# CHEMICAL WARFARE AGENTS IN THE BALTIC SEA

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# **ABSTRACTS**

The practice of sinking German chemical warfare agents (CWA), mainly sulphur mustard, was implemented in the years 1946-1947. At that time nearly 300 thousand tonnes of CWA were deposited, mostly in the Baltic Sea. Due to the dangerous and costly process of CWA recovery and neutralisation, the only possible manner of proceeding consists in their close monitoring. Still, there are occasional reports on sulphur mustard burns of fishermen, holidaymakers or divers.

Key words: chemical warfare agents, the Baltic Sea, hazards for divers, sulphur mustard.

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Chemical warfare agents (CWA) are chemical compounds in the form of gases, liquids or solids, with diversified toxic effects on living organisms, from generally poisonous, asphyxiating, irritating, burning to paralytic and convulsive.

Mass use of CWA took place during World War I in France. In the years 1914-1918 the production reached the total of 180 thousand tons, with 125 thousand tons used in combat. Between 1919-1939 and during the period of World War II, the production of CWA was maintained at the same level. However, the character of the production did change. At that time, newly discovered phosphoorganic compounds began to be used tabun and sarin. Sulphur mustard, lewisite and adamsite on the other hand still maintained their significance among warfare agents.

The issues related to CWA are existent in China, Japan, Italy, England, France, Canada and a number of other countries. Their large quantities, including both the deposits from World War I and World War II and those manufactured in the period between the wars have been and still will be subjected to destructive processes. The destruction of the enormous CWA arsenals was based mostly on their "safe dispersion", burying in the ground, burning in open spaces, and, more seldom, on chemical neutralisation. However, commonly chemical weapons were disposed of by being sunken in the seas and oceans. The locations where chemical ammunition were dumped in large quantities include: the Atlantic Ocean, the Pacific, the Bay of Biscay; and the seas: the Baltic Sea, the North Sea, the White Sea, the Sea of Okhotsk, the Kara Sea, the Barents Sea and the Sea of Japan [1,2,3].

The sinking of German chemical ammunition was executed mainly in the years 1946-1947. Approximately 300 thousand tons were sunk in that period in the North Sea, in the Skagerrak and Kattegat areas as well as in the Baltic Sea, mainly in the Bornholm and Gotland Depth and 26 miles to the north-east from Kołobrzeg, 24 miles to the north-east from Ustka and 5-10 miles to the north-east from Hel.

About 42-65 thousand tons of ammunition containing 6-13 thousand tons of CWA were deposited in the Baltic Sea. The chemical agents were placed in ca. 600 thousand pieces of ammunition and containers. The ammunition mainly consisted of artillery ammunition (105-150 mm), aerial bombs (50, 250, 500 kg), mines, fougasses, flares and smoke grenades. The containers included mainly barrels and canisters [6].

According to current knowledge, the most hazardous CWA sunken in the seas with regard to humans is sulphur mustard. Therefore, our further deliberations will be concerned with this particular toxic substance [7].

As a consequence of postwar liquidation of chemical weapons consisting in their sinkage in different locations, the "king" among the toxic warfare agents – sulphur mustard - has been resting on the bottom of the Baltic, rocked by the waves for several dozen years now. From time to time it enters in to contact (mainly due to the activities of man) with fishermen, or, on rarer occasions, with holidaymakers. Divers are also at risk of interaction with sulphur mustard, especially since diving has become a very fashionable sport. In Poland there are already several hundred thousand people that engage in recreational diving, and this number tends to grow on a year-to-year basis. Diving in the Baltic is particularly attractive as at the bottom of this relatively small and shallow body of water one may find approximately a thousand shipwrecks.

Due to a growing demand for "the Baltic gold" - amber, constant attempts are made at its recovery from the sea bottom, thus leading to an increased risk of coming into contact with sulphur mustard, which may resemble a piece of amber or clay.

Sulphur mustard, the main toxic warfare agent from the group of burning agents, is an oily liquid with dark-brown colour (colourless in chemically pure form) and with a faint scent of garlic or mustard. It easily infiltrates organic materials (skin, wood, rubber) and poriferous materials. It is characterised by poor solubility in water, whereas it is soluble in organic solvents and in fats. Sulphur mustard slowly hydrolyses in water into hydrochloric

acid and thiodiglycol - a non-toxic compound. Chloramines in dichloroethane solution and other solvents react violently with sulphur mustard thus causing its deactivation, which is used in its removal from the skin and equipment.

