

# CHEMSEA FINDINGS

**RESULTS FROM THE CHEMSEA PROJECT –  
CHEMICAL MUNITIONS SEARCH AND ASSESSMENT**





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THE CHEMSEA PROJECT –  
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## GLOSSARY

### **Atomic Absorption Spectrophotometry (AAS):**

AAS is a procedure for quantitatively determining chemical element composition by measuring the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element in a sample to be analyzed such as for example the concentration of metals in a water sample.

### **Acoustic Doppler Current Profiler (ADCP)**

ADCP is a sonar that measures water current velocities at a range of depths. They can be mounted on boats or moorings for short-term surveys or attached to the seabed for long term current and wave studies.

### **Adamsite**

Adamsite is an organic compound traditionally used as a chemical warfare agent. It is an arsenical diphenylaminechlorarsine, an odourless crystalline compound, usually dispersed as aerosol and which affects the upper respiratory tract. It was first synthesized in Germany in 1915 and used during World War I.

### **Baltic Sea Region Strategy (EUSBSR)**

Initiated by the European Parliament and coordinated by the European Commission, the EUSBSR aims to save the sea and increase prosperity in the Baltic Sea Region while shaping the region into a regional cooperation model for the whole EU. The implementation of the strategy is financed from different EU funds in the area including the Baltic Sea Region Programme. The Commission officially launched the Strategy and its Action Plan on 10 June 2009 and it was adopted by the European Council on the 26 October 2009.

### **Bathymetry**

Bathymetry is the study of underwater depth of lake and ocean floors. The information for bathymetric maps today usually comes from an echosounder (a sonar mounted under a boat which sends a beam of sound downward at the seafloor and measures the time it takes for it to bounce off the floor and return) or from remote sensing LIDAR/LADAR systems (same principle but using light or a laser from an airborne device).

### **Bioaccumulation**

Bioaccumulation refers to the accumulation of substances such as chemicals or toxic substances in an organism that occurs when its absorption rate is greater than the rate at which the substance is lost. It can lead to chronic poisoning even if environmental levels of the toxin are not very high. In fish, bioaccumulation can be predicted by models.

### **Biohazard**

A biological hazard refers to a biological substance that poses a threat to the health of living organisms.

### **Biomarker**

A biological marker is an indicator of a biological state. It is a characteristic that is measured and evaluated as an indicator of normal biological or pathogenic processes. Biomarkers are used to indicate an exposure to chemicals in the environment by an organism.

### **Blister agent**

A blister agent, also known as a vesicant, is a chemical compound causing severe skin, eye and mucosal pain and irritation, as do many chemical warfare agents. There are three groups of blister agents: 1) Sulphur mustards (including mustard gas), 2) Nitrogen mustards, and 3) Lewisite (an early blister agent developed but not used during World War I).

### **Chemical munitions**

Munitions containing chemical agents.

### **Chemical warfare agents (CWA)**

CWAs are chemical substances whose toxic properties are used to kill, injure or incapacitate. About 70 different chemicals have been used or stockpiled as chemical warfare agents in the 20th century. CWAs may be in liquid, gas or solid form. They are generally organized into categories according to the physiological manner in which they affect the human body (e.g. blood agents, blister agents, nerve agents, pulmonary agents).

### **Chemical Weapons Convention (CWC)**

The Chemical Weapons Convention or Convention for the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and Their Destruction is an arms control agreement that aims prohibit the development, production, acquisition, stockpiling, transfer or use of chemical weapons by State Parties. It came into effect in 1993 and is administered by the Organisation for the Prohibition of Chemical Weapons (OPCW), an independent organization based in the Netherlands. As of January 2014, 190 state parties have joined the CWC and around 82% of declared stockpiles of chemical weapons have been destroyed.

### **Chloroacetophenone**

Chloroacetophenone is a poisonous crystalline chemical used in solution as a tear gas, irritating the eyes.

### **Clark I**

Clark I is the common name for diphenylarsinchlorid, an odourless toxic liquid compound once used as chemical weapon during World War I. It belongs to the chemicals classified as vomiting agents.

### **Clark II**

Clark II is the common name for diphenylcyanoarsine, a colourless, garlic-smelling crystal chemical that causes nausea, vomiting and headaches. It was used as a chemical weapon during World War I.

### **Ecological risk assessment (ERA)**

Ecological risk assessments are conducted to evaluate the likelihood that adverse ecological effects could result from the exposure to one or more chemical or radiological contaminants in the environment. An ERA provides a way to develop, organize and present scientific information so that it is relevant to environmental decisions.

### **Ecotoxicity**

Ecotoxicity refers to the potential for biological, chemical or physical stressors to affect ecosystems. Ecotoxicity studies measure the effects of chemicals on fish, wildlife, plants and other wild organisms.

### **HELCOM**

HELCOM is The Baltic Marine Environment Protection Commission (Helsinki Commission). It is an intergovernmental organization governing the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention). HELCOM works to protect the marine environment of the Baltic Sea from all sources of pollution.

### **Hydrodynamic model**

Hydrodynamics is the study of the motion of liquids, in particular water. A hydrodynamic model is a tool for describing or representing in some way the motion of water.

### **Inductively coupled plasma mass spectrometry (ICP-MS)**

Mass spectrometry is an analytical technique that measures the ratio of mass-to-charge of charged particles. It is used for determining masses of particles, the elemental composition of a sample or molecule or the chemical structures of molecules. Inductively coupled plasma mass spectrometry is a type of mass spectrometry capable of detecting metals and some non-metals at concentrations as low as one part per trillion (one in 10<sup>12</sup>). In ICP-MS the sample is first ionized (i.e. converting the atom or molecule into an ion by adding or removing charged particles such as electrons or ions) with inductively coupled plasma. This is a type of plasma source in which energy is supplied by electric currents produced by electromagnetic induction (time-varying magnetic fields). A mass spectrometer is then used to separate and quantify the ions.



**Magnetometry**

Magnetometry refers to the study of the magnitude and direction of a magnetic field.

**Multibeam echosounder**

Echo sounding is the technique of using sound pulses to find the depth of water. The interval from the emission of a pulse to reception of its echo is recorded, and the depth calculated from the known speed of propagation of sound through water. Multibeam echosounders were developed in the 1970s to map large swaths of the ocean floor. They produce multiple acoustic beams across a broad swath.

**Mustard gas**

Mustard gas (named also Yperite) is the common name for sulphur gas, a class of chemical warfare agent with the ability to form large blisters on exposed skin and lungs. Sulphur mustards are colourless, viscous liquids with an odour resembling mustard plants or garlic, hence the name. They were originally developed to be produced in large scale for the Imperial German Army in 1916. They are now regulated under the Chemical Weapons Convention.

**Nerve gas/nerve agent**

Nerve agents are a class of phosphorus-containing organic chemicals that disrupt the mechanism by which nerves transfer messages to organs. Some nerve agents are readily vaporized or aerosolized and the primary portal of entry into the body is the respiratory system. Nerve agents can also be absorbed through the skin. They include such chemicals as tabun, sarin and soman. The first class of nerve agents was discovered in Germany in 1936 with the intent of developing insecticides. They were then produced as chemical weapons during World War II, though never used. They are now regulated under the Chemical Weapons Convention.

**Nitrogen mustard**

Nitrogen mustard is a chemical agent similar to mustard gas, also developed as a chemical warfare agent and stockpiled by several nations during World War II. It belongs to the category of blister agents. It is currently regulated by the Chemical Weapons Convention.

**Remotely Operated Vehicle (ROV)**

A remotely operated vehicle is a tethered underwater vehicle that is unoccupied and operated by a person aboard a vessel. It is linked to the ship by a group of cables carrying electrical power, video and data signals back and forth between the operator and the vehicle. ROVs can be equipped with video cameras, lights, sonars, magnetometers, water samplers, thermometers and other instruments.

**Side Scan Sonar (SSS)**

A side scan sonar is a type of sonar used to create images of large areas of the sea floor. Side scan sonar imagery is commonly used to detect debris or other items on the sea floor. The device is usually towed from a surface vessel and functions by emitting conical or fan-shaped pulses down towards the sea floor across a wide angle perpendicular to the path of the sensor through the water. The intensity of the acoustic reflections from the sea floor is recorded in a series of cross-track slices, which when stitched together along the direction of the motion, form an image of the sea bottom within the width of the beam.

**Sulphur mustard**

See mustard gas.

**Tabun**

Tabun is a type of nerve agent. It is an extremely toxic chemical substance that comes in a colourless and tasteless liquid form with a fruity odour. It was produced industrially as a chemical weapon agent during World War II. Today its production is strictly controlled and stockpiling is outlawed by the Chemical Weapons Convention.

**Tear gas**

Tear gas, also known as lachrymatory agent or lachrymator, is a non-lethal chemical weapon that stimulates the eyes to cause tears, pain and even blindness. Tear gas is commonly used as riot control and chemical warfare agents, though military use of tear gas is prohibited by the Chemical Weapons Convention.

**Vessel Traffic Service (VTS)**

Any service implemented by a relevant authority primarily designed to improve safety and efficiency of traffic flow and the protection of the environment. It may range from simple information messages, to extensive organization of the traffic involving national or regional schemes.

**Search and Rescue (SAR)**

"Search and Rescue" means the use of available resources to assist persons and property in potential or actual distress. Several international conventions address SAR at sea and the obligations of a state and of the master of a vessel. States which are parties to the International Convention for the Safety of Life at Sea, 1974 (SOLAS), the 1982 LOS Convention, or the Convention on the High Seas, 1958, are required to set up SAR organizations.

**Maritime Rescue Coordination Centre (MRCC)**

Is where distress calls and all emergency notifications converge and missions are coordinated. Maritime Rescue Coordination Centre is responsible for leading the entire marine SAR mission. The centre provides planning, management, co-ordination, realisation and completion of the SAR interventions.

**Joint Rescue Coordination Centre Trenton (JRCC)**

Is a rescue coordination centre responsible for coordinating the Search and Rescue (SAR) response to both air and marine incidents.

**Harbour Master**

Is an official responsible for enforcing the regulations of a particular harbour or port, in order to ensure the safety of navigation, the security of the harbour and the correct operation of the port facilities.



## INTRODUCTION

Chemical weapons (CW) were produced in mass during both World War (WW) I and II, but those made during WWII were never used in the European Theatre. At the end of WWII vast quantities of German chemical warfare agents (CWA) were stored in Wolgast on the Baltic shore. By far the largest part of these weapons was dumped in the Baltic Sea and Skagerrak Strait on the orders of British, Russian and American occupation authorities. At least 170,000 tonnes of CW were dumped in the Skagerrak, mainly in the Norwegian trench and in the eastern Skagerrak, off the Swedish coast. During most of the dumping operations in the Skagerrak complete ships were sunk with their cargo. In the Baltic Sea at least 50,000 tonnes of CW were dumped and it is assumed that these contained roughly 15,000 tonnes of CWA. The most important dumpsites here are located in the Little Belt, near the island of Bornholm and in the Gotland basin. In most cases, the CW were thrown overboard, either loose (bombs, shells) or in containers, but some ships were also sunk. In most cases those dumped materials contained explosives (burstiers for the CW); in some cases dumping of conventional munitions was carried out in the same locations as CW. There are strong indications that some of the CW were thrown overboard during transport to the Baltic dumpsites, although how many tonnes were dumped in this manner is not known.

The Chemical Munitions Search & Assessment (CHEMSEA) Project resulted from the need to describe in detail CW dumpsites omitted or only partially included in previous investigations. CHEMSEA had the further goal of transforming the scientific discoveries into tools that can be used by maritime administrators to manage risk.

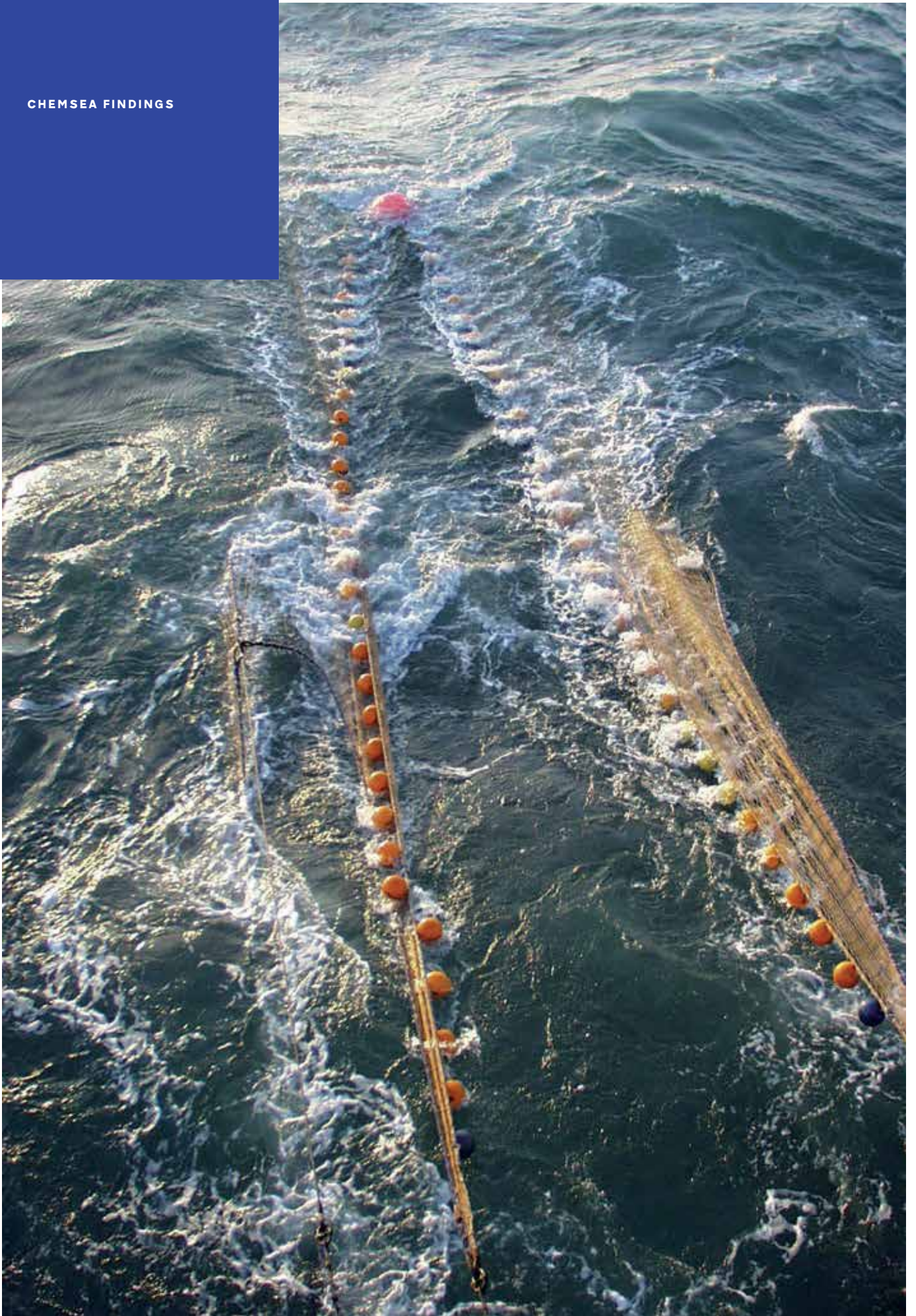
This is inline with current European Union (EU) legislation concerning the chemical status of the marine environment and other strategic documents referring to the Baltic Sea. The seafloor is a resource shared by all countries surrounding the Baltic Sea. Its management requires transnational cooperation, both regarding industrial activity and potential environmental hazards. Use of the Baltic Sea floor continues to grow; many hydro-technical projects have already been implemented or are under implementation. This includes a number of submarine cables and offshore wind farms, a tunnel from Germany to Denmark and several pipelines (e.g. Nordstream, which stretches over 1,224 km on the Baltic bottom from Russia to Germany). Some of these projects are near areas at risk of contamination from CWA degradation products. Also, trawling with bottom contact gear in areas surrounding CWA dumps is very intensive and by-catch of CW is a continuing problem.

CHEMSEA activities cover both environmental threat assessment and risk management issues. The latter is especially important for the multinational community of the Baltic Sea. At present, national regulations, EU legislation and HELCOM documents address the use of Baltic Sea resources and management of threats resulting from CWA. There is a need for introduction of unified, knowledge-based risk management guidelines and contingency strategies.

In order to address both environmental and managerial questions, several goals were formulated for the project:

1. Production of detailed maps of the Gotland and Gdansk Deep dumpsites including location of munitions and areas of contaminated sediments and potentially affected benthic fauna
2. Assessment of the toxicity of CWA degradation products to aquatic life based on in-situ and laboratory studies
3. Development of a model predicting the magnitude and direction of leakage events
4. Integrated assessment of ecosystem risks from CWA dumps
5. Development of novel, unified methodologies for CWA and CWA degradation product analysis to be used in all Baltic countries
6. Formulation of guidelines for different target groups for use when working with contaminated Baltic sediments

The following handbook presents the findings of the project, including the location of dumped chemical munitions, the magnitude of sediment pollution and possible effects on marine organisms. It also summarises guidelines developed for different stakeholders – direct users of marine resources, e.g. fishermen or submarine entrepreneurs, as well as maritime and environmental administrators. The results included here represent the efforts of eleven partner institutions from Finland, Germany, Lithuania, Poland and Sweden, assisted by numerous other associated institutions including international organisations (Helsinki Commission, International Dialogue for Underwater Munitions) and national governmental agencies (ministries of environment, maritime administrations of project countries and many others). The study was partly financed by the European Union Regional Development Fund through the Baltic Sea Region Programme.





## **CHEMICAL MUNITIONS IN THE BALTIC SEA**

- History of chemical weapons warfare
- Dumping areas, transport routes and volume of dumped munitions
- Classification of dumped chemical weapons in the Baltic Sea
- Post Cold War CWA incidents in the Baltic Sea
- CWA relevant conventions/treaties and organisations
- Summary

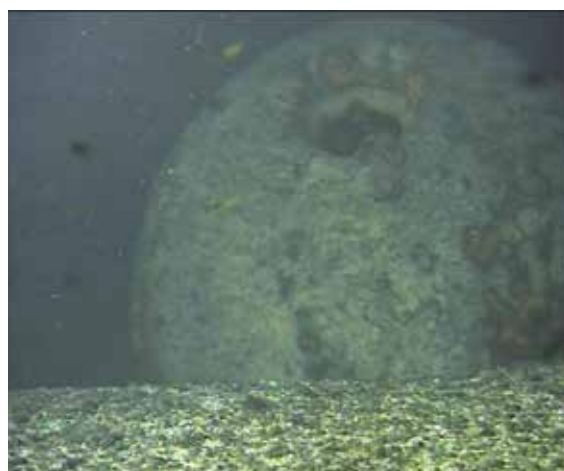
**ACCORDING TO THE HELSINKI COMMISSION (HELCOM) THERE ARE AT LEAST 50,000 TONNES OF CHEMICAL MUNITIONS DUMPED IN THE BALTIC SEA. THESE OBJECTS, RANGING FROM ARTILLERY SHELLS AND AIRCRAFT BOMBS TO CONTAINERS ESTIMATED TO HOLD AROUND 15,000 TONNES OF CHEMICAL WARFARE AGENTS (CWA). DESPITE HAVING BEEN DUMPED IN THE FIFTIES THESE OBJECTS STILL CAUSE INCIDENTS TODAY. WITH INCREASED USE OF THE BALTIC SEA AND THE INDICATION OF NEW AND PREVIOUSLY UNKNOWN AREAS OF DUMPED CHEMICAL MUNITIONS, THERE IS A NEED FOR INCREASED KNOWLEDGE AND UNDERSTANDING OF RISKS RELATED TO THESE OBJECTS. THIS CHAPTER AIMS TO PROVIDE A BACKGROUND ON THE ISSUE AT HAND AND SHOW SOME EXAMPLES OF REPORTED INCIDENTS.**

## **1.1. HISTORY OF CHEMICAL WEAPONS WARFARE**

Chemical weapons (CW) have been used in different forms throughout history. One of the first indications of chemical weapons being used is in references to deadly poison made by civilizations in Babylon, Egypt, India and China. Writings from 1000 BC in China contain recipes for poisonous and harmful vapours for use in war. The use of poisonous weapons had low acceptance from the beginning and several agreements for its restriction have been made, including the Strasbourg Agreement of 1675, the Declaration of St. Petersburg of 1886 and the Haag Declaration 1899. Today CW are defined as "Any chemical which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals. This includes all such chemicals, regardless of their origin or of their method of production, and regardless of whether they are produced in facilities, in munitions or elsewhere."<sup>1</sup> Their use is outlawed since 1997 in accordance with the Chemical Weapons Convention.<sup>2</sup>

Following large-scale use during World War I chemical weapons were banned by the Geneva Protocol (1929) even though production and stockpiling were allowed in order for states to be able to retaliate if attacked with CW. Although never used on the battlefield in Europe during World War II, extensive preparations were made and gases were actively used in Nazi concentration camps (Zyclon B), in Abyssinia by the Italians (mustard gas) as well as by Japan against China (mustard gas, Lewisite and tear gas). European states had been developing agents and strategies during the inter-war years. Through the development of pesticides in the 1930s, Germany discovered the potential of organophosphorous pesticides as a new group of highly toxic weapons, the nerve agents. On the other side of the war, the allied forces were decades behind in the race to synthesize nerve agents. In China, Japanese use of CW between 1937 and 1945 caused an estimated 80,000 casualties. While retreating during the later stages of the war the Japanese forces sought to hide any unused weapons in fear of discovery by the Soviet Red Army. CW were buried on land or submerged, leaving no traces when the Chinese army reclaimed occupied territory. In the same manner, Germany dumped its nerve gas munitions into the Little Belt area and emptied its Tabun factory storage tanks into adjacent rivers prior to the end of the war. Following the end of the war, as victors the Allied forces had to dispose of or destroy any remaining CW.<sup>3</sup>

The outcome of World War II was negotiated in Potsdam in 1945 by the Leader of The Soviet Union Joseph Stalin, President of the United States Harry Truman and Prime Minister of the United Kingdom Winston Churchill. Even though there were numerous disagreements, the three leaders agreed on the disarmament and demilitarisation of Germany. The Potsdam agreement states that *“The complete disarmament and demilitarization of Germany and the elimination or control of all German industry that could be used for military production”*<sup>4</sup> and that *“All arms, ammunition and implements of war and all specialized facilities for their production shall be held at the disposal of the Allies or destroyed. The maintenance and production of all aircraft and all arms, ammunition and implements of war shall be prevented.”*<sup>5</sup> With Germany divided into four zones (American, British, French and Soviet), the Allied parties were responsible for taking care of any CW, CWA and production facilities within their area of oversight, either by including them in their own arsenals or destroying them by any means suitable. This was primarily done by submerging them in oceans and seas.<sup>6</sup>



POST - WAR MUNITION

## 1.2. DUMPING AREAS, TRANSPORT ROUTES, AMOUNTS OF DUMPED MUNITIONS

Germany produced large stockpiles of CWA between 1935 and 1945 and development continued afterwards. The CWA produced in largest volume was mustard gas (in different varieties), accounting for around 40% of the total produced CWA. The majority of munitions produced were aircraft bombs (250 kg) and artillery shells (105 mm and 150 mm). Artillery shells are estimated to contain around 10% active CWA and an aircraft bomb around 60%. Additionally, German forces captured large amounts of chemical munitions from France, Poland, the Soviet Union and other occupied countries. At the end of the war, and up until 1948, a total of 296,103 tonnes of chemical munitions and CWA were found on German territory.<sup>7</sup>


The areas of concern in the Baltic Sea are primarily the official dumpsites east of Bornholm and southeast of Gotland. In addition, there is the Little Belt area as well as transport routes from Wolgast Harbour, where vast amounts of chemical munitions were located. Finally, there are unofficial sites of concern in the Gdansk Deep and the Slupsk Furrow\*. At the time it was considered a cheap method of disposal and it was believed that the vast amounts of water would neutralize the CWA. In contrast to the dumping operations in Skagerrak and Little Belt, where complete ships were sunk, primarily containers and munitions containing CWA were dumped in the Baltic Sea. Dumping was primarily done, with munitions being thrown overboard. During the first dumping operations, objects still packed in wooden crates were thrown overboard causing some of them to drift around before finally sinking. It is stated that on occasions crates washed ashore on the Swedish coast. At the Bornholm site dumping was done in an area with a three nautical mile radius, initially with drifting or sailing vessels dispersing the dumped munitions. Buoys were later dropped marking the dumping sites to improve the accuracy but the ships conducting the dumping operations had only the necessary navigation equipment, making the exact dumping location uncertain in many cases. Furthermore, there are indications of munitions thrown overboard while en route to and from the designated dumping sites and that the routes taken differed from the designated routes in order to further decrease the time spent at sea. Official data suggest that approximately 50,000 tonnes of munitions, containing approximately 15,000 tonnes of CWA were dumped in the Baltic Sea, the majority in the Bornholm Basin.<sup>8</sup>

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\*The sites of Gdansk deep and Slupsk furrow have shown indications worth following up with additional surveys; CHEMSEA has confirmed the presence of chemical warfare agents at these sites.





 Dumping zones for chemical munitions (confirmed and unconfirmed sites)

..... Official transport routes

==== Unofficial (shortcut) transport routes

### 1.3. CLASSIFICATION OF DUMPED CHEMICAL WEAPONS IN THE BALTIC SEA

Types and amounts of dumped chemical munitions in the Baltic Sea vary by location. The Bornholm Basin, containing the largest part, holds over 90% of the chemical munitions dumped in the Baltic Sea. The majority of chemical warfare munitions dumped are aircraft bombs followed by encasements and containers. A typical aircraft bomb is the K.C. 250 (*Kampfstoff Cylindrisch*), 160 cm long, weighing 250 kg and containing approximately

100 kg of CWA, mainly mustard gas. More than half of the chemical munitions dumped (in tonnes) were aircraft bombs containing mustard gas. Due to its chemical properties mustard gas is an agent that can remain stable on the seabed for decades after its metal encasings have corroded. The three different official dumping sites contain different types of CWA: the area of Little Belt contains approximately 5,000 tonnes of munitions (an estimated 750 tonnes of warfare agent) consisting primarily of Tabun, a nerve gas, while the Bornholm Basin and Gotland Deep primarily consist of mustard gas.<sup>9</sup>

Table 1: Quantities and type of munitions in tonnes (HELCOM 1994)

Types	Bornholm Basin	Gotland Deep	Total
Aircraft bombs	7.896	682	8.578
Artillery shells	768	66	834
High-explosive bombs	314	27	341
Mines	42	4	46
Encasements	1.050	91	1.141
Smoke grenades	65	6	71
Containers	924	80	1.004
Drums	18	2	20
<b>Total</b>	<b>11.077</b>	<b>958</b>	<b>12.035</b>

Table 2: Types of Chemical Warfare Agent dumped and amount in tonnes (HELCOM 1994)

Types	Bornholm Basin	Gotland Deep	Total
Mustard gas	7.027	608	7.635
As-cont	2.033	176	2.209
Adamsite	1.428	124	1.552
CAP	515	44	559
Others	74	6	80
<b>Total</b>	<b>11.077</b>	<b>958</b>	<b>12.035</b>

## 1.4. POST COLD WAR CWA INCIDENTS IN THE BALTIC SEA

During the last 20 years, a total of 115 incidents involving submerged CWA where reported to HELCOM. Danish fishermen are compensated for loss of catch and other related costs while ships from other Baltic Sea states are not. Due to this discrepancy in the systems of compensation, the reported cases primarily originate from Danish fishermen through Danish authorities. Although the number of reported incidents has declined during the last decade, incidents are still occurring with potentially serious outcomes. With an increased use of the Baltic Sea, including the construction of wind farms and pipelines, the risks remain high. The following cases described below exemplifies incidents involving fishermen and CWA.

