

FFI RAPPORT

INVESTIGATION AND RISK ASSESSMENT OF SHIPS LOADED WITH CHEMICAL AMMUNITION SCUTTLED IN SKAGERRAK

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Bjørn A Johnsen
Director of Research

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8) ABSTRACT <p>The Norwegian authorities gave in 1945 permission to scuttle ships loaded with captured chemical ammunition on board in an area approximately 14 km X 4 km in size, 25 nautical miles south-east of Arendal. The total amount (gross weight) of chemical ammunition dumped in Skagerrak by the Allies is 168 000 tonnes. A project was carried out by Forsvarets forskningsinstitutt (FFI) in 2002 on behalf of the Norwegian Pollution Control Authority (SFT) to investigate some of the ships scuttled in Skagerrak. This report describes an investigation carried out in two parts in June and September 2002 using the ship KNM Tyr. The aim was to investigate the same wrecks selected in 1989 by using a remote-operated vehicle (ROV) with video cameras.</p> <p>The investigation showed that some of the ammunition was pierced through by corrosion. The content have therefore probably leaked out, which indicate that the release of chemical ammunition to the sea will go on for a long time. The ammunition seen on the seabed has quite thin walls, and many of the shells were pierced through by corrosion. Trying to bring the shells to the surface would most likely not be successful because they will fall into pieces by the movement and the content will leak out. A lot of shrimps and some species of fish were observed close to the bombs. This indicate that no acute toxic effects from the chemical warfare agents in Skagerrak is present, but investigation of the content of chemical warfare agents or degradation products in marine organisms is needed to assess long-term effects.</p>				
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PREFACE

The current report gives a description of the investigation carried out by Forsvarets forskningsinstitutt (FFI) of the wrecks dumped in Skagerrak after World War II with chemical ammunition on board.

The aim of the investigation was to give an evaluation of the conditions of the dumped wrecks and to assess whether the chemical warfare agents have leaked out from the wrecks. This was done by using a remote-operated vehicle with video cameras. Sediment samples were collected and analysed with respect to chemical warfare agents and some related compounds. Temperature and sea current at the sea bottom was measured. This made it possible to give a rough estimate of the risks associated with leaking ammunition. Some recommendation for further work is also given.

Video and still photos were recorded by the photographer Bjørn Fremstad at FFI. We thank him for his high-quality work and assistance during the field work.



CONTENTS

	Page	
1	INTRODUCTION	9
2	INVESTIGATION OF SELECTED SHIPWRECKS	11
2.1	Background	11
2.2	Sea current and temperature	13
2.3	Inspection by a remote operated vehicle	13
2.4	Observations during the investigation	19
2.4.1	The Deep Marine habitat	19
2.4.2	Fishing activity	19
2.4.3	Types of ammunition observed	19
2.4.4	Conditions of the wrecks and ammunition	20
2.5	Sediment and water sampling	21
3	BEHAVIOR OF CHEMICAL WARFARE AGENTS IN SKAGERRAK	22
3.1	Arsenic and arsenic compounds	23
3.2	Adamsite	24
3.3	Chloroacetophenone (CN)	25
3.4	Clark I and II	26
3.5	Sulphur mustard	27
3.6	Viscous sulphur mustard (Zählost)	28
3.7	Phosgene	29
3.8	Tabun	29
4	CHEMICAL ANALYSIS	31
4.1	Sample preparation	31
4.1.1	Preparation of sediment samples	31
4.1.2	Preparation of water samples	31
4.2	Analytical methods	31
4.3	Analytical results	32
4.3.1	Water samples	32
4.3.2	Compounds identified in the soil samples by mass spectrometry	32
4.3.3	Quantification of identified compounds by mass spectrometry	35
4.3.4	Elemental arsenic	36
4.4	Discussion	36
5	RISK ASSESSMENT OF CWA IN SKAGERRAK	37
5.1	Introduction	37
5.2	Risk for fishermen	37

5.3	Exposure to sulphur mustard	38
5.4	Bioaccumulation of arsenicals	39
5.5	Potential effects on local biota	40
5.6	A theoretical scenario of leaking ammunition	40
6	CONCLUSIONS	43
	References	45
A	APPENDIX	49
B	APPENDIX	52
C	APPENDIX	53
D	APPENDIX	54
E	APPENDIX	55
F	RESULTS FROM ANALYSIS BY ICP	69
	Distribution list	77

INVESTIGATION AND RISK ASSESSMENT OF SHIPS LOADED WITH CHEMICAL AMMUNITION SCUTTLED IN SKAGERRAK

1 INTRODUCTION

The first use of chemical weapons was on 22 April 1915 by Germany in World War I in Ypres at the Western Front. As a result of the attack, 15 000 people were injured in French Army positions, 5 000 of them died within the following days. The total amount of chemical warfare (CW) agents produced by the belligerent parties during World War I was more than 130 000 tonnes (Fokin and Babievsky, 1996).

In 1936, during the war in Abyssinia (now Ethiopia), Italy used chemical weapons (in particular sulphur mustard and phosgene) not only against the military forces, but also against civilian population. As a result, the number of chemical war casualties was 15 000. From 1937 to 1943, the Japanese Armed Forces used chemical weapons in China.

During World War II, military research and development centres in the leading industrial countries continued to work on CW agents and technical means for their delivery. As captured German archives show, the annual capacity of plants producing CW agents was in 1943 almost 180 000 tonnes (Fokin and Babievsky, 1996). After the defeat of Germany, the allies found more than 250 000 tonnes (gross weight) of aerial bombs, artillery shells, mines and grenades filled with sulphur mustard, organoarsenicals and nerve agents (tabun and sarin). The total amount of CW agents (net weight) produced by Germany during World War II was between 62 322 tonnes and 65 000 tonnes (Stock, 1996).

Germany had produced and accumulated the following CW agents during World War II (Stock, 1996):

Chloroacetophenone	7 100 tonnes
Diphenylchloroarsine (clark I)	1 500 tonnes
Diphenylcyanoarsine (clark II)	100 tonnes
Adamsite	3 900 tonnes
Arsine oil ¹	7 500 tonnes
Phosgene	5 900 tonnes
Sulphur-Mustard	25 000 tonnes
Nitrogen-Mustard	2 000 tonnes
<u>Tabun</u>	<u>12 000 tonnes</u>
Total (net weight)	65 000 tonnes

¹ Arsine oil: 50 % phenyldichloroarsine, 35 % diphenylchloroarsine, 5 % triphenylarsine and 5 % trichloroarsine (Franke et al, 1976)

According to historical documents, the following amounts of CW were discovered, destroyed, dumped or recycled on German territory between the end of World War II and 1947 (Stock, 1996):

In the American occupation zone	93 995 tonnes
In the British occupation zone	122 508 tonnes
In the French occupation zone	9 250 tonnes
<u>In the Soviet occupation zone</u>	<u>62 505 – 70 500 tonnes</u>
Total (gross weight)	288 258 – 296 203 tonnes

It is reported that ammunition with the nerve agent tabun was sunk at the southern entrance to the Lille Belt at the position 58°48'22"N, 10°13'22"E. This ammunition was in 1959-1960 recovered and dumped west of the Bay of Biscay (HELCOM CHEMU, 1994). One could, however, not exclude the possibility that tabun also was dumped in Norwegian waters.

The Norwegian authorities gave in 1945 permission to scuttle ships loaded with captured chemical ammunition on board in an area approximately 14 km X 4 km in size, 25 nautical miles south-east of Arendal (Fonnum, 1997) (see Figure 1.1).

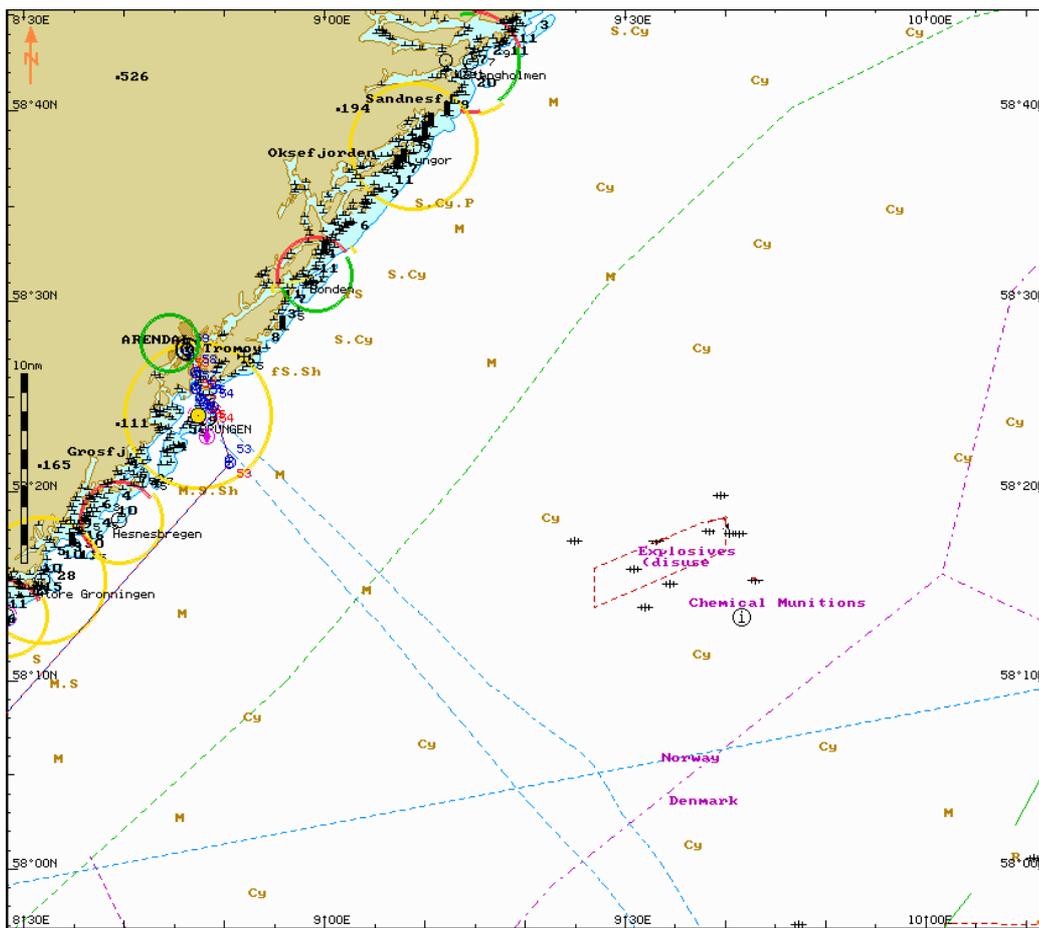


Figure 1.1 The area where Norwegian authorities gave permission to scuttle ships loaded with captured chemical ammunition is marked on navigational charts (chart from KNM Tyr)

The total amount (gross weight) of chemical ammunition dumped in Skagerrak by the Allies was 168 000 tonnes according to US and UK reports to HELCOM CHEMU (HELCOM CHEMU 2/2, 1993 and HELCOM CHEMU 2/2/5, 1993) and SIPRI (Stock, 1996). This includes ships sunk near Måseskär off the Swedish west coast, and in an area 25 nautical miles south-east of Arendal in Norwegian waters (Figure 1.1).

The number of ships sunk with chemical weapons on board is unclear. According to Erling Skjold (Appendix A), 60 ships were sunk in Skagerrak, outside Måseskär in Sweden and outside Lista in Norway, most of them with chemical weapons on board. According to Fonnum (1997), between 13 and 45 ships were scuttled in Skagerrak with chemical ammunition on board. According to Miljøstyrelsen in Denmark (Miljøstyrelsen, 1992) and the Swedish Sjöfartsverket (Sjöfartsverket, 1992), 9 ships with 20 000 tonnes (gross weight) of chemical weapons were sunk outside Måseskär in Sweden. The most likely number of ships sunk in the Norwegian part of Skagerrak is therefore 36.

Depending on the type of ammunition, the content of chemical warfare agents ranges from 10 % (artillery shells) to a maximum of approximately 60-70 % (aerial bombs). A list of German standard ammunition containing chemical warfare agents (Sjöfartsverket, 1992) is shown in Appendix B.

2 INVESTIGATION OF SELECTED SHIPWRECKS

2.1 Background

Chemical weapons dumped in the Baltic Sea have for several years caused problems for fishermen catching the weapons in their nets. The sea depth in the Baltic Sea is, however, quite shallow (30-100 m) and the chemical ammunition was mostly thrown overboard the vessels (HELCOM CHEMU, 1994). In Skagerrak, the sea depth is much larger (Figure 2.1) and whole ships filled with chemical ammunition were sunk. The ammunition dumped in Skagerrak have therefore been regarded as much more safe than the ammunition dumped in the Baltic Sea.

Forsvarets forskningsinstitutt (Norwegian Defence Research Establishment, FFI) carried in 1989 out an investigation of an area 16 km X 8 km in size, 25 nautical miles south-east of Arendal in Norway (see Figure 1.1). During that investigation 15 possible shipwrecks were identified by use of a side-scan sonar. Of those 15 wrecks, 5 were selected, and further investigated by an unmanned remote-operated vehicle (ROV) (Table 2.1). Cameras mounted on the ROV showed bombs of different sizes, some of them pierced through. Water samples were taken close to the wrecks, but no chemical weapons were identified by the methods used at that time (Tørnes et al, 1989).

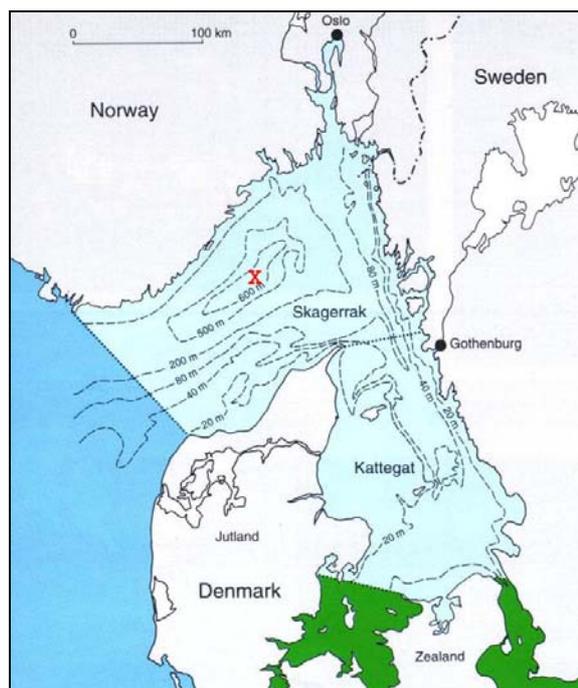


Figure 2.1 Sea depths in Skagerrak (SFT, 1993). The red X indicates the dumping area

Wreck no (from 1989 report)	Position (ED 50)	Depth (m)
5	58°15'53.6''N 9°40'01.9''E	594
6	58°16'08.5''N 9°41'08.6''E	585
11	58°17'28.8''N 9°33'08.5''E	702
13	58°18'47.0''N 9°39'56.2''E	677
14	58°18'31.5''N 9°41'05.7''E	666

Table 2.1 Wrecks investigated by ROV during the expedition in 1989 (Tørnes et al, 1989)

This report describes a new investigation carried out in two parts in June and September 2002 using the ship KNM Tyr. The aim was to investigate the same wrecks selected in 1989 by using a ROV with video cameras. This time it was also decided to take sediment samples close to the wrecks in addition to water samples. Due to bad weather, only four of the selected wrecks were investigated (wreck no 11 was omitted). One and a half wreck was investigated in July 2002 before the mission was stopped due to engine problems. The rest of the wrecks were investigated in September 2002. The project was carried out by FFI on behalf of the Norwegian Pollution Control Authority (SFT).

In addition to the ROV with cameras, a multicorer from Akvaplan NIVA to collect sediment samples and two sea current sensors from Havforskningsinstituttet were used. Two persons from Akvaplan NIVA operated the sediment sampler. Water samples were collected using two Nansen water samplers from Havforskningsinstituttet mounted on the ROV.

2.2 Sea current and temperature

Two RCM 7 current sensors were placed at positions 58°16.392'N 9°40.511'E (S-1) and 58°18.511'N 9°40.119'E (S-2) to measure the sea currents and sea temperature. The sensors logged data for approximately 24 hours with measurements every 10 minutes. The results are shown in Table 2.2 below.

Sensor	Sea temperature (°C)	Mean current direction (span) (degrees)	Mean current speed ± std dev (cm/s)
S-1	6.2	358 (341-13)	2.5 ± 1.5
S-2	6.2	305 (284-325)	2.0 ± 1.1

Table 2.2 Results from the sea current sensors. The sensors logged data for approximately 24 hours

The two sea current sensors gave a somewhat different mean current direction, with one sensor (S-1) showing a current from south to north (358 degrees) and the other sensor (S-2) showing a current towards north-west (305 degrees). The mean current speed from the sensors could be compared with the findings made in the summary report from NGU, (NGU 1997), where a bottom current from 0-19 cm/s is estimated depending on the wind direction. The wind was very variable during the field work in 2002. The wind data recorded at Torungen lighthouse near Arendal showed wind directions from north-west to south-east and wind speeds from 0.5 m/s to 12.3 m/s. The bottom sea current was, however, quite low during the investigation and the direction of the sea current did not seem to depend on the wind direction for the short time the current sensors were operating.

2.3 Inspection by a remote operated vehicle

All of the investigated wrecks were inspected thoroughly by a remote operated vehicle (ROV) with video cameras. In total 6 hours of video was recorded during the investigations. The aim of the investigation was to obtain a visual impression of the condition of the wrecks. The ROV was therefore used to inspect around each of the wrecks in a systematic manner. The positions of the inspected wrecks are given in Table 2.3, where the wrecks were given the same numbers as in the 1989 investigation. Note that different geographical datum were used in the two investigations (ED 50 in 1989 and WGS 84 in 2002). The locations of the investigated wrecks and the position of the current sensor buoys are shown in Figure 2.2.

Wreck no (current investigation)	Position (WGS 84)
5	58°15.87'N 9°39.95'E
6	58°16.10'N 9°41.00'E
13	58°18.79'N 9°39.80'E
14	58°18.53'N 9°41.02'E

Table 2.3 Wrecks investigated during the expedition in 2002

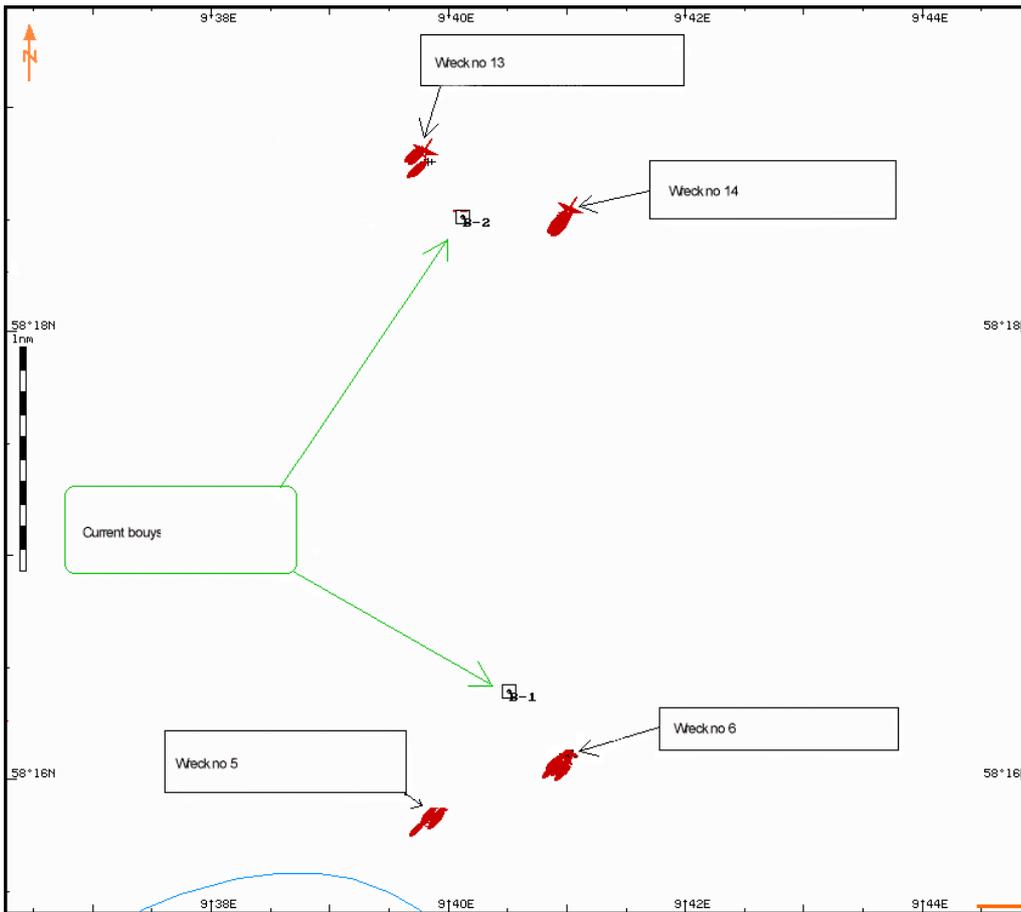


Figure 2.2 Positions (WGS 84) of the sea current buoys (S-1 and S-2) and the wrecks inspected during the investigation in 2002

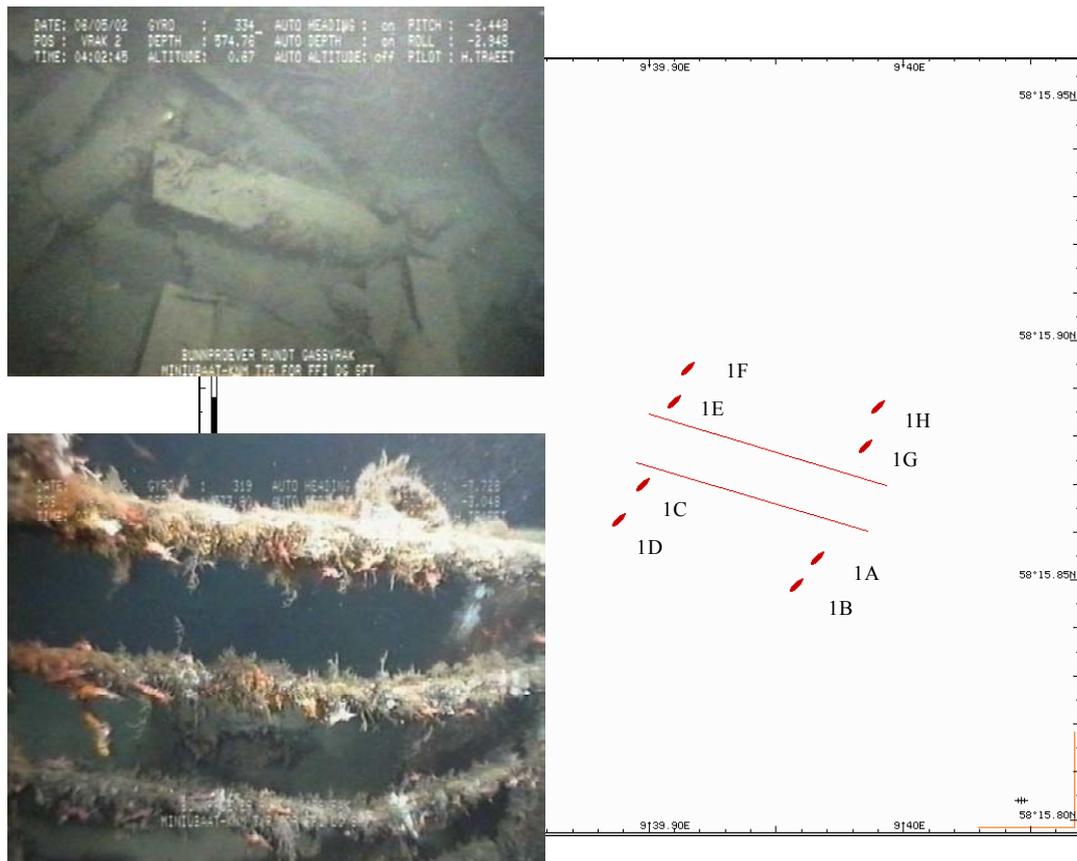


Figure 2.3 Wreck no 5. The red symbols indicate collected sediment samples, with numbering used during the investigation and the red lines indicate position of the wreck

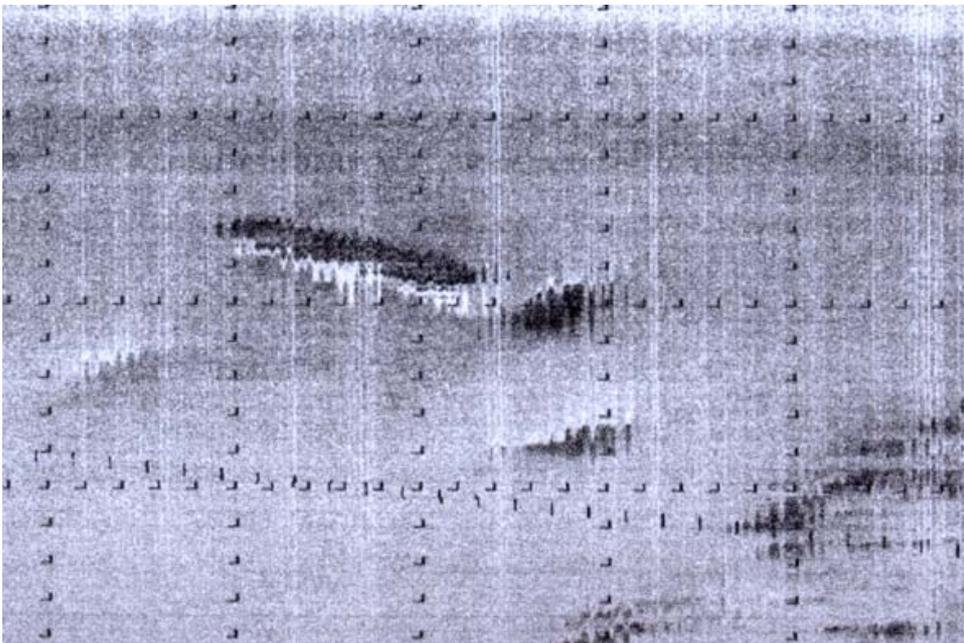


Figure 2.4 Registration of wreck no 5 from side-scan sonar carried out in 1989

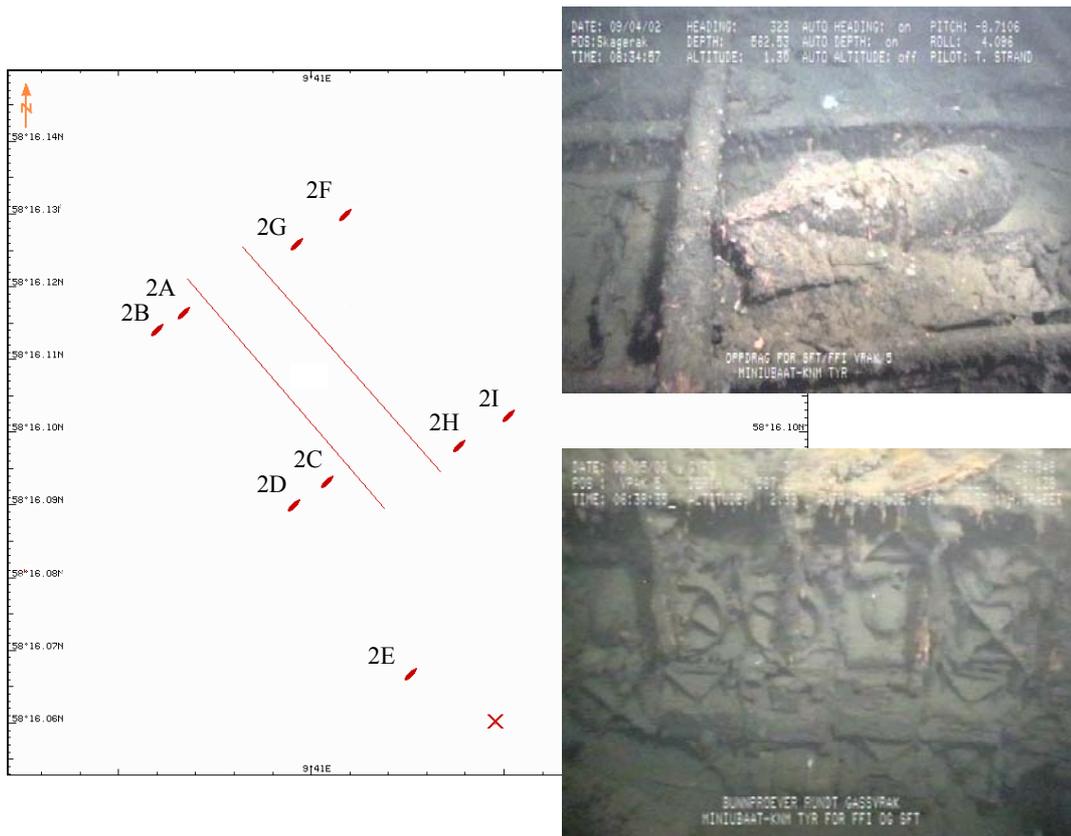


Figure 2.5 Wreck no 6. The red symbols indicate collected sediment samples, with numbering used during the investigation and the red lines indicate position of the wreck. The red X denotes the position of one part of the wreck

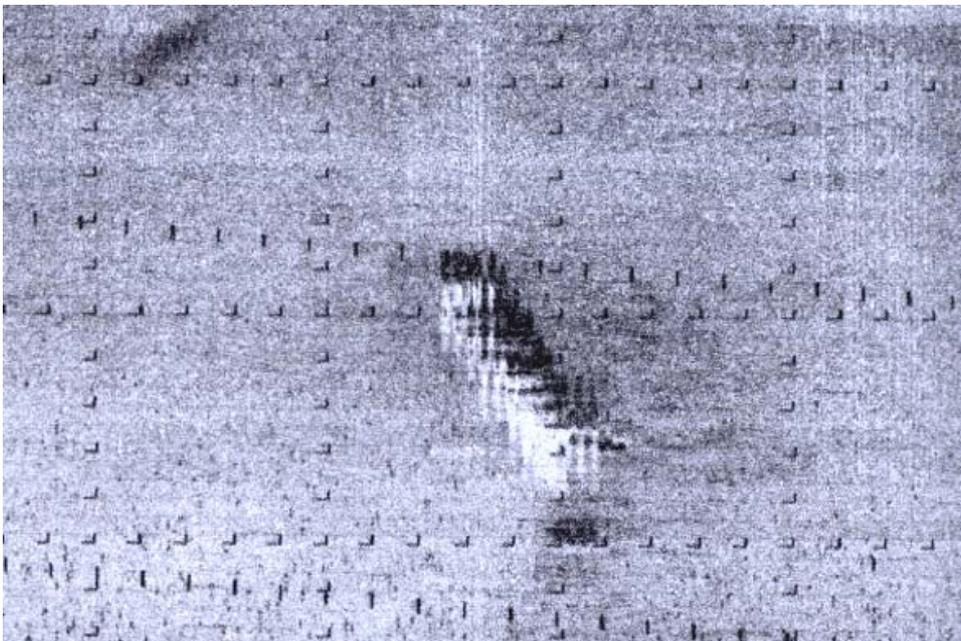


Figure 2.6 Registration of wreck no 6 from side-scan sonar carried out in 1989

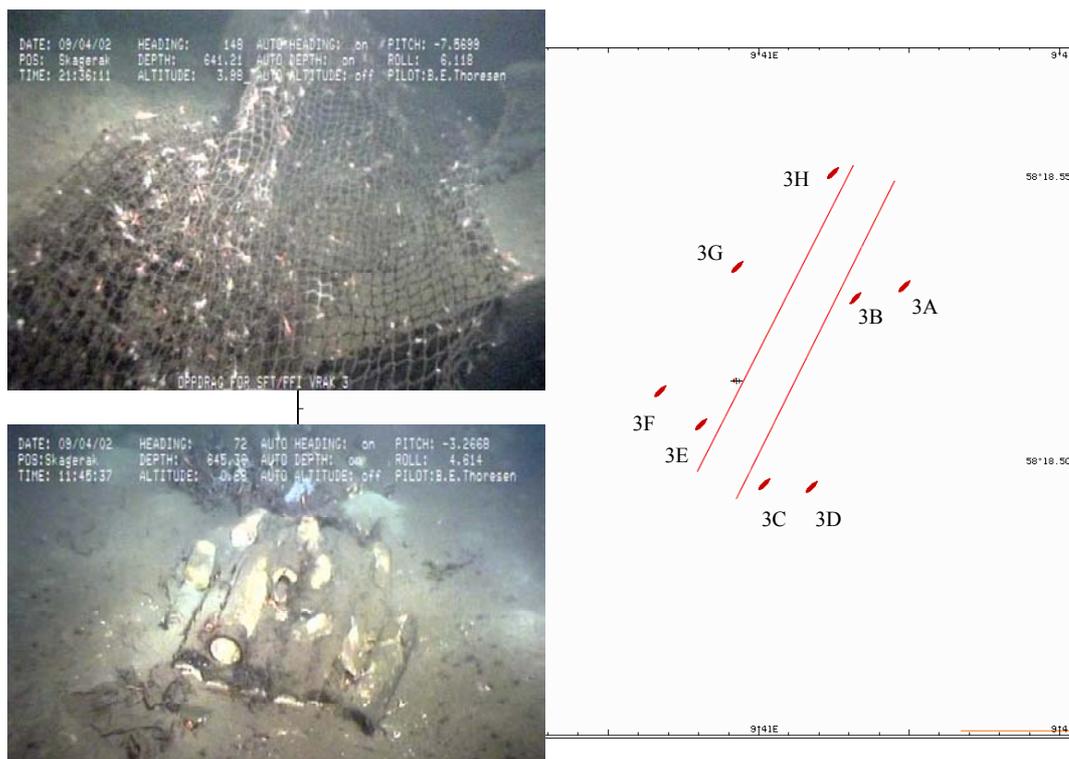


Figure 2.7 Wreck no 14. The red symbols indicate collected sediment samples, with numbering used during the investigation and the red lines indicate position of the wreck. This wreck was identified as SESOSTRIS

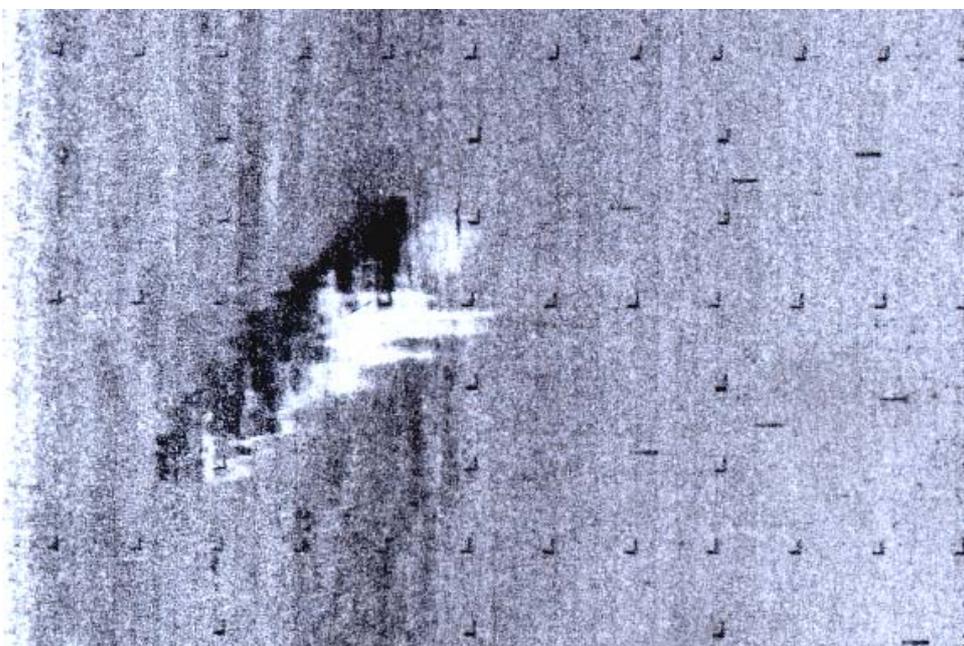


Figure 2.8 Registration of wreck no 14 from side-scan sonar carried out in 1989



Figure 2.9 Wreck no 13. The red symbols indicate collected sediment samples, with numbering used during the investigation and the red lines indicate position of the wreck

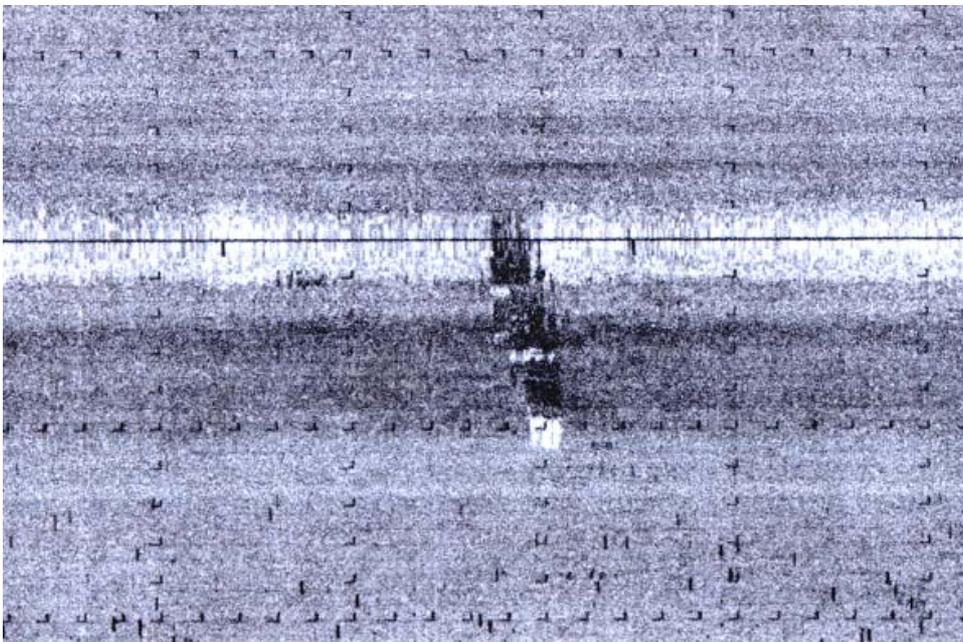


Figure 2.10 Registration of wreck no 13 from side-scan sonar carried out in 1989

2.4 Observations during the investigation

2.4.1 The Deep Marine habitat

Both physical and chemical factors are important for characterising the sea bottom in the deepest part of the Norwegian Deep. The dominant soft muddy sea floor is predominant. The uppermost 10-15 cm of unconsolidated seabed contains a medium brown, quite fluffy substrate. Due to low influx of sediments, the sedimentation process is concentrated along the coast. The central part of Skagerrak is located quite distally from the sediment source, the mainland Norway end Denmark. Hence, the sedimentation rate is very low (1.5-4.5 mm per year, NGU, 1997). Abundant marine organisms observed close to the seabed is the deep-sea shrimp and a lot of crawfish and lithodes. Conical mounds, probably made by burrowing shrimps or crawfish, are localised and observed at every studied location.

Local hardgrounds due to shipwrecks and metal scrap are observed at the soft seafloor. These hardgrounds are substrate for another marine biota than the muddy substrate. Benthos like small branching bryozoans, blade shaped swamps, like sea fans and thin shelled molluscs were seen. Swimming around shipwrecks in a lazy tempo, fish like cusk, pollack, blue ling, the greater silver smelt and rays were recognised. Shipwrecks were probably used as hiding-places for any kind of pelagic biota. The deep water fish assemblage of the Skagerrak is described in Bergstad et al. (2001).

The fauna looked in general very healthy and representative for the deep sea environment. The heavy cold and saline water close to the seafloor is probably well oxygenated. Plankton and nekton in this deep water environment seems to be quite abundant as the benthos is absolutely dependent on this food supply. Only one sediment sample (sample 2H) showed traces of anoxic conditions (black sample with smell of hydrogen disulphide).

2.4.2 Fishing activity

Fishing equipment (trawls) were observed at several places during the investigation and the trawls were hung up on different parts of the wrecks (see Figure 2.7). This is an indication that fishing has taken place in the area close to the dumped wrecks.

2.4.3 Types of ammunition observed

Several different types of ammunition was observed during the inspection of the wrecks. Bombs with different calibre from 50 kg to 250 kg were observed. Artillery shells were also observed, especially outside wreck no 14 (see Figure 2.7). The calibre was difficult to establish, but it looked like 127 mm or larger grenades. It seems that the artillery shells were stored in wooden cases on the ship decks. The cases were carried some distance away from the ships by the sea currents when the ships were sunk. The cases have then rotted away. A list of German standard chemical ammunition at the end of World War II is shown in Appendix B. Examples of German ammunition from World War II are shown in Appendix C.



Figure 2.11 Containers observed at wreck no 13

In addition to bombs and artillery shells, some large containers were observed in a hold in wreck no 13 (Figure 2.11). The purpose of these containers is not known, but it is possible that they contain chemical warfare agents.

2.4.4 Conditions of the wrecks and ammunition

The investigation by ROV showed that the wrecks were in surprisingly good conditions. The corrosion was limited, and not much seems to have happened since the investigation carried out by FFI in 1989 (Tørnes et al, 1989). We can see that the wooden decks have disappeared (possibly removed by shipworms), but the ships themselves seem to be in fairly good shape. At least one of the ships (wreck no 6) had broken into pieces during the dumping operation, possibly because the ship was fired upon to sink. Therefore, many of the bombs that the ship carried have been spread out of the wreck.

The corrosion of ammunition shells is a complex phenomenon. A Russian study (reported in Stock, 1996) concluded that sea current was the important determinant of corrosion rate. Other reports argue that corrosion is very complex and combinations of external factors can create different corrosion rates. Corrosion is usually retarded at great depths because of the low temperature combined with a low oxygen content of water (Fonnum, 1997). The current investigation gave, however, no indication of low oxygen content in the water. The investigation carried out by FFI in 1989 showed that some of the bombs were intact, and some were corroded and the contents were gone (Tørnes et al., 1989). Heavy walled artillery projectiles are likely to remain intact longer than aerial bombs. Bulk cylinders were typically made from relatively thin steel when compared with artillery ammunition. Chemical bombs from World War II often had an inner container of glass holding the ammunition (Fundingsrud, 2002).

The current investigation also showed that some of the ammunition was pierced through by corrosion and the content probably leaked out. The fact that some of the ammunition was observed with the content leaked out, while other ammunition apparently still was intact, indicates that the release of chemical ammunition to the sea will take long time. Ammunition pierced through by corrosion was only seen on aerial bombs, which had thinner walls than artillery grenades.

Wreck number 14 was identified as *SESOSTRIS* by a name found on the side of the ship. This corresponds with the findings during the investigation carried out in 1989. A ship's bell found on the wreck showed the name *LAKE ARTHUR*. This name was an earlier name of the same ship according to Norsk skipsvrakarkiv (Skjold, 2002). According to the German Bundesarchive (German Bundesarchive, 2002), *SESOSTRIS* was loaded with 4 500 tonnes (gross weight) chemical ammunition and sunk in November 1945.

2.5 Sediment and water sampling

The second part of the investigation was to analyse sediment and water samples for arsenic, chemical warfare agents and some of their decomposition products. It was of interest to find out if chemical warfare agents had leaked out from the wrecks. It was also of interest to find out if the agents could be identified at a distance from the wrecks. Sediment samples were therefore collected using a multicorer at 8 positions around each wreck, four close to each wreck (10-15 m) and four a somewhat longer distance from each wreck (20-28 m). Wreck number 6 was broken up into several smaller parts. Here sediments were collected at one additional position close to one of the parts, 50 m away from the main body of the wreck. From each position, at least two sediment cores were taken up to the surface. One of the cores from each position was sliced into three parts (0-1 cm, 1-3 cm and 3-6 cm) which were immediately frozen. The other whole cores were frozen on board the ship and transported back to the laboratory in a freezer. In total, sediment samples from 33 different locations were collected and analysed for arsenic, chemical warfare agents and some of their decomposition products. The multicorer used for sediment sampling is shown in Figure 2.12.

The positions where the sediment samples were collected are shown in Figures 2.3, 2.5, 2.7 and 2.9. In addition, the exact sampling positions are given in Appendix D. Two control samples of sediments were collected at position 58°18.787'N 9°28.841E outside the known dumping area before the sunken ships were investigated.

In addition to the sediment samples, water samples were collected above some of the holds of the wrecks by using a Nansen water-sampling device (Figure 2.13). Two Nansen samplers were mounted on the ROV in such a way that they could be closed by the manipulator arm. This means that maximum two water samples could be collected at each shipwreck. A total of 8 water samples were collected during the expedition, two parallel samples from each wreck.

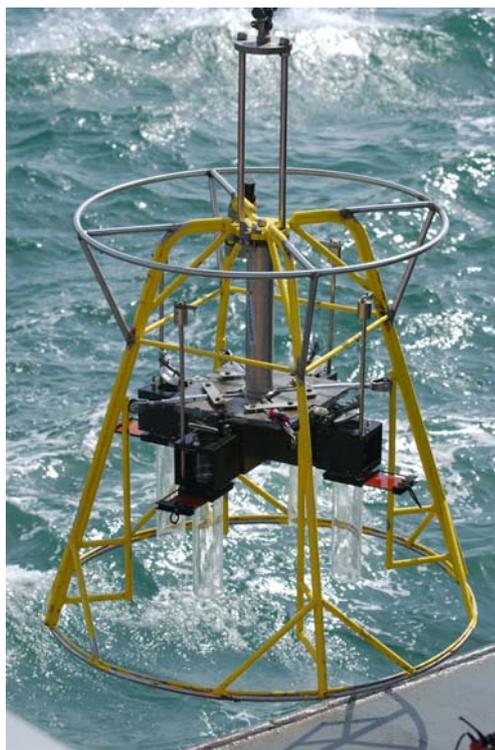


Figure 2.12 Multicorer used for sediment sampling



Figure 2.13 Water samples were collected using a Nansen water-sampling device. This picture is from wreck no 5

3 BEHAVIOR OF CHEMICAL WARFARE AGENTS IN SKAGERRAK

Fate and transport of chemical warfare agents (CWA) in the marine environment depend both on the physio-chemical and chemical properties of the agents, in addition to environmental parameters as temperature, salinity, pH and turbulence in the water. A general survey carried out by the Flødevigen biological station showed that, on average, the oxygen content are 6 ml/l

at a temperature of 5 °C at this depth (Fonnum, 1997). During the current investigation, the temperature at the sea bottom was measured to 6.2 °C (Chapter 2.2). The salinity is estimated to 35 psu (Skogen et al., 1998). Descriptions of the chemical analysis and the analytical results from the investigation of water and sediment samples are given in Chapter 4 and in Appendix E.

The solubility and hydrolysis rate of CWA increase with temperature. As a rule of thumb, a temperature-increase of 10°C, will double the reaction speed. The melting and boiling points for the relevant warfare agents demonstrate that they are liquids or solids under atmospheric pressure at 20°C. Phosgene is a gas at atmospheric pressure with boiling point 8°C (melting point -118°C). At the sea bottom the boiling point will be higher because of the high pressure, phosgene will therefore exist as liquid at the sea bottom.

The density of the agent will determine if the undissolved agent will sink to the seabed or rise to the water surface. From the tables given below, it is shown that with the exception of tabun (density: 1.07 g/cm³), all the agents of concern have a significantly higher density than the water in Skagerrak (1.00 – 1.03 g/cm²). Based upon this, it can be assumed that undissolved chemical warfare agents will normally not rise to the water surface (Stock, 1996).

For the degradation of chemical warfare agents, dissolution in water is the first and most important step. When dissolved in water, the chemical warfare agent will undergo hydrolysis. This reaction leads to new compounds with properties different from those of the chemical warfare agents. In addition, they are less toxic, or no longer toxic (Stock, 1996).

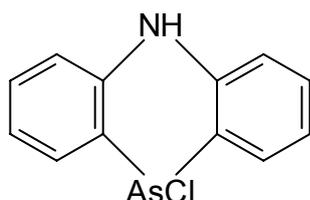
3.1 Arsenic and arsenic compounds

The risk assessment tool prepared by the Norwegian government do not discern the different arsenic compounds (SFT, 1999). Total arsenic is therefore discussed here, using the highest available ecotoxicity data for each species. Concentrations of arsenic in open ocean seawater are typically 1–2 µg/litre (IPCS, 2001). Mean sediment arsenic concentrations range from 5 to 3000 mg/kg, with the higher levels occurring in contaminated areas (IPCS, 2001). A background arsenic concentration of 42.8 – 49.3 mg/kg was found during the current investigation in Skagerrak. Marine organisms normally contain arsenic residues ranging from less than 1 to more than 100 mg/kg, predominantly as organic arsenic species such as arsenosugars (macroalgae) and arsenobetaine (invertebrates and fish). Bioaccumulation of organic arsenic compounds, after their biogenesis from inorganic forms, occurs in aquatic organisms. Bioconcentration factors (BCFs) for arsenic compounds in freshwater invertebrates and fish are lower than for marine organisms. Biomagnification in aquatic food chains has not been observed. Background arsenic concentrations in freshwater and terrestrial biota are usually less than 1 mg/kg (fresh weight). The daily intake of total arsenic from food and beverages is generally between 20 and 300 µg/day. Limited data indicate that approximately 25% of the arsenic present in food is inorganic, but this depends highly on the type of food ingested. Inorganic arsenic levels in fish and shellfish are low (IPCS, 2001).

Parameters	Data	References
Molecular weight	74.9 g/mol	
<i>Ecotoxicology</i>		
Algae	LC ₅₀ = 1.5 mg/l	Kuroiwa et al., 1994
Algae	NOEC = 0.01 mg/l	Toxnet, 2001
Molluscs	LC ₅₀ = 10 mg/l	Toxnet, 2001
Copepoda	LC ₅₀ = 0.024 mg/l	Forget et al., 1998
Annilida	LC ₅₀ = 127.36 mg/l	Fargasova, 1999
Crustacea	LC ₅₀ = 5.8 mg/l	Ensenrink et al., 1991
Crustacea	NOEC > 1 mg/l	Toxnet, 2001
Fish	LC ₅₀ = 18.50 mg/l	Rankin and Dixon, 1994
Fish	NOEC > 1 mg/l	Toxnet, 2001
PNEC ²	0.001 mg/l	Voie et al., 2001
<i>Bioaccumulation</i>		
BCF _{fish}	200	SFT, 1999
<i>Adsorption/distribution</i>		
Solubility in water	Not soluble	IPCS, 2001
Density	3.43 g/cm ³	
K _{dsoil}	30 l/kg	SFT, 1999
<i>Human toxicology</i>		
MTDI(TRV)	1.1×10 ⁻³ (mg/kg · d)	SFT, 1999
Genotoxic TRV	6.0×10 ⁻⁶ (mg/kg · d)	SFT, 1999

Table 3.1 Physical properties and ecotoxicity data for Arsenic

3.2 Adamsite



An estimated K_{OC} value (distribution coefficient between water and organic carbon) of 5.75 × 10³ indicate that adamsite will adsorb to sediments. Adamsite is practically insoluble in water. The agent hydrolyses very slowly in water, where the products are hydrochloric acid and

² PNEC = predicted no-effect concentration (Voie et al, 2001)

BCF_{fish} = concentration in water/concentration in fish at equilibrium

BCF_{estimated} = concentration in water/concentration in biota at equilibrium

K_{OC} = distribution coefficient between water and organic carbon

K_{OW} = distribution coefficient between octanol and water

H = Henrys law constant

MTDI(TRV) = maximal tolerable daily intake (toxicological reference value)

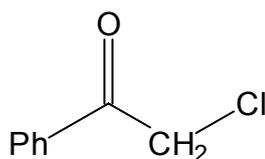
K_{dsoil} = distribution coefficient soil/water

bis(diphenylaminoarsine)oxide. The decomposition product bis(diphenylaminoarsine) oxide has similar toxicity as adamsite (Kopecz et al.). The toxicity of arsenic is summarized in the chapter of arsenic and arsenic compounds (Chapter 3.1). A measured $\log K_{OW}$ of 4.05 and an estimated BCF of 262 indicate some degree of bioaccumulation for adamsite. Even if adamsite should be fully degraded, the product would still contain an undegradable arsenic component that is toxic to humans. The toxicity of arsenic is summarised in the chapter of arsenic and arsenic compounds. Since adamsite is not soluble in water, have a density higher than water, and adsorb to sediments, they are expected to spread very slowly from the wrecks, and only cause a contamination of local sediments.

Parameters	Data	References
Molecular weight	277.57 g/mol	
<i>Ecotoxicology</i>		
Fish	Not soluble	SRC, 2002
PNEC	1×10^{-2} mg/l	Voie et al., 2001
<i>Accumulation</i>		
$BCF_{estimated}$	262	SRC, 2002
<i>Adsorption/distribution</i>		
Solubility in water	Not soluble	Blanch et al, 2001
Density	1.65 g/cm^3	SRC, 2002
H	$3.26 \times 10^{-8} \text{ atm/(mole/m}^3)$	
K_{OC}	5.75×10^3	
$\log K_{OW}$	4.05	

Table 3.2 Physical properties and ecotoxicity data for adamsite

3.3 Chloroacetophenone (CN)



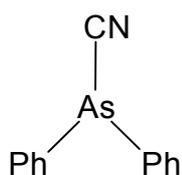
Based on an estimated K_{OC} value of 90 it is not expected that CN adsorb to suspended particles and sediments to a great extent. Evaporation from the water surface is expected based on an estimated Henry's law constant of 3.5×10^{-6} . CN may slowly undergo hydrolysis in water, where the products are hydrochloric acid and hydroxyacetophenone. CN has a higher density than water (1.32 g/cm^3). Thus if CN is released on the seabed, one would expect a high local concentration along the seabed, which would persist until the compound is removed by the process of dilution or degradation. Biodegradation is observed in the laboratory, but it is not known if biodegradation occurs in Skagerrak. An estimated bioconcentration factor (BCF) of 1, and an estimated $\log K_{OW}$ of 1.93, indicates that the potential for bioconcentration in

aquatic organisms is extremely low (HSDB, 2002). Aquatic toxicity data were not found for CN, but toxicological data from mammals indicate low toxicity.

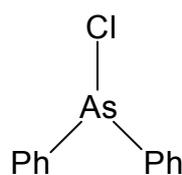
Parameters	Data	References
Molecular weight	154.59 g/mol	
<i>Bioaccumulation</i>		
$BCF_{estimated}$	1	HSDB, 2002
<i>Adsorption/distribution</i>		
Solubility in water	Data varies from none to 1 g/l	Blanch at al, 2001
Density	1.32 g/cm ³	HSDB, 2002
H	$3.5e^{-6}$ atm/(mole/ m ³)	
K_{OC}	90	
Log K_{OW}	1.93	

Table 3.3 Physical properties and ecotoxicity data for Chloroacetophenone (CN)

3.4 Clark I and II



Clark I



Clark II

Based on estimated K_{OC} values of 1.9×10^4 (clark I) and 7.0×10^3 (clark II), these compounds are expected to adsorb to sediments. Clark I and clark II react very slowly with water and produce diphenylchloroarsine and hydrochloric acid (clark I), or cyanide (clark II).

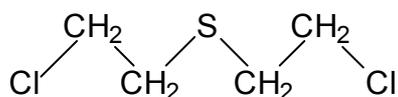
Hydrochloric acid is neutralized by water, while cyanide is quickly broken down.

Diphenylchloroarsine is unstable in water and will subsequently form the highly stable tetraphenyl diarsine oxide. The information about tetraphenyl diarsine oxide is poor, but it is known that it still is a potent warfare agent. Even if clark I and clark II should be fully degraded, the product would still contain an undegradable arsenic component that is toxic to humans. The toxicity of arsenic is summarised in the chapter of arsenic and arsenic compounds (Chapter 3.1). Since clark I and clark II are not soluble in water, have a higher density than water, and adsorb to sediments, they are expected to spread very slowly from the wrecks, and only cause a local contamination of sediments close to the wrecks.

Parameters	Data	References
Molecular weight	264.5 g/mol (I) 255.15 g/mol (II)	
<i>Ecotoxicology</i>		
Crustacea (<i>Daphnia magna</i>)	EC ₅₀ = 0.1 mg/l (48h)	Muribi, 1997
PNEC	1×10 ⁻⁴ mg/l	Voie et al., 2001
<i>Bioaccumulation</i>		
BCF _{estimated}	505 (I), 68 (II)	SRC, 2002
<i>Adsorption/distribution</i>		
Solubility in water	2 g/l	Blanch et al, 2001
Density	1.387 (I), 1.33 (II) g/cm ³	SRC, 2002
H	3.68×10 ⁻⁵ (I) atm/(mole/ m ³)	
K _{OC}	1.9 × 10 ⁴ (I) and 7.0 × 10 ³ (II)	
Log K _{OW}	4.52 (I), 3.29 (II)	

Table 3.4 Physical properties and ecotoxicity data for clark I and clark II

3.5 Sulphur mustard



A log K_{OC} value of 2.12, indicates that sulphur mustard adsorbs to some extent to suspended particles and sediments, which is also confirmed by studies in the laboratory (Waleij, 2001). Evaporation from the water surface is expected based on a Henry's law constant of 2.4×10⁻⁵ atm/(mole/m³). Hydrolysis is an important degradation pathway in aquatic environments, but the low solubility in water prevents hydrolysis. Hydrolysis in seawater is two to three times slower than in fresh water, due to ions in seawater affecting the process. In addition, the rates of hydrolysis are slowed down at low temperatures. Due to a temperature of 5-6°C on the seabed of Skagerrak, sulphur mustard is most likely a solid. In the water column sulphur mustard is hydrolysed with a half-life varying from 15 minutes at 25°C to 175 minutes at 5°C (Stock, 1996). It is observed that the hydrolysis is slowed down or completely prevented by formation of oligomeric and polymeric layers on the outside of the sulphur mustard lumps. It is shown that sulphur mustard may resist degradation in water or soil for years (see for example Stock, 1996). A bioconcentration factor of 0.3, and a log K_{OW} of 1.37 indicates that the potential for bioconcentration is low in aquatic organisms.

No toxicity data are available for thiodiglycol and thioxane, which are degradation products of sulphur mustard.

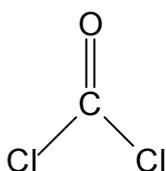
Parameters	Data	References
Molecular weight	159.08 g/mol	
<i>Ecotoxicology</i>		
Algae (<i>Phaeodactylum tricornotum</i>)	NOEC = 1 mg/l	Muribi, 1997
Crustacea (<i>Daphnia magna</i>)	LD _{LO} = 1 mg/l	Waleij, 2001
Crustacea (<i>Daphnia sp.</i>)	LD ₃₀ = 0.03 mg/l	Muribi, 1997
Fish	LD _{LO} = 2 mg/l	Munro et al., 1999
Fish (<i>Pleuronectes sp.</i>)	LD ₅₀ = 3 mg/l	Muribi, 1997
PNEC	3×10 ⁻³ mg/l	Voie et al., 2001
<i>Accumulation</i>		
BCF _{fish}	0.3	Waleij, 2001
<i>Adsorption/distribution</i>		
Solubility in water	0.92 g/l	Munro et al., 1999
Density	1.27 g/cm ³	Munro et al., 1999
H	2.1×10 ⁻⁵ atm/(mole/m ³)	Munro et al., 1999
Log K _{OC}	2.12	Munro et al., 1999
Log K _{OW}	1.37	Munro et al., 1999
<i>Human toxicology</i>		
MTDI(TRV)	2.4×10 ⁻⁵ mg/kg · d	Borges et al., 1996
Skin exposure	EC _{LO} = 0.01 mg/cm ²	Rosenblatt et al., 1995

Table 3.5 Physical properties and ecotoxicity data for sulphur mustard

3.6 Viscous sulphur mustard (Zählost)

Viscous sulphur mustard is sulphur mustard that has been added thickeners. The properties are therefore completely different from ordinary sulphur mustard and it will behave different in the environment. Viscous sulphur mustard looks like wax; it is viscous and sticky. The thickeners (polystyrene or montan wax) prevent dissolution and hydrolysis, which is first possible after the sulphur mustard has diffused out of the thickening medium. In the marine environment, particles will settle on the sticky surface, which conserve the sulphur mustard even further. Thus viscous sulphur mustard may remain on the seabed for many years. Mechanical crushing of viscous sulphur mustard lumps has proven to be very difficult due to the elasticity of the lumps and their protective leather-like surface. Such lumps can be transported by sea current and turbulence along the seabed (HELCOM, 1994). There have been some rumours about lumps of sulphur mustard that rise to the surface and drift there. However, such cases have never been proven and are thought to be speculations (HELCOM, 1994).

3.7 Phosgene

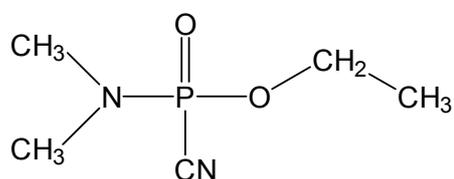


Phosgene hydrolyses quickly in water, but the stability may increase due to slow dissolution. This is also confirmed by studies in the laboratory (Stock, 1996). Hydrolysis produces carbon dioxide and hydrochloric acid. An estimated K_{OC} value of 2.2 indicate that phosgene somewhat adsorb to suspended particles and sediments. Evaporation from the water surface is expected based on a Henry's law constant of $0.02 \text{ atm}/(\text{mole}/\text{m}^3)$. An estimated bioconcentration factor of 3, and an estimated $\log K_{OW}$ of -0.71 , indicates that the potential for bioconcentration is low in aquatic organisms (HSDB, 2002). Aquatic toxicity data were not found for phosgene, but predicted aquatic toxicity data indicate low toxicity (SRC, 2002). Phosgene is heavier than water and is slightly soluble.

Parameters	Data	References
Molecular weight	98.92 g/mol	
<i>Bioaccumulation</i>		
$BCF_{estimated}$	3	HSDB, 2002
<i>Adsorption/distribution</i>		
Solubility in water	Slightly	HSDB, 2002
Density	$1.37 \text{ g}/\text{cm}^3$	
H	$0.02 \text{ atm}/(\text{mole}/\text{m}^3)$	
K_{OC}	2.2	
$\log K_{OW}$	- 0.71	

Table 3.6 Physical properties and ecotoxicity data for phosgene

3.8 Tabun



A K_{OC} value of 22.5, indicates that tabun do not adsorb to suspended particles and sediments. Evaporation from the water surface is not expected based on a Henry's law constant of $1.52 \times 10^{-7} \text{ atm}/(\text{mole}/\text{m}^3)$. An estimated bioconcentration factor of 3, and an estimated $\log K_{OW}$ of 0.38 indicate that the potential for bioconcentration in aquatic organisms is low (SRC, 2002). Hydrolysis is the dominating degradation pathway in the marine environment, and tabun will undergo hydrolysis in seawater with a half-life of 267 minutes at 20°C . The hydrolysis is

slowed down at 5-6 °C. The products from hydrolysis are cyanide and O-ethyl dimethylamidephosphoric acid (Stock, 1996). Tabun do dissolve in water, and with a density similar to seawater (1.00-1.03 g/cm²), tabun is expected to be dissolved in the water during a leakage.

Chlorobenzene is a stabiliser in tabun that can be present in the mixture in percentages of 5 to 20. Its toxicity is much lower than for tabun (Medea, 1997).

Parameters	Data	References
Molecular weight	162.1 g/mol	
<i>Ecotoxicology</i>		
Fish (<i>Pimephales promelas</i>)	LC ₅₀ = 0.6 mg/l	Munro et al., 1999
PNEC	6×10 ⁻⁴ mg/l	Voie et al., 2001
<i>Accumulation</i>		
BCF _{estimated}	3	SRC, 2002
<i>Adsorption/distribution</i>		
Solubility in water	98 g/l	Munro et al., 1999
Density	1.07	Munro et al., 1999
H	1.52×10 ⁻⁷ atm/(mole/m ³)	Munro et al., 1999
K _{OC}	22.5	SRC, 2002
Log K _{OW}	0.38	Munro et al., 1999
<i>Human toxicology</i>		
LD ₅₀ (on skin)	1000 mg/man	USAMRICD, 1999

Table 3.7 Physical properties and ecotoxicity data for tabun

Substance	Species	LC ₅₀ /EC ₅₀ (mg/l)	Referanse
Diemethylphosphoramidic acid	No data		
Dimethylamine	Daphnia magna (2 d)	50	Medea, 1997
	Fish (<i>Ocorhynchus mykiss</i>) (4 d)	17 -118	
Cyanide	Shrimp (<i>Mysidopsis bahia</i>) 4 d)	0.113	
Hydrogen Cyanide	Fish (<i>Lagodon rhomboides</i>)	0.069	

Table 3.8 Toxicity of some hydrolysis products of tabun

4 CHEMICAL ANALYSIS

4.1 Sample preparation

4.1.1 Preparation of sediment samples

The sliced sediment samples were frozen on-board the ship and transported to Kjeller for chemical analysis. After thawing the samples, they were extracted with dichloromethane according to internal procedure C1. This procedure is based on the “Recommended Procedures for Sampling and Analysis in Verification of Chemical Disarmament” (ROP), (The Ministry of Foreign Affairs of Finland, 1994 Edition). In this procedure, 10 g of wet sample was extracted with 2x10ml dichloromethane by sonication for 10 minutes and centrifuged at 2000 G for 5 minutes. The solvent was decanted from the sediment, combined and dried with anhydrous sodium sulphate. The samples were concentrated to about 1 ml with a gentle stream of nitrogen before analysis.

Some of the samples were derivatized to identify decomposition products. 10 g of a new portion of wet sea sediment was extracted with 2x10 ml distilled water by sonication for 10 minutes and centrifuged at 2000 G for 5 minutes. The water was decanted from the sediment and combined and evaporated to dryness by vacuum concentration. The sample was redissolved in 900 μ l acetonitrile and mixed with 100 μ l *N-tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (TBDMS) with 1 % *tert*-butyldimethylsilylchloride. The sample was then heated in a water bath at 60 °C for 30 minutes before analysis.

Dry weight was obtained using internal procedure D1 (dried at 105 °C for 20 hours) on a new portion of wet sea sediment.

4.1.2 Preparation of water samples

The collected water samples were transported back to Kjeller in an expanded polystyrene box, cooled with cooling elements. 10 ml of the water sample was extracted with 2x5 ml dichloromethane for 3 minutes. The combined extracts were dried with anhydrous sodium sulphate and concentrated to about 1 ml with a gentle stream of nitrogen before analysis.

4.2 Analytical methods

The samples were analysed using a Fisons MD800/250 quadrupole mass spectrometer (ThermoQuest, San Jose, CA, USA) in Electron Impact (EI) mode, coupled to a Fisons 8060 gas chromatograph (GC, ThermoQuest). 1 μ l of the sample was injected splitless for 1 min by an autoinjector. The column used was 30 m x 0.25 mm with 0.25 μ m DB-5MS stationary phase from J&W Inc. Helium was used as carrier gas at a flow rate of 1 ml/min (flow controlled). The injector was held at 220 °C, the transfer line at 260 °C and the oven program was 40 °C (1 min) – 10 °C/min - 280 °C (10 min). Other instrumental parameters were: ion

source temperature = 190 °C, electron energy = 70 eV, scan range = 35-600 u, scan cycle time = 0.6 sec and unit resolution. Xcalibur version 1.2 software (ThermoQuest) was used for instrument control and data handling.

The samples where chemical warfare agents or degradation products were found using EI mode, were also subjected to Chemical Ionisation (CI) for further verification. In CI mode, the instrumental parameters were: ion source temperature = 150 °C, electron energy = 70 eV, scan range = 100-600 u, scan cycle time = 0.6 sec and unit resolution. In general, ammonia was used as reagent gas, but isobutane and methane was also used in some cases where no unambiguous molecular ions were found using ammonia.

AMDIS (Automated Mass spectral Deconvolution & Identification System) version 2.0 software from National Institute of Standards and Technology (NIST) was used for screening the analytical data against the FFI library of mass spectra for chemical warfare agents, precursors and degradation products. The analytical data was also screened against a subset of the NIST library of mass spectra. In addition, manual search for some additional compounds not in our libraries but listed in NATO AEP-10 (NATO Restricted) were conducted. Large peaks in the total ion chromatograms were searched against both the full NIST library and the internal FFI library

All samples were also subjected to Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) to analyse for the total arsenic content. Before analysis, the sediment samples were dried overnight at 105 °C. 1 g of each sample was added 7M nitric acid and partly digested by high temperature and high pressure in an autoclave (the samples were not completely dissolved). Control samples were digested together with the authentic samples. After digestion, the samples were diluted to 100 ml with distilled water and analysed by an Optima 4300 DV ICP-AES from PerkinElmer. The wavelength used for arsenic was 188.979 nm. Instrumental uncertainty for this analysis was estimated to 2-5 %.

4.3 Analytical results

4.3.1 Water samples

Four water samples collected above some of the holds of the wrecks were analysed. No compounds related to chemical warfare agents, precursors or degradation products were found in the water samples by GC-MS analysis. The concentrations of elemental arsenic were below the limit of quantification for the ICP analysis (Appendix F).

4.3.2 Compounds identified in the soil samples by mass spectrometry

The structures of identified compounds in the sediment samples are shown in Figures 4.1 and 4.2 below. Chemical names of the compounds are shown in Table 4.1. The mass spectrometric methods used in the identification are given in Appendix E. The underivatized compounds

were found in the dichloromethane extracts of sediments while the bis-TBDMS-derivative of TDG (**2**) was found in the water extracts of sediments.

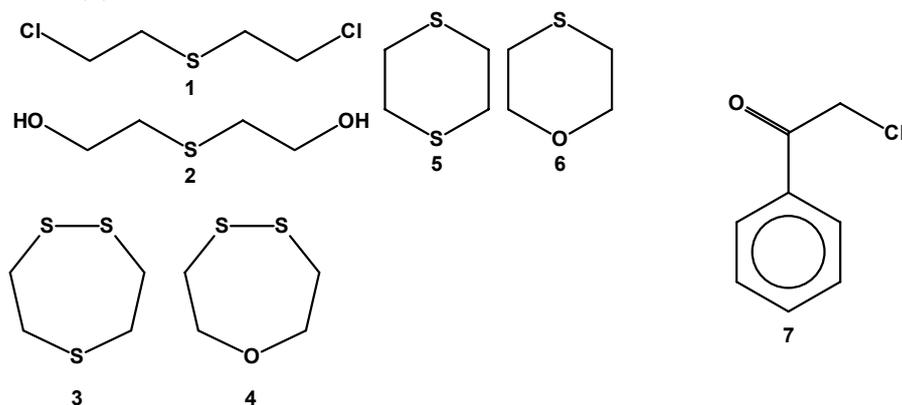


Figure 4.1 Identified riot control agent (**7**) and compounds related to sulphur mustard (**1**)

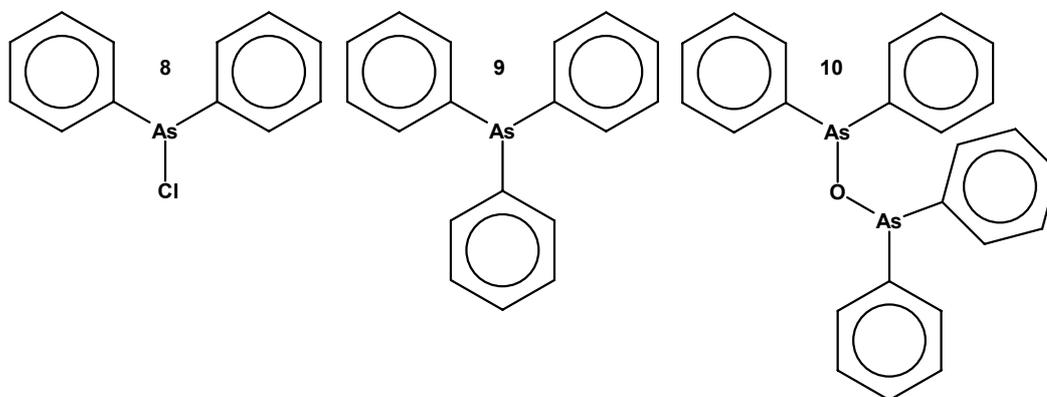


Figure 4.2 Identified arsine compounds (**8-10**)

All of the compounds, except sulphur mustard (**1**), TDG (**2**) (bisTBDMS derivative) and 1,4-Thioxane (**6**), have been identified using at least two independent techniques. In addition, all the compounds have been identified using retention indexes (RI). This last technique is, however, in principle not an independent technique since the RI data are taken from the same runs as the EI data. However, we note that these three compounds related to sulphur mustard were all found only in samples containing several other sulphur mustard degradation products (V02-058 and V02-059, both from the same core) and thus conclude that these three compounds also are present in the samples.

The chemical warfare agent phosgene was not analysed for by the analytical methods used in this investigation. Phosgene is, however, immediately hydrolysed in water to hydrochloric acid and carbon dioxide. It is therefore unlikely that phosgene would have been detected in the samples.

Sample			Results, mg/kg dried sediment								
Sediment sample #	Wreck #	FFI Sample #	Sulphur mustard (H, 1)	1,2,5-Trithiapane (3)	1,4,5-Oxadithiepane (4)	1,4-Dithiane (5)	1,4-Thioxane (6)	2-chloro-1-phenyl-ethanone (CN, 7)	Clark I (DA, 8)	Triphenylarsine (9)	Bis(diphenylarsine) oxide (10)
Mass used for quantification			109	152 ¹	136 ¹	120	104	105	154 ²	152	152 ²
Background (0-1 cm)		V02-011	Nothing identified								
Background (1-3 cm)		V02-012	Nothing identified								
1A (0-1 cm)	5	V02-014								0.03	
1A (1-3 cm)	5	V02-015							0.4		
1D (1-3 cm)	5	V02-024							0.9	7.0	
1E (0-1 cm)	5	V02-026		0.4	0.5	0.2			1.2	0.3	
1E (1-3 cm)	5	V02-027		0.5	0.7	0.2			0.1	0.03	
1F (0-1 cm)	5	V02-029							0.3	0.02	
1F (1-3 cm)	5	V02-030							0.2		
1G (0-1 cm)	5	V02-032							3.0	8.9	
1H (0-1 cm)	5	V02-035							0.2	0.1	
2B (1-3 cm)	6	V02-042								0.1	
2C (0-1 cm)	6	V02-044								0.02	
2E (0-1 cm)	6	V02-050								0.2	
2E (1-3 cm)	6	V02-051							0.2		
2G (1-3 cm)	6	V02-057								3.6	
2H (0-1 cm)	6	V02-058	2.4	0.5	0.1			7.5	178	63	16
2H (1-3 cm)	6	V02-059		0.6	0.5	1.1	1.1		77	3.8	124
2I (0-1 cm)	6	V02-060		0.04					8.0	25	
2I (1-3 cm)	6	V02-061		0.06					2.3	0.3	0.8
3A – 3H	14	V02-062-V02-077	No chemical warfare agents detected in the samples from wreck 14								
10A (0-1 cm)	13	V02-078							2.2	0.3	
10A (1-3 cm)	13	V02-079		0.2					40	18	137
10B (0-1 cm)	13	V02-080		0.2					0.6	0.1	
10B (1-3 cm)	13	V02-081							3.7		0.2
10C (1-3 cm)	13	V02-083							0.4		
10D (0-1 cm)	13	V02-084							0.5		
10F (0-1 cm)	13	V02-088							3.1		
10H (1-3 cm)	13	V02-093							0.6		

Table 4.1 Quantification of identified compounds in the dichloromethane extracts of the sediments (mg compounds pr kg dry sediment). Only samples with identified compounds are shown. The concentrations of the compounds are calculated using *n*-decane as an internal standard

¹No authentic standards available for quantification. As a rough estimate, the same response factor as for 1,4-dithiane related to *n*-decane was used

²Assumed same response factor for clark I, bis(diphenylarsine) oxide and one unknown component in the authentic standard for clark I

4.3.3 Quantification of identified compounds by mass spectrometry

The amounts of each identified compound in the samples were calculated using an internal standard and authentic standards. The results are tabulated in Table 4.1 for dichloromethane extracts of sediments and in Table 4.2 for water extracts of sediments after derivatization. No relevant compounds were identified in the collected water samples. Only samples where agents have been found, are shown in the tables. The location of the samples in relation to each wreck is shown in Figures 2.3, 2.5, 2.7 and 2.9. The exact positions are given in Appendix D.

Sample			Results
Sediment sample #	Wreck #	FFI sample #	Thiodiglycol (TDG, 2), BisTBDMS derivative
Background (0-1cm)		V02-011	Nothing identified
2H (0-1 cm)	6	V02-058	weak
2H (1-3 cm)	6	V02-059	weak

Table 4.2 Identification of compounds in the water extracts of the sediments. None of the two signals for the bis(TBDMS) derivative of TDG (2) were strong enough to be quantified. Only samples with identified compounds are shown

From the results in Table 4.1, we can see that sulphur mustard (H) is found at a concentration of 2.4 mg/kg in the top layer (0-1 cm) of one sample (sample 2H). This sample was collected close (10 m) to wreck number 6, which was divided into several parts, exposing the cargo hold with ammunition (see Figure 2.5). The sample was also collected close to an aerial bomb where the content had leaked out. The same sample also showed the highest amount of clark I (178 mg/kg) found during the investigation. Decomposition products from sulphur mustard (3-7) are found at four additional locations (1E, 2I, 10A and 10B).

In one sample, 2-chloro-1-phenyl-ethanone (chloroacetophenone, CN, 7) was identified. This compound is a riot control agent with low toxicity and low possibility for bio-concentration in aquatic organisms (Chapter 3.3). The compound is practically insoluble in water and very resistant to hydrolysis.

Organoarsenic compounds (compounds 8-10) were found in many samples, both close to the wreck (10 m) and at a somewhat longer distance from the wreck (about 20 m). Most of these samples contain the chemical warfare agent clark I (8) itself. Some of the samples contain triphenylarsine (9) and some samples contain bis(diphenylarsine) oxide (10).

4.3.4 Elemental arsenic

The results from the analysis of elemental arsenic carried out by ICP showed elevated concentrations of Arsenic in some sediment samples (Appendix F). Most of the results are, however, close to the level found in the background sediment samples of 42.8 – 49.3 mg/kg. Elevated concentrations of arsenic ranging from 480 mg/kg to 75 mg/kg were found in four sediment samples (samples 2H [0-1 cm], 2H [1-3 cm], 2I [0-1 cm] and 10A [1-3 cm]). This corresponds well with the samples where the highest concentrations of arsenic-containing compounds, clark I (**8**), triphenylarsine (**9**) and bis(diphenylarsine)oxide (**10**) were found using mass spectrometry (Chapter 4.3.3).

4.4 Discussion

The sediment samples were inspected when brought on board KNM Tyr and only undisturbed samples were selected for further analysis. The analytical results are based on a relatively small number of samples. One could therefore not exclude the possibility that larger concentrations of chemical warfare agents could be present at certain places close to the wrecks. The results indicate, however, that the sediment contamination are very local. This is especially the case for sulphur mustard and its decomposition products which were only found close to the wreck (except for very small concentrations of the decomposition product (**3**) found in sample 2I).

The arsenic containing compounds (**8-10**) were found to be more widespread and were identified both in the samples close to the wrecks and in the samples collected a longer distance (20-28 m) from the wrecks. The reason may be that the compounds are very stable and could be found a long time after they are released from the ammunition. At wreck number 13, the highest concentration of these compounds were not found in the top layer, but were found in the 1-3 cm layer from the core sample. This indicates that these compounds are very stable in this environment and that the leakage has started several years ago. The sedimentation rate in this area is 15-45 cm/100 years (1.5-4.5 mm per year) (NGU, 1997).

Winterlost was the German name for sulphur mustard mixed with phenyldichloroarsine to achieve a lower freezing point than pure mustard (Blanch et al 2001). However, also arsine oil seems to have been used for this purpose (Haas et al 1997, Sjöfartsverket 1992). This can explain the occurrence of both mustard and components of arsine oil in relatively high concentrations in the same samples.

No chemical warfare agents or related compounds were found at wreck no 14. The wreck itself seemed in good shape with little corrosion or other damage. Several small piles of grenades (127 mm or larger) were observed a distance from the wreck. The reason for this is probably that the grenades were transported in wooden cases which eventually have rotted away. The cases might have been transported on deck and then been carried away from the sinking ship. No samples were collected near these piles.

5 RISK ASSESSMENT OF CWA IN SKAGERRAK

5.1 Introduction

In this chapter some of the risks associated with the dumped chemical warfare agents are described. In the last subchapter (Chapter 5.6), we try to estimate the risk from leaking ammunition where we restrict ourselves to one leaking ammunition at a time. This is selected as the most likely scenario because a collapse of the whole wreck leading to an immediate emptying of all its stored CWA would scarcely occur. A more stepwise collapse is more likely, where the extent of a release would be limited to a few kilograms in each step.

5.2 Risk for fishermen

Only 15 of the dumped ships were detected after an investigation by FFI in 1989 (Tørnes et al., 1989). Up to 36 ships might have been dumped in Skagerrak (Chapter 1). Not all of the ships were found inside the area that the allies were allowed to sink the ships. This opens the possibility that the ships in reality were sunk far away from the designated area. As an expert stated, the ships were generally in poor condition, and many could have been lost *en route* to the dumping site because of bad weather. In addition there are information that the *Leipzig* filled with 1000 tonnes of chemical ammunitions, was scuttled in a different area, namely, outside Lista, Norway (UK Ministry of Defence, 1984). If this is the case these ships may pose a risk to demersal trawling in the area. Due to this risk, the area that is marked on the draft for fishers should be increased. However, other information indicates that *Leipzig* did not contain chemical ammunition (Fonnum, 1997). Demersal trawling in the deepest part of Skagerrak should, however, be advised against. We know very little about the situation outside the search area where the investigation with side-scan sonar was carried out in 1989. An effort should therefore be made to locate additional ships.

Fishing equipment (trawls) were observed at several places during the investigation and the trawls were hung up in different parts of the wrecks. This is an indication that trawling has taken place in the area close to the dumped wrecks. This should be avoided, because it might be possible to get chemical ammunition in the nets, which could then be brought up to the surface and poison the fishermen. This has happened in the Baltic sea. It is also a possibility that fishing equipment could damage the wrecks and expose the chemical ammunition to the water, increasing the release of the agents to the environment.

International experience has shown that, wherever possible, public knowledge of the location of CWA dumps has been beneficial in avoiding contact incidents. It has been shown that since a national public inquiry in 1972, when information was released regarding the Japanese dumping sites, there have been no casualties from accidents. This compares with several deaths and dozens of wounded from dumped CWA contacts in the period from World War II to 1972 (Plunkett, 2002).

5.3 Exposure to sulphur mustard

Sulphur mustard was found in the top layer of one sediment sample at a concentration of 2.4 mg/kg, and sulphur mustard decomposition products were found at four additional locations. From the toxicity data in Chapter 3.5 it is shown that sulphur mustard has a low K_{OC} value, meaning that the compound has a low affinity to sediment particles. It is therefore unlikely that the concentration in water reaches a level that could give effects on marine organisms. The rate of hydrolysis is fairly quick (half-life of 175 minutes at 5 °C) (Stock, 1996), meaning that sulphur mustard is hydrolysed almost as soon it is dissolved in water. The dissolution is the rate determining step. The bioconcentration factor (BCF) is 0.3 for fish, meaning that the possibility of accumulation in marine organisms is small. The possibility of fishermen catching marine organisms, e.g. shrimps with a harmful concentration of sulphur mustard is therefore low.

Sediment concentrations of sulphur mustard up to 190 µg/kg were found in Skagerrak in a similar dumping field along the Swedish west coast (Granbom, 1996). Investigations showed that the sediments were not homogenous contaminated and that the highest concentration was found 1 km away from the nearest wreck.

If sediments containing sulphur mustard is brought up to the surface by fishing activities it could hurt fishermen handling the equipment. The maximal tolerable daily intake (toxicological reference value) MTDI(TRV) for sulphur mustard is 2.4×10^{-5} mg/(kg day) (Borgers et al, 1996). A person weighing 60 kg could therefore consume dry sediments containing 1.5×10^{-3} mg H per day without having any adverse effect. With a sediment concentration of 2.4 mg/kg dry sediment or 1.2 mg/kg wet sediment (containing 50 % water) one could consume 1.25 g wet sediment pr day without having any adverse effect. It is very unlikely that this amount is exceeded.

The lowest value publicised for sulphur mustard blistering dose on human skin is 6 µg/cm² (Marrs et al, 1996). Using the same sediment concentration (1.2 mg/kg wet sediment), one could be exposed to 5 g sediment pr cm² skin without seeing any blisters. It is very unlikely that one should be exposed to such large amounts of sulphur mustard-containing sediments, especially because the fishing equipment will be cleaned by the sea-water on the way up to the surface.

These calculations are, however, based on the concentration found in only one sediment sample and it is difficult to draw conclusions based on only one positive sample. It is possible that the sediment concentration of sulphur mustard gas in some areas might be higher than has been found. It is therefore advisable to ban fishing and other bottom activities in the areas of concern.

5.4 Bioaccumulation of arsenicals

The human toxicity of arsenicals is lower than for sulphur mustard. It is stated that for clark I, 0.05 mg/cm² neat agent on skin gives the first signs of damage (Kopecs et al.) It is therefore unlikely that one should be exposed to such large amounts of sediments containing clark I if ammunition is not brought to the surface by fishing or other bottom activities.

Most of the CWAs do not bioaccumulate in marine organisms due to a bioconcentration factor lower than 10. The only compounds of concern are the arsenicals. The bioconcentration factors of these compounds are dependent on the chemical form. The highest bioconcentration factor was found for clark I (BCF = 505), and will be used as a worst-case parameter. If clark or adamsite is accumulated by biota, they will be metabolised to other compounds containing arsenic. Arsenic is therefore the main compound of concern in relation to fish consumption. According to World Health Organisation, the mean acceptable daily intake of arsenic is 40 µg/day. The Norwegian classification system for sediments operates with a criterium of 20 mg/kg as the highest background level of arsenic, based on measurements of background levels in marine sediments (Table 5.1).

A Russian investigation of sediment levels of arsenic in the dumping area located in the Swedish zone of Skagerrak showed sediments concentrations up to 200 mg/kg (Spiridonov and Zhamoida, 1999). The maximum sediment concentration of arsenic in the Norwegian zone found by Inductively Coupled Plasma (ICP) analysis during the current investigation was 480 mg/kg in one sample. The rest of the samples had arsenic concentrations below 100 mg/kg, with background levels of 43-49 mg/kg (two samples).

The number of samples in the different pollution classes are given in Table 5.1 below. Most of the samples (including the background samples) fall in the category “Moderately polluted”. Two samples fall in the category “Markedly polluted” (samples 2H [1-3 cm] from wreck no 6 and 10A [1-3 cm] from wreck no 13) and one sample in the category “Strongly polluted” (sample 2H [0-1 cm] from wreck no 6).

	I Insignificantly – little polluted	II Moderately polluted	III Markedly polluted	IV Strongly polluted	V Very strongly polluted
SFT Classification (mg/kg)	<20	20-80	80-400	400-1000	>1000
Number of samples	1	64	2	1	0

Table 5.1 Classification of arsenic in sediment samples (dry weight) according to the system given by SFT (SFT, 1997)

From the mass spectrometric analysis of the sediment samples, it is shown that several of the samples contain the chemical warfare agent clark I (**8**) and one other arsenic compound triphenylarsine (**9**) contained in “Arsine oil” (Chapter 4.3). Bis(diphenylarsine)oxide (**10**),

which were also found in some samples is a decomposition product from clark I (8). The skin toxicity of clark I is reported as 0,05 mg/cm² for the first damage and 0.5 mg/ cm² for painful damage (P Kopecz). These values are higher (lower toxicity) than for sulphur mustard gas (Chapter 5.3).

Huge amounts of shrimps were observed at the ship wrecks. Assessment of arsenic in marine organisms show that it is accumulated in shellfish (SNT report, 1998). If the concentration of arsenic in water or sediment is known, it is possible to estimate the concentration of arsenic in biota from the BCF or BSAF (Biota Sediment Accumulation Factor). With a BSAF of 0.037 (Song and Breslin, 1999) and a maximum arsenic concentration of 480 mg/kg in sediments found during this investigation, shrimps in this area could have an arsenic concentration of 18 mg/kg. This is similar to what has been measured in shrimps along the Norwegian coast (SNT report, 1998).

Most of the arsenic in shrimps are found as organoarsenic compounds with lower toxicity than inorganic arsenic (Ozretic et al, 1990, Friberg, 1988). This fact, taken together with the estimate of arsenic in biota given above, indicate that there is no health risk associated with eating shrimps from the area with elevated sediment concentration of arsenic.

5.5 Potential effects on local biota

Literature that addresses the effects of CWA exposure on marine biota is very limited. Ecotoxicity data are summarized in the tables containing ecotoxicity data for each compound (Chapter 3). As a conclusion, CWAs seem to have a medium toxicity to marine biota, where tabun seems to be the most toxic with a PNEC of 6×10^{-4} mg/l. The solubility of tabun might explain some of the toxicity compared with the more insoluble CWAs. A toxicological investigation in the Swedish dumping zone studied enzyme activity (acetylcholinesterase) in crabs caged nearby a scuttled wreck. The results showed no statistical changes compared with a control group (Granbom in Kaffka, 1996). The current investigation of the scuttled ships by a ROV, performed by FFI, bore witness of an abundant marine life nearby the ships, indicating non-toxic levels.

5.6 A theoretical scenario of leaking ammunition

The most likely scenario is small leaks from single ammunitions. The investigation of the ship wrecks showed several bombs which were pierced through by corrosion and the content probably leaked out. The corrosion is dependant on the surroundings of each ammunition, especially which materials the bomb or grenade is in contact with (contact corrosion). The leakage will therefore be spread out over many years.

The instant release of arsenicals and sulphur mustard will not result in large toxic plumes. Due to their low solubility and high density, these compounds would be spread as pieces (large or small) and eventually settle on the sea floor, where they could affect local marine organisms. Slow dissolution of the agents would lead to hydrolysis and reduced concentrations.

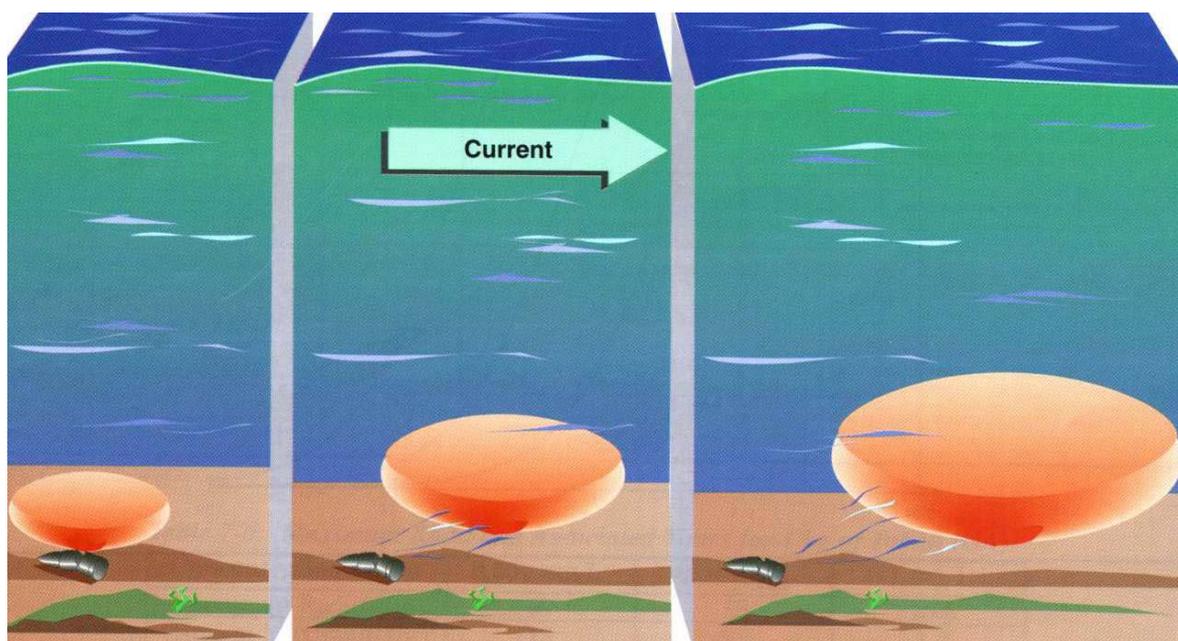


Figure 5.1 Schematic illustration of acutely released chemical warfare agent (Medea, 1997)

The agents causing most concern are the nerve agents. These agents were not found in the water or sediment samples during this investigation, but are included here because the effect of a release might be larger than for the other agents present. Nerve agents are easily soluble in water and have a density close to water, but will hydrolyse fairly quickly to less toxic substances (Chapter 3.8). From Appendix B, it is shown that the nerve agent tabun could be found in 105 mm grenades containing 1.2 litre agent and 250 kg bombs containing 86 kg agent. Medea (Medea, 1997) has estimated a no-effect boundary (0.001 mg/l) at 70 m (radius) from the leaking ammunition if an instant release of 1 kg tabun is modelled and a vertical diffusivity of 0.1 cm/s and a horizontal diffusivity of 1 cm/s is assumed (see Figure 5.2). These diffusivities correspond relatively well with the mean sea current measured during the investigation (mean 2.0-2.5 cm/s). The area with lethal concentration (0.1 mg/l) estimated by Medea as much lower, i.e. 17 m radius.

If a larger bomb with for instance 100 kg tabun is immediately released, the agent will be spread out until the agent is diluted and hydrolysed in water down to a concentration below the no-effect level. If we assume a hydrolysis rate constant of 0.031 h^{-1} at $5 \text{ }^{\circ}\text{C}$ (estimated from known values at higher temperatures), it could be shown that the time before the concentration is below toxic levels due to hydrolysis alone is long. Hydrolysis is therefore not taken into account during this calculation.

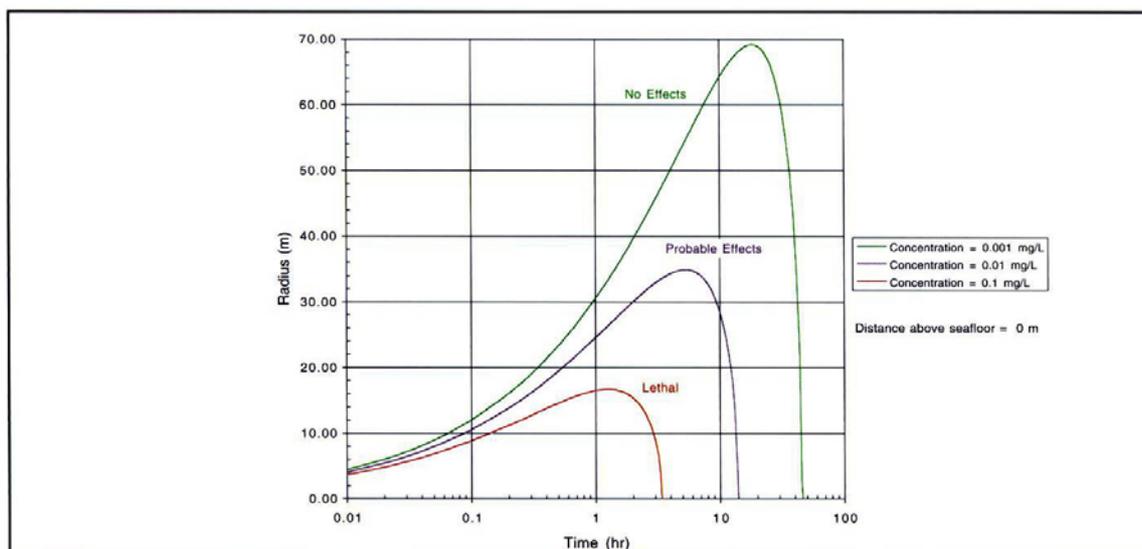


Figure 5.2 Radius of constant concentration on the seafloor for Tabun (Medea 1997)

If we assume that the agent is spread like a half-sphere (volume $V=2/3\pi r^3$), a 100 kg bomb would be diluted to a radius of 360 m before the concentration is below the no-effect level (0.001 mg/l). If the mean sea current is 2.0 m/s, the half-sphere will expand and travel 3 min before the concentration is below this limit. Using a half-sphere as a model for the leak is a rude approximation, but the calculation shows that the time before the concentration is below the no-effect level is fairly short and the volume is quite small.

The most dangerous situation is probably a collapse of a whole ship wreck. All the inspected wrecks were standing upright at the sea floor, probably because the sinking was a slow process. This means that each wreck would orient itself upright before reaching the sea floor. According to wreck specialists, corrosion of the ship structure will eventually cause the metal plates from the sides to collapse outwards and thereby exposing the ammunition to more corrosion. The possibility of a downward collapse of the wrecks with resulting large leaks of the chemical munitions in the holds is assessed as low.

In conclusion, the effect from leaking ammunition would because of rapid hydrolysis and low solubility in water most probably be very local. It is unlikely that chemical warfare agents could affect sea-life over large distances. What has been observed near the wrecks are abundant sea-life, which appear not to be affected by leaking ammunition. The most dangerous situation is when chemical ammunition is brought to the surface by fishing or other bottom activities. The only chemical warfare agent with high solubility in water is tabun. Collapse of a wreck containing tabun could therefore in a worst-case scenario affect a large volume of water.

6 CONCLUSIONS

Four shipwrecks were investigated during the expedition in Skagerrak in 2002. The wrecks showed little sign of corrosion and the conditions of the wrecks seemed to have changed very little since the last investigation in 1989. From the investigation carried out by side-scan sonar in a small area in 1989, 15 possible ships were identified. According to literature, 36 ships might have been sunk in the area south-east of Arendal. The location of the 21 remaining wrecks are not known and an investigation of a larger area should therefore be carried out to locate these ships. It was shown during the investigation in 2002 that the wrecks had caught fishing nets. Demersal trawling should therefore be avoided in all areas that may contain wrecks with chemical ammunition, because it might be possible to get chemical ammunition in the nets, which could then be brought up to the surface and poison the fishermen. It is also a possibility that fishing equipment could damage the wrecks and expose the chemical ammunition to the water, increasing the release of the agents to the environment.

Sulphur mustard was identified in one sediment sample from one location at a concentration of 2.4 mg/kg (dry sediment). The lowest value publicised for sulphur mustard blistering dose on skin is 6 $\mu\text{g}/\text{cm}^2$ (Marrs et al, 1996). Using this sediment concentration (1.2 mg/kg wet sediment), one could be exposed to 5 g sediment pr cm^2 skin without seeing any blisters. It is very unlikely that one should be exposed to such large amounts of sulphur mustard-containing sediments. Decomposition products from sulphur mustard were identified at four additional locations from three wrecks. Sulphur mustard has a relatively low affinity to sediment particles but have a fairly quick rate of hydrolysis. Dissolution in sea water is, however, slow and is therefore the rate determining step. The bioconcentration factor (BCF) is 0.3 for fish, meaning that the possibility of accumulation in marine organisms is low. The possibility of catching marine organisms, e.g. shrimps with a dangerous concentration of sulphur mustard is therefore low.

Arsenic-containing compounds were found in many samples, both close to the wrecks and at a somewhat longer distance from the wrecks. Most of these samples contained the chemical warfare agent clark I. The highest concentration of clark I found during the investigation was 178 mg/kg (dry sediment). Some samples contained other arsenic containing compounds, both decomposition products from clark I and components of the known mixture "Arsine oil". These compounds are poorly soluble in water and resistant to hydrolysis and could therefore be found on the seabed for a very long time. Even when broken down, the end products will contain arsenic. The highest amount of arsenic found in the sediment samples was 480 mg/kg (dry sediment). Arsenic will bioaccumulate in aquatic organisms and might therefore be a health problem. Biomagnification in aquatic food chain has, however, not been observed. With the amount of for instance shrimps consumed (1-3 days pr month), the health risk associated with such consumption from locations close to the wrecks is assessed as low.

Tabun (not found in the investigation) is much more soluble in water than sulphur mustard and the arsenic containing agents. Tabun will, in addition, decompose fairly rapidly to water-

soluble decomposition products. The toxicity is, however, much higher than the other compounds and could in a worst-case scenario affect a large amount of sea-water.

The investigation showed that some of the ammunition was pierced through by corrosion. The content have therefore probably leaked out, which indicate that the release of chemical ammunition to the sea will go on for a long time. It is therefore recommended that a new inspection is carried out within 10 years to assess the condition of the wrecks.

The ammunition seen on the sea bed have quite thin walls, and many of the shells were pierced through by corrosion. Trying to bring the shells to the surface would most likely not be successful because they will fall into pieces by the movement and the content will leak out. It is therefore recommended to leave the ammunition where it is and not to try bringing it to the surface. A lot of shrimps and some species of fish were observed close to the bombs. This indicate that no acute toxic effects from the chemical warfare agents in Skagerrak is present, but investigation of the content of chemical warfare agents or degradation products in marine organisms is needed to assess long-term effects.

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A APPENDIX

Location of sunken gas-ships



POSISJONSANGIVELSE FOR "GASSKIP"

* LOKALISERTE SKIP:

- Krysser Leipzig
- M/S Monte Pascoal
- D/S Philip Heineken
- M/S Schwabenland
- D/S Sesostries
- Torpedojager T 38
- Torpedojager T 39
- Torpedojager TF 1

Følgende fartøyer er antatt senket i Skagerrak. Dumpingsfeltet ser ut til å strekke seg fra Svenskegrensen i øst til Lista i vest. Det kan dokumenteres at det ble senket fartøyer utenfor Arendal (ca 650-700 meters dyp), Måseskjær (ca 200 meters dyp) og sørvest av Lista på ca 300 meters dyp.

ALCOA BANNER	5035brt.	- 58°18,7N 09°36,5Ø
BALKAN	2209brt.	- 58°16N 09°27Ø
BERLIN	2970depl.	
BRANDENBURG - Vs-158	174brt.	
BREMSE	796depl.	- 57°52N 06°15Ø
CLAUS VON BEVERN	861depl.	- 57°52N 06°15Ø
DRAU	5142brt.	
DUBURG	2675brt.	- 58°13.565N 09°32.097Ø / 57°02,5N 10°04,1Ø
EDITH HOWALDT	2067brt.	- 58°14N 09°27Ø
EIDER	3288brt.	
EMMY FRIEDERICH	5066brt.	- 58°14N 09°27Ø
EMPIRE SEVERN	6681brt.	- 58°18N 09°37Ø
ERIKA SCHÜNEMANN	1177brt.	
F 192	240depl.	- 58°08N 10°52Ø
FALKENFELS	6318brt.	
FECHENHEIM	8116brt.	
FREIBURG	5165brt.	
GEORG HAWLEY	7176brt.	- 58°18,5N 09°38,0Ø
GERTRUD FRITZEN	2999brt.	
H.C. HORN	4132brt.	
HELGOLAND	2947brt.	
HERBERT NORKUS	1750depl.	
HUGO OLDENDORFF	1876brt.	
JAMES HARROD (1/2)	7176brt.	- 58°16,0N 09°33,0Ø
JAMES OTIS	7176brt.	- 58°16N 09°32Ø
JANTJE FRITZEN	6582brt.	- 58°18N 09°55Ø
KARL LEONHARDT	6043brt.	- 58°14N 09°24Ø
KSB 13	1724depl.	
Krysser LEIPZIG	6515depl.	- 57°52,011N 06°15,747Ø
LOTTE	2115brt.	- 58°19N 09°40Ø
LOUISE SCHRÖDER	1327brt.	- 58°15N 09°27Ø / 57°25N 10°41Ø
LUDWIGSHAFEN	1923brt.	

Minesveiper M 16	874depl.	- 58°10N 10°42Ø
Minesveiper M 280 (TS14)	775depl.	- 57°40N 06°30Ø
Minesveiper M 522	652depl.	- 58°10N 10°42Ø
MONTE PASCOAL	13870brt.	- 58°10,31N 10°46,13Ø
ODERSTROM	1511brt.	
OLGA SIEMERS	3347brt.	
PATAGONIA	5898brt.	- 58°15N 09°35Ø
PILLAU	1308brt.	
RHÖN	1778brt.	- sannsynligvis sørvest av Arendal
S 7	86depl.	- 58°09N 10°50Ø
S 9	86depl.	- 58°09N 10°51Ø
S 12	92depl.	- 58°09N 10°52Ø
SCHWABENLAND	8631brt.	- 58°10,22N 10°45,24Ø
SESOSTRIS	2013brt.	- 58°18,315N 09°41,057Ø
Torpedojager T 21	1098depl.	- 57°52N 06°15Ø
Torpedojager T 37	2190depl.	- 57°40N 06°30Ø
Torpedojager T 38	2190depl.	- 58°07,48N 10°46,30Ø
Torpedojager T 39	2190depl.	- 58°08,12N 10°47,48Ø
Torpedojager T 63	2566depl.	
Torpedojager T 65	2566depl.	- 58°17,9N 09°37,1Ø
TAGILA	2682brt.	
TAURUS	1158brt.	- 58°16.009N 09°31.152Ø
Torpedojager TF 1	489depl.	- 58°09N 10°50Ø
THEDA FRITZEN	2882brt.	- 58°18N 09°55Ø
TRITON	1620brt.	- ved Jylland = Arendal?
TRUDE SCHÜNEMANN	1260brt.	
Jager Z 29	2657depl.	- 57°52N 06°15Ø
Jager Z 34	2657depl.	

Følgende skip skal ha blitt senket i ”Nordsjøen”. Senkingsområdet er sansynligvis farvannet utenfor Helgoland.

ARTHUR SEAWALL	7176brt.	- tauet ut fra Bremerhaven
DESSAU	5933brt.	
KINDERSLEY	1999brt.	
WILLIAM L. MARCY	7176brt.	

Følgende skip skal ha blitt senket i Biscaya:

DORA OLDENDORFF	2730brt.	- 47°40N 09°22V
EMPIRE CONYNGHAM	1465brt.	- 47°52N 08°51V
EMPIRE CORMORANT	5760brt.	
EMPIRE LARK	4971brt.	- 47°55N 08°25V
EMPIRE NUTFIELD	1561brt.	- 48°03N 08°09V
EMPIRE PEACOCK	6098brt.	- 47°55N 08°30V
EMPIRE SUCCES	5988brt.	
HARM FRITZEN	4818brt.	- 47°55N 08°58V
MARGO	1377brt.	- 47°36N 09°31V

Følgende skip skal ha blitt senket i Atlanterhavet:

EMPIRE CLAIRE	5613brt.	
EMPIRE FAL	4880brt.	- NV av Skottland
EMPIRE SIMBA	5691brt.	- 55°30N 11°00V
EMPIRE WOODLARK	7793brt.	- 59°00N 07°40V
KOTKA	6079brt.	
PHILIP HEINEKEN	2250brt.	- 62°57,0N 01°32,0Ø
VOGTLAND	4969brt.	- Nordatlanteren
WAIRUNA	5826brt.	- 55°30N 11°00V

B APPENDIX

German standard ammunition

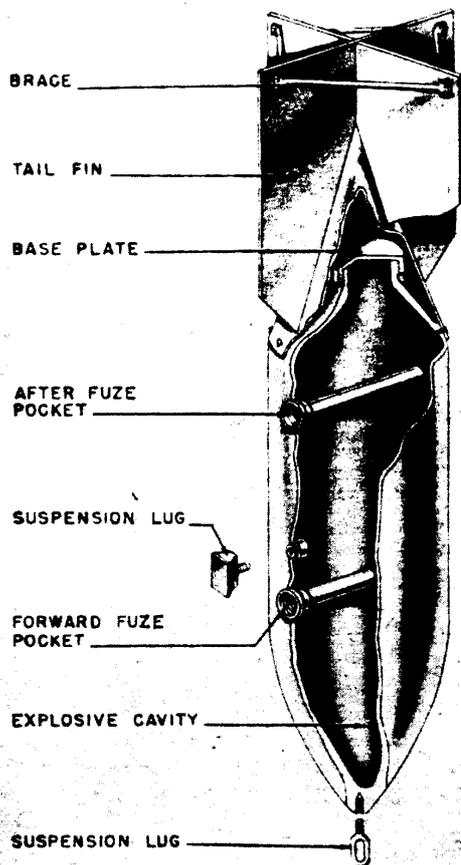
List of German standard ammunition with chemical warfare agents at the end of World War II (Sjöfartsverket, Sweden, 1992)

Calibre	Type	Colour code	Content	
			Agent	Amount
Artillery ammunition				
75 mm	Igr. 18	White ring	Chloroacetophenone	-
105 mm	F.H.Gr.	Yellow ring	Sulphur mustard	1.25 L
105 mm	F.H.Gr. 39	Yellow ring	Sulphur mustard	1.16 L
105 mm	F.H.Gr. 39	Two yellow rings	Thickened sulphur mustard	-
105 mm	F.H.Gr.	Green ring	Sulphur mustard	1.25 L
105 mm	F.H.Gr. 38	Green ring 1	Nitrogen mustard	0.9 Kg
105 mm	F.H.Gr. 39	Green ring 3	Tabun	1.2 L
105 mm	F.H.Gr. 38	Green and yellow rings	Sulphur mustard	0.84 L
105 mm	F.H.Gr.	Blue ring 1	Adamsite	0.5 Kg
105 mm	F.H.Gr. 41	Blue ring 3	Adamsite + nitrocellulose	0.8 Kg
105 mm	F.H.Gr.	White ring	Chloroacetophenone	-
150 mm	Gr. 39	Yellow ring	Sulphur mustard	-
150 mm	Gr. 19	Green ring	Sulphur mustard	3.5 L
150 mm	Gr. 19	Yellow ring	Sulphur mustard	4.8 Kg
150 mm	Gr. 38	Green ring 1	Nitrogen mustard	2.9 Kg
150 mm	Gr. 39	Green ring 3	Tabun	-
150 mm	Gr. 19	Blue ring 1	Adamsite	1.5 Kg
150 mm	Gr. 19	White ring	Chloroacetophenone	3.5 Kg
Rockets				
150 mm	Wgr. 41	Green and yellow rings	Sulphur mustard	3.2 Kg
150 mm	Wgr. 41	Yellow ring	Sulphur mustard	4.6 Kg
150 mm	Wgr. 41	Green ring 1	Nitrogen mustard	3.1 Kg
Rocket launcher ammunition				
100 mm	Wgr. Nb or Nb st	Yellow ring	Sulphur mustard	-
Mines				
10 L	Sprühbüchse 37	Yellow ring	Sulphur mustard	-
10 L	Sprühbüchse 37	Two yellow rings	Thickened sulphur mustard	-
Bombs				
	K.C.250 W.	Two white rings	Chloroacetophenone	100 Kg
	K.C.250 Gr.	Green and yellow rings	Sulphur mustard	100 Kg
	K.C.250 Gb.	Yellow ring	Sulphur mustard	100 Kg
	K.C.250 II Gb.	Two yellow rings	Thickened sulphur mustard	100 Kg
	K.C.250 II Gr.	One or two green rings	Phosgene	100 Kg
	K.C.250 III Gr.	Three green rings	Tabun	86 Kg
	K.C.50 II Bu.	Two blue rings	Adamsite + nitrocellulose	15 Kg

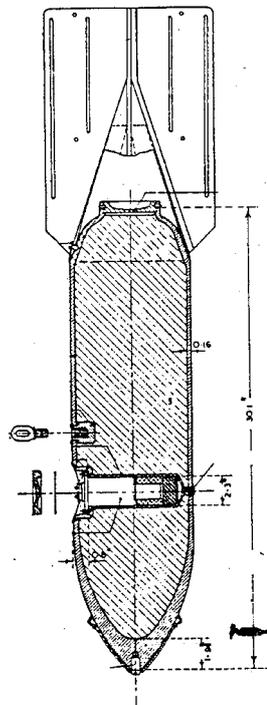
Igr.: Infanterigranat
 F.H.Gr.: Feldhaubitzzgranat
 W.Gr.: Werfergranat
 K.C.: Kampfstoff Cylindrische
 Bu.: Buchse

C APPENDIX

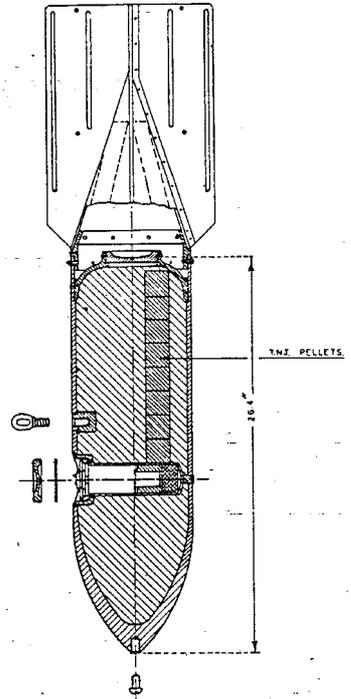
Examples of German ammunition from World War II



Bomb SC 250



GERMAN
SC 50 HE. BOMB GRADE I
MODELS J/B & L



GERMAN
SC 50 HE. BOMB GRADE I
MODELS J/B, J/C, J/J/2

Bomb SC 50

D APPENDIX**Location of sediment samples (WGS 84)**

Wreck no	Sam-ple	Sampling date	Position	Depth	Time	Comments
Background		4 June 2002	58°18.787'N 009°28.841'E	627 m	1400	
5	1A	4 June 2002	58°15.856'N 009°39.969'E	582 m	1920	15 m from wreck
	1B	4 June 2002	58°15.854'N 009°39.963'E	583 m	2041	28 m from wreck
	1C	4 June 2002	58°15.871'N 009°39.901'E	586 m	2141	15 m from wreck
	1D	4 June 2002	58°15.863'N 009°39.890'E	586 m	2248	28 m from wreck
	1E	4 June 2002	58°15.888'N 009°39.913'E	587 m	2352	14 m from wreck
	1F	5 June 2002	58°15.903'N 009°39.901'E	587 m	0058	25 m from wreck
	1G	5 June 2002	58°15.879'N 009°39.987'E	583 m	0227	12 m from wreck
	1H	5 June 2002	58°15.888'N 009°39.993'E	584 m	0325	22 m from wreck
6	2A	5 June 2002	58°16.117'N 009°40.968'E	574 m	0739	12 m from wreck
	2B	5 June 2002	58°16.115'N 009°40.962'E	577 m	0831	26 m from wreck
	2C	5 June 2002	58°16.094'N 009°40.006'E	575 m	0954	12 m from wreck
	2D	5 June 2002	58°16.091'N 009°40.997'E	575 m	1034	26 m from wreck
	2E	5 June 2002	58°16.073'N 009°40.039'E	575 m	1136	Close to grenades, 50 m from main wreck
	2F	4 Sept 2002	58°16.129'N 009°41.008'E	575 m	0300	20 m from wreck
	2G	4 Sept 2002	58°16.125'N 009°40.995'E	575 m	0430	10 m from wreck
	2H	4 Sept 2002	58°16.098'N 009°41.038'E	575 m	0530	10 m from wreck
	2I	4 Sept 2002	58°16.102'N 009°41.050'E	575 m	0640	20 m from wreck
13	10A	5 Sept 2002	58°18.763'N 009°39.794'E	652 m	0420	10 m from wreck
	10B	5 Sept 2002	58°18.765'N 009°39.814'E	652 m	0520	10 m from wreck
	10C	5 Sept 2002	58°18.815'N 009°39.793'E	652 m	0630	10 m from wreck
	10D	5 Sept 2002	58°18.824'N 009°39.772'E	652 m	0720	10 m from wreck
	10E	5 Sept 2002	58°18.829'N 009°39.765'E	652 m	0900	20 m from wreck
	10F	5 Sept 2002	58°18.813'N 009°39.809'E	652 m	0950	20 m from wreck
	10G	5 Sept 2002	58°18.760'N 009°39.827'E	652 m	1100	20 m from wreck
	10H	5 Sept 2002	58°18.759'N 009°39.783'E	652 m	1200	20 m from wreck
14	3A	4 Sept 2002	58°18.531'N 009°41.048'E	646 m	1530	20 m from wreck
	3B	4 Sept 2002	58°18.530'N 009°41.032'E	646 m	1700	10 m from wreck
	3C	4 Sept 2002	58°18.497'N 009°41.002'E	646 m	1820	10 m from wreck
	3D	4 Sept 2002	58°18.496'N 009°41.018'E	646 m	1920	20 m from wreck
	3E	4 Sept 2002	58°18.507'N 009°40.981'E	646 m	2020	10 m from wreck
	3F	4 Sept 2002	58°18.513'N 009°40.967'E	646 m	2120	20 m from wreck
	3G	4 Sept 2002	58°18.535'N 009°40.993'E	646 m	2230	10 m from wreck
	3H	4 Sept 2002	58°18.552'N 009°41.025'E	646 m	2359	At stern

The depth was recorded by a transponder (HPR) connected to the multicorer

E APPENDIX

Results from chemical analysis

E.1 Samples investigated by mass spectrometry

Table E.1 lists the different sample preparation and mass spectrometric techniques used and the estimated dry weight for different sediment samples while Table E.2 is the corresponding table for water samples.

Sample			Dichloromethane extract		H ₂ O extract	
Sediment Sample #	Wreck #	FFI sample #	Sample weight (dried) (g)	Analytical MS method (EI/CI)	Sample weight (dried) (g)	Analytical MS method (EI/CI)
Background (0-1 cm)		V02-011	2.1	EI/CI(NH ₃)	2.2	EI
Background (1-3 cm)		V02-012		EI/CI(NH ₃)		
1A (0-1 cm)	5	V02-014	1.4	EI/CI(NH ₃)		
1A (1-3 cm)	5	V02-015	3.6	EI/CI(NH ₃)		
1B (0-1 cm)	5	V02-017		EI		
1B (1-3 cm)	5	V02-018		EI		
1C (0-1 cm)	5	V02-020		EI		
1C (1-3 cm)	5	V02-021		EI		
1D (0-1 cm)	5	V02-023		EI		
1D (1-3 cm)	5	V02-024	3.0	EI/CI(NH ₃)		
1E (0-1 cm)	5	V02-026	3.5	EI/CI(NH ₃ /i-C ₄ H ₁₀)	3.8	EI
1E (1-3 cm)	5	V02-027	4.0	EI/CI(NH ₃ /i-C ₄ H ₁₀)	4.1	EI
1F (0-1 cm)	5	V02-029	3.3	EI/CI(NH ₃)		
1F (1-3 cm)	5	V02-030	3.8	EI/CI(NH ₃)		
1G (0-1 cm)	5	V02-032	2.4	EI/CI(NH ₃ / i-C ₄ H ₁₀)	2.5	EI
1G (1-3 cm)	5	V02-033		EI		
1H (0-1 cm)	5	V02-035	2.9	EI/CI(NH ₃ / i-C ₄ H ₁₀)		
1H (1-3 cm)	5	V02-036		EI/CI(NH ₃)		
2A (0-1 cm)	6	V02-038		EI		
2A (1-3 cm)	6	V02-039		EI		
2B (0-1 cm)	6	V02-041	2.1	EI/CI(NH ₃)	1.5	EI
2B (1-3 cm)	6	V02-042	3.0	EI		
2C (0-1 cm)	6	V02-044	2.6	EI		
2C (1-3 cm)	6	V02-045		EI		
2D (0-1 cm)	6	V02-047		EI		
2D (1-3 cm)	6	V02-048		EI		
2E (0-1 cm)	6	V02-050	2.4	EI/CI(NH ₃)		
2E (1-3 cm)	6	V02-051	3.2	EI/CI(NH ₃)		
2F (0-1 cm)	6	V02-054	2.7	EI		
2F (1-3 cm)	6	V02-055	2.8	EI		

Table E.1 continued

Sample			Dichloromethane extract		H ₂ O extract	
Sediment Sample #	Wreck #	FFI sample #	Sample weight (dried) (g)	Analytical MS method (EI/CI)	Sample weight (dried) (g)	Analytical MS method (EI/CI)
2G (0-1 cm)	6	V02-056	2.6	EI		
2G (1-3 cm)	6	V02-057	2.8	EI/CI(NH ₃)		
2H (0-1 cm)	6	V02-058	3.1	EI/CI(NH ₃ / i-C ₄ H ₁₀ /CH ₄)	3.1	EI
2H (1-3 cm)	6	V02-059	3.5	EI/CI(NH ₃ / i-C ₄ H ₁₀ /CH ₄)	3.5	EI
2I (0-1 cm)	6	V02-060	2.7	EI/CI(NH ₃)		
2I (1-3 cm)	6	V02-061	3.6	EI/CI(NH ₃)		
3A (0-1 cm)	14	V02-062	2.6	EI		
3A (1-3 cm)	14	V02-063	3.3	EI		
3B (0-1 cm)	14	V02-064	2.6	EI		
3B (1-3 cm)	14	V02-065	3.3	EI		
3C (0-1 cm)	14	V02-066	2.0	EI		
3C (1-3 cm)	14	V02-067	3.2	EI		
3D (0-1 cm)	14	V02-068	2.6	EI		
3D (1-3 cm)	14	V02-069	2.6	EI		
3E (0-1 cm)	14	V02-070	2.2	EI		
3E (1-3 cm)	14	V02-071	2.8	EI		
3F (0-1 cm)	14	V02-072	2.6	EI		
3F (1-3 cm)	14	V02-073	3.0	EI		
3G (0-1 cm)	14	V02-074	2.6	EI		
3G (1-3 cm)	14	V02-075	3.0	EI		
3H (0-1 cm)	14	V02-076	2.2	EI		
3H (1-3 cm)	14	V02-077	3.0	EI		
10A (0-1 cm)	13	V02-078	2.3	EI/CI(NH ₃)		
10A (1-3 cm)	13	V02-079	2.8	EI/CI(NH ₃ / i-C ₄ H ₁₀ /CH ₄)		
10B (0-1 cm)	13	V02-080	2.3	EI/CI(NH ₃)		
10B (1-3 cm)	13	V02-081	2.7	EI/CI(NH ₃)		
10C (0-1 cm)	13	V02-082	1.5	EI		
10C (1-3 cm)	13	V02-083	2.8	EI		
10D (0-1 cm)	13	V02-084	2.5	EI		
10D (1-3 cm)	13	V02-085	3.3	EI		
10E (0-1 cm)	13	V02-086	2.3	EI		
10E (1-3 cm)	13	V02-087	3.5	EI		
10F (0-1 cm)	13	V02-088	2.2	EI		
10F (1-3 cm)	13	V02-089	3.4	EI		
10G (0-1 cm)	13	V02-090	2.6	EI		
10G (1-3 cm)	13	V02-091	3.1	EI		
10H (0-1 cm)	13	V02-092	2.2	EI		
10H (1-3 cm)	13	V02-093	2.9	EI		

Table E.1 List of all collected sediment samples with indication of mass spectrometric methods used. Dry weight is shown for 10 g wet sediment sample.

Water sample		Dichloromethane extract
Wreck #	FFI Sample #	EI/CI
5	V02-053	EI
6	V02-094	EI
14	V02-095	EI
13	V02-096	EI

Table E.2 List of all water samples with indication of analytical mass spectrometric methods used

E.2 Compounds identified by mass spectrometry

The identified compounds in the sediment samples are listed in Table A.3 together with the mass spectrometric methods used in the identification. The underivatized compounds were found in the dichloromethane extracts of sediments while the bis-TBDMS derivative of TDG was found in the water extracts of sediments. The structures for the identified compounds are shown in Figures E.1 and E.2.

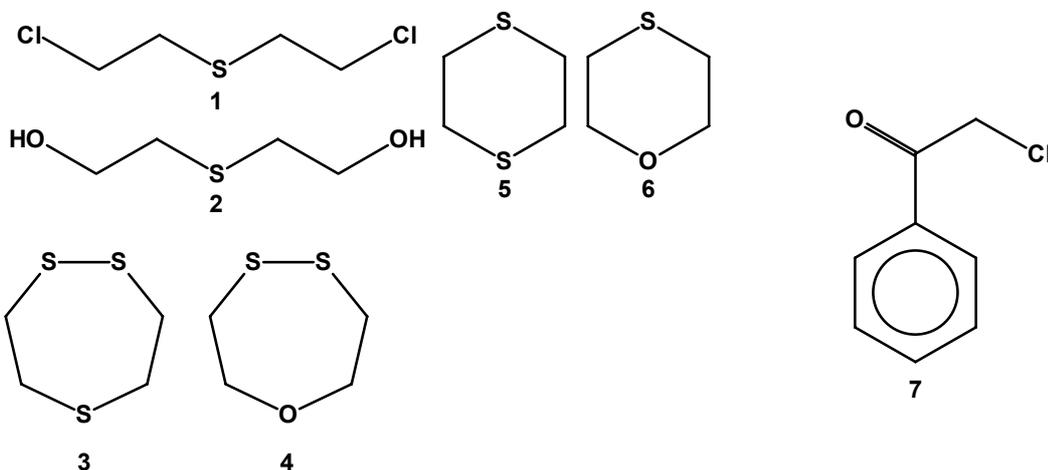


Figure E.1 Identified riot control agent (7) and compounds related to sulphur mustard (1)

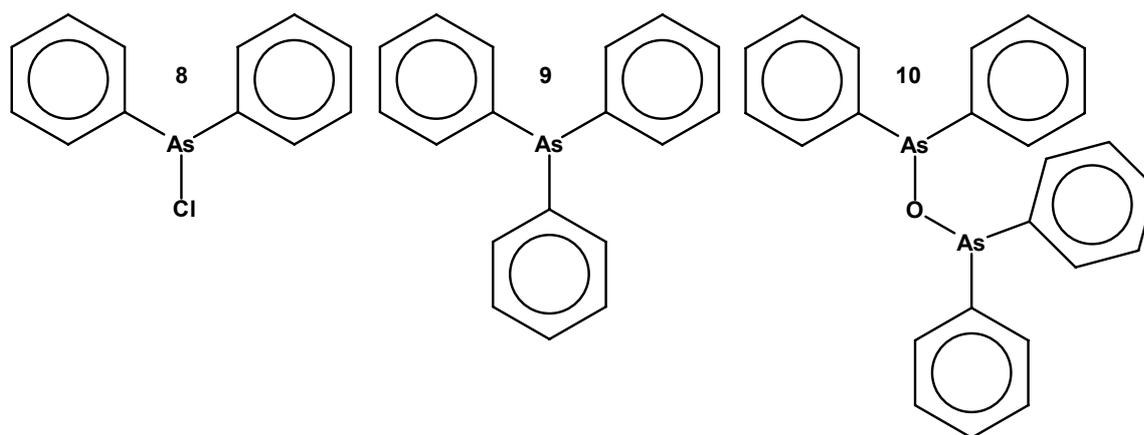


Figure E.2 Identified arsine compounds (8-10)

Identified Compound	RI (retention index)			Sample #	FFI sample #	EI RI	CI		
	Auth ref	FFI ^c	Other				NH ₃	i-C ₄ H ₁₀	CH ₄
Sulphur mustard (1)	1180	1173	1173 ^a 1178 ^b	2H(0-1 cm)	V02-058	1183	-	-	-
TDG (2) (bisTBDMS derivative)	1862	1870		2H(0-1cm)	V02-058	1857	NR	NR	NR
				2H(1-3cm)	V02-059	1857	NR	NR	NR
1,2,5-Tri-thiepane (3)	None		1362 ^a 1375 ^b	1E (0-1cm)	V02-026	1391	-	-	NR
				1E (1-3cm)	V02-027	1391	-	-	NR
				2H (0-1cm)	V02-058	1381	-	+	-
				2H (1-3cm)	V02-059	1381	-	+	-
				2I (0-1cm)	V02-060	1381	-	NR	NR
				2I (1-3cm)	V02-061	1381	-	NR	NR
				10A (1-3cm)	V02-079	1381	-	-	-
1,4,5-Oxa-dithiepane (4)	None		1163 ^a 1172 ^b	1E (0-1cm)	V02-026	1177	-	weak	NR
				1E (1-3cm)	V02-027	1177	-	-	NR
				2H (0-1cm)	V02-058	1178	-	+	-
				2H (1-3cm)	V02-059	1177	-	+	-
1,4-Dithiane (5)	1076	1072	1060 ^a 1068 ^b	1E (0-1cm)	V02-026	1076	-	-	NR
				1E (1-3cm)	V02-027	1076	-	-	NR
				2H (1-3cm)	V02-059	1076	-	+	+
1,4-Thioxane (6)	882	890	880 ^a 877 ^b	2H (1-3cm)	V02-059	885	-	-	-
CN (7)	1290		1283 ^b	2H (0-1cm)	V02-058	1291	+	+	+

Table E.3 continued

Identified Compound	RI (retention index)			Sample #	FFI sample #	EI			
	Auth ref	FFI ^c	Other			RI	NH ₃	i-C ₄ H ₁₀	CH ₄
Clark I (8)	1814		1824 ^a	1A (1-3cm)	V02-015	1813	-	NR	NR
				1D (1-3cm)	V02-024	1812	-	NR	NR
				1E (0-1cm)	V02-026	1812	-	-	NR
				1E (1-3cm)	V02-027	1813	-	-	NR
				1F (0-1cm)	V02-029	1812	-	NR	NR
				1F (1-3cm)	V02-030	1812	-	NR	NR
				1G (0-1cm)	V02-032	1812	-	-	NR
				1H (0-1cm)	V02-035	1812	-	-	NR
				2E (1-3cm)	V02-051	1813	-	NR	NR
				2H (0-1cm)	V02-058	1812	-	+	+
				2H (1-3cm)	V02-059	1812	-	+	weak
				2I (0-1cm)	V02-060	1812	-	NR	NR
				2I (1-3cm)	V02-061	1812	-	NR	NR
				10A (0-1cm)	V02-078	1812	-	NR	NR
				10A (1-3cm)	V02-079	1812	-	+	weak
				10B (0-1cm)	V02-080	1812	-	NR	NR
				10B (1-3cm)	V02-081	1812	-	NR	NR
				10C (1-3cm)	V02-083	1813	NR	NR	NR
				10D (0-1cm)	V02-084	1812	NR	NR	NR
				10F (0-1cm)	V02-088	1813	NR	NR	NR
10H(1-3cm)	V02-093	1813	NR	NR	NR				
Triphenylarsine (9)	2195			1A (0-1cm)	V02-014	2194	-	NR	NR
				1D (1-3cm)	V02-024	2194	+	NR	NR
				1E (0-1cm)	V02-026	2194	+	+	NR
				1E (1-3cm)	V02-027	2194	-	-	NR
				1F (0-1cm)	V02-029	2194	-	NR	NR
				1G (0-1cm)	V02-032	2193	+	+	NR
				1H (0-1cm)	V02-035	2193	-	-	NR
				2B (1-3cm)	V02-042	2194	NR	NR	NR
				2C (0-1cm)	V02-044	2194	NR	NR	NR
				2E (0-1cm)	V02-050	2194	+	NR	NR
				2G (1-3cm)	V02-057	2194	+	NR	NR
				2H (0-1cm)	V02-058	2194	+	+	+
				2H (1-3cm)	V02-059	2193	+	+	weak
				2I (0-1cm)	V02-060	2194	+	NR	NR
				2I (1-3cm)	V02-061	2193	+	NR	NR
				10A (0-1cm)	V02-078	2193	-	NR	NR
				10A (1-3cm)	V02-079	2194	+	+	+
10B (0-1cm)	V02-080	2193	-	NR	NR				
Bis (diphenylarsine) oxide (10)	2987			2H (0-1cm)	V02-058	2994	-	-	-
				2H (1-3cm)	V02-059	2984	+	+	-
				2I (1-3cm)	V02-061	2983	-	NR	NR
				10A (1-3cm)	V02-079	2992	+	+	+
				10B (1-3cm)	V02-081	2984	-	NR	NR

Table E.3 Identified compounds in the sediment samples. The retention index from EI is based on the alkane series and compared with literature and the retention index of authentic compounds, where available. All compounds were found in the dichloromethane extract except the derivative of TDG, which were found in the water extracts after evaporation and derivatization
^aJ R Hancock et al (1991), ^bThe Ministry for Foreign Affairs of Finland (1994),
^cFFI, with another GC-MS instrument
NR Not Recorded.
+ Positive identification
- Negative identification

No compounds related to chemical warfare agents, precursors or degradation products were found in the water samples.

All of the compounds except sulphur mustard (**1**), TDG (**2**) (bisTBDMS derivative) and 1,4-thioxane (**6**) have been identified using at least two independent techniques. In addition, all the compounds have been identified using retention indexes. This last technique is, however, in principle not an independent technique since the RI data are taken from the same runs as the EI data. However, we note that these three compounds related to sulphur mustard were all found only in samples containing several other sulphur mustard degradation products (V02-058 and V02-059, both from the same core) and thus conclude that these three compounds also are indeed present.

E.3 Quantification of identified compounds by mass spectrometry

The amount of each identified compound was calculated using an internal standard and authentic standards. The results are tabulated in Table E.4 for dichloromethane extracts of sediments and in Table E.5 for water extracts of sediments after derivatization. No relevant compounds were identified in the collected water samples. Only samples with identified compounds are shown.

Sample			Results, mg/kg dried sediment								
Sediment sample #	Wreck #	FFI Sample #	Sulphur mustard (H, 1)	1,2,5-Trithiapane (3)	1,4,5-Oxadithiepane (4)	1,4-Dithiane (5)	1,4-Thioxane (6)	2-chloro-1-phenylethanone (CN, 7)	Clark I (DA, 8)	Triphenylarsine (9)	Bis(diphenylarsine) oxide (10)
Mass used for quantification			109	152 ¹	136 ¹	120	104	105	154 ²	152	152 ²
Background (0-1 cm)		V02-011	Nothing identified								
Background (1-3 cm)		V02-012	Nothing identified								
1A (0-1 cm)	5	V02-014								0.03	
1A (1-3 cm)	5	V02-015							0.4		
1D (1-3 cm)	5	V02-024							0.9	7.0	
1E (0-1 cm)	5	V02-026		0.4	0.5	0.2			1.2	0.3	
1E (1-3 cm)	5	V02-027		0.5	0.7	0.2			0.1	0.03	
1F (0-1 cm)	5	V02-029							0.3	0.02	
1F (1-3 cm)	5	V02-030							0.2		
1G (0-1 cm)	5	V02-032							3.0	8.9	
1H (0-1 cm)	5	V02-035							0.2	0.1	
2B (1-3 cm)	6	V02-042								0.1	
2C (0-1 cm)	6	V02-044								0.02	
2E (0-1 cm)	6	V02-050								0.2	
2E (1-3 cm)	6	V02-051							0.2		
2G (1-3 cm)	6	V02-057								3.6	
2H (0-1 cm)	6	V02-058	2.4	0.5	0.1			7.5	178	63	16
2H (1-3 cm)	6	V02-059		0.6	0.5	1.1	1.1		77	3.8	124
2I (0-1 cm)	6	V02-060		0.04					8.0	25	
2I (1-3 cm)	6	V02-061		0.06					2.3	0.3	0.8
3A – 3H	14	V02-062-V02-077	No chemical warfare agents detected in the samples from wreck 14								
10A (0-1 cm)	13	V02-078							2.2	0.3	
10A (1-3 cm)	13	V02-079		0.2					40	18	137
10B (0-1 cm)	13	V02-080		0.2					0.6	0.1	
10B (1-3 cm)	13	V02-081							3.7		0.2
10C (1-3 cm)	13	V02-083							0.4		
10D (0-1 cm)	13	V02-084							0.5		
10F (0-1 cm)	13	V02-088							3.1		
10H (1-3 cm)	13	V02-093							0.6		

Table E.4 Quantification of identified compounds in the dichloromethane extracts of the sediments (mg compounds pr kg dry sediment). Only samples with identified compounds are shown. The concentrations of the compounds are calculated using n-decane as an internal standard

¹No authentic standards available for quantification. As a rough estimate, the same response factor as for 1,4-dithiane related to n-decane was used

²Assumed same response factor for clark I, bis(diphenylarsine) oxide and one unknown component in the authentic standard for clark I

Sample			Results
Sediment sample #	Wreck #	FFI sample #	Thiodiglycol (TDG, 2), BisTBDMS derivative
Background (0-1cm)		V02-011	Nothing identified
2H (0-1 cm)	6	V02-058	weak
2H (1-3 cm)	6	V02-059	weak

*Table E.5 Identification of compounds in the water extracts of the sediments. None of the two signals for the bis(TBDMS) derivative of TDG (**2**) were strong enough to be quantified. Only samples with identified compounds are shown*

E.4 Discussion of mass spectrometry analytical results

Table E.6 lists the compounds identified together with the number of samples where each compound has been identified.

Identified compounds	Found in # samples	Max amount (mg/kg dried sediment)	Lowest amount	
			(mg/kg)	S/N
Sulphur mustard (H, 1)	1	2.4	2.4	511
TDG (2) (bisTBDMS derivative)	(2)	weak	weak	n.m
1,2,5-Trithiephane (3)	8	0.6	0.04	61
1,4,5-Oxadithiephane (4)	4	0.7	0.1	160
1,4-Dithiane (5)	3	1.1	0.2	67
1,4-Thioxane (6)	1	1.1	1.1	258
2-chloro-1-phenyl ethanone (CN, 7)	1	7.5	7.5	925
Clark I (DA, 8)	21	178	0.1	84
Triphenylarsine (9)	18	63	0.02	77
Bis(diphenylarsine oxide) (10)	5	137	0.2	29

*Table E.6 Identified compounds with number of samples the compound were found in and the maximum concentrations found. Lowest concentrations found and the corresponding signal/noise (S/N) ratios using one single mass from the reconstructed ion chromatogram are also shown
n.m. not measured*

Compounds related to both sulphur mustard (**1**) and arsine compounds were found outside wrecks 5, 6 and 13. No compounds of interest were found outside wreck 14.

The chemical warfare agent sulphur mustard (**1**) (a vesicant) was found in a concentration of 2.4 mg per kg dry weight and in one sample only (V02-058, wreck 6). In addition, several decomposition products from **1** were found in a few samples, all in concentrations less than 1.1 mg per kg dry weight per compound.

The riot control agent CN (**7**) was found in a concentration of 7.5 mg per kg dry weight and only in one sample – the same as for sulphur mustard.

Two other chemical warfare agents – clark I (**8**) and triphenylarsine (**9**) were identified in many of the samples. They may be components of the German warfare agent “arsine oil” which contained 50% phenyldichloroarsine (PD), 35% diphenylchloroarsine (clark I, DA, **8**), 5% **9** and 5% trichloroarsine (Franke et al 1976). The core where **1** was identified contained the largest concentration of the arsine compounds, 178 mg **8** and 63 mg **9** per kg dry weight (V02-058). The same core also contained 124 mg per kg dry weight of sediment of the clark I degradation product bis(diphenylarsine) oxide (**10**, V02-059). A large concentration of **8**, **9** and **10** was also observed in sample V02-079 (wreck 13).

Due to budgetary constrains, only a few (6) water extracts of the sediments from the wrecks were worked up and analysed after derivatization. This was only done for samples where other compounds were previously identified in the dichloromethane extract.

Winterlost was the German name for sulphur mustard mixed with PD to achieve a lower freezing point than pure mustard (Blanch et al 2001). However, also arsine oil seems to have been used for this purpose (Haas et al 1997, Sjöfartsverket 1992). This can explain the occurrence of both mustard and components of arsine oil in relatively high concentrations in the same samples.

E.5 Identified compounds and their hydrolysis and oxidation products

E5.1 Arsine compounds

Arsine oil contained 50% phenyldichloroarsine (PD), 35% diphenylchloroarsine (clark I, PFIFFIKUS, DA, **8**), 5% **9** and 5% trichloroarsine (Franke et al 1976).

Clark I (35% in arsine oil, **8**) is not very soluble in water. In bulk form it reacts slowly with water, giving the unstable diphenylarsine hydroxide and hydrochloric acid (Figure E.3). Dimerisation gives the highly stable bis(diphenylarsine) oxide **10** (Blanch et al, 2001). Clark I and **10** are detectable by GC-MS without derivatisation (Haas et al, 1997, Haas, Krippendorf et al, 1998, Haas, Schmidt et al, 1998). Further oxidation gives diphenylarsinic acid, which is not detectable by GC-MS without derivatization (Haas, Schmidt et al, 1998). Diphenylarsinic acid has not been analysed for in this investigation.

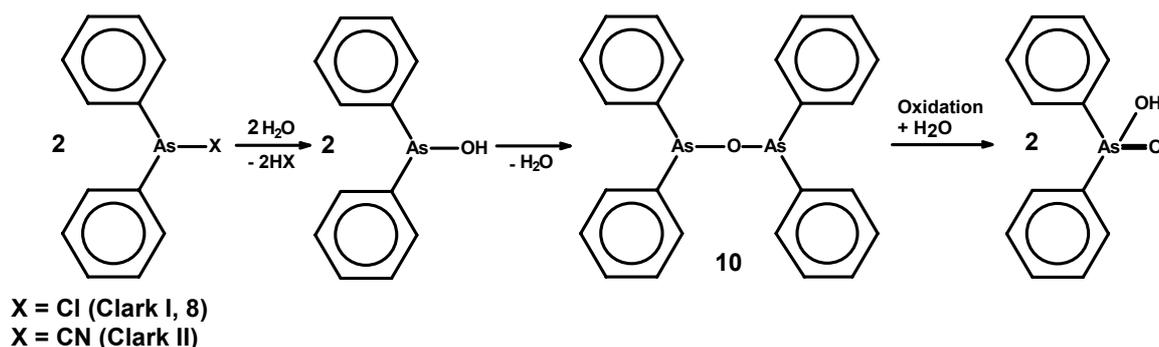


Figure E.3 Hydrolysis of clark I (8) and II followed by dimerisation and oxidation

Clark II (DC, Figure E.3) reacts with water in the same way as for clark I, giving the same hydrolysis and oxidation products in addition to hydrogen cyanide (Haas, Schmidt et al, 1998, Blanch et al, 2001). Clark II is detectable by GC-MS without derivatization (Haas, Krippendorf et al, 1998, Haas, Schmidt et al, 1998). The identified **10** in the samples can thus, in principle, be the hydrolysis product of both clark I and clark II. However, no clark II was found in the samples, only clark I, and it is thus reasonable to assume that the found **10** is the hydrolysis product of clark I.

Triphenylarsine (5% in arsine oil, **9**) is detectable by GC-MS. Triphenylarsine can be oxidised to triphenylarsine oxide (Haas, Schmidt et al, 1998). An authentic sample of triphenylarsine oxide was found not to be detectable by GC-MS and triphenylarsine oxide has thus not been analysed for in this investigation.

E5.2 Sulphur mustard

It is well known that the chemical warfare agent sulphur mustard (H, **1**) hydrolyses in water to give hemimustard which then hydrolyses to TDG (**2**) (Figure E.4). Both reactions take place through a rearrangement of the reactant to an intermediate sulfonium chloride salt (neighbouring group assistance) followed by attack of water to give hemimustard and TDG, respectively. In an alternative reaction, 1,4-thioxane (**6**) is formed through an internal reaction of the intermediate sulfonium chloride salt of the hemimustard (Franke et al, 1976, Mitretek, 2002).

Sulphur mustard can itself act as a nucleophile and attack the sulfonium chloride salt of another sulphur mustard molecule. This gives another sulfonium chloride salt, which upon attack of the salt's chloride ion gives sesquimustard (Q) (Mitretek, 2002). Q was not detected. It has been proposed that Q through an internal reaction can form a 6-ring sulfonium chloride which upon attack by the chloride ion forms 1,4-dithiane (**5**) (Rorbaugh et al, 1997).

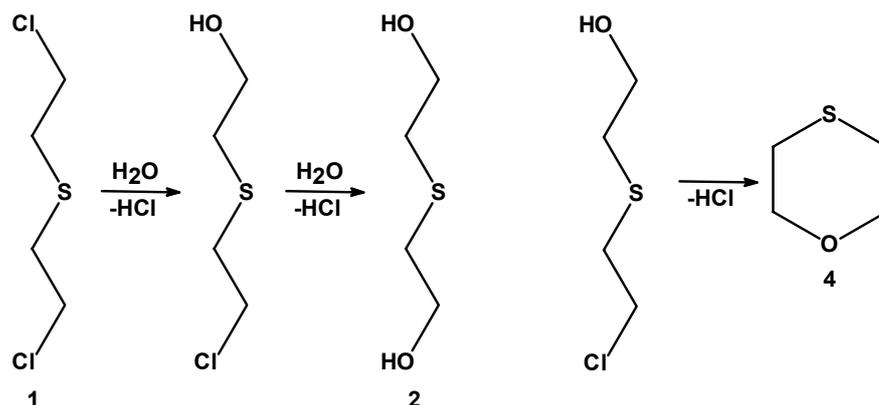


Figure E.4 Hydrolysis of sulphur mustard (H, 1)

If undisturbed, a layer of TDG will build up on the interface between sulphur mustard and water. At this interface, sulphur mustard can also react with TDG, giving stable sulfonium chloride salts. Sesquimustard (Q) may also form sulfonium salts that react with water, mustard, TDG or Q molecules, forming higher homologues of sulfonium salts. The sulfonium chloride salts create a thicker boundary layer. These effects reduce the rate of hydrolysis of sulphur mustard (Mitretrek, 2002).

The stable sulfonium salts have low volatility and thermally degrade to neutral species and are therefore not detected by GC-MS (Rohrbaugh et al, 1997).

1,2,5-Trithiepane (3) and 1,4,5-Oxadithiepane (4) are also considered as related compounds to sulphur mustard (D'Agostino, 1988).

There are many other compounds that are related to sulphur mustard (D'Agostino 1988). In this investigation, only a limited number of them have been searched for.

E5.3 2-Chloro-1-phenyl ethanone (CN)

CN (7) is practically insoluble in water and it is very resistant to hydrolysis. The rate of hydrolysis is so slow that even boiling water will not aid in destroying the compound. Even if a strong base such as sodium hydroxide is added, boiling is required to make the reaction fast enough to be practical. The end product is 2-hydroxy-1-phenyl ethanone (Franke et al, 1976). Only CN was searched for in this investigation.

E6 Other compounds of interest

E6.1 Arsine compounds

Phenyldichloroarsine (50% in arsine oil, PD) reacts with water to give phenylarsenic oxide and hydrochloric acid (Figure E.5). PD is practically insoluble in water. The literature disagrees on the rate of hydrolysis, it varies from resistant to rapid (Blanch et al, 2001). PD can be detected by GC without derivatization. However, the hydrolysis product of PD – phenylarsenic oxide – and the following oxidation product phenylarsonic acid (Figure E.5) are not detectable by GC-MS without derivatization with a dithiol (Haas et al 1997, Haas, Krippendorf et al, 1998, Haas, Schmidt et al 1998). No PD was detected in this investigation despite detection of other constituents of arsine oil. Due to budgetary limitations, hydrolysis and oxidation products of PD have not been analysed for in this investigation.

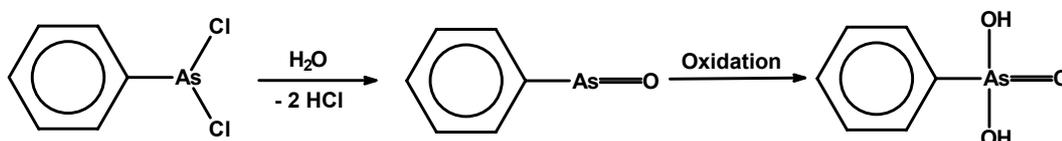


Figure E.5 Hydrolysis of phenyldichloroarsine (PD) followed by further oxidation

Trichloroarsine (5% in arsine oil) reacts quickly with water, giving arsenic acid and hydrochloric acid (Sjöfartsverket, 1992). We did not analyse for this compound.

Adamsite (DM, Figure A.4) is practically insoluble in water, and the rate of hydrolysis is very low if the adamsite is in bulk form, even in hot water. A strong base such as sodium hydroxide is required to speed up the hydrolysis (Blanch et al, 2001). The compound does not hydrolyse after years of storage in water (Sjöfartsverket, 1992). The primary hydrolysis product of DM is bis(diphenylaminoarsine) oxide. Further oxidation gives diphenylamine arsonic acid (Haas et al, 1998). Gas chromatography of DM and its primary degradation product has been reported to give irreproducible results or fail (Schoene et al, 1996, Ministry for Foreign Affairs, 1983). Neither adamsite nor its decomposition products have been analysed for in this investigation.

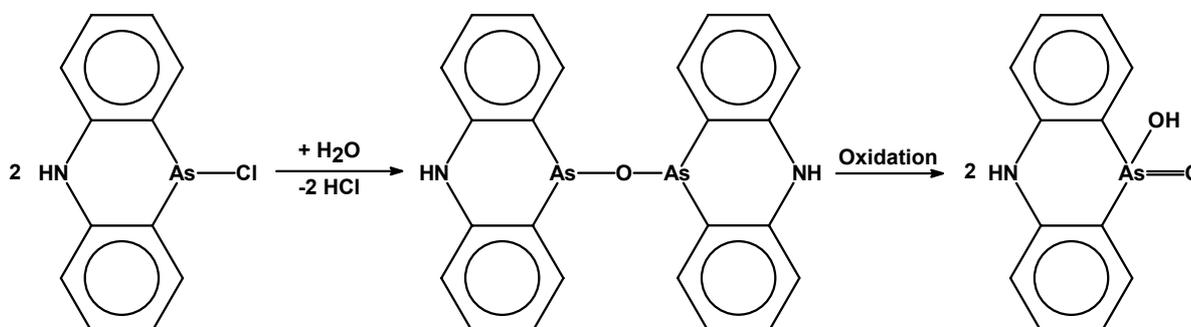


Figure E.6 Hydrolysis of adamsite (DM) followed by oxidation

E6.2 Phosgene

Phosgene (CG) was not searched for in this investigation because it elutes in the void volume of the gas chromatograph. The hydrolysis of phosgene in liquid water is very fast even at low temperatures. It takes 20 seconds for 1 g of phosgene to completely hydrolyse in 100 g water at 0°C. The hydrolysis products are hydrochloric acid and carbon dioxide (Franke et al, 1976). Neither of the hydrolysis products were searched for.

E6.3 Tabun

Tabun (GA) was searched for. In addition, some of its polar decomposition products were searched for. Note that only six samples from the wrecks were analysed for polar decomposition products.

E6.4 Nitrogen mustards

The nitrogen mustards bis(2-chloroethyl)ethylamine (HN1), bis(2-chloroethyl)methylamine (HN2) and tris(2-chloroethyl)amine (HN3) were searched for. Their hydrolysis products are salts (Blanch et al, 2001), which are not detectable by GC-MS.

E6.5 Other

In addition, all the well-known nerve agents and other well-known chemical warfare agents were searched for. Note that only six samples from the wrecks were analysed for polar decomposition products of nerve agents.

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F RESULTS FROM ANALYSIS BY ICP



Forsvarets laboratorietjeneste Teknisk Rapport

Analytisk Laboratorium

Kjemi og materialteknologi

Oppdragsgiver : FFI, Pb. 25, 2027 Kjeller		Oppdragsgivers referanse	
Att: John Tørnes			
Gjenpart :			
Tittel : Bestemmelse av As i innleverte prøver			
Rapportnr : A-02-022	Arkivkode:	Antall sider/vedlegg : 3 inkl. vedlegg	
Dato for mottak av oppdrag :	Jobbnr : A-02-022-1-28	Dato for utgivelse : 22.07.02.	
Utført av : Tove Kristin D. Torstensen		Sjef VLA : Senioring T A Gustavsen	
Sammendrag : Forsvarets laboratorietjeneste har på oppdrag fra FFI bestemt konsentrasjonen av As i innleverte prøver. Bestemmelsen ble gjort ved hjelp av ICP-AES			
Kundenr :	Ordrenr :	MKK :	Artikkelnr :

Utdrag av rapporten må ikke gjengis uten skriftlig godkjenning fra Analytisk Laboratorium.

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1. INNLEDNING

Forsvarets laboratorietjeneste (FOLAT) har på oppdrag fra FFI bestemt konsentrasjonen av As i innleverte prøver. Bestemmelsen ble gjort ved hjelp av ICP-AES.

2. PRØVEMETODER

Prøvene ble tørket i varmeskap ved 40°C. Om lag 1 g prøve ble veid inn, tilsatt 7M HNO₃ og oppsluttet ved høyt trykk og temperatur i autoklav. Dette er en partiell oppslutning, og prøvene ble ikke fullstendig oppløst. Etter oppslutning ble prøvene fortynnet til 100 mL med destillert vann. Det ble oppsluttet både referanseprøver og blindprøver sammen med jordprøvene, dette ble gjort for å ha kontroll med nøyaktigheten og eventuell kontaminering. Den instrumentelle analysen ble utført ved hjelp av ICP-AES (induktivt koblet plasma atomemisjonsspektroskopi). As 188,979 ble brukt til å kvantifisere As.

3. RESULTATER

Resultatene fra analysen av prøvene er gitt i tabell 1 i vedlegget. Konsentrasjonen er gitt som mg/kg. Den instrumentelle usikkerheten estimeres til 2-5 %.

Nøyaktighet:

Funnet konsentrasjon av As i referansematerialet er 101 ± 1 mg/kg. Sertifisert verdi av As er 105 ± 8 mg/kg. Det betyr at gjennfinningen av As var god.

4. KONKLUSJON

As er bestemt i innleverte prøver.

Vedlegg nr. : 1	Ant. Sider : 1	Rapport nr. : A-02-022
Oppdragets tittel : Bestemmelse av As		

Tabell 1. Konsentrasjon av As i innleverte prøver. Konsentrasjonen er gitt som mg/kg tørr prøve.

Prøve ID	Funnet konsentrasjon (mg/kg)
V02-011	49,3
V02-012	42,8
V02-014	43,0
V02-015	37,4
V02-017	43,4
V02-018	42,9
V02-020	26,2
V02-021	32,6
V02-023	40,8
V02-024	39,5
V02-026	22,4
V02-027	17,7
V02-029	37,7
V02-030	32,1
V02-032	44,4
V02-033	42,0
V02-035	33,1
V02-036	32,4
V02-038	44,5
V02-039	42,3
V02-041	49,4
V02-042	42,2
V02-044	43,1
V02-045	35,7
V02-047	29,0
V02-048	35,9
V02-050	42,0
V02-051	42,8



Forsvarets laboratorietjeneste Teknisk Rapport

Analytisk Laboratorium

Kjemi og materialteknologi

Oppdragsgiver : FFI, Pb. 25, 2027 Kjeller		Oppdragsgivers referanse	
Att: John Tørnes			
Gjenpart :			
Tittel : Bestemmelse av As i innleverte prøver			
Rapportnr : A-02-022	Arkivkode:	Antall sider/vedlegg : 3 inkl. vedlegg	
Dato for mottak av oppdrag : 11.09.02	Jobbnr : A-02-022-29-68	Dato for utgivelse : 24.09.02	
Utført av : Tove Kristin D. Torstensen		Sjef VLA : Senioring T A Gustavsen	
Sammendrag : Forsvarets laboratorietjeneste har på oppdrag fra FFI bestemt konsentrasjonen av As i innleverte prøver. Bestemmelsen ble gjort ved hjelp av ICP-AES			
Kundenr :	Ordrenr :	MKK :	Artikkelnr :

Utdrag av rapporten må ikke gjengis uten skriftlig godkjenning fra Analytisk Laboratorium.

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1. INNLEDNING

Forsvarets laboratorietjeneste (FOLAT) har på oppdrag fra FFI bestemt konsentrasjonen av As i innleverte prøver. Bestemmelsen ble gjort ved hjelp av ICP-AES.

2. PRØVEMETODER

Om lag 1 g prøve ble veid inn, tilsatt 7M HNO₃ og oppsluttet ved høyt trykk og temperatur i autoklav. Dette er en partiell oppslutning, og prøvene ble ikke fullstendig oppløst. Etter oppslutning ble prøvene fortynnet til 100 mL med destillert vann. Det ble oppsluttet både referanseprøver og blindprøver sammen med jordprøvene, dette ble gjort for å ha kontroll med nøyaktigheten og eventuell kontaminering. Den instrumentelle analysen ble utført ved hjelp av ICP-AES (induktivt koblet plasma atomemisjonspektroskopi). As 188,979 ble brukt til å kvantifisere As.

3. RESULTATER

Resultatene fra analysen av prøvene er gitt i tabell 1 i vedlegget. Konsentrasjonen er gitt som mg/kg. Den instrumentelle usikkerheten estimeres til 2-5 %.

Nøyaktighet:

Funnet konsentrasjon av As i referansematerialet er 96 ± 2 mg/kg. Sertifisert verdi av As er 105 ± 8 mg/kg. Det betyr at gjennfinningen av As var god.

4. KONKLUSJON

As er bestemt i innleverte prøver.

Vedlegg nr. : 1	Ant. Sider : 1	Rapport nr. : A-02-022
Oppdragets tittel : Bestemmelse av As		

Tabell 1. Konsentrasjon av As i innleverte prøver. Konsentrasjonen er gitt som mg/kg tørr prøve.

Prøve ID	Funnet konsentrasjon (mg/kg)
V-02-054	46
V-02-055	46
V-02-056	44
V-02-057	45
V-02-058	480
V-02-059	93
V-02-060	75
V-02-061	58
V-02-062	41
V-02-063	37
V-02-064	47
V-02-065	41
V-02-066	48
V-02-067	41
V-02-068	46
V-02-069	49
V-02-070	57
V-02-071	54
V-02-072	47
V-02-073	38
V-02-074	49
V-02-075	42
V-02-076	54
V-02-077	42
V-02-078	56
V-02-079	99
V-02-080	58
V-02-081	51
V-02-082	52
V-02-083	48
V-02-084	55
V-02-085	47
V-02-086	47
V-02-087	38
V-02-088	52
V-02-089	47
V-02-090	48
V-02-091	49
V-02-092	54
V-02-093	57



Forsvarets laboratorietjeneste Teknisk Rapport

Analytisk Laboratorium Kjemi og materialteknologi

Oppdragsgiver John Tørnes FFI BM Postboks 25 2007 Kjeller		Oppdragsgivers referanse
Gjenpart		
Tittel Bestemmelse av As i sjøvann		
Rapportnr A-02-025	Ordrenr	Antall sider/vedlegg 2/0
Dato for mottak av oppdrag 15.10.02	Jobbnr A-01-025	Dato for utgivelse 24.10.02
Utført av Oing Tove Kristin D. Torstensen Oing E Larsen		Sjef VLA Senioring T A Gustavsen
Sammendrag Forsvarets laboratorietjeneste (FOLAT) har på oppdrag fra FFI bestemt As i sjøvann.		

Utdrag av rapporten må ikke gjengis uten skriftlig godkjenning fra Analytisk Laboratorium.

1. INNLEDNING

Forsvarets laboratorietjeneste (FOLAT) har på oppdrag fra FFI bestemt As i sjøvann.

2. PRØVEMETODER

Prøveløsningen ble analysert ved hjelp av As-hydrid generering.

Den instrumentelle analysen ble utført med ICP-AES (induktivt koblet plasma atomemisjonsspektroskopi). Valgt bølgelengde for As var 188,979 nm.

3. RESULTATER

Resultatet av analysen er gitt i tabell 1. LOD er deteksjonsgrensen og LOQ er kvantifiseringsgrensen.

Tabell 1: Konsentrasjon av As i vannprøvene [$\mu\text{g/l}$].

Prøve	As
Blind	6
Vann1A V02-053A	9
Vann2 V02-094A	8
Vann3 V02-095A	7
Vann10 V02-096	13
LOD	5
LOQ	20

Det er høyere usikkerhet til verdiene som ligger mellom LOD og LOQ enn de som er høyere enn LOQ.

Den instrumentelle usikkerheten estimeres til 2-5 % .

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