Its local effects include lesions on the skin, in the respiratory tract, in the conjuctiva and the eyeballs as well as in the alimentary tract. The duration of its latent effect ranges from 2 to 24 hours, depending on the quantity, the place of absorbance and individual properties of a given organism. Sulphur mustard settling on human skin in the form of drops, fog and vapour is absorbed quickly, without causing pain. After several hours, red marks and swelling appear on the skin, producing an itching sensation. The erythema recedes after a certain time, first adopting a violet and then brown colour. In more severe cases, blisters occur at the end of the first 24-hour period, and usually later become combined into larger ones, filled with transparent yellow liquid. The blisters are highly sensitive to mechanical injuiries and secondary infections. The occurrence of blisters is commonly accompanied with general weakness and an increased body temperature. After 2-3 days the blisters burst and turn into deep and hard to heal (for weeks) skin ulceration. Often, granulation begins to form as late as after the lapse of 30-40 days. The minimum dose causing skin erythema amounts to 0.07 mg/cm<sup>2</sup>. Sulphur mustard is a cellular poison that easily combines with various cell components such as aminoacids, peptides and protein through their alkylation. The cytotoxic effects take the form of metabolic disorders in a cell, such as damaging of cellular enzymes, irregular cell division and disintegration. The macroscopic image reveals the formation of blisters and ulceration of the skin and, damageing toof the bone marrow and parenchymal organs.

Within the Polish economic zone of the Baltic Sea, 23 contacts with CWA were reported, mainly in the 1950s and 1970s. This is shown in tab. 1.

Tab 1.

The number of contacts with sulphur mustard recovered from the Baltic Sea in particular years.

| Year | Quanti-<br>ty | - Year | Quanti-<br>ty |
|------|---------------|------|---------------|------|---------------|------|---------------|------|---------------|--------|---------------|
| 1952 | 3             | 1953 | 1             | 1954 | 3             | 1955 | 1             | 1961 | 1             | 1971   | 2             |
| 1974 | 2             | 1976 | 2             | 1977 | 4             | 1979 | 3             | 1997 | 1             |        |               |

The cases of burns with sulphur mustard recovered from the Baltic Sea were reported: in 1955, on a beach, affecting 120 children from Żywiec having a summer camp; in 1961 four fishermen from Kołobrzeg were burned with sulphur mustard; in 1976- six fishermen from Darłowo; in 1977 - twelve fishermen from Kołobrzeg, Darłowo and Ustka; in 1979 - four fishermen from Kołobrzeg and Władysławowo; in 1997 - four fishermen from Władysławowo. In total 165 people, including 45 fishermen, were contaminated due to contact with sulphur mustard [4,5,6].

However, this number should be expanded to include an additional 92 people, these being: 60 Polish fishermen delivering fish on Bornholm as well as another 32 Polish workers at a fish-processing plant on Iceland, processing fish caught in the Baltic Sea.

Moreover, fishermen from Denmark, Germany and Sweden are known to come into contact with sulphur mustard. For instance since 1976, 439 such contacts were reported in Denmark, with 101 of them taking place in 1991 (in Denmark each fishermen who has a confirmed contact with sulphur mustard in areas beyond the CWA dumping sites is compensated financially, whereas Polish fishermen unfortunately are not entitled to any such benefits).

At the moment, there are no recently publicised reports on the issues related to the CWA deposits in the Baltic Sea. However, after the incident of 1997 involving fishermen from Władysławo, a number of articles were published with such sensational titles as: "A Bomb Dumpster", "The Mustard Sea", "Death Waiting in the Baltic", "The Skull-Marked Baltic".

The last contact of Polish fishermen with sulphur mustard took place on 09/01/1997. On that day, the crew of a fishing boat WŁA-206 was fishing 20 miles to the north of Władysławowo. The catch consisted of ca. 30 kg of fish and ca. 6

kg of a substance resembling a piece of amber. During the next trawl there was a failure and the boat returned to port, where the unidentified substance was thrown away into a dumpster. On 10/01/1997 at 12.00 pm, a medical officer of PPiUR (Fisheries and Fishery Services Company) "Szkuner" from Władysławowo informed via telephone the National Sanitary Inspectorate in Puck on having examined patients with burns on the hands and face due to contact with an unknown chemical substance - these were the fishermen from the fishing boat WŁA-206. This information was reported by an employee of the Inspectorate to:

- 1. State Local Sanitary Inspection in Gdańsk,
- 2. Labour Inspection in Gdańsk,
- 3. Maritime Office in Gdynia,
- 4. Institute of Marine and Tropical Medicine in Gdynia,
- 5. Veterinary Sanitary Inspection in Puck,
- 6. Management of PPiUR "Szkuner" in Władysławowo,
- 7. Port Authorities of Władysławowo,
- 8. Border Guard Units in Władysławowo.

This took place on Friday between 12.00 pm-2.00 pm. The operation revealed a complete lack of knowledge among people answering the phones with regard to procedures adopted in such situations. Some of them even recommended waiting until Monday, as it was the end of the working day on a Friday before the weekend.

On the same day, at 6.20 pm a group of experts from the 55<sup>th</sup> Company for the Protection of Chemical Warfare Agents of the Polish Navy arrived and began neutralisation of the boat, dumpster and the landfill onto which the contents of the dumpster had been transported. Eight fishermen with burns were transferred to the Naval Hospital in Gdańsk. In the admission room, four of the patients were qualified for hospitalised treatment and four for out-patients' clinic treatment.

The applied treatment involved local therapy, antibiotic therapy and surgical treatment (removal of skin necrosis).

Patient T.C., aged 19, hospitalised from 10.01. to 05.02.1997 due to: I/II° chemical burns of the face in the frontal areas, areas of the orbital cavities and cheeks. II° burn of the dorsum of the penis. I° burn in the neck and nape areas. In total, the burns covered approximately 7% of the body. The first symptoms in form of burning erythematous changes appeared after more than ten hours from the recovery of unknown substance. On the third hospitalisation day, blisters filled with serous fluid were formed in the frontal area of the face, the outer corner of the right eye, as well as on the skin on the dorsum of the penis. After the blisters burst, they were replaced with erosions and shallow, difficult to heal ulceration. The applied treatment resulted in healing of all the cutaneous lesions.

Patient M.J., aged 34, hospitalised from 10/01 to 29/01/1997 due to: I° chemical burn of the skin on the left cheek and orbital cavity, I/II° chemical burns of the  $1^{st}$ ,  $4^{th}$  and  $5^{th}$  fingers of the left hand and the  $2^{nd}$  finger of the right hand.

In total, the burns covered approximately 4% of the body. Patient T.C., aged 41, hospitalised from 10.01. to05.02.1997 due to: I/II° chemical burn of the face in the right eye area, and the areas of the neck and nape. I/II° chemical burn of interdigital spaces between the  $2^{\text{nd}}$ - $3^{\text{rd}}$  and  $2^{\text{nd}}$ - $4^{\text{th}}$  fingers of the left hand. I/II° chemical burn of the skin of

the dorsum of the penis. In total, the burns covered 8% of the body. According to the patient's relation, an object was recovered when the fishing net was being pulled up, which he then transferred onto the deck, and, after reaching the port, again from the deck into the quay.

Patient T.C., aged 46, hospitalised from 10.01. to 05.02.1997 due to: I/II° chemical burns of the skin (both upper extremities, upper areas of the hands, forearms and arms). In total, the burns covered approximately 16% of the body.

The non-hospitalised fishermen were diagnosed with I° burns on the hands or face, affecting small areas that did not exceed 1% of the body surface. The diversity in the intensification of skin contamination was caused by differences in the duration and surface of the contact with a toxic substance, i.e. the sulphur mustard. It should also be noted that the burns of the lowest intensity occurred in persons wearing protective gloves. The only explanation for the detection of burns in persons not having direct contact with sulphur mustard was the fact of using a shared towel as well as other objects present on the deck of the contaminated boat by crew members. The occurrence of cutaneous lesions on the covered parts of the body was a consequence of touching them with contaminated hands. All of the hospitalised patients were discharged in good condition [4,5].

## THE PROCEDURE IN THE CASE OF A DIRECT CONTACT OF HUMANS WITH CWA

- 1. The unidentified objects recovered on the beach or in the waters of the Baltic Sea (for instance, resembling a clump of clay or a piece of amber) must not be touched with bare hands.
- 2. An unknown substance should be removed from the skin with dry gauze or cotton wool.
- 3. The contaminated area should be washed with warm water and soap.
- 4. Wash the contaminated area with 5% monochloramine solution.
- 5. Use the Individual Anti Chemical Set IPP.
- 6. Do not use organic solvents (alcohol, petrol, petroleum, fuel oil).
- 7. Notify the nearest military unit, police department, border guard service or health care service.

After the incident involving the burning of fishermen from Władysławowo with sulphur mustard in January 1997, Maritime Offices prepared an "Instruction for proceeding in the case of recovery of chemical ammunition". Such an instruction may now be found on each fishing boat, and the crews are required to be familiarised with its content and know how to use the Individual Anti-Chemical Sets.

The Individual Anti-Chemical Set (IPP) contains a powder decontaminator and an organic decontaminator in the form of an aerosol. IPP was prepared by employees of the Institute of Marine and Tropical Medicine of Gdynia as well as employees of the Military Institute of Chemistry and Radiometry of Warsaw (KBN grant no. 0 T00A 054 20 entitled "The methodology and security measures against contamination with sulphur mustard and lewisite sunken in the Baltic Sea with regard to navigating crews", in the years 2001-2002; the head of the grant: Prof. Romuald Olszański, Ph.D., M.D.).

In discussing the problem related to large quantities of CWA lingering on the bottom of the Baltic Sea, ecologists try to consider the possibilities of recovering and neutralising at least some of the substances which are particularly hazardous to humans. However, specialists estimate that such an operation, although being technically possible, would be exceptionally difficult and dangerous. It is commonly known that even if it is possible to recover chemical weapons from water, their neutralisation is 10 times more expensive than their production.

Thus far, no cost simulation has been executed with regard to such an operation. However, several firms specialised in performing works at sea have come forward with

a proposal to cover the chemical ammunition with a layer of concrete or polymer. In the opinion of the opponents of this undertaking, such a solution would be unbelievably costly and could provide no guarantee regarding the achievement of the desired effects. Hence, due to the dangerous and costly process of CWA recovery and neutralisation, the only viable procedure consists in the monitoring of their dumping **SITES** in the Baltic Sea.

## **CONCLUSIONS**

- 1. Fishermen and divers should be aware of the risks connected with the presence of CWA in the Baltic Sea.
- 2. It is essential to comply with the agreed procedure in the case of suspicion of a direct contact with CWA (e.g. a clump of clay or a piece of amber).
- 3. Organisers of camps and diving schools should be equipped with individual antichemical packages and familiarise the participants with their use.

In 2011, an international research project was activated within the 8th Regional Programme for the Baltic Sea (2007-2013) under the name "Chemical munitions search and assessment" (CHEMSEA). The originator and initiators of the project were the Naval Academy of Gdynia and the Institute of Oceanology of the Polish Academy of Sciences of Sopot. The project associates 11 research institutions from 5 Baltic countries: Poland, Sweden, Finland, Germany and Lithuania.

The executors of the CHEMSEA project have undertaken to verify a hypothesis on the chemical ammunitions sunk around the Depth of Gdańsk and the Gotland Depth, estimate the concentration of chemical warfare agents and products of their degradation in seabed sediment in the vicinity of the finding, as well as assess the risk related to accidental or natural release of those substances into the pelagic zone. The end product of the project will consist in the production of maps of contaminated regions, models allowing the estimation of contamination spread in the case of damage to containers or contaminated seabed sediment and a complex risk assessment related to the chemical weapons lingering on the bottom of the Baltic Sea.

## **BIBLIOGRAPHY**

- 1. Andrulewicz E., Wielgat M., Anticipated fate of the chemical ammunition and chemical warfare agents (CWA) sunken in the Baltic Sea, Materials from scientific symposium, 22.04.1997 r. "Chemical weapons sunken in the Baltic Sea", AMW, Gdynia, 1998.
- 2. Barański J., Chemical ammunition sunken in the Baltic Sea, an unpublished work, Gdynia 1997.
- 3. Fabisiak J., Olejnik A., Sunken chemical ammunition in the Baltic Sea research and risk assessment CHEMSEA Scientific Programme, Bulletin PTMiTH no. 2, 2012. Gdynia.
- 4. Filipek B., Olszański R., Chemical warfare agents in the Baltic Sea proceeding in the case of a direct contact with CWA. Safety aspects regarding water and underwater practices and flights over the sea, DMW, Gdynia 2001.
- 5. Filipek B., Olszański R., Harmata W., Chemical warfare agents vs. diving in the Baltic Sea. Safety aspects regarding water and underwater practices and flights over the sea, DMW, Gdynia 2002.
- 6. Kasperek T., Sunken chemical weapons in the Baltic Sea, Wydawnictwo A. Marszałek, Toruń 1999.
- 7. Report from the implementation of a research project no. 0 T00A 054 20 entitled "The methodology and security measures against contamination with sulphur mustard and lewisite sunken in the Baltic Sea with regard to navigating crews" Warsaw 2003.

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