Table 3: Numbers of reported incidents where chemical munitions have been caught by fishermen (HELCOM)

Year	Numbers of incidents	Weight of active gas in kg
1993	3	N/A
1994	3	N/A
1995	6	40
1996	10	210
1997	9	184
1998	5	290
1999	3	185
2000	11	512
2001	11	514
2002	10	345
2003	25	1110
2004	4	160
2005	4	105
2006	1	6
2007	2	58
2008	1	0
2009	1	1.5
2010	3	65
2011	2	63
2012	1	45



### Katrine Søe

In 2011, the crew of the Katrine Søe had been fishing for five weeks, during which time they caught, among other things, an object containing mustard gas. The crew chucked the object together with other pieces of junk caught during the cruise. Back at the harbour, the crew spent three weeks making repairs with the hazardous object and other pieces of junk still located onboard. When done with the repairs the crew prepared to take to sea. They discarded the junk on the quay before setting sail. The following day one of the harbour staff members identified signs and symptoms of contact with mustard gas and alerted authorities. The grenade was found among the pieces of junk and the ship was ordered back to harbour due to the risk of further contamination and to ensure that neither the captain nor his crew had been exposed to the chemical agent. The object was disposed of by authorities.<sup>10</sup>



*Since we were to sail on Wednesday, we threw all the junk that we had caught in the nets on the quay, where all the others had put theirs.<sup>11</sup>*



### WŁA 206

In January 1997, the crew of the Polish fishing vessel WŁA 206, trawling 30 nautical miles north of Władysławowo harbour, extracted an est. 5-7 kg clay-like object that proved to be a lump of mustard gas. The lump where dumped in a port rubbish container before anyone identified symptoms of exposure. The next day, all of the crewmembers experienced "adverse skin reactions, a sort of burning sensation, skin lesions and reddening."<sup>12</sup> The lump resulted in serious burns and injuries for the eight crewmembers. Four were treated, and released home, while the other four hospitalised due to severe skin burns before finally being released home after a few weeks.

† Denmark is the only Baltic Sea state compensating its fishermen for destruction of potentially contaminated.

The lump of mustard gas were taken care of by the Military Decontamination Unit in the Polish Navy. Deaths were avoided only thanks to the low, January temperatures, which stopped gas from evaporation.<sup>13</sup>



### SG Delfin

In 2001, the Swedish trawler *SG Delfin* caught an aircraft bomb, later confirmed to contain mustard gas. Believing it would be easier for authorities to handle, the crew transported the bomb into Nordersund port and late in the evening placed it on the quay before finally informing the Swedish Coastguard. The Coastguard relayed the information forward to local emergency services that assumed responsibility. During the following day, several governmental agencies were involved in confirmation and the process of handling the incident. Finally, confirmed as an aircraft bomb containing mustard gas, authorities evacuated several houses and around 100 people had to leave their homes. After authorities disarmed the bomb, they neutralized the chemical warfare agent using decontaminants supplied by the Swedish Armed Forces. The management of the incident took around two days.<sup>14</sup>



### Hildarstindür

Although the incident with *Hildarstindür* took place in 1984, it shows the potential severity of incidents related to submerged chemical munitions. Trawling southeast of Gotland, seven fishermen on board a Faroese trawler unknowingly brought mustard gas onboard their vessel. During the night, the crew caught an object while trawling. Due to the time of day they did not identify it as unknown and dangerous to the crewmen and mustard gas was present not only on the ship deck but also inside the cabins. The crew suffered severe injuries and when they finally receive aid from authorities, they required medical evacuation to Copenhagen.<sup>15</sup>

## 1.5. CWA RELEVANT CONVENTIONS/TREATIES AND ORGANISATIONS

The Chemical Weapons Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction, commonly referred to as the Chemical Weapons Convention, entered into force on April 29, 1997. It is one of the world's most widely accepted conventions, ratified by 190 states parties and lacking the participation of only six states. It aims to resolve the issue of CW stockpiles and ensure their destruction. The implementing body of the convention is the Organisation for the Prohibition of Chemical Weapons (OPCW) seated in The Hague. Parties of the convention are obliged to declare any CW in their possession and, under the supervision of OPCW, ensure its destruction as well as the destruction of any production facilities. State parties are prohibited from using chemical weapons or any military preparation to use them. Additionally, states are responsible for any CW they have abandoned on another state's territory. This, however, only applies to chemical weapons abandoned on land since 1977 or dumped at sea since January 1, 1985. Originally, the convention aimed for the complete destruction of CW ten years after it entered into force. This deadline included a one-time possibility of extension for a period of an additional five years, i.e. 2012. As of September 2013, OPCW declared that 81.10% of the world's chemical weapon stockpiles had been destroyed. During the Third Review Conference of the Chemical Weapons Convention in spring 2013, the conference declared its determination to destroy all existing chemical weapons in the shortest time possible. Although CW and their use are banned in a large part of the world, there are still confirmed incidents taking place, but progress is also being made. In 2013 a UN investigation team confirmed use of the nerve agent Sarin in Syria. In June and October, 2013, Somalia and Syria joined the Chemical Weapons Convention as the 189<sup>th</sup> and 190<sup>th</sup> state parties. On October 11, 2013, the Norwegian Nobel Committee awarded the Nobel Peace Prize to the OPCW for "*its extensive efforts to eliminate chemical weapons*".<sup>16</sup>

‡ Israel and Myanmar have not yet (mid 2013) ratified the convention. Angola, Egypt, North Korea, South Sudan have neither signed nor acceded the convention.

The Helsinki Commission (HELCOM), is an intergovernmental cooperation between the European Community and the states of Denmark, Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM works to protect the marine environment from all sources of pollution. Within HELCOM there are six working groups with the Monitor and Assessment Group (MONAS) and the Response Group (RESPONSE) which concern the issue of submerged chemical munitions.

## 1.6. SUMMARY

Following the large-scale use of chemical weapons during World War I, extensive preparations were made to further develop chemical warfare and increase its capacity. Even though it was never used on the European battlefield, large amounts of CW remained after the end of the war. The victors decided that they were responsible for the disposal any chemical munitions found in their area of oversight. In addition to being a cheap method of disposal, the belief was that the vast amounts of waters in the oceans would neutralize and absorb the dangerous

substances. The Soviet Union dumped at least 50,000 tonnes of chemical munitions containing an estimated 15,000 tonnes of CWA in the Baltic Sea, primarily in the Bornholm Basin. Other official dumping sites are the Little Belt area and the Gotland Deep. In addition to these sites, dumping took place en route from Wolgast, where vast amounts of chemical munitions were located. Furthermore, CHEMSEA has found indications pointing to the unofficial dumping sites of Slupsk Furrow and the Gdansk Deep.

Due to discrepancies in the systems of compensation for fishermen involved in incidents with submerged chemical munitions, only statistics from Denmark are deemed valid. During the last ten years (2003 – 2012), there were 44 reported incidents. Even though the incidents are declining in numbers, the problem remains; there are dangerous objects in the Baltic Sea inside and outside known locations. Activities undertaken on the seabed of the Baltic Sea need to acknowledge the presence of chemical munitions and the potential dangers they constitute. Additionally, there are environmental factors that need to be taken into account as the CWA remain on the seabed far longer than originally believed.

<sup>1</sup> Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction Article 1(b)

<sup>2</sup> Martha K. Lenhart (ed.) 2008 . Medical aspects of chemical warfare, Ch.2 History of Chemical Warfare

<sup>3</sup> Martha K. Lenhart (ed.) 2008 . Medical aspects of chemical warfare, Ch.2 History of Chemical Warfare; Deng, Hongmei, and Peter O'Meara Evans. "Social and environmental aspects of abandoned chemical weapons in China." The Nonproliferation Review 4.3 (1997): 101-108.

<sup>4</sup> Agreement following the Postdam Conference Article 2: A3i

<sup>5</sup> Agreement following the Postdam Conference Article 2: A3i(b)

<sup>6</sup> The Berlin (Potsdam) Conference, July 17-August 2, 1945 (a) Protocol of the Proceedings, August 1, 1945

<sup>7</sup> Martha K. Lenhart (ed.) 2008. Medical aspects of chemical warfare, Ch.2 History of Chemical Warfare; HELCOM CHEMU, 1994. Report on Chemical Munitions Dumped in the Baltic Sea. Report to the 16th Meeting of Helsinki Commission from the ad hoc Working Group on Dumped Chemical Munitions

<sup>8</sup> HELCOM CHEMU, 2013. Report on Chemical Munitions Dumped in the Baltic Sea. Report of the ad hoc Expert Group to Update and Review the Existing Information on Dumped Chemical Munitions in the Baltic Sea (HELCOM MUNI)

<sup>9</sup> HELCOM CHEMU, 1994. Report on Chemical Munitions Dumped in the Baltic Sea. Report to the 16th Meeting of Helsinki Commission from the ad hoc Working Group on Dumped Chemical Munitions; Helcom Response Manual 2002, Volume 2, chapter 6.

<sup>10</sup> Nordjyske Medier - Fisker tvunget i havn af granat [Fishermen forced to harbor due to grenade], (accessed 2013-05-24) <<http://nordjyske.dk/nyheder/fisker-tvunget-i-havn-af-granat/520362e0-0bc5-43c1-bc20-6a6bfa762782/4/1513>>; Dagbladet Politiken - Mand i Thyborøn skadet af sennepsgas [Man in Thyborøn injured by mustard gas] (accessed 2013-05-24) <<http://politiken.dk/indland/ECE1227427/mand-i-thyboroen-skadet-af-sennepsgas/>>; TV MIDTVEST - Her er granaten [Here is the grenade], (accessed 2013-05-24) <<http://www.tvmidtvest.dk/indhold/her-er-granaten>>

<sup>11</sup> Nordjyske Medier - Fisker tvunget i havn af granat [Fishermen forced to harbor due to grande], (accessed 2013-05-24) Available at <<http://nordjyske.dk/nyheder/fisker-tvunget-i-havn-af-granat/520362e0-0bc5-43c1-bc20-6a6bfa762782/4/1513>>

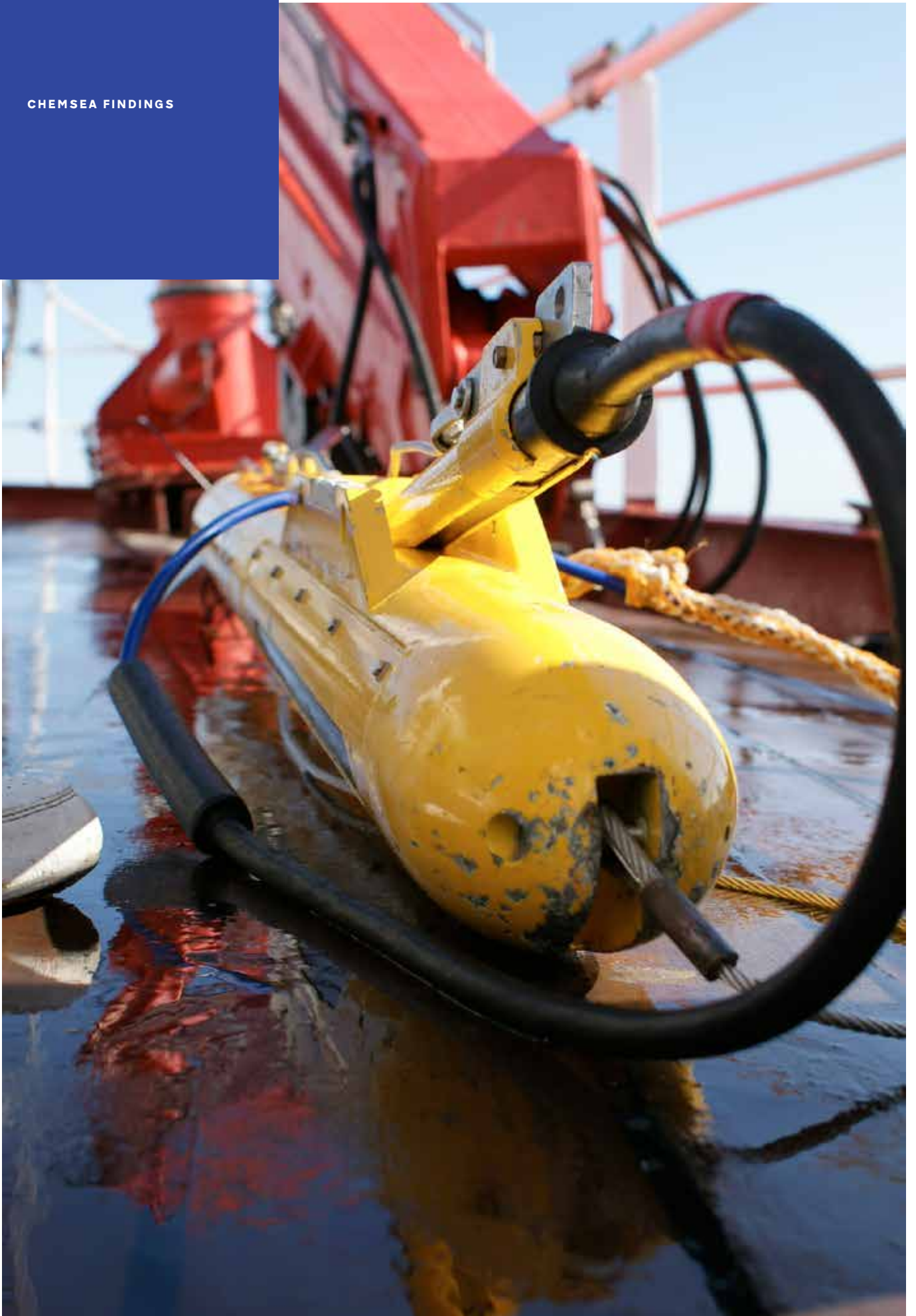
<sup>12</sup> Gonenc, I. Ethem., Ambrose, Robert B., Koutitonsky, Vladimir G., Rashleigh, Brenda. & Wolflin, John P., Assessment of the Fate and Effects of Toxic Agents on Water Resources [electronic resource], Springer, Dordrecht, 2007, p. 313.

<sup>13</sup> Gonenc, I. Ethem., Ambrose, Robert B., Koutitonsky, Vladimir G., Rashleigh, Brenda. & Wolflin, John P., Assessment of the Fate and Effects of Toxic Agents on Water Resources [electronic resource], Springer, Dordrecht, 2007.

<sup>14</sup> Waleij, Annica. "Dumpade C-stridsmedel i Skagerrak och Östersjön, en uppdatering." [Dumped chemical warfare agents in skagerrak and the Baltic Sea, an update.] Totalförsvarets Forskningsinstitut (2001).

<sup>15</sup> Waleij, Annica. "Dumpade C-stridsmedel i Skagerrak och Östersjön, en uppdatering." [Dumped chemical warfare agents in Skagerrak and the Baltic Sea, an update.] Totalförsvarets Forskningsinstitut (2001); FOI, Faktasamling CBRN - Kemiska stridsmedel, beskrivningar [Collection of facts CBRN – Chemical weapons, descriptions]

<sup>16</sup> The Organisation for the Prohibition of Chemical Weapons, (accessed 2013-09-21) <<http://www.opcw.org/>>; United Nations Mission to Investigate Allegations of the Use of Chemical Weapons in the Syrian Arab Republic, "Report on the Alleged Use of Chemical Weapons in the Ghouta Area of Damascus on 21 August 2013" Available at [http://reliefweb.int/sites/reliefweb.int/files/resources/Secretary\\_General\\_Report\\_of\\_CW\\_Investigation.pdf](http://reliefweb.int/sites/reliefweb.int/files/resources/Secretary_General_Report_of_CW_Investigation.pdf); The Official Web Site of the Nobel Prize – The Nobel Peace Prize for 2013 (accessed 2013-10-20) <[http://www.nobelprize.org/nobel\\_prizes/peace/laureates/2013/press.html](http://www.nobelprize.org/nobel_prizes/peace/laureates/2013/press.html)>



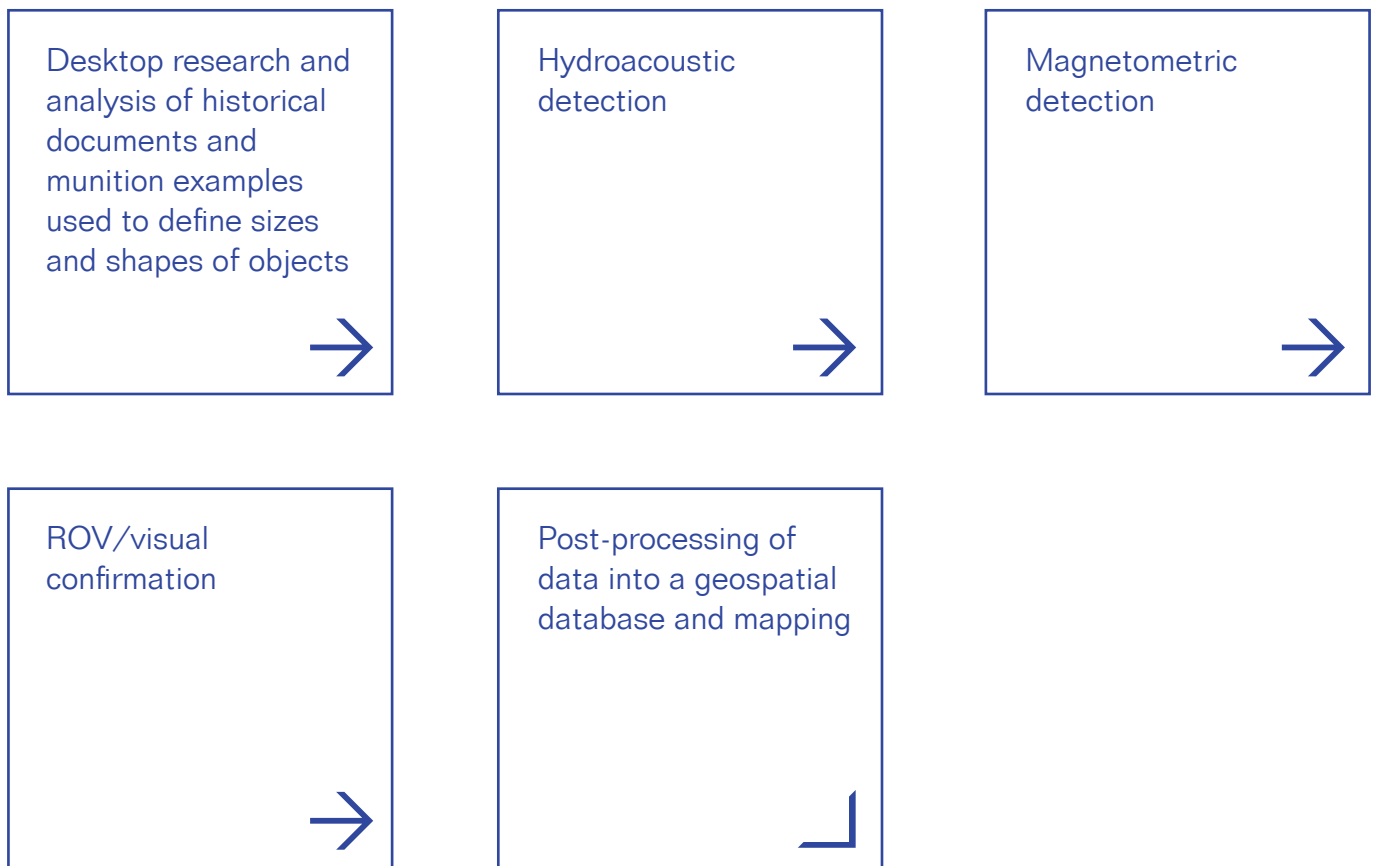


## **DETECTION OF CWA, CLASSIFICATION AND MAPPING OF CWA DUMPING SITES**

- Hydroacoustic CWA detection methods
- Magnetometric survey
- Oceanography – bottom currents
- Geospatial database and mapping
- CHEMSEA findings summary

**DETAILED KNOWLEDGE ABOUT THE POSITION OF CWA IS A MARITIME SECURITY PREREQUISITE IN THE CONTEXT OF FISHING OR THE INSTALLATION OF UNDERWATER INFRASTRUCTURE LIKE CABLES OR PIPELINES. THUS, IT WAS ONE OF THE CHEMSEA AIMS TO VERIFY AND UPDATE INFORMATION ON THE LOCATION OF CHEMICAL MUNITIONS IN THE BALTIC SEA. THE CHEMSEA CONSORTIUM SET OUT TO COLLECT THE NECESSARY DATA BY MEANS OF SONARS, ECHOSOUNDERS AND MAGNETOMETERS OPERATED FROM VESSELS OR BY IMAGES AND SAMPLES TAKEN WITH UNDERWATER REMOTELY OPERATED VEHICLES (ROV). THIS DATA WAS EVENTUALLY PROCESSED INTO GIS ARCMAP MAPS SHOWING ACTUAL MUNITION POSITIONS AND THE RANGE OF POLLUTED SEDIMENTS IN ORDER TO UPDATE NAUTICAL CHARTS.**

5-Steps of CWA detection and characterization of dumpsites:





## 2.1. HYDROACOUSTIC CWA DETECTION METHODS

The Polish Naval Academy (PNA) and the Swedish Maritime Administration (SMA) conducted several research cruises on board the vessels *Baltica* and *Oceania* to detect and verify CWA in the Gdansk and Gotland Deep areas.

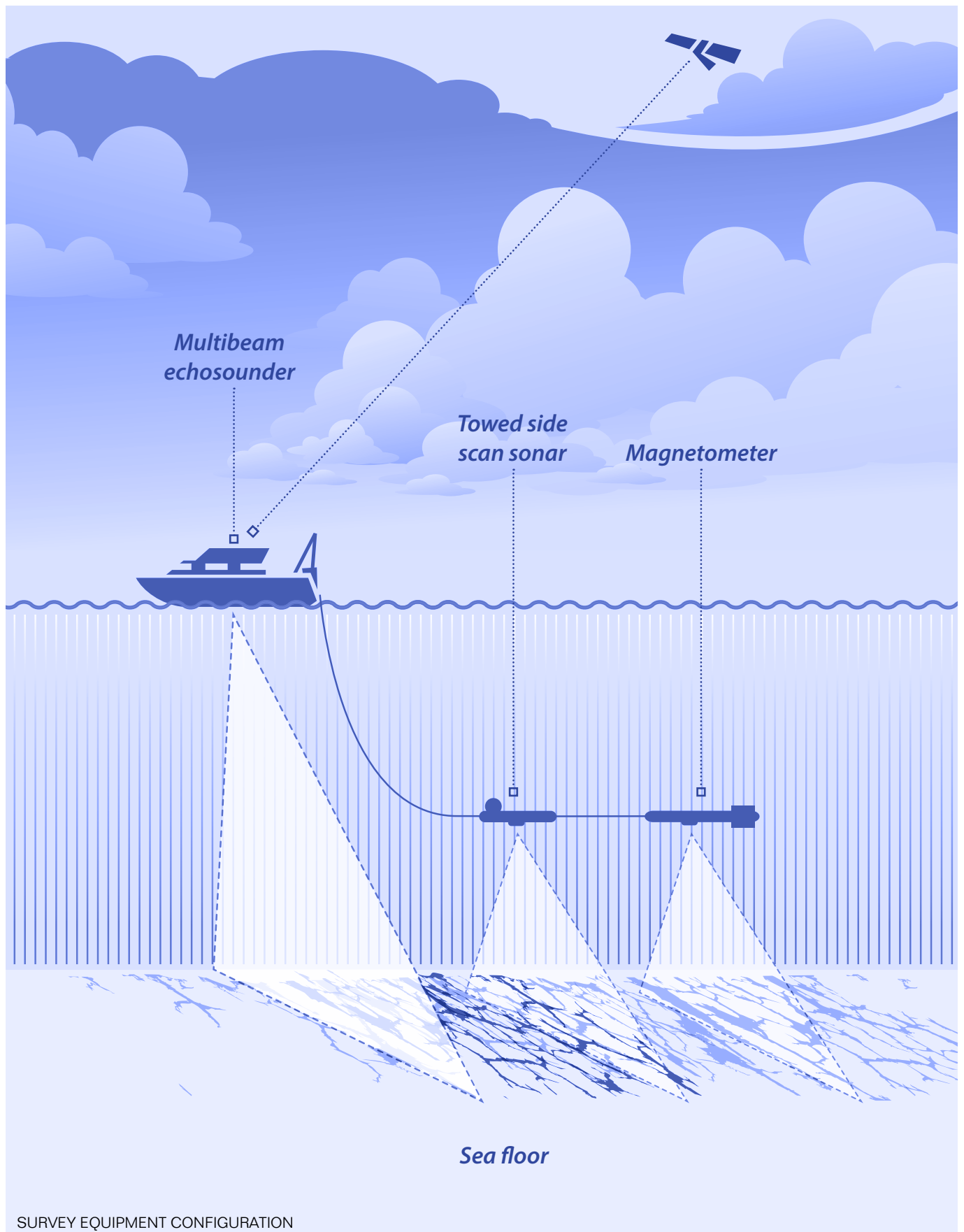
In a first step, the size of containers used to store chemical munitions was defined – based on the analysis of historical documents – as 150 mm artillery shells and steel barrels. Multibeam echosounder (MBS) and towed side scan sonar (SSS) were used in order to reveal the potential location of bottom objects that may be recognised as chemical munitions, containers or wrecks potentially containing chemical munitions.



R/V BALTICA



R/V OCEANIA



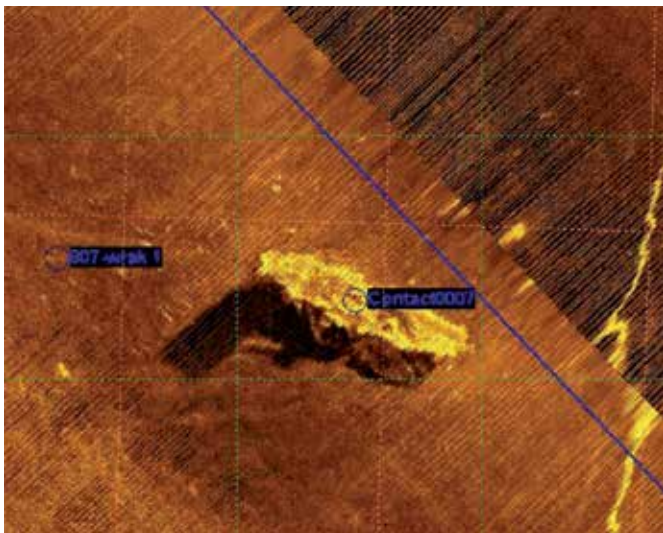
SURVEY EQUIPMENT CONFIGURATION

The research area of the official dumping site in Gotland Deep, with a total surface of 1,760 km<sup>2</sup>, was divided into 40 sub-areas each with a size approximately 13,000 x 3,000-5,000 m.

