a length scale of $L_H = \sqrt{K_H / k}$;

  (c) Along with the current, v, with a length scale $= L_H \sigma$, where σ is the dimensionless current $\sigma = v / \sqrt{K_H / k}$.

- Values of these quantities defining the critical spatial scales are tabulated below:

Quantity	Tabun	Sarin	Mustard	Lewisite Agent	Arsenic
L_H (m)	46	29	17	0.7	274
L_v (m)	14.5	9.1	5.3	0.2	87

- Interaction of CW agents released on the seafloor in the locations of interest is not expected to result in significant quantities appearing near the sea surface.

- The primary exception to this could be a large steady state source of Lewisite generating quasi-stable organic arsenic which has the potential for vertical mixing to the surface for shallow water depths such as at Site 134 in the southern Barents Sea, which has a depth of approximately 30 to 60 m.

7.5 TOXIC LEVELS FROM AN IMPULSIVE (ACUTE) RELEASE

In order to gain a simple understanding of some of the general properties of the solutions, only an integrated quantity, linear mass density, has been examined thus far. However, before biological impacts can be assessed, it will be necessary to have actual concentrations and this requires addressing the three-dimensional problem and solving Equation 7-1. This will be done generically for the two classes of sources being considered, impulsive and steady state, followed by numerical calculations for the various CW agents.

7.5.1 Generic Results

For an impulsive source, $S = Q\ \delta(t)\ \delta(x)\ \delta(y)\ \delta(z)$, where Q is the total mass of agent injected. The solution which is in a half-space ($z \geq 0$), with the boundary condition of zero flux across the seafloor at $z=0$, is found to be:

$$C(x, y, z, t) = \left[\frac{Q}{4(\pi t)^{3/2}\ K_H \sqrt{K_v}} \right] e^{-kt}\ e^{-\left[\left(\frac{(x-vt)^2}{4tK_H} \right) + \left(\frac{y^2}{4tK_H} \right) + \left(\frac{z^2}{4tK_v} \right) \right]}$$

(7-14)

This solution, when integrated over any two of the spatial coordinates, reproduces the results of Section 7.4 and, when integrated over all three spatial coordinates, gives the total mass of agent remaining in the ocean, $M = Q\ e^{-kt} = M_o\ e^{-kt}$.

For simplicity here, the previous results, showing at water depths of interest that there is no appreciable concentration reaching the sea surface, have been used to eliminate the upper boundary condition, justifying the applicability of this half-space solution.

It is clear that this solution describes a pulse, singular at t=0, moving along the x-axis at speed v with its amplitude decreasing away from the peak at {vt,0,0} according to the Gaussian functions. The role of the various constants can be appreciated more easily by introducing the following scaled dimensionless coordinates,

$$\xi = x/L_H, \; \psi = y/L_H, \; \zeta = z/L_V, \; \tau = kt, \sigma = v/\sqrt{K_H k}$$

(7-15)

and the concentration becomes:

$$C = \left[Q \middle/ 4L_H^2 L_v \pi^{3/2} \tau^{3/2} \right] e^{-\tau} e^{-\left[\left(\frac{(\xi-\sigma\tau)^2}{4\tau} \right) + \left(\frac{\psi^2}{4\tau} \right) + \left(\frac{\zeta^2}{4\tau} \right) \right]}$$

(7-16)

At these coordinates, the peak at {στ,0,0} has a width in all three dimensions of $(2\tau)^{1/2}$ and an amplitude factor of mass (Q) per the natural volume ($L^2_H L_V$) and a hydrolysis decay rate of unity. In rewriting Equation 7-16,

$$C = C_1 F(\xi, \psi, \zeta, \sigma) \; , \; C_1 = Q \middle/ L_H^2 L_v = M_0 \middle/ L_H^2 L_v$$

(7-17)

with C_1 being the total mass remaining, divided by the volume defined by the natural units $L_H \times L_H \times L_V$ and with F_1 involving only non-dimensional coordinates and the non-dimensional parameter σ,

$$F_1(\xi, \psi, \zeta, \sigma) = (4^{-1} \pi^{-3/2} \tau^{-3/2}) e^{-\tau} e^{-\left[\left(\frac{(\xi-\sigma\tau)^2}{4\tau} \right) + \left(\frac{\psi^2}{4\tau} \right) + \left(\frac{\zeta^2}{4\tau} \right) \right]}$$

(7-18)

it is seen that apart from the factor C_0, the concentration C when expressed in terms of {ξ,ψ,ζ} and with the scaled speed σ, is "universal," i.e., it is the same for all values of diffusivity and hydrolysis rates. The contours of constant concentration are seen to be circles, centered at {ξ=στ,ψ=0, ζ=0}. A schematic illustration of the general appearance of such a cloud of CW agent is shown in Figure 7-12, which depicts a growing cloud moving with the current v.

The magnitude of the spatial distribution of concentration in three dimensions can be seen by integrating C over a cube of size 1x1x1 in these scaled coordinates, that is, over L_H x L_H x L_V in x,y,z coordinates. The result is the mass $M_B(t)$ contained within a box having the natural volume $V = L_H^2 L_V$,

Figure 7-12: Schematic Illustration of Acutely Released CW Agent
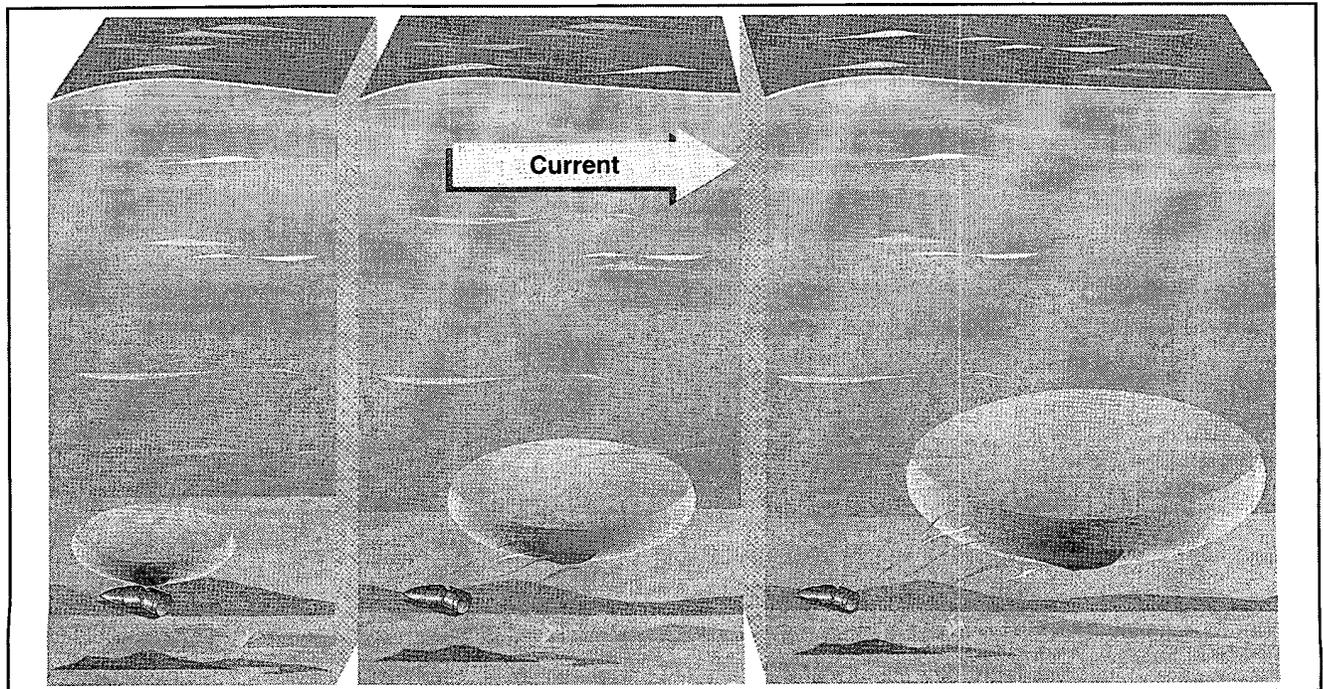
given by Equation 7-19.

$$M_B(t) = Q e^{-\nu t} erf^3(\tau^{-1/2}/2) = M_T(t) erf^3(\tau^{-1/2}/2)$$

$$(7-19)$$

where $erf(\bullet)$ is the usual error function, becoming 1 as $\tau \to 0$ and 0 as $\tau \to \infty$.

Figure 7-13 shows M_B/M_T vs. τ for three box volumes $L^2_H Lv$, $8L^2_H Lv$, and $64L^2_H Lv$. The conclusion to be drawn is that at times of interest, say $t < 10\ t_{1/2}$, almost all of the remaining mass from an impulsive injection of CW agent will be contained within a box whose dimensions are several multiples of the mixing lengths.

7.5.2 Acute Release of Specific CW Agents

If the release rate is much faster than the other relevant processes of hydrolysis, diffusion, and advection, then the release can be adequately modeled as an impulsive event, a delta function in time. Since we are still considering release from a single munition, the spatial distribution of the source will again be a delta function. An impulsive release generates a "fuzzy ball" of contamination, moving with the current and becoming less toxic with time due to the twin effects of hydrolysis and dilution. As noted in Section 7.5.1, the contours of constant concentration, in any plane, for an impulsive source are circles in scaled coordinates and circles or ellipses in x, y and z coordinates. According to Equation 7-14, the shape of the three-dimensional surface C(x,y,z,t) is an oblate spheroid bisected by the seafloor (z=0).

The radius of the iso-concentration contours in the x-y plane can be written as

$$R^2(t) = -4L^2_H \tau\ Ln\left[4\pi^{3/2}\ (C/C_1) e^\tau\ \tau^{3/2}\right]$$

$$(7-20)$$

Figure 7-13: Fraction of Agent Mass Contained in a Box of Volume $xL_H L_H L_V$

7-20
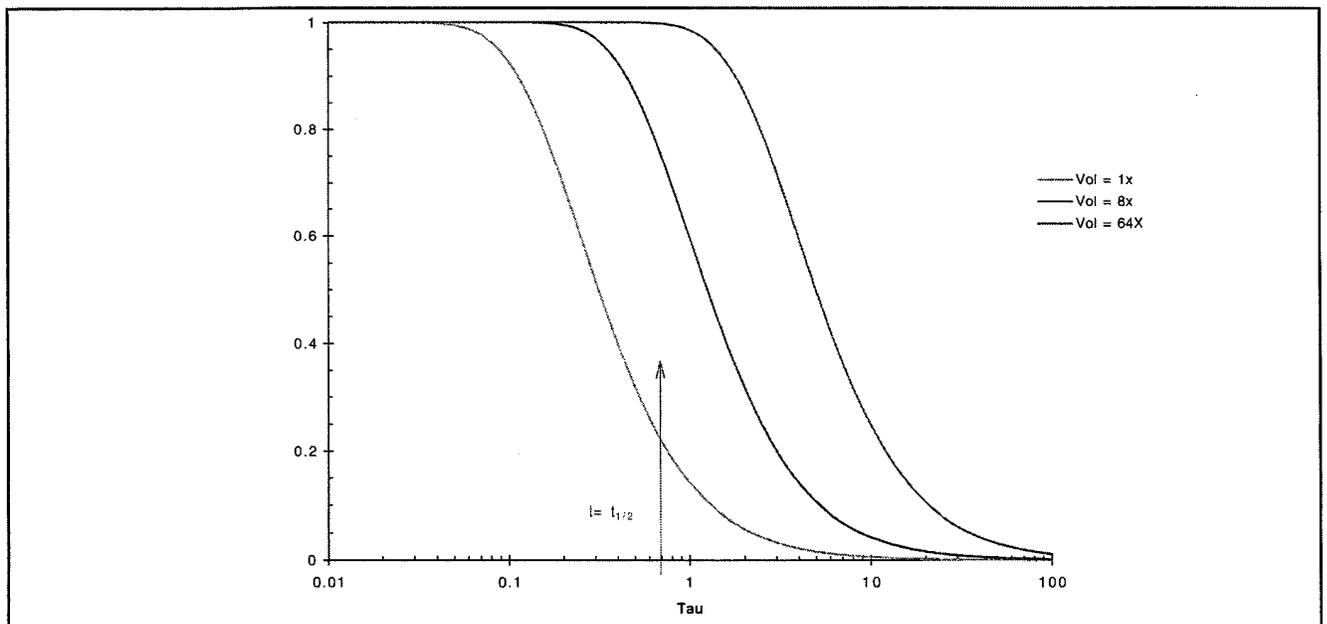
where C_1 is defined by Equation 7-20 and C is the fixed concentration of interest. The maximum height or the semi-minor axis of the truncated oblate spheroid that a specific concentration surface reaches above the seafloor is

$$h(t) = R(t) \sqrt{K_V/K_H} \qquad (7\text{-}21)$$

Figure 7-14 shows the radii of concentration on the seafloor as a function of time for the case of a sudden release of 1 kg of Tabun.

The maximum radius and associate times for these three cases are tabulated in Table 7-6 for convenience.

The general shape of these curves can be understood as primarily the result of dilution through the turbulent mixing process being modeled here in a coarse grained

sense. Initially, the point source has no radius at any finite concentration, so an increase in R is all that can happen. However, as dilution proceeds, abetted by some hydrolysis, concentrations drop. The half-life of Tabun is forty hours by which time a concentration of 0.01, for example, has vanished entirely in approximately thirteen hours, thus showing that the effects seen are primarily due to dilution. This conclusion is not general however, since if enough agent is injected initially, some will survive at any given concentration until the passage of time allows hydrolysis to become effective.

For the values of vertical and horizontal diffusivities used here (0.001 m^2s^{-1} and 0.01 m^2s^{-1}), the maximum height above the seafloor at the three concentrations in Figure 7-15 is, by Equation 7-17, 0.316 R(t) or 22 m for C=0.001 mg L^{-1}. This is consistent with the results in Section 7.3, where the solution for linear

Figure 7-14: Radius of Constant Concentration on the Seafloor for Tabun (GA)
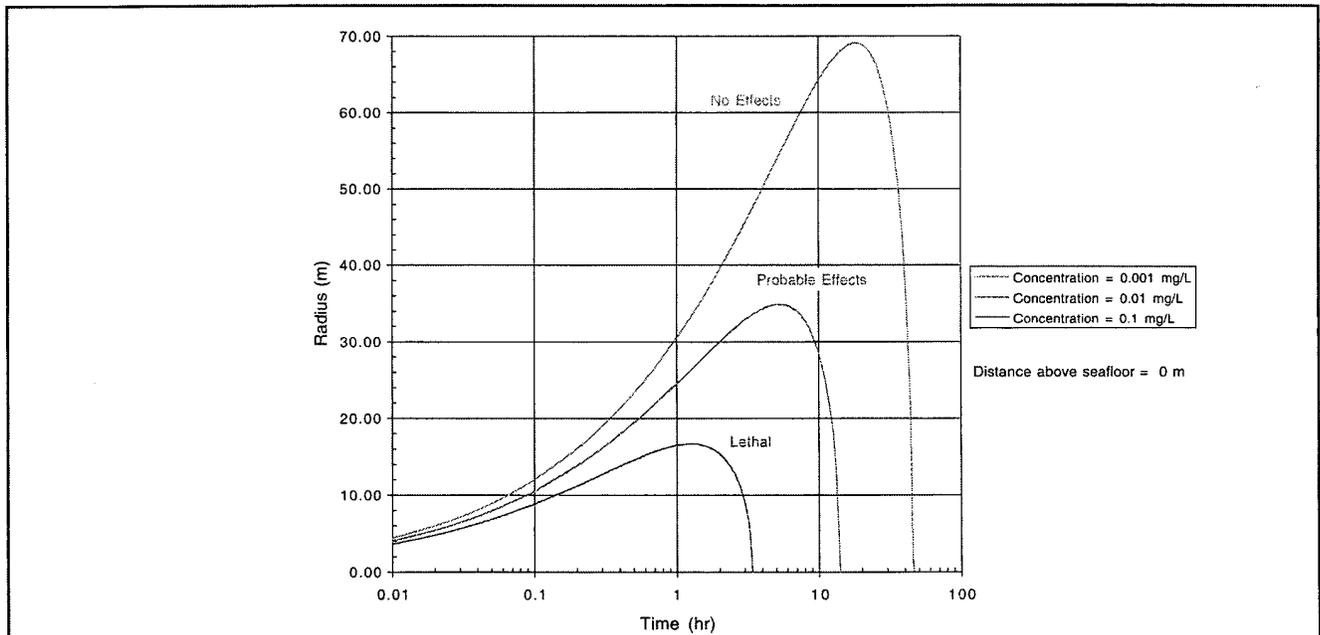
Table 7-6: Maximum Radii and Associated Times for 1 kg of Tabun (GA)

Concentration of GA	0.001 mg L^{-1}	0.01 mg L^{-1}	0.1 mg L^{-1}
Maximum Radius (m)	69	35	16.6
Time at Maximum (hr)	18	5.3	1.2

7-21

mass densities incorporating the sea surface boundary condition was used to argue that this boundary condition was irrelevant. The additional quantities of interest are the enclosed volume, $V=(2/3)\pi R^3(K_V/K_H)^{1/2}$ and the area on the seafloor ($A=\pi R^2$) of the oblate spheroid.

Figure 7-15 shows the associated volume of the oblate spheroid defined by the same three levels of concentration for the case of an acute release of 1 kg of Tabun.

For the case of release of 1 kg of Tabun from a single munition, these curves represent a metric that is rather close to what is needed to assess biological implications, the volume of water affected. The effects of the current in transporting this contaminated volume

are not accounted for in Figure 7-15, in the sense that this volume "sweeps out" water along the direction of the current moving a distance vt in time t.

Before further discussing this phenomenon, it will be useful to summarize the instantaneous volumes for all three agents that can lead to an impulsive release of Tabun, Sarin, and arsenic from Lewisite. Figure 7-16 shows the corresponding curves for all three agents at the concentrations corresponding to non-toxic and toxic levels. In the case of 1 kg of Lewisite, the initial mass of arsenic is 361 grams and the toxicity levels shown are those associated with arsenic.

The maximum volumes, areas on the seafloor, and associated times are summarized in Table 7-7.

Figure 7-15: Instantaneous Volumes for Three Concentrations of Tabun (GA)
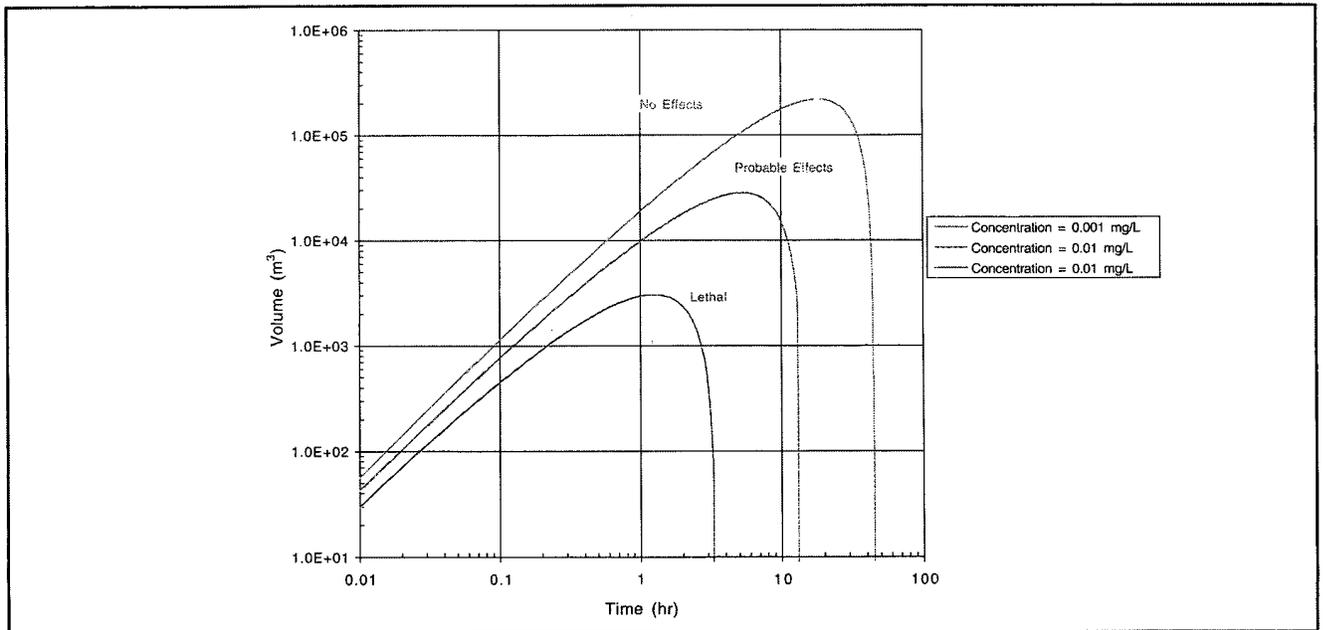
Figure 7-16: Instantaneous Volumes for Release of 1 kg of Three Agents
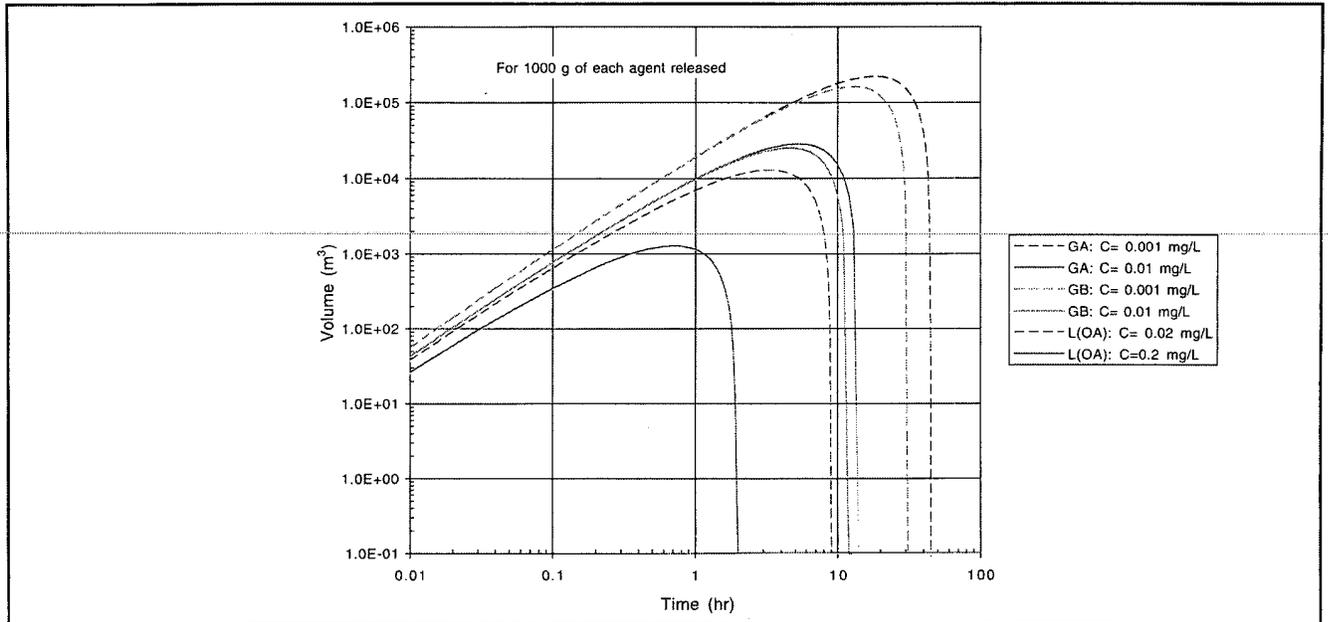
Table 7-7: Maximum Instantaneous Volumes and Associated Times
(1 kg of agent released)

Agent/Concentration	Maximum Volume (m³)	Maximum Area on Seafloor m²	Time at Maximum (hr)
GA			
Probable Effects	2.8×10^4	9.6×10^2	4.4
No Effects	2.2×10^5	1.5×10^4	12
GB			
Probable Effects	2.5×10^4	3.5×10^3	4.6
No Effects	1.6×10^5	1.2×10^4	13
L			
Probable Effects	1.3×10^2	475	0.7
No Effects	1.3×10^3	2120	3.3

In addition to these areas and times, we need to account for the advection of the mass of toxic water. This is accounted for in Equation 7-16, but the areas and volumes discussed above were instantaneous quantities, i.e., time t=x/v. If we are entitled to argue that the important quantity for assessing biological effects is the *total* volume of water swept out at a specified concentration, then the relevant volume is that of cones, bisected by their intersection with the seafloor, increasing in radius from zero at t=0, to a maximum and then decreasing again to zero.

This volume can easily be shown as $V_s=(1/3)\pi R_{max}^2 v\Delta t$, where R_{max} is the maximum radius reached, and Δt is the elapsed time from initial release until the radius at the specified concentration vanishes. Likewise, there is an area swept-out on the seafloor shown by $R_{max} v\Delta t$. These volumes and areas, which are now integrated quantities that do not change with time, are given in Table 7-8 along with the elapsed time. The volumes and areas are not contaminated over this entire period; elapsed time is the total event time. These areas and volumes are seen to be significantly larger than their instantaneous counterparts, as would be expected since over the total elapsed times, the 0.1 kt current will sweep the contamination up to several kilometers.

Since the effects of the current are to transport the toxic region downstream only (in this model we have assumed that diffusivities can be specified independently of the current), the effects of the current

on the total volumes and areas is simply linear. That is, for twice the current, i.e., 0.2 kt, the toxic water is transported twice the distance in the same time hence both seafloor area and swept-out volume are doubled. The dependence on other parameters, Q for example, is not so simple.

7.6 STEADY STATE (CHRONIC) RELEASE OF CW AGENTS

7.6.1 Generic Results

Based on the one dimensional results in Section 7.4, we expect to obtain plume solutions for the steady state source S = Q δ(x) δ(y) δ(z). The steady state (half space) solution to Equation 7-1 for this source can be shown as:

$$C(x, y, z) = \left[\frac{Q}{4\pi k L_H^2 L_v \rho} \right] e^{\sigma x/2L_H} e^{-\gamma \rho} \tag{7-22}$$

where the scaled radial distance ρ is given by

$$\rho^2 = (x^2 / L_H^2) + (y^2 / L_H^2) + (z^2 / L_V^2) \tag{7-23}$$

and γ is given by $\gamma^2 = (1 + \sigma^2/4)$ with σ still meaning scaled speed. The plume character of this solution can be seen by examining the case of y=z=0. The result can be written as

Table 7-8: Total Volumes, Areas, and Times for 1 kg Releases Into a 0.1 kt Current

Agent/Concentration	Total Area on Seafloor (m³)	Total Volume (m³)	Elapsed Time (hr)
GA			
Probable Effects	1.7 x 10⁴	3.1 x 10⁵	13
No Effects	1.2 x 10⁵	4.2 x 10⁶	45
GB			
Probable Effects	1.4 x 10⁴	2.4 x 10⁵	11
No Effects	6.9 x 10⁴	2.3 x 10⁶	30
L			
Probable Effects	1.9 x 10³	2.6 x 10⁴	0.4
No Effects	1.9 x 10⁴	5.6 x 10⁵	1.9

$$C(x,0,0) = \left[\frac{Q}{4\pi k\, L_v L_H x}\right] e^{-(x/L_H)[\pm(1+\sigma^2/4)^{1/2} - \sigma/2]}$$

(7-24)

where $\pm$ means + for $x>0$ and - for $x<0$. Note that for $\sigma \gg 2$ the exponential decay in x becomes $(-x/L_H)[(1+\sigma^2/4)^{1/2}-\sigma/2]\approx -xL_H\sigma$, indicating the expected behavior of the plume. Increasing currents (σ) cause the length of the plume ($L_H\sigma$) to be extended in the downstream direction.

Since $4K_H k/v > 0$, C decays exponentially with x increasing in the positive direction with the current, but *less* rapidly than it does with x increasing negatively against the current. This, with the increasing transverse width already shows the characteristics of a plume, and as with the time dependent solution, it is a plume closely confined to the region near the seafloor.

Introducing the same scaled dimensionless coordinates as before, Equation 7-22 can be written as

$$C(\xi,\psi,\zeta) = \left[\frac{(Q/v)}{4\pi\,(L_H^2 L_v)\,\sqrt{\xi^2+\psi^2+\zeta^2}}\right] e^{\sigma\xi/2}\, e^{-\gamma\sqrt{\xi^2+\psi^2+\zeta^2}}$$

(7-25)

The factor, Q/v, has the dimensions of mass and is the mass injected in the hydrolysis time v^{-1}, and the factor, $L_H^2 L_v$ is just the "natural" volume encountered previously. Hence the factor multiplying $(1/4\pi\rho)$ is again mass per natural volume, and

$$C(\xi,\psi,\zeta) = C_0 F_2(\xi,\psi,\zeta) \quad \text{with} \quad C_0 = \left[\frac{(Q/v)}{(L_H^2 L_v)}\right]$$

(7-26)

For illustration, as in Figure 7-17, the plume function F_2 is shown as a function of ξ, *i.e.*, of scaled x for several values of σ, where scaled y = 0.01 to avoid having a singularity on the x-axis. The asymmetry due to the current is evident, with mixing having a large effect against the current and much less with it.

While specific results for the CW agents of interest will be given in the following sections, it should be noted here that the scale factors on horizontal distances are on the order of tens of meters, and the scale factors on time of the order of 1/100. For example, a half-life of ten hours in a 0.1 kt current make σ approximately equals 117. In terms of the real problems at hand,

Figure 7-17: Dimensionless Plume Function vs. Scaled x-coordinate

7-25
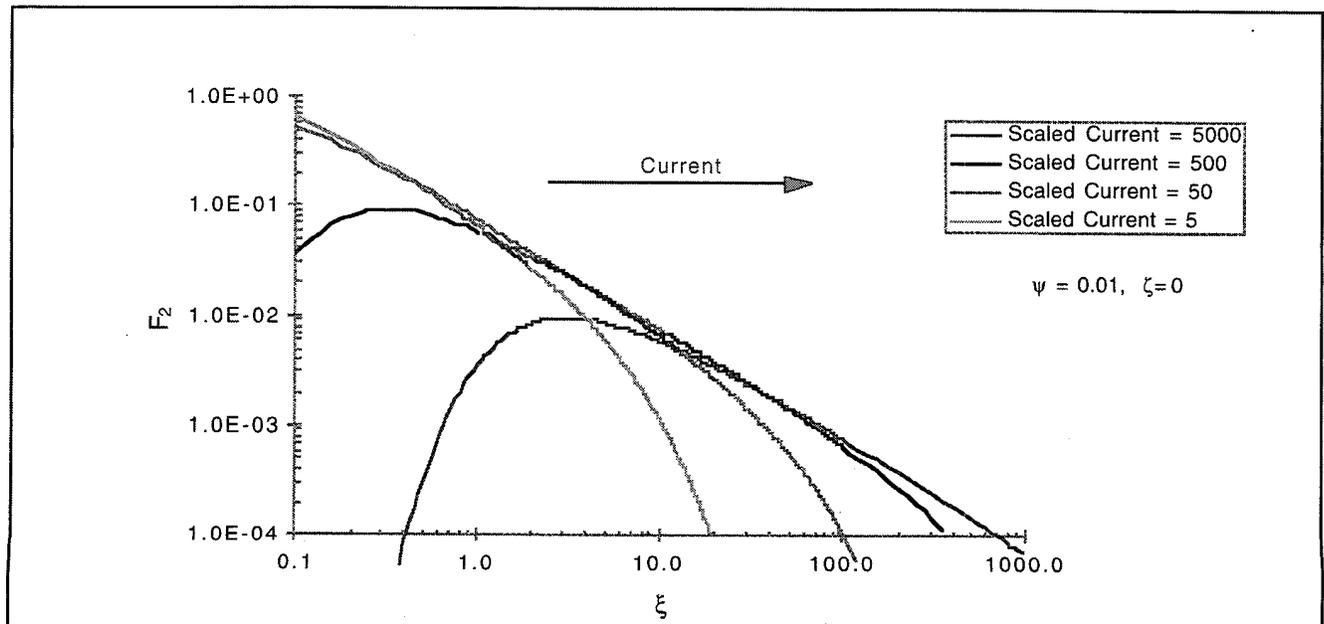
$\xi = 10$ might be on the order of 1 km and $\sigma = 500$ might be a current on the order of 0.1 kt (see Section 7.4.1), and 5,000 might be a current on the order of 1 kt. What is seen here is that at fixed concentration, (*i.e.*, fixed F_2), say 0.001, the peak of the plume moves away from the source and the larger the scaled current, the further the peak moves away. The general appearance of such a plume of CW agent is depicted schematically in Figure 7-18, with some exaggeration of the vertical scale.

If the release rate is much slower than the other operating processes hydrolysis, diffusion, and advection, then the release can be regarded as being constant over a long enough period to establish steady state conditions.

It can be shown that x_P, the approximate on-axis length of the plume on the seafloor ($z=y=0$) at a given concentration, is given by Equation 7-27.

$$x_P \approx x_0\left(1 - x_0/L_H \sigma\right) \ , x_0 \ = \ C^{-1}\left(Q/4\pi L_H L_v k\right) \ = \ C^{-1}\left(Q/4\pi\sqrt{K_H K_v}\right)$$

$$(7\text{-}27)$$

Likewise, at a distance from the source of x, the plume width y is given by Equation 7-28.

$$y \ \approx \ 2\sqrt{-xL_H\sigma^{-1}\ \ln(x/x_0)}$$

$$(7\text{-}28)$$

The maximum width, y_P, can be shown to occur at $x=x_0 e^{-1}$, at which point the plume width, y_P, is given by Equation 7-29:

$$y_P \ \approx \ 2\sqrt{x_0 L_H \sigma^{-1}\ e}$$

$$(7\text{-}29)$$

Equations 7-27 and 7-28 are valid only for $x_P \ll L_H \sigma$. It should be observed that for small currents, *i.e.*, small σ, x_P is linear in Q. It also should be noted that to the first order, the plume length is independent of both the current and the hydrolysis rate. This is simply a reflection of the fact the plume is dominated by diffusion and not by hydrolysis. At $\sigma=0$, we have the pure diffusion result $x_P \approx x_0.(1-. x_0./. L_H.)$.

Figure 7-18: Schematic Appearance of a Toxic Plume
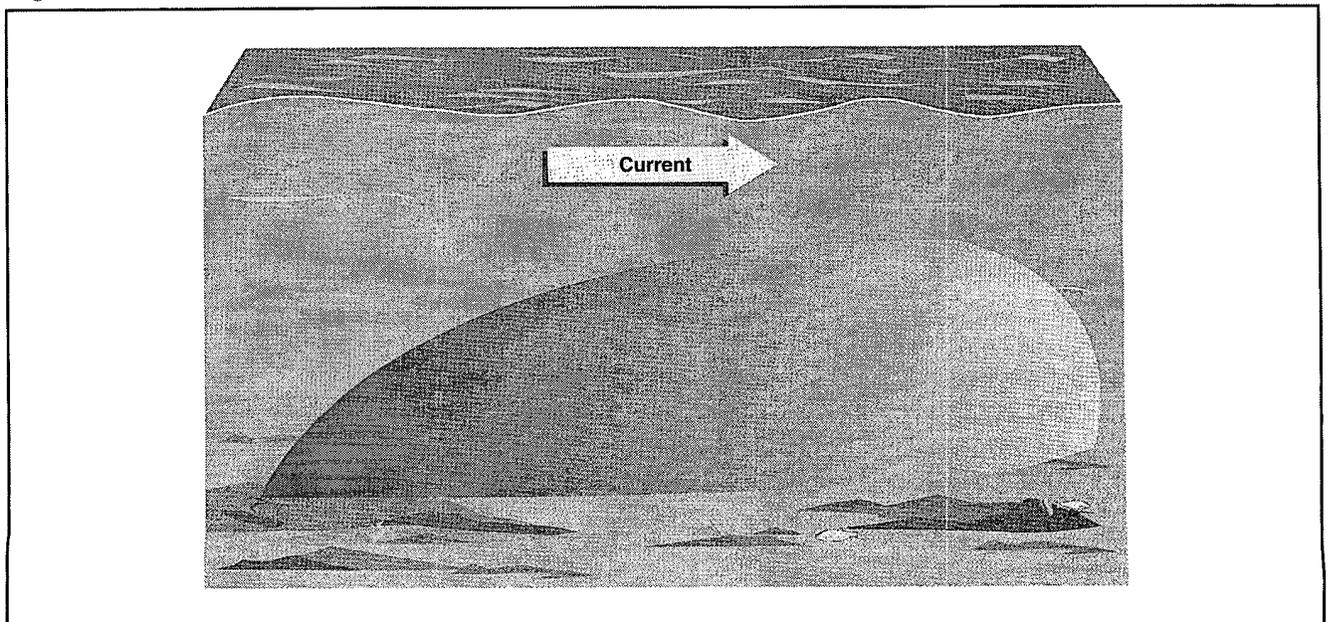
By approximating the area on the seafloor as an ellipse, it can be estimated using the approximations in Equations 7-27 and 7-28, giving

$$A \approx (\pi x_0/2)\sqrt{L_H x_0/e\sigma} \approx Q^{3/2} v^{-1/2} C^{-3/2}.$$
(7-30)

In a similar vein, the height of the plume at fixed concentration z_P, can be approximated as

$$z_p \approx L_V\left[4x_0/L_H e\sigma\right]^{1/2}.$$
(7-31)

The volume of the plume within a fixed concentration, using an ellipsoidal approximation to its shape, is given by

$$V \approx (2\pi/3) X_p (y_p/2) z_p \approx (2/3)A z_p$$
(7-32)

with the volume of the plume behaving approximately as
$$V \approx C^{-2} Q^2 v^{-1}.$$
(7-33)

In the sections to follow, numerical results will be shown for the various agents, but we can see here that the volume of water contaminated at a specified concentration is more sensitive to release rate Q than to the current v.

7.6.2 The Case of Mustard

Because of the slow dissolution rate of mustard, it is clear that a steady state release is the only reasonable approximation. Figure 7-19 shows that following complete disintegration of the casing of a munition containing mustard, dissolution of a typical 1 kg mass would take on the order of 150 days or approximately 3,500 hours and not greater than 250 days or approximately 5,900 hours. Since the other time scales in the problem operate on the order of hours, it is clear that the approximate model is a steady state process over the lifetime determined by the mass of mustard available, which is 1 kg in our usual model.

A 1 kg mass completely dissolving in 3,500 hours would have an average release rate of 0.007 kg day^{-1}. The concentrations of the plume along the x-axis in the direction of the current on the seafloor (z=y=0) based

Figure 7-19: Mustard (H) Concentration on the Seafloor Along the Plume From a 1 kg Munition Charge

7-27
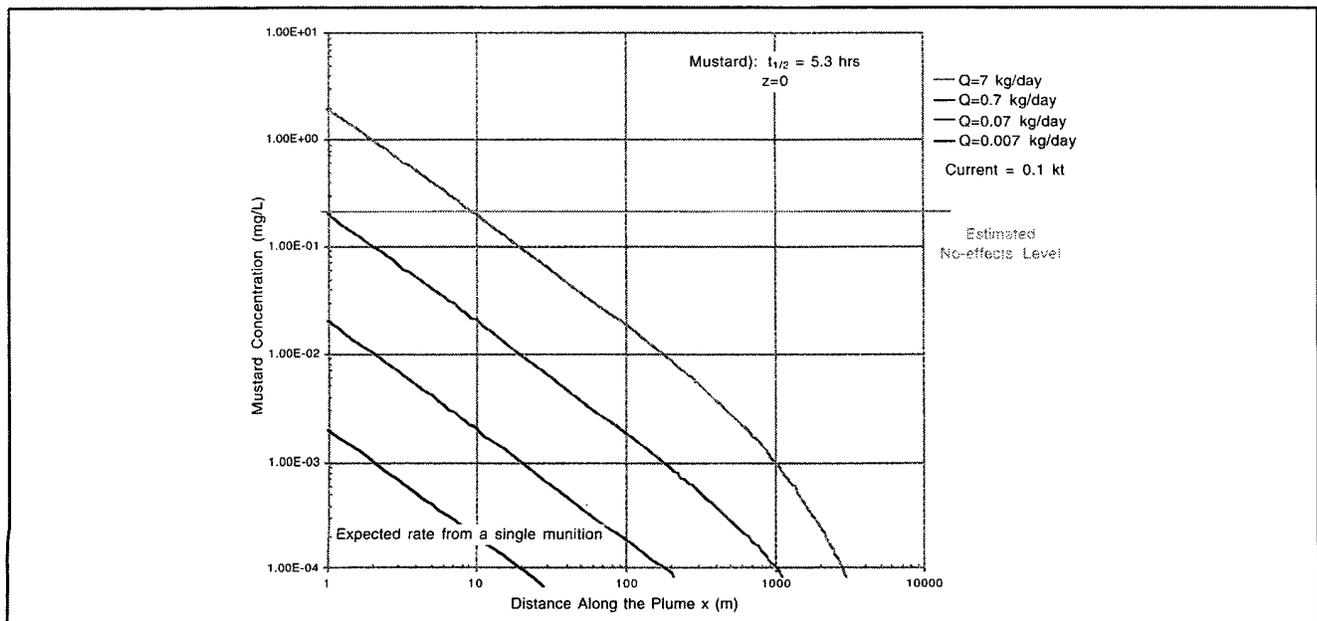
on Equation 7-24 are shown in Figure 7-19. The expected release rate are examined in addition to greater rates.

The ENEC level is highlighted in this figure, from which it is clear that the dissolution rate of mustard is so low that even at a distance of one meter downstream, the maximum concentration will be two orders of magnitude *below* this safe level. In Chapter 5, we estimated release rates for 1 kg clumps of mustard, finding that the largest instantaneous value would be 0.2 kg day^{-1} (see Figure 5-4). At this release rate, mustard concentrations just reach the non-toxic level at 14 cm from the source. Since the source is a pancake 27 cm in diameter, levels at or above the non-toxic threshold are confined to a layer a few centimeters thick. This conclusion is an upper bound since it was based on a release rate for a very thin pancake, possible only for rather low viscosity mustard. In somewhat purer form, mustard is a solid whose shape would lead to even lower rates and shorter distances.

There is a cautionary note that must be applied to these results for mustard. The spatial dimensions of the plumes are sufficiently small that the treatment using

the advective diffussion model is itself suspect. That is not to say that a more detailed treatment of turbulent mixing would lead to large plume dimensions, only that the details here should not be taken too seriously.

7.6.3   Tabun and Sarin

The only way that the highly soluble agents Tabun and Sarin could have a steady state release from a single munition would be from pinhole leaks that would allow release to be extended over a period of days. Figure 7-20 shows the resulting concentration of the plume on the seafloor along the current as a function of distance from the leaking munition (x) parameterized by the release rate.

With a single munition holding 1 kg of agent and with perhaps one hour needed to establish a steady state, the steady state model estimates that the maximum release rate would be a few kg day^{-1}. At the level of C=0.001, the plume for this release rate is some 270 m in length along the seafloor. In this regime the plume length is linear with C, so the length at the toxic level, C=0.01 for Tabun, is approximately 29 m in length.

The results for Sarin are essentially identical, with the

Figure 7-20: Downstream Plume Concentrations of Tabun (GA) in a 0.1 kt Current
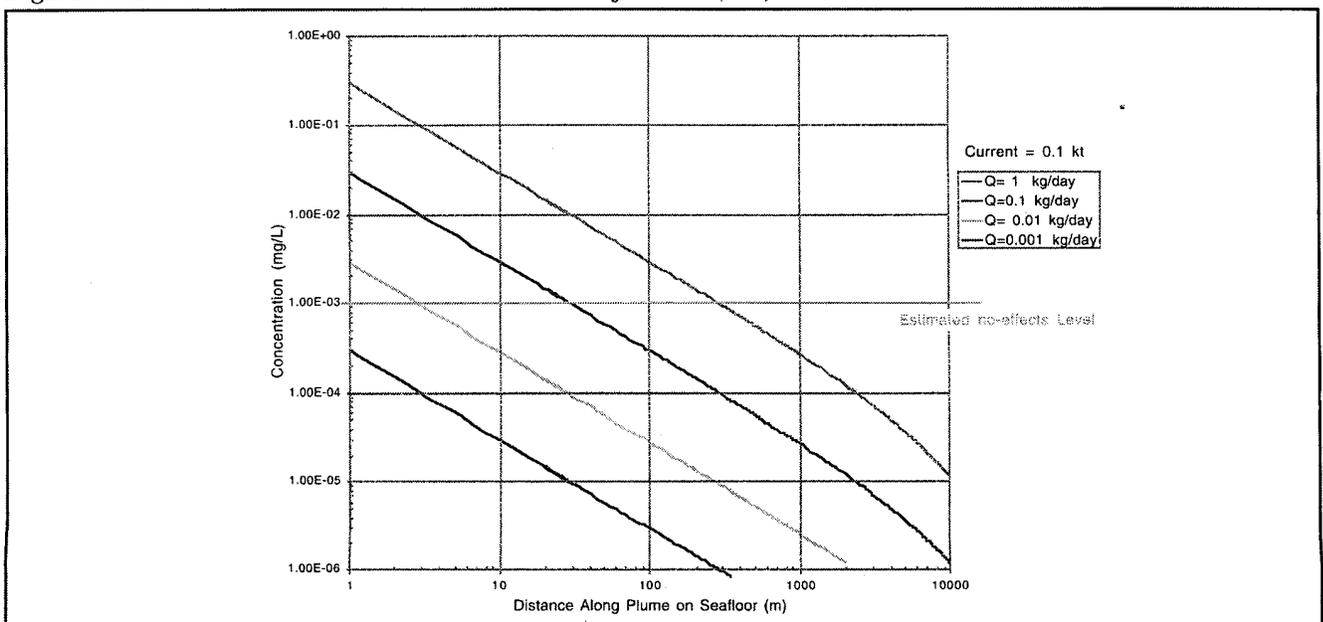
relevant toxic levels being the same and the half-lives differing only slightly.

In addition to the behavior on the seafloor along the plume axis (x), it is illuminating to examine the concentration in the transverse direction (y). Figure 7-21 shows C versus y at several positions downstream, all located on the seafloor. It will be observed that at y=0 and x=100 m, the concentration is the same as in Figure 7-21.

One conclusion that can be drawn from these figures is that if the release rate of Tabun or Sarin is less than 0.001 kg day^{-1}, the extent of the plume at the concentration corresponding to the "just safe" level will be less than one meter at the seafloor. Plausibly we could take this, or if necessary, one order of magnitude less, 0.0001 kg day^{-1}, to establish a threshold for being ignorable, especially since the width and thickness of the plume will be an order of magnitude less.

Figures 7-22 through 7-24 show the contours on the seafloor of the plume corresponding to no effects, probable effects, and lethal levels for release rates of 1 kg day^{-1}, 0.1 kg day^{-1}, and 10 kg day^{-1}, respectively.

In all cases the current is 0.1 kt. These results apply equally to Tabun and Sarin.

Figure 7-25 shows the same situation as Figure 7-24, except that the current is 1.0 kt rather than 0.1 kt.

It should be noted that the plume dimensions, particularly its length, correspond quite closely with the approximate results obtained earlier in, for example, Equation 7-27, which gives a plume length for Figures 7-22 and 7-25 of 29 m.

Beyond these individual depictions of plume characteristics, it was necessary to know the volumes of water and associated seafloor areas contained within plumes generated by various release rates. Figure 7-26 shows, for both Tabun and Sarin, the area of the seafloor under the plume as a function of the release rate ranging from approximately 8.6 g day^{-1} to approximately 86 kg day^{-1}, at three concentrations and for a current of 0.1 kt. Figure 7-27 shows the area for Tabun and Sarin for a current of 1 kt.

As noted previously, when $\sigma \gg 2$, the plume dimensions become independent of the hydrolysis rate.

Figure 7-21: Concentration of Tabun (GA) Across a 0.1 kt Current
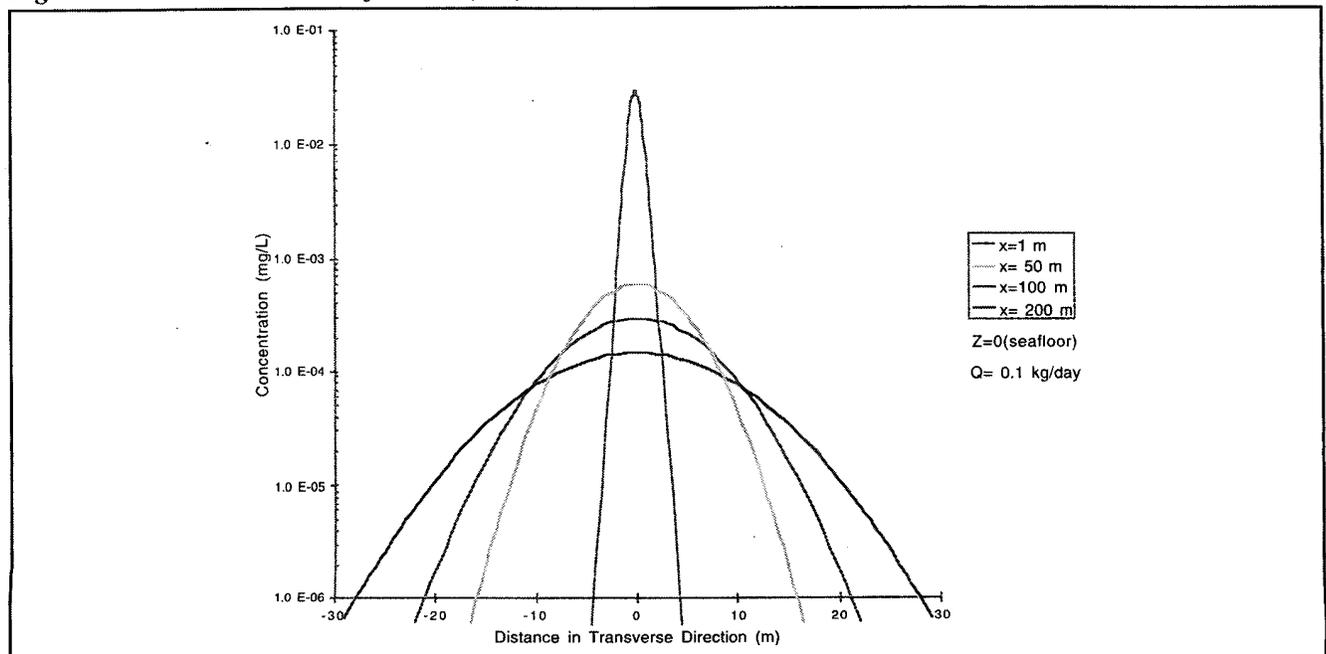
Figure 7-22: Seafloor Plume for Tabun (GA)/Sarin (GB) (Q = 0.1 kg day⁻¹)
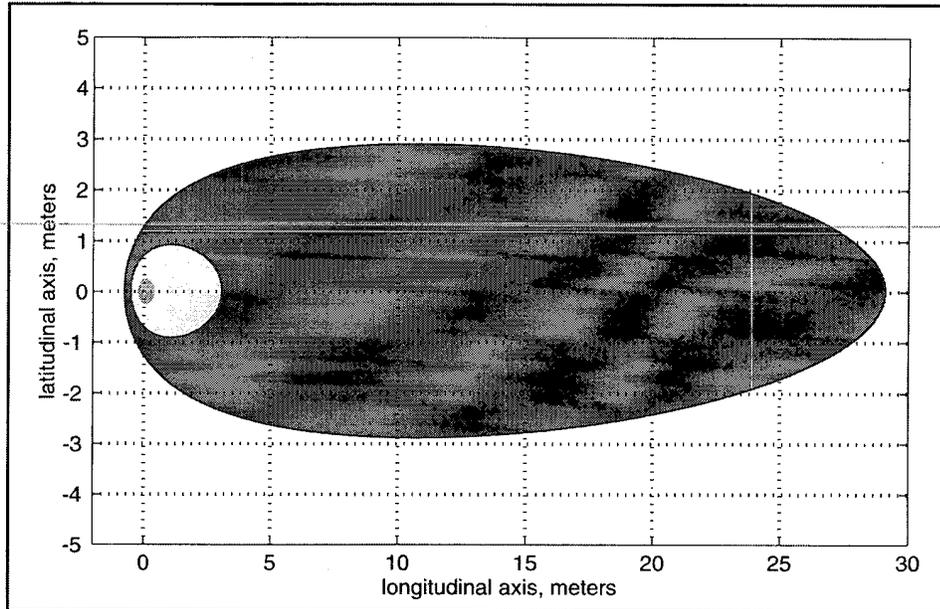
Figure 7-23: Seafloor Plume for Tabun (GA)/Sarin (GB) (Q = 0.01 kg day⁻¹)
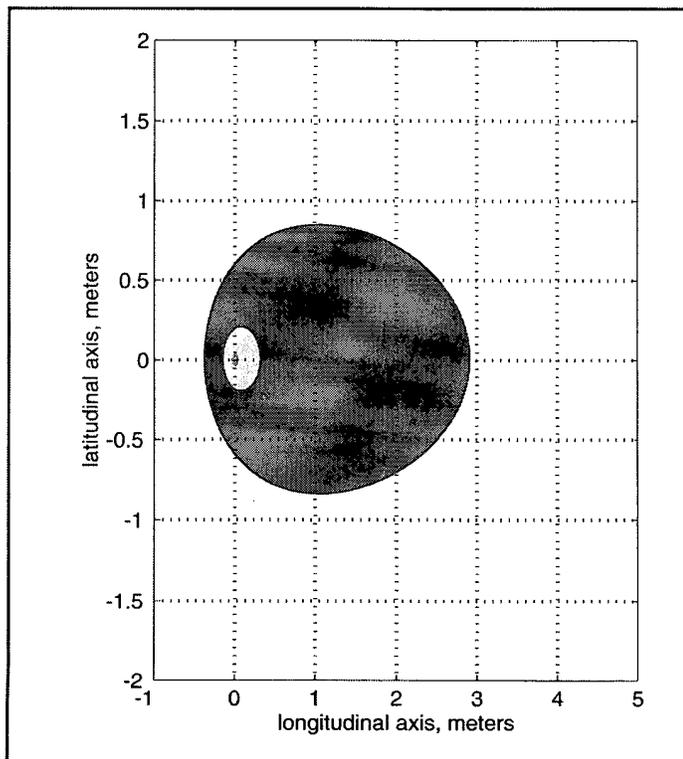
Figure 7-24: Seafloor Plume for Tabun (GA)/Sarin (GB) (Q = 1 kg day⁻¹)
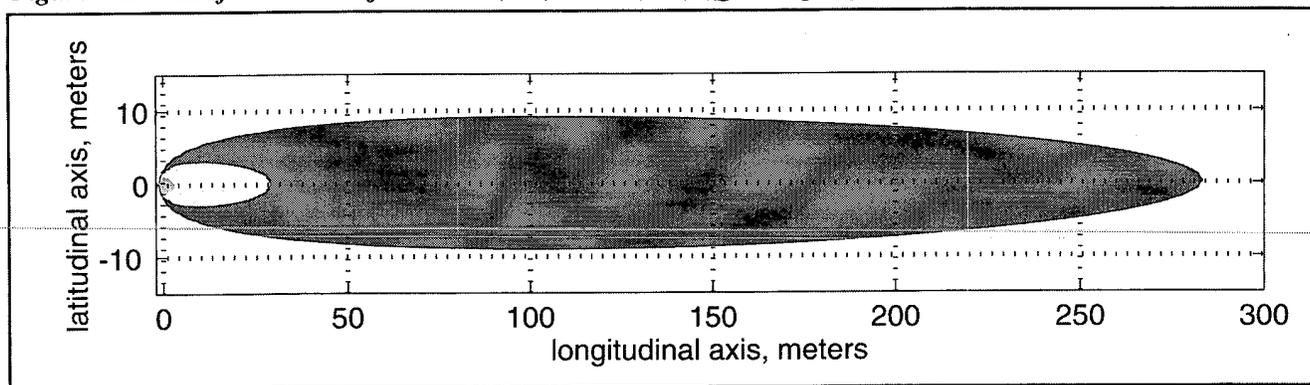
Figure 7-25: Seafloor Plume for Tabun (GA)/Sarin (GB) (v = 1 kt, Q = .1 kg day⁻¹)
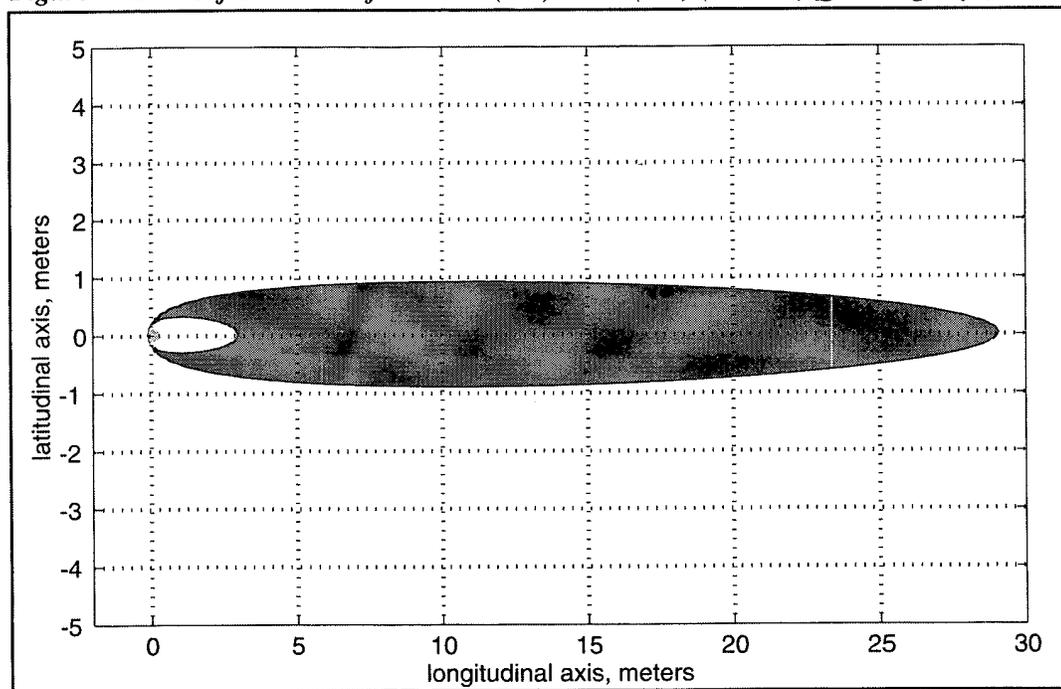
This means that the plume is formed by advection and mixing in a time that is relatively short compared to the time scale of hydrolysis. In such a circumstance, the hydrolysis rate has nothing to do with the plume size.

The associated plume volumes are depicted in Figures 7-28, applying to both Tabun and Sarin, at a current of

0.1 kt, and in Figure 7-29 at a current of 1 kt.

7.6.4   Plume Results for Lewisite

As argued earlier, the key issue for Lewisite is organic arsenic and that remains true even for a steady state release.   Figure 7-30 shows an organic arsenic concentration along the length of a plume which

Figure 7-26: Plume (Seafloor) Area for Tabun (GA)/Sarin (GB) in a 0.1 kt Current
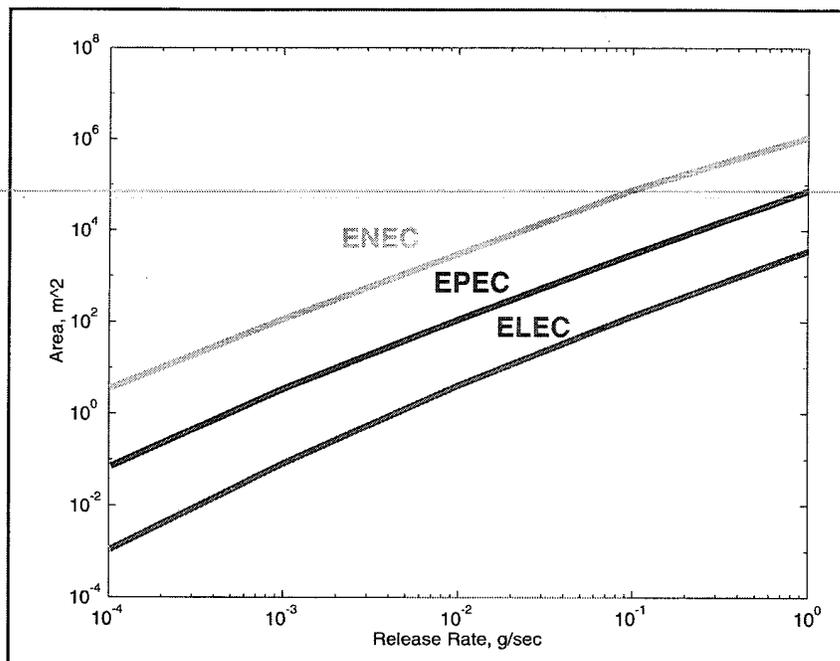
is across the seafloor for various release rates of Lewisite. The estimated no-effects level of 0.02 mg L^{-1} is highlighted.

The major conclusion to be drawn from this figure is that the release of Lewisite from a single munition, at rates less than 0.1 kg day^{-1}, will result in toxic levels at distances measured in tens of meters or less. Furthermore, release rates lower than approximately 0.1 kg day^{-1} will produce toxic plumes on the order of a few meters or less.

For release rates relevant to munitions containing approximately 1 kg of Lewisite and persisting long enough for a steady state solution, an upper bound on the release rate would be 24 kg day^{-1} (0.28 gs^{-1}). This rate would produce a short-lived plume having a volume at the no-effects level of approximately 10^4 m^3 and occupying a seafloor area of approximately 10^3 m^2. We can regard these as being upper bounds on the sizes of an arsenic plume, but it is important to note that their lifetimes will be short, that is, approximately one hour in the case of a 1 kg munition. However, it is

easy to imagine that in the course of corrosive development of leaks, that there first would be the appearance of pinholes allowing only much smaller rates, resulting in much smaller toxic volumes and areas.

7.7   TOXIC LEVELS AT THE DUMP SITES

There were two ways to proceed from this point, one potentially offering more generality than the other, although because of our state of ignorance about the dump sites they could end up being the same.

The first approach would have been to develop a statistical source distribution function (*i.e.*, giving the probability that at location (x,y) there is a leaking munition) for each dump site and, recognizing that the solutions already obtained, C(x,y,z,t) are Green's functions, convolve the two and compute expectation values, *e.g.*, the mean concentration.

The second approach, the path taken, was to recognize

Figure 7-27: Plume (Seafloor) Area for Tabun (GA)/Sarin (GB) in a 1 kt Current
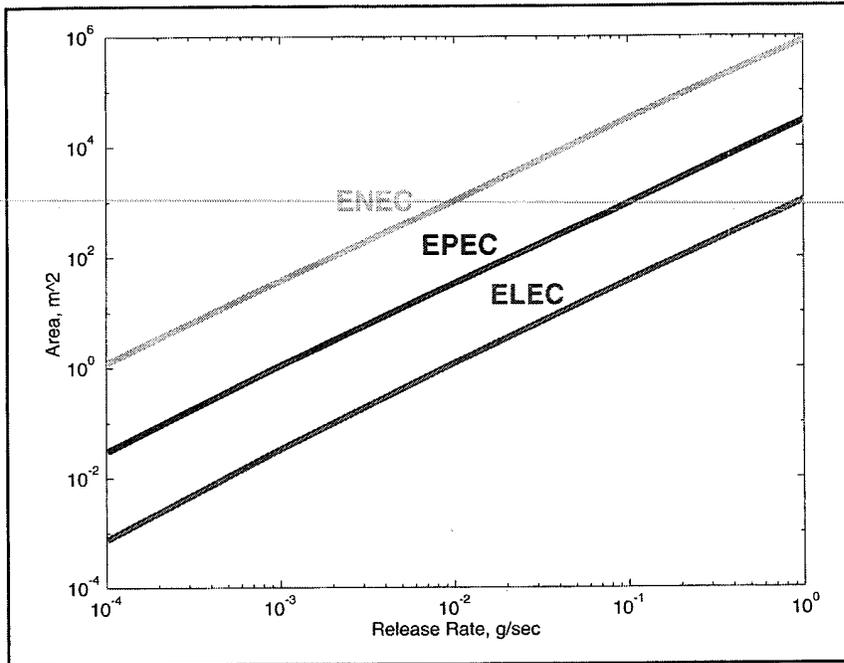
Figure 7-28: Plume Volume vs. Q for Tabun (GA)/Sarin (GB) in a Current of 0.1 kt
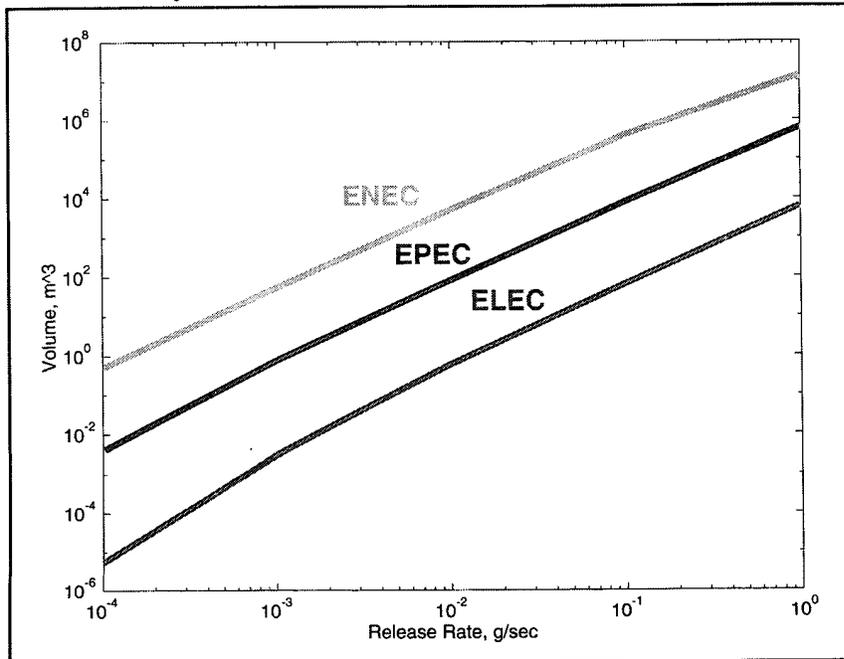
Figure 7-29: Plume Volume vs. Q for Tabun (GA)/Sarin (GB)
in a Current of 1 kt
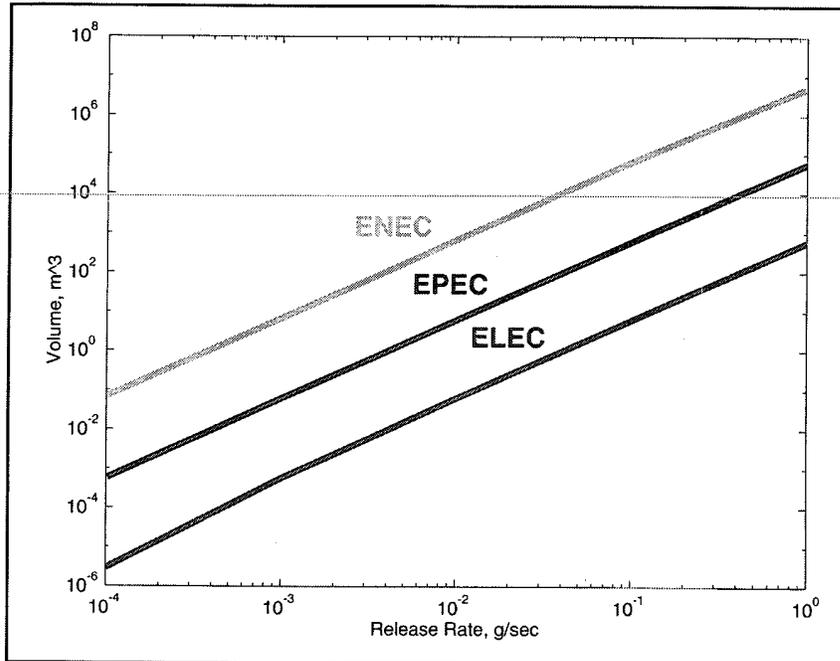
that because the estimated mean separation between leaking munitions will be generally larger than the sizes of the plumes or the toxicity fields generated by a sudden release, an "independence" approximation will be very good. This will be especially true for total dump site lifetimes greater than the expected lifetime of twenty years. Further, we will assume that the munitions are distributed uniformly across the site. With these assumptions, the total volume of contaminated water was obtained simply by multiplying the size of the contaminated volume from a single munition by the mean number of munitions leaking over the interval, which is determined by the time it takes to empty a munition.

Under the assumptions of uniform distribution and independence, these two approaches yield the same result. The convolution in the first approach becomes the sum of leaking munitions whose concentrations do not overlap at any relevant levels.

7.7.1 Toxicity from Rapid (Impulsive) Release of Agent

As we have learned, an abrupt or impulsive release of CW agent could possibly apply to Tabun, Sarin or Lewisite, but not to Mustard where the slow dissolution rate forces consideration of a plume description. Table 7-9 summarizes the total areas and volumes that can be contaminated at the ENEC and EPEC levels for these three agents.

To obtain the real extent of toxicity, we now need to combine these results with the conclusions of *Chapter 5* which provided the density of munitions on the seafloor. Since there is so much uncertainty about the duration of the primary release period, five, ten, twenty, forty years, or perhaps longer, as well as the spatial distribution of munitions, it will be useful simply to compute the maximum areas and volumes using all the agent thought to have been dumped. As

Figure 7-30: Concentrations of Arsenic in a Lewisite (L) Plume (0.1 kt current)
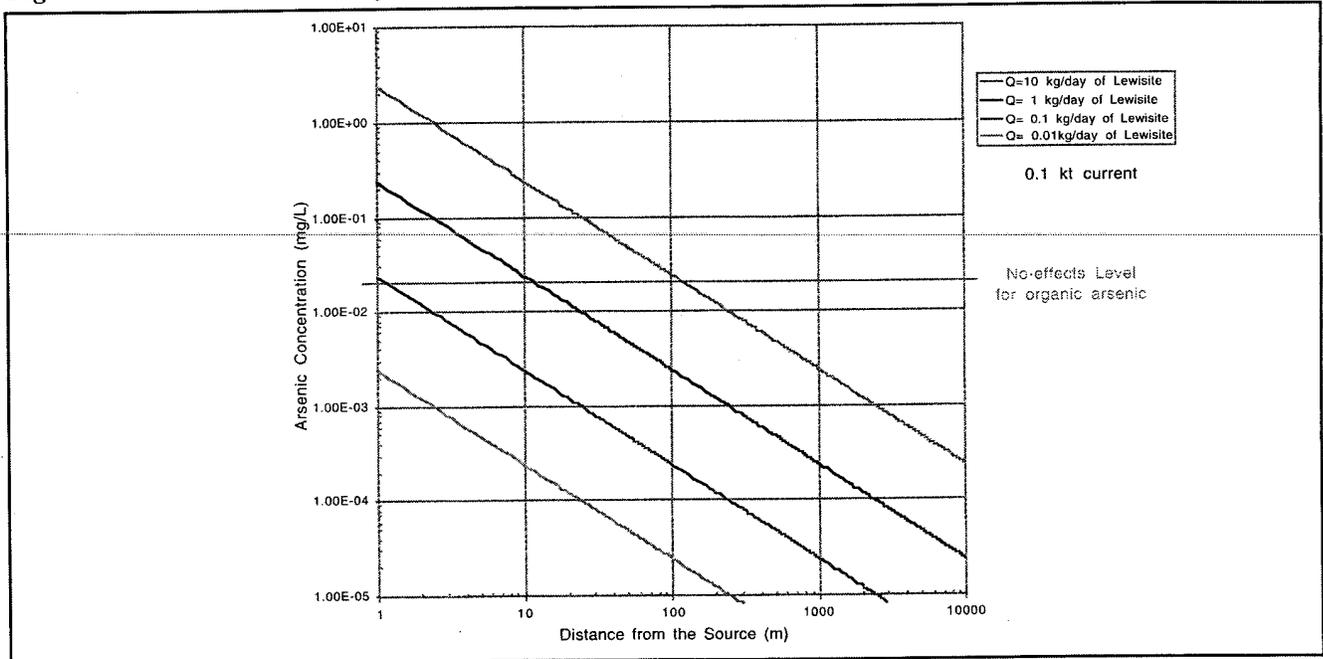
has been shown, the maximum volumes that can be contaminated by the agent from a single munition would arise from a single impulsive release.

Taking the results from Chapter 5 and the volumes and areas from Table 7-8, we have the results in Table 7-9. It should be appreciated that these areas and volumes are "one-time," with the toxic levels indicated extending over time given in Table 7-8. These values are simply the sums over all the areas and volumes taken independently, whether they result from a single, massive, simultaneous release from all munitions or the addition of the individual areas and volumes disregarding the times.

The magnitude of these values can be appreciated by realizing that the largest, Tabun, is comparable to the Kara Sea in both area and volume. These volumes and areas are those "swept out" by the toxic water moving with the current. However, these volumes cannot be realistically produced and we must introduce the primary release period in order to obtain something approaching a realistic picture.

Figure 7-31 shows the volume estimate as a function of

the total release period for both ENEC and EPEC levels. It should be understood that these volumes are maintained over the entire release period, whereas those in Table 7-9 were "one-time". That is, if we thought that the release period was at least ten years, then the maximum volume that could be contaminated by Tabun at the EPEC level would be no greater than 1.4 km³ and this volume would persist for at least ten years.

The results in Figure 7-31 have nothing to do with the spatial distribution of the munitions, except to assume that they are spread sparsely to result in independent areas and volumes of toxicity. For release periods greater than five years, this is a good assumption.

With this as background, we can complete the analysis for *impulsive release* by introducing the assumption of a uniform spatial distribution over the sites and the munitions quantities assigned to the sites in Chapter 5. Figure 7-32 shows the volumes by site for the initial release of five percent of the munitions and Figure 7-33 shows the areas. It was assumed here that this initial release was a single event, whereas in reality, with munitions being dumped from ships

Figure 7-31: Volumes of Direct Toxicity at EPEC for All Munitions
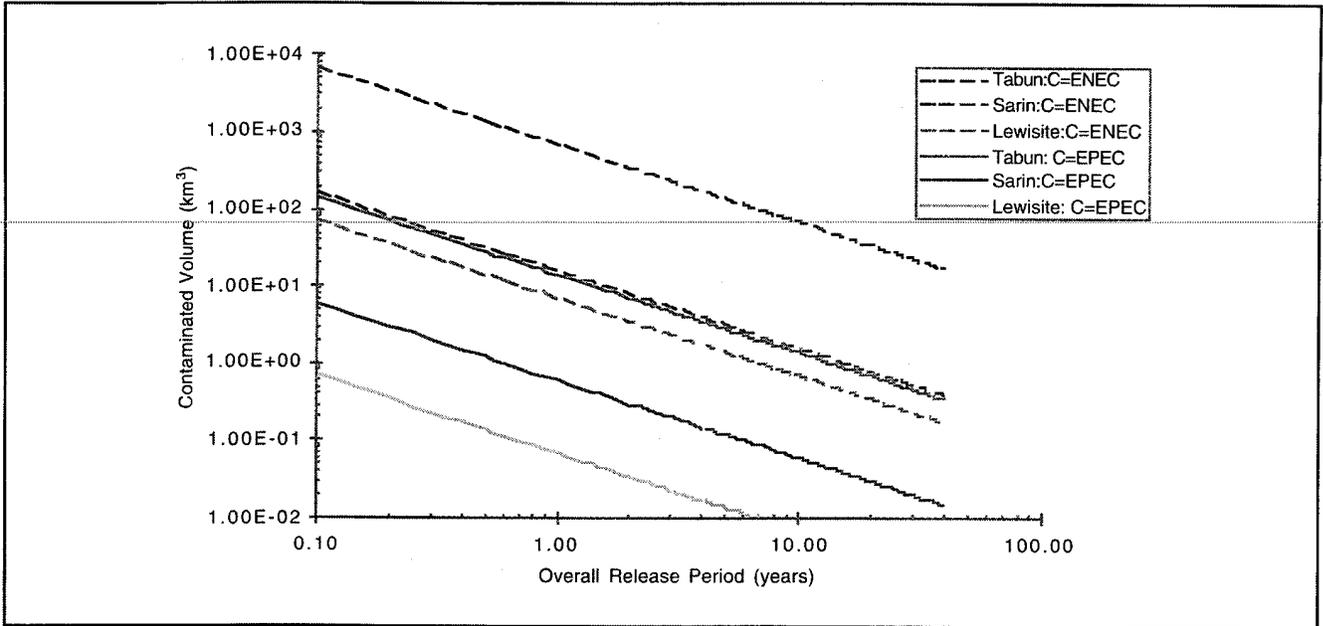
Table 7-9: Maximum Extent of Contamination From Simultaneous Release of All Munitions Dumped in Arctic Seas

Agent	# Equivalent	Maximum Seafloor Area	Maximum Water Volume
GA 30 KT	3×10^7		
EPEC		5.1×10^5	9.3×10^3
ENEC		3.6×10^6	1.3×10^5
GB 2 KT	2×10^6		
EPEC		2.8×10^4	4.8×10^2
ENEC		1.4×10^5	4.6×10^3
L 58 KT*	5.8×10^7		
EPEC		1.1×10^5	1.5×10^3
ENEC		1.1×10^6	3.2×10^4

*As before, this assumes that the 115KT of H+L is equally divided.

7-36

arriving over months if not years, even this "initial" five percent event would be spread out in time. If this were taken into account, the volumes and areas would be reduced, perhaps by factors as great as two orders of magnitude.

The sites producing the most contamination are Site 123 in the Kara Sea, Site 121 in the White Sea, and Site 134, the shallow site in the southern Barents Sea. With the assumption of a single release of five percent of the munitions, these volumes and areas are very large. The total volume of the Kara Sea, for example, is approximately 100,000 km^3 with an area of approximately 880,000 km^2.

It is important to appreciate that the volume and area shown are "one time," based on an impulsive release from five percent of the munitions dumped. This is in contrast to the steady state problem discussed below, where the result will be contaminated areas and volumes existing over periods of years, even decades.

7.7.2   Steady State Release

The first issue to be confronted is the release rate Q, since, as we have seen in Section 7.6, contaminated volumes and areas are quite sensitive to Q. In Section 6.1, it was shown that the contaminated area and volume were proportional to $Q^{3/2}$ and Q^2, respectively. Since what we want to do is to obtain *upper bounds* on the contaminated areas and volumes, it will be sufficient to use as large a value of Q as is consistent with both plausibility and with the use of the steady state solution. This will be taken to be approximately 1 kg day^{-1} for Tabun, Sarin, and Lewisite and 0.01 kg day^{-1} for mustard. It should be understood that this *is not necessarily the most likely rate*–which may be two orders of magnitude smaller in many cases–it is a high rate, possibly near the maximum. At this rate we have a duration for each single, 1 kg munition of one day except for mustard, which has a duration of 100 days.

Figure 7-32: Contaminated Volumes by Site for the Initial Five Percent Release
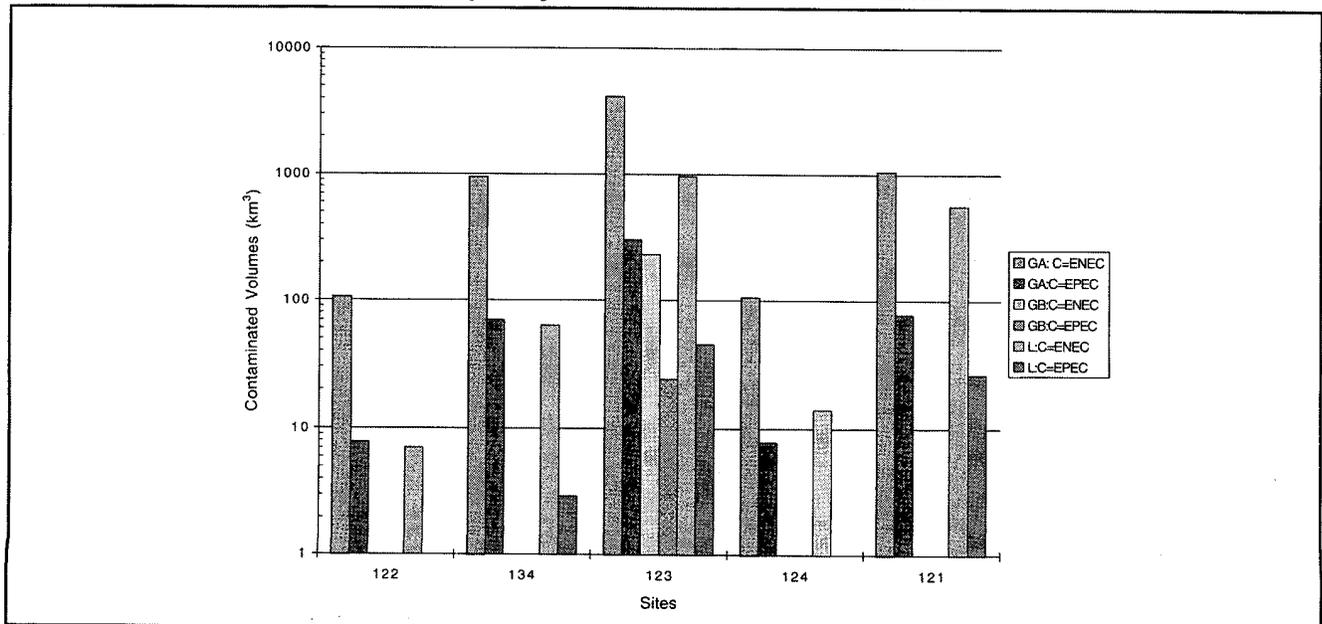
Figure 7-33: Contaminated Areas for the Initial Five Percent Release
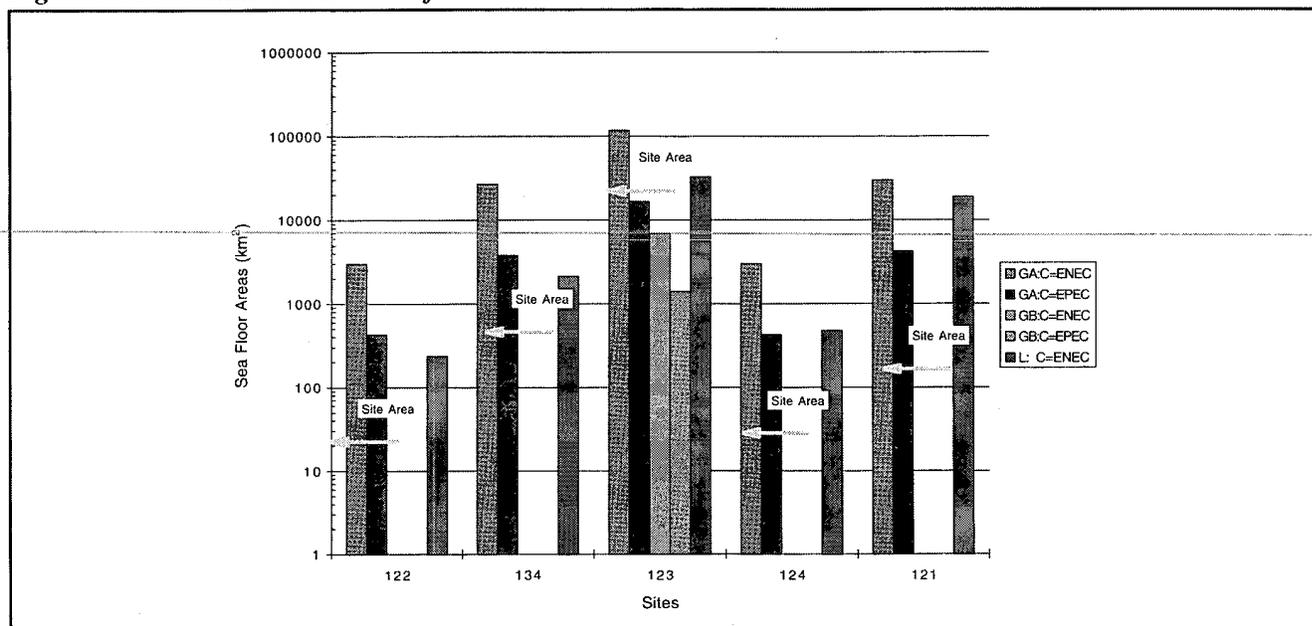
Given the plume volumes and associated seafloor areas previously estimated and the spatial and temporal distribution assumptions of Chapter 5, we can arrive at estimates for the areas and volumes associated with entire dump sites. These are given in Figures 7-34 and 7-35 where they are referred to with respect to the volumes and areas of the relevant seas.

In all cases, the volumes are usually very much less than 1 km³. It is important to appreciate that since, in this model, the initiation of a release is assumed to be uniformly distributed over time T, taken to be 5 years or 50 years, the volumes indicated are present for these entire periods. Of course, the munitions that are actually releasing will vary from one time to another. It is only the number that is being held constant.

The associated areas on the seafloor are given in Figures 7-36 and 7-37.

The most important conclusion to be drawn from the estimates given for contaminated areas and volumes is that both are a very small function of the areas or volumes of the seas in which the sites are located.

Moreover, the contaminated areas are even a small fraction of the site areas. Both conclusions are true even for a total release period of five years, which is unrealistically short.

7.8 POTENTIAL FOR ACCUMULATION OF CONTAMINANTS IN THE SEDIMENTS

After release to the water column, chemical agents, additives, and breakdown products can remain in solution or suspension, where they may undergo additional breakdown reactions and continue to be diluted in the regional waters. Some contaminants may be carried to the sediment where persistent contaminants could increase greatly in concentration over background amounts.

Arsenic in Lewisite is the only contaminant likely to be carried to the sediments in significant quantity and to remain for long periods.

Figure 7-38 shows the areas over which a given quantity of arsenic would need to be distributed in

Figure 7-34: Contaminated Volumes for Steady State: T = Five Years
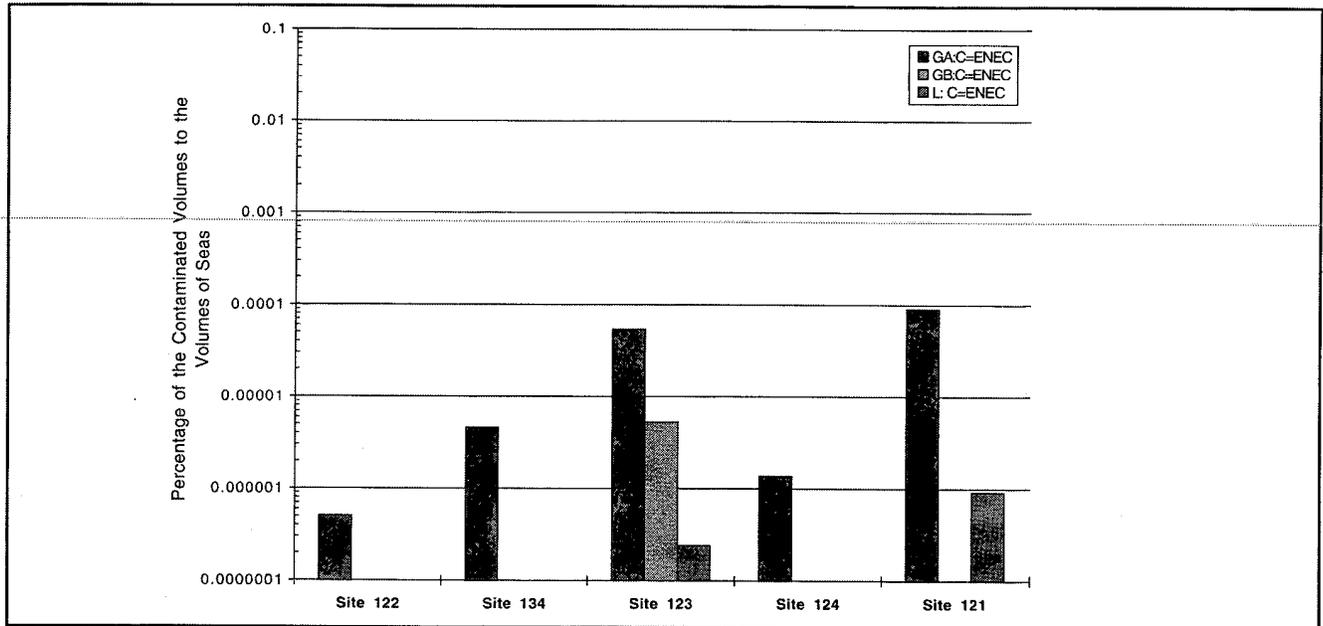
Figure 7-35: Contaminated Volumes for Steady State: T = Fifty Years
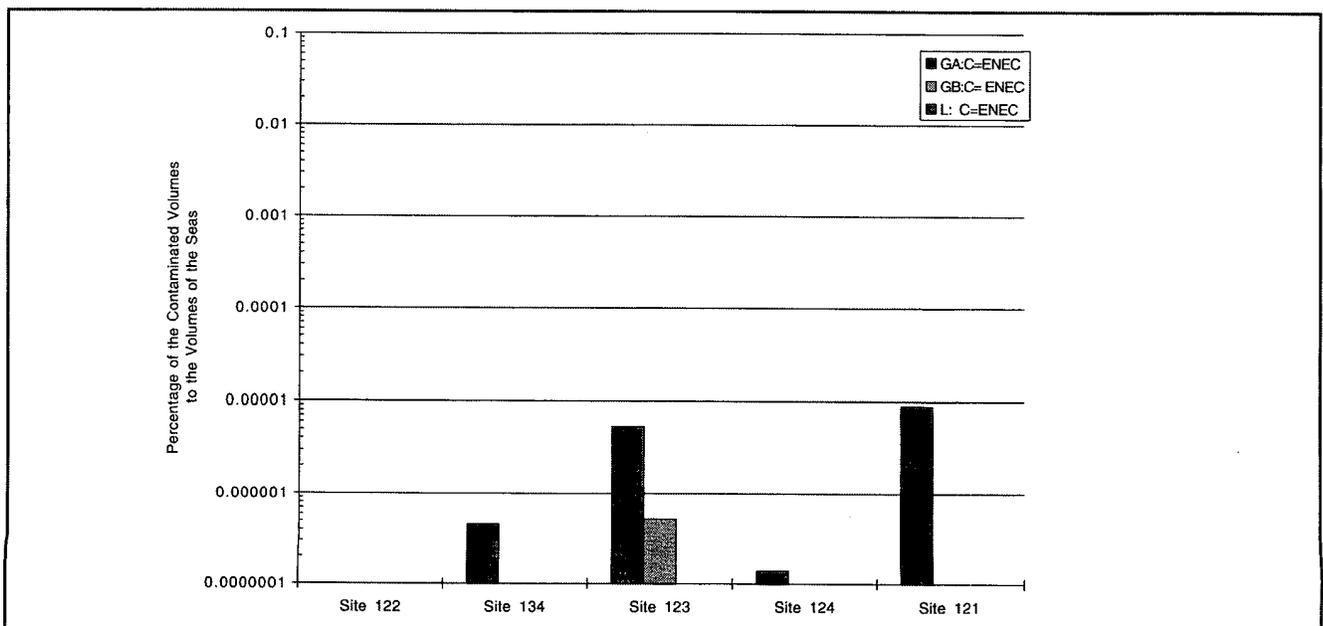
Figure 7-36: Contaminated Areas for Steady State Release: T = Five Years
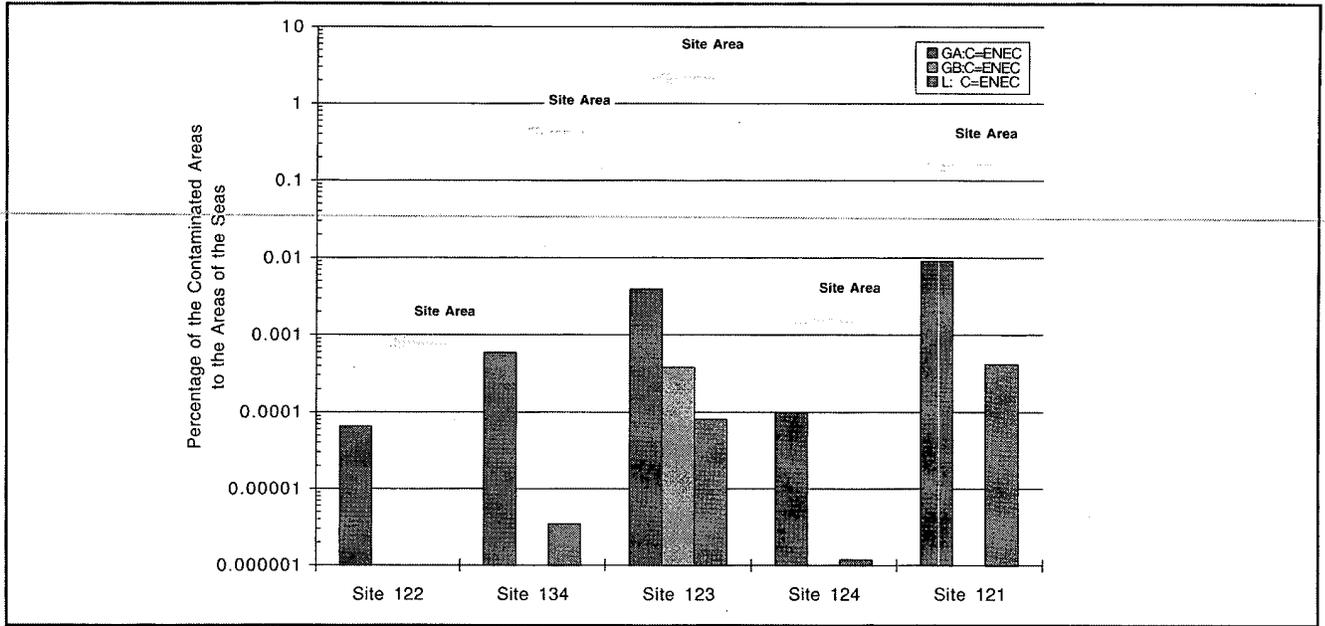
Figure 7-37: Contaminated Areas for Steady State Release: T = Fifty Years
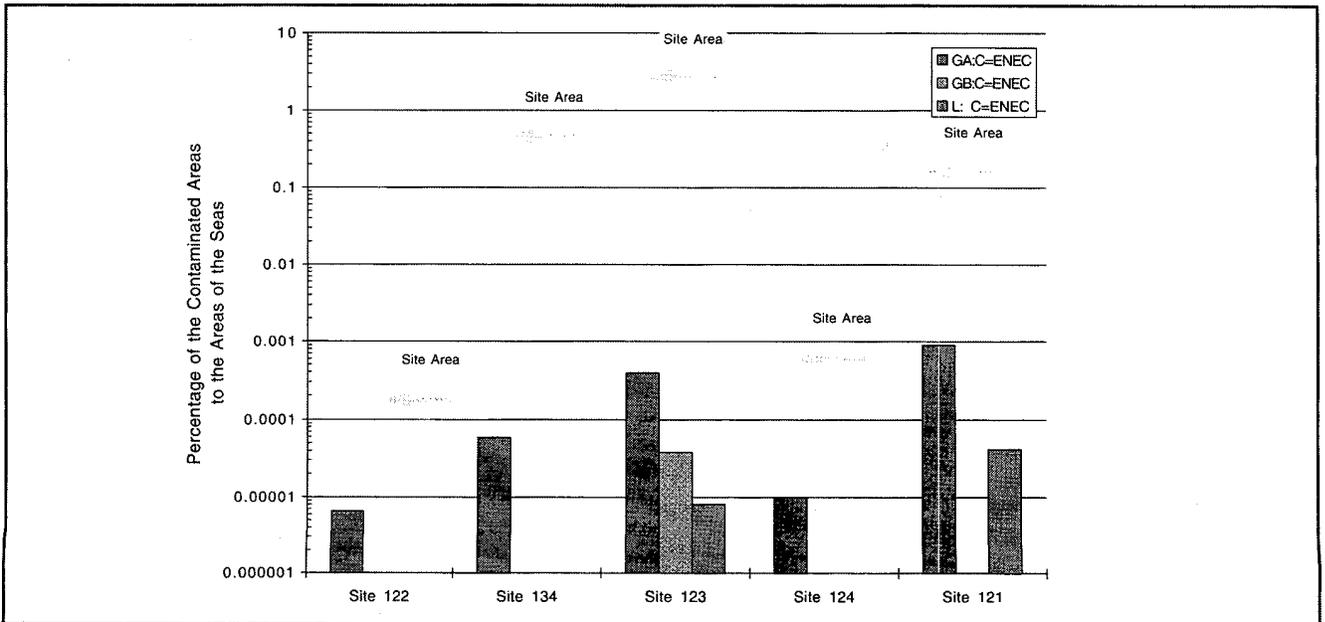
order to produce a given concentration. The range of naturally occurring background levels is highlighted.

These values assume a uniform distribution in area and a depth of 1 cm. If, as we mentioned earlier, mixing through bioturbation to a depth of 10 cm is plausible over long periods, then these values would be divided by ten.

7.8.1 Fate of Chemical Agents and Organic Breakdown Products

The reactions of chemical agents in the marine environment have been discussed in Chapter 4. Although the long-term reactions of these compounds are not well known, it is likely that most of the organic products will continue to undergo breakdown reactions in the water or in the sediments. Most of these compounds would probably not be long-lived in the environment.

The short-lived contaminants are not likely to be carried to the sediments, as indicated by their very low or negative octonal-water partition coefficient (K_{ow}), (see Tables 4-18 through 4-21 in Chapter 4). Chemicals with log K_{ow} greater than four have the greatest affinity for adsorption in sediments or onto suspended matter that can sink to the bottom.[7]

The estimated log K_{ow} for Lewisite is two to three, which is greater than most of the other compounds, but still less than the lower end of the range of greatest adsorption. It is unlikely that Lewisite would be carried to sediments in significant concentrations because the very large hydrolysis rate discussed earlier in this chapter would not allow it to persist for sufficient time for this process to be effective.

Only rough estimates of log K_{ow} for the organic breakdown products of Lewisite are available from the phosphorus analogues. The relatively low K_{ow} estimates are consistent with the expected degree of disassociation at the pH of the marine waters of the

study area. This disassociation makes it likely that these compounds would stay in solution in preference to sorption to sediments.

For Tabun, no measurement or estimate of log K_{ow} could be found for two of the organic breakdown products. These acids are significantly disassociated in seawater at pH 8.1 and are likely to have low toxicity. Accumulation in sediments at concentrations that could produce toxic effects is unlikely. In any case, we have shown that significant Tabun concentrations must be restricted to the site itself.

7.8.2 Arsenic

Arsenic in Lewisite is released from munitions in organic forms. Since organic arsenic compounds are readily oxidized in aerobic waters,[8] such as in the study region, it is likely that these compounds would continue to undergo reactions to inorganic forms and enter the natural cycle of arsenic in the physical and biological environment of the region. Significant quantities of arsenic are likely to remain in sediments.

Adsorption of arsenic into sediments and coprecipitation may be important controlling factors in the fate of arsenic in the environment.[9,10] Arsenic may be sorbed onto clays, aluminum hydroxide, iron oxides, and organic material. Coprecipitation or sorption with hydrous oxides of iron is an important process. The log K_{ow} of 2.84 for arsenic indicates a modest affinity for sorption on sediments. Oxyanions of both arsenic and arsenous acid can coprecipitate with hydrous iron and manganese oxides. The rate of adsorption decreases with increasing salinity. The formation of ferromanganese concretions in the Barents and Kara Seas[11] could indicate that this mechanism would operate in the study region.

The prevalent form of inorganic arsenic in seawater is $HASO_4^{2-}$.[12,13] The inorganic form is probably the predominant form in marine sediments, although the method of extraction for measurement can change the

[7] Baird, C. 1995. *Environmental Chemistry.* W.H. Freeman and Company, New York, NY.

[8] U.S. Environmental Protection Agency. 1979. *Water-Related Environmental Fate of 129 Priority Pollutants. Volume II.* EPA-440/4-79-029b. U.S. Enviromental Protection Agency, Washington, DC.

[9] Tamaki, S. and W. T. Frankenberger, Jr. 1992. *Environmental Biochemistry of Arsenic. Reviews of Environmental Contamination and Toxicology* 124: 79-110.

[10] Reference 9.

[11] Ingri, J. 1985. "Geochemistry of Ferromanganese Concretions in the Barents Sea." *Marine Geology* 67: 101-119.

[12] Sillen, L.G. 1961. "The Physical Chemistry of Seawater." *In* Sears, M. (ed.), *Oceanograph Publication No. 67.* American Association for the Advancement of Science, Washington, DC.

[13] Reference 10.

Figure 7-38: Concentration of Arsenic vs. Area (Uniform Distribution)
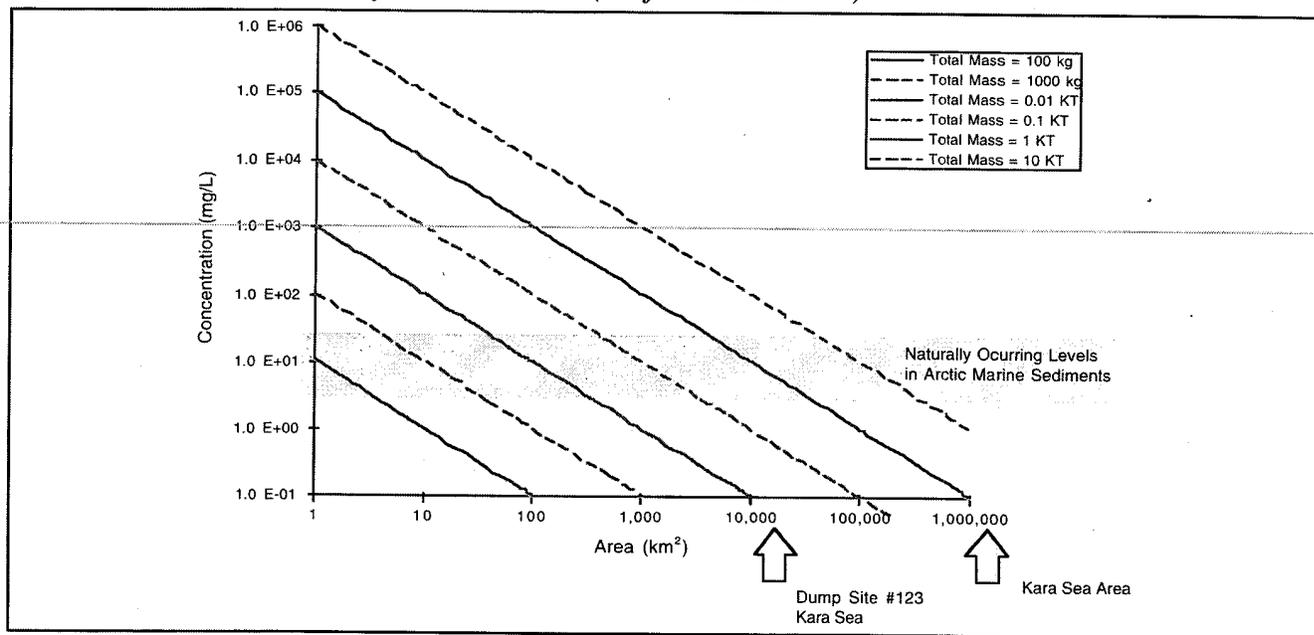
form. Methylated forms were not detected in oceanic sediments measured.[14]

7.8.3 Cyanide

Once produced, Tabun can exist in several different forms in the aquatic environment. The primary toxic agent of concern is free cyanide, which consists of HCN and the cyanide ion in equilibrium:

$$HCN \leftrightarrow H^+ + CN^-$$

Cyanide is a hydrolysis product of Tabun. Cyanide would likely remain as free cyanide in the form of HCN. It is likely that the fate of this acid primarily will be governed by biodegradation and volatilization, if brought to the surface.

The pK_A for HCN is 9.4 at 25°C and 9.6 at 10°C.[15] HCN is far more toxic to aquatic species than the

cyanide ion, presumably because it can more easily penetrate the gills. Except under extreme conditions of high pH, HCN would be the dominant form in aqueous solutions. In marine waters, which are well-buffered by the carbonate system at a pH near eight, probably 95 percent of the free cyanide would exist as HCN.

Although it is well-known that free cyanide can be chemically oxidized to cyanate (CNO^-), data on the chemical oxidation of cyanide in natural aquatic systems is not available.[16]

No data was found on the absorption of free cyanide to suspended particulates or bottom sediments in natural systems, but it has been demonstrated that the cyanide ion is not strongly adsorbed or retained in soils.[17] It is unlikely that cyanide would strongly partition to the sediments in aquatic systems. Furthermore, insoluble metal cyanides are unlikely to precipitate in natural waters because of the low metal concentrations

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[14]Francesconi, K.A. and J.S. Edmonds. 1993. "Arsenic in the Sea." *Oceanography and Marine Biology Annual Review* 31:11-151.
[15]Leduc, G., R.C. Pierce, and I.R. McCracken. 1982. *The Effects of Cyanides on Aquatic Organisms With Emphasis Upon Freshwater Fishes.* Publication No. NRCC 19246. National Research Council of Canada, Ottawa.
[16]Reference 15.
[17]Eisler, R. 1991. *Cyanide Hazards to Fish, Wildlife, and Invertebrates - A Synoptic Review.* Biological Report 85(1.23). U.S. Fish and Wildlife Service, Washington, DC.

encountered. Because of its high solubility in water, hydrogen cyanide is not strongly adsorbed to sediments or suspended material.[18]

Most of the research on the fate of cyanide-containing compounds is based on investigations of industrial wastewaters containing cyanide in concentrations in the mg l^{-1} range and usually in association with other contaminants, such as metals. Some of the mechanisms that have been shown to affect cyanide concentrations are biodegradation, volatilization, chemical oxidation, photolysis, and precipitation. However, very little information is available about the fate of cyanide compounds in natural waters.

There are many inorganic cyanide complexes that can form with the transition metals and this formation serves to remove cyanide from aquatic systems. These complexes have the following general formula:

$$[M^{n+} (CN)_x]^{(n-x)}$$
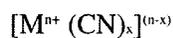
These complex ions are variable in their stability. The copper complexes are moderately stable. The iron complexes are very stable and can serve to reduce the availability of free cyanide. The high stability of the ferric hydroxides, however, keeps the ferric ion activity so low that the extent of iron complexation is limited. Overall, it is probable that metals in seawater would form complexes with dominant anions such as hydroxide, chloride, sulfate, and carbonates and that cyanide would be present in concentrations too low to permit significant complex formation.[19]

If cyanide complexes form, there remains a potential for later release of cyanide. For example, although iron-cyanide complexes are not toxic, ultraviolet or visible light can liberate the cyanide ion.[20]

Hydrogen cyanide is volatile, having a vapor pressure

of 360 Torr at 7°C.[21] Volatilization, particularly in turbulent waters, may be a significant means of removing free cyanide from aqueous systems. In deep marine environments and during periods of ice cover, this mechanism would be unimportant. In shallow systems, circulation could bring water in contact with the atmosphere and volatilization could occur.

Cyanides at low concentrations are biodegraded by almost all organisms,[22] making this an important process in the aquatic fate of this contaminant. Under aerobic conditions, cyanide salts in the soil are degraded microbially to nitrites or they form metallic complexes.[23] Under anaerobic conditions, cyanides denitrify to nitrogen compounds. Cyanides do not seem to persist in aquatic environments. In small, cold lakes treated with 1 mg NaCN/l, acute toxicity was negligible within forty days. In warm, shallow ponds, toxicity disappeared within four days.[24]

7.8.4   Chlorobenzene

Chlorobenzene can be released as a mixture with Tabun. Chlorobenzene is resistant to hydrolysis and could be persistent in the marine environment.[25] It is likely that chlorobenzene would not accumulate in sediments in significant amounts.

Chlorobenzene has a log K_{ow} of 2.84, which suggests a low to modest affinity for adsorption onto sediment and particulate matter. The adsorption coefficient, K_{oc}, for chlorobenzene is in the range of 83 to 389. This coefficient is a measure of the affinity to sorb onto organic matter. K_{oc} values in this range indicate there is little affinity for adsorption onto sediment.[26]

Chlorobenzene has a vapor pressure of 11.8 Torr at 25°C, which indicates it will partition to the air in a surface environment.[27] In quiescent water, the evaporative half-life of chlorobenzene has been estimated to be nine hours.[28] In agitated waters, such as

[18]Reference 9.
[19]Morel, F.M.M. 1983. *Principles of Aquatic Chemistry.* John Wiley and Sons, New York.
[20]Reference 15.
[21]Reference 9.
[22]Reference 9.
[23]Reference 18.
[24]Reference 15.
[25]Reference 9.
[26]Ney, R.E., Jr. 1995. *Fate and Transport of Organic Chemicals in the Environment, Second Edition.* Government Institutes, Inc., Rockville, MD.
[27]U.S. Environmental Protection Agency, 1988. "Chlorobenzene." *In* Ware, G.E. (ed.), *Reviews of Environmental Contamination and Toxicology* 106:37-49.
[28]Reference 9.

white capping in the ocean, the rate would be higher. In deep waters, chlorobenzene would not have the opportunity to volatilize, but in shallow areas this could be an important mechanism by which the substance is lost from the aquatic system.

Photolysis potentially can reduce chlorobenzene concentrations. Chlorobenzene at 2 to 5 ppm in river water photodegraded to phenol and chlorophenol when exposed to artificial sunlight.[29]

The half-life of chlorobenzene in sediments has been reported as 75 days.[30] At this rate, over 95 percent of the compound would be degraded within one year. The temperature regime for this estimate was not reported. Biodegradation of chlorobenzene in aquatic systems is likely to be slow.[31]

7.9   SUMMARY OF RESULTS

At the beginning of this chapter seven key questions were posed. These questions were developed in such a way that their answers would serve as the departure point for the assessment of the ecosystem effects to be carried out in Chapter 8. The most succinct way to summarize the substantial quantity of material in this chapter is to provide answers to these questions.

1. *Following release from a single munition, how does the total quantity of the remaining CW agent change with time due to chemical reactions?*

   The total quantity of agent present in the ocean decreases as a result of chemical reactions (hydrolysis), the rates of which have been established (Chapter 4). In some cases the reaction products are relatively non-toxic, in others they are less toxic than the CW agent, but long-lived.

   In the cases of mustard and Sarin, all the hydrolysis products are very much less toxic than

the agent and after approximately ten hydrolysis half-lives essentially no toxic material remains.

In the case of Tabun, after approximately ten half-lives essentially all the agent has been hydrolyzed into relatively non-toxic compounds except for the stable toxic compound HCN (hydrogen cyanide) of which approximately 170 g is produced per 1 kg of agent.

In the case of Lewisite, there is first a very rapid hydrolysis, occurring on the order of seconds, producing organic arsenic, which has substantial toxicity. Subsequently, very much slower reactions, occurring on the order of a few months, convert this organic arsenic to toxic, inorganic forms.

The values for *ten* hydrolysis half-lives of these agents are:

Agent	Ten half-lives
Mustard	53 hours
Lewisite	seconds (to organic arsenic, months to inorganic arsenic)
Tabun	400 hours (20% stable HCN produced)
Sarin	159 hours

2. *Following a sudden release of CW agent, what is the spatial extent of toxic contamination and how does it change with time?*

   It is expected that sudden release could occur only if a munition were fractured upon impacting the seafloor following dumping, or upon being impacted by a fishing (bottom) trawl. After a sudden release of all the agent in a munition, a "cloud" of contaminated water will be produced. This cloud grows in size because of mixing via eddy diffusion and is transported downstream by the local ocean current. Meanwhile, the process of hydrolysis continues to alter its chemical composition.

[29]Montgomery, J.H. and L.M. Welkom. 1990. *Groundwater Chemicals Desk Reference.* Lewis Publishers, Chelsea, MI.
[30]Howard, P.H. 1989. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume I.* Lewis Publishers, Chelsea, MI.
[31]Reference 9.

Because mixing upward in the benthic boundary layer is much slower than mixing horizontally, this cloud has an oblate spheroidal shape. For sudden release of 1 kg of an agent, the radius on the seafloor of this cloud at the ENEC level can grow to tens of meters over a few tens of hours. Its thickness or height above the seafloor will be less by a factor of $(K_V/K_H)^{1/2}$. Subsequently, the combined effects of mixing and hydrolysis then rapidly reduce the volume of toxic contamination to zero.

At one hydrolysis half-life, when the quantity has been reduced by 50 percent, approximately 90 percent of the remaining agent is contained within a box having the dimensions L_H x L_H x L_V, where these lengths are the horizontal and vertical mixing distances.

The instantaneous radius of this cloud of contamination is proportional to the first power of the quantity of agent released, and to L_H^2.

As a cloud of contamination is transported downstream by the current, it "sweeps out" a volume of seawater that is much larger than the volume of the cloud itself. For the agents considered, this volume could be as large as approximately 300,000 m³ at an EPEC level in a 0.1 kt current. By contrast, the instantaneous volume of the cloud would be no larger than approximately 30,000 m³ at EPEC.

3. *What is the spatial extent of the toxic plume that is expected to form if a CW agent is slowly released into the ocean over a long period of time?*

The size of the toxic plume formed by the slow release of an agent depends on the release rate Q, the two eddy diffusivities K_H and K_V, the specified concentration C and the local ocean current v. The maximum dimension of a plume is its down-current length along the seafloor, which is given approximately by $Q(4\pi C)^{-1}(K_H K_V)^{-1/2}$. The thickness of the plume is very much less, both because of the action of the current and because the vertical eddy diffusivity is much smaller,

probably by a factor of ten or more, than the horizontal diffusivity.

The volume of water contained within a plume of specified toxic concentration and the associated area of the seafloor beneath the plume, are important measures of the potential for causing significant biological effects. The volume of a plume is proportional to $C^{-2} Q^2 v^{-1}$ and its area on the seafloor area to $Q^{3/2} v^{-1} C^{-3/2}$.

Plume volumes at the ENEC level for a rate of release of Tabun or Sarin that would empty a 1 kg munition in twenty-four hours would be approximately 3,000 m³, with a corresponding seafloor area of 1,500 m². The thickness of such plumes will typically be only a few meters as would be expected from the volume/area ratio in the foregoing example.

Because of its very low dissolution rate, plumes generated by mustard have dimensions on the order of a few tens of centimeters, or less. Because the ENEC and EPEC values of organic arsenic are less than those for Tabun or Sarin. The volumes of the plumes at the same release rate are less by C^{-2}. These dimensions are, in fact, so small that the physical model used in this study is probably not applicable.

The most important result concerning the sizes of toxic plumes generated by single munitions is that their maximum dimensions are on the order of tens or hundreds of meters, not kilometers much less tens or hundreds of kilometers.

4. *To what degree are the answers to Questions 1 through 3 sensitive to details of the local ocean environment?*

Hydrolysis rates do depend on temperature and pH. However, temperature at the bottom of arctic seas is very stable as is the pH. In any case, the appropriate temperature and pH were used in Chapter 4 to develop values for the hydrolysis rates used in this chapter. There is, therefore, essentially no sensitivity to the answer to Question 1.

The dimensions of the cloud of contamination produced by sudden release of a CW agent do depend on the diffusivities with its radius proportional to LH and to the logarithm of other parameters and its height (thickness) additionally proportional to $(K_V/K_H)^{1/2}$. Moreover, the extent of the region swept out by the downstream transport of the cloud by the local ocean current clearly depends on the magnitude of that current. There is some substantial sensitivity to these parameters, but the values for the extent of toxic concentrations developed are upper bounds based on maximum expected values for diffusivities and cases were worked out for several values of local ocean current.

The same statements as in the foregoing paragraph also apply to the estimates of the extent of toxic plumes. The results carried forward into estimates of dump site contamination and into Chapter 8 are believed to be plausible upper bounds based on parametric analysis guided by an empirical understanding of the important physical quantities.

5. **What is the potential for the transport of toxic concentrations by ocean currents over great distances?**

There is essentially no possibility that contamination from a single munition due to any of the agents considered in this chapter could be transported at toxic levels over basin-wide distances, or even across regional scales.

For the short-lived compounds such as Tabun or Sarin, the process of hydrolysis sets an upper limit on the duration that is relevant, approximately ten hydrolysis half-lives. Even neglecting the very considerable effects of dilution (mixing) over such times, a few tens or hundreds of hours is insufficient to involve general ocean circulation resulting in arctic-wide transport.

When the effects of turbulent mixing are included, the effective spatial scales for the short-lived compounds are reduced to a few tens, perhaps a few hundreds, of meters. The concentrations of the long-lived compounds, *e.g.*, arsenic, are also diluted by mixing. Moreover, they are expected to

accumulate on suspended particulates and be carried to the sediments where stable long-term burial results. Given the quantities of Lewisite that were probably dumped, the sizes of seafloor areas that could be contaminated by arsenic at levels significantly above natural background do not appreciably exceed site dimensions.

6. **What is the total extent, including water volumes and affected areas of the seafloor, of toxic concentrations produced at a dump site?**

The best estimate that can be developed based on available information shows that at any of the dump sites considered here, the size of the seafloor area that can be contaminated at the ENEC level is much less than the area of the site.

If all of the dumped munitions are assumed to release their agents over a period of five years, the largest area found was for Site 121 in the White Sea where the area contaminated at ENEC was still a very small fraction of the site area for Tabun and still less for the other agents. In no case did the estimated size approach much less exceed the site area, and still less were the contaminated volumes or areas comparable with those of the regional seas.

The well-documented Baltic Sea experience suggests rather strongly that corrosion of CW munitions takes place over long periods, with some munitions releasing agents very soon after dumping and some remaining intact after fifty years. Thus it is plausible, though not conclusive, that the size of the area contaminated at ENEC will be a very small fraction of the total site area. The area contaminated at EPEC or ELEC will be smaller by orders of magnitude. The area of the plume generated by a single munition is proportional to $C^{-3/2}$, giving a reduction of 32 for EPEC, and 1,000 for ELEC, relative to ENEC.

Since the extent of toxic concentrations at ENEC or greater is confined to a few meters of the seafloor by the low vertical eddy diffusivity in the benthic boundary layer, the volumes of contaminated seawater are a small fraction of the site area multiplied by a few meters.

The methodology used did not permit estimating the time delay after the dumping until corrosive disintegration leads to the formation of toxic concentrations at the sites. Parametric analysis was used to bound the consequences of release once begun and to account for the possibility that a small fraction, five percent, of the munitions might fracture and release agents immediately upon dumping.

7. **What is the sensitivity of the answer to Question 6 to uncertainties in the analysis?**

There is significant sensitivity to uncertainties in the quantities of munitions that were dumped and to the condition of the munitions at the dump site with the passage of time. If there are reasons to think that agents not considered here, V-gas for example, had been dumped in arctic seas, the conclusions of this assessment would not apply.

There is less sensitivity to uncertainties in the description of the local ocean environment in the sense that upper bounds were obtained for the extent of toxic concentrations based on upper bounds for expected eddy diffusivities. This study sheds little light on the question of determining when toxic concentrations can be expected to appear at the dump sites. The uncertainty in this remains significant.

As long as it can be safely assumed that there are no additional dump sites located in very shallow waters, particularly in the southern Barents Sea where biological productivity is high, there is little sensitivity to dump site location.

There is a considerable sensitivity of contaminated volume to the toxicity being considered (*i.e.*, the concentration). The volume of a toxic plume is proportional to C^{-2}, and there could be order-of-magnitude uncertainty in the levels at a specific degree of biological effect, especially across all marine species.

CONCLUSIONS

- <u>Potential Sources of Environmental Effects from Chemical Munitions:</u> The main potential sources of environmental effect from chemical munitions present at the dump sites are acute toxicity of released agents and associated breakdown products, adverse effects from bioaccumulation of contaminants in the food web, and the long-term effects of permanently contaminating sediments with arsenic contained in Lewisite. Plumes of contaminants at toxic concentrations could be produced by Lewisite, Tabun, and Sarin. Mustard would not produce toxic plumes, but would be present for decades on the bottom as viscous liquid. Toxic plumes would aeffect the entire area of the disposal site for as long as it takes to empty the munitions that are present at the site. Arsenic could settle in large quantities of sediments at adverse concentrations and could affect an area up to several times the disposal site.

- <u>Potential for Released Contaminants to Bioaccumulate in the Food Web:</u> Most chemical agents and their breakdown products have no or very low potential to bioaccumulate in the food web. Arsenic has a low to moderate potential to bioaccumulate in organisms most closely associated with arsenic-contaminated sediments. At the deep disposal sites, bioaccumulation of arsenic in higher trophic levels would be very small because of the small contribution of the benthos to the pelagic food web. At the shallow disposal site, some bioaccumulation would occur in higher trophic levels because the benthos are more important in the food web at this site.

- <u>Potential Effects at Deep Disposal Sites Nos. 121, 122, 123, and 124:</u> Benthic and demersal organisms would be lost or reduced in number by toxic plumes and contamination of sediments by arsenic. Loss of benthic and demersal organisms would have a small effect on the ecosystems of the deep disposal site regions because the contribution of the benthos is small to the predominantly pelagic food web of the deep waters of the region. Marine mammals, which include endangered species, are at low risk at the deep disposal sites. Depths are at the limit or are too great for bottom feeding by seals and walrus. Whales are unlikely to come in contact with the bottom or enter the water near the bottom containing toxic plumes.

- <u>Potential Effects at Shallow Disposal Site No. 134:</u> Benthic and demersal organisms would be lost or reduced in number by toxic plumes and contamination of sediments by arsenic. Effects on the seal and bird populations of the Kolguev Island region would be moderate to large because the loss of carrying capacity from the site is large relative to the marine area supporting these populations. The size of bird and mammal populations on the island could decline to match the resources available. Ecosystem effects on the Pechora Sea region would be moderate to small. This would depend mainly on the size of the area affected deleteriously by arsenic in sediments. This would add to an existing large area of contamination.

  Some bioaccumulation of arsenic could occur at higher trophic levels because of the importance of the benthos in the food web of the region and the accessibility of contaminated sediments to seals and walrus.

- <u>Potential Effects on Human Health and Safety:</u> The risk of increased cancer to consumers eating fish contaminated with arsenic from the sites is near the upper limit of the risk deemed acceptable by U.S. regulatory agencies. Indigenous people eating large quantities of contaminated fish could have a small to moderate increased risk. Fishing boat crews would be at risk of injury or death from capturing mustard lumps or munitions containing agent in trawl nets fished on the bottom. Oil and gas workers are at a small risk of injury or death during activities that could bring an agent to the surface or could contaminate drilling or pipelaying equipment.

- <u>Potential Economic Effects:</u> Commercial fish stocks near Site 134 in the Pechora Sea could have increased body burdens of arsenic, especially the demersal species, which could exceed arsenic standards for Finland (5 ppm) and the United Kingdom (one ppm) and some other non-European countries. Economic effects would be small because stocks can be sold in countries without standards, although there could be some temporary effect while new markets are found. Economic effects could be greater if other countries or consumers become concerned about arsenic contamination in fish from the region.

  Oil and gas resources within Sites 121, 123, and 134 could not be exploited if drilling could not be carried out from within the site boundaries. If operations can take place within sites, exploration and exploitation costs could be significantly increased if munitions must be cleared from an area before undertaking activities.

8.1 INTRODUCTION

The data presented in the previous chapters shows that the chemical warfare munitions and agents at disposal sites in the Barents, Kara, and White Seas pose a threat to the arctic marine ecosystems, to the regional economy based on exploitation of these ecosystems, and to human health and safety. These threats include the following:

- Acute toxicity to marine organisms of agents and breakdown products released into the water,

- Chronic toxicity on marine organisms of long-lived contaminants in the sediments,

- Bioaccumulation or biomagnification of released contaminants in the food web,

- Human health effects from consuming marine organisms that have accumulated released contaminants,

- Threat to human safety if munitions are caught in commercial fishing nets or encountered during oil and gas resource development activities,

- Regional economic effects if commercial fish stocks are reduced in size, if sales of commercially important species are affected by contamination with released agents or breakdown products, or if additional large areas are closed to fishing and oil and gas resource development activities.

This chapter assesses the possible magnitude of the environmental, human health and safety, and economic effects that could result from the above environmental threats. The results of the analyses presented in the previous chapters provide much of the input for estimating the likely effects. The starting point for the assessment is the description of the regional ecosystems (Chapter 3). The types, quantities, and distribution of munitions and chemical agents in the disposal sites (Chapters 2 and 5) establish the magnitude of the chemical threat that could be present at the sites. Chapter 7 describes how these chemical agents would react and spread in the environment when released from the munitions; and on the amount of bottom area and water volume affected at

contaminant concentrations injurious to aquatic organisms are estimated (Chapter 7). This information is the basis for estimating the magnitude of the effect on biological communities in the site regions. The data in Chapter 4 on chemical properties of the agents and their breakdown products is used to determine if these contaminants can bioaccumulate or biomagnify in the food web to harmful concentrations (Chapter 4). Chapter 6 establishes the environmental concentrations of agents and breakdown products that can be harmful.

Other activities besides the disposal of chemical munitions have also affected the regional environment. Effects from chemical munitions disposal would add to the environmental impacts resulting from these other past, current, and future activities. Environmental effects from these other activities include the following:

- Possible over-exploitation of the commercial fish stocks and damage to benthic habitats by the large commercial fishery in the Barents Sea,

- Release of contaminants and damage to benthic habitats from exploration and exploitation of regional oil and gas resources,

- Release of radioactive contaminants from testing of nuclear weapons in the atmosphere and the disposal of nuclear wastes,

- Emissions and effluents from mining activities on the Kola Peninsula,

- Long-range transport of contaminants into the region from elsewhere in Europe and Russia.

Details of the assessment of the threats to the environment, human health and safety, and the region economy are given in Sections 8.3 through 8.9. Table 8-1 provides a summary of the main findings of this assessment.

Table 8-1: Summary of Potential Environmental, Health, Safety, and Economic Effects From the Presence of Chemical Munitions in the Barents, Kara, and White Seas

Potential Effects	Deep Disposal Sites	Shallow Disposal Site 134
Potential for bioaccumulation of contaminants in the food web	Measured or estimated log k_{ow} values negative or very small for most agents and breakdown products. None are likely to bioaccumulate. Chlorobenzene could have a low but not significant bioaccumulation. Arsenic would have low tendency towards bioaccumulation, but would not biomagnify in higher trophic levels. Arsenic increase likely in trophic levels closely associated with contaminated sediments.	
Acute Toxicity Effects **Presence of viscous mustard**	Seals could ingest mustard, however sites may be too deep or unattractive for feeding. Sites too deep for walrus feeding. Whales have low potential for contacting bottom.	Walrus and bottom-feeding seals at risk because bottom within diving range. Risk may be low because of low encounter rate or possible learned avoidance of lumps. Whales have low potential for contacting bottom at site. Humpback whale could contact bottom with jaw if certain feeding behavior used. Effect would likely be blistering or lesions.
Toxic plumes of Lewisite, GA and GB	Benthic biomass eliminated or reduced over entire site for period of release of agent from all munitions. Effect of productivity loss small to dominant pelagic ecosystem present at deep water sites. Risk of mortality or injury small to marine mammals because sites unattractive as feeding areas. Whales unlikely to enter toxic plume near bottom. *Recovery:* Slow, requiring ten to perhaps twenty years to regain biomass and diversity.	**Kolguev Island Region** Benthic biomass eliminated or reduced over entire site for period of release of agent from all munitions. Effect of productivity loss moderate to large because of reduced carrying capacity for island seal and bird populations supported by resources in site vicinity. Risk of mortality or injury greatest for seals and walrus during five-year release period because forty percent of site bottom area covered by toxic plumes on any day. Only six percent covered on any day for forty-year release period. *Recovery:* Slow, requiring ten to perhaps twenty years to regain biomass and diversity in site area. Island seal and bird populations would recover as region carrying capacity is regained. **Pechora Sea Region** Benthic biomass eliminated or reduced over entire site for period of release of agent from all munitions. Effect of lost productivity on 528 km^2 site small on roughly 110,000 km^2 region shallower than 100 m. Arcto-Norwegian cod and haddock stocks could be affected in vicinity of site, but stocks are very large and widespread in region. Polar cod spawning of pelagic eggs occurs over region large in relation to area of site. Marine mammals distributed over area very large in relation to site area. *Recovery:* Slow, requiring ten to perhaps twenty years to regain biomass and diversity in site area. Small loss of carrying capacity regained for region.

Table 8-1: Summary of Potential Environmental, Health, Safety, and Economic Effects From the Presence of Chemical Munitions in the Barents, Kara, and White Seas (continued)

Potential Effects	Deep Disposal Sites	Shallow Disposal Site 134	
		Kolguev Island Region	**Pechora Sea Region**
Permanent arsenic contamination of sediments	Arsenic could permanently contaminate up to 2420 km² at sites in Barents and Kara Seas and 1290 km² at White Sea site at biological benchmark concentration of 90 mg kg⁻¹ which is likely to cause effects on benthic community. Contaminating maximum area very unlikely. Benthic and demersal organism biomass and diversity could be greatly reduced in contaminated region. Low effect on region because of small contribution of benthic community to pelagic food web. Arsenic would increase in tissues of benthic and demersal organisms. Low potential for transferring arsenic to higher trophic levels.	Arsenic could permanently contaminate an area up to four or five times the 528 km² site at biological benchmark concentration of 90 mg kg⁻¹ which is likely to cause effects on benthic community. Contaminating maximum area very unlikely. Biological effects: Benthic and demersal organism biomass and diversity could be greatly reduced in contaminated region. Loss of carrying capacity from largest area could have large effect on island bird and seal populations. Bioaccumulation: Arsenic would increase in tissues of benthic and demersal organisms. Moderate potential for transferring arsenic to higher trophic levels because of importance of benthos in food web. Possibility of transferring arsenic in phytoplankton lipid compounds if arsenic is mixed to surface during spring bloom period. Transport in ice: Potential that arsenic could be incorporated into ice and transported away from area.	Site area contaminated added to 5000 km² area already contaminated in the sea. Biological effects: Upper bound total of about 7400 km² for two contaminated areas would be in range of five to ten percent of region area shallower than 100 m. Carrying capacity of region could begin to be affected if largest area contaminated at site. Contaminating maximum area very unlikely. Bioaccumulation: Arsenic would increase in tissues of benthic and demersal organisms in contaminated area. Moderate potential for transferring arsenic to higher trophic levels because of importance of benthos in food web. Some potential for arsenic increase in commercial fish stocks, mainly demersal species.
Seasonality of effects	Migratory stocks such as cod, haddock, and whales not present during ice-cover period. Potential slightly greater during warm period because migratory stocks present and biological productivity high near water surface. Small interaction of benthic community and near-bottom water with surface waters.	Risk to ice-associated species, such as seals, walrus, and polar bears, greatest during ice formation and ice melt when ice is present over and near site. Risk to migratory species greatest when present during warm period. Possibility of transferring arsenic in phytoplankton lipids greatest during intense bloom period in spring and summer when biological productivity is greatest.	

8-4

Table 8-1: Summary of Potential Environmental, Health, Safety, and Economic Effects From the Presence of Chemical Munitions in the Barents, Kara, and White Seas (continued)

Potential Effects	Deep Disposal Sites	Shallow Disposal Site 134
Economic threat to commercial fishery	Low possibility of effect. Size of pelagic stocks or arsenic in tissues not likely to be affected because of small contribution of benthos to food web. Bottom trawling not currently a harvest method at sites.	Fish sales: Stock size not likely to be effected significantly, although some potential if large area affected by arsenic. Increased arsenic in tissues of demersal fish and shellfish species, and possibly some pelagic species, in vicinity of contamination. Finnish and United Kingdom standards likely to be exceeded in demersal species and possibly in some pelagic species. Temporary economic effect if sales are shifted to other markets. Large economic effect possible if other nations ban sales or consumers develop negative attitude toward regional fish products because of concern over arsenic contamination. Fish oil: No effect likely because refining process likely to reduce arsenic to concentration less than regulatory concern. Closure of fishing area: Fishing currently discouraged in site area. Presence of munitions would result in continuation of current situation.
Effects on oil and gas exploration and exploitation activities	No activities within site: Current directional drilling technologies could access resources only within a few km of boundaries. Most resources under sites 121 and 123 could not be reached. Sites 122 and 124 could potentially be exploited by directional drilling. Activities within site: Costs increased if survey for munitions or munitions clearing required. Costs potentially high for munition clearing.	No activities within site: Current directional drill technologies could access resources only within a few km of boundaries. Activities within site: Costs increased if survey for munitions or munitions clearing required. Costs potentially high for munition clearing.
Threat to human health and safety		Consumers of arsenic-contaminated fish: Risk of cancer small for consumption at high end of U.S. range. Risk is below range of regulatory concern set by U.S. agencies responsible for human health. Risk to indigenous people who consume large quantities of fish is small to moderate. Upper end of risk range within lower end of range of regulatory concern set by U.S. agencies responsible for human health. Consumers of fish oil: Insignificant risk of cancer because refining process likely to reduce arsenic contamination to low amounts Fishing boat crews : Could be exposed to injury and death if munitions or mustard lumps are captured in trawl nets fished on the bottom. No reports of incidents from study region were found in literature reviewed. Oil and gas resource exploration and exploitation crews: Crews could be exposed to agent contaminating equipment that comes in contact with bottom or enters toxic plumes near bottom. Crews could also be exposed to agents brought to the drilling platform in drilling muds or circulated to the waters surface.

Table 8-1: Summary of Potential Environmental, Health, Safety, and Economic Effects From the Presence of Chemical Munitions in the Barents, Kara, and White Seas (concluded)

Potential Effects	Deep Disposal Sites	Shallow Disposal Site 134
Cumulative impacts	Environmental effects from chemical munitions would add to effects of other past and ongoing activities in the regional marine environments. These include the possible over exploitation of commercial fish stocks and damaging of benthic habitat by the large commercial fishery in the Barents Sea, contaminant release and habitat alteration from the exploration and production of regional oil and gas resources, release of radioactive contaminants from testing of nuclear weapons in the atmosphere on Novaya Zemlya, disposal of liquid and solid nuclear materials, emissions and effluents released by mining activities on the Kola Peninsula, and long-range transport of contaminants into the region from elsewhere in Europe and Russia.	

8.2 ANALYTICAL APPROACH

The potential sources of impacts on the biological communities and ecosystems of the study region are the acute toxicity of the released agents and breakdown products, the permanent contamination of sediments with arsenic, and possible bioaccumulation of contaminants in the food web. Described below are the considerations important in determining the kinds and magnitude of effects that can be caused by these sources of impact.

The type of food web present at a disposal site is also important in determining how released agents can affect the biological community. This issue is considered when determining whether the disposal sites must be analyzed separately or can be grouped for analysis.

8.2.1 Grouping of Disposal Sites for Analysis

Chapter 3 describes the structure and function of the biological communities and ecosystems in the study region. In deep water areas, the biological productivity and energy flow take place primarily in the water column. The contribution of the benthic community to the biological activity in the water column is small. Thus there should be relatively little exchange of materials between the upper ocean ecosystem and materials near the seafloor. In shallow water, the benthic community is a much more important component of the biological system.

When we examine the characteristics of the disposal sites as given in Chapter 3, we see that four sites (Site 120 in the White Sea, Site 122 in the Barents Sea, and Sites 123 and 124 in the Kara Sea) are in water deeper than 200 m and are similar in temperature, salinity and stratification. These sites are grouped together for analysis because they are likely to have pelagic food webs that are similar. Site 134 in the southeastern Barents Sea, however, is in much shallower water (about 30 - 50 m) and is likely to have a bentho-pelagic food web. This site is analyzed separately.

8.2.2 Determining the Potential for Contaminants to Bioaccumulate or Biomagnify in the Food Web

Log K_{ow} values are used to estimate the bioaccumulation potential of the chemical agents and breakdown products discussed in Chapter 4. These values are given in Tables 4-18 through 4-21.

Bioaccumulation of contaminants is the net accumulation of a substance by an organism as a result of uptake from all environmental sources. Environmental contaminants can accumulate in the tissues of organisms or bioaccumulate throughout the food web at concentrations that are many times greater than in the water or sediments to which the organisms are exposed. Organisms can be adversely affected if the accumulated concentration is great enough.

Of particular concern in bioaccumulation is the special process of biomagnification of concentration through the food web. Hydrophobic chemicals, such as DDT and other chlorinated organic compounds, are particularly prone to exhibit this phenomenon. Biomagnification occurs when an absorbed or ingested contaminant is not metabolized or excreted but, instead, is stored preferentially in fatty tissue. It accumulates and is passed on to the next level in the food web. As a result, the quantity of the contaminant in the body increases dramatically at each level. This process affects organisms at the top of the food web, such as polar bears and sea birds, even though the contaminants are present at very low, non-toxic concentrations in the water. It results in accumulated amounts that are orders of magnitude greater than the amounts found in the water or sediments that serve as the source of the contamination.

The potential to bioaccumulate and biomagnify has been measured experimentally for many chemicals and can be estimated from chemical properties using several methods. For organic chemicals, the octanol-water partition coefficient (K_{ow}) can be used as an indicator of bioaccumulation potential. Values of K_{ow} for the agents of interest are tabulated in Chapter 4, Tables 4-18 through 4-21.

K_{ow} is determined experimentally by adding a chemical of interest to a two-phase system consisting of water and the alcohol 1-octanol. This alcohol is a good surrogate for lipids, such as fish fatty tissue. After the mixture is shaken, the amount of the chemical dissolved in the water and alcohol phases is measured. Kow is defined as the ratio of the amount of chemical in the alcohol phase to that in the water phase. The result is often reported as the logarithm of the ratio.

The greater the log K_{ow} value, the greater is the affinity of a chemical for lipids and the greater is the potential for a chemical to bioaccumulate or biomagnify in the food web. Chemicals with log K_{ow} in the 4 to 7 range bioaccumulate to the greatest degree and are of greatest concern.[1]

8.2.3   Analyzing the Acute Toxicity Effects of Mustard

Mustard exposed by the corrosion of munitions would exist as a solid or viscous liquid on the bottom. In Section 7.6.2, the analysis shows that the rate of dissolution of this mass is so slow that no toxic concentration of mustard would be produced in the water surrounding the mustard lump. Individual mustard lumps of 1 kg, once exposed to water, would last for many months, taking from 150 to 250 days to dissolve completely. Because the munitions at a site would constantly be corroding through, mustard lumps are likely to be present at a site for the many years that it takes for complete disintegration of all munitions. It is assumed in this analysis that mustard is present at the site for the entire period of agent release.

The effects of mustard in the environment would result from contact of organisms with the lumps. The magnitude of the effect would be a function of the probability of such contact and the injury or death that results.

8.2.4   Analyzing Acute Toxicity Effects of Lewisite, Tabun, and Sarin

In Section 7.6.3 and 7.6.4, we can see that it is possible for munitions leaking Lewisite, Tabun, and Sarin to release agent or breakdown products into the surrounding water at concentrations potentially toxic to marine organisms. The resulting downcurrent plume would remain on the bottom and mix vertically only a few to a few tens of meters. The size of this plume is dependent on the rate of leakage. Toxicity could be confined to within only a few centimeters to a meter of a leaking munition at the low, but plausible, leakage rates analyzed. At the high release rates of 1 to 10 kg day^{-1}, the toxic plume could extend a few to a few tens of meters along the bottom. Because the plumes

produced stay on and near the bottom, the main effects would be on benthic organisms covered by the plume and on mobile species, such as marine mammals and fish schools, that could swim into the plume near the bottom.

The ecosystem effect of toxicity to benthic organisms is determined by the loss of biomass and productivity and by the importance of the benthic community to the food web at that location. This effect would be partly determined by the size of the area affected and the length of time the effect remains.

At the high release rates of 1 to 10 kg day^{-1}, it is likely that the benthic communities would be reduced in biomass or eliminated over much of the site because of the likely random nature of release from individual munitions over time and the slow recovery rate of arctic benthic communities. As munitions randomly release their contents over the five to fifty year periods analyzed in Chapter 7, each plume would affect a small area of benthic community for a period of one day to perhaps 10 or so days. This same bottom area would soon be affected once again by the plume from another nearby munition when its contents were released. The return period of effect on an area of bottom could vary from a few days to a few months depending on the length of the period over which all munitions released their contents and the number of munitions present at a site. Because the recovery rate for benthic communities in arctic waters may be a decade or longer, the overall effect within the site is that the entire bottom area would be affected for the entire release period. Benthic recovery rate is discussed in more detail in later sections of this chapter.

For mobile organisms, such as marine mammals, the potential to be exposed to harm is largely a function of the probability of swimming into an area of toxicity near the bottom. This probability would be determined by the area of bottom covered and volume of water at harmful concentrations that exists on any day during the period of release. The area of bottom covered calculated in Section 7.7 has been used in this analysis.

Lewisite breakdown products are arsenicals. Since inorganic forms of arsenic have toxicity, these

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[1]Baird, C., 1995. *Environmental Chemistry*. W.H. Freeman and Company, New York, NY.

breakdown products could have continued toxicity as they are transformed in the marine environment. As discussed below, the first toxic breakdown products of Lewisite are organic compounds and are about as toxic as Lewisite. Inorganic arsenic compounds shown in Table 6-1 are toxic at a concentration about one-third that of Lewisite. Therefore, any toxicity from inorganic arsenic, if it occurs, would be encompassed within the plume dimensions of Lewisite breakdown product.

Chlorobenzene is an additive in German-produced Tabun and would be released with Tabun. The acute toxicity of chlorobenzene is three orders of magnitude less than Tabun, so it is likely that chlorobenzene would not be released in toxic concentrations.

Cyanide is a breakdown product of Tabun. Cyanide is three to four times less toxic than Tabun. Therefore, any toxicity from cyanide would be encompassed within the plume dimensions of released Tabun.

Fluoride and dimethylamine are breakdown products of Tabun and Sarin. Their toxicity is two orders of magnitude less than Tabun and Sarin. Any toxic concentrations from these substances would be encompassed within the plumes of Tabun and Sarin.

8.2.5 Analyzing Contamination of Sediments with Arsenic

Arsenic released from munitions in Lewisite would be distributed in the marine environment by currents and other natural transport phenomena. It is anticipated that much of it would be carried to the sediments eventually. How much the sediment concentration increases beyond its natural background concentration would depend on how widely the arsenic is dispersed and diluted before settling into the sediments. The concentration of arsenic in the sediment is important because it determines the ecological effect. Benchmark concentrations of sediment arsenic concentrations are used to determine how large an area could be contaminated at biologically harmful concentrations.

The Barents and Kara Seas are not likely to be widely contaminated by anthropogenic sources of arsenic and, thus they should have sediment arsenic concentrations in the range of naturally occurring values for marine sediments. A mean arsenic concentration of 13 mg kg^{-1} has been measured at uncontaminated sites in U.S. coastal and estuarine locations and 25 mg kg^{-1} for similar sites worldwide.[2] Thus, tthe natural background sediment concentration of arsenic in the Barents and Kara Seas is estimated to be 10 mg kg^{-1}.[3]

No measurement of arsenic in White Sea sediments has been found in the literature. The White Sea receives effluents from human activities and may be contaminated with arsenic. For purposes of this study, the estimate of arsenic concentration in the sediments of the deep basin in the White Sea is 20 mg kg^{-1}.

Benchmark concentrations for arsenic in sediment that cause no biological effect and the median value that has been demonstrated to cause biological effects have been determined by Long and Morgan.[4] The lower value, called effects range-low, is the sediment concentration at the low end of the range in which biological effects were observed. This value was estimated to be 33 mg kg^{-1}. The higher value, called effects range-median, is the sediment concentration median for reported values associated with biological effects. This value was estimated to be 85 mg kg^{-1}. The benchmark values selected for analysis of biological effects at CW disposal sites are 40 mg kg^{-1} and 90 mg kg^{-1}, which are rounded approximations of the Long and Morgan values.

The distance that arsenic, released from Lewisite, travels before settling in the sediments cannot be estimated with precision. This issue is important, however, because transport distance determines dilution and spatial distribution of the arsenic before deposition and adsorption occurs.

[2] Cantillo, A.Y. and T.P. O'Connor. 1992. "Trace Element Contaminants in Sediments From the NOAA National Status and Trends Programme Compared to Data From Throughout the World." *Chemistry and Ecology* 7:31 50.

[3] Loring, D.H. et al. 1995. "Arsenic, Trace Metals, and Organic Micro Contaminants in Sediments From the Pechora Sea, Russia." *Marine Geology* 128:153-167.

[4] Long, E.R. and L.G. Morgan. 1990. *Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program.* NOAA Technical Memorandum NOS OMA 52. PB91-172288, National Technical Information Service, Springfield, VA.

Bounds on the area contaminated at the biological benchmark sediment concentrations can be estimated. These bounds are calculated by determining how large an area the quantity of arsenic potentially present at a disposal site must be spread over and mixed 10 cm deep into the sediments to increase the total arsenic concentration to the benchmark concentrations. This assumes that the background concentrations for arsenic presented above are present. A depth of 10 cm was used as a reasonable depth for mixing by organisms that live in the sediments (bioturbation). Figure 7-38 also shows the sediment concentration of arsenic as a function of area for a range of arsenic quantities released, but for a mixing depth of only 1 cm.

8.3 POTENTIAL OF RELEASED CONTAMINANTS TO BIOACCUMULATE IN THE FOOD WEB

Measured and estimated values for log K_{ow} for agents and breakdown products are listed in Chapter 4, Tables 4-18 through 4-21. The log K_{ow} values for most of the compounds are very low or negative. Therefore, many of these contaminants are not likely to exhibit any tendency to bioaccumulate in the food web. In contrast, the estimated log K_{ow} value for Lewisite is near the lower end of the range of greatest concern for bioaccumulation given in Section 8.2.2. Since Lewisite is short-lived and therefore is unlikely to be released to the environment in any significant quantity, it is unlikely that it would bioaccumulate to any significant extent.

Chlorobenzene, an additive to Tabun, has a log K_{ow} value of 2.84 and a bioconcentration factor of 645.[5] It is likely that some bioaccumulation of chlorobenzene could occur at the lowest trophic levels. However, it is also likely, given the log K_{ow} value, that there is a low potential to bioaccumulate at higher trophic levels.

Arsenic does not biomagnify in the food web,[6,7] most likely because animals convert arsenic to organoarsenic compounds that can be excreted. However, arsenic does bioaccumulate in marine organisms at concentrations greater than in the water surrounding the organism. The log of the bioconcentration factor for arsenic in fish is 2.5.[8] A bioconcentration factor is the ratio of the concentration of a chemical measured in the tissue of an organism to the concentration in the surrounding water. High concentrations of arsenic have been measured in organisms from environments with abnormally high levels of arsenic in the sediment or water,[9,10] such as areas polluted by mining wastes or industrial wastewater discharges. Concentrations are often greater in mollusks and crustaceans than in fish.[11]

8.4 ECOLOGICAL EFFECTS AT DEEP DISPOSAL SITES

The deep disposal sites are analyzed together. As discussed in Section 8.2.1, these sites have similar physical characteristics and the biological community is likely to be a pelagic food web, so the environmental effects from agent release are likely to be similar at the sites.

As can be seen in Chapter 7, agents released from leaking munitions would stay near or on the bottom and the arsenic released from Lewisite would eventually end up as a long-term contaminant in the sediments. Therefore, the acute and chronic toxicity would be exerted mainly on benthic communities and on any mobile organisms that swim near the bottom or feed on benthic organisms.

The ecological effects at the deep disposal sites should be small because of the small amount of benthic area affected and the small contribution (biological coupling) of the benthic community to the pelagic food

[5]U.S. Environmental Protection Agency. 1979. *Water-Related Environmental Fate of 129 Priority Pollutants, Volume I: Introduction and Technical Background, Metals and Inorganics, Pesticides and PCBs.* EPA-440/4-79-029a. Office of Water Planning and Standards, Washington, DC.
[6]United Nations Environmental Program, 1988. "GESAMP: Arsenic, Mercury and Selenium in the Marine Environment. UNEP Regional Seas Reports and Studies No. 92." *GESAMP Reports on Studies No. 28.* New York, NY.
[7]Biddinger, G.R. and S.P. Gloss. 1984. "The Importance of Trophic Transfer in the Bioaccumulation of Chemical Contaminants in Aquatic Ecosystems. *Residue Reviews* 91:103-145.
[8]U.S. Environmental Protection Agency. 1989. *Assessing Human Health Risks from Chemically Contaminated Fish and Shellfish: A Guidance Manual.* EPA-503/8-89-002. Washington, DC.
[9]Reference 6.
[10]National Research Council of Canada, 1978. *Effects of Arsenic in the Canadian Environment.* Publication No. NRCC 15391. Ottawa, Ontario.
[11]Tamaki, S. and W.T. Frankenberger, Jr., 1992. "Environmental Biochemistry of Arsenic." *Reviews of Environmental Contamination and Toxicology* 124:79-110.

web likely to be present. However, in other marine ecosystems, resting or larval stages of various organisms may spend part of their existence in the bottom sediments. These forms later return to the upper ocean either when conditions improve or as the organisms mature. This would provide a pathway between the benthic and upper ocean communities. It is not known if such processes are significant at the deep disposal sites, but the evidence suggests that this is not the case.

8.4.1 Effects of Mustard

Mustard may be present in a viscous form on the seafloor somewhere on the site for many years. Benthic organisms would be killed when exposed to or contact with mustard. The exposed surface area of mustard is small and therefore, the number of benthic organisms killed by contact with mustard would be a very small loss to the food web and unlikely to have measurable effects.

Marine mammals could be injured or killed by ingesting or coming into contact with the mustard substance, however, this risk is likely to be very low. Injury or death to seals from ingesting or coming into contact with mustard while feeding on the bottom is possible, but is likely to be small at the deep disposal sites because benthic feeding species are not attracted to the deep locations for feeding. The depth of the sites is within the diving range of the harp seal which is able to dive to depths of 300 m. They feed on benthic fishes and crustaceans.[12] Bearded seals feed on benthic invertebrates.[13,14] This species occurs on ice over waters of depths of 200 m or less, so the sites would be at the limit of their diving range. The low benthic biomass at the Kara Sea sites (less than 10 g m^{-2}) will likely make these areas unattractive for feeding by seals that forage on benthic organisms. Site No. 123 at the northern end of Novaya Zemlya may be too deep for seal feeding if the munitions are in the deeper sections of the site. Benthic biomass at the White Sea site is not known, but may be low because of the muddy sediments present. Site No. 122 in the Barents

Sea has greater biomass (possibly 50-200 g m^{-2}) than the other sites and could be used by seals during the period when ice conditions are favorable for seals to be present.

Walrus are found in the vicinity of the Kara and Barents Sea sites. It is an endangered species that feeds predominantly on mollusks and other benthic organisms. The sites, however, are too deep for walrus foraging because they are limited to a diving depth of about 80 m.[15] No walrus live in the White Sea.

Whales would not ingest mustard because there are no bottom-feeding whales in the study region. Most whales inhabiting, the disposal sites, feed in the water column and would have a very low probability of contacting the bottom. Humpback whales, however, may come in contact with the bottom during certain feeding behaviors[16] and would have a slight possibility of coming into contact with mustard if this behavior occurs in the study region. The expected effects include lesions from the vesicant action of the mustard, most likely in the jaw region. While it is unlikely that this effect would be significant within the humpback whale population in the region, any effect on these whales is of concern because of their status as an endangered species.

8.4.2 Toxic Effects of Lewisite, Tabun, and Sarin

Benthic and demersal organisms would be eliminated or significantly reduced in numbers or species diversity over the area of the disposal site for the entire period of agent release from the munitions present at the site. The effect is independent of the period of release because of the slow recovery rate of arctic benthic organisms, as discussed in Section 8.2.4.

The effect of the loss of benthic organisms and productivity on higher trophic levels in the region of the sites would likely be small. The food web and energy flow of the deep water areas is located predominantly in the near-surface waters. The organic matter produced by the phytoplankton when light is

[12]Lydersen, C. et al. 1991. "Feeding Habits of Northeast Atlantic Harp Seals (Phoca groenlandica) Along the Summer Ice Edge of the Barents Sea." *Canadian Journal of Fisheries and Aquatic Science* 48:2180-2183.

[13]Dayton, P.K., 1990. "Polar Benthos." *Polar Oceanography, Part B: Chemistry, Biology, Geology*. Academic Press, New York, NY.

[14]Lewbel, G.S. (ed.)., 1983. *Bering Sea Biology: An Evaluation of the Environmental Data Base Related to Bering Sea Oil and Gas Exploration and Development*. LGL Alaska Research Associates, Inc., Anchorage, AK, and SOHIO Alaska Petroleum Company, Anchorage, AK.

[15]Reference 14.

[16]Hains, J.H.W. et al. 1995. "Apparent Bottom Feeding by Humpback Whales on Stellwagen Bank." *Marine Mammal Science* 11(4):464-479.

available is consumed heavily by zooplankton and other nekton within the surface water layers. Fecal material produced by these grazers may sink to the seafloor where it will be available to the benthic community. The higher trophic levels of fish, birds, and mammals that feed on the upper ocean are found predominantly in the near-surface water where the food is available. In this system, benthic biomass is low and the benthic community contributes only small or modest amounts to the pelagic food web because of the small biomass of organisms available and the depth of the water.

Risk of mortality or injury to marine mammals would be small. The risk of injury to seals would largely be based on the probability of swimming into a plume of agent at a harmful concentration near the bottom; the more area covered at any time, the greater is the possibility of encountering such a plume. The area of bottom covered at any time during the release period has been estimated in Section 7.7. As would be expected, the amount of area covered and volume affected is greatest for a five-year release period and least for a fifty-year release period (see Figures 7-34 through 7-38). For seals, the depth of the sites and the likely small quantity of biomass present, as discussed above for mustard, makes these areas unattractive feeding locations. There would be no risk to walruses because the sites are too deep for feeding. Whales would only be affected if they enter the toxic plume near the bottom, which is unlikely because no bottom-feeding whales inhabit the region of interest.

There is some uncertainty in the above analysis because it is possible for a disposal area to be located in a habitat important for a particular species or for a particular life stage of an organism. No detailed data are available on the biological communities of the disposal sites. However, the data reviewed for this study does not suggest that the disposal sites are located in any areas of special significance.

Recovery of benthic and demersal communities would occur when toxic plumes are no longer present. Data on the rate of recovery of benthic and demersal communities at deep arctic locations was not found. Benthic organisms may grow slowly, have long individual life spans, and low turnover rates.[17,18] Many organisms brood their young rather than release pelagic larvae.[19] Dispersal of brooded young into a site would be slow. Pelagic larvae would colonize the site much faster. It is likely that the rate of regeneration would be slow, perhaps requiring a period of one or two decades to recover to the original biomass and diversity.

8.4.3 Long-Term Effects of Arsenic-Contaminated Sediments

Arsenic, a persistent contaminant from Lewisite, would be added permanently to the sediments and be available for uptake by marine organisms. Because arsenic is potentially toxic, there could be chronic toxic effects from its long-term presence in the sediments of the regional environment.

Marine organisms can be exposed to arsenic in sediments in several ways. These include absorption of dissolved arsenic from the water or sediments through the skin and gills, eating other organisms containing arsenic in their tissue or gut, ingesting contaminated sediments as a food source or incidentally while feeding on benthic organisms, and filtering contaminated particles from the water.

Arsenic is biologically available primarily in the inorganic dissolved form.[20] Organic arsenic breakdown products of Lewisite will ultimately be converted to inorganic forms and enter into the natural arsenic cycle. Marine phytoplankton and macroalgae readily take up the inorganic form arsenate[21] and convert it to water-soluble and lipid-type compounds, primarily ribosides. Animals convert arsenic compounds into low-toxicity organic forms, primarily arsinobetaine.[22] The organic arsenics are readily excreted by animals.

[17]Grebmeier, J.M. and J.P. Barry. 1991. "The Influence of Oceanographic Processes on Pelagic-Benthic Coupling in Polar Regions: a Benthic Perspective." *Journal of Marine Systems* 2:495-518.

[18]Grebmeier, J.M., H.M. Feder, and C.P. McRoy. 1989. "Pelagic-Benthic Coupling on the Shelf of the Northern Bering and Chukchi Seas, II. Benthic Community Structure." *Marine Ecology Progress Series* 51:253-268.

[19]Reference 17.

[20]Reference 11.

[21]Phillips, D.J.H. 1990. "Arsenic in Aquatic Organisms: a Review, Emphasizing Chemical Speciation." *Aquatic Toxicology* 16:151-186.

[22]Francesconi, K.A. and J.S. Edmonds. 1993. "Arsenic in the Sea." *Oceanography and Marine Biology Annual Review* 31:11-151.

Several factors determine whether arsenic in sediments could have adverse effects on regional marine ecosystems. These include the concentration of arsenic in the sediment, the total area affected by concentrations that could have adverse affects, the bioavailability of the arsenic, and the potential of arsenic to bioaccumulate or biomagnify in the food web.

8.4.3.1 Estimate of Arsenic Contamination of Sediments at Biological Benchmark Concentrations

In Section 8.2.5, arsenic sediment concentrations of 40 mg kg^{-1} and 90 mg kg^{-1} were selected as biological benchmarks for analyzing the possible effects of arsenic on benthic populations.

Table 8-2 shows the area of sediment that could be contaminated at these biological benchmark concentrations by different quantities of arsenic that could be present at a disposal site. These areas were calculated by the method discussed in Section 8.2.5. Figure 7-38 also shows the sediment concentration of arsenic as a function of area for a range of arsenic quantities released. This area calculation assumes a uniform distribution of arsenic mixed into sediment at a depth of 1 cm. To match the data in Tables 8-2 and 8-3 the mixing depths must be reduced by an order of magnitude.

The quantities of Lewisite in Tables 8-2 and 8-3 are bounding values. The highest value of 75,000 tons disposed at a site is highly unlikely. It could only occur if all munitions dumped in the Kara or White Seas were filled with Lewisite and that they all were disposed of at only one site, a highly unlikely scenario.

Large areas could be affected if large quantities of Lewisite are present at a site. Figure 8-1 and 8-2 show the size of the area that would be contaminated at 90 mg kg^{-1} by the largest quantity of Lewisite given in Table 8-2.

Table 8-3 shows the concentration that would result if all the arsenic remained in the sediments within the disposal site boundary. Very high concentrations would occur at the small circular sites in the Barents and Kara Seas. Sediment arsenic would increase only a little in the site in the St. Anna Trough because the site is so large. Increases at the White Sea site would be modest because less Lewisite is likely to have been disposed there than at the other sites.

Table 8-2: **Area of Arsenic-Contaminated Sediment at Two Biological Benchmark Concentrations at the Deep Disposal Sites**

| | Quantity (tons) | | Area of Sediment Contaminated at the Benchmark Concentration[b] | |
Location	Lewisite[a]	Arsenic	40 mg kg^{-1} [c,e]	90 mg kg^{-1} [d,e]
Kara and Barents Seas	75,000	27,100	6450 km² (80 km)	2420 km² (49 km)
	37,500	13,550	3230 km² (57 km)	1210 km² (35 km)
	7,500	2,710	650 km² (25 km)	240 km² (16 km)
White Sea	40,000	14,500	3440 km² (59 km)	1290 km² (36 km)
	20,000	7,230	1720 km² (41 km)	650 km² (25 km)
	4,000	1,450	340 km² (19 km)	130 km² (11 km)

[a]Greatest value is from Chapter 2. Other values are one-half and one-tenth of greatest value.
[b]0.1 m deep.
[c]Increase to 40 mg kg^{-1} from background of 10 mg kg^{-1} in the Barents and Kara Seas and 20 mg kg^{-1} in the White Sea.
[d]Increase to 90 mg kg^{-1} from background of 10 mg kg^{-1} in the Barents and Kara Sea and 20 mg kg^{-1} in the White Sea.
[e]Number in parentheses is the approximate length of the sides if area is square.

Figure 8-1: Maximum Size of Area in the Barents and Kara Seas That Could Be Contaminated With Arsenic From Lewisite at the 90 mg kg⁻¹ Biological Benchmark Concentration
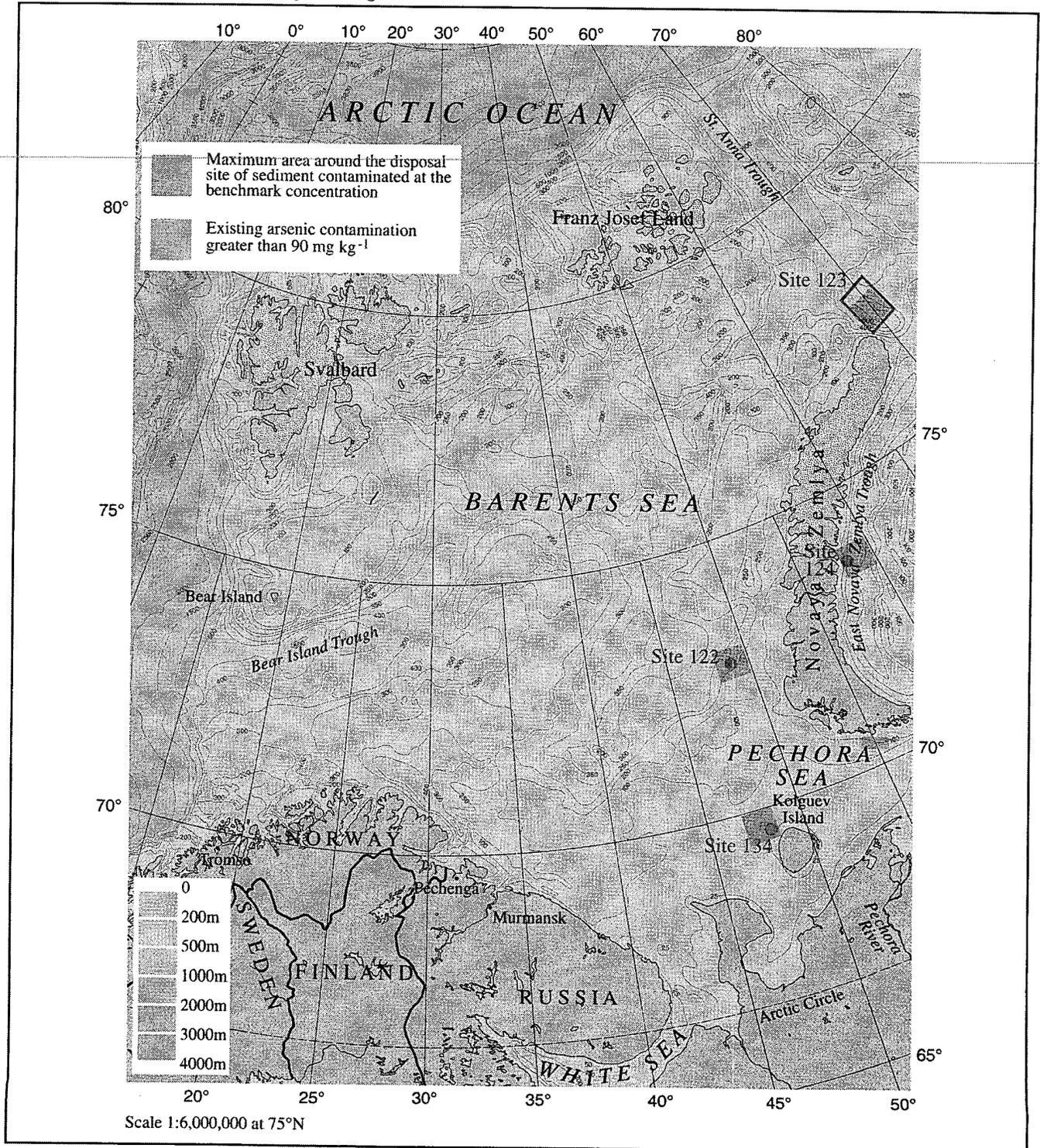
Figure 8-2: Maximum Size of Area in the White Sea That Could Be Contaminated With Arsenic From Lewisite at the 90 mg kg^{-1} Biological Benchmark Concentration
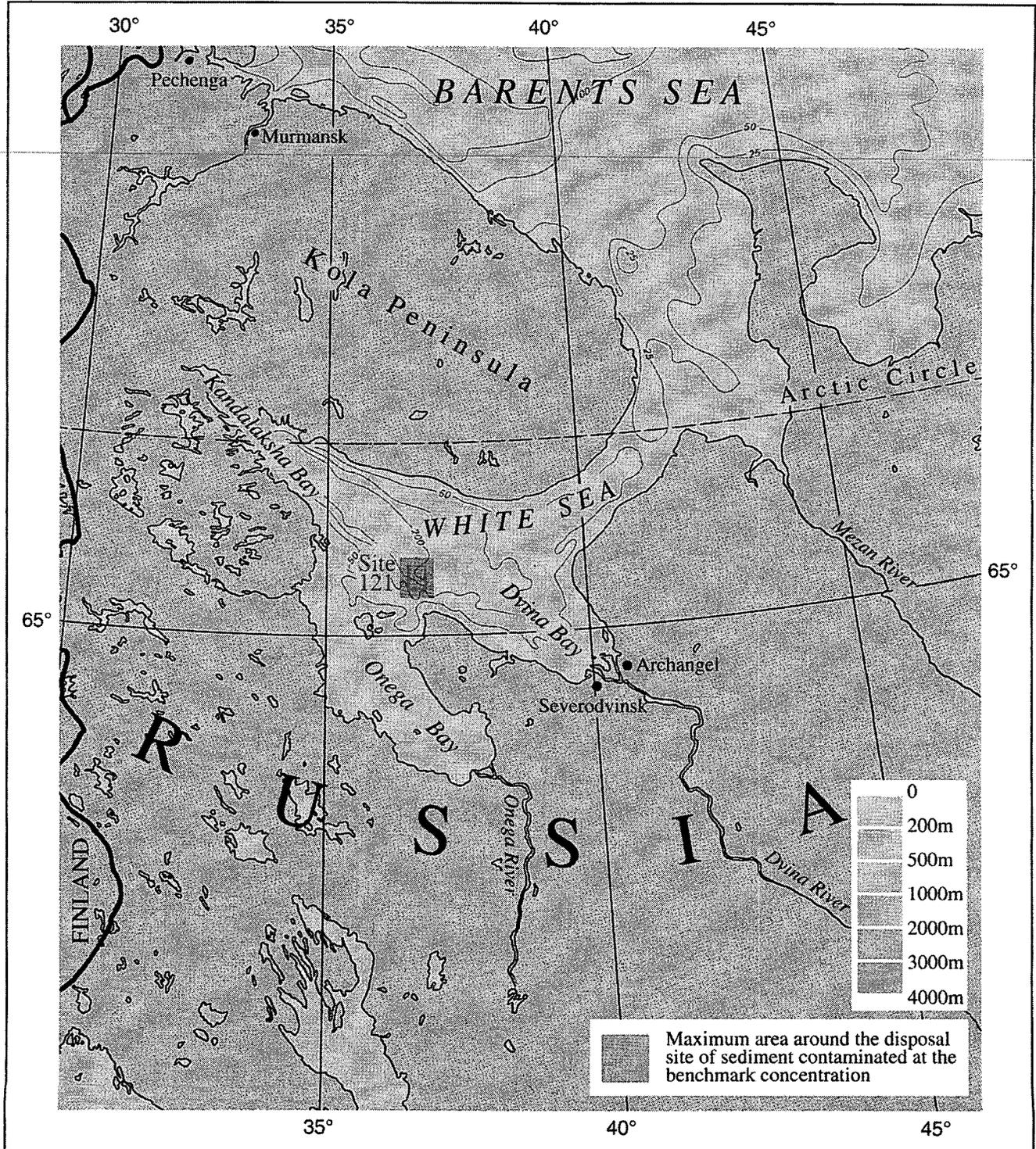
Table 8-3: Sediment Arsenic Concentrations That Would Result if All Contamination is Retained Within the Boundaries of the Deep Disposal Sites[a,b]

Disposal Site	Area (km^2)	Quantity of Lewisite (tons)		
		75,000	37,500	7,500
122 - Barents Sea	43	4,510 mg kg^{-1}	2,260 mg kg^{-1}	460 mg kg^{-1}
123 - Kara Sea	17,150	20 mg kg^{-1}	16 mg kg^{-1}	11 mg kg^{-1}
124 - Kara Sea	20	9,870 mg kg^{-1}	4,940 mg kg^{-1}	995 mg kg^{-1}
		~~40,000~~	~~20,000~~	~~4,000~~
121 - White Sea	292	375 mg kg^{-1}	195 mg kg^{-1}	55 mg kg^{-1}

[a]Arsenic quantity mixed 0.1 m deep into sediment.
[b]Arsenic from Lewisite is added to naturally occuring concentration of 10 mg kg^{-1} in the Barents and Kara Seas and 20 mg kg^{-1} in the White Sea.

8.4.3.2 Ecosystem Effects

The potential exists that large areas of sediments could be contaminated at the 90 mg kg^{-1} benchmark for arsenic, which could produce effects on benthic organisms. The main effect would be to reduce or eliminate benthic organism biomass and reduce species diversity. Demersal organisms could also experience some toxic effects because of their close association with the sediments and reduction or loss of benthos as a food source. Contamination could have a greater effect on early life stages, such as eggs and larvae, than on adults.

The ecosystem effects of sediment contamination is likely to be small in the White Sea and the Kara Sea because of the very low biomass of benthos in the vicinity of the disposal sites and the likely small coupling of the benthic community with the predominantly pelagic system, as discussed above for acute toxicity.

Site No. 122 in the Barents Sea may have greater benthic biomass (possibly 50-200 g m^{-2}) than the other sites and is adjacent to shallow areas of high benthic biomass between the site and Novaya Zemlya. The nearby productive area could be affected if arsenic from the site were spread to the east. Although current direction at the site has not been measured, it is likely that bottom currents would be to the north and west.[23] It is likely that this is also the main flow direction at the bottom. Bottom water is formed during a freeze-up. This water would flow downslope to the northwest and toward the deep West Novaya Zemlya Trough and the Central Basin. It is unlikely that any significant quantity of arsenic would be transported to the east.

8.4.3.3 Potential for Bioaccumulation of Arsenic in Higher Trophic Levels

It is highly probable that the marine organisms associated with the areas of increased arsenic concentration in sediments contaminated by released Lewisite would have greater quantities of arsenic in their tissues. This increase would be greatest in benthic organisms, which are directly and constantly exposed to the contaminated sediments, and in demersal species, which are exposed to these sediments and feed on contaminated benthic organisms. At the deep disposal sites, transfer of arsenic from benthic organisms to pelagic organisms is likely to be very small because of the small contribution of the benthos to the food web in these deep waters and the fact that arsenic does not biomagnify in the food web, as discussed in Section 8.3.

The production of lipid-soluble arsenic compounds by phytoplankton increases the risk of bioaccumulation at higher levels in the food web. Phytoplankton store a large quantity of lipids during the spring and summer period of intense growth and these lipids are passed up the food web, as described in Chapter 3. Arsenic in this form has a high potential to affect higher trophic levels.

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[23]Figures 3-2 and 3-8 in Chapter 3 show surface current flow to the north on the west side of Novaya Zemlya.

The risk of transferring arsenic in phytoplankton lipids is low at the deep disposal sites. To be available to phytoplankton, the arsenic must be mixed into the surface 20 to 50 m of water. As shown in Chapter 7, the plumes released from munitions on the bottom remain near the bottom. No strong mechanisms exist to mix the water column to the depths of the site. Also, the water column is stratified strongly in the surface 50m during the bloom period because melting ice lowers salinity and increasing insolation warms the water. It is highly unlikely that significant quantities of arsenic could be mixed into the productive surface waters and be available for phytoplankton uptake.

8.4.4 Seasonality of Ecosystem Effects

The risks to the ecosystem of the regions of the sites vary somewhat over the year. These risks would be reduced during the winter period of ice cover and increased during the warm months when the ice cover is gone.

During the cold period of ice cover, the risks would be reduced for migratory species that leave the shelf regions. These include important commercial fish stocks such as Arcto-Norwegian cod, herring, and haddock. Whales also are not present during this period. The potential for arsenic to be incorporated into phytoplankton lipid compounds would be very low during this period because of greatly reduced solar insolation and low primary production.

The risk is slightly greater during the warm period. Phytoplankton grow rapidly near the surface. Migratory stocks of fish are present in large numbers and whales are present. Based on the bloom of phytoplankton productivity, there is a high rate of flow of material and energy in the surface waters. However, the interaction of the benthic community and the near-

bottom water with the surface waters is generally small, as discussed in Section 8.4.3.3.

8.5 ECOLOGICAL EFFECTS AT SHALLOW DISPOSAL SITE

Disposal Site No. 134, located near Kolguev Island in the southeastern Barents Sea, represents a different physical and ecological situation than the deep disposal sites considered above. As can be seen in Figure 3-1, this area of the Barents Sea, called the Pechora Sea, is shallow with water less than 100 m deep. Water depths in Site No. 134 are 30 to 50 m.

Chapter 3 describes the bentho-pelagic food web that occurs in the shallow portions of the study region. The food web at Site No. 134 is likely to be of this type, although data specific to the structure of the biological communities in the Pechora Sea region was not found in the English language literature collected for this study. In the bentho-pelagic food web, much of the organic matter produced by the phytoplankton in the water column sinks to the bottom and is available as food to the benthic community. Because of this food source, the biomass of benthic organisms is greater in these shallow areas than in the deep waters, as can be seen in Figure 3-6. In these shallow waters, the benthic biomass is also within the diving depths of the walrus and several species of seals that feed on benthic organisms.

Site No. 134 is close to Kolguev Island, which is reported to have large populations of seals and sea birds.[24] These populations forage in the marine waters near their roosting and haulout areas and are supported by the biological productivity of these waters.[25] The disposal site waters are within the foraging range of birds and seals on the northern and western shores of the island.

[24]Matishov, G.G., 1991. *Barents Sea: Biological Resources and Human Impact.* Map prepared in cooperation with Murmansk Marine Biological Institute of Academy of Sciencies of the USSR, Norwegian Polar Research Institute, and Institute of Oceanology of the Polish Academy of Sciences. Apatity, Russia.
[25]McRoy, C.P. 1974. "Bird and Mammal Island Subsystems of Higher Latitudes." *In* H.T. Odum, B.J. Copeland, and E.A. McMahan (eds.). *Coastal Ecological Systems of the United States, Volume II.* The Conservation Foundation. Washington, D.C.

The Pechora Sea also supports an important commercial fishery, as described in Section 3.3. The benthic community is important to this fishery, and bottom trawls are used extensively as a method of harvest.

It is clear, then, that the benthic community in shallow waters is an important component of the food web and is closely coupled to the productivity of the overlying water column. In this situation, the potential threat posed by released agent that primarily affects the bottom community, as described in Chapter 7, could be great.

8.5.1   Effects of Mustard

As discussed for the deep water sites, it is possible for mustard to be present in a viscous form on the sea floor somewhere on the disposal site for many years. Although a 1 kg quantity of mustard exposed to seawater at the site would dissolve in less than one year (see Chapter 7), new mustard would constantly be exposed as shells corroded at different rates, as discussed in Section 8.2. Benthic organisms in contact with the mustard would be killed. However, the area occupied by exposed mustard at any one time would be small compared to the area of the disposal site. Therefore, the number of benthic organisms killed by mustard would be a very small loss to the food web and unlikely to have measurable effects.

Unlike the deep water sites, ingestion of or contact with mustard in the shallow water sites is a more likely potential source of injury or death to seals feeding on the bottom. A map produced by Matishov[26] shows Kolguev Island waters as having abundant occurrences of ringed, bearded, and Greenland seals. Although most seals feed predominantly on fish and other pelagic organisms in the water column, some bottom feeding takes place.[27] The bearded seal feeds primarily on bottom organisms.[28,29] Benthic biomass at the site is likely to be in the range of 50-200 g m^{-2}.[30] The attractiveness of the disposal site for seal feeding is not known but is likely to be typical of the region.

The magnitude of the mustard risk to seals is difficult to estimate, but is likely to be low even in these shallow water sites. This conclusion is based on several considerations. The number of mustard lumps exposed at any time should be small so that the rate of encounter is low. If seals are using sight during foraging, it is possible that they would avoid lumps after the first encounter that results in an irritation or injury. Also, no mention of unusual seal mortalities or injuries in this region were found in any of the English language literature reviewed during this assessment. This suggests that no mortality or injury from mustard lumps occurs or that it occurs at a low rate not noticed as unusual. It is also possible that no mustard is present.

The disposal site is within the range of the walrus,[31] which feeds on benthic organisms in water up to 80 m deep.[32] Mollusks are a dominant food organism of walrus[33] and are a major component of the benthic biomass in the region of the disposal site.[34,35] No data was found to determine if walrus populations are present on nearby Kolguev Island, and the map of Matishov[36] does not show walrus present. It is possible, however, that walrus are present during the period when ice is advancing or retreating over the area. As with seals, the risk of injury or death to walrus is difficult to estimate but is likely to be low for reasons similar to those for seals. Because of the endangered status of walrus, any potential for effects would be of some concern.

[26]Reference 24.
[27]Reference 13.
[28]Reference 13.
[29]Demel, K. and S. Rutkowicz. 1966. *The Barents Sea (Morze Barentsa).* Translated from the Polish by the U.S. Department of the Interior and the National Science Foundation. Clearinghouse for Federal Scientific and Technical Information, Springfield, VA.
[30]Zenkevitch, L., 1963. *Biology of the Seas of the USSR.* Interscience Publishers, New York, NY.
[31]*Atlas of the Arctic.* 1985. Lenin Arctic and Antarctic Scientific Research Institute. Moscow.
[32]Reference 14.
[33]Reference 14.
[34]Reference 30.
[35]Zatsepin, V.I., 1970. "On the Significance of Various Ecological Groups of Animals in the Bottom Communities of the Greenland, Norwegian and the Barents Sea." In J.H. Steele (ed.). *Marine Ecosystems.* Oliver & Boyd, Edinburg. Reprint by Otto Koeltz, Antiquariat, Koenigstien-Ts./B.R.D., 1973.
[36]Reference 24.

It is possible for whales to be present in this disposal site region. The main threat is contact with mustard when foraging near the bottom. Ingestion of mustard is not a threat because there are no bottom-feeding whales in the study region. The shallow Pechora Sea region is in the range of the beluga whale,[37] which occurs in large numbers.[38] This species feeds primarily on fish and squids[39,40] and is not likely to come in contact with the bottom. Minke whales are common in the deeper waters to the north and west[41] but no data was found on their occurrence in disposal site waters. This species is a baleen whale feeding on pelagic organisms and would not come in contact with the bottom. Humpback whales, which may come in contact with the bottom during certain feeding behaviors,[42] do not occur in the disposal site area.[43] It is likely that the threat of injury to whales from contacting mustard is very low.

8.5.2 Toxic Effects of Lewisite, Tabun, and Sarin

As discussed in Chapter 7, Lewisite, Tabun, and Sarin released from leaking munitions would stay near or on the bottom, and the arsenic released from Lewisite would eventually end up as a long-term contaminant in the sediments. Therefore, the acute and chronic toxicity would be exerted mainly on benthic communities and on any mobile organisms that swim near the bottom or feed on benthic organisms. The importance of the benthic community in the food web of the disposal site region was discussed at the beginning of Section 8.5.

The magnitude of the ecological effect at the disposal site would be largely determined by the amount of benthic productivity lost due to the toxicity of the agent plumes and the long-term effects on productivity and species diversity due to arsenic contamination of the sediments. This issue must be analyzed at two regional scales. One scale is the region of Kolguev Island and the populations of birds and seals found

there. The other region is that of the Pechora Sea, defined as the area within the 100 m depth contour.

At the greater agent release rates considered in Chapter 7, the benthic organisms and demersal species would be eliminated or significantly reduced in numbers or in species diversity over the entire disposal site area for the period of agent release from all the munitions present (see Section 8.2). The loss of this important benthic productivity at the base of the food web would affect higher trophic levels by reducing the carrying capacity of the region. Carrying capacity is the quantity of organisms at all trophic levels that can be sustained in a region by the biological production that is available to support them.

The effect of the loss of carrying capacity would be one of scale. The greatest effect would be on the populations of birds and marine mammals on Kolguev Island near the site because these populations are mostly supported by the marine environment and the disposal site is a large fraction of the total area. There would be less effect on the larger Pechora Sea region ecosystem because of its size relative to the disposal site. More details on these two regions follow.

8.5.2.1 Kolguev Island Region

At this disposal site, the loss or reduction of benthic biomass and productivity and demersal species would be a moderate to large effect because the area of the site is large compared to the area of the Kolguev Island region. A likely effect would be a reduction in the size of resident seal and marine bird populations on the northern and western shores of Kolguev Island. These populations are supported by the biological productivity of the adjacent marine ecosystems, which includes the disposal site area. A significant loss of food resources in their region of foraging reduces the carrying capacity for these populations. With a smaller carrying capacity, population sizes would decline

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[37]Reference 31.
[38]Reference 24.
[39]Reference 29.
[40]Reference 14.
[41]Schweder, T. et al. In press. *Abundance of Northeastern Minke Whales, Estimates for 1989 and 1995.* Reports of the International Whaling Commission, Vol. 47. (International Whaling Commission document number SC/48/NA1). The Red House, Cambridge CB44NP, England.
[42]Reference 16.
[43]Reference 29.

to a level that could be sustained by this reduced biological productivity.

The magnitude of the effect in the Kolguev Island region cannot be estimated easily with the data available. However, it is likely that the loss would be in proportion to the reduction in productivity in the area used by the populations most affected. This productivity is determined by both the local area and the much larger region of the Pechora Sea and the Barents Sea. The loss of productivity is likely to be less than the proportion of bottom area in the disposal site to the larger area supporting the Kolguev Island populations. Those species feeding directly on benthic and demersal organisms, such as bearded seals, would be affected to a greater extent than species feeding on primarily pelagic species.

No data are available on the effect of the chemical agents on marine mammals. Examination of the plume characteristics analyzed in Chapter 7 indicates that a large part of the plume volume would be between the ENEC and EPEC levels (see Section 6.3 for a discussion of these toxicity levels). It is possible, then, that injury rather than death would be the most likely effect. It is also possible that seals and walrus could learn to avoid the disposal site area because of irritation or injuries received and because the reduction or elimination of food sources makes the area unattractive for foraging.

For marine mammals, the probability of encountering toxic plumes at the disposal site would be a function of the area of the site near the bottom covered by plumes on any day. This area is dependent on the agent release period, as shown in Figures 7-34 through 7-38. If all the agent is released over a five-year period, approximately 40 percent of the disposal site area is covered with plumes at the ENEC on any day. For a fifty-year release period, six percent of the area is covered by toxic plumes.

8.5.2.2 *Pechora Sea Region*

The ecosystem effect on the larger Pechora Sea region would be small. The area of the disposal site, 528 km^2, is modest compared to the approximate 100,000 to 110,000 km^2 area of the Pechora Sea region. The likely benthic biomass of 50-200 g m^{-2} at the site is a medium amount for the Barents Sea, but less than the high biomass of 200-500 g m^{-2} found in the northern portion of the Pechora Sea region (see Figure 3-6). Loss or reduction of benthic biomass in the disposal site could be small when considering the total regional productivity of benthic communities.

The effects on marine mammals would be small. These populations are distributed over an area large in comparison to the disposal site area.

The distribution of fish in the Pechora Sea region is not well documented but data are available on Arcto-Norwegian cod, haddock, and polar cod.[44] The first two species are important components of the regional commercial fishery. The polar cod spawns in the region, but is less important to the fishery.

Immature Arcto-Norwegian cod exist in large numbers in the fall and winter in the Pechora Sea region (see Figure 8-3). Spawning takes place in the Norwegian Sea and cod are widely distributed in the Barents Sea. They feed predominantly on pelagic species. The loss of productivity of the disposal site area could possibly affect the abundance of cod locally but is unlikely to have an effect on the large Barents Sea stock. Any effect would be indistinguishable from the large year-to-year variations in stock size that occur naturally.

Adult haddock occur in the Pechora Sea region in the summer and fall (see Figure 8-4). Spawning takes place in the Norwegian Sea. Adult haddock feed predominantly on benthic and demersal species.[45,46] The loss in the disposal site area for feeding by haddock could result in a small reduction of the stock size that

[44]Reference 29.
[45]Reference 30.
[46]Reference 29.

Figure 8-3: Regions of Arcto-Norwegian Cod Congregation in the Barents Sea[47]
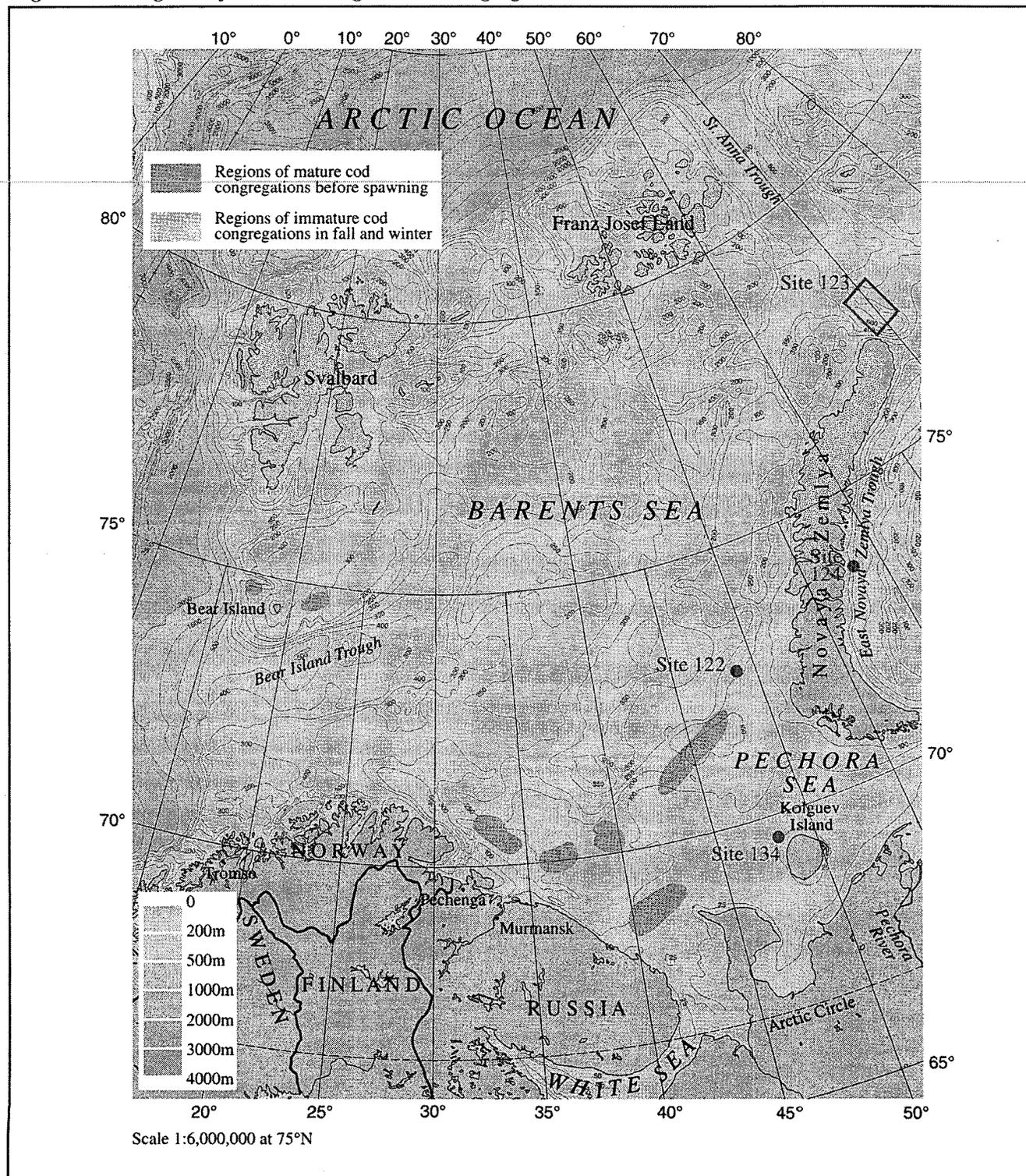
Figure 8-4: Regions of Haddock Congregation in the Barents Sea[48]
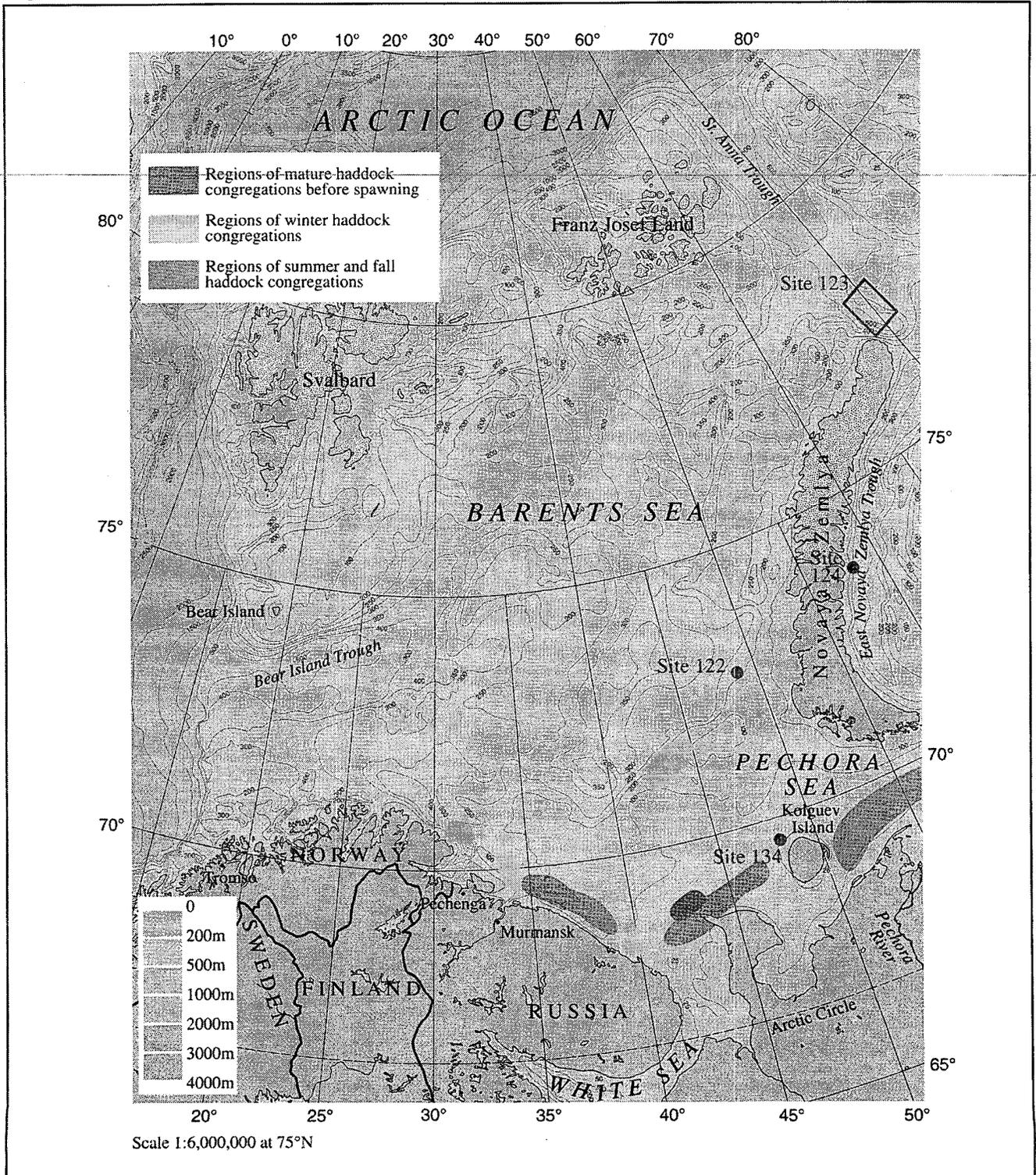
48Reference 29.

could be supported in the Pechora Sea region. The effect on the larger Barents Sea stock probably would be very small.

The polar cod spawns off the west coast of Novaya Zemlya in the fall and under the ice in the Pechora Sea region in January and February.[49] Eggs are pelagic. Eggs and larvae that enter the contaminated water near the bottom in the disposal site would likely be killed. The effect of this egg and larvae mortality on the regional stock is difficult to estimate, because the factors affecting stock size are not well known for this species. However, the effect is estimated to be small.

8.5.2.3 Recovery of Benthic and Demersal Communities

Toxic effects on benthic and demersal communities would not be permanent. The benthic habitat affected would not be altered permanently and recovery would occur once the toxic plume is no longer present. Currents would bring pelagic larvae of benthic organisms to the site from the surrounding bottom areas. Demersal species from nearby areas would move into the disposal area.

Data was not found on the rate of recovery of benthic and demersal communities at shallow arctic shelf locations, such as the disposal site. It is likely that the rate would be slow, perhaps requiring a decade or two to recover to the original biomass and diversity. Several factors are important to the rate of recovery. Benthic organisms may grow slowly and have long individual lifespans and low turnover rates.[50,51] Many organisms brood their young rather than release pelagic larvae.[52] Dispersal of brooded young into a site would be slow. Pelagic larvae would colonize the site much faster. Recovery rate of demersal species would be dependent on the recovery of the benthic community on which they feed. As the benthic productivity is restored, the carrying capacity of the area would return to the previous level. Populations of birds and seals on Kolguev Island would return to previous sizes.

8.5.3 Long-Term Effects of Arsenic-Contaminated Sediments

Arsenic is a persistent contaminant from Lewisite that would remain permanently in the sediments and be available for uptake by marine organisms. Because arsenic is potentially toxic, there could be chronic toxic effects from its long-term presence in the sediments of the regional environment, as discussed in Section 8.4.3 for the deep disposal sites. This issue is a concern at the shallow disposal site because the benthic community is important in the food web of the regional ecosystem.

Most of the Pechora Sea sediments are at natural background arsenic concentrations.[53] However, a large area of arsenic contamination exists in the northern Pechora Sea off the south coast of Novaya Zemlya (see Figure 8-1). The contaminated area estimated to be greater than 90 mg kg^{-1} is about 500 km^2. The source of the arsenic is not known.[54]

8.5.3.1 Estimate of Arsenic Contamination of Sediments at Biological Benchmark Concentrations

Table 8-4 shows the area that could be contaminated at the biological benchmark arsenic concentrations and the concentrations that would result if all of the arsenic were spread only over the area of the disposal site. Figure 8-1 shows the area contaminated at the 90 mg kg^{-1} benchmark concentration if the largest quantity of Lewisite is present at the site. The areas were calculated as described in Section 8.2. Figure 7-38 also shows the sediment concentration of arsenic as a function of area for a range of arsenic quantities released. This area calculation assumes a uniform distribution of arsenic mixed into sediment at a depth of 1 cm. To match the data in Tables 8-2 and 8-3 the mixing depths must be reduced by an order of magnitude.

[49]Reference 29.
[50]Reference 17.
[51]Reference 18.
[52]Reference 17.
[53]Reference 2.
[54]Reference 2.

Table 8-4: Potential Arsenic Sediment Concentrations at Disposal Site No. 134 in the Pechora Sea Region

Quantity (tons)		Area of Sediment Contaminated at Benchmark Concentrations[b]		All Arsenic in Disposal Site[f] (527 km²)
Lewisite[a]	Arsenic	40 mg kg⁻¹ [c,e]	90 mg kg⁻¹ [d,e]	
75,000	27,100	6450 km² (80 km)	2420 km² (49 km)	377 mg kg⁻¹
37,500	13,550	3230 km² (57 km)	1210 km² (35 km)	194 mg kg⁻¹
7,500	2,710	650 km² (25 km)	240 km² (16 km)	47 mg km⁻¹

[a]Greatest value is from Chapter 2. Other values are one-half and one-tenth of greatest value.
[b]0.1 m deep.
[c]Increase to 40 mg kg⁻¹ from background of 10 mg kg⁻¹.
[d]Increase to 90 mg kg⁻¹ from background of 10 mg kg⁻¹.
[e]Number in parentheses is the approximate length of the sides if area is square.
[f]Sediment arsenic concentration that would result if the entire quantity of arsenic released remained with the boundary of the disposal site and mixed into sediments to a depth of 0.1 m. Includes background concentrations of 10 mg kg⁻¹.

The quantities of Lewisite given are bounding values. The highest value of 75,000 tons is highly unlikely. It could only occur if all vesicant munitions dumped were filled with Lewisite and they all were disposed of at Site No. 134, a highly unlikely scenario.

8.5.3.2 Ecosystem Effects

As can be seen from Table 8-4, arsenic has the potential to contaminate large areas of sediments at the 90 mg kg⁻¹ benchmark. It is possible that the main effect would be to reduce or eliminate benthic organism biomass and species diversity. Demersal organisms could also experience some toxic effects because of their close association with the sediments and reduction or loss of benthos as a food source. Contamination could have a greater effect on early life stages, such as eggs and larvae, than on adults.

The maximum area affected at the 90 mg kg⁻¹ biological benchmark would be on the order of four times the size of the disposal site (see Table 8-4). Since some effects could still occur in the concentration range between 40 mg kg⁻¹ and 90 mg kg⁻¹, deleterious effects could take place over perhaps five times the area of the disposal site. If small quantities of arsenic were released, however, the deleterious zone would be only the size of the disposal site or less.

The likely effect in the deleterious zone would be to reduce the biomass of benthic and demersal organisms present. The diversity of species could also be reduced or changed because the effect of arsenic is likely to vary for different species.

Reduction or loss of benthic biomass would reduce the carrying capacity significantly in the Kolguev Island region, for similar reasons detailed above for toxic plumes. A significant loss of productivity over an area five times the size of the disposal site would probably result in a large effect on the population of seals and birds on Kolguev Island. The loss due to arsenic contamination would be very long term, lasting as long as the arsenic contamination remained in the biologically active zone of the top 10 cm of sediment. Since sediment deposition rates in the Barents Sea are 1-3 cm per 1,000 years, some effect could remain for 3,000 to 10,000 years.

The ecosystem effect on the larger Pechora Sea region could be small to moderate if the contamination reaches 2410 km². This area would be added to the 500 km² region already contaminated in the northern Pechora Sea. It is noted that no data are available from this region to determine if benthic biomass and diversity has actually been affected. The total of the

two areas is a few percent of the area of Pechora seawaters within the 100 m isobath.

8.5.3.3 Potential for Bioaccumulation of Arsenic at Higher Trophic Levels

Arsenic in sediments of the disposal site and surrounding area would be readily available for interaction with the food web of the region because of the importance of benthic organisms in this community. The risk of bioaccumulation of arsenic in higher trophic levels is modest, however, because arsenic does not biomagnify in the food web and may not bioaccumulate much beyond the lowest trophic levels, as discussed in Section 8.3. Bearded seals and walrus would be most exposed to arsenic contamination by feeding on benthic organisms, which can include ingesting contaminated sediments during feeding.

Arsenic in tissues of benthic organisms would increase significantly in the area of contamination, as observed in other arsenic-contaminated aquatic environments. The biomass at the site may be dominated by organisms that filter the overlying water to obtain their food (filter feeders). Fewer organisms may be present that directly ingest contaminated sediments or bottom organic matter.[55] Filter feeders would have somewhat less exposure to arsenic because they primarily would be ingesting material suspended in the water. However, resuspension of arsenic-contaminated material from the bottom into the water may be frequent. Turbulence from strong surface winds can resuspend sediments during the ice-free period if strong density stratification in the surface water layer is not present. Sinking dense water formed when brine is rejected during ice formation can also impinge on the bottom with enough velocity to resuspend sediments.

The potential for body burden of arsenic in demersal fish and invertebrates would also increase significantly in the contaminated area. Demersal invertebrates, such as crabs and shrimp, feed directly on benthic organisms, sediments, and organic matter. Demersal fish feed on benthic organisms or other fish and invertebrates living on or near the bottom. Demersal fish, such as the flatfishes and skates, are common in the region and may be affected.[56]

Walrus would be directly exposed to arsenic through consumption of contaminated benthic organisms and by incidentally ingesting contaminated sediments while feeding. If walrus occur in the region, they would experience some increase in arsenic body burden.

Polar bears are not shown to be present on Kolguev Island, but are shown to be present on Novaya Zemlya.[57] Bears could have some access to the contaminated area near the disposal site during winter ice cover and spring ice melt but the exposure is likely to be brief. Ringed seals, which feed mainly on fish, are the principal food source of polar bears, and this species is present in the Kolguev Island region in large numbers. The polar bear would only be exposed to arsenic indirectly through the food web from eating contaminated seals. Because of the low bioaccumulation of arsenic, polar bears would have low potential to increase their body burden of arsenic. Any bear exposure to arsenic could add to stress caused by high concentrations of chlorinated hydrocarbons that may exist currently.[58]

It is possible that some food web transfer of arsenic could occur by incorporation into lipids in phytoplankton. For this to occur, soluble inorganic arsenic would have to be mixed into the surface photic layer while primary production is occurring. It is

[55]Reference 35.
[56]Reference 29.
[57]Reference 24.
[58]Klungsoyr J., R. Saetre, L. Foyn, and H. Loeng. 1995. "Man's Impact on the Barents Sea." *Arctic* 48(3):279 296.

possible that some arsenic could reach the surface layers during strong winds that mix the entire water column and then could be available for phytoplankton uptake. The water column is likely to stratify during ice melt, which is the period of greatest primary production. No data are available from the site or its environs to determine the potential for water column mixing and arsenic transport to the surface, so no estimate can be made of the magnitude of this arsenic transfer mechanism. If it occurs at the site, arsenic could be transferred to higher trophic levels much more efficiently than by other mechanisms.

8.5.3.4 Potential for Transport of Arsenic in Ice

Because the disposal site is shallow, it is possible that arsenic could be incorporated into ice during freezing. This can occur if sediments are resuspended while ice is forming over the contaminated area and by incorporation into anchor, slush, and frazil ice that forms in contaminated areas. Arsenic could then be carried to other areas as ice moves in the region.

Resuspension of sediments into the water occurs in two ways. One is turbulence induced by strong winds that blow over the site while ice is forming. In the Bering Sea, wind turbulence has been measured to depths of 50 m. The second mechanism is by the rejection of brine during ice formation. The heavy water produced sinks and impinges the bottom. In shallow water, the impingement velocity can sometimes be great enough to resuspend sediments.

Sediments can also be incorporated into an overlying ice cover by two other mechanisms that can occur if the total water column is less than 50 m deep.[59,60] Once the entire water column becomes slightly supercooled, small frazil ice crystals can nucleate throughout the column. Once formed they gradually float to the surface where they become incorporated in the overlying ice sheet. During their rise they scavenge any suspended particles that are to be found in the water column. In a somewhat related process, supercooled water swept down from the ocean surface can feed the growth of ice crystals that nucleate on materials lying on the seafloor. Once these anchor ice crystal masses become large, their buoyancy is sufficient to lift materials directly off the seafloor, ultimately transporting them to the overlying ice cover. Once incorporated in the ice masses at the sea surface, the potential exists for the sediment to be transported outside of the local region.

No data are available to determine if incorporation of sediments into ice occurs in the region of the disposal site, nor can an estimate be made of the magnitude of transport if it occurs. However, the potential exists for these mechanisms to operate in the region.

8.5.4 Seasonality of Ecosystem Effects

The risk to components of the regional ecosystem would vary over the year. Risk to ice-associated species such as polar bears, walrus, and possibly seals could be greatest when ice is present because these species would be present in and adjacent to the disposal site. Risk to migratory species of birds, whales, and fish stocks would be much greater during the warm months when these populations are present in the Pechora Sea region. The potential to incorporate arsenic into phytoplankton lipids would be greatest during the spring and summer periods of the greatest primary production in surface waters.

8.6 ECONOMIC EFFECTS

Commercial fishing is an important economic activity in the Barents and White Seas. There are several threats to the commercial fishery from the presence of chemical munitions in the region. These include changing or reducing the size of the commercially important stocks, contaminating fish products rendering them unable to be sold in the marketplace, and closing areas to commercial fishing because of the presence of munitions or the contamination of the area by agents or breakdown products.

[59]Reimnitz, E., M. McCormick, K. McDougall, and E. Brouwers. 1993. "Sediment Export by Ice Rafting From a Coastal Polynya, Arctic Alaska, USA." *Arctic and Alpine Research* 25(2):83-98.
[60]Pfirman, S.L., H. Eicken, D. Bauch, and W.F. Weeks. 1995. "The Potential Transport of Pollutants by Arctic Sea Ice." *The Science of the Total Environment* 159:129-146.

8.6.1 Change or Reduction of Fish Stocks

Commercial fish stocks in the regions of the deep sites are pelagic species such as capelin and Arcto-Norwegian cod. It is likely that these stocks would not change or be reduced in size because of munitions at the sites. Contamination would be confined to benthic and demersal organisms as discussed in Section 8.4. Because benthic communities in these deep areas contribute little to the food web, pelagic fish stocks are not likely to be altered significantly at the deep sites. In the region of shallow site No. 134, only a small effect is likely on the commercially important species Arcto-Norwegian cod and haddock (see Section 8.5).

8.6.2 Contamination of Fish Flesh by Chemical Agents and Breakdown Products Other than Arsenic

Chemical agents and their breakdown products could contaminate commercial fish stocks by bioaccumulation or bioconcentration in the food web, preventing or affecting the sale of fish flesh in the commercial market. As discussed in Section 8.3, the bioconcentration potential of the chemical agents and their breakdown products is low. These contaminants are not likely to be present in commercial fish flesh in significant quantities.

8.6.3 Contamination of Fish Flesh by Arsenic

The analyses in Sections 8.4.3 and 8.5.3 indicates that the arsenic concentration in sediments in and near the disposal sites would increase from the release of arsenic to the water. The amount of arsenic in fish will increase in their tissue, and because arsenic is a human carcinogen, the amount of arsenic in commercial fish products (flesh and oils) is of concern.

An arsenic standard in fish and fishery products, ranging from 0.1 to 10 ppm, has been established by a number of nations.[61] In Europe, Finland and the United Kingdom have established limits of 5.0 ppm and 1.0 ppm, respectively.

Concentrations of arsenic in commercially important fish in the Barents Sea are probably low although only a few measurements were found. Values in Barents Sea cod were 0.7 ppm for muscle and 2.2 ppm in liver. Values for cod taken off Norway and in Oslofjord were reported as 4.2 to 5 ppm for muscle and 10 ppm for liver.

Demersal fish, which feed mostly on organisms in, on, or near the bottom are likely to have a greater increase in arsenic in their bodies than pelagic species, which reside and feed mostly in the water column. Arsenic concentrations in flounder, a demersal fish, were reported to be considerably greater than in cod, a pelagic fish, for specimens taken in Norwegian waters.[62]

8.6.3.1 Deep Disposal Sites

At the deep disposal sites, contamination of commercial species with arsenic is not likely to be a significant problem. Arsenic could increase in demersal fish, which interact with the arsenic-contaminated sediments and benthic organisms. These species, however, are not likely to be harvested in significant numbers in the trawl fishery because bottom trawling is not used in the deep areas. Some transfer of arsenic to pelagic species could occur by transfer through the food web. The amount is likely to be small because of the small contribution of the benthic community to the predominantly pelagic food web in these areas.

8.6.3.2 Shallow Disposal Site No. 134

The shallow waters of the Pechora Sea region are fished extensively (see Figure 8-5). Arcto-Norwegian cod and haddock constitute the large majority of the catch. Polar cod, plaice, and halibut are also harvested.[63]

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[61]Reference 8.
[62]Savinova, T.N., G.W. Gabrielsen, S. Falk-Petersen. 1995. *Chemical Pollution in the Arctic and Sub-Arctic Marine Ecosystems: An Overview of Current Knowledge.* NINA-fagrapport 1.68 pp. Trondheim, Norway.
[63]Reference 29.

Figure 8-5: Fishing Intensity in the Barents Sea[64]
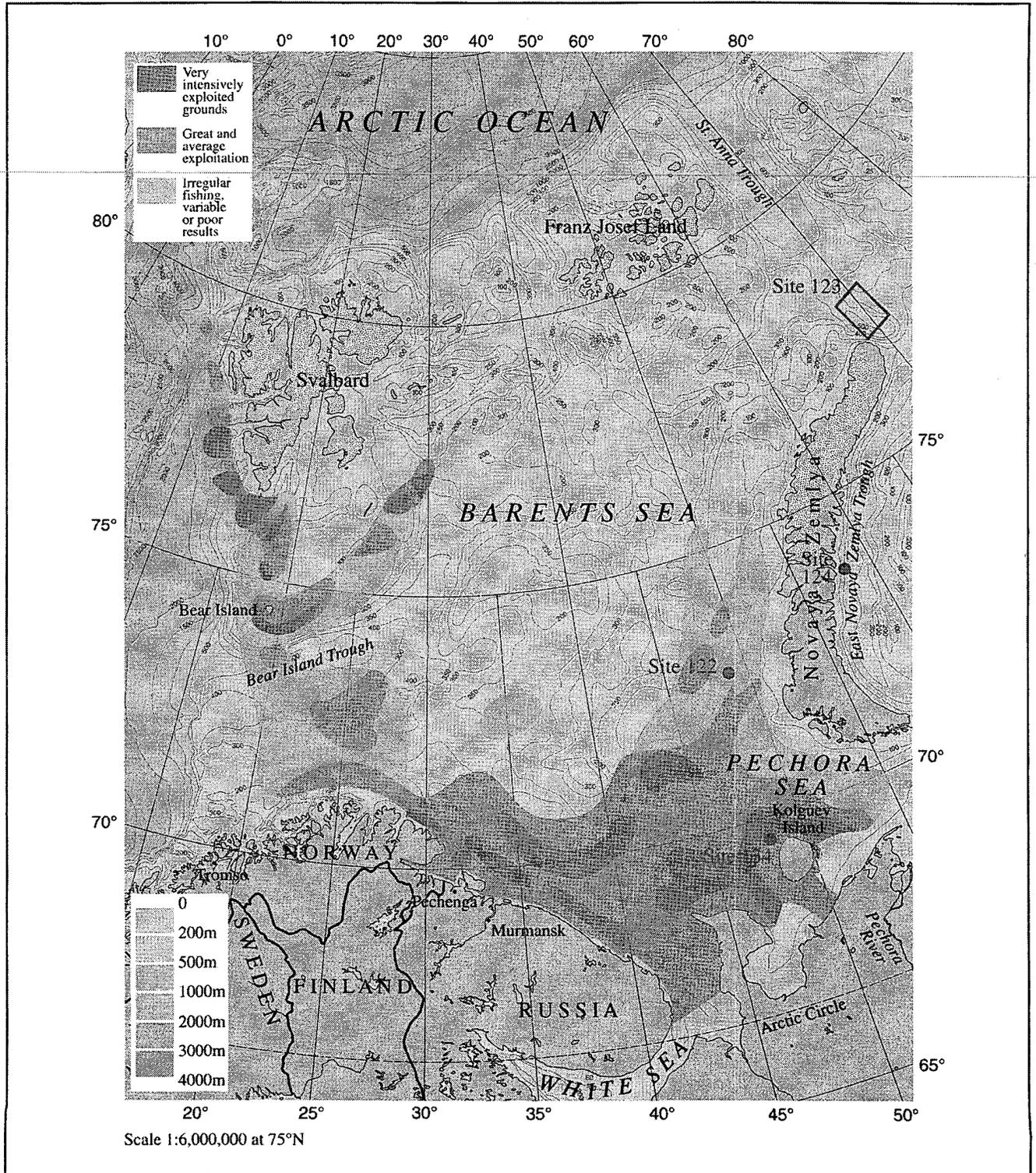
[64]Reference 29.

Increased arsenic concentrations are likely in commercial fish species near Site No. 134. The increase is likely to be greatest in demersal species, such as haddock, plaice, and halibut. Some arsenic would be passed to the pelagic fish, such as the cods. The area with significantly increased arsenic concentrations could be several times the size of the disposal site if large quantities of munitions containing Lewisite were dumped there.

Fishing is discouraged within the disposal site, according to postings on Russian navigation chart No. 650. It is possible that contaminated fish could move outside the marked areas and be caught because trawling takes place in the vicinity of the site. Demersal, as well as pelagic species, are potential catches because of bottom trawling. It is likely that the area of arsenic-contaminated sediments near the southern coast of Novaya Zemlya is also contributing to the amount of arsenic in commercial species in the region.

It is difficult to quantify the increase in arsenic amounts that is likely to occur in commercial species near the disposal site. However, it is probable that the body burdens in demersal species within the contaminated zone would exceed the 1.0 ppm limit for arsenic established by the United Kingdom and it is likely that the Finnish limit of 5.0 ppm could also be exceeded in many individual fish. It is possible that pelagic species that remain and feed in and near the contaminated area could also exceed both limits.

The economic effect of fish contaminated with arsenic would likely be insignificant under current conditions. Information was not found on the market distribution of fish caught in the Kolguev Island and Pechora Sea region, so it is not known if any of the catch could be barred from Finland and United Kingdom markets. If that occurs, the catch could be shifted to other European or world markets that do not have arsenic standards for fish. There could be some temporary economic effects while new markets are developed.

The economic effect could be large if, in the future, other national governments become concerned about arsenic contamination of fish from the region and impose bans on sales. Sales could also be reduced if consumers develop negative attitudes toward fish from the region because of the possibility of arsenic contamination.

8.6.4   Contamination of Commercial Fish Oils

Commercial fish oils could become contaminated with arsenic if prepared from species contaminated by arsenic in the shallow Pechora Sea. It is likely, however, that refining processes used in fish oil manufacturing can greatly reduce contaminant concentrations. For example, refining of menhaden oil reduces arsenic concentrations from 10.4 ppm to less than 0.7 ppm.[65] Refining crude fish oil reduced DDT and PCB concentrations by two orders of magnitude.[66] It is unlikely that there could be a significant economic effect on fish oil products.

8.6.5   Closure of Fishing Areas

Commercial fishing activities could be affected if areas were to be closed to fishing because either fish stocks are contaminated with hazardous materials or chemical munitions could be captured by fishing nets. Loss of fishing areas could substantially reduce the quantities of catch and increase fishing pressure on the remaining area.

The waters over the deep disposal areas are not currently closed to fishing. Because these areas are not currently productive for bottom trawling, the commercial fishery would experience no change in limiting the area for bottom trawling.

It is not likely that pelagic fish stocks in and near the deep sites would experience significant contamination from arsenic released to sediments at these sites. It is unlikely that the waters in and around the disposal sites would be closed to fishing for health reasons.

[65]Elson, C.M., E.M. Bern, and R.G. Ackerman. 1981. "Determination of Heavy Metals in Menhaden Oil After Refining and Hydrogenation Using Several Analytical Methods." *Journal of American Oil Chemistry Society* 58:1024-1026.
[66]Ackman. R.G., 1980. "Fish Lipids." Pgs 86-103. *In* Connell, J.J. (ed.). *Advances in Fish Science and Technology.* Fishing News Books, Ltd. West Byfleet, UK.

Fishing is currently discouraged in disposal Site 134 according to postings on Russian navigation chart No. 650. Chemical munitions, if present on the seafloor, could cause the area in and around the disposal site to remain closed to fishing in the future. The closure would need to continue at least until it could be determined that all agents had been released from the munitions. The length of this period cannot be estimated with certainty because of a lack of information on corrosion rates in arctic waters. Experience with mustard disposed in the Baltic Sea[67] and the Sea of Japan[68] indicates mustard munitions can last for many decades in cold marine environments.

8.7 EFFECTS ON OIL AND GAS EXPLORATION AND EXPLOITATION ACTIVITIES

The Barents and Kara Seas are areas of active oil and gas exploration and oil production (see Section 3.8.3). The presence of chemical munitions could increase costs or prevent the development of oil and gas resources if exploration and exploitation activities were to take place in the disposal sites.

If resources were discovered in the disposal Sites 121, 123, and 134, it is possible that they could not be exploited if drilling could not be carried out from within the site boundaries because of their extent. The use of directional drilling technology from locations outside the site boundaries could reach only a few kilometers into the site area limiting access to other portions of the sites. Access to Sites 122 and 124 is possible if conditions are appropriate for directional drilling because they are smaller.

If it were determined that operations could take place within the disposal sites, resource exploration and development costs would potentially be increased. Finding munitions and ensuring that the area of interest is clear would drive up costs. Activities that could result in contact with agents include some seismic techniques, exploratory drilling, developing production infrastructure, and pipelaying. Costs to locate the presence of munitions could be small compared to the costs of operating in the regional environment. Costs to clear munitions before exploration or exploitation activities take place could be potentially large.

8.8 THREAT TO HUMAN HEALTH AND SAFETY

Human health and safety is potentially at risk in several ways from the presence of chemical munitions in the arctic marine environment. Viscous pieces of raw mustard or munitions containing chemical agent could be ensnared in the trawling nets of commercial fishing boats. There are similar threats to oil and gas exploration crews when they conduct activities that could contact munitions on the bottom. Consumers of commercial fish products could ingest arsenic. Indigenous peoples could be exposed to contaminated fish and mammals in their traditional diets or lose traditional subsistence food sources because of contamination or reduced populations.

8.8.1 Consumers of Fish

Consumption of arsenic-contaminated fish from the study region could potentially affect the health of consumers. Consuming arsenic in drinking water has been shown to be associated with skin cancer in a large epidemiological study.[69] On the basis of this study, inorganic arsenic has been classified as a class A human carcinogen by the U.S. Environmental Protection Agency. Class A carcinogens are substances proven to be carcinogenic in humans.

Consumers of fish products in those countries that currently have a standard for maximum arsenic concentration in fish and fish products are protected against potential adverse health effects of arsenic.[70] Consumers in other countries, including the United States, would be exposed to arsenic-contaminated products because the arsenic content of fish products is

[67]Jorgensen, B.S., B. Olesen, and O. Berntsen, *Mustard Gas Accidents on Bornholm*, AFMIC-HT-111-86, July 1988. AD-B102076, Defence Technical Information Service. Translation from Danish in Ugeskr Laeger, 1985, 147(28):2251-2254.
[68]Kurata, H. 1980. "Lessons Learned From the Destruction of the Chemical Weapons of the Japanese Imperial Forces." *In Chemical Weapons: Destruction and Conversion*. Stockholm International Peace Research Institute. Taylor and Francis, London.
[69]Tseng. W.P., 1977. "Effects and Dose Response Relationships of Skin Cancer and Blackfoot Disease with Arsenic." *Environmental Health Perspectives* 19:109-119.
[70]Reference 8.

not regulated. The potential cancer risk to these consumers is estimated below using the methods of human health risk assessment.

The slope factor[71] for calculation of cancer risk from a daily averaged lifetime dose of inorganic arsenic is 1.75 mg kg^{-1} day^{-1}. Table 8-5 shows the calculated cancer risk resulting from applying this slope factor to several scenarios of normally occurring arsenic ingestion or ingestion rates that have been deemed acceptable by organizations concerned with human health. The estimated normal intake of arsenic in food, for example, is 50 µg per day,[72] which corresponds to a cancer risk of 1.25 x 10^{-3}. The World Health Organization has established a tolerable daily intake of arsenic of 2 µg kg^{-1} body weight day^{-1}, which corresponds to a daily intake of 140 µg per 70 kg per adult and a cancer risk of 3.5 x 10^{-3}. The U.S. Food and Drug Administration has established a tolerance for 2 ppm of arsenic in food. This concentration supports a scenario of a daily intake of 1000 µg per adult if 500 gms of such food is ingested. This corresponds to the highest regulated risk in Table 8-5 of 25 x 10^{-3}.

Table 8-6 shows the lifetime cancer risk from consuming fish containing 1 to 10 ppm of inorganic arsenic. The concentration of 1 ppm is well within the naturally occurring concentration of arsenic in marine fish and shellfish. The concentration of total arsenic in fish, especially demersal species, could increase to 10 ppm in the areas of arsenic-contaminated sediments. The variables in addition to concentration that affect the calculated risk value are the grams of fish consumed per day and the fraction of total fish consumption that is contaminated. Consumption of forty grams per day is the 95th percentile of fish consumption in the United States.[73] The consumption of 700 grams per day (about 1.5 pounds) is the maximum possible daily consumption by a subsistence fisherman eating three meals of fish per day of about 0.5 pounds of fish per meal.

The lifetime cancer risk due to consumption of fish containing total arsenic at 1 ppm ranges from 1 x 10^{-3} for the 95th percentile U.S. consumption to 18 x 10^{-3} for the subsistence scenario. The risk for the 95th percentile U.S. consumption is well within the range of

Table 8-5: Arsenic Cancer Risk of Some Regulated or Background Scenarios

Scenario	Standard	Daily Arsenic Intake for a 70 kg Adult (µg)	Arsenic Dose (µg kg^{-1} day^{-1})	Cancer Risk Due to Arsenic Consumption
USFDA tolerance for arsenic in food	2 ppm	1000 (0.5 kg)	14.2	25 x 10^{-3}
WHO tolerable daily intake of arsenic	2 µg kg^{-1} day^{-1}	140	2	3.5 x 10^{-3}
Drinking water: USEPA MCL, WHO guideline, USFDA	0.05 mg l^{-1}	100 (2 liters)	1.42	2.5 x 10^{-3}
Estimated daily intake of arsenic in food	50 µg day^{-1}	50	0.7	1.25 x 10^{-3}

USEPA - U.S. Environmental Protection Agency
USFDA - U.S. Food and Drug Administration
MCL - Maximum Contaminant Limit
WHO - World Health Organization

[71]The slope factor is a measure of the carcinogenic potency of a substance. The larger the slope factor value, the greater the potency.
[72]U.S. Department of Health and Human Services. 1993. *Toxicological Profile for Arsenic.* Washington, DC.
[73]U.S. Environmental Protection Agency. 1989. *Exposure Factors Handbook.* EPA/600/8-89/043. Washington, DC.

Table 8-6: Cancer Risk of Consumption of Fish Contaminated With Arsenic

Arsenic in Fish (ppm)	Fish Consumed (g day^{-1})	Fish Contaminated (percent)	Cancer Risk Due to Arsenic Consumption
1	40[a]	100	1.0×10^{-3}
1	40	50	0.5×10^{-3}
1	700[b]	100	18×10^{-3}
1	700	50	9.0×10^{-3}
10	40	100	10×10^{-3}
10	40	50	5.0×10^{-3}
10	700	100	180×10^{-3}
10	700	50	90×10^{-3}

regulated or background scenarios shown in Table 8-5. The subsistence scenario risk is close to the risk from consuming food containing the U.S. Food and Drug Administration tolerance standard. If only half of the fish consumed are contaminated, the cancer risk is also halved. At the higher concentration of 10 ppm, the risks are higher by an order of magnitude.

The risk values in Tables 8-5 and 8-6 are probably overestimates because the slope factor used in the calculations is for inorganic arsenic. Approximately 99 percent of the arsenic in fish would be in an organic form[74] that is not carcinogenic.[75] Organic arsenic is not converted to inorganic forms by humans and is excreted unchanged in form.[76] If only one percent of the total arsenic consumed in the calculations used is in the inorganic form, the risks would be reduced by two orders of magnitude from those given in the table.

In addition, the slope factor used in the calculations assumes that the daily intake rate used in the calculation continues for a lifetime. If subsistence fishermen spend less than a seventy-year lifetime consuming 700 grams of fish per day, the risk would be reduced proportionately. Similarly, if the subsistence food source was fish for only half of the year and meat, such as reindeer, was consumed during the other half of the year, the cancer risk due to arsenic would be reduced by one-half.

If the risk calculated above is reduced by two orders of magnitude because arsenic consumed is mostly organic in form, the increased risk to consumers eating fish quantities at the high end of the range for the United States is likely to be small to modest. The increased risk from consuming fish contaminated with arsenic at 10 ppm of total arsenic (ten times the likely natural concentration) is in the range of one in 10,000 to one in 100,000. This is at the upper end of the range of increased risk usually acceptable to regulatory agencies concerned with human health. This estimate could be conservative because it is based on the assumption that fifty to one hundred percent of the fish consumed over a seventy-year lifetime is contaminated at 10 ppm.

A moderate risk exists for indigenous peoples consuming fish contaminated with arsenic at 10 ppm as a significant portion of their diet. Increased risk is in the range of one in 1,000 to one in 10,000. The high end of this range is at the lower limit of risk considered of regulatory concern to U.S. regulatory agencies concerned with human health. The upper end of this range is a conservative estimate because it is based on consuming contaminated fish at all meals for a seventy-year lifetime.

[74]Reference 11.
[75]Goldman, M. and J.C. Dacre. 1989. "Lewisite: Its Chemistry, Toxicology, and Biological Effects." *Reviews of Environmental Contamination and Toxicology* 110:75-115.
[76]Reference 11.

8.8.2   Consumers of Commercial Fish Oils

Exposure of consumers of fish oil products to significant arsenic concentrations is likely to be low. Refining of fish oils to produce the finished product for sale can reduce the concentration of metals by two orders of magnitude,[77] making it unlikely that consumers could receive significant doses of arsenic from these products.

8.8.3   Health and Safety of Fishing Boat Crews

Munitions containing agents or viscous pieces of raw mustard can be captured during bottom trawling by commercial fishing boats, exposing boat crews to injury and death when the net is brought on board. Recovery of chemical munitions and injury and death of fishing boat crew members has been documented in Japan[78] and the Baltic Sea.[79]

No reports of chemical munitions captured during commercial fishing operations in the study region have been found in a search of news sources, government reports, or technical literature. Several explanations exist that could account for this. Munitions could have been dumped only in deep areas where bottom trawling is not used. If munitions were dumped in shallow waters, the sites used could be in areas closed to fishing or are in areas with bottom characteristics that are unsuitable for the use of bottom trawling gear. It is also possible that no chemical munitions have been dumped in regional waters and that the reports reported in Chapter 2 are not accurate.

If chemical munitions are present in regional waters, fishing boat crews could be exposed to injury or death in the future, under some conditions. Bottom trawling could be used at deep locations if changes in gear technology make this fishing method productive and profitable. Opening shallow areas currently closed to fishing would expose any munitions or agent still present.

8.8.4   Health and Safety of Oil and Gas Resource Exploration and Exploitation Crews

The presence of chemical munitions could threaten the safety of crews involved in oil and gas exploration and exploitation activities within disposal sites although this risk is probably low. Any activities that contact the bottom could contaminate equipment with an agent. Seismic surveying crews are also at risk when using certain techniques. Drilling crews could be exposed if agent contaminates drilling muds or drill strings, which are brought to the drilling platform. Crews installing production infrastructure are at risk from contaminated construction equipment. Pipelaying crews installing gathering systems and trunk lines could be exposed to agent released to the water or contaminating equipment during trenching and pipelaying operations.

8.9   CUMULATIVE IMPACTS

A variety of past and current activities in the Barents, Kara, and White Seas have affected the marine environment.[80,81] Any adverse environmental or economic effects resulting from the presence of chemical munitions would add to these effects.

8.9.1   White Sea

Little data on the effects of past and current human activities on the White Sea was found in the English-language publications reviewed for this study. Some things, however, were identified as occurring in the region.

The White Sea is receiving some effluents from industrial activities associated with mining on the Kola Peninsula. These effects are occurring primarily in Kandalaksha Bay. Acid deposition, caused by atmospheric transport of emissions from the burning of

[77]Reference 65.
[78]Reference 68, see also, Chapters 1 and 5.
[79]Reference 67.
[80]Matishov, G.G., 1993. *Anthropogenous Destruction of the Ecosystems in the Barents and the Norwegian Seas.* Kola Scientific Center, Russian Academy of Sciences. Apatity, Russia.
[81]Reference 58.

fossil fuels in Europe, is occurring in the region. Acidification of regional soils may be a consequence of this deposition and may be causing the release of some metals from the soils into runoff into the sea.[82] A spill in 1990 of "thousands of tons" of rocket fuel into Dvina Bay from the Russian military base at Severodvinsk caused an enormous kill of invertebrates, fish, and seals in a large area of the bay. Fishing was suspended by the local government during this period.[83]

If munitions filled with Lewisite were dumped into the White Sea at disposal Site No. 120, the long-term effect would be an area of permanent arsenic contamination in the sediment of the deep basin. The size of this area would depend on the quantity of Lewisite disposed at the site but could be several times the size of the disposal area.

8.9.2 Barents Sea

A variety of activities have affected the Barents Sea ecosystem. These include nuclear weapons testing in the atmosphere on Novaya Zemlya and in the offshore waters, disposal of liquid and solid radioactive materials, oil and gas exploration and production, and possible over-exploitation of the fishery. Large areas of benthic habitat may be damaged by bottom trawling in the shallow central and southern areas of the Barents Sea although the magnitude of the damage is not known.[84]

Benthic productivity could be lost at one or both Barents Sea disposal sites from the toxicity of leaking chemical agents and breakdown products and by

deposition of arsenic in the sediments if munitions containing Lewisite were disposed of at these sites. The effect of toxic agent plumes on the benthos would be temporary but could last for a decade or several decades. Any loss of productivity from contamination of sediments by arsenic would be permanent in the time scale of human activities.

Benthic productivity losses from munition disposal would be additive with the other activities that could temporarily and permanently affect benthic habitat and productivity. Large areas may have been damaged by bottom trawling. The magnitude of this damage is not stated, but loss of some productivity would be likely. Oil and gas exploration and production activities have been modest to date, but the potential exists for extensive activities in the future. Benthic systems would be affected by disposal of drilling muds and cuttings, discharge of produced waters, and installation of gathering and trunk pipeline systems from areas of production.

8.9.3 Kara Sea

Little data on the effects of past and current human activities on the Kara Sea was found in the English-language publications reviewed for this study. Disposal of radioactive material in fjords and bays on the east coast of Novaya Zemlya and testing of nuclear weapons in the atmosphere on Novaya Zemlya may be the main activities that could affect the marine ecosystem. Arsenic contamination of sediment at the deep disposal sites would be an additional effect in the near-shore region of Novaya Zemlya.

[82]Kristoforova, N.K., 1994. "Chemicoecological Characterization of Kandalaksha Bay (White Sea) by the Content of Heavy Metals in Mollusks and Algae." *Russian Journal of Marine Biology* 20(2):117-123.
[83]Economist Publications. 1990. *A major disaster in the White Sea.* News report dated August 30, 1990.
[84]Reference 80.

SUMMARY

V-gas

- There is no reason to believe that V-gas has been dumped in arctic seas. However, against the possibility of a mistake having been made, or the potential for future dumping, a brief investigation was carried out. Thus, the seawater chemistry of V-gas was investigated, and the principal reactions, reaction products, reaction rates, and other parameters obtained.

- V-gas (an isomer of the U.S. agent VX) is estimated to have a half-life of 5.4 years in seawater at 0° C. The principal reaction product, an analog of EA 2192, is stable.

- The toxicity of V-gas to marine species is estimated, on the basis of aquatic toxicity data, to be less toxic than Sarin by a factor of approximately five. Toxicity data in laboratory animals, however, shows VX to be five times more toxic than Sarin. The toxicity of EA 2192 is estimated to be roughly half that of the parent compound.

- Because of its high toxicity and long persistence, V-gas may not pose a simply local problem in the ocean environment. Some ocean processes may be important that were not necessary to consider in the local problems posed by mustard, Lewisite, Tabun, or Sarin.

- A credible case for dumped V-gas generating pan-arctic environmental problems cannot be made. However, there is clearly the potential for the release from *single* munitions generating concentrations having significant biological effects at distances of kilometers from the leaking munition.

- No estimate of the environmental impact of the release of V-gas from a large quantity of munitions was carried out.

Munition Burial

- If the munitions dumped in arctic seas were to be buried in seafloor sediments, the process of corrosion, and the resulting time delay to release of agent, could be affected. Also, the potential for disturbance of munitions by trawling would be lessened with buried munitions, and the likelihood of agent release or dangerous encounters by fishermen reduced.

- Dumped munitions could become buried by impact burial upon dumping, and by gradually being covered by sediments, where no initial impact burial occurred.

- Estimates of terminal velocities of sinking pallets were found to be low, no greater than 2-7 ms⁻¹. Given the firm sediments at these sites, it is concluded that impact burial of palletized munitions is very unlikely.

- Sedimentation rates at the sites was also investigated with the conclusion that the rates are far too low ($\approx$ several cm per 1000 years) to cause significant burial in the several decades since dumping occurred.

- Information from the literature was reviewed to support estimates of sediment characteristics at the dump sites. The conclusion reached was that the sediments are thought to be rather compact, largely because of the high content of terreginous material. This, together with the rather low estimated impact velocities, suggests that impact burial of these munitions upon dumping is unlikely.

This chapter considers two topics that have been deferred in previous chapters, the highly toxic, third generation, CW agent V-gas and the potential concern over munitions dumped from ships being buried in the sediments.

In the case of V-gas, there are *no known reasons to think that this agent was disposed of by the USSR by ocean dumping.* However, it may be interesting to ask a hypothetical question concerning the environmental impact should some nation contemplate future arctic seas disposal of this agent. Also, one might wish to consider the consequences of a possible mistake having been made in the past resulting in ocean dumping of limited quantities of V-agent.

In prior chapters of this study, it has been assumed that the dumped munitions lie on the seafloor, exposed to corrosion and damage by trawling. However, burial of CW munitions could perhaps occur, either as a result of impacting the seafloor at sufficient speed to directly bury in soft sediments or as a result of sedimentation over the years as the munitions lie on the seafloor.

9.1   V AGENTS

The V agents are the most recently developed of the conventional nerve agents. They were discovered independently by Ranaji Goshem, of ICI, and Lars-Erik Tammelin, of the Swedish Institute of Defense Research, in 1952. Shortly thereafter, the U.S. Army began a systematic investigation of this class of compounds at Edgewood Arsenal and as a result, VX

was developed.[1] An isomer referred to as V-gas was developed later by the USSR.

9.1.1   Chemistry of V Agents in the Ocean Environment

V agents, including VX (methylphosphonothioic acid, S-[2-[bis(1-methylethyl)amino]ethyl] O-ethyl ester) and its isomer "V gas" (methylphosphonothioic acid, S-[2-(diethylamino)ethyl] O-2-methylpropyl ester), are members of the phosphorylthiocholine class of compounds.

VX was produced and stockpiled by the United States; V-gas was produced and stockpiled by the Soviet Union. VX is colorless and odorless. Both VX and V-gas have the formula $C_{11}H_{26}NO_2PS$ and molecular weight 267.37. The Chemical Abstracts Service registry number for VX is 50782-69-9; for V-gas the registry number is 159939-87-4.

One group gives hydrolysis rate constants for VX as 8.4×10^{-3} hr^{-1} ($[VX]_o = 2$ percent) and 12.1×10^{-3} hr^{-1} ($[VX]_o = 0.5$ percent) in distilled water at 21°C.[2] 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.[3] Rate constants have been measured at pH 7.7 in a synthetic seawater solution at several temperatures between 15°C and 45°C; $k_{obs} = 4 \times 10^{-3}$ hr^{-1} at 25°C.

The rate constant as a function of temperature at pH 7.7 in seawater obeyed the following expression:

$$\log k_{obs} = 24.286 - \frac{7954 \text{ K}}{T},$$
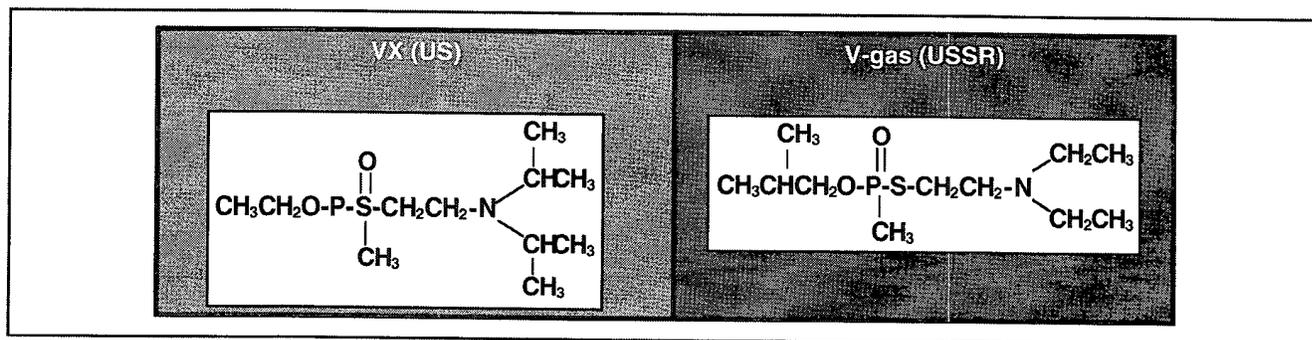
[1]Antonov, N., *Chemical Weapons at the Turn of the Century*, LN 72-96, p. 32.

[2]Szafraniec, L. J., L. L. Szafraniec, W. T. Beaudry, and J. R. Ward, "On the Stoichiometry of Phosphonothiolate Ester Hydrolysis," *CRDEC-TR-212*, July 1990, AD-A250773.

[3]Epstein, J., J. J. Callahan, and V. E. Bauer, "The Kinetics and Mechanisms of Hydrolysis of Phophonothiolates in Dilute Aqueous Solution," *Phosphorus*, 1974, 4, 157-163.

where k_{obs} is in hr^{-1}.[4] Extrapolating to 0°C with this expression, the rate constant is calculated as 1.47×10^{-5} hr^{-1}. This corresponds to a half-life of 5.4 years in seawater under conditions of this study; VX is thus extremely long-lived in the ocean. For purposes of this study, the value of 5.4 years will be used for the half-life of V-gas.

The first step in the basic hydrolysis of VX is the attack of hydroxide on the phosphorous to form an intermediate, which then can decompose in one of two ways. In the first mode, the anion of diisopropylaminoethanethiol is expelled to give the ethyl ester of methylphosphonic acid:
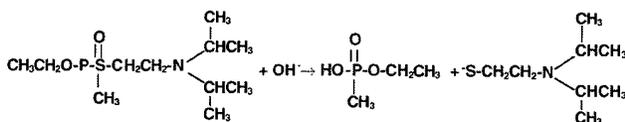
This reaction accounts for 34 to 37 percent of VX hydrolysis in distilled water.[5] In the second, ethoxide is expelled to give EA 2192:
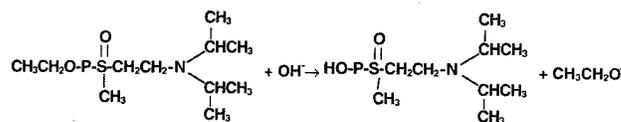
This reaction accounts for 42 to 50 percent of VX hydrolysis. The remainder of VX, roughly 10 percent, hydrolyzes via displacement of a thiophosphonate anion from a carbon atom.

The amounts of the compounds produced during the hydrolysis reaction are given in Table 9-1. The log K_{ow} value for VX is 2.06.[6] Of these products, only EA 2192 is known to have significant toxicity. EA 2192 is very long-lived; under comparable conditions, i.e., 22°C, pH 13-14, EA 2192 undergoes hydrolysis 3,700 times more slowly than VX.[7] If the same is true under the conditions of this study, EA 2192 would have a half-life of over 5,000 years.

Table 9-1: Hydrolysis Products From VX

Compound	MW	Solubility, g l^{-1}	Estimated log K_{ow}[8]	Product produced from 1 kg VX, g
EA 2192	239.32	–	1.52	413
Ethanol	46.07	miscible[9]	-0.31	79
Methylphosphonic acid, ethyl ester	124.08	–	-0.15[10]	165
Diisopropylaminoethanethiol	161.31	–	2.29	214
Methylphosphonothioic acid, ethyl ester	140.14	–	0.00	52
Diisopropylaminoethanol	145.25	78.6[11]	0.88	54
Methylphosphonic acid	96.02	"very"[12]	-0.70	359

[4]Demek, M. M. et al., "Behavior of Chemical Agents in Seawater," *EATR 4417*, August 1970, AD-873242.
[5]Reference 2.
[6]Estimated using Syracuse Research Corporation, LOGKOW version 1.50; see W.M. Meylan and P.H. Howard, *J. Pharm. Sci.* 1995, 84(1): 83-92.
[7]Yang, Y. C., L.L. Szfraniec, W.T. Beaudry, and C.A. Bunton, *Perhydrolysis of nerve agent VX*, J. Org. Chem., 1993, 58, 6964-6965.
[8]Reference 6.
[9]*The Merck Index, 11 ed.*, Budavari, S., M.J. O'Niel, A. Amith, and P.E. Heckelmanm, (Eds.), Merck & Co.: Rahway, N.J. 1989, p. 594, compound no. 3716.
[10]Experimental value from Hansch, C. and A.J. Leo, MEDCHEM Project, Issue No 26, Claremont, CA: Pomona College, 1985.
[11]EPA ASTER database.
[12]Weast, R.C., (ed.), *Handbook of Chemistry and Physics, 56th ed.*, CRC Press, 1976.

The hydrolysis chemistry of the Soviet V-gas is expected to be similar. Compounds produced during hydrolysis of the Soviet V-gas are likely to include:

- Methylphosphonothioic acid, S-[2-(diethylamino)ethyl] ester (the analog of EA 2192)

$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}-S-CH_2CH_2-N\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_2CH_3}{}}$$
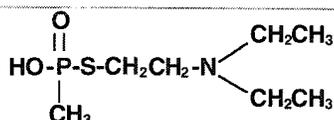
- 2-Methyl-1-propanol

- Methylphosphonic acid, 2-methylpropyl ester

- 2-(Diethylamino)ethanethiol

- Methylphosphonic acid

9.1.2 Toxicity of VX, V-gas and Their Breakdown Products

The LD_{50} values of VX and its major toxic breakdown product, EA 2192, for various laboratory animals are shown in Table 9-2. Comparison with the data in Table 6-6 shows that VX is roughly twice as toxic in rabbits, and five times as toxic in guinea pigs, as Sarin.

The major breakdown product, EA 2192, is roughly half as toxic as the parent compound VX, when compared in rabbits, e.g., LD_{50} of 0.017 mg kg⁻¹ for EA 2192 compared to 0.008 mg kg⁻¹ for VX. Thus, the degradation of VX with a half-life of 5.4 years, will reduce the toxicity to the marine environment by only a factor of two.

The acquatic toxicity of VX is illustrated in Table 9-3. The most sensitive species, striped bass, has an LC_{50} of 0.035 mg l⁻¹. Consistent with the methodology used for other agents, applying a multipler of 0.1 to this number yields an ENEC of 3.5 μg l⁻¹. While this is a 3.5-fold higher than the ENEC for Tabun and Sarin, indicating a lesser toxicity, the use of this as a benchmark for marine toxicity should consider two significant facts regarding VX. One is the fact that available data indicates that VX is approximately 5-fold more toxic to mammalian species than Sarin or Tabun. Two is the fact that VX undergoes relatively slow hydrolysis, with a half-life of 5.4 years, to a compound that is only half as toxic to mammals and orders of magnitude more persistent than the parent compound.

This is a very different situation from the release of the other agents analyzed, whose more rapid hydrolysis reduces toxicity by several orders of magnitude.

Table 9-2: LD_{50} Values for VX and EA 2192 in Laboratory Animals

Substance	Species	LD_{50}
VX	Rabbits	0.008 mg kg⁻¹ (iv)[13]
	Rabbits	0.0154 mg kg⁻¹ (sc)[14]
	Guinea Pigs	0.0084 mg kg⁻¹ (sc)[15]
EA 2192	Rabbits	0.017 mg kg⁻¹ (iv)[16]

Table 9-3: Twenty-Four Hour LC_{50} Values for VX in Aquatic Species[17]

Species	Blue Crab	White Perch	Striped Bass
LC_{50} mg l⁻¹	29	0.046	0.035

[13]Yang, Y.C., L.L. Szfraniec, W.T. Beaudry, and D.K. Rohrbaugh, 1990. "Oxidative Detoxification of Phosphonothiolates." *J. Am. Chem. Soc.* 112(18): 6621-6627.

[14]Gordon, J.J. and L. Leadbeater. 1977. "The Prophylactic Use of 1-Methyl, 2-Hydroxyiminomethyl- Pyridinium Methanesulfonate (P2S) in the Treatment of Organophosphate Poisoning." *Toxicology and Applied Pharmacology* 40: 109-114.

[15]Reference 14.

[16]Reference 13.

[17]Weimer, J.T. et al. 1970. *Toxicity of VX and GD in Aquatic Animals Indigenous to the Carrol Island Test Area Water.* Edgewood Arsenal Technical Report 4441.

No toxicity data are available for V-gas. It can be plausibly assumed from its structural homology to VX that the mechanism and potency of the toxicity of V-gas and its breakdown products are similar to VX, and that an ENEC of 3.5 µg l⁻¹ would be appropriate for V-gas as well. The remaining two benchmark levels, EPEC and ELEC, can be obtained in the same fashion as for the four agents previously considered (multiplication by factors of 10 and 100, respectively). Thus, the benchmark levels that would be used in an analysis of the extent of V-gas marine toxicity, such as that carried out for other agents in Chapter 7, are given in Table 9-4.

Table 9-4: Estimated Benchmark Toxic Concentrations for V-gas

Agent	ENEC mg l⁻¹	EPEC mg l⁻¹	ELEC mg l⁻¹
V-gas	3.5	35	350

It should be appreciated that the values in Table 9-4 are for V-gas, but its major breakdown product, EA 2192, has a toxicity higher than the agent by a factor of two. However, with the half-life of V-gas being more than five years, the rate of production of EA 2192 would be sufficiently low that, to first order, direct toxicity will be driven by the concentration of the agent.

9.1.3 Dispersal by Ocean Processes

Once V-gas is released from munitions into the sea, dilution through turbulent mixing, transport by ocean currents, and hydrolysis all will take place, as seen in Chapter 7. However, in the case of V-gas, the combination of a very long half-life and high toxicity suggest that we must reexamine the previous conclusion that dispersal is a local problem.

The first and most obvious conclusion to be drawn about dispersal of V-gas released into the ocean environment is that hydrolysis to benign compounds will *not* place a useful upper bound on the relevant time scales. The half-life of 5.4 years means that after eighteen years, approximately 10 percent of the initial mass of agent will remain in the ocean. Such times are *comparable with those of general arctic circulation* and suggest that the problem might be pan-arctic, this "suggestion" ignores dilution through turbulent

mixing, which will place much more stringent limits as seen below. Moreover, the principal hydrolysis product, EA 2192, is stable and even more toxic than the agent. However, both V-gas and EA 2192 have small values of Log K_{ow} indicating little likelihood for adsorption onto particulates.

In advance of doing any estimates of dispersal, one has a physical picture suggesting that the effective extent of toxicity is governed primarily by dilution as a result of the turbulent mixing processes generated by the prevailing currents. To gain some appreciation for the limits of toxicity of V-gas, Figure 9-1 shows the total volume (in km³) of seawater that could be contaminated at the three benchmark concentrations as a function of the quantity (in kg) of agent.

It is only when quantities on the order of kilotons are considered that water volumes approaching the volume of the White Sea, or an appreciable fraction of the Kara Sea, can be contaminated at the lowest concentration of interest, ENEC. Thus, there is no possibility that the entire Arctic Ocean, or even the entirety of the Barents or Kara Seas, could become toxic to marine life even if at some future date V-gas were dumped in kiloton quantities. If there were any reason to have concern over dumping of V-gas in quantities greater than 100,000 metric tons in the White Sea, then greater than 10 percent of the water volume could reach the ENEC for very long periods of time before hydrolysis or flushing into the Barents reduced the concentration.

Of course this does not rule out contamination of volumes sufficiently large to pose significant environmental hazard. A quantity of 100 tons of V-gas could contaminate up to 100 km³ of seawater if diluted to the level of significant biological effects, EPEC. In the southern Barents and Pechora Seas, with a mean water depth of less than 100 m, this would encompass an area greater than 30x30 km. There would certainly be significant direct biological effects from such contamination and because of the persistence of V-gas, an impact on the regional ecosystem could not easily be ruled out.

The foregoing simplified view, while containing an important bound, ignores two important dimensions of the issue, one of which can be addressed in a

Figure 9-1: Contaminated Volumes at Three Concentrations vs. Quantity of V-gas
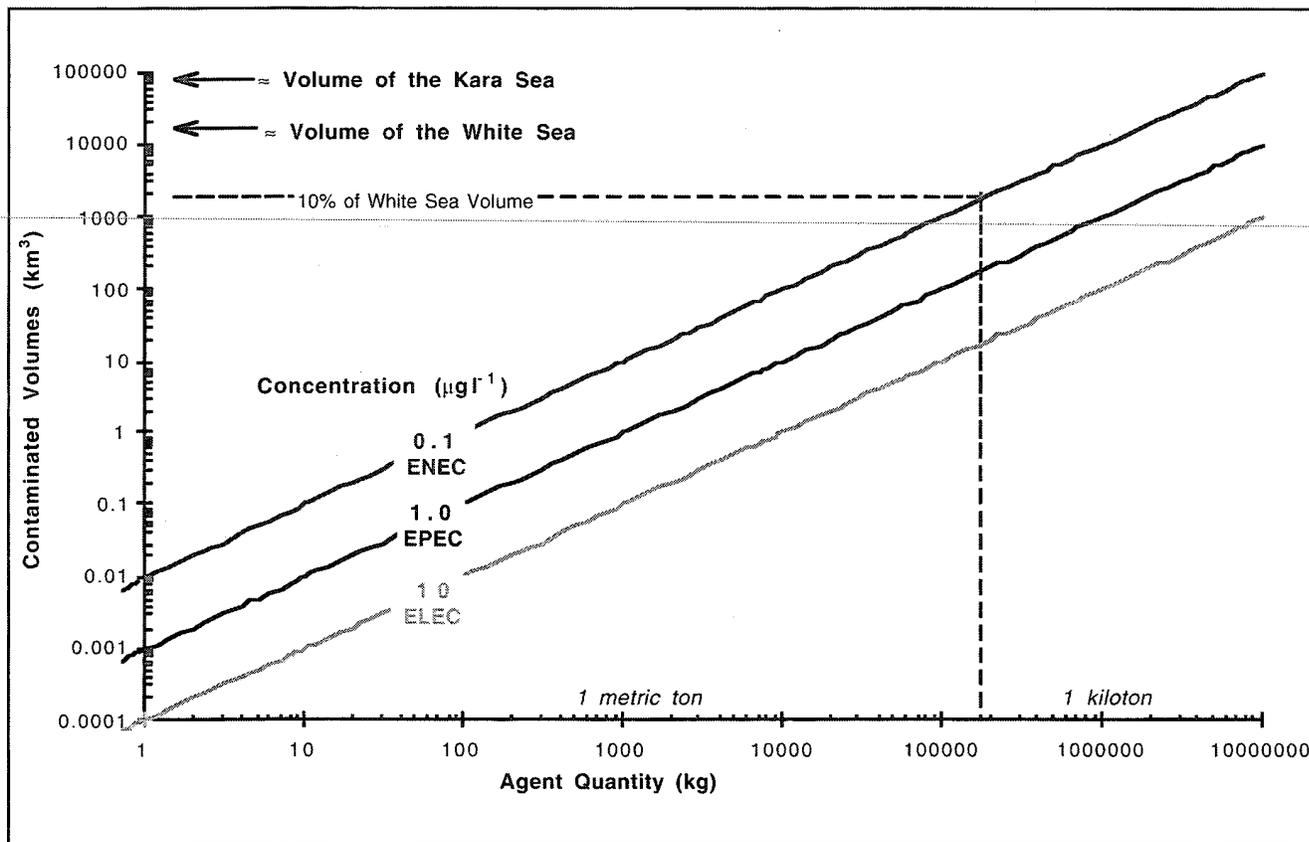
straightforward fashion using the methods of Chapter 7. The linear extent of toxicity in plumes subjected to transport by ocean currents will establish the spatial extent of slowly released agent. However, this spatially averaged view encompassed by the advective-diffusion equation does not consider "pockets" of higher concentration trapped in turbulent eddies which, because of the very long hydrolysis half-life, have the potential to be transported long distances before being smoothed by mixing and molecular diffusion. Addressing this second concern lies beyond the scope of this study.

As we found in Chapter 7, contamination generated by leaking munitions has concentrations that vary with two length scales, one in the horizontal and one in the vertical. These two key length scales are $L_H = \sqrt{K_H / k}$, and $L_v = \sqrt{K_v / k}$, where

K_H and K_v are the horizontal and vertical diffusivities that parameterize the average effects of turbulent mixing. Because of the long half-life of V-gas, these lengths, $L_H \approx 1600$ m and $L_v \approx 500$ m, are significantly longer than in the case of Tabun. This already suggests that the spatial scales of the V-gas problem would be much greater than the ones encountered previously in this study.

It was shown in Chapter 7 that the spatially averaged concentration, parameterized by the advective-diffusion equation, the length of a plume at concentration C generated by release of agent at a rate Q is given approximately by:

$$x_P \approx C^{-1} \left(Q / 4\pi \sqrt{K_H K_v} \right) \qquad (1)$$

9-6

For a release rate of 0.1 kg day⁻¹, the length of a plume of Sarin at ENEC was shown to be approximately 30 m. Thus, the corresponding plume length for V-gas released at the same rate would be larger by a factor of ten, the ratio of concentrations, yielding 300 m for V-gas. At the release rate of 1 kg day⁻¹ the plume length at the ENEC would be 3,000 m. Of course these dimensions only bound the ENEC region whereas most of the mass of a long-lived compound like V-gas is actually located outside the plume at much reduced concentrations. With the larger plume dimensions for V-gas, relative to the other agents considered, and the long half-life, the extrapolation to the extent of contamination at a site containing many munitions may not be done as simply as what has been done previously. Here, too, it is not at all clear that the "local view" adopted throughout this study is applicable. A simple estimate of the contaminated site volumes obtained, assuming that leaking munitions were widely separated and subjected to the same uniform ocean current, is certainly suspect.

Since there is no reason to believe that V-gas has been dumped in arctic seas and because some elements of the methodology developed here for other agents is suspect when applied to V-gas, it would not be useful to speculate on potential environmental effects. However, while it is clear that while pan-arctic contamination resulting from dumping of V-gas in kiloton quantities is unlikely, extensive regional effects could occur and a finer grained analysis than that conducted here would be needed to quantify the environmental impact.

9.2   BURIAL OF DUMPED MUNITIONS

It has been assumed in this study that most munitions dumped at the disposal sites did not significantly penetrate into the sediments upon impact and were not buried subsequently by natural sedimentation. In this section, this assumption is revisited based on an assessment of the likely sediment characteristics at the disposal sites, on estimates of the impact velocity on the seafloor of palletized munitions during dumping and on natural rates of sedimentation in the study region.

9.2.1   Munitions Packing at Time of Disposal

No information is available on how munitions were packed when they were disposed of in the Barents, Kara, and White Seas. It is highly likely, however, that most munitions were packaged in groups on pallets, since this method is a common way of packing munitions for ease of handling during storage, transport, and deployment to points of use. It is likely that very few munitions were disposed of as individual rounds, since handling of individual rounds would have been unsafe and very difficult logistically, given the volume of munitions that seem to have been disposed. (See Chapter 2.) Therefore, since there are no reports of the disposal of chemical weapons in arctic seas by sinking loaded ships, and since dumping of individual rounds is impractical on a large scale, it will be assumed here that the preferred method was the dropping of palletized munitions overboard.

9.2.2   Impact Velocity of Dumped Munitions

Palletized munitions dumped into the water at the disposal sites would accelerate to a terminal sinking velocity well before reaching the bottom. The terminal velocity would be determined by the mass and shape of the sinking object, with its resulting buoyancy and the drag resistance exerted on the object by seawater. Depending on the nature of the sediments and the terminal velocity of the objects, the munitions could become buried in the sediments upon impact.

The forces acting on an object immersed in an incompressible fluid are the weight (W) of the object, the buoyant force (F_B) of the fluid and the drag force (F_D) of the fluid on the object. At the terminal velocity (u) of a sinking object, the sum of the forces acting in the downward direction will be balanced by the buoyancy and drag forces. In its simplest form, $W = F_B + F_D$; where F_B = (unit weight of the fluid) x (volume of the object); and $F_D = C_D(\rho_f u^2/2)A$, where C_D is the dimensionless drag coefficient, ρ_f is the density of the fluid at specified conditions, u is the terminal velocity, and A is the frontal area of the sinking object.

Graphical forms of analytical or quasi-analytical solutions for the drag coefficient of certain shapes can be found in various engineering handbooks and texts.[18] The drag coefficient is normally plotted against the

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[18] For example: White, F.M., 1991. *Viscous Fluid Flow (2nd ed)*. McGraw-Hill New York, NY.

Reynolds number, a dimensionless number which relates the viscous forces of the fluid acting on the immersed object to the inertial force on the object. The relationship is given as $R_e = VL/v$, where V is the speed of the sinking object, L is a representative dimension of the object, and v is the kinematic viscosity. Determining the range of possible Reynolds numbers will establish the region of the curves to be used for estimating the drag coefficients.

As a means of establishing the range of Reynolds numbers, velocities of 2 ms^{-1} and 20 ms^{-1} were selected as encompassing the spectrum of physically plausible speeds. The munitions dumped at sea were, in all likelihood, either palletized or containerized in such a manner that a representative dimension would be the length of one side of a shipping pallet, which was estimated to be about seven feet (approximately 2 m). The kinematic viscosity, *i.e.*, dynamic viscosity/ density, of seawater at 0° C and a salinity of 35 ppt[19] is 1.83 x 10^{-4} m^{2}s^{-1}. At 2 ms^{-1} the Reynolds number is estimated to be $R_e \approx 2.6 \times 10^6$, and at 20 ms^{-1}, $R_e \approx 26 \times 10^6$. Inspection of the curves for cylinders, spheres or discs suggest that for this range of Reynolds numbers the drag coefficient will range between 0.4 and 1.1.[20] Thus, as a preliminary guide, we can expect that drag coefficients would be within this or possibly a somewhat greater range.

A 1987 document prepared for the U.S. Chemical Demilitarization Program catalogs several different munitions including their physical characteristics and shipping configurations.[21] The following five munitions and container payloads were selected as being representative of the types that may have been dumped at sea:

1. Six 8-inch projectiles, placed vertically on a pallet.
2. Twenty-four 105 mm projectiles, placed vertically on a pallet.
3. Eight 155 projectiles, placed vertically on a pallet.

4. Six 750-pound bombs, stacked horizontally (3-2-1) on a pallet.
5. A 1- ton cylindrical container.

Terminal sinking velocities for each of these configurations were calculated over a range of drag coefficients that extends from 0.2 to 1.2. This range is broader than the range identified above. The expanded range provides conservative upper and lower estimates of possible terminal velocities.

Using the approximation that the pallets could be represented as rectangular prisms, terminal velocities were estimated for four palletized munition types and a bulk container using U.S. configurations as examples. The results are summarized in Table 9-5.

Table 9-5: Estimated Terminal Velocities of Sinking Munitions

Type of Pallet		Terminal Sinking Velocity[a] (ms^{-1})
Munition	No./pallet	
8-inch projectiles	6	1.9 - 4.6
105 mm projectiles	24	2.6 - 6.3
155 mm projectiles	8	2.8 - 4.7
750 lb. bomb	6	2.0 - 4.9
Ton container		1.9 - 4.6

[a]Range given is for different drag coefficients.

9.2.3 Sediment Characteristics at Disposal Sites

Characteristics of the sediments at the disposal sites were determined from qualitative descriptions of the regional sediments, as discussed in Chapter 3. None of these descriptions indicated that sediments were flocculent, which would allow palletized munitions to sink deeply into the sediment.

[19]Baumeister, T. (ed. in chief). 1979. *Marks' Standard Handbook for Mechanical Engineers,* Chapter 3. McGraw-Hill, New York, NY.
[20]Daugherty, R.L. and J.B. Franzini, 1977, *Fluid Mechanics with Engineering Applications,* pp. 294-307. McGraw-Hill, New York, NY.
[21]U.S. Army Chemical Stockpile Disposal Program. 1987. *Risk Analysis of the Onsite Disposal of Chemical Munitions.* Report SAPEO-CDE-18-87010. Aberdeen, MD.

White Sea sediments in the deep basin are covered with a shallow, very fine-grained, brown, clayey mud about 20 cm thick. Bedrock is exposed in some places. The thinness of this layer means that munition pallets could not sink deeply into the sediments, even if the low impact velocity and firmness of the sediments did not prevent it.

Sediment at disposal sites in the Barents Sea is probably fairly firm because of the sand content. Site 122 west of Novaya Zemlya is likely to be silty sand or sandy silt, which could have a sand content of 25 to 75 percent. Sediment at disposal Site 134 in the Barents Sea off Kolguev Island is sand or sandy silt, which would be very firm.

Sediment at disposal Site 123 in the Kara Sea at the northern end of Novaya Zemlya is greater than 8 percent sand and gravel, ranging up to 47 percent near the southern end of the disposal area.[22] These sediments would be fairly firm.

Sediment at disposal Site 124 in the East Novaya Zemlya Trough is silty. It is possible that pallets could sink a little way into these sediments upon impact, but it is unlikely that they would be completely covered.

9.2.4   Munition Burial

Terminal velocities at the low end of the range estimated in Section 9.2.2 represent the postulated munitions bundles or rectangular prisms with relatively high drag coefficients, i.e., not streamlined. Low drag coefficients were used to conservatively bound the velocity calculation. These coefficients resulted in the somewhat higher terminal velocities. Overall, however, these velocities are relatively slow and the kinetic energy on impact would be equivalent to a 1.5 ton automobile crash test of between 2.5 and 14 mph.

While the specific characteristics of the sediments at the disposal sites are not known, the dominant sedimentation processes and high content of coarse terrigenous material suggests rather compact sediments at the disposal sites. This implies that the low energy impacts have limited potential for impact burial of the munitions bundles. Table 9-6 provides estimated penetration depths for the postulated munitions bundles. The basic principle is that the energy of impact will be dissipated by the cohesive material on the ocean floor.[23] The equation governing the energy transformation is given below:

Another factor is that the sedimentation rates in the

$$1/2m\, V^2 = q_{(ultimate)} * A * \rho * x_{(max)}$$

where

m	=	mass
V	=	terminal velocity
$q_{(ultimate)}$	=	bearing capacity of sediment (based on dimensionless bearing capacity coefficients as described in reference 22 Section 3.9.1)
A	=	area (frontal area of falling object)
ρ	=	specific weight of seawater (~9810 N/m³)
$x_{(max)}$	=	penetration depth

[22]Andrew, J.A. and J.H. Kravitz. 1974. "Sediment Distribution in Deep Areas of the Northern Kara Sea." pp.231-256. In Herman, Y. (ed.). Marine Geology and Oceanography of the Arctic Seas. Springer-Verlag, New York, NY.
[23]Schenck, Hilbert, Jr., 1975. Introduction to Ocean Engineering, Chapter 3. McGraw-Hill, New York, NY.

Table 9-6: Estimated Penetration Depths for Postulated Munitions Bundles

Type of Pallet		Terminal Sinking	Estimated Range of
Munition	No./Pallet	Velocity (m s^{-1})	Penetration Depths (m)
8 inch projectiles	6	1.9 - 4.6	0.1 - 0.4
105 mm projectiles	24	2.6 - 6.3	0.1 - 0.5
155 mm projectiles	8	2.8 - 4.7	0.14 - 0.4
750 lb. bomb	6	2.0 - 4.9	1.9 - 4.0
Ton container		1.9 - 4.6	1.8 - 3.9

study region are variable but, generally, are very slow. For the Barents Sea, the rate is reported to be about 1 to 3 cm per 1,000 years.[24] In the central part of the White Sea, the location of Site 121, the rate of accumulation of the very fine grained, brown, clayey mud is 2 cm per 1,000 years. On the western margin of the Kara Sea, in the Novaya Zemlya Trough, the sedimentation rate is cited as being 3 to 10 cm per 1,000 years.[25] These rates are much too slow to bury munitions pallets or single munitions on the sediment surface during the period of corrosion and subsequent release of agent, which is likely to be on the order of twenty to fifty years.

[24]Fairbridge, R.W. (ed.). 1966. *The Encyclopedia of Oceanography.* Reinhold Publishing Corporation. New York, NY.
[25]Pfirman, S.L., J. Kogeler and B. Anselme. 1995. "Coastal Environments of the Western Kara and Eastern Barents Seas." *Deep-Sea Research* 42(6): 1391-1412.

The objective of this study was to develop a credible assessment of the potential for significant adverse impact on the environment arising from CW munitions dumped in arctic seas. In the view of the authors, a credible assessment required addressing all of the zeroth order processes involving agent release, seawater chemistry, physics of ocean dispersal, biological interactions, and the like. The intent was to quantify the magnitude of the effects of these processes on ecosystems. Moreover, given the nature of the U.S. Government request for this study, the intent was not to conduct an assessment of compliance with U.S. law or international convention regarding ocean dumping of CW munitions.

Since we are dealing with chemical munitions developed for military operations, it is obvious that once dumped into the sea, any CW agent leaking out is likely to have some level of adverse impact on the environment. The issue for this assessment was to quantify this impact to the degree possible and to determine its significance. The test for significance was taken to mean an effect large enough to have some potential importance for national security perhaps, for example, through impact on fish stocks, on human health and safety, on exploitation of natural resources, or on international relations.

To this point, the assessment has proceeded according to the logic in Figure 10-1.

Each chapter in this flow contains several levels of summary material which are not reproduced here. In the next section the primary results obtained throughout this lengthy analysis are recast in terms of answers to a number of key questions that bear directly on the purposes for which this assessment was conducted.

10.1 FINDINGS

As mentioned above, the findings of this assessment are put forth as the answers to a series of key questions.

1. **Is it probable that large quantities of CW munitions were dumped by the USSR in the arctic seas?**

   Yes, highly probable. Ocean dumping of CW munitions was a fairly common international practice during the Cold War era. All information available strongly suggests that the USSR extensively dumped CW munitions in a variety of ocean areas, including arctic waters.

Figure 10-1: Analysis Flow
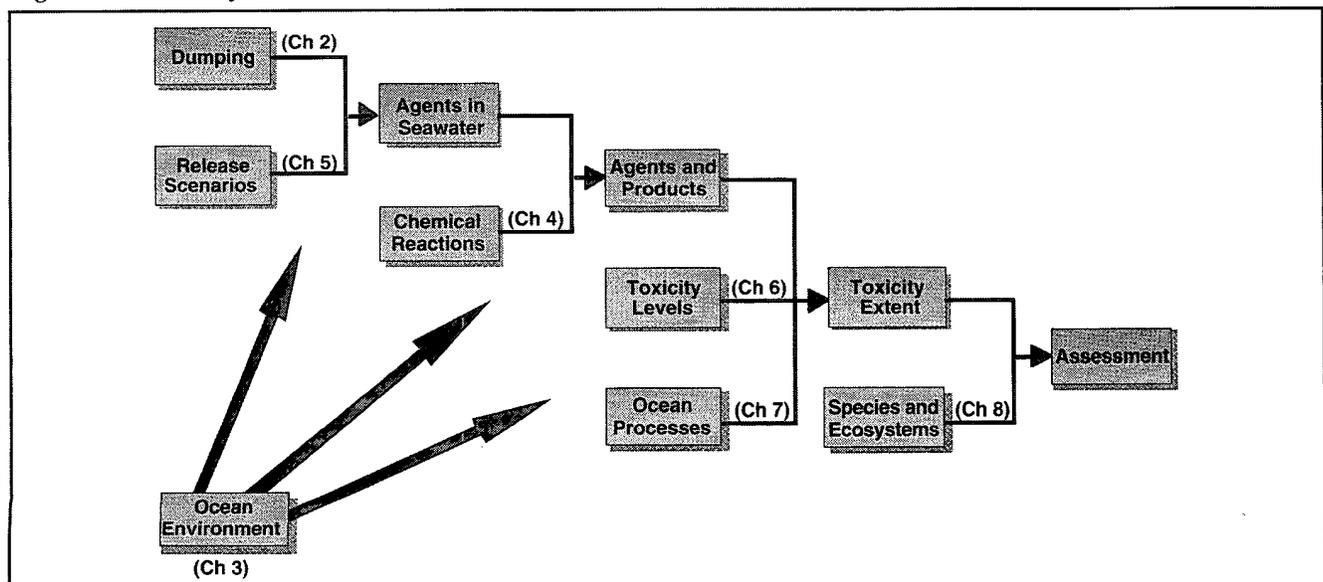
In the final years of World War II, chemical munitions certainly were dumped at sea by Germany and Japan. In the years immediately following the war, it is well-documented that there was extensive ocean dumping by the Allied powers in the Baltic and in Japanese waters. There is a considerable, though poorly documented, history throughout the subsequent Cold War years of dumping of CW munitions at sea by several nations, including the United States.

At the end of World War II, large ammunition depots were discovered in Germany containing mustard gas grenades and mustard gas, sneezing gas and tear gas bombs. From 1946 to 1947, an estimated 50,000 to 150,000 tons of chemical munitions were dumped at a depth of approximately 100 m in the Bornholm Basins, fifteen miles off the Danish island. Approximately 2,000 tons of chemical munitions, predominantly mustard gas and sneezing gas, were dumped in the Gotland basins off the coast of Sweden.

Details of dumping operations in Japanese waters were not widely known until 1972 when the Japanese Prime Minister commissioned a national inquiry to investigate the status of the chemical weapons disposed of in the 1940s. Numerous accidents in the 1960s and early 1970s prompted the inquiry.

Open source reporting on the dumping of chemical agents and weapons in the arctic seas by the USSR during the Cold War years is ambiguous and incomplete. The major source has been Russian scientists, especially Lev Federov who has written several recent books on the subjects of CW weapons and their disposal. The open press has described alleged incidents in which obsolete Soviet chemical weapons, as well as German chemical munitions captured after World War II, were dumped in the northern and far eastern seas surrounding Russia. In contrast to well-characterized campaigns of chemical weapons dumping in the Baltic Sea by the Allies in the 1940s, reports of such dumping in the arctic regions by the USSR have never been confirmed officially.

Not surprisingly, compiling and accurately documenting statistics on USSR dumping activities in the arctic seas would be difficult and would require the cooperation of the Russian government. However, the accumulation of sources reporting specifics of ocean dumping and the continuity with what had become common international practice during the Cold War, is convincing that such dumping did occur. Moreover, it extended over many years, and may have involved large quantities and a variety of CW agents.

2. **Is it known where and when this dumping may have occurred, what agents may have been dumped and in what quantities?**

Little is known with any certainty. However, it is highly probable that thousands of metric tons of munitions containing the CW agents Tabun, Sarin, mustard, and Lewisite were dumped in the White, Kara, and Barents Seas. Other agents may have been dumped as well, but even less is known and it is very likely that, if such dumping occurred, the quantities were much smaller.

Identification of sites for this assessment was based upon the following:

- Delineation of restricted or hazardous areas on Soviet and Russian navigation charts for the arctic seas of interest;

- Dumping areas shown on maps prepared by Genady G. Matishov of the Murmansk Marine Biological Institute (MMBI) of the Russian Academy of Sciences, in cooperation with the Norwegian Polar Research Institute and the Institute of Oceanology of the Polish Academy of Sciences;

- Recent writings of Russian scientists; and

- Defense Mapping Agency maps.

The Barents Sea has two candidate locations for CW munitions dumping: one site is west of Novaya Zemlya located at 72°N50' 49°E00'; the

second is north of Kolguev Island at 69°N35' 47°E55'.

In the Kara Sea, eight explosive and military materials dumping areas are identified at the northern end of Novaya Zemlya, off Cape Zhelanyia, in the region bounded by 77-78°N 68-70°E, encompassing an area of roughly 17,150 km².

Two closely related dump sites have been identified in the White Sea, northeast of the Solovetsk Islands. Both sites are identified in DMA charts and in Area 121 at 65° 25'N, 36° 40'E. Many activities are prohibited at these sites, including anchoring, bottom fishing, and undersea work, suggesting that there are real hazards from dumped munitions.

A 1995 open press report from Moscow indicated that 40,000 tons of mustard and Lewisite were dumped in the White Sea during the 1950s and 1960s. Lacking any other quantitative reporting, this value has been used to represent the level of dumping in the White Sea in the present study.

However, combined production of mustard and Lewisite in the Soviet Union between 1941 and 1945 is estimated to have reached 115,000 tons. The balance, 75,000 tons of mustard and Lewisite, is taken as the total quantity dumped in the Barents and Kara Seas, jointly or severally.

Reports in the open press on the dumping of Tabun in the arctic seas are scarce and only anecdotal. There are descriptions of the capture of German production facilities for Tabun by the Soviet Army at the end of World War II. Allied data indicated that the German facility had produced 12,000 tons of Tabun. For purposes of this assessment, it was assumed that no more than 30,000 tons of Tabun were dumped in arctic seas. This is possibly too high, if one takes into account the German production only. It was taken as an upper bound for purposes of this study.

Sarin apparently was not produced successfully by the Soviets until the late 1950s. It is generally understood that a German production facility was under construction at the end of World War II and that the German equipment for its production, including pilot quantities, was captured by the Soviet Army and transported to the Soviet Union after World War II. It is not known if stocks of German Sarin weapons were captured by the Soviet Army. For the present study, the assumption was made that no more than 2,000 tons of Sarin were dumped in the Russian arctic seas.

3. **What is the condition of the dump sites; how long after dumping would the CW agents be contained in the munitions?**

There is no information concerning the current condition of the probable arctic CW dump sites, nor is there information concerning their past condition. There is only anecdotal and inferential support for the view that the period may be very long, even decades, over which chemical munitions could remain intact on the seafloor before corrosion of the casings allows the agents to be released into the sea. We cannot exclude the possibility that a large fraction of the munitions dumped in arctic seas could remain intact today, with any consequent impact on the ecosystems yet to occur.

Figure 10-2 shows a compilation of both medical records involving actual harm to fishermen, anecdotal Baltic data involving fishermen recovering CW weapons, and various incidents from Japan. It presumed that the greater numbers of yearly data points in the 1976-1991 study than in the 1946-1984 study are because the latter involve incidents serious enough to have generated medical reports whereas the former only involve recovery of weapons debris.

The Baltic experience shows conclusively that if fishing, especially trawling, occurs at the dump sites, munitions on the seafloor can be disturbed leading to harm to fishermen and sometimes death. From 1946 to 1984, there were a total of 197 patients suffering from mustard gas exposure in the Baltic Sea. A total of 171 were treated as ambulatory patients and 26 were admitted to the hospital. In both 1947 and 1948, there were two reported deaths resulting from a mustard disposal

Figure 10-2: CW Munitions Related Incidents
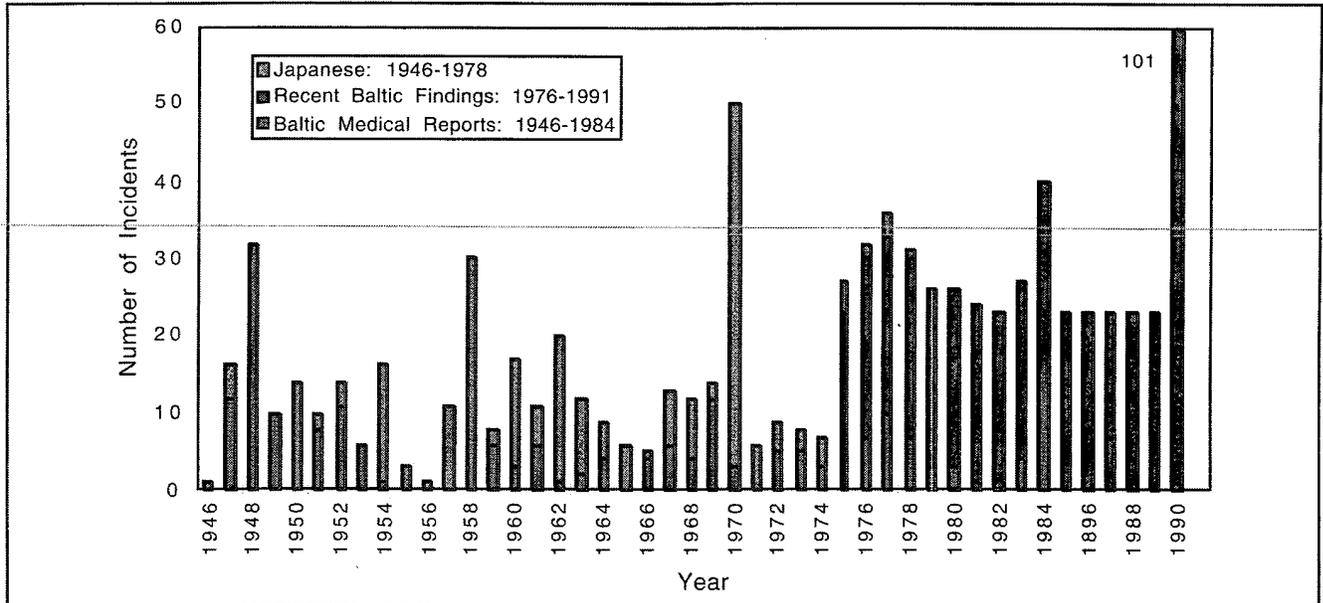
mishap. As recently as 1990, 101 incidents of fishermen recovering CW munitions debris were reported, though none apparently resulted in injury.

The Baltic experience clearly suggests that some munitions remain intact on the seafloor after fifty years. *There is no evidence to suggest that a major release of agents from the CW munitions dumped into arctic seas has already occurred.* The corrosive disintegration period, T_1, is defined as the elapsed time after dumping and before corrosion begins to release agents from *large numbers* of munitions. The primary release period, T, is the time period during which most of the munitions at any site could be expected to undergo corrosive disintegration. This release period was treated parametrically in this assessment, with T bounded by five and fifty years, as shown in Figure 10-3.

There is no information that exists to indicate what T_1 is, except for discovery of munitions on the seafloor of the Baltic after fifty years. Unlike the Baltic, there are no widespread reports of fishermen in arctic seas encountering chemical

weapons. This could be because of the "Hazardous Dump Site" warnings on charts have limited the scope of trawling activities at these sites and the munitions have laid undisturbed for decades. This study sheds no further light on the period T_1, referring only to the empirical Baltic experience for insight.

4. **Once CW agents begin to leak into the sea, are any chemical reactions that may occur understood well enough to support reliable estimates of the quantity of toxic compounds that could be produced?**

Yes. An understanding of the chemical trans-formations that CW agents are likely to undergo are critical to assessing their impact on the environment. The chemistry of CW agents in the marine environment is dominated by hydrolysis, the reaction of the agents with water. The important reaction products have been identified and the rate constants determined.

The key features of the chemistry of CW agents in the marine environment are as follows:

Figure 10-3: Schematic Illustration of the Distribution of Release Events
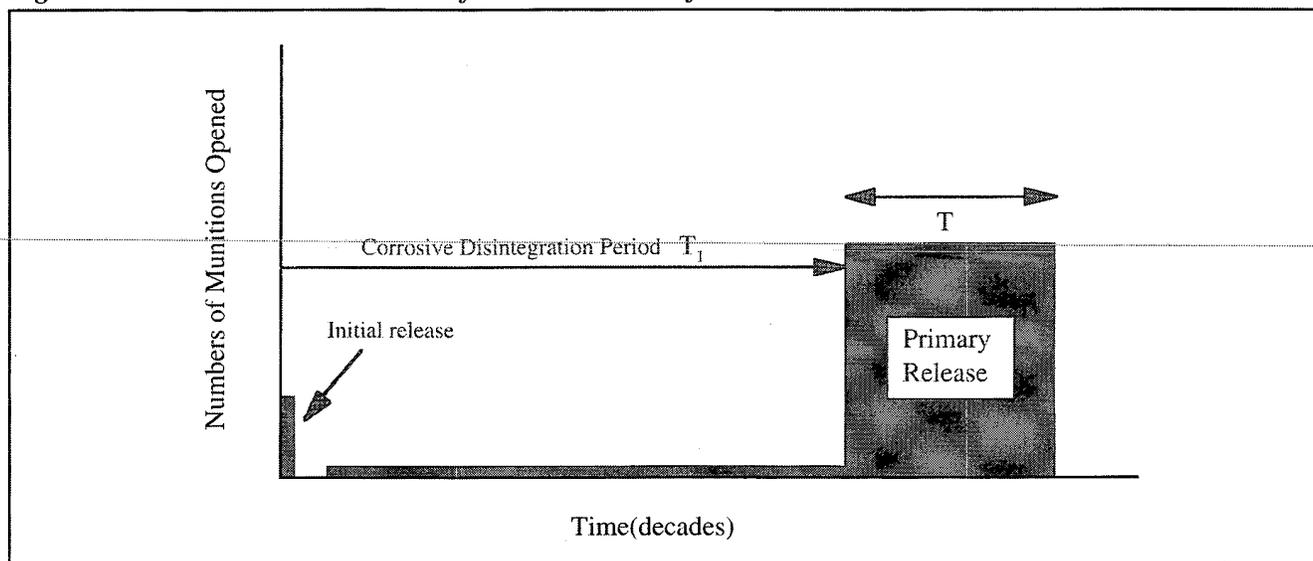
- Tabun is fairly soluble in water and hydrolyzes with a half-life of forty hours. The principal toxic breakdown product is a stable cyanide compound, HCN;

- Sarin is miscible, that is, it mixes in all proportions with water and hydrolyzes with a half-life of sixteen hours into relatively non-toxic reaction products;

- Dissolved mustard hydrolyzes relatively rapidly, with a half-life of five hours. However, the persistence of mustard in the marine environment is controlled by the rate at which it dissolves. Dissolution is much slower than hydrolysis, allowing clumps of exposed mustard to persist in the sea for months, for kilogram quantities, or years for hundred kilogram quantities.

- Lewisite is soluble in water and hydrolyzes very rapidly, i.e., in seconds. The initial hydrolysis products of Lewisite are also very toxic and persist in seawater for months or longer.

- The major toxic Lewisite reaction products, (2-chloroethenyl) arsonous acid and inorganic arsenic, appear in quantities of approximately

80 percent and 30 percent, respectively, of the mass of Lewisite. The half-life of (2-chloroethenyl) arsonous acid is several months, whereas the inorganic arsenicals are stable.

5. **What is the toxicity of the CW agents and products to organisms in the marine environment?**

There is little information bearing directly on the toxicity of the CW agents to marine species. However, there is a great deal of information on toxicity to other organisms, which has been synthesized to produce estimates for three benchmark levels. These levels are to be applied to all marine organisms equally. Of the non-persistent agents, Tabun and Sarin are the most toxic. Of the persistent compounds, organic arsenic (2-chlorovinyl)arsenous acid, a hydrolysis product of Lewisite, is the most toxic.

LC_{50}, defined as the concentration of a substance which results in the death of 50 percent of the exposed organisms during the specified time interval, was the most useful measure in assessing the toxic effects of these chemicals in seawater. The reported lethal dose fifty LD_{50} values, which

are the doses of a substance resulting in the death of 50 percent of the exposed organisms during the specified time interval, were also used to estimate toxicities where LC_{50} values were limited or not available. The values of LC_{50} vary with the organism tested, reflecting the variation in sensitivity of different species to different chemicals.

For the purpose of estimating a toxic threshold for the compounds of concern, one-tenth of the lowest reported LC_{50} was selected as the concentration at which marine organisms would not experience acute toxicity. This value is identified as the *estimated no effects concentration* or ENEC and is to be understood as the highest concentration which is unlikely to produce observable biological effects. For the purpose of defining volumes that would show toxic effects of these chemicals, the ENEC was multiplied by ten to yield *estimated probable effects concentrations*, EPEC, and by one hundred to yield *estimated lethal effects concentrations*, ELEC.

Because of the sparseness of studies of long-term non-lethal effects at low concentration, the benchmark levels established here are considered more reliable at ELEC and EPEC levels than at ENEC levels. For simplicity and because data did not exist on those agents to support a better analysis, these levels are taken to apply equally to all marine species.

Tabun and Sarin are of approximately equal toxicity. They were both assigned an ENEC of 1 μg l^{-1}. mustard is orders of magnitude less toxic, with an ENEC of 200 μg l^{-1} and Lewisite has intermediate toxicity with an ENEC of 20 μg l^{-1}.

Cyanide and dimethylamine are breakdown products of Tabun and were assigned ENEC of 7 μg l^{-1} and 115 μg l^{-1}, respectively. Chlorobenzene, a component of the Tabun formulation, is present up to 20 percent. Chlorobenzene was assigned an ENEC of 1,000 μg l^{-1}.

Most of the breakdown products of Sarin have toxicities six orders of magnitude less than Sarin. Fluoride is the only exception to this and was

assigned an ENEC of 200 μg l^{-1}.

Mustard breakdown products are thiodyglycol, with an ENEC of 1,470,000 μg l^{-1} and 1,4-thioxane with an ENEC of 26,000 μg l^{-1}.

Lewisite hydrolyzes to (2-chlorovinyl)arsenous acid, which was assigned an ENEC of 20 μg l^{-1}, the same as the parent compound, Lewisite. Inorganic arsenic is the ultimate degradation product of Lewisite, with an ENEC of 90 μg l^{-1}.

6. **Once CW agents leak out of a single munition, what is the extent of toxic concentration, how long can this persist and how does it differ for the various CW agents?**

For the four types of CW agents considered, estimates were made that show that contamination by leaking single CW munitions will be a local one, that is, one confined to small areas having dimensions on the order of hundreds of meters or less. This conclusion was found to be valid at all concentrations of any environmental concern. There is little possibility that ocean circulation could disperse toxic levels throughout the entire arctic, or even over the extent of the regional sea. This does not mean that the extent of toxic contamination from an entire dump site is limited to such a small area (see Question 7).

The rate of appearance of dissolved mustard is determined primarily by the surface of the mass of mustard following the abrupt and complete corrosion of a munition casing. The total lifetime for a 1 kg quantity is approximately 150 to 250 days, although quantities on the order of 100 kg, from bombs could persist up to three years after being completely exposed.

After the last of the mustard is dissolved, the remaining agent in solution hydrolyzes rapidly and, within five to ten hydrolysis lifetimes or approximately twenty-five to fifty hours, it can be regarded as being completely eliminated from the environment.

Moreover, mustard, once it is released, can lead to concentrations at toxic levels *only in the immediate*

vicinity of the disintegrated munition, generating a plume only tens of centimeters in length and several centimeters thick. *This is an upper bound.*

The most plausible form of release of agents other than mustard is through pinholes formed by corrosion. It is expected that once pinholes develop, the leaking of agent into the sea will be a process lasting days, even weeks or months. Once released, agents will cause toxic plumes that have their maximum extent on the seafloor. These plumes will have dimensions on the order of a few hundred meters or less in the direction of the current, a few tens of meters across the current and a few meters thick. The volumes of contaminated seawater contained in such a plume can be expected to be no greater than a few thousand cubic meters and may be much less.

Plumes will persist for the time period that CW agent is releasing from the munition, the slower the release the longer the period. However, it also follows that the slower the release, the smaller the plume. The maximum volumes of contamination, a few thousand cubic meters, can occur only for release rates that would empty a typical artillery shell in a day.

7. **What is the extent and duration of toxic contamination over the ocean areas surrounding the arctic dump sites?**

The extent of toxic contamination at the dump sites will be limited to a very small fraction of the area of the dump site itself and to a volume up to a few meters above the seafloor. In the worst case, less than a fraction of a percent of the total area of the dump site could be contaminated to ENEC levels and remain so for years. However, this could occur only if all the munitions containing a specific agent located at the site were to release an agent over a few year period. This period is viewed as being unrealistically short, possibly by an order of magnitude. At the shallow dump site in the southern Barents Sea (Site 134), there are sufficient munitions estimated to have been dumped to extend the contamination of arsenic throughout much of the water column.

If all of the CW agent of a given type dumped at the various sites were to be released over a single five-year period, it was estimated that the volumes of water that could be contaminated to the ENEC level would be approximately 0.0001% of the volumes of the seas in which the sites are located. For example, for Site 121 in the White Sea, the volume of seawater that could be contaminated to ENEC by a five-year release of Tabun would be approximately 0.0001% of the volume of the White Sea. The volumes at ENEC for the other three agents would be significantly less. For the same five-year release period, the seafloor areas contaminated to ENEC by dumped Tabun would be approximately 0.01% of the areas of the associated seas, and significantly less for the other agents. For Tabun at Site 121 in the White Sea, the seafloor area directly contaminated by toxic plumes could be as great as one-thirtieth of the site area. When, after dumping, the five year period occurs is of no consequence to these conclusions. With the assumption that a release is uniformly distributed in time, a release over fifty years rather than five years would reduce the foregoing values by a factor of fifty.

8. **What are the major *potential* threats to the arctic environment and to humans posed by the dumping of chemical weapons in arctic seas?**

The main threats to the marine ecosystems from the release of chemical agents at the disposal sites occur from immediate effects, i.e., acute toxicity of released agent and associated breakdown products; long term effects such as bioaccumulation in the food web; and the long-term contamination of sediments with arsenic contained in Lewisite.

Potential threats to human health and safety are the consumption of fish contaminated with arsenic, the snaring of munitions and mustard lumps in trawling nets, and the exposure of crews to agents during oil and gas drilling or during exploitation of seafloor mineral resources.

Economic threats could include the loss of commercial fish markets because of arsenic contamination and increased costs in exploring and

developing offshore oil and gas resources.

Effects from chemical munitions would be cumulative with the adverse effects caused by other activities in the regional marine environments, including industrial pollution.

9. **What is the likelihood that there could be a major catastrophe to the regional or even the entire arctic ecosystem?**

There is almost no possibility that a major catastrophe to the regional ecosystems, much less the entire arctic environment, could occur as result of the release of chemical agents at the disposal sites. This conclusion should not obscure the fact that sufficient CW agents were apparently dumped at the arctic sites to affect individual organisms, even in large numbers (see Question 10).

The maximum bottom area that could be affected by acutely toxic plumes would be much less than the area of the disposal site. The plumes would be present only within a few meters of the bottom. The worst-case effect would be the loss of benthic biomass and productivity in the disposal site area for a period that could last a few decades. A recovery period of perhaps ten to twenty years would take place because of the slow growth and long-lived nature of benthic organisms in very cold arctic waters. Moreover, the sites are not located where biomass concentration is the greatest, so even if the extent of toxicity were to be much greater than our estimates show, a calamitous effect on the total biomass would be unlikely.

At the deeper sites, the effect of losing this productivity on the local ecosystem would be small because of the limited contribution of the benthic community to the predominantly pelagic food web waters deeper than 200 m. Effects on marine mammals would be small. Walrus and seals, which can dive to those depths, would find the low benthic biomass to provide unattractive feeding areas. It is important to remember that the benchmark levels used in this study to define regions of toxicity are based on exposure times sufficiently long to enable mobile species, *e.g.*, the

walrus, to move out of the contaminated area.

Catastrophic effects of direct toxicity are also highly unlikely at the shallow disposal site, number 134 in the southern Barents Sea. The size of bird, walrus, and seal populations on the northern and western shores of Kolguev Island could be moderately and possibly significantly affected. The loss of benthic productivity within a site area would reduce the carrying capacity of the marine region supporting these populations. However, effects on the larger Pechora Sea region would be small because the benthic area affected is small relative to the entire shallow water area of high biological productivity.

10. **What is the likelihood that dominant fauna could be affected at a level that would imperil the viability of populations?**

There is a very low likelihood that dominant regional stocks could be affected so as to imperil stock viability.

Because toxic concentrations are confined to the near-bottom region, benthic and demersal organisms would be the main communities affected. However, only a small portion of these communities would be affected and large unaffected areas would be available as a source for recovery of larvae and juveniles. The major vertebrate and invertebrate populations are distributed over regions very much larger than the disposal sites. The contribution of benthic communities at deep disposal sites to pelagic stocks is small. The loss of carrying capacity at the shallow site is small compared to the very large regions that support the major stocks of invertebrates, fish, marine mammals, and birds but could be large for populations of seals and birds on Kolguev Island.

11. **Can there be significant economic effects on the commercial fishery or on the development of offshore oil and gas resources?**

Economic effects on the commercial fishery are likely to be small to moderate.

As discussed above, the effects of contamination on the viability of commercial fish stocks would be very small. Moreover, bottom trawling is currently not a harvest method used at the deep disposal sites and fishing has been strongly discouraged at the shallow disposal site. Some fish in the vicinity of the shallow disposal site are likely to see increased body burdens of arsenic. As a result, the sale of fish harvested from this area could be banned in Finland and the United Kingdom, which are the only countries in the region that have standards for the maximum arsenic concentration allowed in commercial fish products. If other countries become concerned about arsenic contamination and ban sales, the economic effect could be large. Sale of fish oils would not be affected because the refining process greatly reduces the content of contaminants.

The effects on offshore oil and gas resource development would be small if the munitions are present only at the identified disposal sites. Presence of munitions would not prevent exploration, *i.e.*, seismic profiling and development of the resource would be a "point" problem. Resources under the disposal sites could be reached by directional drilling if drilling could not be carried out within the disposal site. Pipelines required to gather and bring the resource to shore could be routed around the disposal sites.

12. **Can human health and safety be adversely affected by direct contact with contaminants released at the disposal sites?**

   There is very little chance that there could be significant and direct human contact with toxic contamination due to CW agents at locations remote from the dump sites, e.g., at beaches where contamination was carried ashore by currents. Commercial fishing and offshore drilling and pipe laying crews could be directly exposed to contact with chemical agents if these activities are carried out within the disposal sites.

   Munitions with agents or solid lumps of mustard would likely be captured in trawling nets if bottom trawling occurs at these sites. Boat crews, then, would be at significant risk of injury or death when the nets are brought on board, as had occurred for many years in the Baltic Sea and Japanese waters. However, there is essentially no chance that dissolved agents or reaction products could be carried to remote shores in concentrations sufficient to directly affect humans having contact with the sea. This conclusion is a consequence of the effects of turbulent mixing in diluting agents to harmless concentrations over distances much less than the distances from dump sites to beaches, as well as the effects of hydrolysis in reducing agents to compounds of much lower toxicity over times much shorter than the time to advect compounds to remote shores.

   Drilling crews could be exposed to chemical agents that contaminate drilling mud or drill strings, which are materials and items that return to the drilling platform when drilling operations are carried out. Pipe laying crews could be exposed to agents brought to the water surface on equipment used for pipeline construction. However, both of these are "point problems" that would occur only in connection with activities on the seafloor at the dump sites, if this, indeed were permitted.

13. **Can human health and safety be adversely affected by contaminants from the disposal sites entering the food web?**

   Fish in the vicinity of the shallow disposal site in the southern Barents Sea would likely have arsenic concentrations greater than naturally occurring background amounts for fish in the Barents Sea, although the potential effects to humans would be low. The region where this site is located is an area of intense commercial fishing. Inorganic arsenic is a proven carcinogen in humans. However, up to 99 percent of arsenic in fish tissue are in organic forms, which are not known to be carcinogenic.

   The increased risk from consuming fish contaminated at 10 ppm of total arsenic (ten times the natural concentration in fish) is in the range of one in 10,000 to one in 100,000. This is at the

upper end of the range of increased risk usually acceptable to U.S. regulatory agencies concerned with human health. This estimate could be conservative because it is based on the assumption that 50 to 100 percent of the fish consumed over a seventy year lifetime is contaminated at 10 ppm.

The risk to indigenous peoples consuming fish contaminated with arsenic at 10 ppm as a significant portion of their diet could be moderate. Increased risk is in the range of one in 1,000 to one in 10,000. The upper end of this range is a conservative estimate because it is based on consuming contaminated fish at all meals for a seventy-year lifetime.

14. What are the other activities affecting the regional marine ecosystems that are cumulative with the effects of chemical agents and munitions? What is the likelihood that toxicity of chemical agents, even if insufficient to affect ecosystems or populations, could be the critical additional stress on top of existing anthropogenic contamination and would produce large scale effects?

A variety of past and current activities in the Barents, Kara, and White Seas have adversely affected the marine environment. Any environmental or economic effects resulting from the presence of chemical munitions would certainly add to these effects. However, there is insufficient information concerning the baseline burden of anthropogenic contamination to allow quantifying the cumulative effects of contamination due to chemical warfare agents at the arctic dump sites.

The White Sea receives industrial and domestic wastewater effluents from human activities. A spill in 1990 of thousands of tons of rocket fuel into Dvina Bay from the Russian military base at Severodvinsk caused an enormous kill of invertebrates, fish, and seals in a large area of the bay. Acid deposition, caused by atmospheric transport of emissions from the burning of fossil fuels in Europe, is also occurring in the region. Acidification of regional soils may be a consequence of this deposition and may be causing

the release of some soil metals into runoff into the sea.

A variety of activities have affected the Barents Sea ecosystem. These include nuclear weapons testing in the atmosphere on Novaya Zemlya and in the offshore waters, disposal of liquid and solid radioactive materials, oil and gas exploration and production, and possible over-exploitation of the fishery. A very large proportion of the area of benthic habitat in the shallow central and southern areas of the Barents Sea may be damaged by bottom trawling, although the magnitude of the damage is not known. This claim of damage has been disputed.

In the Kara Sea, disposal of radioactive material in fjords and bays on the east coast of Novaya Zemlya and testing of nuclear weapons in the atmosphere on Novaya Zemlya could have affected the marine ecosystem.

The main effect of chemical agent release would be the loss of benthic productivity from toxic plumes and high arsenic concentrations in sediments. These effects would likely be additive to other benthic disturbances roughly in proportion to the area affected. However, it seems unlikely that the effects caused by the release of chemical agents alone would cause large-scale regional effects when added to the effects of other human activities.

15. What would be the first indications of a large-scale effect on the ecosystem or species populations?

Release of chemical agents at the disposal sites is highly unlikely to produce large-scale effects on populations or ecosystems of the region. However, first indications of such an effect, would be high mortality or significant decreases in fish populations that could not be readily explained by natural processes or known detrimental human activity. Chemical agent effects on fish stocks may be difficult to distinguish from the large fluctuations in population size that occur naturally. Of course, a scientific sampling program to monitor water quality, sediment contamination,

and fish catches, if carried out in a sustained manner, would offer the first opportunities to detect a developing problem.

16. **What is the likelihood that endangered species could be affected? Which endangered species are most susceptible? Could the numbers affected be large enough to affect the viability of populations?**

The following animals known to live or capable of living in the region are considered by Russian sources to be threatened or endangered: the polar bear, the Atlantic walrus, the gray seal, the narwhal, the bowhead whale, the beluga whale, the harbor porpoise, and Dall's porpoise. There is little data available to indicate the size of the populations or their degree of fragility at or near any of the arctic CW disposal sites. Thus, a scientific assessment of the potential damage from CW agents is difficult if not impossible. However, it seems unlikely that these species would be affected at the deep disposal sites, although there may be some risk of appreciable adverse effects at the shallow disposal site.

At the four deeper sites, the near-bottom confinement of high concentrations of CW agents will provide a significant isolation of these endangered species from effects due to direct toxicity. On this basis, it would be expected that adverse consequences at the population level would not be significant unless these populations are in a highly fragile condition.

The Atlantic walrus has the greatest potential of any endangered species to be affected at the shallow site. This species feeds predominantly on benthic organisms and, thus, could be exposed to toxic plumes and contaminated sediments. The site is in the historic range of this species, although data on its occurrence at this site was not found. The potential for effects on this species is likely to be small because the current occupied range of this species is large compared to the contaminated area. There is some risk to the other marine mammals in entering the toxic plumes near the bottom while feeding in the water column.

17. **Can agents or breakdown products bioaccumulate in the food web? If so, what are the effects on the ecosystem?**

Most chemical agents and breakdown products would not bioaccumulate in the food web. Arsenic has a modest potential to bioaccumulate in the trophic levels most closely associated with arsenic-contaminated sediments. Some increase would occur in higher trophic levels. Biomagnification resulting in high concentrations in high trophic levels would not occur. Significant effects on the ecosystem due to arsenic bioaccumulation are not likely. The potential exists, however, for economic effects on the commercial fishery, as discussed above.

18. **How large an area of the seafloor could be permanently contaminated by the arsenic contained in Lewisite and what are the long-term ecosystem effects?**

Arsenic in Lewisite is released from munitions in organic forms. These compounds would continue to undergo reactions to inorganic forms and enter the natural cycle of arsenic in the physical and biological environment of the region. The transport and fate processes for arsenic in the marine environment are not well understood. However, there is sufficient arsenic in the Lewisite dumped at the arctic sites to allow contamination well above natural background levels over areas somewhat greater than those of the dump sites themselves.

The area of sediment affected at 90 mg kg⁻¹ of arsenic was estimated for several quantities of Lewisite in order to bound the problem. This is the concentration likely to have significant effects on benthic organisms. For Lewisite quantities at Barents and Kara Sea sites ranging from 7,500 tons to 75,000 tons, the area affected would be 240 to 2,420 km². For Lewisite quantities at the White Sea site ranging from 4,000 to 40,000 tons, the area affected would be 130 to 1,290 km². The likely effect of arsenic in sediments at 90 mg kg⁻¹ would be to reduce permanently benthic biomass and species diversity.

Ecosystem effects at the deep disposal sites would be small because of the small contribution of the benthic community to the dominant pelagic food web occurring in the deep waters of the region.

Effects at the shallow disposal site would be a reduction in carrying capacity of the Kolguev Island region and some contamination of the food web with arsenic, as discussed above. The area at the site would add to an existing area of about 5,000 km² contaminated with arsenic in the Pechora Sea off the southern coast of Novaya Zemlya. If a large area is contaminated at the disposal site, the total contaminated area could reach 10 percent of the Pechora Sea region shallower than 100 m. Permanent loss of some benthic productivity over a region of this size could have a modest effect on the carrying capacity of the Pechora Sea region.

19. Are there uncertainties that could significantly affect the answers to the foregoing questions and, if so, how might they be removed?

While there are many uncertainties that could alter details in this assessment, there are only a small number that could significantly alter the top-level findings. They include the following:

- *Total quantities of CW munitions dumped into arctic seas could be less than indicated here, with correspondingly reduced likelihood for environmental impact.*

- *If third generation CW materials, such as V-agent, have been dumped into arctic seas, one could not easily exclude the possibility of environmental impact on a very much wider basis than found here. It is not believed that disposal of third generation munitions has occurred.*

- *The benchmark levels of toxicity developed in this study and applied uniformly to all marine organisms contain significant uncertainty, both in the numbers themselves and their universal applicability. Only the use of what are believed to be highly conservative levels for ENEC prevents this factor from driving the*

uncertainty equation. As a result, it is believed that there is little chance that biological effects could be worse than portrayed here, but could be very much less.

- *If bottom trawling does occur at the arctic CW dump sites, then the release of agents could be significantly accelerated. Direct acute harm to individuals and to fish catches is possible.*

There are several uncertainties important to the analysis of environmental effects. These include the rate of agent release from munitions, the transport and fate of arsenic in Lewisite, the number and type of munitions present at each site, and knowledge of the physical conditions and biological components and processes at each site and its vicinity.

The rate of release of an agent from a corroded munition determines whether acute toxicity is an issue at a site. At slow but plausible release rates, no toxic plume would be produced. In this situation, there would be no effects from acute toxicity. Additional analysis of corrosion processes could provide some additional insight.

The distance that arsenic is transported, before depositing in the sediments, determines the concentration of arsenic contamination as does the rate of bioturbation, which mixes the arsenic into the top of the sediment column. More detailed modeling of arsenic transport could provide better definition of the area affected at each site, as would measured data.

Data specific to the disposal sites and vicinity are needed in order to analyze site-specific effects. This data includes the benthic community structure and biomass, the main components of the food web, the occurrence of endangered species, the trophic relations in the food web, the current speed and direction, and the sensitivity of species to the agent and breakdown product toxicity. Without site-specific data, conclusions were drawn based on general data for the large region or other areas in the arctic with environments that could be similar.

10.2 CONCLUSIONS AND RECOMMENDATIONS

This study has found only a very small likelihood that the past dumping of chemical weapons in arctic seas would cause such a large or widespread impact on the arctic environment that it would be of concern to U.S. national security, however broadly that is interpreted. However, local adverse impacts may be present but the uncertainties in this dimension of the assessment are large. The assessment carried out in this study is believed to be conservative in the sense that any adverse environmental effects that may be encountered are unlikely to be larger than the estimates developed here.

The most important information gaps involve the location and condition of the dump sites, the types and amounts of munitions dumped, when they were dumped, and the toxicity of CW agents and reaction products to marine species. In addition, no reports were found similar to the various European studies of the Baltic tracking reports of fishermen encountering CW munitions.

It is our recommendation that the U.S. Government *not* approach this information gap solely as a conventional intelligence problem. Rather, it should be viewed largely as a *scientific problem*, one where the intelligence and the scientific communities could collaborate.

Russian cooperation should be solicited to share information regarding past ocean dumping in both United States and Russian waters. Both countries could carry out an oceanographic survey of one of the dump sites considered in this assessment. That survey would include collection of water, sediment, biological samples, and underwater photography of the condition of the munitions. Advantage should be taken of any serendipitous opportunity that arises in connection with a planned oceanographic cruise in order to collect sediment, water samples, and even underwater photographs from one of the dump sites.

In addition, a low-level ongoing effort might be put in place to monitor local fishing conditions and, especially, to collect any information regarding encounters with chemical weapons debris in fish catches. These efforts should draw heavily from the Baltic experience, beginning with a comprehensive review of existing studies and site surveys of the various Baltic CW dump sites.

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