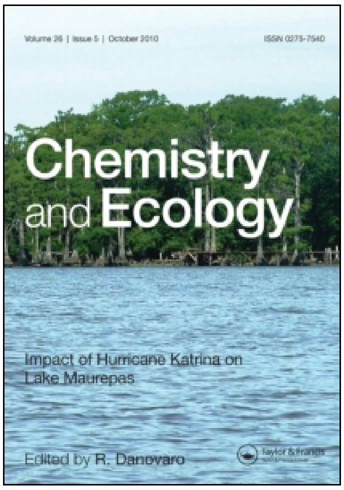


Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

The Baltic Sea as a dumping site of chemical munitions and chemical warfare agents

Aleksandra Szarejko[a]; Jacek Namieśnik[a]
[a] Department of Analytical Chemistry, Chemical Faculty, Gdañsk University of Technology, Gdañsk, Poland

To cite this Article Szarejko, Aleksandra and Namieśnik, Jacek(2009) 'The Baltic Sea as a dumping site of chemical munitions and chemical warfare agents', Chemistry and Ecology, 25: 1, 13 — 26
To link to this Article: DOI: 10.1080/02757540802657177
URL: http://dx.doi.org/10.1080/02757540802657177

Chemistry and Ecology
Vol. 25, No. 1, February 2009, 13–26

RESEARCH ARTICLE

The Baltic Sea as a dumping site of chemical munitions and chemical warfare agents

Aleksandra Szarejko and Jacek Namieśnik*

Department of Analytical Chemistry, Chemical Faculty, Gdañsk University of Technology, Gdañsk, Poland

(*Received 30 July 2008; final version received 1 December 2008*)

In this paper, the problem of chemical weapons dumped in the Baltic Sea by the Allied and Soviet forces after World War II is presented. The types and properties of the chemical warfare agents found in the Baltic, as well as the known dumping regions, are described. The potential hazards for the environment arising from the long-term disposal of munitions under the water are also described. Based on a study of the literature, possible analytical methods for the detection of chemical warfare agents are discussed.

Keywords: Baltic Sea; sea contamination; World War II; chemical weapons; chemical munitions; ammunition chemical warfare agents, types, threats

1. Introduction

It is well known that large quantities of chemical weapons were dumped into the Baltic Sea after World War II, following the decision of the Potsdam Conference which took place in July 1945.

Chemical munitions were used for the first time by Germany on 22 April 1915 during World War I [1]. As a result, about 100,000 people died and about 1,200,000 were injured [2]. During World War II, large-scale production of various toxic warfare agents took place. The production of Chemical Warfare Agents (CWA) exceeded 137,000 tonnes. Germany itself produced around 65,000 tonnes of toxic agents. The most significant was the sulfur yperite, also known as mustard gas [3]. After the war, around 296,000 tonnes of chemical weapons were discovered in Germany. The largest amount of weapons was dumped in the Baltic Sea and Skagerrak Strait on the order of the British, Soviet and American military administrations in Germany. At least 150,000 tonnes of chemical weapons were dumped into Skagerrak, and about 50,000 chemical munitions containing around 13,000 tonnes of CWA are known to have been dumped in the Baltic Sea. However, due to the inadequate documentation of these operations, as well as the possible destruction of records, the actual amount could be much higher [4,5].

---

*Corresponding author. Email: chemanal@pg.gda.pl

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540802657177
http://www.informaworld.com

From the quantity of chemical ammunition and chemical toxic agents found in containers in Germany after the war, some must have been destroyed, and some dumped in the Baltic Sea and Skagerrak. The method preferred by the Western Allies was to sink damaged ships loaded with the weapons. However, four ships containing 15,000 tonnes of CWA munitions were sunk southwest of Bornholm under the supervision of the British Military Administration [3].

In addition, an unknown amount of munitions were thrown overboard on their way to the dumping area. Most probably, ships were sailing in the vicinity of the Polish coast, which has been confirmed by accidents taking place every few years [6]. Moreover Polish, Swedish and Danish fishermen are aware of the devastation that the recovered CWA canisters may cause. Every few months, dangerous objects are found which are immediately thrown back into the water. As a result, fishermen very often become burnt by the yellow liquid leaking out of corroded and leaking containers and bombs [1].

The lack of any attention to this problem over many years is surprising, despite the accidents regarding munitions. No systematic study or inventory was carried out until 1992. Finally, the Baltic Marine Environment Protection Commission (Helsinki Commission) decided to form a special working group to deal with problems connected with the dumped chemical ammunitions in the Baltic Sea and an *ad hoc* Working Group on Dumped Chemical Munitions (HELCOM CHEMU) [6].

A number of investigations have shown that a significant amount of chemical weapons became corroded, resulting in the increased rate of release of the chemicals enclosed in them. Even though an enormous amount of toxic chemical compounds undergo hydrolysis into non-toxic, or forms with low toxicity, some of them do not. According to one prognosis put forward by some specialists, the corrosion rate of the metallic canisters is about 0.5 mm/year. These canisters are 2–3 cm thick, and would therefore be completely corroded after 40–60 years [2].

The construction of the North Stream gas pipeline presents an additional problem which requires further consideration of dumped munitions. Its route will pass over the dumped weapons, which may accelerate the release of chemical warfare agents into the marine environment when disturbed [6]. It is obvious that any activities undertaken within or close to these dumped areas should be subject to a full assessment of the potential risk.

2. Types and quantities of dumped munitions and chemicals

CWA are chemical compounds which are able to interfere with the physiological functions of humans through chemical or biochemical reactions. They are used during war in order to reduce the combat ability of soldiers and they lead to death. CWA occur in gaseous, liquid or solid forms and may be sprayed or released into the air [2].

During various investigations of wrecks in the Baltic sea, several types of ammunition were found. These included bombs, artillery shells and large containers. The calibre of bombs varied from 50 kg to 250 kg. The calibre of artillery shells was difficult to define but they were estimated to be 127 mm or larger grenades. The shells were stored in wooden cases. The purpose of the large containers which were also found is not yet known but, according to several sources, it seems that they contain CWA [7].

So far, the following types of dumped toxic agents have been discovered:

- Tabun
- Sarin
- Soman
- Mustard gas
- Nitrogen mustard

- Sulfur mustard
- Phosgene
- Diphosgene
- Chloride
- Chloroacetofenon
- Hydrogen cyanide
- Cyanogen chloride
- Arsine
- Clark I
- Clark II
- Adamiste
- Lewisite
- Additives

Based on the effects caused by chemical warfare agents, we can classify them, as shown in Table 1.

The total amount of chemical agents produced by Germany during World War II has been estimated to be between 62,320 and 65,000 tonnes. The exact types of CWA produced are presented in Table 2. It is believed that there are about 60 places where ammunition was dumped in Baltic Sea waters. However, three regions are widely known: the Little Belt, Bornholm Basin and Gotland Basin. The last two are the most affected. The types and amounts of ammunition and warfare agents dumped in the Helsinki Convention Area are presented in Table 3 [2].

In addition to the estimated 35,000 tonnes of chemical weapons dumped in the east of the Bornholm Deep by the Soviet Union, the British also dumped about 8,000 tonnes of weapons, and a small amount of weapons were dumped by the German Democratic Republic. The precise amount of the dumped ammunition is very difficult to estimate. There may still be many unknown dumping sites or a number of sunken weapons which were drifting for long distances in the sea after they were thrown overboard during transportation [10].

Table 1. Classification of chemical warfare agents [2,8].

Type	Examples
Lachrymators (tear gases)	Chloroacetophenone (CAP), tear gases, pepper spray
Choking agents (pulmonary)	Phosgene, diphosgene, chlorine, hydrogen chloride
Nerve gases	Tabun, sarin, soman
Asphyxiant (nose and throat irritants)	Clark I, Clark II, Adamsite, cyanogen chloride
Blister gases	Sulfur mustard, nitrogen mustard, Lewisite
Behavioural altering agents	Ex: monochlorobenzene

Table 2. CW agents produced and stored by Germany [9].

Chloroacetophenone (CAP)	7100 tonnes
Diphenylchloroarsine (Clark I)	1500 tonnes
Diphenylcyanoarsine (Clark II)	100 tonnes
Adamsite	3900 tonnes
Arsine oil	7500 tonnes
Phosgene	5900 tonnes
Sulphur mustard	25,000 tonnes
Nitrogen mustard	2000 tonnes
Tabun	12,000 tonnes
Total (net weight)	65,000 tonnes

Table 3. Total number of chemical weapons and warfare agents dumped in the east of Bornholm and south-east of Gotland (south-west of Liepaja) [2].

Warfare agents → Munitions ↓	Mustard gas (iprit)	As-cont.	Adamsite	CAP	Others	Total
Aircraft bombs	6432	984	642	520	–	8578
Artillery shells	729	–	66	39	–	834
High-explosive bombs	341	–	–	–	–	341
Mines	46	–	–	–	–	46
Encasements	87	221	753	–	80	1141
Smoke grenades	–	–	71	–	–	71
Containers	–	1004	–	–	–	1004
Drums	–	–	20	–	–	20
Total	7635	2209	1552	559	80	12,035

3. Areas of dumped warfare weapons

Following the agreement at the Potsdam Conference of 2 August 1945 the way in which ammunition found in Germany was to be removed and destroyed was outlined. Each occupation authority was responsible for managing the stocks of munitions found in its zone. Each had its own programme of disposal [3]. The amounts of CW found in each of the occupation zones are given in Table 4.

The decision to dump the weapons into the sea was probably based on the fact that biodegradation would take too much time and destruction would be too expensive. The easiest way of disposal was therefore by simply dumping them into the sea. This method was relatively quick, easy and effective in those times. Nobody then thought about the ecological consequences of this action. Furthermore, as a result of improper actions, some of the loads were thrown overboard at unknown locations. Moreover, agents which were placed in wooden boxes floated on the water, and could drift for very long distances [9]. Munitions could therefore be located anywhere in the southern part of the Baltic Sea. Accidents take place every few years which confirm this conclusion. However, according to different publications and reports, the official areas of dumped ammunition in the Baltic Sea are assumed to be in the south-east part of the Gotland Basin, the eastern and southern parts of the Bornholm Basin and the Little Belt. At least 170,000 tonnes of chemical weapons were disposed of in the Skagerrak. In most cases, whole ships loaded with munitions were sunk there [10]. This method of dumping was a little better because it prevented the munitions from being deposited beyond the immediate area and the further spreading of the warfare agents.

British and Soviet occupation authorities sank about 42 ships at two dumping sites – in the Norwegian Trench and the Skagerrak (Table 5). However, the number of chemical weapons sunk by these authorities in the Atlantic and near Helgoland still remains unknown. It is reported that four ships loaded with 15,000 tonnes of chemical munitions were sunk in the southwest area of Bornholm under the British supervision in Germany [11].

It has also been confirmed that the American authorities disposed of an enormous amount of ammunition in the Skagerrak between Denmark and Norway and sank eight ships in the Kattegat Strait. Both these regions are frequently visited by Swedish and Danish fishermen and are situated not far from large harbours [12]. According to some reports, about 1500 tonnes of organoarsenic

Table 4. Chemical munitions found on German territory after World War II [9].

American occupation zone	93,995 tonnes
British occupation zone	122,508 tonnes
French occupation zone	9250 tonnes
Soviet occupation zone	62,505–70,500 tonnes
Total	288,000–296,000 tonnes

Table 5. Areas and quantities of munitions and chemical warfare agents dumped in the Baltic Sea [4].

Region	Quantities of munitions (t)	Estimated quantities of warfare agents (t)
Bornholm Basin	35,300 43,300 (uncertain)	5300–6500
S.W. area of Bornholm	Up to 15,000 (uncertain)	2250
Gotland Basin	2000	300
Little Belt	5000	750

irritants were dumped by the French Military administration in the Skagerrak. The Soviet authorities, however, decided to sink their part of the chemical weapons in bulk in two Baltic regions. They dumped 35,000 tonnes of chemical weapons (560,090 units with 11,077 tonnes of CWA) near Bornholm Island at a depth of about 100 m, and about 2000 tonnes (48,392 munitions units containing 958 tonnes of CWA) at a depth of 120 m between Liepaja and Gotland Island [12,13].

In addition, one report confirmed that the shallow waters of the southern Little Belt also became a dumping site for the Allies after World War II. Around 5000 tonnes of chemical weapons filled with tabun and phosgene were sunk there under German surveillance. However, those munitions have been raised and sunk in the Bay of Biscay after being encased in concrete blocks.

4. Characteristics of dumped warfare agents

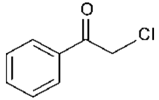
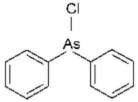
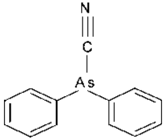
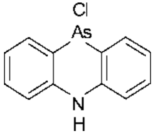
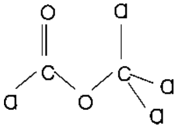
According to the Chemical Weapons Convention, an arms control agreement which outlaws the production, stockpiling and use of chemical weapons [14], chemical weapons in general mean 'munitions and devices, specifically designed to cause death or other harm through the toxic properties of the toxic chemicals which would be released as a result of the employment of such munitions and devices'. However they could also be 'any equipment specifically designed for use directly in connection with the employment of munitions described earlier' [15].

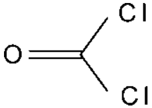
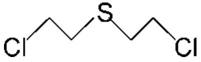
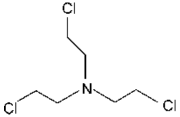
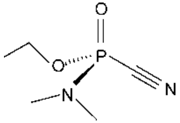
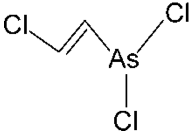
Chemical warfare agents are defined as poisonous chemicals that are utilised to cause death or disable the enemy during war or other military operations due to physiological effects. They are characterised by lethal or harmful action on people, animals and plants. They are fundamental components in chemical weapons [16]. Chemical toxic agents are most frequently liquids or solids but rarely gaseous. During war, they are used in the form of vapours and aerosols. The vapours of liquid toxic agents are generally heaver than air. Vapour buoyancy, volatility, boiling points and freezing points are very variable. Most toxic agents are soluble in fats and organic solvents. With some exceptions, they are rarely soluble in water [6].

The way that chemical warfare agents behave in the marine environment is strongly related to their physical and chemical properties, as well as to external factors. Those factors include temperature, salinity and pH. However, the average pH value of sea water is 8 (slightly alkaline). The main factors influencing the chemical reactions are therefore salinity and temperature. The solubility of the compounds as well as the speed of the chemical reactions increases with temperature. If the temperature is increased by 10 °C, then the speed of reaction almost doubles. The temperature of Baltic Sea waters varies from 0 °C to 20 °C. The reactions that occur at 20 °C are four times faster than at 0 °C. Waters above the seabed in the Baltic Sea are colder and the temperature varies from 2–12 °C. Marine currents can also accelerate the decomposition processes [2,17].

Another factor which influences the behaviour of the CWA in water is density. The density value decides whether the CWA will float at the water surface or sink to the sea-bed. Almost all of the mentioned warfare agents are characterised by a higher density than Baltic seawater (approx. 1.08 g/cm^3). As a result, they stay at the bottom of the sea after being released. The exception is tabun, with its density 1.07 g/cm^3 [18]. The most important properties of the described chemical warfare agents are shown in Table 6.

Table 6. Physicochemical properties of selected chemical warfare agents (hydrophobicity – log K_{ow}; sorption coefficient – K_{oc}; dissipation half life – DT_{50}; biodegradability – Biodeg) [1,2,24].

Chemical Warfare agent	Structure	Melting point (°C)	Boiling point (°C)	Vapour pressure (mmHg) 20 °C	Density (g/cm^3)	Water solubility (g/dm^3)	log K_{ow}	K_{oc}	Biodeg
Chloroacetophenone		54–56	244	13×10^{-3}	1.32	1	1.93	89	Not Pers
Clark I		38–44	307–333	16×10^{-4}	1.422	2	4.53	19,000	Not Pers
Clark II		30–35	290–346	47×10^{-6}	1.45	2	3.29	6980	Not Pers
Adamsite		195	410	2×10^{-13}	1.65	2×10^{-3}	4.05	5,000	Pers
Diphosgene		−57	127	10.3	1.65	Insoluble	1.49	17.4	Pers

Phogsene		−128	7,6	1.178	3.4	5	−0.71	2.2	Not Pers
Sulfur mustard		14	228	0.72	1.27	0.8	1.37	275	Pers
Nitrogen mustard		−4	235	11×10^{-3}	1.24	0,16	1.53–2.27	188–672	Pers
Tabun		−50	246	0.07	1.07	120	0.29	22.5	Not Pers
Lewisite		−18	190	0.35	1.89	0,5	2.56	18.6	Pers

The mechanism of toxic action depends on the type of CWA. The classification of those agents is shown in Table 1, but this classification is not unequivocal in many cases because some CWA are characterised by complex toxic actions. Yperite and Lewisite, for example, may cause general toxicity in addition to a burning action [2].

From the military point of view, CWA can have either lethal or incapacitating effects. It is basically connected with the class of agent, its concentration, as well as the period of exposure. CWA may also be classified as 'persistent' and 'non-persistent'. The persistent type of CWA includes the blister and nerve agents, whereas the non-persistent agents are more volatile and do not remain in an open environment for a long time.

The most frequently used and stored chemical agents are the blister agents, which cause the formation of blisters on the skin. The best known are yperite and lewisite [19].

Yperite is 2,2'-dichloro-diethyl-sulphide, and is also known as sulfur mustard. In the form of liquid or vapour, it causes skin irritation, temporary or permanent blindness as well as respiratory system disorders. Yperite is mostly found as an oily yellowish liquid which slowly vaporises at room temperature. Because of its properties, it may persist on the ground for a long time if protected from wind and rain. Sometimes other chemicals like thickeners are added in order to make it more viscous and to enhance its resistance to hydrolysis and cause its persistence to last longer [20]. Mustard gas undergoes hydrolysis under water only when dissolved. Its hydrolysis products are hydrochloric acid and thiodiglycol. However, mustard gas is only sparingly soluble in water and may persist in water for a long time. The rate of hydrolysis may be enhanced by alkalinity and higher temperature [21]. Hydrolysis in seawater may be even three times slower than in fresh water. The rates of hydrolysis are also slowed down at low temperatures. In the Skagerrak, the sulphur mustard is solid due to the temperature being 5–6 °C on the seabed. Its hydrophobicity log K_{ow} of 1.37 proves that the potential bioconcentration of yperite in aquatic organisms is rather unlikely.

The properties of viscous sulphur mustard are completely different from ordinary mustard and it behaves in a different way in the environment. It looks like wax and may remain on the seabed for many years [7]. Sulphur yperite toxicity is characterised by causing death of particular parts of an organism. It has cytotoxic, mutagenic, and blistering potential. Its chemical reactivity is based on its ability to undergo internal cyclisation of an ethylene group ($-CH_2CH_2-$) in order to form a highly reactive episulfonium ion [22]. Mustard mostly affects organs like skin, eyes, and airways when those organs are in direct contact with mustard. The first signs of skin burning after contact with yperite appear after a latent action period of 4 to 24 or more hours, depending on the dose. It is characterised by burning in the form of reddening. Small blisters start to occur after about one day, which after a while start to join to form one big blister filled with serum on the skin. The lethal dose of sulfur yperite is 40–60 $\mathrm{mgkg^{-1}}$, whereas the average lethal dose is LD_{50}-20 per kilogram of body weight. The typical signs of paralysis through the respiratory track occur after 4–6 hours and these are a painful cough, disappearance of voice and sometimes pneumonia. When yperite affects the eyes, ophthalmia, eyelid swelling and suppuration, as well as temporary blindness occur. Permanent blindness occurs after direct eye contact with a liquid drop. Toxic properties of nitrogen mustard are very similar to those described above [6,22].

Adamsite is a phenarsazine chloride and is classified as asphyxiant or a vomiting agent. It is also hardly soluble in water and therefore persists in the environment for long periods. Adamsite dissolves well only in trace amounts [4,11]. When a material is covered with water, an insoluble film forms which prevents it from further hydrolysis. Its hydrolysis products are diphenylarsenious oxide $[NH(C_6H_4)_2\,As]_2O$ and hydrochloric acid. Diphenylarsenious oxide is of the same toxicity as adamsite itself. It may be toxic through inhalation, ingestion, or skin contact. As a result, it may cause serious illness which can cause death. It can cause eye irritation, mucous membranes, cough, sneezing, severe headache, vomiting or acute pain and tightness in the chest [21]. The K_{ow} (octanol-water partition coefficient) value of 4.05 and BCF (bioconcentration factor) of 262 proves that it may be bioaccumulated in aquatic organisms [7].

Chloroacetophenone (CAP) is 2-chloro-1-phenylethanone. CAP is classified as tear gas and is insoluble in water. It may undergo very slow hydrolysis to produce hydrochloric acid and hydroxyacetophenone which are non-toxic and could decompose completely in seawater. It causes flow of tears and irritates the skin. The estimated BCF of 1 and K_{ow} of 1,93 indicates that it does not bioaccumulate in aquatic organisms [7,21,23].

Clark I and II are diphenyl arsine chloride and cyanide, respectively. Both undergo very slow hydrolysis to produce diphenylchloroarsine and hydrochloric acid (C-I), or cyanide (C-II). Diphenylchloroarsine is unstable in water and forms tetraphenyl diarsine which is more stable. The rest of the hydrolysis products are neutralised and broken down in water. Physico-chemical properties of Clark I allow us to assume that its hydrolysis products may stay on the sea floor for long periods and that it may also bioaccumulate in marine organisms [23]. Although Clark I and Clark II are both degradable, their products still contain arsenic, which is not degradable and remains toxic to humans. Both are very similar in their toxic action. They cause irritation of the eyes as well as the mucous membrane and upper respiratory track irritation. The paralysis signs are most frequently lacrimation of the eyes, coughing, sneezing, lung pain and difficulty with breathing. In most cases, those symptoms disappear after a while. However, at high concentrations, they may even lead to death as a result of permanent respiratory track paralysis [6,7].