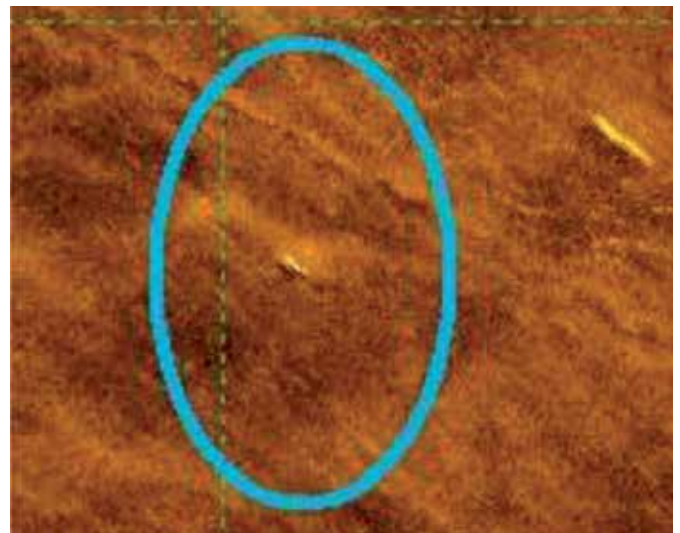
The study of the official chemical munitions dumping area within the Gotland Deep revealed that this region is characterised by the presence of a large quantity of discarded waste material. In some areas, chains of sea mines measuring tens of nautical miles were recognised and their position catalogued. On the basis of the collected SSS images a preliminary classification and an estimate of local densities and clusters of small bottom targets was performed along with their mapping.

Targets with features characteristic for mine-like objects, classified on the SSS images as potential munitions

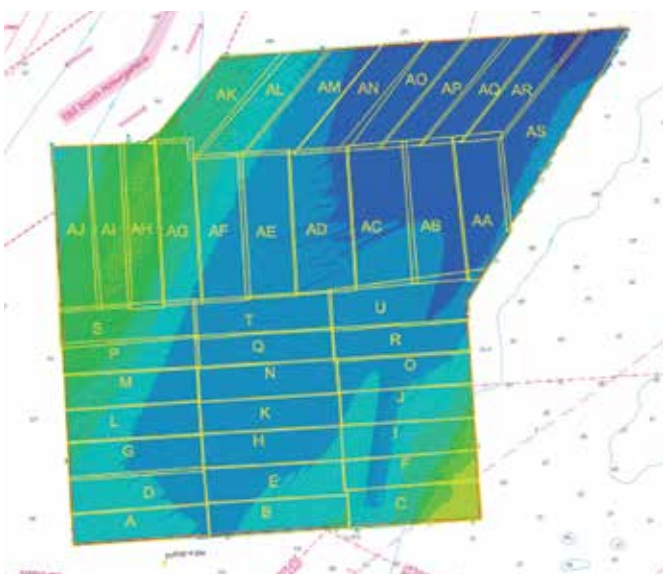
required visual checking. 198 objects were investigated through ROV operations (the total number of ROV dives by SMA and PNA was over 250). ROV operations including video recognition and water and sediment sampling resulted in an authentication and classification rate exceeding 50%, thus proving that SSS checks of the sea bottom at relatively high ship speeds are sufficiently detailed, while remaining more time and cost effective than other methods of detection.



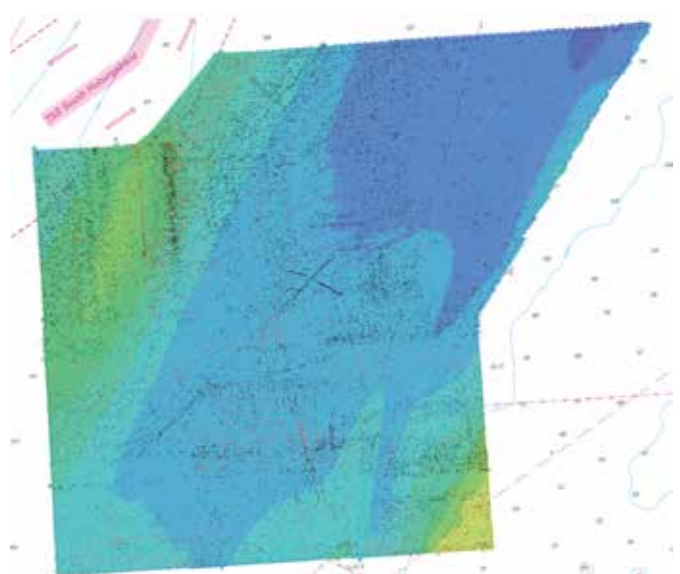
LARGE BOTTOM OBJECT (LBO)



SMALL BOTTOM OBJECT (SBO)



GOTLAND DEEP DUMPING SITE'S DIVISION



DISTRIBUTION OF DETECTED OBJECTS

## 2.2. MAGNETOMETRIC SURVEY

The main aim of the magnetometric survey, conducted in a small test area of Gdansk Deep, by the Maritime Institute in Gdansk, was to find correlations between geographical positions of objects identified on the seabed during the hydroacoustic survey and the positions of Earth magnetic field disturbances.

A number of magnetic anomalies were detected in the area of research, plus one more outside the region designated by PNA, indicating the presence of ferromagnetic objects. Not all the objects pointed by PNA gave magnetic anomalies response. It is probable that the objects detected with the SSS are objects with no magnetic properties, such as shipwrecks (or parts of wrecks) made of wood. There is also a significant probability that some of the identified anomalies do not indicate the actual place of ferromagnetic object deposition. The applied processing technique used to find small magnetic anomalies involves

the deep processing of recorded raw data and may in certain situations lead to errors due to the formation of 'nodes', where the sum of the errors contributes to form 'false' objects. However, the places where the positive dipoles are shown next to the negative dipoles may be considered as highly reliable.

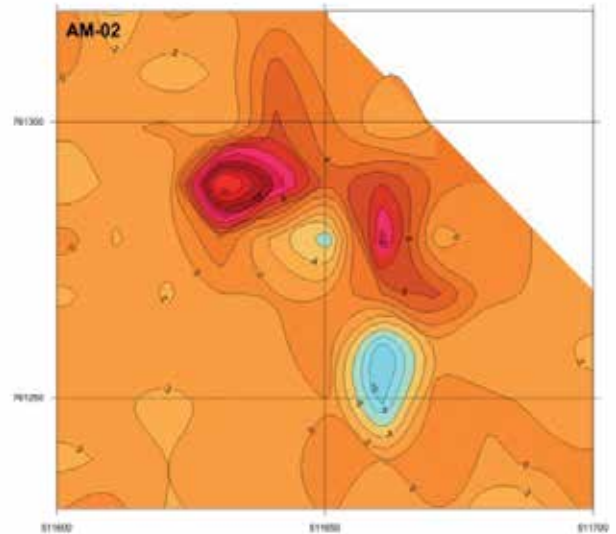
Due to the low mass of searched objects the signal recorded by the measuring device was deliberately amplified in order to enhance local anomalies. The values shown in the diagrams are higher than the actual values. However, this method allows locating the places of slightly increased values in the magnetic field of the area.



RESEARCH VESSEL OF THE MARITIME INSTITUTE IN GDANSK – R/V „IMOR”



SEAQUEST MAGNETOMETER AND SIDE SCAN SONAR



ANOMALY AM-02

Reference: Report of the magnetometric survey in the area of the Deep of Gdansk, Report of the magnetometric survey in the area of the Deep of Gdansk 2012-05-15, Version: 1.01, Agnieszka Brzezińska, Dorota Cichowska, Łukasz Gajewski, Wojciech Konieczny, Maria Kubacka, Jarosław Nowak

### 2.3. BOTTOM CURRENTS, SEDIMENT RE-SUSPENSION AND TRANSPORT

The detection and classification of dumped CW is the first step in assessing the risk for the marine environment and coastal communities. In addition, it is necessary to improve the knowledge regarding what happens when chemical agents actually start to leak from corroded munitions or are re-suspended with sediments in the water column. Understanding when near-bottom currents exceed the critical friction velocity that causes the re-suspension of a contaminated sediment type and which direction these contaminants may then drift is essential for the classification of CWA dumpsites, risk assessment and effective counter measures in case of leakage.

Against this backdrop, IO PAN set out to investigate and characterise dense currents in the project's CWA dumping sites in the Baltic proper: Bornholm Basin, Gdansk Basin and Slupsk Furrow. During the summer of 2012 IO PAN deployed three moorings to measure current velocity profiles in the Slupsk Furrow and the Gdansk Basin, where additionally temperature, salinity, oxygen and turbidity were measured at about 1 m above the bottom. The mooring results were combined with two long-term

vessel-mounted current profiler datasets originating from 38 regular cruises of the research vessels R/V Oceania and R/V Baltica in 2001-2012 organised by IO PAN and the Polish National Marine Fisheries Research Institute (NMFRI).

So far, mean circulation and current speed in the three CWA dumpsites were mainly predicted by numerical models. Now, for the first time, relatively long (several months) in-situ observations of near-bottom currents can be presented. This makes the results from the bottom current measurements within the CHEMSEA project unique. Generally, the observations show that the currents' speed across the Baltic proper was around 12 cm/s in the whole water column, with a stronger flow in the regions above the sills in the Bornholm and Slupsk Channels, reaching on average of about 20 cm/s except in the lowest layer (8-20 m from the sea bed) where the speed reached a maximum of 35 cm/s. These figures suggest that the investigated regions are important areas of intense vertical mixing. The results also show that current velocities and directions in the three basins are highly variable.



Route of the R/V Oceania

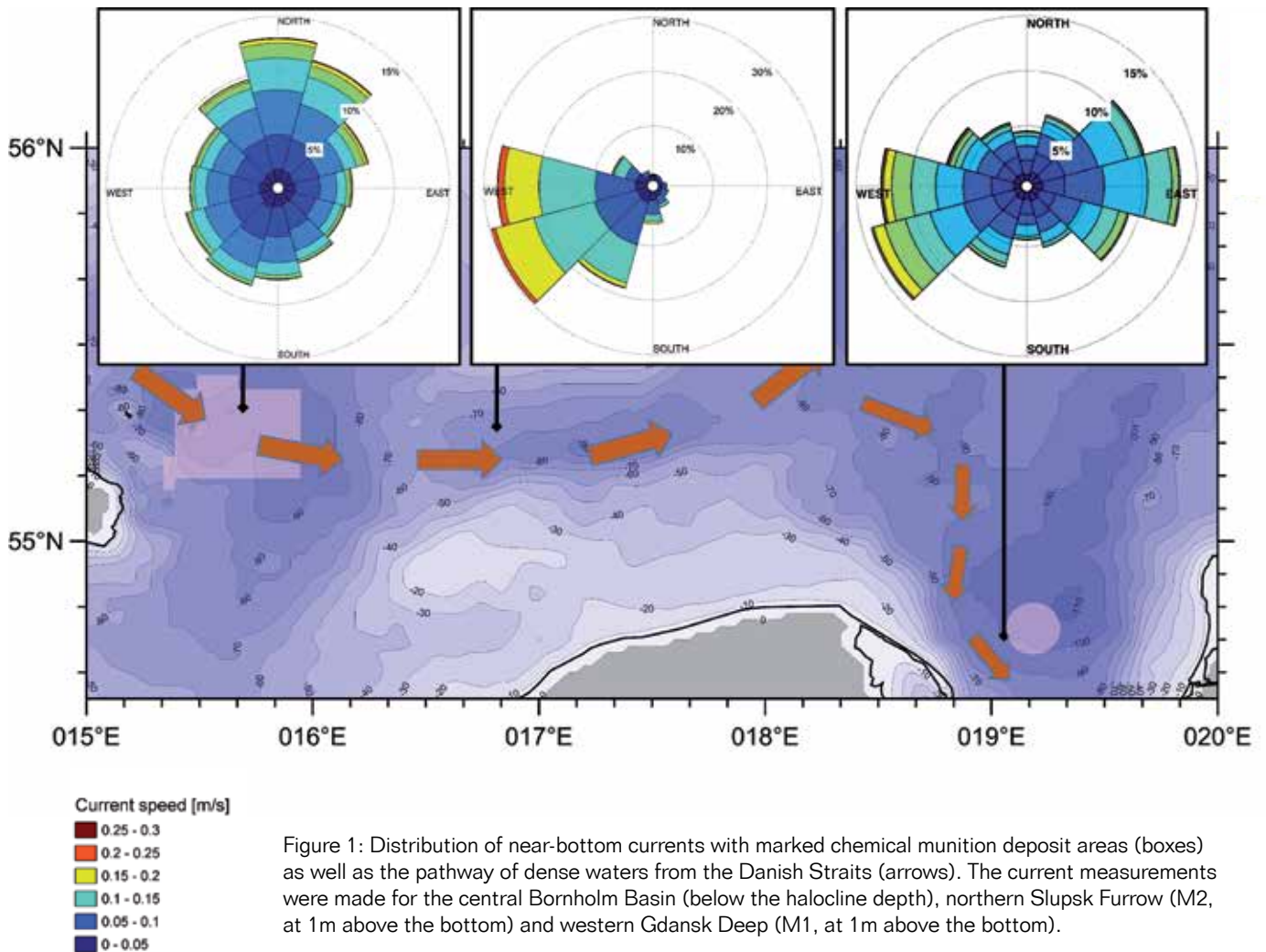


Figure 1: Distribution of near-bottom currents with marked chemical munition deposit areas (boxes) as well as the pathway of dense waters from the Danish Straits (arrows). The current measurements were made for the central Bornholm Basin (below the halocline depth), northern Slupsk Furrow (M2, at 1 m above the bottom) and western Gdansk Deep (M1, at 1 m above the bottom).

They are mainly determined by four factors: the impact of atmosphere-ice-water, water exchange through the Danish Straits, river supply and topography. The near-bottom currents information were taken from the moorings deployed one meter above the sea bed on the pathway of the inflow waters. Those dense waters accumulate on the area northeast of the island of Bornholm, above the primary chemical dump site. The average currents at this site are shown in Figure 1. The average currents direction were very variable but over 30% of them were northern with  $\pm 45$  degree spread. During the whole deployment period low current speed were observed (ca 7 cm/s).

The Slupsk Furrow (SF) has bi-directional flow, northern part of the furrow is westerly directed, southern part is easterly directed. At the M2 in SF, with a narrow spread over 80% currents were south-westerly directed. Relatively strong currents speed exceeding 15 cm/s occurred during 17 % of time (10 days). During the deployment time, very weak northern and eastern currents were measured with a speed up to 5 cm/s.

From SF through Hoburg Channel, inflow waters are transported to the deeper parts of the Baltic Sea. However, part of the inflow waters are transported to the Gdansk Deep (GD). This basin act as a buffer in which part of the water, circulates. At M1 located in GD dump site region, flow was directed easterly or westerly for almost 60% of the time (90 days). However, westerly currents speed were slightly greater. Strong currents that exceeded 10 cm/s occurred relatively briefly. Northern and Southern currents were weak, speed ca 8 cm/s.

The bottom mixed layer occupies at least 10% of the water column and the turbulent mixing induced by near-bottom currents is likely to produce local sediment resuspension and transport in all three sub-basins. The near-bottom currents exceeding critical friction velocity for a given sediment type cause resuspension of sediments into the upper water column and their transport with the flow, or a bed load transport of coarser sediments. Sediments can be transported from BB through Slupsk Sill to deeper parts of the Baltic Sea and partly to the GD. However,

the probability of long-term transport of BB originated WOCMD (waste originating from chemical munitions dumpsites) to GD is low, they might still reach the area via subsequent deposition/resuspension cycles as observed in other areas of the Baltic. Gdansk Deep can act both as a transport and source area. Sediments originated in Gotland Deep can be transported to the northern part of the Baltic Sea. During the year, transport of sediments from the WOCMD to the shallow areas can occur in 10% of time. More complex approach needs simulations made by the numerical models.

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Reference: Bulczak A. I., Rak D., Schmidt B. (forthcoming): Observations of near-bottom currents in three deep sub-basins of the Baltic Proper: Bornholm Basin, Slupsk Furrow and Gdansk Deep.

## 2.4. MAPPING

The Polish Naval Academy designed a geospatial database based on ArcGIS Geographic Information System developed by ESRI to store all the measurement data obtained during the course of the CHEMSEA project. This includes, in the first step, the bathymetric data obtained with the Multibeam Echosounder (MBES) by the research vessels R/V Baltica and R/V Oceania, along with the sea bottom mosaic picture composed of sonograms collected by towed SSS. Subsequently, the database was also filled with oceanographic and biochemical data reflecting results of laboratory analyses of sediment samples and studies of biota tissues.

The vast amount of GIS data refers to hydrographic survey conducted at the official Gotland Deep dumping ground, located in the south-easternmost Swedish EEZ border to Latvia, Lithuania and Poland. Altogether, MBES and SSS measurements revealed the presence of 39,260 bottom

objects in the area. In order to select bottom objects for further detailed investigation with ROV<sup>1</sup>, it was necessary to categorise them.

The primary target categorisation into five classes was based on the size of highlights of detected objects and their acoustic shadows. Typically acceptable size and shape for Class 1 objects – the most probable munition pieces – are within dimensions of 1.8 x 0.5 m. Class 2 contains targets with strong echo and clearly visible pit/shadow but that are the wrong size – in general too big to be recognised as munition pieces. Hardly recognisable targets (most likely sunken in the mud or covered with fine sands) characterised by strong hydroacoustic reflection but without the pit/shadow encompass Class 3 objects. Finally, any detected wrecks were classified as Class 4 and other unrecognised targets as 'Class 5'.

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<sup>1</sup> Remotely Operated Vehicle

Table 1. The number of targets catalogued into classes

Class		Number
1	Probable munition	17.267
2	Other strong echoes	6.476
3	Unrecognizable, in sediments or flat objects	12.476
4	Wrecks	33
5	Other echoes	3.008
<b>Total</b>		<b>39.260</b>

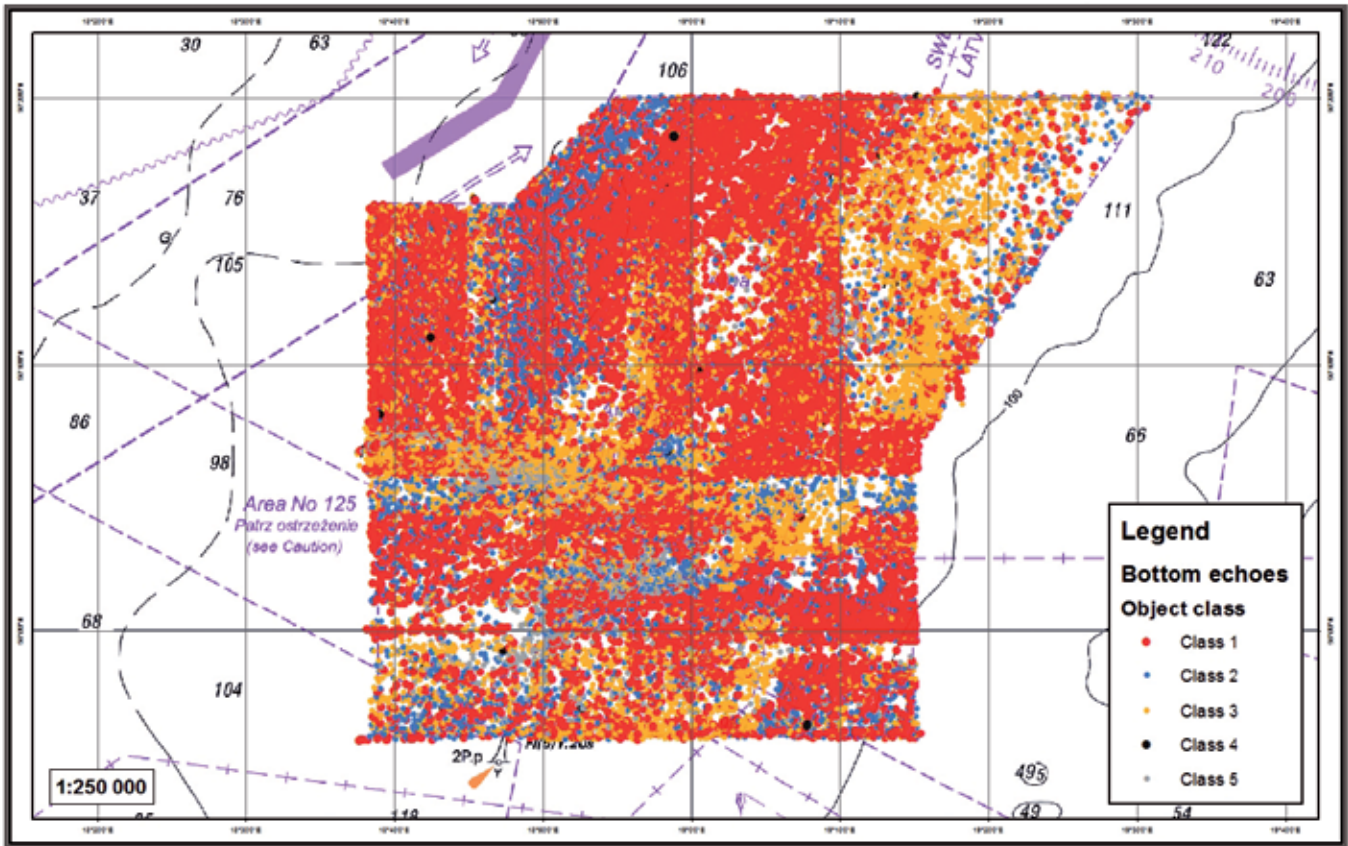


FIG. 1. DISTRIBUTION OF BOTTOM OBJECTS IN THE AREA OF GOTLAND DEEP

The distribution of bottom objects detected in the Gotland Deep with classification results is depicted in Figure 1. Classification of targets was based on analysis of sonograms done by experts of the Swedish Maritime Administration and Swedish Navy, Mine Warfare Data Center (MWDC) and supported with artificial intelligence tools, such as the neural networks used by IO PAN experts to analyse both sonograms and raw recordings of SSS signals.

In order to verify the correctness of target classification, selected Class 1 objects were verified visually during underwater ROV operations. Figure 2 depicts the positions of ROV operations conducted by scientists of PNA and SMA in the framework of the CHEMSEA project.

Although the main effort of ROV operations was focused on the Gotland Deep area, ROV operations were also conducted in Bornholm Deep and Gdansk Deep in order to correlate the results of the CHEMSEA project with the earlier, EU-financed MERCW research programme, which focused only on Bornholm Deep, and to verify the hypothesis of CWA dumping in Gdansk Deep.



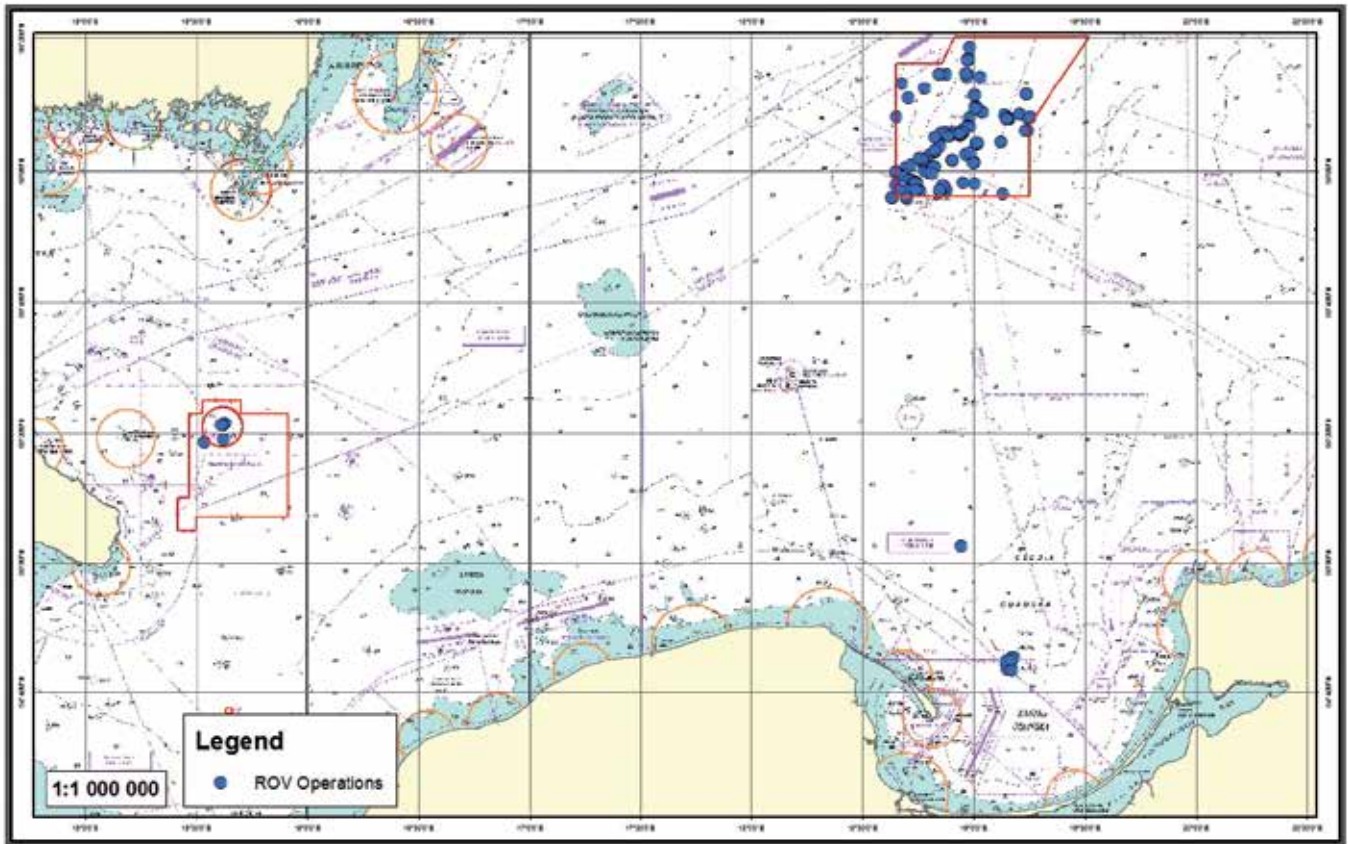
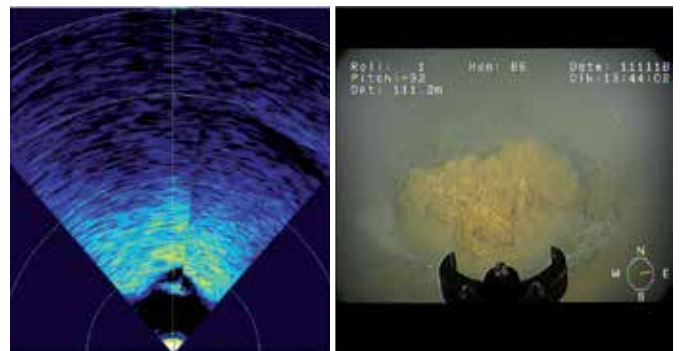
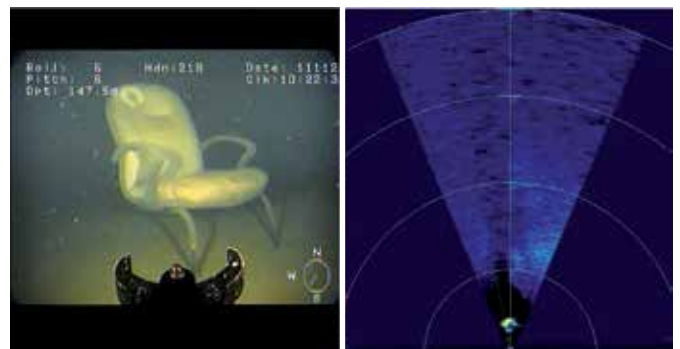


FIG. 2. POSITIONS OF ROV UNDERWATER OPERATIONS CONDUCTED WITHIN THE FRAMEWORK OF CHEMSEA PROJECT

It was not possible in every single case to visually confirm the presence of objects detected by SSS on the sea bottom. Moreover, in a few cases, visual inspection of underwater objects revealed that the automatic or semi-automatic classification of targets was incorrect.



ROV INSPECTION ON CORRECTLY CLASSIFIED OBJECT



ROV INSPECTION ON MISCLASSIFIED OBJECT

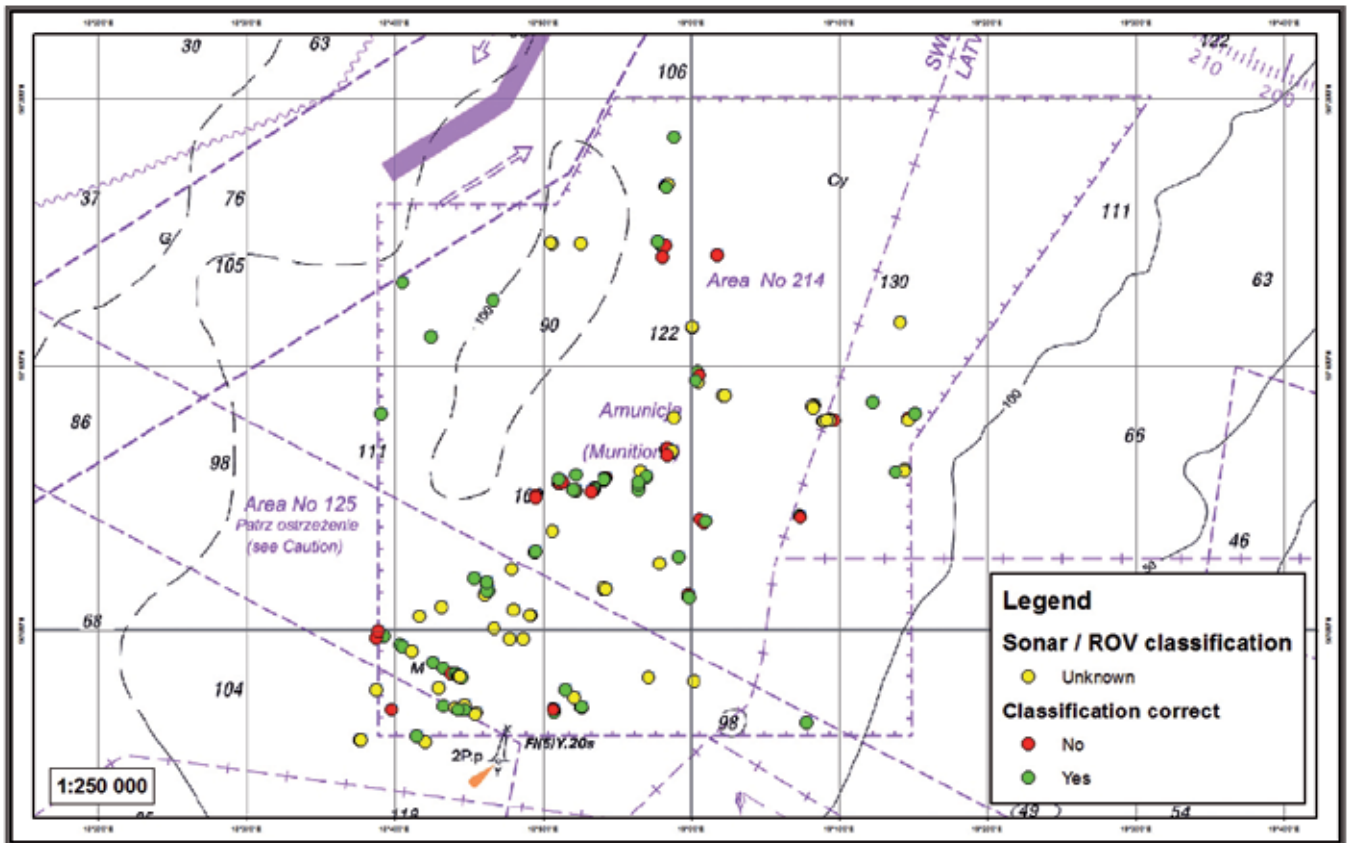


FIG. 3. CORRECTNESS OF 'CLASS 1' TARGETS' CLASSIFICATION

Figure 3 depicts ROV operations conducted by SMA in Gotland Deep, showing the correctness of target classification. Targets classified primarily as Class 1 and visually confirmed as Class 1 are depicted as green dots. Targets visually confirmed to be classes other than Class 1, i.e. misclassified, are depicted as red dots. Yellow dots represent cases in which the ROV was not able to visually confirm the presence of a target on the sea bottom or in which the physical state of the detected target did not allow classification to any given class.

The ROV mission was not only to confirm the correctness of target classification and document targets by means of video and photo techniques, but also to collect samples of sediments in the direct vicinity of the underwater objects for further chemical laboratory tests.

In addition to the ROV, sediment samples were also taken with other sampling tools (i.e. Box corer and Van Veen grab sampler). The positions of sediment samples obtained with the aforementioned tools are depicted with red dots in Figures 4 and 5.

Additionally, the positions of fish sampling stations (described in Chapter 3) are depicted with green dots.

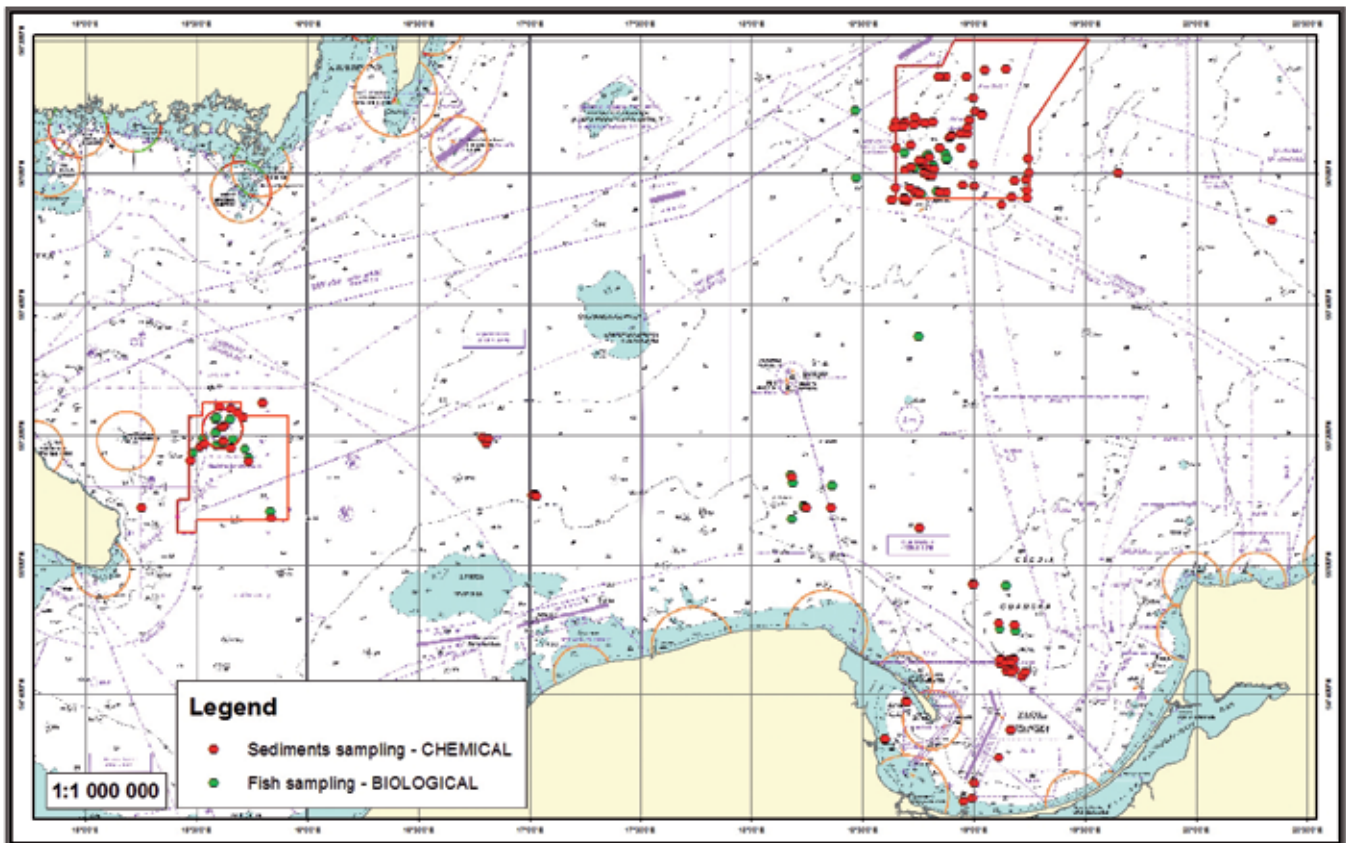


FIG. 4. POSITIONS OF SEDIMENTS SAMPLING AND FISH SAMPLING STATIONS

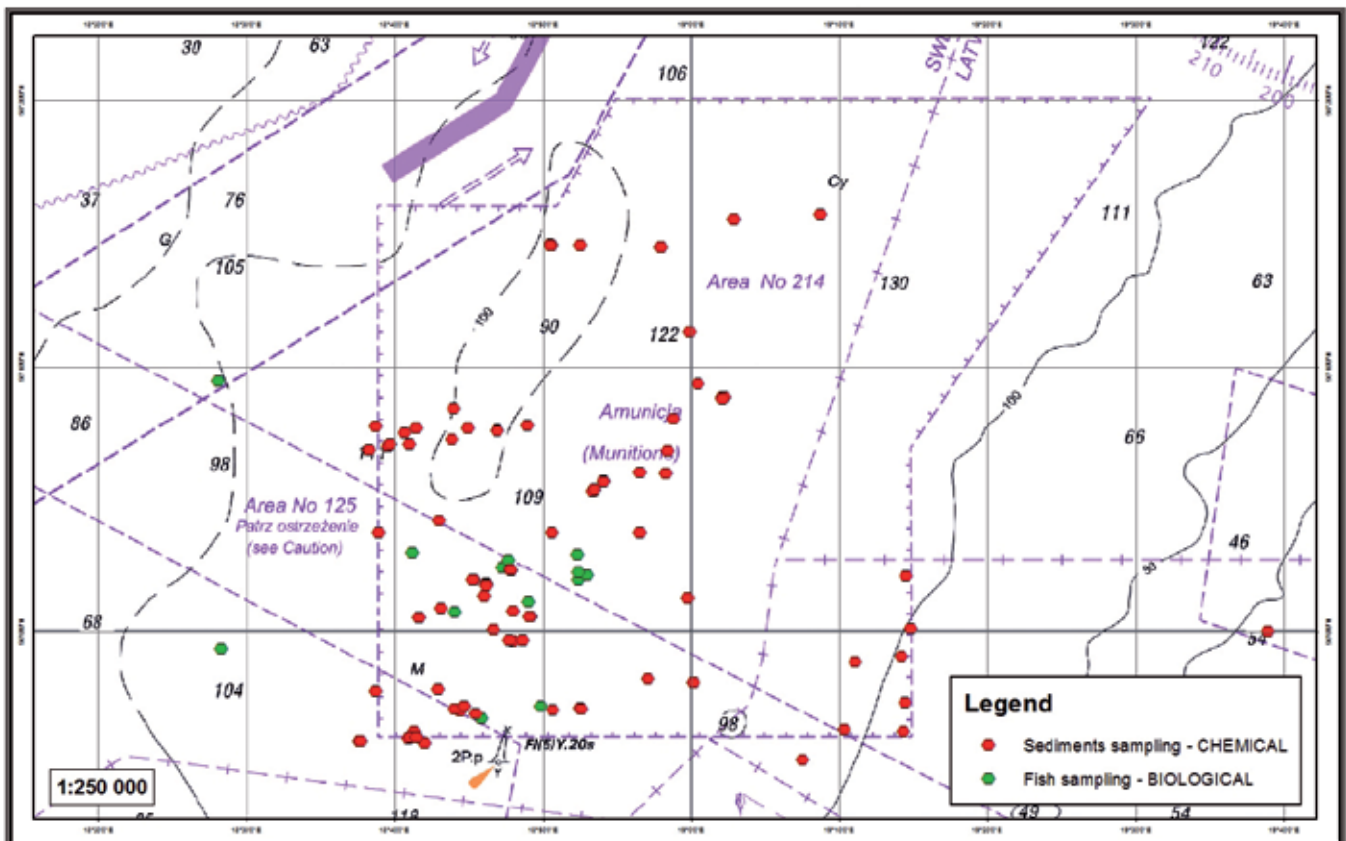


FIG. 5. POSITIONS OF SEDIMENTS SAMPLING AND FISH SAMPLING STATIONS – GOTLAND DEEP DUMPING SITE

After receiving the results of the laboratory analyses of sediment samples, the GIS database was enhanced with data on the concentration levels of multiple chemicals, allowing for correlation of sampling positions with contamination levels. General classification of contaminants into two groups of arsenic-related substances and CWA allowed to draw a map of contaminant concentration levels and positive detections of CWA and their degradation products.

Figures 6 to 9 depict the concentration levels of total arsenic in sediments and the positions of positive detections of CWA and their degradation products, respectively.

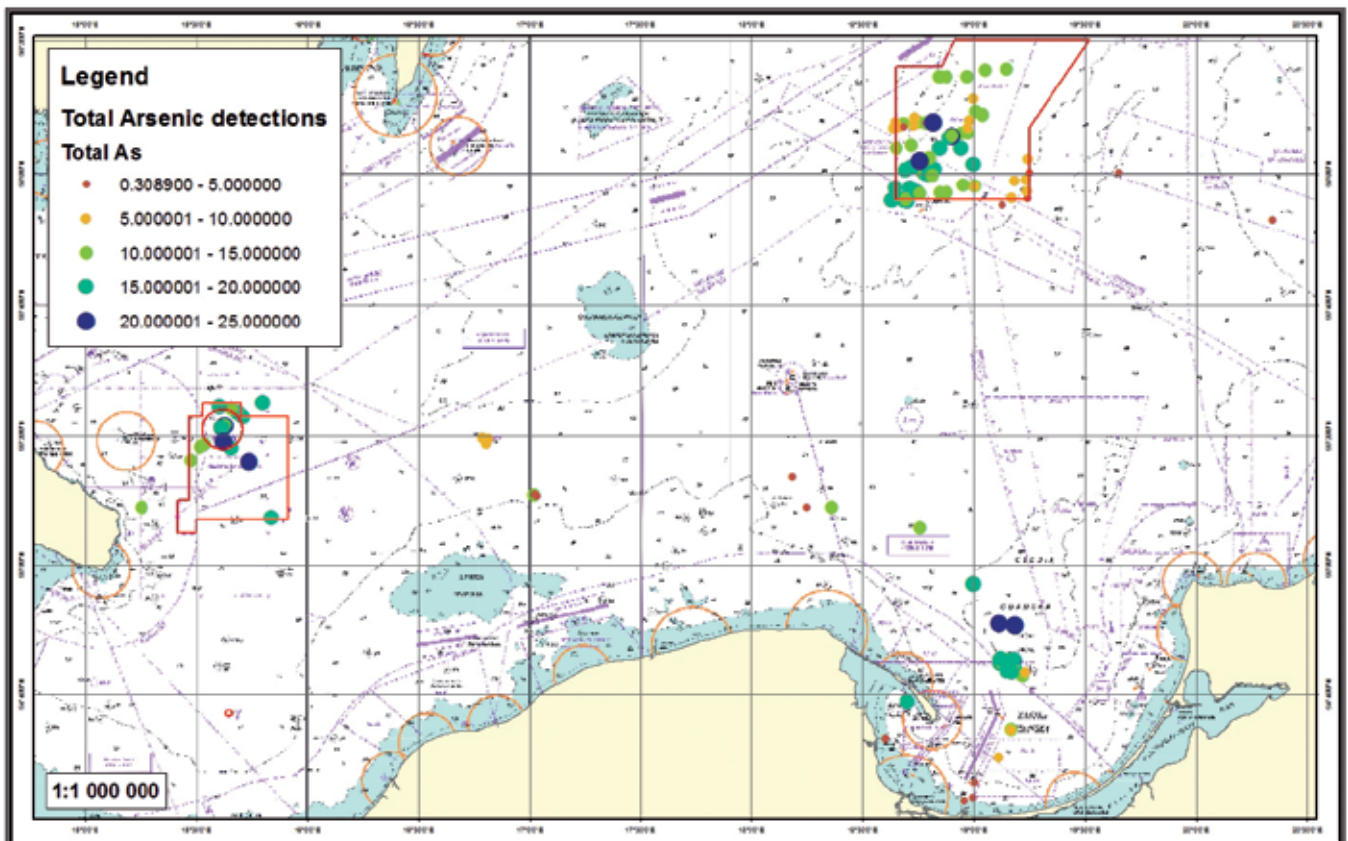


FIG. 6. CONCENTRATION LEVELS OF TOTAL ARSENIC IN SEDIMENTS

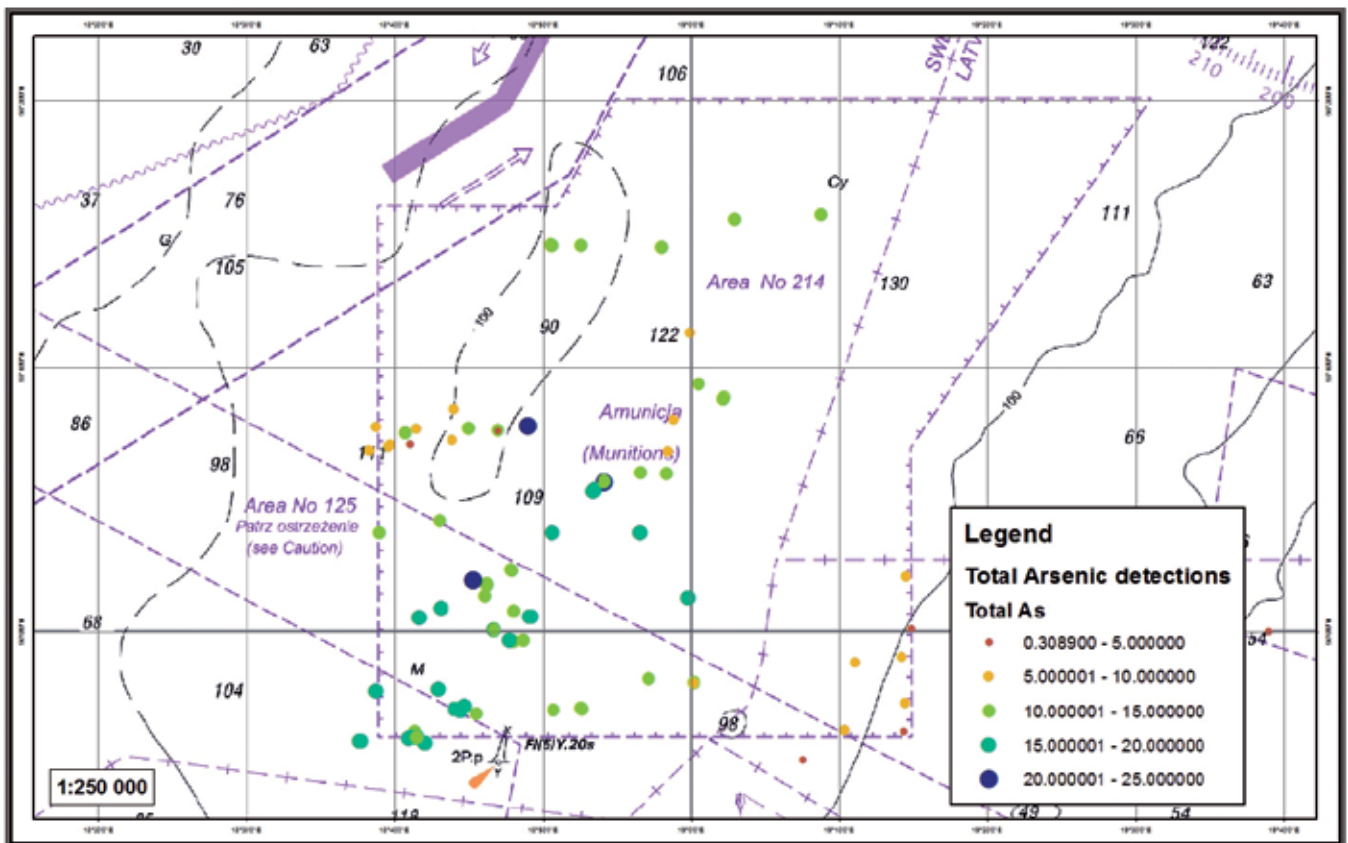


FIG. 7. CONCENTRATION LEVELS OF TOTAL ARSENIC IN SEDIMENTS – GOTLAND DEEP DUMPING SITE

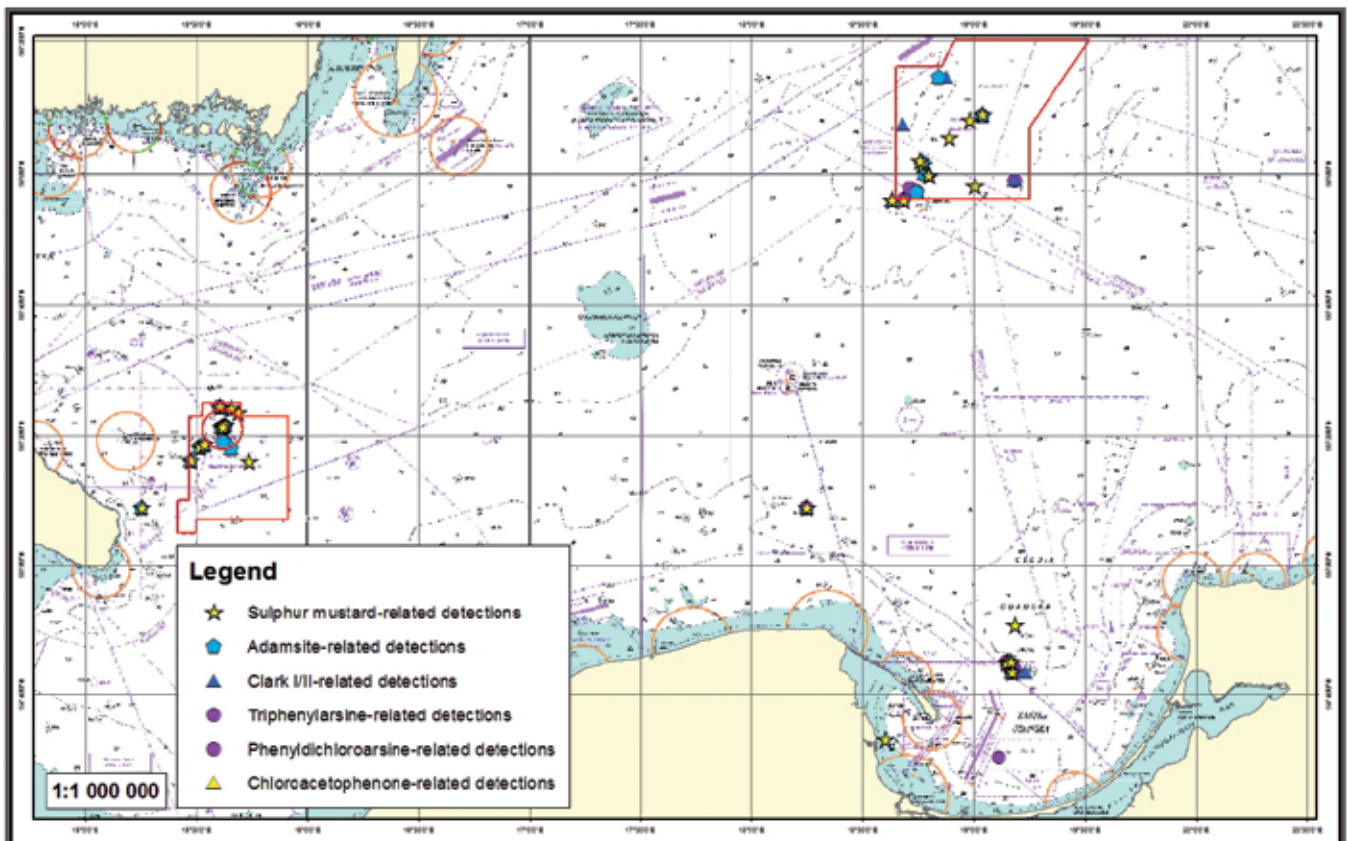


FIG. 8. POSITIONS OF POSITIVE DETECTIONS OF CHEMICAL WARFARE AGENTS AND THEIR DEGRADATION PRODUCTS

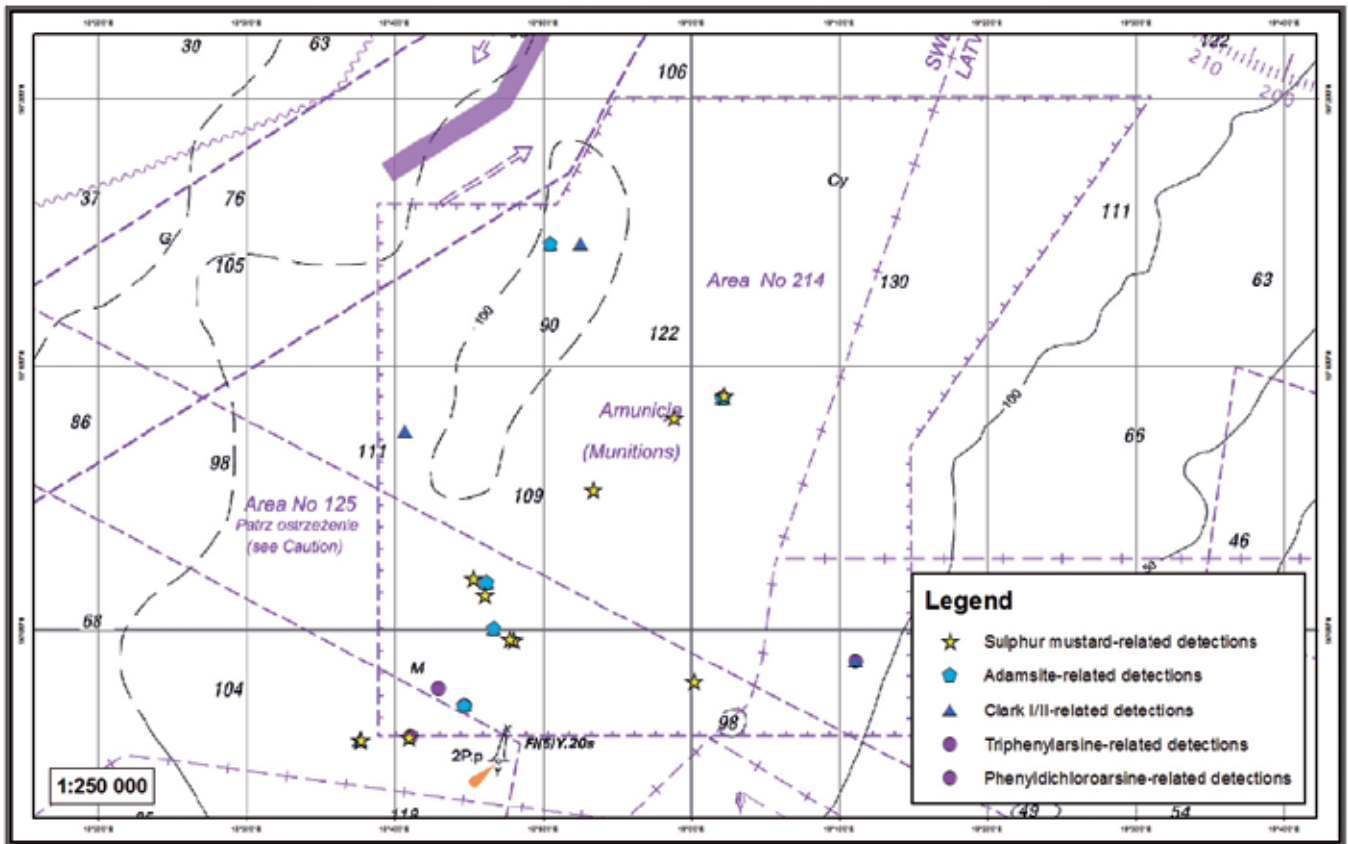


FIG. 9. POSITIONS OF POSITIVE DETECTIONS OF CHEMICAL WARFARE AGENTS AND THEIR DEGRADATION PRODUCTS – GOTLAND DEEP DUMPING SITE

## 2.5. SUMMARY

The rapid growth of the offshore industry raises new issues related to munitions (both conventional and chemical) dumped at sea. The use of the seabed for offshore activities such as resource extraction or construction is rapidly developing and increases the likelihood of encounters with dumped munitions.

Many temporary or permanent facilities will be deployed on the seafloor in the near future, resulting in increased risk of coming into contact with CWA. Operations conducted directly on or in the sediment layer may damage the encasements of chemical munitions that have not yet lost their integrity, generating threats to humans and the environment.

Therefore, prior to any offshore operation, appropriate methodologies for risk assessment must be followed. The model approach has been introduced during the biggest investment in recent years in the Baltic Sea area, i.e. the Nord Stream pipeline construction. The documented experiences of the Nord Stream pipeline laying project between 2005 and 2011 could be a model for future project plans.



## NORD STREAM

### Planning

The proposed route, including the 15 m wide installation corridor, was planned in such a way as to avoid known dumpsites, based on available historical and scientific data.

### Area Wide Assessment

The screening survey included a 2 km zone around the actual activities, followed by a detailed geophysical survey of a 180 m zone along the final planned pipeline route and inspections of the close vicinity (a 20 m zone) with a resolution high enough to identify objects of sizes >10 cm. Employed technologies included multi-beam echo sounders (MBES), high-resolution side-scan sonars (SSS), sub-bottom profilers and

a magnetometer. MBES and SSS provided a detailed picture of the contours of the sea floor and of objects lying on the seabed. The sub-bottom profiler penetrated deep into the material at the sea bottom to show a cross-section of the mud, silt and bedrock that make up the seabed. The magnetometer provided information on ferrous (iron-based) materials.

### **Detailed Survey**

The second stage used a 6.7 m wide 12 sensor gradiometer array mounted on a ROV to detect any ferrous metals on the seabed and provided coverage of the full installation corridor. Concurrently with the gradiometer survey, visual coverage of the seabed was also achieved. The gradiometer data was processed within a digital terrain model to allow objects to be located for further visual inspection.

### **Inspection**

In a third stage, Nord Stream visually inspected the targets located during the previous two stages. This allowed experts to examine and identify any questionable objects.

### **Monitoring**

Pre- and post- lay monitoring was performed in the vicinity of five discovered CW objects. This included both visual inspection and analysis of CWA degradation products in sediments. Baseline levels were established prior to pipe laying. With the monitoring programme, Nord Stream was aiming at documenting any changes in the level of CWA in the sediment due to project activities resulting in the disturbance of contaminated sediments originating from dumped chemical munitions. Sampling was conducted at 29 stations along the midline of the pipelines. At six of these stations, a transect consisting of 15 stations was sampled. Three sampling campaigns – baseline and after installation of the first and the second pipelines were performed. Samples were analysed in two certified laboratories.

In order to facilitate Area Wide Assessment and Detailed Survey phases within the model methodology, CHEMSEA worked out a framework of detection, classification and mapping of CWA, which consisted of:

- Desktop research of historical documents and munitions examples in order to define sizes and shapes of the objects searched for
- Hydroacoustic detection with multiple survey tools
- Magnetometric detection
- ROV / visual confirmation
- Post-processing of data into a geospatial database and mapping

Based on CHEMSEA research, a hydroacoustic survey would be advised as the first step in both environmental impact assessment and work site selection in the area where suspected dumped munitions are located. It is advisable to perform a sonar survey using side scan sonars, multi beam echosounders and sub-bottom profilers. To exclude natural or non-munition objects, the sonar survey should be complimented with other techniques, such as magnetometry used for detecting ferrous items.

The aforementioned survey techniques generate enormous amounts of data, which needs to be fused and processed using GIS computer software, widely available on the commercial market. The resulting output represents an enhanced graphic display of the surveyed area in the form of detailed charts aimed to support decision-making processes in the area of human maritime activities.

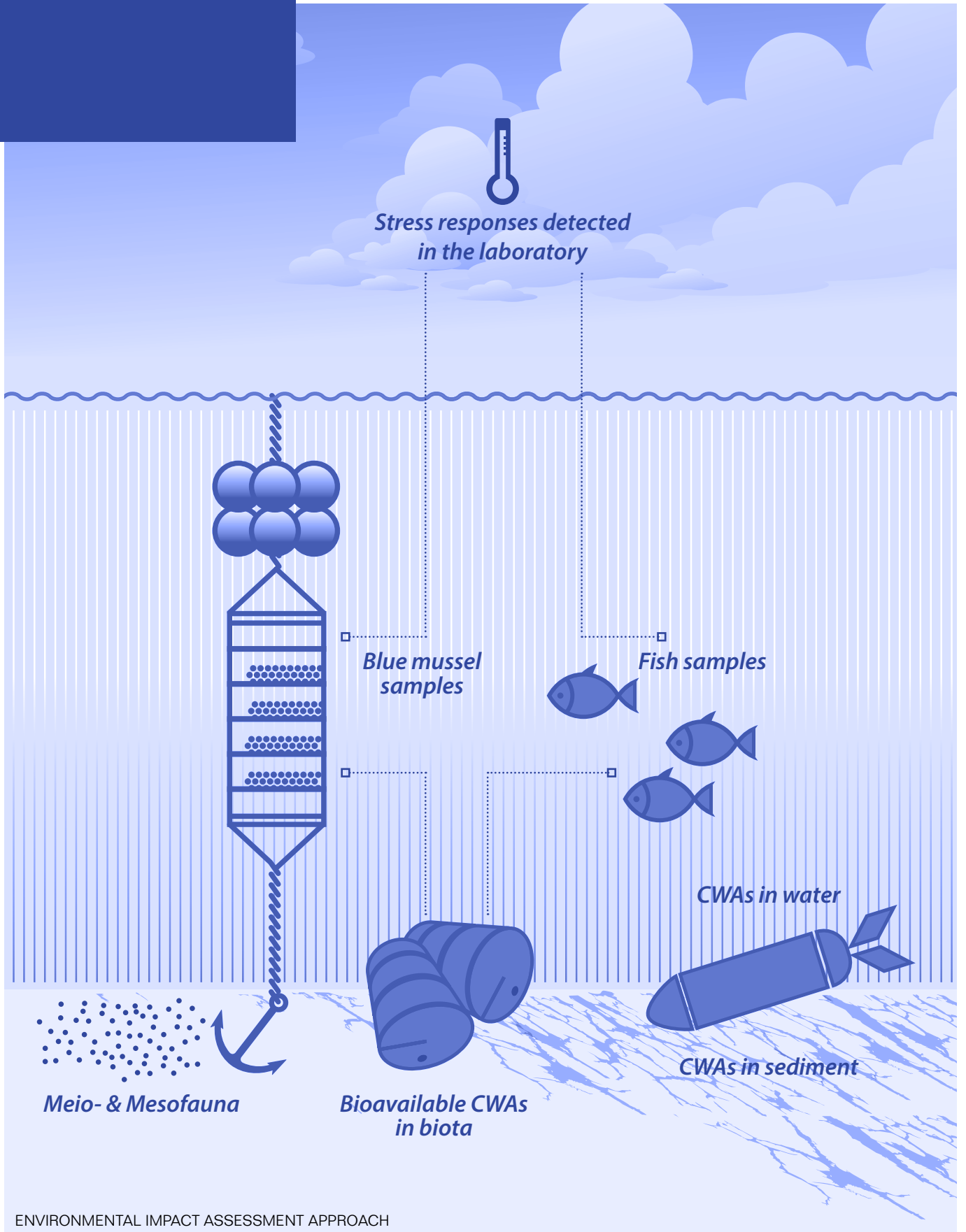






## **EFFECTS OF CWA LEAKAGE ON BIOTA AND SEDIMENTS AT DUMPING SITES**

- Effects of CWA on biota at dumping sites
- CWA in sediments



**OCEAN WATERS ARE IN A CONSTANT FLUX, MAKING THE STUDY OF EFFECTS OF CWA ON FISH, PLANTS AND OTHER MARINE BIOTA A CHALLENGING TASK. SEVERAL APPROACHES WERE USED TO EVALUATE THE ENVIRONMENTAL STRESS GENERATED BY CWA IN SEDIMENTS AND THE WATER COLUMN. THEY INCLUDED THE STUDY OF INFAUNA COMMUNITIES AS WELL AS THE HEALTH EFFECTS ON COD AND MUSSELS. HUNDREDS OF SEDIMENT, WATER AND TISSUE SAMPLES WERE COLLECTED AND SUBSEQUENTLY ANALYSED IN THE LABORATORY.**

### **3.1. EFFECTS OF CWA ON BIOTA AT DUMPING SITES**

#### **3.1.1. Macro- and Meiofauna**

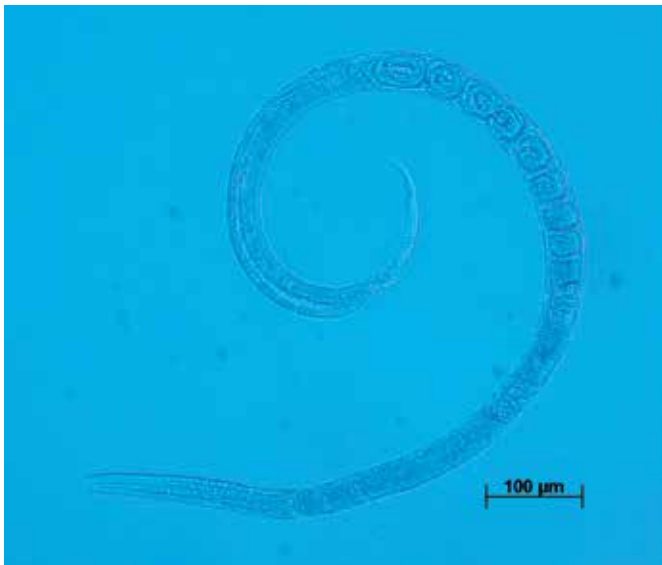
Benthic organisms, i.e. those living in the bottom substratum of a body of water, especially in the bottom-most oceanic sediments are called macro- and meiofauna. Meiofauna are small benthic invertebrates that live in both marine and freshwater environments passing unharmed through a 0.5 – 1 mm mesh but retained by a 30 – 45  $\mu\text{m}$  mesh. Mesofauna are macroscopic sediment invertebrates such as arthropods or nematodes. Organisms belonging to macro- as well as meiofauna are widely used benthic ecological indicators for monitoring the health of an environment or ecosystem.

In the CHEMSEA project three sampling sites were selected to investigate the macro- and meiofauna communities: Bornholm Deep, Gotland Deep and Gdansk Deep. Fauna collected from these locations was compared with fauna from a reference area located between the study regions in an area of similar depth, i.e. deeper than 80 m. In total six scientific cruises were conducted in different seasons between 2011 and 2013. During the first, second and third expeditions macrofauna was collected using box-core and Van-Veen grab sampling equipment. Sub-samples for meiofauna were collected using a plexiglass core with a 10 cm<sup>2</sup> surface grip. During subsequent cruises a remote operating underwater vehicle (ROV) equipped with a sampling device for faunal material was used. This offered the opportunity to collect

samples in the immediate vicinity of buried objects that may be a potential source of chemical pollution.

The first results show that macrofaunal and meiofaunal communities in CW dumping sites are very poor in terms of abundance and number of taxa in comparison with the reference area. A complete lack of any representatives of macrozoobenthos in all investigated dumping sites was noted. The Baltic deeps are inhabited only by nematodes, mostly in very low densities. Therefore nematodes were used as a key species to explore the meiobenthic communities inhabiting chemical dumping sites in the Baltic deeps.

In total 48 genera of nematodes belonging to 21 families were noted in all investigated areas. The most frequently occurring were nematodes belonging to the genus *Sabatieria* and *Terschellingia*. The dominating species were *Tripyloides marinus* and *Terschellingia longicaudata*. A first Baltic Sea record of viviparous nematodes (*Halomonhystera*) was observed. All listed species are resistant to low oxygen concentrations in the external environment. The direct effects of CWA on benthic faunal communities, however, are difficult to determine due to hypoxic or even anoxic conditions. Although the lack of oxygen near the bottom at sampling sites located below 80-100 m depth is probably the main factor in determining the occurrence of living organisms, in combination with this, the low nematode density and diversity at dumping sites can also be regarded as the consequence of the higher toxicity levels in the sediments.



HALOMONHYSTERA SPP. COLLECTED DURING CHEMSEA PROJECT IN THE AREA OF GOTLAND DEEP. ©IO PAN

Reference: Kotwicki, Lech; Grzelak, Katarzyna (2013): Summary of adverse ecological effects to infauna. CHEMSEA Report.

### 3.1.2. Cod (*Gadus morhua* L.)

Cod is the most abundant gadoid species in the Baltic Sea and with landings of around 70.000 t/year it is of major economic importance. Given its value as a fishery resource, the ecology and stock structure of cod have been thoroughly studied and changes in stock performance are assessed regularly by all countries around the Baltic Sea involved in cod fishing. In addition to stock assessment surveys, some countries have been monitoring the health status of cod since the 1980s, mainly as part of national environmental monitoring programmes. From these studies, long-term health data are available that have previously been used for the analysis of spatial and temporal patterns in disease occurrence. These data are therefore of major relevance for the CHEMSEA project as reference information. Besides being a well-studied fish species, cod was selected for the CHEMSEA project as target species primarily because it is a demersal and benthic-pelagic species and thus is at risk of being in direct contact with dumped CWA. Furthermore, it is widely distributed in the Baltic Sea and also inhabits areas

with dumped CW. Actually, some of its major spawning grounds are located in the deep basins at Bornholm and Gotland, the main CW dumping areas after World War II. For the CHEMSEA project, the Thünen Institute of Fisheries Ecology (FI), the Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research (AWI), the Finnish Environment Institute (SYKE) and the Nature Research Centre (NRC) assessed the health status of cod at CW dumpsites and in reference areas in the Baltic Sea. Sampling took place during four campaigns between December 2011 and September 2013 onboard the fishery research vessel Walther Herwig III. Cod was sampled by means of pelagic (at the dumpsites) and bottom trawling (at the reference sites), covering official and suspected dumpsites (Bornholm, Gotland, Belt Sea, Gdansk Deep) as well as a number of reference sites in the western (Arkona Sea) and eastern Baltic Sea (outside the Gulf of Gdansk). In addition to studies on grossly visible external and internal diseases and parasites and biometric characteristics carried out directly onboard the vessel, a large number of tissue samples were taken for subsequent analyses of contaminant concentrations as well as for the analysis of biochemical, physiological, pathological, neurotoxic and genotoxic responses to CWA exposure (see Table 1).

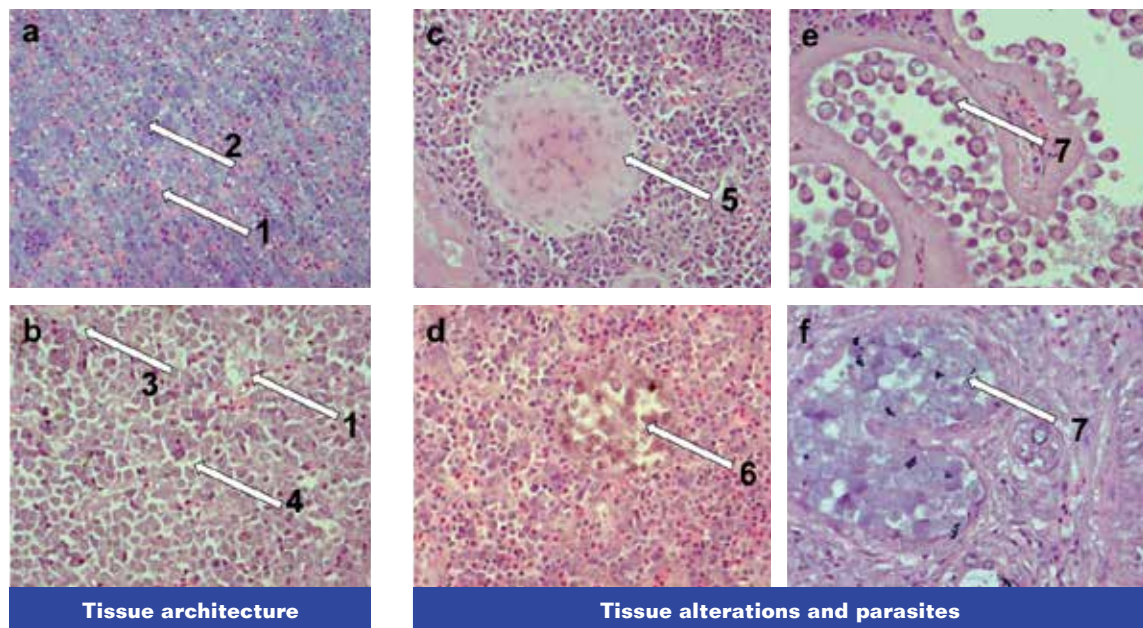
Summarising the results of these analyses and of all campaigns, the data reveal no significant overall health effects in cod from CW dumpsites compared to the reference areas. However, when looking at single parameters some differences were noted, possibly reflecting responses to CWA exposure. As an example, tissue samples of the blood generating head kidneys of cod from 2011 showed more alterations and less compact tissue architecture in individuals caught at the dumping sites compared to those from the reference area (Figure 1).

The latter finding influences the risk of cod getting in contact with CWA. As an example, Figure 2 shows results of the studies on externally visible diseases and parasites of cod carried out in December 2011 and 2012. While the mean Fish Disease Index (FDI) value at the Bornholm dumpsite was high in 2011, it was significantly lower in 2012 and did not indicate differences between CWA dumpsites and the reference areas (B09, B10 and B11). Thus, it cannot be excluded that health risks posed by CWA vary on the short and the long term scales. In a variable environment like the Baltic Sea, the implementation of regular monitoring and assessment of CWA risks should therefore be considered.

Table 1: Health and fitness indicators measured in cod from CWA dumpsites and reference sites

<b>Fitness</b>	Condition factor
	Liver somatic index
	Spleen somatic index
	Gonadosomatic index
<b>Disease and pathology</b>	Gross diseases and parasites
	Liver histopathology
	Head kidney pathology
	Lysosomal membrane stability
	Differential blood cell counts
<b>Cyto-/genotoxicity</b>	Morphological alterations in red blood cells
<b>Neurotoxicity</b>	Acetylcholinesterase (AChE) inhibition
<b>Oxidative stress</b>	Antioxidant defence enzymes (e.g. catalase, glutathione reductase)

Figure 1: Histopathological alterations in head kidney of cod (*Gadus morhua*)



**Photo a:**

Healthy tissue, displaying many blood vessels, dense cluster of HC, no interspace between cells and low vacuolisation.

**Photo b:**

Disturbed tissue architecture, with low number of blood vessels, large interspace between cells, less dense HC cluster and marked vacuolisation.

**Photo c-f:**

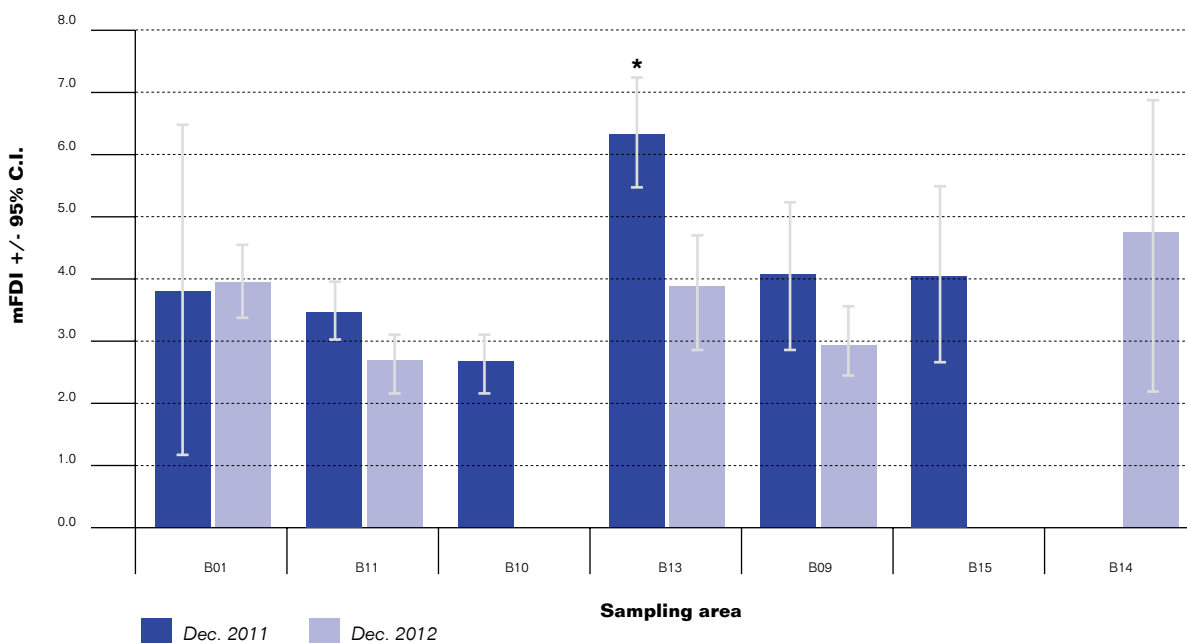
Tissues of head kidneys showing alterations such as granulomas (a), macrophagic aggregates (d) and parasites in the head kidney ducts (e, f)

- 1 Blood vessel
- 2 Cluster of haematopoietic cells (HC)
- 3 Vacuolisation
- 4 Large interspace between cells
- 5 Granuloma
- 6 Macrophagic aggregate
- 7 Parasites in head kidney ducts



BALTIC COD IN ITS NATURAL HABITAT

Figure 3: Fish Disease Index (FDI)



Fish Disease Index (FDI) in cod (*Gadus morhua*) from CHEMSEA sampling areas and campaigns in Dec. 2011 and 2012, summarising data on the presence of 7 externally visible diseases and parasites (skin ulceration, skeletal deformities, epidermal hyperplasia/papilloma, fin rot/erosion, pseudobranchial pseudotumour, *Lernaeocera branchialis*, *Cryptocotyle lingua*). High values reflect elevated disease prevalences. (B13: Bornholm dumpsite, B15: Gotland dumpsite, B01: close to dumpsite in the Belt Sea, B14: suspected dumpsite Gdansk Deep, B09: reference site outside Gulf of Gdansk, B10 and B11: western reference sites Arkona Sea) (\* indicates significant difference between sampling campaigns)

References: Chemical Munitions Search & Assessment – a complex evaluation of the dumped munitions problem in the Baltic Sea. Jacek Beldowski\*, Zygmunt Klusek, Marta Szubska, Raisa Turja, Anna I. Bulczak, Daniel Rak, Matthias Brenner, Thomas Lang, Lech Kotwicki, Katarzyna Grzelak, Jaromir Jakacki, Nicolai Fricke, Anders Ostin, Ulf Olsson, Jacek Fabisiak, Galina Garnaga, Jenny Rattfelt Nyholm, Katja Broeg, Paula Vanninen, Stanislaw Popiel, Kari Lehtonen, Rune Berglund to be published in Deep Sea Research.

### 3.1.3. Blue mussels (*Mytilus edulis* L.)

Blue mussels are widely used as sentinel species for studying the accumulation and biological effects of a variety of contaminants present in the marine environment. CWA present in the sea bottom of the Bornholm Basin study area may induce a variety of adverse biological effects in organisms exposed to them. Using the mussel as a model organism, the aim of the study was to use various biomarker methods representing different biological functions and levels of biological organisation to allow prediction of potential risks of dumped chemicals to aquatic organisms.

Within the frame of the CHEMSEA project specially designed cages were deployed at two different depths between May and August 2012 at two selected hotspot sites and one reference site in the Bornholm dumping area. Based on this hydrographical data, the cages were placed at 35 and 65 m depth at all stations. The poor oxygen conditions ( $<1$  mg O<sub>2</sub> l<sup>-1</sup>) prevailing in the main CW dumping area (average depth ca. 95 m) made caging closer to the sea bottom unfeasible.

Mussels for the caging experiment were collected by scuba divers on the east coast of Bornholm in Svenske Havn. The mussel cages deployed in the Bornholm Basin in late May 2012 were successfully retrieved during the COMBINE 3 cruise of the R/V Aranda in late August 2012 (total exposure time 2.5 months). About 400 mussels were deployed per cage and an additional 400 mussels were collected to be dissected immediately for the “start” condition. In addition, the cages were equipped with POCIS (Polar Organic Chemical Integrative Sampler) passive samplers to record the accumulation of selected organic contaminants as well as hydrography sensors with automatic loggers measuring temperature, salinity and oxygen at 30 min intervals.

Mortality of the mussels in all 6 cages was in general very low and oxygen conditions were relatively good also at the depth of 65 m (ca. 4.9 mL/L). Dissecting of the mussels for chemical and biomarker analyses started immediately and all samples were stored as appropriate for each analysis type. Tissue samples taken were analysed in close cooperation of three CHEMSEA project partners: the Finnish Environment Institute (SYKE), the Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research (AWI) and the Nature Research Centre (NRC). Samples were analysed for a selected battery of biomarkers including genotoxic, cytotoxic and neurotoxic effects, oxidative stress and lysosomal responses. Integrated biomarker response index, sex and gamete development, bioenergetic status and concentrations of CWAs and their metabolites were assessed for a holistic determination of the health status of the caged mussels. In addition, samples were also taken for chemical analysis to detect CWAs and CWA metabolites in the tissues. In



BLUE MUSSELS

a final step, about 400 mussels were collected by scuba divers from the same place (Svenske Havn) as in May 2012 in order to document “end” condition in the natural population.

First results show highest biomarker responses at both hotspot sites at 65 m. Markedly lower lysosomal membrane stability observed in 65 m cages at hotspot stations indicated significantly impaired haemocyte function compared to all other stations. A somewhat lower LMS value at the 65 m reference station compared to 35 m stations possibly shows the effect of increased general stress due to the e.g. lower oxygen at the 65 m. Environmental parameters recorded at those depths showed that the salinity and the concentration of dissolved oxygen fluctuated, indicating mixing of the near bottom water in the sub halocline water layer. Thus, this makes it likely that mussels at 65 m were exposed to CWAs and other contaminants present in the sediment or near bottom water resulting in the observed biological effects. However, it has to be kept in mind that mussels were also exposed to lower oxygen concentrations that could, at least for a short period of time, induce the change from aerobic to anaerobic metabolism and contribute to the variation in the observed biological responses.

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References: Anu Lastumäki, Raisa Turja, Kari Lehtonen, Katja Broeg and Matthias Brenner. Plan and report of the in situ mussel caging experiment. CHEMSEA Report 2012.

### 3.1.4. Water fleas (*Daphnia magna*)

In addition to blue mussels water fleas are also an indicator genus to test the effects of toxins on an ecosystem. Water fleas are particularly useful due to their short lifespan and reproductive capabilities. For the CHEMSEA project water fleas were exposed at the Swedish Defence Research Agency (FOI) to slurries and water extracts from sediment samples from the Gotland Deep CW dumping site.

The experiment was set up as a static acute toxicity test. Glass beakers (50 ml) were filled with 25 ml test solution at a concentration of 50% sediment extract. *Daphnia* culture medium was used as diluent. Two experiments were run on sediment extracts using *Daphnia magna* as test animal: testing the effect on survival and galactosidase activity (*Daphnia* IQ-test) and testing the effects on juvenile growth.

**IQ-test and survival:** The survival test included juvenile (< 24 h old) water fleas exposed for 48 h to sediment extracts. At the end of experiments number of live individuals was counted. In the IQ-test, 4 days old animals were used, and exposure lasted the same time. The galactosidase activity was measured at the end of this test.

**Juvenile growth:** at the start of the test the animals were not older than 18 h. The duration of the exposure was maximised to 120 h. During the exposure the animals were fed daily with green algae at a density of  $10^7$  cells/L. Ten animals were used in each of two replicates per extract. The length of the animals, from the top of the head to the base of the spine, was measured at the beginning and at the end of the experiment. The animals were photographed with a reference (mm). From the photo, the length was measured using a calliper.

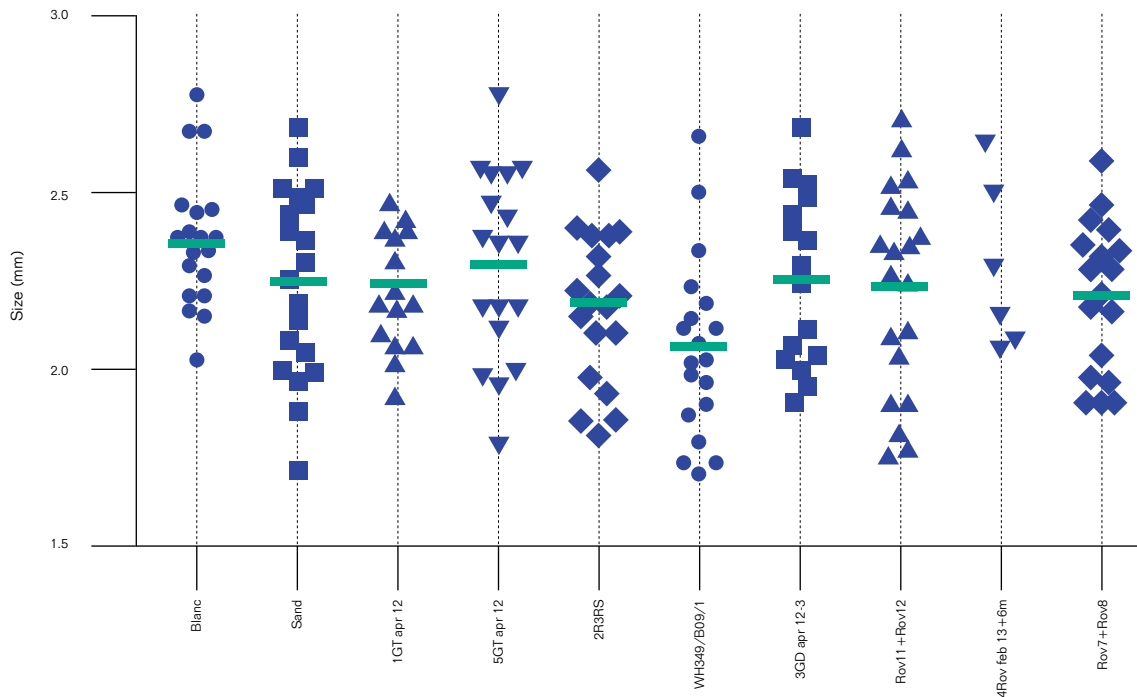
The results of the laboratory experiments showed that the slurries of the sediments were not toxic to the animals. In the experiment on sediment extracts two of the extracts affected both the survival and the galactosidase activity. In the growth study one extract decreased the growth of the juveniles significantly. However, the analysis of the sediment samples indicates that none of the three toxic samples actually showed traces of compounds related to the presence of CWA. Which compound in the three sediments samples actually affected the water fleas is yet unknown.



DAPHNIA MAGNA - FEMALE ADULT



Size of *Daphnia magna* after 120 h incubation to sediment extracts from the baltic sea.  
© FOI/CHEMSEA



Effect of sediment extract on survival and galactosidase activity (fluorescence) in juvenile *Daphnia magna* after 48 h exposure. © FOI/CHEMSEA

Sediment extracts 50%	Blank	1	2	3	4	5	6	7	8	6
% live animals	100	94	100	100	50	89	100	44	72	100
% fluorescent of live animals	100	100	100	100	78	100	100	63	85	94

Sample number:

1 = 3GD Apr. 12; 2 = ROV4; 3 = ROV7+ROV8; 4 = 5GT Apr. 12; 5 = 1 GT Apr. 12; 6 = 2R3RS; 7 = 4ROV Feb. 13+6 m; 8 = ROV11+ROV12; 9 = WH349/B09/1

Reference: Berglind, R.; Johansson, T.; Akfur, M. C. (forthcoming): Effect of sediment extract on survival, galactosidase activity and juvenile growth in *Daphnia magna*.

### 3.1.5. Chemical analysis of cod and mussel tissues

In the evaluation of the risks of dumped CWAs, triphenylarsine (TPA) is thought to pose the highest risk to the fish community followed by sulphur mustard (H), Adamsite (DM) and Clark I (DA)<sup>1</sup>. The exact effects of these chemicals in fish are not known and no information is available concerning the relative intake and detoxification rates of CWAs in fish tissues or other marine organisms, such as mussels<sup>2</sup>. The human metabolites of CWAs could give a hint about the structure of the fish metabolites but the metabolism of fish or other marine organisms may be quite different.

The liver is a site of detoxification and chemicals are thought to accumulate in it prior to transformation and excretion into bile and urine. Fish muscle is also important for analysis as it is the part of the fish usually consumed and the intact nonpolar chemicals could accumulate in the muscle tissue. For these reasons, cod urine, bile and muscle tissues were chosen for chemical analysis in addition to the whole blue mussels from caging experiments. From each of the three stations, 20 fish samples were analysed from all selected tissues, a total of 180 samples. The total number of pooled blue mussels was 24.

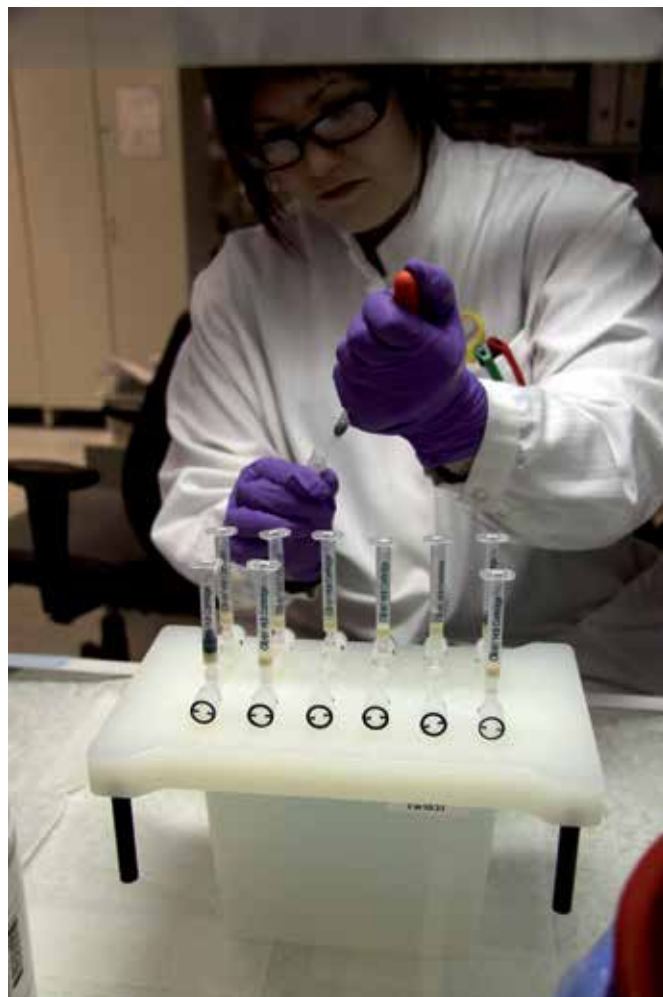
Prediction of metabolites, also called chemical biomarkers, is difficult when information about the metabolism of CWAs in fish is lacking. However, typical and probable metabolic reactions are both hydrolysis and oxidation, which occur mainly in the liver. These products could be excreted into urine or metabolised further. In addition, conjugation reactions are also possible along with other metabolic reactions.

Sulphur mustard hydrolyses quickly into thiodiglycol (TDG) in aqueous environments. TDG was analysed from cod urine and bile as well as from whole mussels. TDG could also be found in its oxidised form as thiodiglycol sulfoxide and it is reduced to TDG at the beginning of sample preparation. Analyses were performed using combined gas chromatography–tandem mass spectrometry (GC-MS/MS) and the TDG was detected as its heptafluorobutyrylimidazole (HBFI) derivative. There are also two unequivocal biomarkers of sulphur mustard,  $\beta$ -lyase metabolites (SBMSE and MSMTESE), which were also analysed from cod urine and bile samples as their reduced form as SBMTE using GC-MS/MS. Reduction was performed with titanium chloride ( $TiCl_3$ ). These metabolites are the result of conjugation reactions between sulphur mustard and glutathione (GSH). All samples were treated with solid-phase extraction (SPE) prior to analysis.

DM, DA and TPA are more lipophilic chemicals than sulphur mustard. They were analysed as their oxidation products using liquid chromatography–tandem mass spectrometry (LC-MS/MS) from cod muscle and mussel samples.

The sample preparation for these analyses is laborious and includes homogenisation, multiple extractions, dispersive SPE (dSPE) for lipid removal and filtration. TPA was also analysed as an intact chemical from muscle and mussel tissues since its nonpolar structure enables the accumulation into tissues. This method is under development.

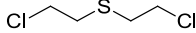
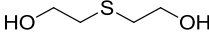
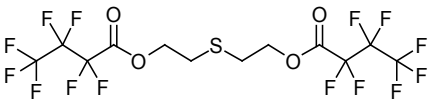
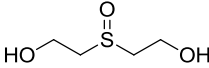
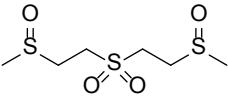
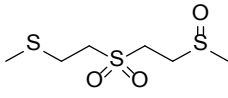
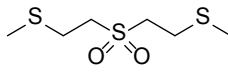
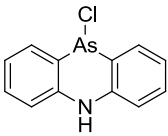
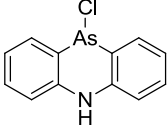
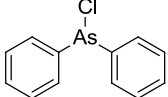
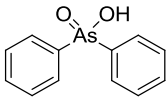
All the target chemicals and their analysis methods for various tissues are combined in Table 2. The analysis of cod and mussel tissues to find possible biomarkers for CWA exposure are in progress. Analysis results will be available by the end of the CHEMSEA project.

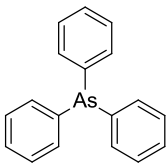
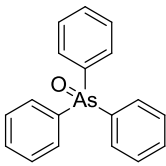


<sup>1</sup> Sanderson, H.; Fauser, P.; Thomsen, M. and Sørensen, P. B. Human health risk screening due to consumption of fish contaminated with chemical warfare agents in the Baltic Sea, *Journal of Hazardous Materials* 162 (2009) 416-422.

<sup>2</sup> MERCW Deliverable 3.3.4, Literature review of methods for analysis of chemicals related to sea-dumped chemical weapons in fish tissues and some other biological samples (2008).

Table 2: Target chemicals for screening cod and mussel samples  
 HFBI = heptafluorobutyrylimidazole;  $\text{TiCl}_3$  = titanium chloride

	Chemical (acronym) CAS	Structure	Description	GC-based			LC-based		Method available
				intact	HFBI	$\text{TiCl}_3$	intact	$\text{H}_2\text{O}_2$	
<b>1</b>	Sulphur mustard (H) 505-60-2		Dumped CW agent	<b>Not analysed as such</b>					
<b>1.1</b>	Thiodiglycol (TDG) 111-48-8		Hydrolysis product of <b>1</b>	<b>Not analysed as such</b>					
<b>1.1F</b>		HFBI derivative of <b>1.1</b>	<b>Urine (60) Bile (60) Mussel (24)</b>	<b>Yes Yes Under development</b>					
<b>1.1O</b>	Thiodiglycol sulfoxide 3085-45-8		Oxidation product of <b>1</b> (either natural or with $\text{H}_2\text{O}_2$ )	<b>Not analysed as such (analysed as 1.1F after <math>\text{TiCl}_3</math> reduction and HFBI Derivatisation)</b>					
<b>1.8</b>	$\beta$ -lyase metabolite (SBMSE) 137371-96-1		Prime urine metabolite of <b>1</b> in human	<b>Not analysed as such</b>					
<b>1.9</b>	$\beta$ -lyase metabolite (MSMTESE) 137371-97-2		Prime urine metabolite of <b>1</b> in human	<b>Not analysed as such</b>					
<b>1.9R</b>	$\beta$ -lyase metabolite (SBMTE) 197371-98-3		Reduction product of <b>1.8</b> and <b>1.9</b>	<b>Urine (60) Bile (60)</b>	<b>Yes Yes</b>				
<b>2</b>	Adamsite (DM) 578-94-9		Dumped CW agent	<b>Not analysed as such</b>					
<b>20</b>	5,10-Dihydrophenoarsazin-10-ol 10-oxide 4733-19-1		Oxidation product of <b>2</b> and all of its degradation products (either natural or with $\text{H}_2\text{O}_2$ )		<b>Muscle (60) Mussel (24)</b>	<b>Yes Yes</b>			
<b>3</b>	Clark I (DA) 712-48-1		Dumped CW agent. Also component in dumped arsine oil.	<b>Not analysed as such</b>					
<b>30</b>	Diphenylarsinic acid 4656-80-8		Oxidation product of <b>3</b> (either natural or with $\text{H}_2\text{O}_2$ )		<b>Muscle (60) Mussel (24)</b>	<b>Yes Yes</b>			

	Chemical (acronym) CAS	Structure	Description	GC-based			LC-based		Method available
				intact	PrSH	BSTFA	intact	H <sub>2</sub> O <sub>2</sub>	
4	Triphenylarsine (TPA) 603-32-7		Component in dumped arsine oil						Under development
40	Triphenylarsine oxide 1153-05-5		Oxidation product of 4 (either natural or with H <sub>2</sub> O <sub>2</sub> )						Muscle (60) Yes Mussel (24) Yes

### 3.1.6. Summary: CWA impact on biota

The results of studies on cod health indicate no significant generic health effects in cod from CW dumpsites compared to reference sites. However, at lower organisational levels, such as organ, tissue, cellular and subcellular levels, some stress responses could be recorded in cod from CW dumpsites using the applied suite of biomarkers. Supporting this, higher stress responses were also observed in mussels deployed closer to the dumped CW (65 m) compared to the respective reference site and to mussels caged closer to the water surface (35 m).

The often anoxic conditions in the water bodies surrounding the dumped CW in the deep basins of the Baltic Sea limit the potential of common biological effect monitoring approaches in the field. If oxygen concentrations fall below 2 ml/L in the bottom water, marine organisms tend to migrate to more oxygenated waters. Therefore, a direct exposure of living organisms to the most polluted water bodies is unlikely to occur. However, it is well known that species such as cod can be found in water layers with very low oxygen levels and thus at least a temporary risk of direct contact of cod or other species with munitions or released toxic compounds of CWA cannot be excluded.

It seems necessary to extend research and monitoring activities both on a time scale, to reduce variability coming from changes in environmental conditions, and on a geographical scale, so that dumping areas without oxygen depletion (e.g. Skagerrak) can be included to create a comprehensive monitoring approach. Further, more efforts should be placed on conducting laboratory exposures using different ecologically relevant key species to assess biological effects and uptake mechanisms of toxic compounds leaking from dumped CW on exposed organisms.

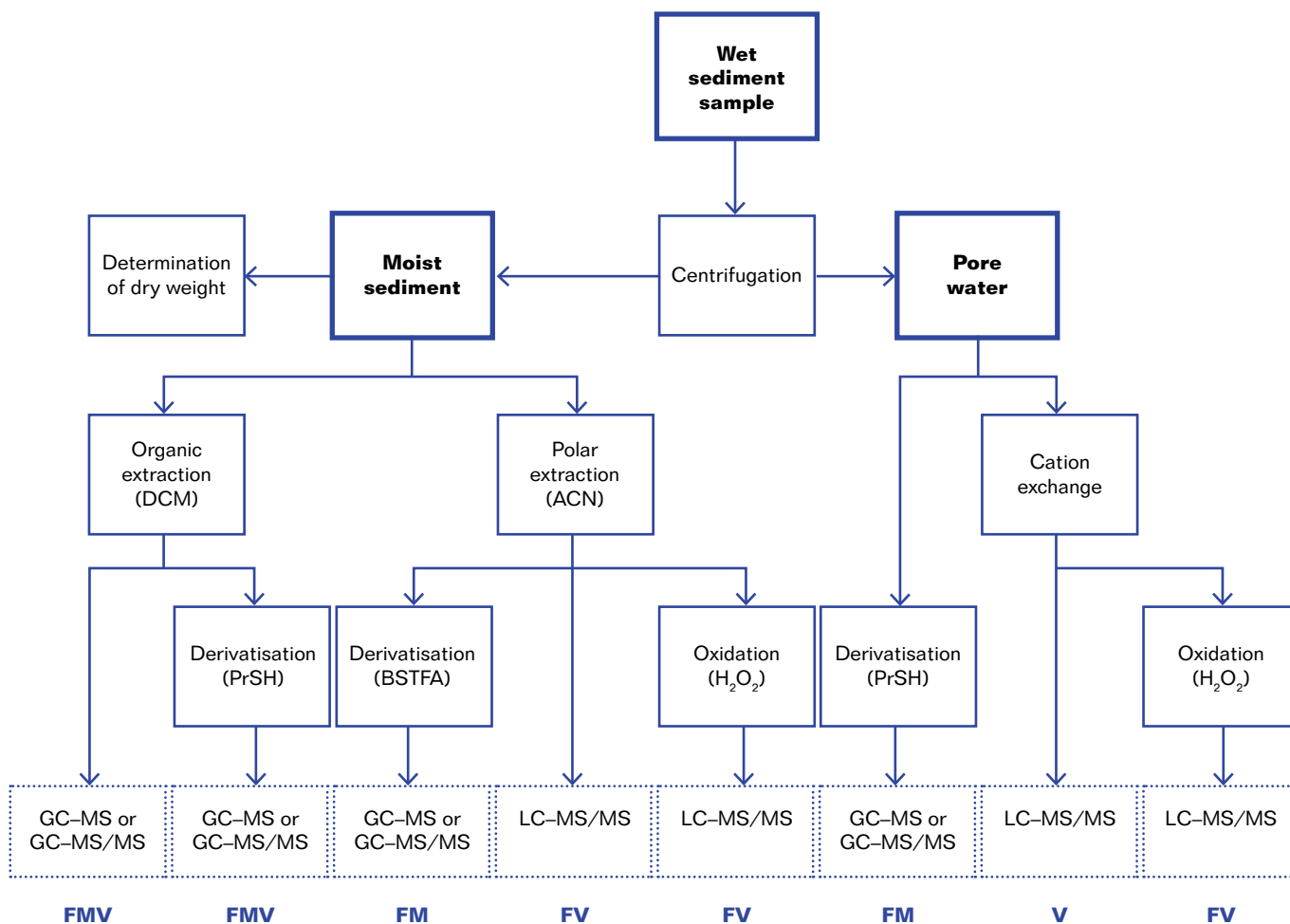
## 3.2. CWA IN SEDIMENTS

### 3.2.1. Screening methods for CWA products

Prior to sediment sampling and analysis CHEMSEA partners reviewed analytical screening methods and agreed on relevant CWA related compounds to identify the presence of the active agent or degradation, hydrolysis or biological markers that could demonstrate a history of presence and/or exposure to CWA related material. The choice of analytical methods and suitable marker chemicals was based on a CHEMSEA methodological review and VERIFIN experience in the analysis of samples taken during the MERCW project in the Bornholm Deep.

In order to catch the widest range of degradation products the sediment was extracted using both organic and polar solvents. After consideration the selected solvents were dichloromethane (DCM) and acetonitrile (ACN), respectively. The DCM extract as well as its derivatised fractions (using propanethiol) were analysed using either gas chromatography-mass spectrometry (GC-MS) or gas chromatography-tandem mass spectrometry (GC-MS/MS). ACN extracts and their oxidised fractions (using hydrogen peroxide) were analysed using liquid chromatography-tandem mass spectrometry (LC-MS/MS). ACN extracts and their oxidised fractions (using hydrogen peroxide) were analysed using liquid chromatography-tandem mass spectrometry (LC-MS/MS).

### CHEMSEA FLOW CHART FOR ANALYSIS OF THE TARGET CHEMICALS IN SEDIMENT SAMPLES



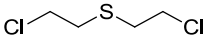
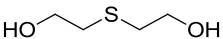
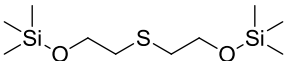
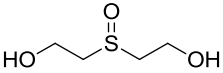
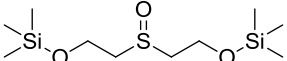

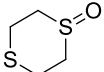
F – FOI, M – MUT, V – VERIFIN




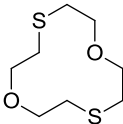
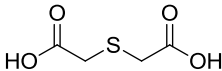
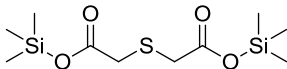
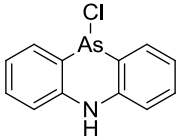
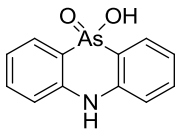
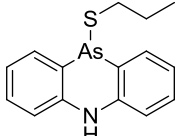
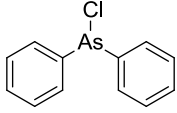
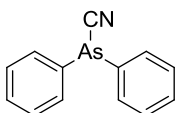
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Additionally, silylated fractions of the ACN extracts were analysed using GC-MS or GC-MS/MS. As the instrumentation available at the three analysis laboratories was different, different solutions for the sample preparation had to be taken to allow the full range of target chemicals to be analysed.

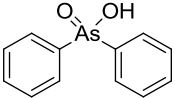
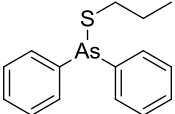
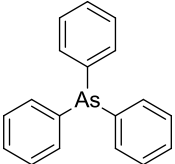
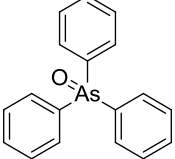
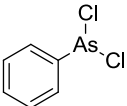
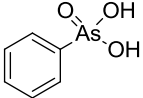
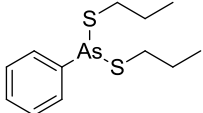
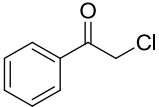
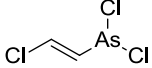
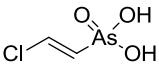
All the selected analysis methods were targeted to the analytes to achieve the best possible sensitivity. Therefore, either selected ion monitoring (SIM) or selected reaction monitoring (SRM) methods were used. This also means that no chemicals outside the list of selected targets could be detected.

Table 3: Target chemicals for analysis of sediment samples in CHEMSEA project  
PrSH = propan-1-thiol; BSTFA = (N,O-bis(trimethylsilyl) trifluoroacetamide); Laboratories: F = FOI, M = MUT, V = VERIFIN

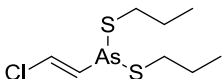
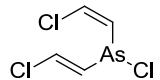
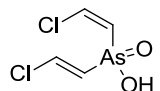
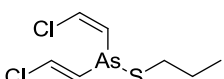
	Chemical (acronym) CAS	Structure	Description	GC-based			LC-based	
				intact	PrSH	BSTFA	intact	H <sub>2</sub> O <sub>2</sub>
<b>1</b>	Sulphur mustard (H) 505-60-2		Dumped CW agent	<b>FMV</b>				
<b>1.1</b>	Thiodiglycol (TDG) 111-48-8		Hydrolysis product of <b>1</b>				<b>V</b>	
<b>1.1S</b>	Bis(2-siloxyethyl) sulfide 20486-03-7		BSTFA derivative of <b>1.1</b>			<b>FM</b>		
<b>1.1O</b>	Thiodiglycol sulfoxide 3085-45-8		Oxidation product of <b>1</b> (either natural or with H <sub>2</sub> O <sub>2</sub> )				<b>FV</b>	
<b>1.1OS</b>	Bis(2-siloxyethyl) sulfoxide		BSTFA derivative of <b>1.1O</b>			<b>M</b>		
<b>1.2</b>	1,4-Dithiane 505-29-3		Degradation product of <b>1</b>	<b>FMV</b>				
<b>1.2O</b>	1,4-Dithiane oxide 19087-70-8		Oxidation product of <b>1.2</b>	<b>M</b>			<b>FV</b>	

	Chemical (acronym) CAS	Structure	Description	GC-based			LC-based	
				intact	PrSH	BSTFA	intact	H <sub>2</sub> O <sub>2</sub>
<b>1.3</b>	1,4-Oxathiane 15980-15-1		Degradation product of <b>1</b>	FMV				
<b>1.4</b>	1,4,5-Oxadithiepane 3886-40-6		Degradation product or by-product of <b>1</b>	FMV				
<b>1.5</b>	1,2,5-Trithiepane 6576-93-8		Degradation product or by-product of <b>1</b>	FMV				
<b>1.6</b>	1,7-Dioxa-4,10-dithiacyclododecane 294-95-1		Degradation product or by-product of <b>1</b>	FMV				
<b>1.7</b>	Thiodiglycolic acid (TDGA) 123-93-3		Bacterial metabolite of <b>1.1</b>				FV	
<b>1.7S</b>	Bis(trimethylsilyl) 2,2'-thiodiacetate 20486-03-7		BSTFA derivative of <b>1.7</b>			FM		
<b>2</b>	Adamsite (DM) 578-94-9		Dumped CW agent				Not analysed as such	
<b>2O</b>	5,10-Dihydrophenoarsazin-10-ol 10-oxide 4733-19-1		Oxidation product of <b>2</b> and all of its degradation products (either natural or with H <sub>2</sub> O <sub>2</sub> )				FV	
<b>2T</b>	10-(propylthio)-5,10-dihydrophenarsazinine 7269-24-1		Derivative of <b>2</b> and all of its degradation products			FM		
<b>3a</b>	Clark I (DA) 712-48-1		Dumped CW agent. Also component in dumped arsine oil.				Not analysed as such	
<b>3b</b>	Clark II (DC) 23525-22-6		(Possibly) dumped CW agent				Not analysed as such	

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	Chemical (acronym) CAS	Structure	Description	GC-based			LC-based	
				intact	PrSH	BSTFA	intact	H <sub>2</sub> O <sub>2</sub>
<b>30</b>	Diphenylarsinic acid 4656-80-8		Oxidation product of <b>3a</b> and <b>3b</b> and all of their degradation products (either natural or with H <sub>2</sub> O <sub>2</sub> )					<b>FV</b>
<b>3T</b>	Diphenylpropylthioarsine 17544-92-2		Derivative of <b>3a</b> and <b>3b</b> and all of their degradation products		<b>FMV</b>			
<b>4</b>	Triphenylarsine (TPA) 603-32-7		Component in dumped arsine oil	<b>FMV</b>				
<b>40</b>	Triphenylarsine oxide 1153-05-5		Oxidation product of <b>4</b> and all of its degradation products (either natural or with H <sub>2</sub> O <sub>2</sub> )	<b>M</b>				<b>FV</b>
<b>5</b>	Phenyldichloroarsine (PDCA) 696-28-6		Dumped CW agent. Also component in dumped arsine oil.					<b>Not analysed as such</b>
<b>50</b>	Phenylarsonic acid 98-05-5		Oxidation product of <b>5</b> and all of its degradation products (either natural or with H <sub>2</sub> O <sub>2</sub> )					<b>FM</b>
<b>5T</b>	Dipropyl phenylarsonodithioite 1776-69-8		Oxidation product of <b>8</b> and all of its degradation products (either natural or with H <sub>2</sub> O <sub>2</sub> )		<b>FMV</b>			
<b>6</b>	α-Chloroacetophenone (CN) 532-27-4		Derivative of <b>8</b> and all of its degradation products	<b>FMV</b>				
<b>7</b>	Lewisite I (L1) 541-25-3		Dumped CW agent					<b>Not analysed as such</b>
<b>70</b>	2-Chlorovinylarsonic acid 64038-44-4		Oxidation product of <b>7</b> and all of its degradation products (either natural or with H <sub>2</sub> O <sub>2</sub> )					<b>F</b>



	Chemical (acronym) CAS	Structure	Description	GC-based			LC-based	
				intact	PrSH	BSTFA	intact	H <sub>2</sub> O <sub>2</sub>
<b>7T</b>	Dipropyl 2chlorovinyl arsonodithioite 677354-97-1		Derivative of <b>7</b> and all of its degradation products		<b>FMV</b>			
<b>8</b>	Lewisite II (L2) 40334-69-8		Dumped CW agent				<b>Not analysed as such</b>	
<b>8O</b>	Bis(2chlorovinyl) arsenic acid 157184-21-9							<b>FMV</b>
<b>8T</b>	Bis(2chlorovinyl) propylthioarsine 677355-04-3				<b>FMV</b>			

### 3.2.2. Inter-calibration study

As the analysis of both organic chemicals and heavy metals in the CHEMSEA project was divided between different laboratories it was necessary to verify that the results obtained by these laboratories would be comparable. Therefore, a transnational inter-calibration study was organised to test the methods selected and the performance of the laboratories for analysis of the selected sea dumped CW and/or their degradation products as well as for arsenic. The inter-calibration study was coordinated by VERIFIN.

Samples were sent to four other partners: IO PAN, MUT, FOI and LEPA. MUT, FOI and VERIFIN analysed the samples for organic CW and/or their degradation products and IO PAN, MUT and LEPA analysed the samples for organic and total arsenic. The results of the inter-calibration study were satisfactory and confirmed that all five partners could produce reliable results.

### 3.2.3. Concentrations in sediments

Sediment samples were collected during five cruises of the R/V Oceania (IO PAN) from March 2012 to April 2013 and a cruise of the R/V Vėjūnas organised by the Lithuanian Environment Protection Agency in April 2013. The sampling stations at the dumpsites were chosen near Class I objects according to sonar data obtained by scanning the sea floor by the Swedish Maritime Administrations (SMA). Several samples were collected with an ROV as close as possible to visible objects resembling munitions.

In addition to the sediment sampling, macrozoobenthos samples were collected and hydrological parameters measured (water current speed and direction, water temperature, salinity and dissolved oxygen). After analysing all samples and parameters the data showed no drastic changes in the environment at the chemical munitions dumpsite compared to previous research, although the number of the macrozoobenthos species had decreased notably.

Sediment samples were divided into subsamples and distributed among three different laboratories for CWA analysis – the Military University of Technology (MUT), the Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN) and the Swedish Defence Research Agency (FOI) – and three laboratories who analysed sediments for arsenic concentrations as an indicator of arsenic containing CWA – the Lithuanian Environment Protection Agency (LEPA), MUT and IO PAN.

#### CWA

The location of samples, where CWA degradation products were detected is presented in Maps section, on figure 6. A number of CWA and their degradation products were analysed in laboratories with the use of techniques based on liquid and gas chromatography coupled with mass spectrometry (GC–MS and LC–MS). The details concerning the methods used will be published later. The list of target chemicals presented in Table 3 includes: chemicals related to sulphur mustard, several arsenic-containing chemicals as well as a tear gas,  $\alpha$ -chloroacetophenone.

From the 179 sediment samples as many as 57 contained at least one target chemical. Chemicals related to mustard were found in 37 samples and arsenic-containing chemicals in 39 samples. Both types of chemicals were detected in 19 samples. Comparison of the distance between contaminated and non-contaminated samples leads to the conclusion that the pollution of sediments with CWA is local and strongly depends on the type of seabed, the condition of the munitions and the prevailing bottom currents. This finding is in line with findings by the MERCW project.

During the MERCW project, only minor traces were found

of sulphur mustard, which represents a large portion of all dumped agents. Therefore, new chemicals related to sulphur mustard were included in the list of target chemical in the CHEMSEA project compared to the MERCW project. This proved successful as mustard-related chemicals were detected in 57 of the 179 samples. The best indicators for previous presence of sulphur mustard proved to be two cyclic mustard degradation products: 1,4,5-oxadithiepane and 1,2,5-trithiepane (chemicals 1.4 and 1.5 in Table 3).

The most typically identified arsenic-containing chemicals were degradation products of Clark I. Degradation products for Adamsite were detected in 13 samples. Triphenylarsine, which is a component of arsine oil used both in arsenic containing and mustard related munitions, was detected in 19 samples.

When the samples were divided for analysis among the three laboratories, portions of the same sediment samples were delivered to two laboratories if enough sample was available. Most samples could be divided and only a few samples had to be analysed in only one laboratory. Although the analysis procedure differed slightly between laboratories, it was expected that in several cases positive identification would be made from both divided portions. It was noted that sediment samples were not homogenous and that portions of one sample can differ greatly in composition. Therefore, if a sample was not identified as positive by both laboratories it does not mean that the analysis is incorrect.

#### Bornholm Deep

A large portion of the 21 samples taken at the Bornholm Deep (86 %) was positive i.e. contained one or more target chemicals. 16 samples contained arsenic-containing chemicals. These findings are in line with the results obtained during the MERCW project. It was also noted that half of the samples (12) contained both mustard-related and arsenic-containing chemicals. Intact sulphur mustard was found at a very low level in one sample that was taken from the primary dumpsite located in the Bornholm Deep.

In the Bornholm area, many of the positive identifications were made by both laboratories analysing the divided samples. This makes these identifications very reliable.

#### Gotland Deep

More than half of the samples (108 samples) were taken in Gotland Deep. Ten of the samples were collected by LEPA in the Lithuanian part of Gotland Deep. Here 21 % of the samples were

found positive: 12 samples containing mustard related chemicals and 12 with arsenic containing chemicals. Only one sample contained both types of target chemicals. Contamination in Gotland Deep is clearly lower than in Bornholm Deep. In Gotland Deep, only one split sample was found positive in two laboratories. However, several chemicals were found by at least one laboratory.

### Gdansk Deep

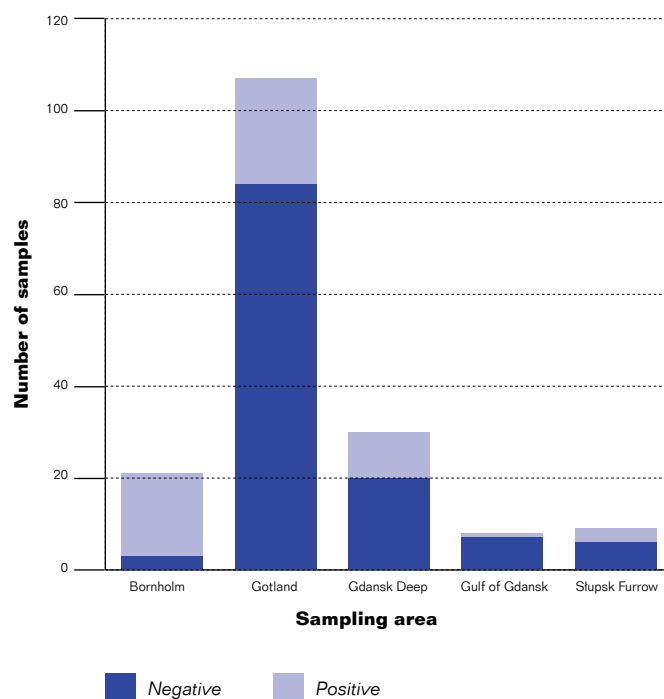
In the addition to the previously known dumpsites in Bornholm and Gotland Deep, 30 samples were taken from the Gdansk Deep, a potential CW dumpsite and 8 from nearby region of Gulf of Gdansk. According to the analysis results 10 samples from the Gdansk Deep and one sample from the Gulf of Gdansk contained target chemicals.

According to these results it seems that the suspicions that the Gdansk Deep was also used as a chemical dumpsite are correct. This, however, still requires final confirmations as nine of the eleven positive identifications were made by the same laboratory. The other two laboratories did not find these samples positive although the detected concentrations were relatively high.

### Slupsk Furrow

In addition to the known or suspected dumpsites, 10 samples were also taken in Slupsk. Three of these samples showed contamination. One sample out of three from a reference area located near Rozewie was found positive. This may indicate that CW were dumped in the transport route between harbours and areas designated as the official dumping sites. The findings from Slupsk Furrow also require final confirmation as they were made only by one laboratory, the same as in the case of Gdansk Deep.

Number of positive and negative samples in different sampling areas



### Arsenic

Concentrations of Arsenic in sediments is presented in maps section on figure 7. Total arsenic concentrations in sediments from chemical munition dumpsites and reference areas did not exceed the concentration of 24  $\mu\text{g/g}$ . Obtained results of As concentration remain in the range of geochemical background which amounts from 20 to 30  $\mu\text{g/g}$  depending on the literature source. Only 13 samples from a total of 179 had concentrations exceeding 20  $\mu\text{g/g}$ . The lowest value was detected in the Gulf of Gdansk (0.31  $\mu\text{g/g}$ ) and the highest in Gotland Deep, in the area of the official dumpsite (23  $\mu\text{g/g}$ ). Total arsenic concentrations differed significantly within individual areas. In the reference areas of Slupsk Furrow, Gulf of Gdansk and the Lithuanian EEZ in close vicinity to the dumpsites mean concentrations ranged from 5.7 to 9.0  $\mu\text{g/g}$ . The highest mean concentration of As was measured in the area of Bornholm Deep and amounted to 17  $\mu\text{g/g}$ . The station with the highest concentration (22  $\mu\text{g/g}$ ) was located in the middle of the dumpsite. Mean concentrations of As were also higher in the Gotland Deep and Gdansk Deep than those in the reference areas and amounted to 13 and 15  $\mu\text{g/g}$ , respectively. In 7 of the total 40 samples in which arsenic containing CWAs and/or their degradation products were detected, the concentrations of As exceeded 20  $\mu\text{g/g}$  and in 16 samples the concentration exceeded 15  $\mu\text{g/g}$ .

Organic arsenic contents in sediment showed neither spatial differences between sampling sites nor a correlation with total arsenic, organic matter and heavy metals. This may indicate that different methods should be developed for easy and inexpensive estimation of arsenic containing CWA based on arsenic analyses.

### 3.2.4. Degradation pathways

In general, as time progresses, the metallic mantles of munitions and bulk containers rust and are subject to mechanical erosion. At some point, hull integrity will be breached and contact between seawater and the chemical contents of a munition will be established.

Both CWA mixtures and explosives contained in the munition (ie. as bursting charges) are chemicals that may have reacted with other materials in the container or with themselves. Effectively, this aging process may have changed the properties of the chemical contents. With regard to CWA, compounds with less pronounced or without warfare capabilities may have emerged. Explosives, on the other hand, may have lost their handling safety and become sensitive to shocks and thus more dangerous.

When seawater comes into contact with these chemicals, it may act as a solvent or suspension agent. Consequently, the chemicals will leak into the environment, first spreading locally, possibly entering a sediment sorption / desorption equilibrium process and with time will, be distributed on a larger scale by hydrological processes and anthropogenic activities.

Once under the influence of environmental factors, chemicals may also undergo changes by abiotic (e.g. reactions with sea water and its components like dissolved oxygen or hydrogen sulfide, or closer to the surface, sunlight-mediated degradation) or biotic processes (e.g. bacteria-mediated biotransformation).

The propensity to undergo chemical transformations and the pathways and modes of environmental distribution, taken together the environmental fate of a chemical, depend on the nature of the chemical (e.g. reactivity, polarity) and on the prevailing ambient conditions (e.g. temperature, reaction partners, bacterial population). Resulting from these transformations are chemicals that may have properties similar to or quite unlike the parent compounds.

Some parent or transformation chemicals will undergo fast reactions, in other cases transformations will occur only very slowly. The latter chemicals are persistent in the environment and, given suitable hydrophobic (fat-soluble) properties, have the potential to bioaccumulate in living organisms via food webs (food chains). Persistent organic pollutants (POPs) are one of the principal issues in environmental pollution.

With regard to organic chemicals, the highest possible stage of chemical breakdown is mineralisation - conversion to e.g. carbon dioxide, ammonia, water and hydrogen sulfide. In the case of organometallic (e.g. organoarsenic-based CWA) or inorganic (e.g. metals from containers or the primary explosive lead (II) azide from detonators) chemical warfare materials, transformations will lead to inorganic species of heavy metals which can be converted to different organometallic species through biotic processes. These latter inorganic and organometallic species do occur naturally and their toxic properties depend on the chemical "wrapping", oxidation state and nature of the metal atom and may either be pronounced or negligible (e.g. arsenobetaine). Nonetheless, since the amounts of bioavailable heavy metals introduced by anthropogenic activities are considerable in comparison to the naturally bioavailable amounts, discharge of heavy metals into the environment is one of the principal issues of environmental pollution.

The behaviour of the CW munitions on the Baltic seafloor depends on two things. The first is how the munitions corrode and start leaching. The second is how the chemicals in the munitions behave in contact with the marine environment.

### Leaching

To assess the threat to the marine environment, Makles and Śliwakowski (Makles and Śliwakowski, 1997) developed a model according to which, depending of the type of ammunitions (containers), mustard gas will escape in the following way:

- Barrels: start 23 years after dumping, complete loss of containment after 60 years
- Bombs: start 46 years after dumping, complete loss of containment after 120 years
- Shells: start 69 years after dumping, complete loss of containment after 265 years

It was later observed that the containers often start leaching after point corrosion. This means that a hole is corroded through the wall material at a weak point. The effect of this is that the start of the leaching process is quite unpredictable and can occur faster than expected. Witkiewicz (Witkiewicz, 1997) claims that the transition of toxic agents into the surrounding water will take place mainly by way of diffusion. It is, by nature, a slow process and will additionally be hindered by the fact that the toxic agents escaping the ammunition and containers may be covered by a layer of seabed sediments. Therefore, he claimed that the concentration of toxic agents in the surrounding water will not be high and that the concentration of products of hydrolysis of the toxic agents will be small.

In the years 2000 through 2003, a significant increase in the number of incidents with sulphur mustard was



observed in the Baltic. The causes of the increase have not yet been identified (CBWCB, 2004, 2005, 2009), but the observation correlates well with the period of complete loss of containment of barrels.

### **CWA behaviour on the sea bottom**

The behaviour of chemical substances in the marine environment depends both on the chemical and physico-chemical properties of the substances and on the impact of environmental factors. Dissolution of CWA in the sea is considered to be an important first stage of their decomposition.

The maximum solubility of CWA in water is about 2,300 mg/l (triphenylchloroarsine). Hydrogen cyanide (also known as Zyklon B) is an exception as its solubility in water amounts to about 95,000 mg/l (Sanderson et al., 2008). In real conditions in the seawater, the maximum concentration of CWA will be less than 10 % of their theoretical solubility, and that only for a short period of time. As a result of further dissolution, dilution and the reaction of decomposition, the possibility of occurrence of high concentrations of CWAs in the seawater is unlikely. For phosgene and tabun, which easily solve in water, the initial concentration after release may be much higher.

In the marine environment tabun hydrolyses into phosphoric acid and hydrogen cyanide, which further breaks down to formic acid. At the temperature of 7 °C its half-life time equals approximately 5 hours. Thus, it poses a rather short-term threat to the marine environment, only when it occurs in high concentrations (Korzeniewski, 1996).

Phosgene hydrolysis is even faster, as the half-life even at 0 °C equals 20 seconds (for a 1 % solution). This is caused by the pH of the seawater, which buffers HCl and CO<sub>2</sub> resulting from phosgene decomposition (Korzeniewski, 1996).

Remaining CWA are characterised by lower breakdown rates and can be considered persistent pollutants.

Despite the initial rapidity of the hydrolysis reaction, sulphur mustard persists in the marine environment for decades. During such a long exposure to the impact of seawater and sediments, the hydrolysis of dissolved mustard is usually relatively fast, whereas the hydrolysis of un-dissolved mustard is slow, so both the hydrolysis rate and the dissolution rate of mustard gas must be taken into account. This factor causes the mustard degradation process to take weeks or years. Many varieties of mustard are present in the Baltic Bottom, this includes relatively pure sulphur mustard as well as various types of mixtures which can be more viscous or contain arsine oil (winter-grade mustard). The main mustard gas degradation pathway is supposed to be thiodiglycol and hydrochloric acid, while sulphur mustard degradation reaction is similar but even slower due to the presence of water insoluble thickening agents. Mustard is known to

also form various cyclic degradation products in addition to many other products. The degradation products are typically less toxic than mustard and hydrolysis products are more water soluble.

### **Degradation pathways for sulphur mustard**

In the years 1998-99, detailed laboratory tests of the mustard gas lump caught on 9 January 1997 were performed in the Military University of Technology in Warsaw. During the tests, chromatographic techniques (GC-MS, GC-AED) were employed. About 50 various chemical compounds of differing toxicity were found in the lump of mustard gas, while their chemical structure was identified in 30 cases. Those included sesqui mustard and its analogues as well as oxidized compounds. However, no thiodiglycol was detected, probably due to the high solubility of this compound (Mazurek et al., 2001).

Pursuant to the MEDEA report, the most probable time of decomposition of mustard gas lumps weighing 1 kg amounts to about 8 months (typical chemical ammunition), about 18 months for lumps weighing 10 kg (chemical artillery shell) and about 31 months for lumps weighing 100 kg (air bomb). However, mustard gas has the tendency to form gels with a jelly or rubbery consistency, with a polymer skin preventing further decomposition (Mazurek et al., 2001).

Besides mustard gas, arsenic-containing compounds (Clark I and II, Lewisite and Adamsite), as well as  $\alpha$ -chloroacetophenone are not readily water soluble either and hydrolyse even harder than mustard gas. During MERCW project research, a lump was found on one of the wrecks. Its analysis revealed that it was  $\alpha$ -chloroacetophenone. The chemical structure of this compound suggests that no biodegradation could occur. After dehalogenation (due to hydrolysis), non-toxic compounds are created, which might decompose completely in the seawater.

Clark I hydrolysis in water will lead to diphenylarsinous acid and hydrochloric acid and Clark II will lead to hydrogen cyanide and diphenylarsinous acid. Both hydrochloric acid and hydrogen cyanide are toxic but they will be detoxified quickly in water, so the toxic effects are short-term and local. Both arseno-organic compounds decompose later into toxic, inorganic arsenic compounds which are assimilated by organisms, adsorbed to the sediments and suspensions, desorbed and transported in dissolved form in the water column.

Adamsite hydrolyses into phenarsazin-10(5H)-ol and hydrochloric acid. Degradation of Adamsite is very similar to that of the clarks and degradation products are persistent, spread slowly and can undergo bioaccumulation.

Lewisite reacts with water to form chlorovinyl arsine oxide, which can be further decomposed into toxic arsenic acid and acetylene.

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### 3.2.5. Summary: Concentrations in sediments

Different environmental factors like temperature, salinity, oxygen presence or depletion, sediment type and chemistry or presence of bacteria, as well as their specific combination affect chemical processes in the marine environment. Chemicals undergo constant transformations and change their structure and properties. Therefore the main interest in detecting CWA in environmental samples is on their different degradation products. Derivatives or oxidation products of sulphur mustard, Adamsite, Clark I and Clark II, triphenylarsine, Lewisite I and Lewisite II were found in sediments. Despite the differences between parent chemicals and derivatives, most of the CWA degradation products have similar toxic properties to those of the chemicals they originate from. Furthermore, remaining CWA derivatives have lower breakdown rates and can be considered as persistent pollutants. Nearly one third of samples collected in the CHEMSEA project contained at least one trace of chemical munitions. In comparison only in one sample was intact sulphur mustard detected.

Pollution with CWA is most clearly visible in the Bornholm Deep. In this area nearly all analysed samples contained CWA derivatives. Arsenic containing CWA were found in 14 of the 21 total samples collected in the Bornholm Basin area. Total arsenic concentrations were also elevated in that region compared to background levels. Only in samples taken on the transect in growing distance from the primary or secondary Bornholm dumpsite did concentrations of arsenic decrease and no arsenic containing CWA were found in the sediment.

In the Gotland Deep dumping area the situation is more diversified. A number of sediment samples were free from CWA pollution and total arsenic concentrations did not show contiguous spatial distribution despite high mean concentration. It can thus be suggested that pollution

of sediments with CWA is local and strongly dependent on spot environmental features. This also shows that the disposal of chemical weapons was more spread within the Gotland dumpsite.

In the Gdansk Deep area considered to have been a potential dumping site, pollution with CWA was confirmed in half of the samples and mean arsenic concentration was also elevated in comparison with the reference area.

In all areas of interest there is a relation visible between total arsenic concentration and presence of arsenic containing chemicals related to CW although in very few cases did arsenic contents exceed the biogeochemical background estimated for the whole Baltic Sea.

According to the estimates of corrosion and leaching duration and the natural processes affecting CWA transformations and environmental conditions there is a possibility that the transition of toxic chemicals from the remaining weapon to the surrounding environment will constantly increase in time. Further monitoring of chemical pollution in dumping areas is necessary. It is important both for estimating the status of chemical ammunition and containers and for further survey of pollution threats to the environment.

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## **REACTION AGAINST THREATS: CONTINGENCY PLANS AND GUIDELINES**

- Unified model of contingency plans
- CHEMSEA Awareness Trainings
- Guidelines on CWA contamination at sea
- Recommendations for hazardous waste disposal
- Technical aspects of CWA contaminated sediments disposal

**ACCORDING TO A CHEMSEA ASSESSMENT, EXISTING NATIONAL CONTINGENCY PLANS FOR EVENTS OF CWA LEAKAGE AND ACCIDENTLY-FISHED MUNITIONS IN THE BALTIC SEA REGION ARE OFTEN OUTDATED AND INCOHERENT. CHEMSEA PARTNERS DEVELOPED JOINT GUIDELINES FOR RISK GROUPS, UNDERWATER OPERATIONS AND CONTAMINATED SEDIMENT TREATMENT AND DEVELOPED A BLUEPRINT FOR A JOINT CONTINGENCY PLAN.**

#### **4.1. UNIFIED MODEL OF CONTINGENCY PLANS**

The Baltic States, acting in accordance with the HELCOM CHEMU Report of 1995 and taking the safety of crewmen into account, have prepared instructions for fishermen to follow in the event of catching post war chemical munitions. However, nowadays such instructions seem too general and out-dated, leading to numerous difficulties in defining a EU-unified code of conduct that ship captains should follow in case of accidental catch of CW.

Moreover, the lack of regulations and knowledge concerning the responsibilities of national authorities in the area of decontamination procedures usually results in re-dumping of dangerous chemicals back into the sea, without reports to the appropriate authorities.







Therefore, one of the main goals of the CHEMSEA project was to develop a unified code of conduct in case of accidental catch of chemical munitions at sea or shoring on the beach, that may be implemented in all Baltic States, resulting in a unification of reaction procedures and national contingency plans.

A framework of research was developed which is focused on current national contingency plans and national threat reaction models. The study included, but was not limited to, the following research questions:

1. Are national procedures in case of CW catching / shoring already in existence?
2. Are national bodies responsible for contingency planning already designated?
3. Is the contact information for such bodies well known and widely available?
4. How are CW treated in case of accidental catching / shoring?
5. Which body initiates the response operation in case of a CW related threat?
6. Are standard forms of CW related incident documentation available?
7. Are national decontamination procedures established?
8. Do national guidelines for crew men exist and are they up-to-date?



Table 1. The matrix of the national contingency plans analyses

						
<b>1.</b>	+	+	+	+	+	+
<b>2.</b>	+	+	+	+	+	+
<b>3.</b>	+	+	+ / -	+ / -	+	+ / -
<b>4.</b>	ADS	AF	AF	AF	AF	CG
<b>5.</b>	VTS / MRCC	MRC	MRCC	MRCC	VTS / MRCC	SMA / JRCC
<b>6.</b>	decentralized	decentralized	n.d.	decentralized	decentralized	n.d.
<b>7.</b>	deployable	deployable	n.d.	n.d.	deployable	deployable
<b>8.</b>	yes '90	yes '97	no	n.d.	yes '98	yes '90

n.d. – no data

ADS - Ammunition Disposal Services of Schleswig-Holstein and Mecklenburg-Western Pomerania  
 AF - Armed Forces' units  
 CG - Coast Guard  
 VTS - Vessel Traffic Service  
 MRC - Maritime Rescue Centre  
 JRC - Joint Rescue Centre  
 MRCC - Maritime Rescue Coordination Centre  
 JRCC - Joint Rescue Coordination Centre  
 SAR - The Maritime Search and Rescue Service (SAR Service)

The matrix of research results allowed reaching the following main conclusions:

1. The Baltic States possess national services and agencies capable of taking action in order to minimise the threat posed by fished / shored CW, but their actions differ significantly.
2. The authority to be notified first in case of CW related accidents at sea would be the VTS / MRC (JRC) / MRCC (JRCC) officer – SAR Service in general.
3. Accident documentation, where available, is decentralised and incoherent.
4. Guidelines for fishermen exist in selected states but are out-dated.
5. Guidelines or routines (Standard Operating Procedures) for national contingency planning bodies are incoherent and require unification.

The research proved that current procedures and safety recommendations for accidentally or deliberately recovered CW munitions are regulated primarily by national legislation, taking HELCOM recommendations and guidelines into account. Common practice seems to be that accidentally recovered munitions are deliberately re-dumped, which does not comply with the Chemical Weapons Convention (OPCW 1997), but may be in particular the only way to ensure the safety of crewmen. In order to get rid of identified discrepancies CHEMSEA drafted, consulted and endorsed a unified process or model of reaction against the threat posed by accidentally recovered or shored CW. The model was developed and introduced in the context of two generalised scenarios of contact with CW:

1. CW threat at sea – the sea scenario,
2. CW accident on the beach – the land scenario.

Fig. 1. The model of reaction against threat posed by CWA – Sea Scenario

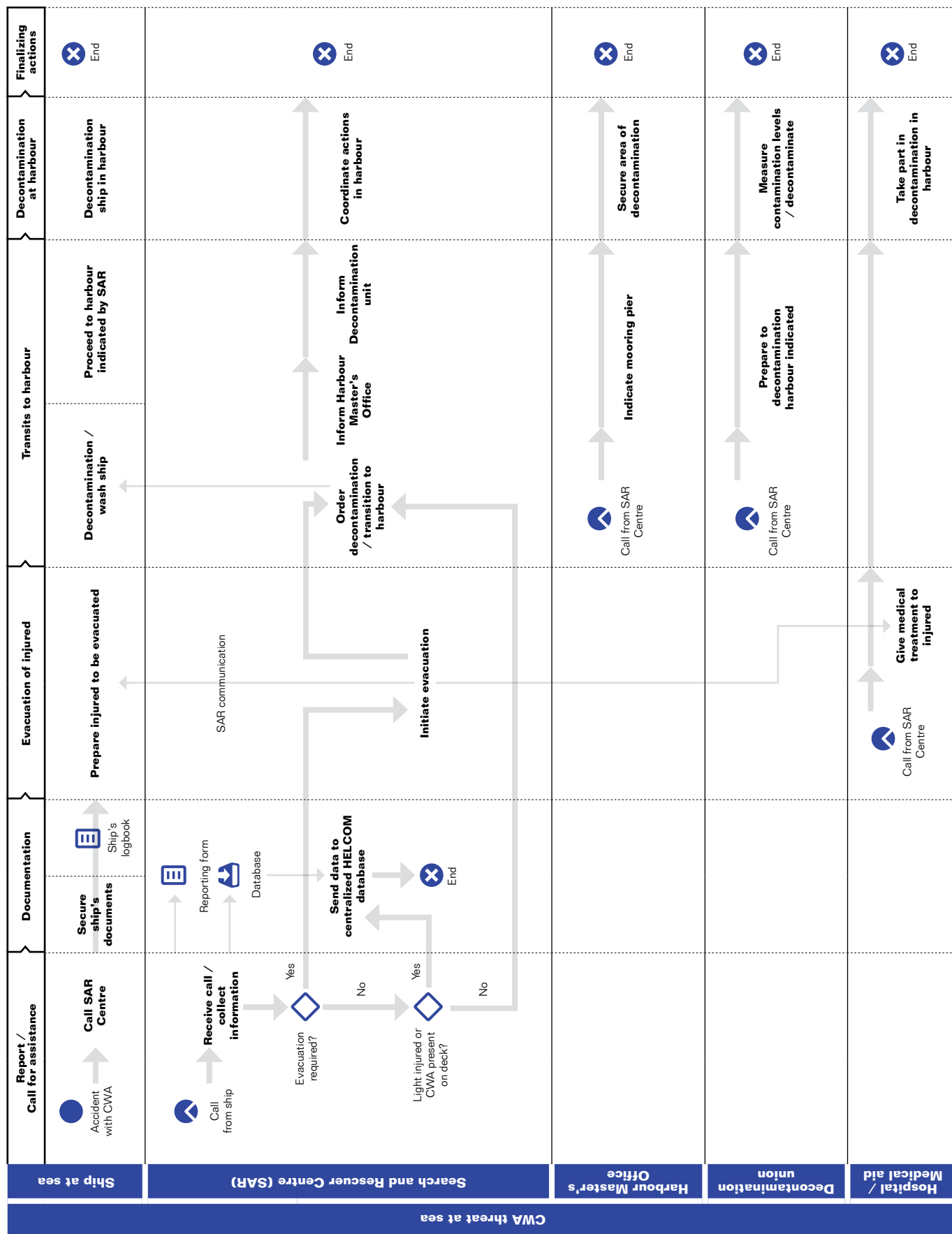
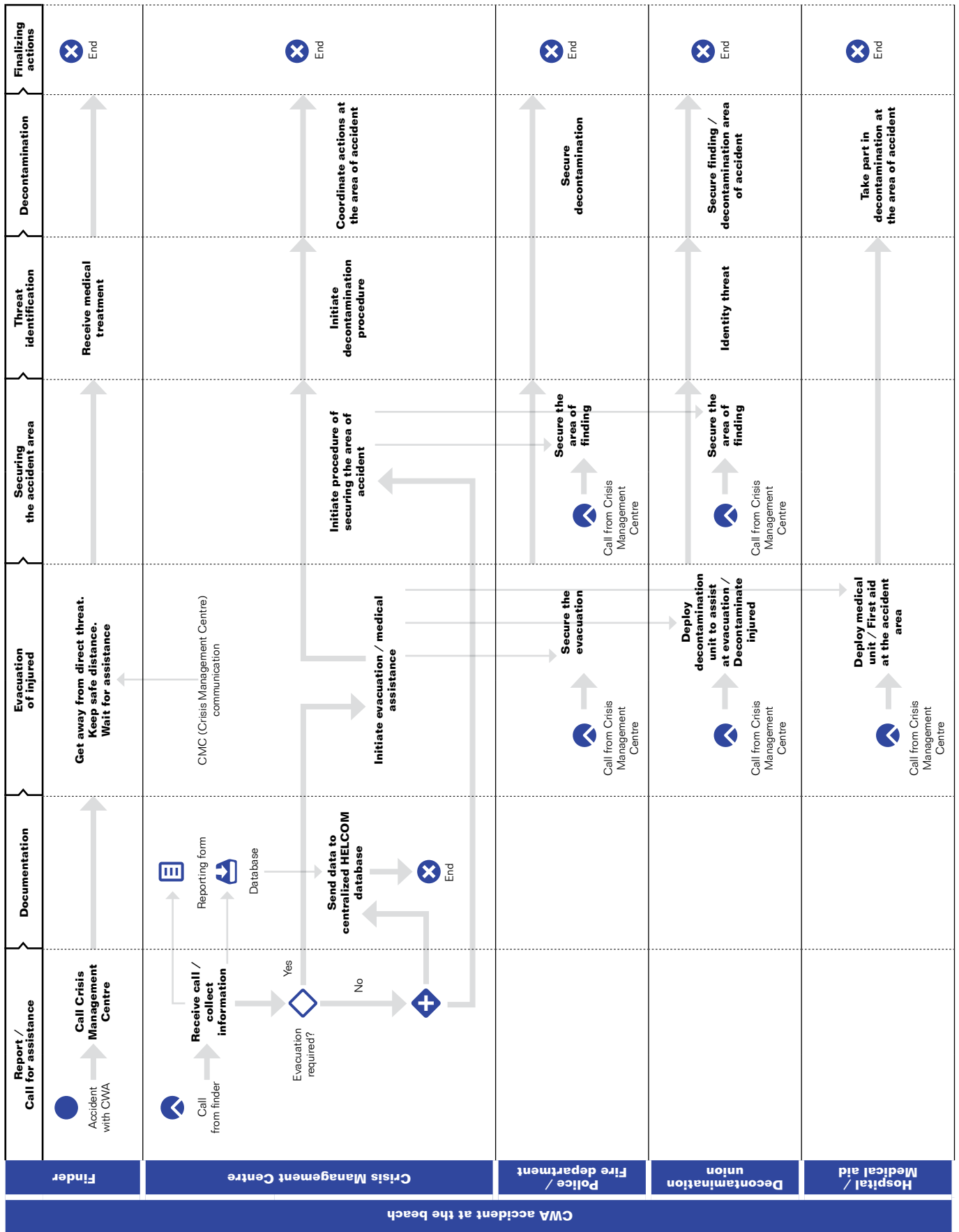


Fig. 2. The model of reaction against threat posed by CWA – Land Scenario



Both models identify bodies responsible for reacting against the threat and actions to be conducted in order to secure both people and the environment.

The key elements of the sea scenario, depicted in Figure 1, are:

- Ship at sea: endangered after accidental catch of suspicious items in the fishing or dredging gear
- Search and rescue centre (SAR): initiates rescue operation after being notified about the accident and being called for assistance
- Harbour master's office: prepares and isolates the mooring pier in order to conduct the ship's decontamination operation
- Decontamination unit: conducts ship's decontamination
- Medical aid personnel: takes care of injured crewmembers brought to the harbour or evacuated from the vessel at sea

Vessel crewmembers should be alert for the following signs that a chemical munition or chemical agents are present onboard:

- Unusual odour from equipment or fish
- Stinging sensations in the eyes
- Burning or irritated skin
- Presence of an oily liquid
- Corroded containers or suspicious clay-like lumps

In the case of catch or extraction of such a substances the ship's captain is obliged to take every possible precautionary measure to remove the dangerous substances from the vessel (Note: If a munition is encountered while in harbour, the land scenario should be initiated). When the dangerous substances have been removed from the vessel the captain should:

- Note the position of removal (re-dumping) of dangerous materials
- If possible, mark the position with a buoy of yellow colour

Afterwards, the SAR Centre should be immediately notified and provided the following information:

- The vessel's position (use World Geodetic System 1984 [WGS-84] for reporting). If the exact position is unknown, approximate coordinates should be given or a range and bearing from a charted feature.
- The activity (e.g. fishing, clamming, dredging) being conducted when the munition was encountered.
- A general description of the munition's key features (e.g. size, shape, fins, markings) and overall condition, if observed or known.
- Any unusual odours.

- The actions taken (e.g., secured munition on deck, munition carefully returned to the water, washed off deck where munition was retrieved to protect the crew).

The ship's captain should maintain a radio watch in order to be provided with further instructions and should strictly follow any instructions received. Particularly, vessels that may have come in contact with chemical agents should not bring their catch ashore, unless instructed to do so. Prior to entering the harbour, the appropriate harbour master's office should indicate a mooring pier, located as far as possible from other vessels already moored in the harbour. It is forbidden to unload or get any materials off the vessel before the decontamination unit arrives to inspect and decontaminate the vessel.

The key elements of the land scenario, depicted in Figure 2, are as follows:

- Potential finder: usually unaware of possible threat connected with suspicious object washed ashore
- Crisis management centre: represents the local emergency services called by a finder requesting assistance
- Police / fire departments: take in situ actions to isolate and secure the area of the finding
- Decontamination unit: conducts decontamination of people and finding
- Medical aid personnel: provides medical assistance to the injured or burned

Similarly to the sea scenario, the finder should be alert for the following signs that a chemical munition or chemical agents are present in the object washed ashore:

- Unusual odour of the object found
- Stinging sensations in the eyes
- Burning or irritated skin
- Presence of an oily liquid
- Corroded containers or suspicious clay-like lumps

In case of finding a suspicious object ashore, it is strictly forbidden to approach, move, dismantle or touch the object. Additionally, a safe distance should be kept at all times. Notification of the finding should be directed to the nearest police or fire department station or emergency response centre.

Having received a notification concerning a CW related accident ashore, the emergency response centre forwards the notification to local police stations, rescue departments (fire departments) and medical ambulance services. Resources and manpower are sent to the scene of the accident in order to secure the area and transport routes (police), diagnose the accident scene (rescue /

## CHEMSEA FINDINGS

fire department) and provide medical assistance (medical ambulance).

If initial diagnosis of the accident scene confirms the presence of CWA, a specialised decontamination unit is called in to conduct the decontamination, remedy the consequences of contamination and restore the environment to an appropriate state.

The above general models of reaction against threats posed by accidentally recovered or shored CW were compared with national contingency plans in order to reveal strengths and weaknesses of state specific solutions. As a result, CHEMSEA encouraged national authorities of Baltic States to introduce improvements to their current procedures.

### 4.2. CHEMSEA AWARENESS TRAININGS

In addition to focusing on national contingency plans and unified reaction models against CW threats, CHEMSEA conducted research to evaluate the level of awareness of working groups that may potentially come in contact with CW. This primarily included fishermen and offshore industry employees.

Despite the existence of national plans concerning trainings for fishermen and offshore industry employees, CHEMSEA disclosed negligence in the implementation of such trainings. As this confusion has adverse consequences for the safety of maritime operations, an independent Awareness Training Program was prepared and conducted in Baltic States to spread knowledge on chemical munitions dumped at sea and to introduce best practices in minimising the threats posed by CWA.

The primary target group addressed by the CHEMSEA Awareness Trainings were fishermen. CHEMSEA cooperated closely with local fishermen's associations and organised a number of trainings for fishermen in harbours, e.g. trainings in Hel, Władysławowo, Krynica Morska (Poland), Klaipeda (Lithuania), and Helsinki (Finland).

Information delivered during the trainings included:

- Location of CW in the Baltic Sea
- Possible effects on humans and the environment
- Appropriate protective measures
- Proper behaviour in case of potential contamination
- First aid in case of contamination

The main part of each awareness training focused on measures to be taken onboard in order to secure crew members in case of contact with CW at sea.



FIG. 3. AWARENESS TRAINING FOR LITHUANIAN FISHERMEN AT KLAIPEDA (AUGUST 2013)



### 4.3. GUIDELINES ON CWA CONTAMINATION AT SEA

As far as any type of munitions present a potential explosive or chemical agent hazard, they should not be moved, disturbed or handled. However, at sea and depending on the circumstances, precautionary actions may be required to protect the vessel and crew members. Therefore, in case of catch or extraction of hazardous or noxious substances of military origin, particularly CWA, the following actions should be taken:

- Do not touch neither caught or extracted materials nor the fishing equipment or potentially contaminated parts of the vessel
- Keep contaminated parts of the vessel leeward, if possible
- Close hatches and windows of the wheelhouse and compartments
- Collect the clothing of crew members who came into contact with contaminants in the foil sacks and tighten them firmly
- Report the accident to the SAR officer / Harbour master, providing the following information:
- What, where, when and by whom has been caught or extracted
- Crewmembers who may have been contaminated or injured
- Keep a radio watch in order to be provided with further instructions
- Follow instructions given by the SAR officer / Harbour master,
- If ordered, steer the vessel to the forefront of the nearest harbour

When a munition is recovered by the fishing gear but not brought onboard:

- Stop all fishing operations immediately
- Do not try to bring the munition or gear containing the suspected object / contaminant onboard
- Do not allow the munition to come or remain alongside the vessel, where sea waves could cause the munition to contact the hull
- Lower the fishing gear carefully back into the water, note its position and report it to the SAR officer / Harbour master,
- If possible, mark the position with a yellow buoy
- Await assistance and follow further instructions, as ordered by the SAR officer / Harbour master.

When the munition has been brought onboard:

- Immediately secure the munition to prevent its movement
- Keep the crew upwind and away from the munition / contaminant
- Minimise handling and decide whether it is safest to return the contaminant to the water or retain it onboard.

When the munition remains onboard:

- Keep the crew upwind and away from the munition / contaminant
- Minimise handling and avoid disturbing any part of the munition
- Secure the munition on deck to prevent its movement; do this as far away as possible from heat sources, vibrations and crew members
- Cover the munition with wet blankets or wet cloths to reduce the potential for deterioration of metal parts and release of its contents and to reduce the risk of explosives drying up and becoming more sensitive to shock
- Immediately contact the SAR officer / Harbour master for assistance
- Await assistance and follow further instructions as ordered by the SAR officer / Harbour master

If, despite precautionary actions taken, any crew member comes into contact with CWA:

- Immediately remove any lumps or drops of toxic substance from the skin using the back side of a knife or similar object, clean pieces of fabric, etc.
- Carefully wash the contaminated skin with fresh water mixed with soap
- After drying, decontaminate the skin using the decontamination package (if available)
- Do not perforate the blisters on the skin – they keep the body from further penetration by the chemical agents
- Report the accident to a SAR officer / Harbour master and request assistance
- Place contaminated crew members in a separate compartment or on a windward deck and wait for professional assistance, as ordered by the SAR Officer / Harbour master

In case of eye irritation:

- Never rub the eyes, even if they sting
- Wash the eyes with large amounts of fresh water, in the direction from the nose toward the external corners
- After washing, close the eyelids and wash the skin around the eyeballs with freshwater mixed with soap
- Do not use any ointments, do not bandage the eyes

Visible skin symptoms of CWA contamination may not appear immediately, only following hours or days.

Therefore, in every single case when the crew member observes a suspicious object in the fishing gear or an unusual smell in the caught fishes or the fishing gear itself resulting in stinging of the eyes or throat, it should be assumed that the vessel might have been contaminated with chemical munitions and all the precautionary actions, described above should be taken.

#### 4.4. RECOMMENDATIONS FOR HAZARDOUS WASTE DISPOSAL

In order to effectively manage hazardous waste (contaminated sediments, fish, etc.), all stakeholders, crews of fishing vessels and offshore companies operating on the seabed should follow three basic principles:

##### 1. MINIMIZE EXPOSURE

Take all necessary precautions when working with contaminated sediments and other materials. As a means of minimising potential exposure, do not touch anything with bare hands and do not breathe vapours.

##### 2. DO NOT UNDERESTIMATE RISKS

Ensure that the risk associated with each sample of contaminated sediment or other material is assessed, understood and communicated to the appropriate personnel. It is very important to assume that all contaminated sediments and other materials are very dangerous and that they should be handled with great caution.

##### 3. USE PROPER COUNTERMEASURES

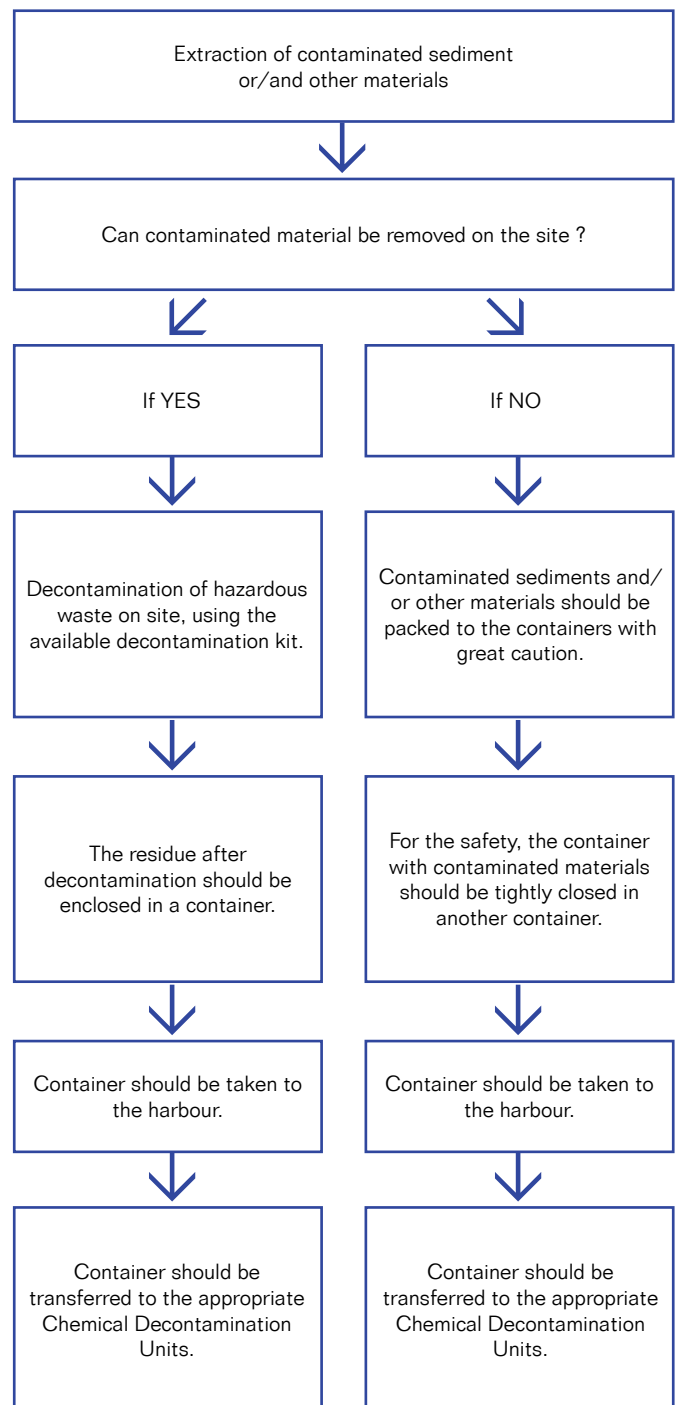
The use of personal protective equipment, and limitation of protection it offers, together with proper administrative procedures should be understood by all users. Ensure that all staff are properly trained in accordance with regulatory requirements so that they can perform their tasks safely. The following are key management issues for handling contaminated materials, including sediments. Regulations regarding the proper storage of hazardous materials are complex. The schematic procedures for dealing with contaminated sediments are shown in Figure 4 below.

Different methods for treating and handling sediments are currently being developed. They include isolating the contaminants from the rest of the sediments by separating the smallest grains (since contaminants tend to stick to them) and separating the oily part of the sediment (which contains most of the toxic organic compounds).

Sometimes sediment is incinerated in order to destroy organic contaminants. Other times, setting agents such as cement are added to solidify the sediment and prevent contaminants from being released into the environment. Bacteria and fungi may also be added to break down the contaminants; this process is called bioremediation.

Advanced treatment approaches such as these are promising but often expensive.

Fig.4. Schematic procedure of dealing with contaminated sediment and/or other contaminated materials





ROV SAMPLING OF CONTAMINATED SEDIMENTS

CHEMSEA proposes two strategies for dealing with contaminated sediments and/or other materials. The first strategy is based on the knowledge and available equipment possessed by the interested companies and the ship's crew. In this strategy, the contaminated sediments and/or other materials are disposed of on site. **This strategy is only possible when workers and the vessel's crew are properly trained and possess appropriate equipment for decontamination.** In this situation decontamination of the sediments and/or other materials can be carried out on site, **but can only be performed by qualified personnel!!!** After decontamination, all sediments and/or other materials should be sealed in containers and delivered to the harbour. Extraction and decontamination of sediments and/or other materials should be reported to the appropriate regional and/or national authority. The residue present after decontamination should be passed on to the unit responsible for chemical retrieval (Chemical Decontamination Unit).

The second strategy applies to the company employees, ship crew and other personnel who do not possess proper equipment and/or proper training to conduct decontamination of sediments and/or other materials. **All operations performed on contaminated sediments and/or other materials must be done with extreme caution!!!** Contaminated sediments and/or other materials should be packed in sealed containers. All operations involving the sealing of containers with contaminated sediments should be performed wearing protective gloves. Vapours from

contaminated sediments and/or other materials should not be inhaled. Containers with contaminated sediments and/or other materials should be tightly closed in a second container and must then be delivered to the harbour. Extraction of contaminated sediments and/or other materials should be reported to the appropriate regional and/or national authority. The contaminated sediment and/or other materials should be passed on to the unit responsible for the chemical retrieval (Chemical Decontamination Unit).

#### 4.5. TECHNICAL ASPECTS OF CWA CONTAMINATED SEDIMENTS DISPOSAL

Offshore-industry operations carried out in the Baltic Sea, particularly in areas close to CWA dumpsites, require that worst-case scenarios be anticipated. Specifically, it is probable that sludge extracted from the Baltic seabed could contain extremely hazardous CWA, e.g. Sarin or Tabun.

The worst-case scenario leaves no time for deliberations of what should be done with a CWA hazardous find. When discovering a dangerous chemical from the group of organophosphoric compounds in the excavated sediments, actions must be taken immediately.

Therefore, guidelines on methods and techniques for destruction or decontamination of CWA hazardous compounds in place were reviewed within the CHEMSEA framework in the perspective of agents dumped to

Table 2. Guidelines on CWA decontamination methods and technologies – main reactive systems for decontamination

Technology of decontamination	Decontaminant applicable against	Media, which should be decontaminated (water, soil, building, sludge, wastewater, equipment, etc.)	Comments & remarks
Water (steam, sea water, supercritical water, etc.)	<b>All agents</b>	Multiple media; including personnel uncovered parts of the body (e.g. skin). Steam for multiple media, including possible building ductwork	Immediate response in absence of more specific decontamination formulations; improved decontamination/neutralization with addition of soap (see below) and heat; salt-water may increase efficiency due to pH; heated water and steam augment hydrolysis
Soap and water wash	<b>All agents</b>	Multiple media; including personnel uncovered parts of the body (skin)	Immediate response in absence of more specific decontamination formulations; effective for physical removal of contamination from personnel, vehicles, aircraft, loading docks, building exteriors, etc.
Hypochlorite including: <ul style="list-style-type: none"> <li>Chlorine bleach</li> <li>High test hypochlorite [HTH];</li> <li>Super tropical bleach [STB];</li> <li>Hydantoin (dichlorodimethylhydantoin)</li> </ul>	<b>All agents; especially effective in relation to G-agents, less effective against VX at high pH; hydantoin could be used to detoxify HD</b>	Select media – high potential for caustic damage; not recommended for personnel (skin) unless extremely dilute	Corrosive to materials; non-dilute solutions are extremely irritating to skin and respiratory system; 0.5% solution of NaOCl may be used to decontaminate human skin; potential for ignition if undiluted HTH comes in contact with VX, HD; HTH not recommended for shipboard use; dry STB inconsistent with HD, it could be a cause of the ignition
Fichlor (sodium N,N-dichloroisocyanurate) and Fichlor-containing formulations including CASCAD®	<b>VX</b>	Select media – potential caustic damage; not recommended for personnel	Stable, general disinfectant; corrosive; contact with combustible materials may cause fire
Chloramine-B (sodium N-chlorobenzenesulfonamide)	<b>HD, VX</b>	Multiple media – potential caustic damage; not for direct skin/human decontamination	Less corrosive than bleach
Oxone (potassium peroxymonosulfate; KHSO5) formulations including L-Gel	<b>HD, VX</b>	Multiple media; Not designed for human decontamination	Stable; low toxicity but irritating to skin and respiratory system
m-Chloroperoxybenzoic acid (m-CPBA; C7H5ClO3)	<b>HD, VX</b>	Multiple media. Not designed for human decontamination	Unstable
Magnesium monoperoxyphthalate (MMPP; [HO2CC6H4CO3]2 Mg)	<b>HD, VX, GD</b>	Multiple media. Not designed for human decontamination	Stable, mild oxidizer; low toxicity
Sodium hydroxide (NaOH)b	<b>Nerve agents</b>	Select media – high potential for caustic damage; not recommended for personnel (skin) unless extremely dilute	Caustic
Decontamination Solution 2 (DS2): <ul style="list-style-type: none"> <li>70% diethylenetriamine,</li> <li>28% ethylene glycol monomethyl ether,</li> <li>2% sodium hydroxide)</li> </ul>	<b>All agents</b>	Select media – high potential for caustic damage; not recommended for personnel (skin) unless extremely dilute	Military-unique decontamination solution; corrosive and destructive to many materials, metals, protective equipment and human tissues; flammable, inconsistent with STB and HTH
Hydrogen peroxide (H2O2) with activators and co-solvents; Vaporized H2O2	<b>HD, nerve agents</b>	Multiple media; including possible buildings/ductwork; not designed for human decontamination	Unstable; forms non-toxic products that may nevertheless pose clean-up issues; current commercial use is as general disinfectant; toxic at high concentrations
Sandia Foam formulations (contains H2O2)	<b>HD, nerve agents</b>	Multiple media; not designed for human decontamination	Same action as H2O2; provides visible means to identify applied decontaminant; and to maximize adherence times. Greater cost than traditional methods; resulting non-toxic residues may present an additional clean-up issue
Decon Green (H2O2, potassium carbonate, potassium molybdate, propylene carbonate, surfactant)	<b>All agents</b>	Multiple media – Not designed for human decontamination	Forms nontoxic products; designed as replacement for DS2; means to identify applied decontaminant and to maximize adherence times; some residue and cost disadvantages as above

the Baltic, and the state they might be in, to support decontamination operations.

The main reactive systems for decontamination of all types of chemical warfare agents have been collected in Table 2 and are described below. The list was created upon assumption of taking such decontaminants into account, that could be used for disposal of CWA toxic substances, ensure effectiveness and versatility and remain stable during storage.

### 1. