Long-time behaviour of mustard gas dumped in the Bornholm Basin

BO₂X WIN

Technical report no.6

Thomas Hellström[1] & Malin Ödalen[2]

Naturvetenskapliga fakulteten

GÖTEBORGS UNIVERSITET

Long-time behaviour
of mustard gas dumped
in the Bornholm Basin

BO₂X
WIN

Technical report no.6

Thomas Hellström[1] & Malin Ödalen[2]

[1]Thellva HB, Källskuruvägen 2, 137 71 Dalarö, Sweden

[2]Department of Earth Sciences, University of Gothenburg, BOX 460, 405 30 Göteborg, Sweden

Abstract

The amount of mustard gas (a liquid at room temperature) originally dumped in the Baltic Sea is uncertain, but is probably 10,000 – 25,000 tons. The main dumping site is situated east of Bornholm, in the Bornholm Basin, and at least 7,000 tons of mustard gas is expected to have been dumped here. It is unknown how much of this remains today, but it is likely to be the major part. Most of the mustard gas dumped was enclosed in munitions (bombs, artillery shells etc.) and the major part of these munitions is probably buried in the sediments. Most munitions that stayed on the sediment surface are expected to be completely corroded. Lumps of mustard gas, originating from the corroded munitions, can be observed at the sediment surface. What has and will happen with the munitions deeper in the sediments is uncertain. Proper investigations are lacking and based on present knowledge it is not possible to quantify the rate of leaching and degradation of the dumped mustard gas. Mustard gas will be dissolved in contact with water. This is a slow process and the rate of dissolution is also strongly retarded by a solid cover forming around each lump of mustard gas. This cover grows thicker with time and smaller lumps of mustard gas are today solid straight through. Studies of the rate of dissolution with this solid cover are lacking. Dissolved mustard gas will through hydrolysis form thiodiglycol (TDG). This is a process which is fairly rapid. TDG is microbiologically degradable by aerobic microorganisms and its toxicity is low. The dumping sites are at depths of around 100 m, which means that these bottom waters are often anoxic. In the case of anoxic bottom water, the water containing TDG has to be mixed with oxic water before degradation can occur. Oxygenation of even the deepest bottoms by artificial deepwater ventilation, as suggested by the BOX-WIN project, may give more favourable conditions for degradation of mustard gas through hydrolysis and degradation of the hydrolysis product.

Sammanfattning

Den mängd senapsgas (en vätska vid rumstemperatur) som dumpats i Östersjön är osäker, men uppskattas till 10 000 – 25 000 ton. Största delen av dumpningen av kemiska stridsmedel skedde öster om Bornholm, i Bornholmsbassängen, och åtminstone 7 000 ton senapsgas dumpades i detta område. Hur mycket som finns kvar idag är inte känt, men troligen återstår merparten. Det som dumpades var huvudsakligen inneslutet i flygbomber och artillerigranater varav merparten troligen befinner sig nere i sedimenten. De bomber och granater som hamnat på sedimentytan förväntas nu vara helt sönderrostade. Från dessa har vätskan läckt ut och därför kan klumpar av senapsgas observeras på sedimentytan. Vad som sker med senapsgas längre ner i sedimenten är osäkert, då undersökningar saknas. Det är också svårt att, baserat på den kunskap som idag finns tillgänglig, uppskatta urlakning och nedbrytning av den dumpade senapsgasen. Senapsgas i kontakt med vatten går i lösning, vilket är en långsam process. Lösligheten är också starkt begränsad av det fasta skal som bildas runt varje senapsgasklump. Skalet växer sig tjockare och tjockare med tiden och mindre senapsgasklumpar är numera helt fasta rakt igenom. Undersökningar kring hur senapsgasen diffunderar ut genom sådana skal saknas. Löst senapsgas kommer relativt snabbt att hydrolyseras och bilda thiodiglykol (TDG), som har låg toxicitet. TDG bryts ner mikobiologiskt under oxiska förhållanden. Dumpningsområdena är på djup upp till 100 m, vilket betyder att bottenvattnen där ofta kan vara anoxiska. Hydrolysprodukten TDG måste under sådana omständigheter först nå syresatt vatten innan nedbrytningen kan äga rum. Syresättning av också de djupaste bottnarna genom haloklinventilation med hjälp av pumpar, så som föreslagits i projektet BOX-WIN, skulle kunna skapa bättre förutsättningar för nedbrytning av senapsgas genom hydrolys och nedbrytning av hydrolysprodukten.

Table of Contents

List of Figures

List of Tables

Preface

In 2008, Formas and Naturvårdsverket (Swedish EPA) announced available funding for research on the possibility to use deepwater oxidation as a mean to combat eutrophication in the Baltic Sea. Two projects, BOX, "Baltic deepwater OXygenation" and PROPPEN were funded at the end of December 2008. These projects have shown that phosphorus leakage from anoxic bottoms in small coastal basins may be stopped by oxygenation. BOX has shown that this also is true for the Baltic proper. The BOX-WIN project "winddriven oxygenation by pumping and generation of electrical power" builds on BOX.

Results from the BOX-WIN project will be presented in a series of reports from the Department of Earth Sciences at University of Gothenburg. A wide range of subjects are covered by BOX-WIN. Technological, environmental, economical and legal facts and circumstances must be considered to develop and locate a full-scale Demonstrator composed of a self-supporting, floating wind turbine unit with a generator producing electric power for deepwater oxygenation by pumping and for delivery to the grid. The Demonstrator will be developed for the Bornholm Basin, which at times has anoxic water in its deepest parts. The Demonstrator developed by BOX-WIN will hopefully be built to conduct tests in the Bornholm Basin. This would be an important step towards installation of a regional system of full-scale floating wind turbine units with pumps in the Bornholm Basin. An updated list of BOX-WIN reports is included at the end of the report.

The present report "BOX-WIN Technical report no. 6 – Long-time behaviour of mustard gas dumped in the Bornholm Basin" is written by Thomas Hellström and Malin Ödalen. The work is funded by the Swedish Agency for Marine and Water Management and by the Baltic Sea Action Plan Fund via the Nordic Investment Bank.

Gothenburg 20 May 2013

Anders Stigebrandt

1. Introduction

Mustard gas, a chemical warfare agent, was first invented for use during World War I and was used in a number of places at that time. The gas produced during World War I contained several impurities. This gas is often called H or Levinstein mustard in the literature. During World War II, distilled mustard gas, called HD, was produced, though this gas was not used. After World War II large amounts of munitions filled with chemical warfare agents were dumped into the sea. The chemical warfare agents dumped in the Baltic Sea were mainly in the form of munitions ready to use, deriving from Germany. In the North European seas alone the dumping of chemical munitions runs into hundreds of thousands of tons since the end of World War I (Sanderson et al., 2010).

The major dumpsite in the Baltic Sea is situated east of Bornholm at maximum depths of around 100 m. Another dumpsite is situated southeast of Gotland, also at depths of about 100 m or somewhat less. The dumping activities in the Bornholm Basin were ordered by the Soviet Military Administration in Germany, but were carried out in cooperation with the British military. The British mainly carried out the dumping East of Bornholm, while the dumping southeast of Gotland was performed by the Soviets themselves. There are indications that dumping also took place while the ships were en route, on their way to the main dumping areas (CHEMSEA project, 2013). The dumping sites and dumping methods are described more in detail by HELCOM (1994), and are also displayed in Fig. 1.

The main known problem with the dumped chemical munitions so far is that fishermen get hurt when they by accident catch mustard gas in their fishing trawls. However, fishing in the dumping areas is not recommended. Reported accidents have decreased during the latest decade (HELCOM, 2010a), which may indicate that the problem is decreasing.

The areas chosen as dumpsites are deeper regions of the Baltic Sea. At these sites there is often a lack of oxygen. The BOX-WIN project aims to investigate what it takes to achieve permanent oxygenation of the bottom waters and sediments in the Bornholm Basin. In this context, the possible effects on the dumped chemical munitions will be an important issue to evaluate.

Figure 1. Confirmed and unconfirmed dumping sites for chemical munitions (red), official transport routes (dashed red) and unofficial transport routes (dashed purple). Reproduced with the permission of the Institute of Oceanology of the Polish Academy of Sciences (IOPAN), CHEMSEA Project (2013).

2. Dumped chemical warfare agents

2.1 Amount of dumped material

The main warfare chemical agents dumped into the sea were in the form of bombs and artillery shells, hence munitions "ready for use". From 1946 onwards, it is estimated that around 300,000 tons of chemical weapons were dumped into the seas worldwide (Brewer and Nakayama, 2008). The estimates of how much munitions and other warfare material that has been dumped in the Baltic Sea, and of the amount of chemical warfare agents associated with this material, have varied strongly between reports. Bizzigotti et al. (2009) state that about 50,000 – 150,000 tons of chemical munitions have been dumped into the Baltic Sea after World War II. Sjöfartsverket (Naval authority of Sweden, 2011) estimate that more than 55,000 tons of chemical munitions have been dumped in the Baltic Sea. They also state that most of this is still left in the bottoms.

HELCOM (1994, 2010b) report that dumping of chemical munitions in the Baltic Sea amounted to about 40,000 tons. Their numbers are thus somewhat lower than numbers in the above mentioned reports by Bizzigotti et al. (2009) and Sjöfartsverket (2011). HELCOM also estimate that the dumped chemical munitions in total contained a maximum of 13,000 tons of chemical warfare agents. Glasby (1997) has given slightly lower values for the tonnage of dumped chemical warfare agents. In the HELCOM (1994) study, it is specified that between 32,000 tons (reliable data) and 40,000 tons (unreliable data) of munitions were dumped in the Bornholm Basin and that these munitions are expected to have contained about 11,000 tons of chemical warfare agents. About 7,000 tons of these are expected to be mustard gas. According

to the Federal Maritime and Hydrographic agency in Germany (1993) from 35,300 tons (reliable data) to 43,300 tons (unreliable data) of chemical munitions were dumped in the Bornholm Basin (east of Bornholm) and that these munitions contained 5,300 to 6,500 chemical warfare agents. In the area southwest of Bornholm up to 15,000 tons (unreliable data) (HELCOM, 1994; Federal Maritime and Hydrographic agency, 1993) were dumped and additionally about 2,000 tons were dumped in the Gotland Basin (HELCOM, 1994). The positions of the official dumping sites in the Baltic Sea are described in HELCOM (1994).

Berglind and Östin (2013) estimated that, of all dumped chemical weapons, the chemical warfare agents comprise about half of the tonnage and that those warfare agents are dominated by mustard gas. Duursma and Surikov (see Beddington and Kinloch, 2005) have estimated that about 25,000 tons of mustard gas has been dumped in the Baltic Sea. The remaining dumps of other chemical warfare agents represent about 50 % of the amounts of dumped mustard gas and are dominated by As-compounds (Missiaen et al., 2010). The dumping southeast of Gotland represents around 10 % of the dumping east of Bornholm (Missiaen et al., 2010). There are no estimates of the dissolution and degradation which have taken place.

Non-verified information indicates that 4 ships filled with chemical weapons have been sunk in the Arkona Basin southwest of Rønne, Bornholm (HELCOM, 1996). At the dumpsite east of Bornholm, loaded ships have probably been sunk. There is diverging information about the number of ships, from zero or just some barges to a number of ships. HELCOM (1996) states that 9 ships loaded with chemical warfare agents were sunk in the area, but this is not verified. At the dumping site southeast of Gotland, no ships or barges were reported sunk.

The estimates summarized above show that the amount of mustard gas dumped in the Baltic Sea is uncertain. It is likely to be in the range of 10,000 – 25,000 tons of which the major part is suspected to have been dumped in the Bornholm Basin. The figures generally do not take into account degradation of the chemical warfare agents, but it is stated that most of the dumped material probably still remains.

2.2 Composition and state of the dumped material

According to HELCOM (1994) mustard gas constitutes 63% of the dumped chemicals and various arsenic compounds about 31 %. Hence, of the 13,000 tons of chemical warfare agents expected to have been dumped at the Baltic Sea dumpsites according to this study, approximately 8,200 tons are estimated to be mustard gas. Similar proportions of the dumped chemicals are mentioned by Missiaen et al. (2010).

At the dumpsite east of Bornholm, the dumped chemicals can, according to HELCOM (1994), be split up as in Table 1. These numbers only include the Bornholm Basin dumping area.

Found bombs and shells are either empty or heavily corroded (HELCOM, 2005; Sanderson and Fauser, 2008, referred to in Missiaen et al., 2010). Bombs and shells found deeper in the sediments are more intact. The munitions caught by fishermen nowadays are completely corroded and the chemical warfare agents appear as solid brittle lumps (Sanderson et al., 2010). Mustard gas found at the sediment surface is also in lumps with a harder surface cover, which grows thicker with time. Smaller lumps are solid straight through. According to Missiaen et al. (2010), this is due to polymerization that occurs when the mustard gas comes in contact with water.

Table 1. Different types of munitions and other containing vessels for chemical warfare agents dumped East of Bornholm and estimates of tonnage of chemical warfare agents associated with the type of containing vessel. (HELCOM, 1994)

Containing vessel	Mustard gas (tons)	As-compounds (tons)	Other agents
Bombs	6234	1497	479
Artillery shells	671	61	36
Mines	42		
Encasements	80	896	74
Containers		924	
Other types		83	
Total	**7027**	**3461**	**589**

2.3 Distribution of the dumped material

Missiaen et al. (2010) have carried out an investigation of the dumpsite east of Bornholm. They found 4 wrecks but do not exclude that there can be more. Except the wrecks, they also detected a number of objects. The detection limit for these objects was about 2 m. Almost nothing was found at the sediment surface. Most detected objects were found at depths of 0.5 – 1 m beneath the sediment surface. This indicates that most of the bombs and shells are buried to a depth of at least 0.5 m. 80 % of objects found were at a level of 70 cm under sediment surface. 60 % of the detected objects had a size less than 2 m. Wrecks were covered by some decimetres of sediments, which means that most of the objects have sunk deeper in the soft sediments and are not just covered with new sediments.

65 samples of the upper 5 cm of the sediments were analysed. Most of the samples were taken within the officially given dumping area, but many far outside as well. Just one sample showed traces of mustard gas. Traces of arsenic compounds were found in most samples. Since mustard gas is more easily adsorbed to sediments compared to arsenic compounds, it does not spread as easily and contamination is generally limited to a small radius around the source. According to the authors, that is probably one reason for why traces of mustard gas or its degradation products were not found in most of the analysed samples. Another reason is the crust which forms around lumps of mustard gas (see section 5.1.). Water samples taken just above the sediments did not show any contamination by chemical warfare agents.

The spatial distribution of the sediment concentrations was patchy. For example, a sample 10 m from a wreck could show no contamination at all. Meanwhile, traces of chemicals could be found far away from the stated dumping area. Because of the patchy distribution, the occurrence of mustard gas in samples appears random. The authors mean that the "patchiness" is probably due to leaching. The patchiness seems to indicate that whether gas traces are detected or not depends on if a bomb or shell is buried in the sediments just below where the sediment sample was taken. It is worth noting that only one sample showed traces of mustard gas (thiodiglycol). Since mustard gas was the main chemical dumped and has caused the most problems for fishermen, traces of mustard gas should be expected to be found more frequently.

Another factor which is likely to cause "patchiness" is that the officially stated dumping area is not valid and that the dumping area in reality has been several times larger. It has been reported that dumping took place "en route", as ships were on their way to the main dumping areas (HELCOM, 1994; Missiaen et al., 2010). Fishermen have also caught mustard gas and shells in their nets far outside the stated dumping area. Reliable information about where the dumping took place is apparently lacking. Some redistribution of the dumped material by fishing trawls may also have occurred (Missiaen et al., 2010).

In the above described study by Missiaen et al. (2010) it is also mentioned that bombs and artillery shells often were stored in wooden boxes. When dumped, these were not likely to reach deeper sediments in the same way as single artillery shells. This may thus have affected the distribution of the dumped material.

The authors state that they have not been able to locate all bombs and shells at their investigated sites. Most bombs and shells have most likely not been detected, since they are buried too deep in the sediments. They also point out that further investigations on dumped chemical warfare agents in the area are needed.

3. Corrosion of dumped munitions

Munitions at the sediment surface are probably so corroded that their content of mustard gas is in contact with water. Munitions, or traces thereof, caught by fishermen during later years have been heavily corroded. For munitions situated further down in the sediments, which probably are anoxic, the situation is unknown. As traces of arsenic compounds have been found in many sediment samples, this indicates that munitions buried further down in the sediments are leaching, i. e. they have corroded so that the content is now in contact with water.

Corrosion of steel in sea water is rather uniform. The rate of corrosion has been estimated to be 0.1 mm per year (Sjöfartsverket, 2011). The rate of corrosion imbedded in anoxic sediments without bacterial activity can be as low as 0.01 mm per year. A combination of anoxic conditions and sulphur reducing bacteria can lead to a corrosion rate of 0.3 – 0.8 mm per year (Sjöfartsverket, 2011). Sanderson et al. (2008) have estimated the corrosion rate of the bombs and shells to be 0.05 – 0.575 mm per year depending on shell type. Bombs have a thinner steel cover than shells and are therefore corroded more rapidly. They also contain more chemicals per object.

In the MSc Project by Courtney-Green (1990), referred to in Beddington and Kinloch (2005), it is argued that a large calibre shell would decay by corrosion over a period of approximately 300 years and its high explosive filling would dissolve slowly in seawater for a period in the order of 10,000 years. According to the National Report of the Russian Federation (1993; see Beddington and Kinloch, 2005), the total period of unsealing of chemical munitions can last for 10 to 400 years.

4. Mustard gas

Mustard gas has got its name from a slight smell of mustard. Its chemical formula is $(Cl\text{-}CH_2CH_2)_2S$ (CAS no 505-60-2). Mustard gas has got many names: 1,1′-thiobis[2-chloroethane], bis(2-chloroethyl) sulphide and yperite. The boiling point of this chemical agent is 217 °C, the melting point is about 14 °C and, thus, it occurs in liquid form at room temperature (OPCW, 2013). At 13°C mustard gas has a density of 1.34 g cm^{-3} (ATSDR, 2003). The current NATO designation for mustard gas that was distilled is HD.HD was produced during World War II. H is the designation for undistilled mustard gas (also known as Levinstein mustard), which was produced during World War I. Data on the properties of mustard gas according to Sanderson et al. (2010) are given in Table 2. The same study states that water solubility of up to 1 g L^{-1} at 25 °C has been reported. The influence of temperature on water solubility is limited, see section 5.1 below.

K_{OW} (dissolution in octanol/dissolution in water) is a measure of the ability to bioaccumulate. The values indicate that mustard gas bioaccumulates to some degree. The theoretically estimated BCF (bioconcentration factor; conc. in biota/conc. in water) based on K_{OW} indicates a value of 14. According to Sanderson et al. (2009), the measured value is only 3, while Östin (2012) reports a value of 25. K_{OC} is a measure of the ability to be adsorbed to organic matter in the sediments. The value indicates that most of the gas will be attached to the sediments unless the bottom material is pure sand or rocks. This is not the case here. The sediments are in general muddy and soft and are likely to contain a large proportion of organic matter.

The data reported on the properties listed in Table 2 are not consistent. To some degree it can depend on whether H or HD has been studied. H includes some impurities which can affect the results. Although distilled mustard gas (HD) originally is rather pure, substances have often been added to control viscosity or to lower the freezing point. This can be a reason why reported values vary. Impurities and added substances that alter the freezing point also make it difficult to predict whether the dumped mustard gas would be in liquid or solid form at the prevailing temperatures of the Bornholm Basin deepwater.

Table 2. Properties of mustard gas (after Sanderson et al., 2010)

K_{OW}	K_{OC}	Water solubility (mg L^{-1})	Vapour pressure (mm Hg)	Molecular weight
23 - 257	100 - 269	605	0.217	159.07

5. Dissolution and degradation of mustard gas

Dissipation of chemical warfare agents has been described under laboratory conditions, but little is known about the dissipation of these chemicals in the deep sea (>100 m) (Sanderson et al., 2010).

According to Munro et al. (1999), most chemical warfare agents including mustard gas will be hydrolysed after they have dissolved. The hydrolysis products of mustard gas are microbiologically degradable. In this chapter, the processes involved in the degradation of mustard gas and their consequences are investigated.

5.1 Dissolution

Mustard gas is only sparingly soluble in water. Levinstein mustard (H) is considerably more resistant to dissolution in water than pure distilled mustard gas (HD) (Price et al., 1947). It can

be assumed that the mustard gas dumped in the Baltic Sea is HD, since it derives from World War II.

Literature values for water solubility vary from 0.5 to 1 g L^{-1}. Brookfield et al. (1942, see Bizzigotti et al., 2009) established an equation for the rate at which pure mustard gas dissolves in quiescent water as a function of temperature. With this equation it can be estimated that rate of dissolution at 5 ^{o}C is about 10 % less than at 20 ^{o}C. Missiaen et al. (2010) mention that low temperatures of 3 – 4 °C, which are similar to temperatures at the bottom of the Bornholm Basin, are expected to decrease the rate of dissolution. In water, the rate of dissolution is limiting, not the subsequent hydrolysis. One problem is that various laboratory tests have been carried out during mixing, which does not reflect the real circumstances (Wang et al., 2012). Due to this, laboratory dissolution rates exceed real values (Ashmore and Nathanail, 2008). Demek et al. (1970, see Bizzigotti et al., 2009) measured the rate of sulphur mustard dissolution as $3.4 \cdot 10^{-7}$ gm cm^{-2} s^{-1} at 4 °C in a current of 7.7 cm s^{-1}. These measured rates are obviously strong overestimations, see below. Otherwise all superficial mustard gas at the sea bottom should be dissolved by now, which is not the case.

One uncertainty factor is that, to increase viscosity, chemicals like polysulfides have often been added to the mustard gas. This can limit the rate of dissolution of the gas (Yang et al., 1992; Rosenblatt et al., 1996 and Talmage et al., 2007). To withstand freezing temperature, "winter mustard" was produced. It contained 37 % arsenic, which created a viscous substance that some say is practically insoluble (e.g. Paka, see Beddington and Kinloch, 2005). It is estimated that 20 % of Germany's entire mustard gas production was "winter mustard" (Lietuvos.net; HELCOM, 1994). Arsine oil is one example of added chemicals. Arsine oil, which is also a chemical warfare agent, consists of a mixture of 50 % phenyldichloroasine, 35 % diphenyl-chloroarsine, 5 % triphenylarsine and 5 % trichloroarsine (Franke, 1977, see Missiaen et al., 2010).

Various polymer materials, such as alloprene and polymethyl methacrylate (PMMA), were sometimes combined with sulphur mustard to lower its freezing temperature, and solvents such as chlorobenzene, have also been combined with sulphur mustard (Beddington and Kinloch, 2005). Water insoluble thickening agents as polystyrene and montan wax, which could be added to the gas, have a crucial effect on its behaviour in the marine environment, as they prevent the mustard gas from reacting with the sea water (Yang et al., 1992).

A solid surface of mustard gas will develop when the gas comes in contact with water. Some have stated that this is a result of a kind of polymerization, which occurs when hydrolysis products of the mustard gas react with the gas itself during incomplete hydrolysis (see e.g. ATSDR, 2003; Missiaen et al., 2010). Sulphur polymers are suspected to be built up on the surface of the lumps of mustard gas, which limits both further dissolution and hydrolysis (MacNaugton et al., 1994; Small, 1984). The rate of dissolution is therefore very uncertain.

The chemical composition of the tarry exterior is not well understood, partly because it varies from case to case. The chemistry and behaviour of this solid matter are thus more or less unknown, and so are the diffusivity through this crust layer and the thickness of the layer. It is, however, known that the hard shell or crust which develops around the lumps of mustard gas will grow thicker and thicker. Lumps of mustard gas found some decades ago had a liquid centre with mustard gas. Lumps found nowadays are either solid straight through or have a black viscous matter in the centre (Berglind and Östin, 2013). This formed matter will strongly limit dissolution of mustard gas. Mainly due to the crusts, formed lumps of mustard gas may remain after the munition bodies have largely corroded away. (Hart, 2000, see Beddington and Kinloch, 2005). Mazurek et al. (2001) have analysed a partly solid lump of mustard gas (weight about 5 – 6 kg) from the Bornholm basin and detected 50 compounds with the formula $C_uH_vCl_xS_y(O_z)$ with various numbers on the indexes u, v, x, y and z. They assume that at least half of them derive from mustard gas. Only 14 – 20 % of the lump was mustard gas. What to notice is that they did not find thiodiglycol (hydrolysis product of mustard gas, see Section 5.2), which they explain to be due to its water solubility.

Yang et al. (1988) mention that a mustard "heel", which is a solid material, is formed in mustard gas munitions upon prolonged storage. It is composed of occluded liquid mustard gas in a mixture of iron salts and S-(2-chloroethyl)-1,4-dithianium chloride. The mustard heel is soluble in water, but the authors have been unable to locate any quantitative data on the fate of mustard heel once it dissolves in water. It can be expected to be relatively non-volatile, although it has been shown to react with water within several hours (Stahmann et al., 1946).

Sanderson et al. (2010) summarize the findings associated with the dissolution and degradation of mustard gas and indicate further necessary investigations. The conclusion is that dissolution rates of mustard gas are uncertain but rather low.

5.2 Hydrolysis

Dissolved mustard gas will be hydrolysed to form thiodiglycol (TDG in short, with chemical formula $C_4H_{10}O_2S$ or $OH-CH_2-CH_2-S-CH_2-CH_2-OH$), which is microbiologically degradable and fairly harmless (Munro et al., 1999). There are also some other possible reactions (Munro et al., 1999), but those are considered insignificant in this context. A problem is that, during incomplete hydrolysis, produced TDG can stay at the surface of a lump of mustard gas and limit further dissolution (see also section 5.1.).

Dissolved mustard gas has a half-life of minutes when it hydrolyses in pure water, while hydrolysis in sea water occurs more slowly. Low temperatures also decrease the rate of hydrolysis (Missiaen et al., 2010). The hydrolysis of dissolved mustard gas is retarded by chloride in marine water (Yang et al., 1988). Then, half-life is measured in hours. This time

scale applies only to dissolved mustard gas. Because mustard gas is relatively insoluble, the slower dissolving process becomes the limiting factor.

Research groups have measured rate constants (k) for hydrolysis of mustard gas with water. Ogston (1948) reported values at 25 °C of k = 0.174 min^{-1} and Bartlett and Swain (1949) reported values at 25 °C of k = 0.155 min^{-1}. Munro et al. (1999) report that half-lives through hydrolysis in distilled water are 4 – 8 minutes. Yang et al. (1988), Winemiller and Sumpter (2008) and Dell´Amico et al. (2009) have found similar or somewhat larger half-lives. Small (1984) found half-lives of hydrolysis of 158 min at 0.5 ^{o}C and of 1.5 min at 40 ^{o}C. A group of U.S. Army researchers have measured the half-life (t½) and present rates of hydrolysis (k) of mustard gas in seawater at several different temperatures (Bizzigotti et al, 2009). These values are given in Table 3. According to their results, the effect of chloride in sea water compared to fresh water is to slow the rate of hydrolysis by a factor of 3.8 at 25 °C. Dissolved mustard gas can thus be considered as relatively short-lived.

The sulphur mustard degradation half-lives on ambient concrete at 22 ^{o}C ranged from 3.5 to 54 weeks. When the substrates were moistened, the degradation half-lives at 22 ^{o}C ranged from 75 to 350 hours (Brevett et al., 2008).

Generic site specific parameters suggests that hydrolysis in estuaries is approximately four times lower than in freshwater environments and even lower further away from land. For the predicted persistent chemical warfare agents it would be recommended to use default marine mineralization half-lives of >150 days (Sanderson et al., 2010).

Table 3. Half-lives (t½) and rates (k) of hydrolysis of mustard gas in seawater at different temperatures (after Bizzigotti et al., 2009)

T (°C)	t½ (min)	k (min^{-1})
5	175	0.004
15	49	0.0141
25	15	0.046

5.3 Microbial degradation

Microbiological degradation of mustard gas has not been observed. This is most likely due to its high toxicity. However, Medvedeva et al. (2008, 2009) found that the hydrolysis product TDG was microbiologically degradable. This was carried out by microorganisms identified as *Achromobacter* sp., *Pseudomonas* sp., and *Arthrobacter*. All three isolated bacterial strains

were aerobic, oxidase and catalase-positive, two were gram-negative and one was gram-positive. All three strains grew between 0 and 30 ^{o}C, with the optimal growth temperature around 25 ^{o}C. These were all capable of metabolizing TDG at a low temperature. The time required for TDG degradation (t½) was 30 – 45 days at 20 and 25 ^{o}C, but 180 – 210 days were required to degrade TDG at 5 ^{o}C.

The degrader microorganisms also grew more actively under aeration. For example, the biomass gain for *Achromobacter* sp. 75-1 under aeration was 8 times that under static conditions. The growth rate at 20°C (µmax = 0.23 – 0.31 g/g/d) was about 3 – 5 times more rapid than the growth rate at 5 °C. Cultures also took longer time to degrade TDG at 5 °C; t½ was 1.5 – 2.5 months, compared to a t½ of 0.5 month at 20 ^{o} C.

The temperatures at the dumping sites are 7 ± 4 ^{o}C (Sanderson et al., 2008), which indicates that the degrader microorganisms here should operate on the longer time scales (~2 months).

Degradation by the same microorganisms has also been detected in soil contaminated with mustard gas (Medvedeva et al., 2008, 2012; Dell'Amico et al., 2009; Ermakova et al., 2004).

At the dumping sites increased numbers of these microorganisms have been detected in the bottom waters, with significant amounts of bacterial cultures tolerant to mustard gas products (both chlorinated and non-chlorinated) in the near-bottom water. The tolerant microorganisms were found at about 40% of the stations in the dump site areas (Medvedeva et al., 2009). Outside of the dumpsites, the concentration of mustard gas hydrolysis products tolerant microorganisms in near-bottom water was only between 0% and 3% (Sanderson et al., 2010). Bacterium collected at the mustard dumpsites in the Baltic Sea showed reduced diversity of microbiota (Östin, 2012).

In the microbiological degradation, thiodiglycol sulphoxide is first formed. This will then be further degraded into hydrochloric acid and acetic acid (Creek et al., 2010; D'Agostino and Provost, 1992).

5.4 Traces of dissolved mustard gas in the environment

Sanderson et al. (2008, 2009) have theoretically estimated the concentrations of dissolved mustard gas in the water east of Bornholm, see Table 4. They have made a number of assumptions, of which some are rather uncertain, especially the rate of dissolution. They assume a continuous and homogenous release, over 60 years, of the total dumped mass on the seabed to the water phase. The total chemical mass is assumed to be homogenously distributed on either the primary (worst case) or secondary (more realistic) dumpsite areas. A south-easterly bottom water current of 5 cm s^{-1} was assumed and a vertical dispersion coefficient of 0.2 cm^{2} s^{-1} was used, as given by Stigebrandt (1987). Sedimentation, diffusion

to sediment, degradation (hydrolysis) and accumulation in sediment are also included in the calculations. In the calculations, the rate of hydrolysis has a half-life of 56 days.

The horizontal location of the maximum concentration of dissolved mustard gas predicted at 20 cm above the seafloor is, at the dump site, in principle directly above the sediment, whereas the maximum concentration 20 m above the sediment is calculated to be around 30 km east of the dumpsite boundary. The estimated concentrations in Table 4 are overestimations, which the authors also write. The used dissolution rates from the sediments are probably more than 10 times higher than reality.

Mustard gas has been found to persist in soil or even in water for periods of decades (Assennato et al., 1942, see Bizzigotti et al., 2009). This is believed to be due to the low solubility of sulphur mustard in water and the slow rate at which mustard dissolves in water (Bizzigotti et al., 2009). Also TDG has been observed in soils and in groundwater at sites contaminated by mustard gas 60 years ago (Muir et al., 2012). Soil organic matter adsorbs about 90%, which may be a reason (Ashmore and Nathanail, 2008). Adsorption can also be suspected to take place in sediments.

Since traces of mustard gas hydrolysis products (Missiaen et al., 2010) and altered microbial composition (Medvedeva et al., 2009) can be detected in the water it means that leaching of mustard gas occurs. This may derive from superficial lumps of mustard gas, which are not uniformly spread. Most of the dumped mustard gas is probably more permanently stored deeper in the sediments and is thus expected to be more stationary.

Table 4. Predicted maximum water concentrations of dissolved mustard gas at 20 cm and 20 m above the sediment surface. (after Sanderson et al., 2008)

Concentration (µg L^{-1}) in lower water layer (20 cm above sediment)		Concentration (µg L^{-1}) in upper water layer (20 m above sediment)	
Primary dump site	Secondary dump site	Primary dump site	Secondary dump site
0.4	0.08	$1 \cdot 10^{-4}$	$1 \cdot 10^{-5}$

5.5 Effects of anoxia on degradation of mustard gas

The dumping sites are situated rather deep in the Baltic Sea, where the water is often anoxic. This means that the sediments are likely to be more or less permanently anoxic. If the water is anoxic, degradation of TDG will take place in other locations. In case the water above the sediments was permanently oxic, the sediments would also become oxygenated. This would mean that microorganisms would be able to degrade TDG already in the sediments.

Sanderson et al. (2010) report suggestions that the time scale of the threat from dumped chemical munitions under low oxygen conditions is limited to < 100 years, by which time the released chemical warfare agents will have been significantly hydrolysed and mineralized, at least when situated on the sediment surface.

5.6 Amount of degraded mustard gas

Due to the many uncertainties regarding the limitations on dissolution of mustard gas, e.g. caused by added substances or formation of polymer substances on the surface of the lumps, it is difficult to estimate how much of the dumped mustard gas that has been dissolved and then further degraded by hydrolysis and microbial processes. Even though material is expected to have leaked out from the corroded munition shells, the retarding processes that are limiting dissolution are expected to be efficient enough for most of the dumped mustard gas to still remain on the bottom of the sea.

6. Harmful effects of mustard gas

Mustard gas is poisonous to biota, and spread in soil it has been noticed to affect microorganisms (Medvedeva et al., 2008). No effects on fish in the Baltic Sea have been reported according to the literature cited in this study. Effects on fish have however been reported from dumped chemical warfare agents outside Italy (Della Torre et al., 2010; Amato et al., 2006), but the reported effects in that study were not caused by mustard gas. Sanderson et al. (2009) write that the fish community at the Bornholm dumpsite could potentially be at risk from exposure to chemical warfare agents. Reported contaminated fish catches have been dominated by mustard gas (HELCOM, 1994), but these contaminations were due to lumps of mustard gas caught together with fish in the nets.

An EU-project is currently investigating the risks for mussels to be affected by chemical warfare agents in the Baltic Sea. According to Berglind and Östin (2013), effects have been suspected, but it is currently not possible to state how severe these effects are. Die-off of bottom fauna, mussels in particular, in the Bornholm Basin in the late 1940's and early 1950's was hypothesized to have been caused by chemical warfare agents (Demel and Mankowski, 1951, see Gerlach, 1994). Later, it has however been argued that this mass mortality was more likely caused by changing hydrographic conditions causing anoxia in the previously well oxygenated basin (Gerlach, 1994). These issues are further treated in Section 7.

Surikov (see Kaffka, 1996) argues that mustard gas lying on the sea bottom maintains high toxicity for 400 years. On humans, the harmful effects of mustard gas include damaging to the skin, eyes and respiratory system (Gupta, 2009). Mustard gas is also carcinogenic. The safe

oral dose (reference dose, RfD) for humans of mustard gas is as low as $7 \cdot 10^{-6}$ mg kg^{-1} body weight per day (Sanderson et al., 2010). Today there is generally no risk for such levels of oral exposure (for example by eating fish) and, overall, humans are not expected to be exposed to mustard gas. Fishermen, who may still catch lumps of mustard gas in their fishing gear, do however risk harmful exposure. The question is whether biota at the bottoms can be affected. As mentioned above, current investigations are attempting to find this answer.

TDG as a product of hydrolysis of mustard gas is not very toxic (Munro et al., 1999; Reddy et al., 2005). Estimated LC$_{50}$- and EC$_{50}$ -levels are in the range of 0.5 to more than 1 g L^{-1}. Thus, lethal concentrations and effective concentrations for various biota and algae are by far higher than the levels that are considered possible for water at the dumping sites, see calculations by Sanderson et al. (2008).

In summary, undissolved mustard gas, which has not been hydrolysed, is expected to be much more harmful to humans as well as to biota in general than its hydrolysis product TDG. Toxic effects of mustard gas are however expected to be concentrated to a radius of no more than a few metres surrounding the source (Missiaen et al., 2010).

7. Evolution of hydrographical and ecological conditions since the time of dumping

During the first half of the 20th century, before World War II, salinities in the Baltic proper were relatively low compared to the conditions after the war (1948 – 1970) and the position of the halocline was deeper (Gerlach, 1994). The prevailing hydrographic conditions before the war allowed for good oxic conditions and a healthy bottom community. Investigations made after the war showed that this bottom community was still present, with high abundance of various species of e.g. mussels and polychaetes in the Southern Baltic (Demel and Mulicki, 1958).

Mass mortality of the bottom fauna in the Baltic Sea was first reported from the Gulf of Finland in 1948 (Seire, 1992, see Gerlach, 1994), hence not in the vicinity of the main dumpsites of chemical warfare agents. However, in the same year the mussel species *Macoma calcarea* was reported to have disappeared in the Gdansk Basin and parts of the Bornholm Basin (Demel and Mankowski, 1951, see Gerlach, 1994). This disappearance was hypothesized to be caused by poisoning due to the dumping of chemical warfare agents.

However, later studies suggest that the die-off was more likely caused by a change in the hydrographic conditions in combination with an increase in nutrient loading, which caused oxygen depletion in the deepwater (Gerlach, 1994). This hypothesis is strengthened by the changes of the salinity structure observed in the Gotland Deep beginning already in 1933 and

continuing for four decades until the late 1970's (Gerlach, 1994), with overall increases in salinity especially in the deepwater and a rising halocline. Oxygen data from the 1960's and 1970's from the same area, showing increasing hypoxia and anoxia (Hansson et al., 2011), also supports this argument. It is expected that the general hydrographic trends during this period were similar in the entire Baltic proper area including the Bornholm Basin. The clam *Astarte borealis*, which is highly tolerant to anoxia compared to *Macoma calcarea*, was found in the Bornholm Basin until 1958 whereas *Macoma calcarea* had disappeared already in 1956. Since some biota survived much longer, it seems unlikely that poisoning by chemical warfare agents was the main cause for the die-off.

During the period 1978 to 1992, inflows of new deepwater to the Baltic Sea were scarce (Hansson et al., 2011). Salinity in the Baltic proper generally decreased and the halocline was lowered (Gerlach, 1994; Hansson et al., 2011). In the Bornholm Basin, this trend was not as clear, but salinity is lower in 1985 – 1992 (Ödalen and Stigebrandt, 2013). During this period with lowering of the halocline, areas which had previously been severely affected by low oxygen conditions and completely lacking macrofauna were oxygenated. Recolonization of previously dead bottoms was observed in many areas including parts of the Bornholm Basin (Gerlach, 1994), despite the presence of dumped chemical warfare agents in this area.

After the major inflow that occurred in 1993, the halocline started ascending again and in recent years it has been at approximately the same level as before it started descending in the late 1970's (Hansson et al., 2011). During these past 20 years, the deepwater salinity in the Baltic proper has generally been high and this is also observed in the Bornholm Basin together with low availability of oxygen (Ödalen and Stigebrandt, 2013). Since larger water volumes are again affected by oxygen deficiency, the areas of the Bornholm Basin that were recolonized in the early 1990's are not likely to have had a healthy bottom fauna during the late 2000's.

It is likely to assume that the increased supply of organic material due to increased nutrient input, linked to both spreading anoxia and eutrophication after World War II, has led to a higher rate of sedimentation and thus softer sediments in this area over time. This sedimentation will have caused the dumped munitions and escaped lumps of mustard gas to be buried to a higher degree today than when they were initially dumped. Deep burial of the lumps of mustard gas should decrease the risk for recolonizing bottom fauna to come into contact with the poisonous compound, though it should be noted that it is unclear how or if the lumps move within the sediments towards the sediment surface.

8. Removal solutions for dumped chemical warfare agents

Dumping of chemical warfare agents has occurred in many places around the world. Discussions about how to approach the problems caused by these warfare agents have been going on for a long time. The idea to remove the chemicals has generally been turned down. It is a widely held view that recovery of dumped munitions is not technically feasible at present (Beddington and Kinloch, 2005; HELCOM, 2010a). The main reasons are that it is expensive and that the removal itself can cause more problems, since the environment can be more exposed at least for a time. Therefore, the conclusion so far is that the chemicals have to stay where they are (Kaffka, 1996).

A number of destruction methods have been proposed (Creber et al., 2009; Hess, 2009; Pham et al., 1996; Popiel et al., 2005, 2008; Saxena et al., 2012; Sharma et al., 2006, 2009; Singh et al., 2009). Bleaching-powder and chloramines, for example, react violently with mustard agent, whereupon non-poisonous oxidation products are formed. These substances are often used for the decontamination of mustard agent. Incineration is also a method that has been used. The disadvantage is that all of these methods require that the dumped mustard gas is transported to land.

9. Conclusions

It is likely that approximately 10,000 – 25,000 tons of mustard gas have been dumped in the Baltic Sea. More precise numbers for the Bornholm Basin suggest that approximately 7,000 tons of mustard gas were dumped here. Most of the dumped mustard gas is assumed to remain in the sediments of the dumping areas.

Based on what is known today it is not possible to quantify the rate of leaking and degradation of dumped mustard gas. The main problem concerns the effect of the crust or shell formed around lumps of mustard gas, which limits dissolution. Therefore, the rate of dissolution is not possible to estimate, but it is expected to be rather low. Hydrolysis and microbial degradation of hydrolysis products such as TDG are expected to be much faster, but the slow rate of dissolution will be the limiting step for degradation of mustard gas.

Most of the dumped mustard gas is likely to be buried deep in the sediments and it is rather uncertain how mustard gas moves in the sediments towards the surface. There is a need for a number of laboratory tests of the lumps of mustard gas which are now present at the dumping sites. Especially, better knowledge of the dissolution of mustard gas and the adsorption effects of the sediments is needed. Studies have shown that, even though mustard gas has been dumped to a larger extent than other chemical warfare agents, it is more common to encounter contamination caused by other chemical compounds than by mustard gas (see Missiaen et al.,

2010). This is likely to be due to the capsulation caused by the polymerized crust of the lumps of gas.

A problem with the dumping sites in the Baltic Sea is that the sites are often anoxic, which for example limits the microbial degradation of TDG. This, in itself, is no major environmental problem, since TDG is not very toxic. Oxygenation of the deepwater is not expected to have any major effect on dissolution and hydrolysis of the poisonous mustard gas. However, in case the bottom waters were permanently oxygenated the degradation of the hydrolysis products could take place already in the sediments. This would likely improve the rate of degradation of mustard gas to some degree, as the rate of dissolution can be suspected to increase slightly when the concentration of TDG in the water decreases.

Despite the presence of mustard gas and other chemical warfare agents in the area, recolonization of dead bottoms has been observed during natural oxygenation events in the past. It is thus likely that the positive effects on biota due to oxygenation would be greater than the negative effects on the colonizing species caused by dumped chemical warfare agents.

It is clear that there are many uncertainties regarding dissolution and behaviour of mustard gas in the dumping areas. Therefore, it is recommended that oxygenation by artificial mixing, e.g. by pumping down water from above the halocline as suggested by the BOX-WIN project, is accompanied by a monitoring program aiming to clarify the effects of oxygenation on mustard gas and other remnants of dumped chemical warfare agents. Before the initiation of such a project, it is also important that the current situation is properly monitored to allow for a quantitative comparison of the conditions before and during pumping.

10. Acknowledgements

11. References

Amato, E., Alcaro, L., Corsi, I., Torre, C. D., Farchi, C., Focard, S., Marino, G. and Tursi, A., 2006. An integrated ecotoxicological approach to assess the effects of pollutants released by unexploded chemical ordnance dumped in the southern Adriatic (Mediterranean Sea). *Mar. Biol.* 149, pp. 17-23.

Ashmore, M. H. and Nathanail, C. P., 2008. Review article: A critical evaluation of the implications for risk based land management of the environmental chemistry of Sulphur Mustard. *Environ. Int.*, 34 (8), pp. 1192-1203.

ATSDR (Agency for Toxic Substances and Disease Registry), 2003. Toxicological Profile for Sulfur Mustard (Update), Public Health Service, U.S. Department of Health and Human Services, Sep. 2003, Atlanta, U.S.A.

Bartlett, P. D. and Swain, C. G., 1949. Kinetics of hydrolysis and displacement reactions of beta, beta1-dichlorodiethyl sulfide and of beta-chloro-beta1-hydroxydiethyl sulfide. *J. Am. Chem. Soc.*, 71 (4), pp. 1406-1415.

Brewer, P. G. and Nakayama, N., 2008. What Lies Beneath: A Plea for Complete Information, *Environ. Sci. Technol.*, 42 (5), pp. 1394-1399.

Brevett, C. S., Sumpter, K. B. and Wagner, G. W., 2008. Degradation of Sulfur Mustard on Moist Sand as Determined by 13C Solid-State Magic Angle Spinning Nuclear Magnetic Resonance. *Spectrosc. Lett.*, 41 (1), pp. 29-39.

Beddington, J. and Kinloch, A. J., 2005. Munitions Dumped at Sea: A Literature Review. IC Consultants Ltd, London.

Berglind, R. and Östin, A., 2013. Personal communication, FOI, Umeå.

Bizzigotti, G. O., Castelly, H., Hafez, A. M., Smith, W. H. B. and Whitmire, M. T., 2009. Parameters for Evaluation of the Fate, Transport, and Environmental Impacts of Chemical Agents in Marine Environments. *Chem. Rev.*, 109 (1), pp. 236–256.

Federal Maritime and Hydrographic agency, 1993. Chemical munitions in the Southern and Western Baltic Sea, 1993. Complication, assessment and recommendations. Hamburg, Germany.

CHEMSEA Project, 2013. Characterization & Mapping. Chemical Munitions Search & Assessment, CHEMSEA Project, partly financed by the European Union ERDF funds. <http://www.chemsea.eu/Characterization_&_Mapping,8.html>, image retrieved 2013-04-16.

Creber, K. A. M., Samuleev, P. V. and Andrews, W. S., 2009. An investigation into the use of ionizing radiation for the destruction of sulphur mustard. *J. Radioanal. Nucl. Chem.*, 282 (2), pp. 597-600.

Creek, J. A., McAnoy, A. M. and Brinkworth, C. S., 2010. Rapid monitoring of sulfur mustard degradation in solution by headspace solid-phase microextraction sampling and

gas chromatography mass spectrometry. *Rapid. Commun. Mass Spectrom.*, 24 (23), pp. 3419-3424.

D'Agostino, P. A. and Provost, L. R., 1992. Determination of chemical warfare agents, their hydrolysis products and related compounds in soil. *J. Chromatogr.*, 589 (1), pp. 287-294.

Dell'Amico, E., Bernasconi, S., Cavalca, L., Magni, C., Prinsi, B. and Andreoni, V., 2009. New insights into the biodegradation of thiodiglycol, the hydrolysis product of Yperite (sulfur mustard gas). *J. of Appl. Microbiol.*, 106 (4), pp. 1111-1121.

Della Torre, C., Petochi, T., Corsi, I., Dinardo, M. M., Baroni, D., Alcaro, L., Focardi, S., Tursi, A., Marino, G., Frigeri, A. and Amato, E. 2010. DNA damage, severe organ lesions and high muscle levels of As and Hg in two benthic fish species from a chemical warfare agent dumping site in the Mediterranean Sea. *Sci. Total Environ.*, 408 (9), pp. 2136-2145.

Demel, K., Mulicki, Z., 1958. The zoobenthic biomass in the Southern Baltic, *J. Cons. perm. int. Explor. Mer.*, 24, pp. 43-54.

Ermakova, I. T., Safrina, N. S., Starovoitov, I. I., Lyubun, E. V., Shcherbakov, A. A., Makarov, O. E., Petrova, A. A. and Shpilkov, P. A., 2004. Microbial Degradation of Mustard Gas Reaction Masses: Isolation and Selection of Degradative Microorganisms, Analysis of Organic Components of Reaction Masses, and Their Biodegradation. *Microbiology -AIBS- c/co of Mikrobiologiia*, 73 (3), pp. 300-304.

Gerlach, S. A., 1994. Oxygen conditions improve when the salinity in the Baltic Sea decreases. *Mar. Pollut. Bull.* 28 (7), pp. 413-416.

Glasby, G. P., 1997. Disposal of chemical weapons in the Baltic Sea. *Sci. Total Environ.*, 206, pp. 267–273.

Gupta, R. C. (ed.), 2009. Handbook of Toxicology of chemical warfare agents, Academic Press, Elsevier Inc., USA/UK. ISBN: 978-0-12-374484-5.

Hansson, M., Andersson, L., Axe, P., 2011. Areal extent and volume of anoxia and hypoxia in the Baltic Sea, 1960-2011. Report Oceanography no. 42, SMHI Swedish Meteorological and Hydrological Institute.

HELCOM, 1994. Report on Chemical Munitions Dumped in the Baltic Sea, Report to the 16th Meeting of the Helsinki Commission 8-11th March 1994 from the Ad Hoc Working Group on Dumped Chemical Munitions, HELCOM CHEMU.

HELCOM, 1996. Third periodic assessment of the state of the marine environment of the Baltic Sea, 1989 – 1993. Executive summary & background document, *Baltic Sea Environ. Proc.*, 64A, 64B.

HELCOM, 2005. Press release regarding chemical weapons dumps in the Baltic. Helsinki Commission. <www.helcom.fi/press_office/news_helcom/en_GB/ChemicalMunitions11 15039886140/>

HELCOM, 2010a. Activities of the Helsinki commission with regard to chemical munitions dumped in the Baltic Sea. <http://meeting.helcom.fi/c/document_library/get_file?p_l_id=16324&folderId=1270009&name=DLFE-43386.pdf>

HELCOM, 2010b. Chemical weapons dumps in the Baltic. <http://www.helcom.fi/environment2 /hazsubs/en_GB/chemu/>

Hess, G., 2009. Army depot plans to destroy mustard gas. *Chem. Eng. News*, 87 (24), pp. 21-26.

Kaffka, A. V. (ed), 1996. Sea-Dumped Chemical Weapons: Aspects, Problems and Solutions. Kluwer Academic Publishers, Dordrecht.

Lietuvos.net, 'Chemical Weapon Dumping in the Baltic Sea', Lithuanian Website at: <http://lietuvos.net/zinios/gas_ww2.htm>

MacNaughon, M. G., Brewer, J. H. and Ferril, J. L., 1994. Field manual on environmental chemistry and fate of chemical warfare agents. SwRI project 01-5864. San Antonio. Southwest research institute.

Medvedeva, N., Polyak, Y., Kuzikova, I., Orlova, O. and Zharikov, G., 2008. The effect of mustard gas on the biological activity of soil. In Special Section: 8th International Conference on the Protection and Restoration of the Environment, *Environ. Res.*, 106 (3), pp. 289-295.

Medvedeva, N., Polyak, Y., Kankaanpää, H. and Zaytseva, T., 2009. Microbial responses to mustard gas dumped in the Baltic Sea. *Mar. Environ. Res.*, 68 (2), pp. 71-81.

Medvedeva, N., Polyak, Y. O., Zaytseva, T. and Zharikov, G., 2012. Destruction of mustard gas hydrolysis products by marine and soil bacteria. *Biol. Bull.*, 39 (1), pp. 77-84.

Missiaen, T., Söderström, M., Popescu, I. and Vanninen, P., 2010. Evaluation of a chemical munition dumpsite in the Baltic Sea based on geophysical and chemical investigations. *Sci. Total Environ.*, 408, pp. 3536-3553.

Muir, R. L. H., McFarlane, N. R., Soilleux, R. J., Yu, X., Thompson, I. P. and Jackman, S. A., 2012. Soil biotransformation of thiodiglycol, the hydrolysis product of mustard gas: understanding the factors governing remediation of mustard gas contaminated soil. *Biodegradation*, 24 (1), pp. 125-135.

Munro, N. B., Talmage, S. S., Griffin, B. D., Waters L. C., Watson, A. P., King, J. F. and Hauschild, V., 1999. The sources, fate and toxicity of chemical warfare agent degradation products. *Environ. Health Persp.*, 107 (12), pp. 933 – 974.

Mazurek, M., Witkiewic, Z., Popiel, S. and Śliwakowski, M., 2001. Capillary gas chromatography-atomic emission spectroscopy-mass spectrometry analysis of sulphur mustard and transformation products in a block recovered from the Baltic Sea. *J. Chromatogr. A*, 919 (1), pp. 133–145

Ödalen, M., Stigebrandt, A., 2013. Hydrographical conditions in the Bornholm Basin of importance for oxygenation of the deepwater by pumping down oxygen saturated water

from above the halocline. BOX-WIN Technical Report no. 1, Report C96, ISSN 1400-383X, Dept. of Earth Sciences, University of Gothenburg.

Ogston, A.G., 1948. The reactions of mustard gas in aqueous solution. *Biochem. J.*, 42 (2), pp. 25-31.

OPCW – Organisation for the Prohibition of Chemical Weapons, www.opcw.org, 'Mustard agents: description, physical and chemical properties, mechanism of action, symptoms, antidotes and methods of treatment', Information retrieved 20 May 2013, <www.opcw.org/about-chemical-weapons/types-of-chemical-agent/mustard-agents/#c187>

Östin, A., 2012. Review of Analytical Methods for the Analysis of Agents Related to Dumped Chemical Weapons for the CHEMSEA project Chemsea, Umeå. European CBRNE Center 901 87 Umeå, Sweden

Price, C. C. and Bullitt, O. H. Jr., 1947. Hydrolysis and oxidation of mustard gas and related compounds in aqueous solution. *J. Org. Chem.*, 12 (2), pp. 238-48.

Popiel, S., Witkiewicz, Z. and Szewczuk, A., 2005. The GC/AED studies on the reactions of sulfur mustard with oxidants. *J. Hazard. Mater.,* 123 (1), pp. 94-111.

Popiel, S., Witkiewicz, Z. and Chrzanowski, M., 2008. Sulfur mustard destruction using ozone, UV, hydrogen peroxide and their combination. *J. Hazard. Mater.*, 153 (1-2), pp. 37-43.

Pham, M. Q. K., Harvey, S. P., Weigand, W. A. and Bentley W. E., 1996. Reactor comparisons for the biodegradation of thiodiglycol, a product of mustard gas hydrolysis. *Appl. Biochem. Biotech.,* 57 (8), pp. 779-789.

Reddy, G., Major, M. A. and Leach, G., 2005. Toxicity assessment of thiodiglycol. *Int. J. Toxicol.* 24 (6), pp. 435-442.

Rosenblatt, D. H., Small, M. J., Kimmell, T. A. and Anderson, A. W., 1996. Background chemistry for chemical warfare agents and decontamination processes in support of delisting waste streams at US. Army dugway proving ground. Argonne national laboratory. Washington D.C.

Sanderson, H., Thomsen, M., Fauser, P. and Sørensen, P. B., 2008. Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea, *J. Hazard. Mater*., 154, pp. 846-857.

Sanderson, H., Fauser, P., Thomsen, M. and Sørensen, P. B., 2009. Human health risk screening due to consumption of fish contaminated with chemical warfare agents in the Baltic Sea. *J. Hazard. Mater.,* 162 (1), pp. 416-422.

Sanderson, H., Fauser, P., Thomsen, M., Vanninen, P., Soderstrom, M., Savin, Y., Khalikov, I., Hirvonen, A., Nliranen, S. and Missiaen, T., 2010. Environmental Hazards of Sea-Dumped Chemical Weapons. *Environ. Sci. Technol.,* 44 (12), pp. 4389-4394.

Saxena, A., Srivastava, A. K., Singh, B. and Goyal, A., 2012. Removal of sulphur mustard, sarin and simulants on impregnated silica nanoparticles. *J. Hazard. Mater*. 211-212, pp. 226-232.

Sharma, A., Saxena, A., Singh, B., Sharma, M., Suryanarayana, M. V., Semwal, R. P., Ganeshan, K. and Sekhar, K., 2006. In-situ degradation of sulphur mustard and its simulants on the surface of impregnated carbon systems. *J. Hazard. Mater*. 133 (1-3), pp. 106-112.

Sharma, A., Singh, B. and Saxena, A., 2009. Polyoxometalate impregnated carbon systems for the in situ degradation of sulphur mustard. *Carbon*. 47 (8), pp. 1911-1915.

Singh, B., Saxena, A., Nigam, A. K., Ganesan, K. and Pandey, P., 2009. Impregnated silica nanoparticles for the reactive removal of sulphur mustard from solutions. *J. Hazard. Mater*., 161 (2/3), pp. 933-940.

Sjöfartsverket (Naval authority of Sweden), 2011. Miljörisker från fartygsvrak. Regeringsuppdrag 2009/4683/TR. 2011-01-14 (in Swedish)

Small, M. J., 1984. Compounds found from the chemical decontamination of HD, BG and VX and their environmental fate, Tech. rpt 8304:AD A149515. US. Army medical bioengineering research and development laboratory.

Stahmann, M. A., Fruton, J. S. and Bergmann, M. 1946. Chemical reactions of mustard gas and related compounds.VI. The chemistry of sulfonium salts related to mustard gas. *L. Org, Chem*., 11 (46), pp. 704-718.

Stigebrandt, A., 1987. A model for the vertical circulation of the Baltic deep water. *J. Phys. Oceanogr.*, 17, pp. 1772–1785.

Talmage, S. S., Munro, N. B., Watson, A. P., King, J. F. and Hauschild, V., 2007. The fate of chemical warfare agents in the environment. In: Chemical warfare agents: Toxicology and Treatment. 2nd ed. Marrs T.C., Maynard, R. L., Sidell and F. R. (eds.), John Wiley & Sons, Ltd.

Wang, Q. Q., Begum, R. A., Day, V.W. and Bowman-James, K., 2012. Sulfur, oxygen, and nitrogen mustards: stability and reactivity. *Org. Biomol. Chem.* 10 (44), pp. 8786-8793.

Winemiller, M. and Sumpter, K., 2008. Products of Sulfur Mustard Degradation: Synthesis and Characterization of 1-(2-Chloroethoxy)-2- [(2-chloroethyl)thio] Ethane, Related Compounds, and Derivatives. *Phosphorus, Sulfur & Silicon & the Related Elements*, 183 (9), pp. 2309-2317.

Yang, Y. C., Szafraniec, L. L., Beaudry, W. T. and Wa, J. R., 1988. Kinetics and mechanism of the hydrolysis of 2-chloroethyl sulfide. *J. Org. Chem*., 53, pp. 3293-3297.

Yang, Y. C., Baker, J. A. and Ward, R. J., 1992. Decontamination of chemical warfare agents. *Chem. Rev*. 92 (8), pp. 1729-1743.

BOX-WIN Technical Reports Series

1. Ödalen, M. & Stigebrandt, A., 2013. Hydrographical conditions in the Bornholm Basin of importance for oxygenation of the deepwater by pumping down oxygen saturated water from above the halocline, BOX-WIN Technical Report no. 1, Report C96, ISSN 1400-383X, Dept. of Earth Sciences, University of Gothenburg.

2. Ödalen, M. & Stigebrandt, A., 2013. Factors of potential importance for the location of wind-driven water pumps in the Bornholm Basin, BOX-WIN Technical Report no. 2, Report C97, ISSN 1400-383X, Dept. of Earth Sciences, University of Gothenburg.

3. Stigebrandt, A., Kalén, O., 2012. Improving oxygen conditions in the deeper parts of Bornholm Sea by pumped injection of winter water, *Ambio*, 41, no. 8, Dec 2012, doi: 10.1007/s13280-012-0356-4 (BOX-WIN Technical Report no. 3)

4. Eriksson, H., Kullander, T., 2013. Assessing feasible mooring technologies for a Demonstrator in the Bornholm Basin as restricted to the modes of operation and limitations for the Demonstrator, BOX-WIN Technical Report no. 4, Report C98, ISSN 1400-383X, Dept. of Earth Sciences, University of Gothenburg.

5. Eriksson, H., Kullander, T., 2013. Assessing important technical risks from use of a floating wind turbine unit equipped with pumps for oxygenation of the deepwater, BOX-WIN Technical Report no. 5, Report C99, ISSN 1400-383X, Dept. of Earth Sciences, University of Gothenburg.

6. Hellström, T., Ödalen, M., 2013. Long-time behaviour of mustard gas dumped in the Bornholm Basin, BOX-WIN Technical Report no. 6, Report C100, ISSN 1400-383X, Dept. of Earth Sciences, University of Gothenburg.