Phosgene is carbonyl chloride. It undergoes hydrolysis readily to produce carbon dioxide and hydrochloric acid. It is classified as a choking agent. An estimated BCF of 3 and log K_{ow} of -0.71 indicate a low potential for accumulation in aquatic organisms. The predicted aquatic data indicates that it has a low toxicity. It also belongs also to an unstable group of toxic agents. Some of the symptoms are coughing with blood-red expectoration, difficulties with breathing, accelerated breathing rate, and slower heart-beat. Veins on the face and neck may also expand [7,21].

Tabun is P-cyano-N,N-dimethyl phosphoramid acid ethyl ester. It is classified as a nerve agent. It is said to be stable for many years when stored in containers at normal temperature. Tabun is a relatively persistent compound. At low temperatures, it has low vapour pressure (0.04 mm Hg at 20 °C). It is also soluble in water and typical organic solvents like alcohols, ethers, oils or fats. It does not adsorb on suspended particles or sediments. Its relatively low log K_{ow} value of 0.29 indicates that the potential for bioaccumulation in aquatic organisms is rather low. The hydrolysis products of tabun depend on the factors such as pH or reaction times. They may include cyanide ion, hydrocyanic acid, the monoethyl ester of dimethylphosphoramidic acid, ethanol, dimethylamine and phosphoric acid. The presence of phosphate increases the rate of tabun hydrolysis. Signs of paralysis with tabun include runny nose, tightness of chest, difficulty with breathing, headache, coma and narrowing of pupils. They may be followed by cessation of breathing and death [4,7,21,22].

Sarin is also known as isopropyloxymethylphosphoryl fluoride. It is classified as a nerve agent and is miscible with water. Its hydrolysis products depend on the pH of water. It produces hydrogen fluoride under acidic conditions and isopropyl alcohol and polymers under alkaline conditions. It is known that the presence of calcium and magnesium in water may accelerate hydrolysis. Sarin has very high toxicity and acts very fast. Death may occur within 15 minutes of absorption of a fatal dose. Signs of paralysis are very similar to tabun but additional symptoms may occur such as excessive sweating, vomiting, nausea, involuntary defecation and urination, and jerking [21,22].

Lewisite is a blister agent. It contains arsenic in its structure as a poisonous element. The name lewisite usually describes a technical product which is actually a mixture of three chemical isomers: 2-chlorovinyldichloroarsine (lewisite-1), bis-(2-chlorovinyl) chloroarsine (lewisite-2), and tris-(2-chloroethenyl) arsine (lewisite-3). The most poisonous agent ingredient is lewisite-1, which possesses the strongest toxic properties. It can penetrate into an organism through the skin and respiratory track. In addition to signs of poisoning, it can lead to lung oedema, diarrhea, restlessness, weakness and low blood pressure. In addition, breathing in excessive amounts of lewisite vapours may cause chronic respiratory disease, while extensive exposure of the eye may cause permanent blindness. Lewisite is insoluble in water and hydrolysis is therefore limited. Its hydrolysis products are hydrochloric acid and chlorovinyl arsine oxide. The latter products undergo further reaction in an alkaline environment to form arsenic acid and acetylene. Organisms are not able to detoxify lewisite [6,8,21].

5. Potential hazards

Because the Baltic Sea is a relatively shallow, semi-enclosed basin with limited water exchange with the North Sea, choosing the Baltic as one of the principal dumping areas for chemical weapons was not well considered. Those features make the Baltic Sea particularly sensitive for contamination. The average depth of its waters is 65 m and the amount of water which escapes to the North Sea each year does not exceed 5%. Corrosion is a major problem with dumped munitions. As corrosion proceeds, the probability of the CWA being released increases. It has been estimated that the corrosion rate of bombshells is approximately 0.05–0.5 mm/year, depending on the type of the shell. It is assumed that the CWA will be completely released after 25–265 years when 50% of the shell surface has decayed. Mustard gas is expected to be released about 125 years after dumping [4,18,24].

In some countries such as Finland, Norway, Sweden, Germany and Russia, systematic studies are being carried out to estimate the condition of the dumped weapons, and to predict the effects of their presence in the Baltic Sea. Studies are being made on actual ammunition that was recovered from the sea or observations of the munitions resting on the seabed [25].

The condition of the dumped ammunition depends on many factors: the initial thickness of the shells, bombs and other kind of munitions; the material from which these weapons were made (steel and aluminum alloys); the way it was dumped (sunk in a ship or in concrete blocks); the type of sea bottom at the dumping site, and the mechanical influence of sea currents in the area [17].

Investigations of chemical weapons carried out by the German Navy showed that artillery ammunition with a wall thickness greater than 10 mm resting on sand or gravel has corroded only a few millimetres in depth. Some of the ammunitions showed an inner overpressure caused by gases released during the decomposition of the chemical warfare agents. This creates the risk of an explosion during the excavation. Shells that are covered with mud on the sea floor are usually in rather good condition and some are even suitable to be used again, because of the suboxic conditions in the mud. However, ammunition with a casing thickness of 1.5–3.0 mm, resting on a hard bottom where the munitions are exposed to seawater, are rusted away and no longer contain chemical warfare agents [17,26].

The behaviour of the released warfare agents depends on the physical–chemical properties of the agents, as well as other external environmental factors, of which solubility is the most important. The reaction of CWA with water depends on hydrolysis that leads to the formation of new compounds with properties and toxicity different from the original CWA [11]. The solubility of warfare agents in water varies from high (like tabun) to very low (like adamsite and solid yperite). Decomposition is much slower when the agent has very low solubility. All these substances react with sea water. The products of hydrolysis are usually less toxic and in most cases dissolve well in water [23]. There have not been many investigations concerning the behaviour of individual warfare agents, which is why there is usually a lack of detailed information about ongoing processes [17]. The behaviour of each warfare agent present in the Baltic Sea has been described above.

5.1. *Coastal threat*

Two possible ways of relocating CWAs have been considered by HELCOM: relocation by currents and relocation by fishing. It has been concluded that chemical agents cannot be washed ashore while their density is higher than 1 (with the exception of tabun). In addition, the currents acting at the seabed are too weak to move heavy munitions far from the place where they were dumped or to the upper water layers. The same refers to the lumps which are formed from viscous mustard gas in seawater which have a density of 1.3–1.5 g/cm^3. Relocation of munitions by fishing crews who unwillingly bring them in their nets to the harbours seems to be more realistic [2]. Presently, only Clark I and II, adamsite and viscous yperite pose a threat when being fished up or washed ashore [26].

During the 1950s, 1960s and 1970s, various shells and aerial bombs were found on Polish beaches. They were washed onto the coast during storms mainly in the western and central part of the coast near Kołobrzeg, Mielno, Darłówko, Jastarnia and Hel [25]. The most serious accident took place in Darłówko in July 1955, when the waves washed a corroded barrel ashore, from which a brown-black liquid was leaking. As a result, over 100 children were injured, with irreversible eye injuries found in four of them. This was probably due to special care being given too late [27]. Access to the beach was immediately closed, and the contaminated area neutralised with 3 tonnes of chlorinated lime ($CaOCl_2$) poured out during the next 7 days and by harrowing the area. The beach was opened after three months following laboratory confirmation that all the yperite had disappeared [26].

The most recent case of mustard lump poisoning occurred on the Dziwnów beach in 1997. A fishing crew had been fishing about 30 miles from the harbor, when they accidentally caught a 5 kg heavy lump which they brought into the harbour in a net. As a result, eight people were burned [27]. All reported accidents concerning found chemical ammunitions are presented in Table 7.

5.2. *Threat to humans*

Except for the case of the burned children in Darłówko, the only people who have been injured by the munitions so far are fishermen. Information presented in Table 7 confirms this fact. Most

Table 7. Places of ammunition dumping, with reported cases of human injuries and fishing boats poisonings [30].

	Object	Place	Date	Kind of munition	Human poisoning
1	Beach	Dziwnów	June 1952	Ammunition with yperite	–
2	Boat	E. Bornholm	June 1952	Ammunition with yperite	–
3	Beach	Kołobrzeg	September 1952	Ammunition with yperite	–
4	Beach	Dziwnów	February 1953	Ammunition with yperite	–
5	Boat	E. Hel Peninsula	June 1954	Ammunition with yperite	–
6	Boat	Hel Peninsula	September 1954	Yperite	–
7	Beach	Hel Peninsula	November 1954	Yperite	–
8	Beach	Darłówek	July 1955	Ammunition with yperite	120 children
9	Marine dune	Jarosławiec precincts	May 1957	Cistern cont. arsenoorganic compounds	–
10	Boat	N. Kołobrzeg	May 1961	Yperite	4 fishermen
11	Boat	N. Hel Peninsula	February 1971	Yperite	–
12	Boat	N. Hel Peninsula	August 1971	Yperite	–
13	Boat	S.E. Bornholm	June 1974	Yperite	–
14	Boat	S.E. Bornholm	July 1974	Yperite	–
15	Boat	Bornholm	June 1976	Ammunition with yperite	3 fishermen
16	Boat	E. Bornholm	July 1976	Yperite	3 fishermen
17	Boat	Bornholm	June 1977	Yperite	12 fishermen burned in 1977
18	Boat	E. Bornholm	June 1976	Yperite	–
19	Boat	S.E. Bornholm	July 1977	Yperite	–
20	Boat	Bornholm	July 1977	Yperite	–
21	Boat	Bornholm	May 1979	Yperite	–
22	Boat	S.E. Bornholm	May 1979	Yperite	–
23	Boat	N.W. Hel Peninsula	June 1979	Yperite	1 fisherman
24	Boat	N.E. Władysławowo	January 1997	Yperite	4 fishermen

often munitions were accidentally caught in their nets when trawling. Very often, munitions were brought on board, where they injured fishermen unaware of the danger [28].

Because of its low solubility in water, hardened yperite presents the biggest threat of being fished up and contaminating fish and fishing equipment. During hydrolysis of yperite, a solid layer is formed, which impedes further mixing with water and makes further hydrolysis impossible. Complete dissolution of such a lump could last a very long time. Yperite lumps are probably the only toxic agent that is deposited in large amounts at the bottom of the Baltic Sea, which could cause serious damage to humans and other living organisms. However, particularly when talking about the sticky yperite, we are not aware of environmental contamination on a massive scale. So far, fishermen have only been poisoned as a result of direct contact of yperite with the skin [23].

Mustard gas as a solid or liquid causes severe damage to people when in contact with unprotected skin. It can penetrate clothing or even rubber gloves and cause blistering of the skin and irritation of the eyes. Mustard gas occurs most frequently in the east of Bornholm. Fishermen who operate in this area frequently find bombs, shells and lumps of yperite in their trawl nets [2,4]. So far, Denmark and Sweden have implemented serious rules about fisheries in risky areas, such as an obligation to carry protective clothing and first aid equipment in the vessel. There are also detailed regulations on behaviour and handling of the caught munitions. According to the decision at the 9th Meeting of the Helsinki Commission in 1988, if the caught munitions pose a threat of explosion, they will be dumped again. However, when experts do not find any risk of explosion, the munitions will be brought ashore and transported safely for destruction [2].

5.3. *Threat to the marine environment*

Almost all the chemical warfare agents dissolve in sea water. They break down at different rates into less toxic, water soluble compounds. In the type of deposition, they do not cause a significant threat to the environment. However, some of them are characterised by extremely low solubility and slow degradability. Especially, in the case of yperite, Clark I, Clark II and adamsite, we may expect them to stay in the environment for long periods and affect the environment [2]. In the case of very soluble substances, the initial concentrations of released chemicals could be high but these will decline below the toxicological limit during a relatively short period of time. The probability of the toxic concentrations of CWA staying in a large body of water for a long period of time is almost impossible. The ability of CWA to reach the surface of the sea or to contaminate masses of water to the scale that could cause an ecological catastrophe can also be excluded [23]. The probability of several weapons to be corroded at the same rate at the same time and release chemical agents into the marine environment simultaneously is unlikely [17].

In addition, when a chemical agent is released from its shell, its high concentrations would damage only those marine organisms which are present in the nearest vicinity for only a short period of time. During experiments carried out in an aquarium, acute toxicity of yperite to algae, crustaceans and fish took place at concentrations of 1–10 mg/l [17].

Viscous yperite poses a more serious problem because it hardly dissolves in water and solid lumps are being formed during its hydrolysis that can rest at the sea bottom for a long period. Its complete decomposition may last hundreds of years. Yperite lumps are probably the only CWA that is present in large quantities in the Baltic Sea that can cause injuries for humans and other living organisms under mechanical influence. Marine animals which are contaminated by mustard may be expected to develop skin lesions similar to those in humans, but the fish will not be poisonous to humans. On the other hand, these lumps do not occur in ecologically dangerous amounts [17,29].

Clark I, II and adamsite hydrolyse to form compounds containing arsenic which are still toxic and remain in water for a long time. Some of them are poisonous to marine animals at a concentration of 0.2 mg/m^3. Theoretically, Clark I and II may also be accumulated in certain marine organisms and be regarded as an environmental problem. However, this has not been reported so far [29].

Overall, knowledge of the effects that dumped munitions cause to the marine environment remains rather limited. It is still not known in detail what happens if the warfare agents are released. According to the HELCOM annual report of 1994, some ecotoxicological investigations on the effects on various types of marine organisms have been carried out for some toxic agents. The emphasis was put on mustard gas and warfare agents containing arsenic. In order to define the potential bioaccumulation of mustard gas in fish, three research series were carried. Each series did not indicate that mustard gas can bioaccumulate in fish. Experts emphasised that the arsenic still persists as an inorganic arsenic compound even after complete degradation of the substances. However, these inorganic compounds are less toxic than the warfare agents. It has never been demonstrated that arsenic bioaccumulates in marine organisms or is enriched in the surrounding sediments above background level. There have also been no cases of fish poisoning reported due to the presence of toxic agents in the Baltic Sea [2].

Information based on present knowledge permits us to conclude that a widespread risk to the marine environment from dissolved warfare agents can be excluded. No threat is posed to marine flora and fauna because of the very limited extent of the agents. Increased levels of Clark, adamsite or viscous yperite could be present on the sea floor in the vicinity of dumped ammunition. However, according to current reports, they pose no threat for the fauna and flora because of their limited extent [17].

6. Conclusion

Even though HELCOM CHEMU concludes in its final report that a threat to the coastal areas of the Helsinki Convention Area (the Baltic Sea and the entrance to the Baltic Sea bounded by the parallel of the Skaw in the Skagerrak at 57 44.43′N) caused by residues of warfare agents or chemical munitions washed ashore is rather unlikely, it still should be considered as a threat not only to the brittle and incredibly sensitive ecosystem of the Baltic Sea but also for the health and life of people, especially for fishing crews. The number of accidents that have taken place as a result of munitions either caught by fishing crews or suddenly found on the beach should be seen as sufficient evidence. Research undertaken so far permits us to localise sectors of chemical warfare dumping areas and to understand at least something about the influence of dumped stock on the ecosystem. Legal solutions, as well as the introduction of some additional methods to treat the dumped weapons, have contributed to better environmental protection. Nevertheless, new challenges and threats constantly appear in front of communities from countries located on the Baltic coasts. The major current problem is the progressive corrosion which attacks the ammunition cases and containers with CWAs, so that their content may be more readily released. Trying to move and raise the munitions for safe destruction from the present dumping sites seems to pose serious danger, as the movement may cause rapid and extensive release of the chemical agents. Nevertheless, it would be possible with some modern techniques and equipment, although the cost of such operations would be extremely high.

The planned North European Gas Pipeline (Nord Stream) construction represents another serious problem, which may have a negative influence on ammunition storage on the Baltic seabed, and which may accelerate the potential for ecological catastrophe. Only determined legal and investigative actions may solve this problem.

Acknowledgements

We are grateful to Dr G.P. Glasby for his constructive comments and suggestions and for extensive editing of this manuscript.

References

[1] H. Sanderson, P. Fauser, M. Thomsen, and P.B. Sorensen, *PBT screening profile of chemical warfare agents*, J. Hazard. Mater. 148 (1997), pp. 210–215.

[2] HELCOM. *Report on chemical munitions dumped in the Baltic Sea*. Report to the 16th Meeting of Helsinki Commission, 8–11 March 1994, HELCOM CHEMU 1994, 43.

[3] J. Matousek, *Environmental threats posed by the sea-dumped and earth-buried chemical weapons in the Central-European and Baltic region*. Proceedings of the 6th International Symposium on Environmental Contamination in Central and Eastern Europe and the Commonwealth of Independent States, Prague, 2003, pp. 146–152.

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

[5] OSPAR Commission 2005, *Overview of Past Dumping At Sea of Chemical Weapons and Munitions in the OSPAR Maritime Area*, Biodiversity Series: OSPAR Commission; available at: http://www.ospar.org/documents/dbase/publications/

[6] T. Kasperek, *Chemical Weapons Dumped in the Baltic Sea*, Adam Marszałek Publishing, Toruñ, 1999.

[7] J.A Tørnes, Ø.A. Voie, M. Ljønes, A.M. Opstad, L.H. Bjerkeseth, and F. Hussain, *Investigation and risk assessment of ships loaded with chemical ammunition scuttled in the Skagerrak*, SFT Internal Report TA-1907/2002.

[8] S. Chauhan, S. Chauhan, R. D'Cruz, S. Faruqi, K.K. Singh, S. Varma, M. Singh, and V. Karthik, *Chemical warfare agents*, Environ. Toxicol. Pharmacol. 26 (2008), pp. 113–122.

[9] E. Andrulewicz, *War gases and ammunition in the Polish economic zone of the Baltic Sea*, in *Sea-Dumped Chemical Weapons: Aspects, Problems and Solutions*, A.V. Kaffka, ed., NATO ASI Series 7 (1996), pp. 9–15.

[10] W. Paka, *Deployment, Toxicity and Influence on the Environment and Other Issues Connected with Sea-Dumped Chemical Weapons*, Shirshov Institute of Oceanology, Kaliningrad, 2007.

[11] E. Andrulewicz, *Chemical Weapons Dumped in the Baltic Sea*, in *Assessment of the Fate and Effects of Toxic Agents on Water Resources*, I.E. Gönenç, V.G. Koutitonsky, B. Rashleigh, R.B. Jr Ambrose, and J.P. Wolfin, eds., Springer, New York, 2006, pp. 299–319.

[12] A. Pilarczyk, *Martwe Morze*. Magazyn Wileñski [*Dead Sea*. Vilnius Magazine] 2 (2006), pp. 26–28.

[13] G.V. Lisichkin, *Chemical weapons on the seabed*, in *Sea-Dumped Chemical Weapons: Aspects, Problems and Solutions*, A.V. Kaffka, ed., NATO ASI Series, 7 (1996), pp. 121–128

[14] Wikipedia. 'Chemical Weapons Convention'. Available at: www.wikipedia.org

[15] Organization for the prohibition of chemical weapons. The CW convention. Available at: http://www.opcw.org/html/db/cwc/eng/cwc_frameset.html

[16] Y. Sun and Y. Ong Kwok, *Detection Technologies for chemical warfare agents and Toxic Vapours*, CRC Press LLC, New York, 2004.

[17] E. Smolnicka, *Amunicja Chemiczna w Morzu Bałtyckim*. (Eng: Chemical ammunition in the Baltic Sea) Source: *Chemical Munitions In the Southern and Western Baltic Sea*, Report by the Federal/Lander Government Working Group, 1993.

[18] T. Stock, *Sea-dumped chemical weapons and the chemical weapons convention*, in *Sea-Dumped Chemical Weapons: Aspects, Problems and Solutions*, A.V. Kaffka, ed., NATO ASI Series, 7 (1996), pp. 49–66.

[19] D.H. Moore and S.M. Alexander, *Emergency response to a chemical warfare agent incident: domestic preparadeness, first response, and public health considereations*, in *Chemical Warfare Agents – Toxicity at Low Levels*, J.A. Romano and S.M. Somani, eds., CRC Press, USA, 1996, 414–419.

[20] B. Riley, *The toxicology and treatment of injuries from chemical warfare agents*, Curr. Anaes. Crit. Care 14 (2003), pp. 149–154.

[21] S.L. Hoenig, *Compendium of Chemical Warfare Agents*, Springer Science, LLC, 2007.

[22] P. Kikilo, V. Fedorenko, and A.L. Ternay, *Chemistry of chemical warfare agents*, in *Chemical Warfare Agents – Chemistry, Pharmacology, Toxicology and Therapeutics*, J.A. Romano Jr, ed., CRC Press, New York, 2008.

[23] E. Andrulewicz, *Przewidywane losy amunicji chemicznej i bojowych środków trujących (BST) zatopionych w Morzu Bałtyckim*. [Predicted fate of chemical ammunition and toxic warfare agents dumped in the Baltic Sea], Morski Instytut Rybacki w Gdyni.

[24] H. Sanderson, P. Fauser, M. Thomsen, and P.B. Sørensen, *Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea*, J. Hazard. Mater. 154 (2007), pp. 846–857.

[25] S. Popiel, Z. Witkiewicz, and A. Świątkowski, *Amunicja Chemiczna Zatopiona w Morzu Bałtyckim*. [Chemical Ammunition dumped In the Baltic Sea], Military Academy (WAT), Warsaw, 1996.

[26] K. Korzeniewski, *Bojowe środki trujące w wodach południowego Bałtyku*. [War Gases in the Southern Baltic Sea], Wiadomości Chemiczne, 50 (1996), pp. 9–10.

[27] P. Miller, *Bałtyk Nadziewany Chemią*, available at: http://militaria.wp.pl/kat,27305,wid,9299951,wiadomosc.html

[28] Noblis website. Available at: http://www.noblis.org/OceanDumpingOfChemicalWeapons.htm

[29] F. Fonnum, *Examination of CV Ammunition in the Norwegian Sea – Possible Environmental Impact*, NILU, Kjeller, Norway, 1993.

[30] Raport *II Konferencja Naukowa, Zarządzanie Kryzysowe*, [Report on the II Scientific Conference, Recessionary Management], Szczecin, 2004. Available at: http://www.wsm.szczecin.pl/userfiles/File/konferencje/wiet/IIzzk.pdf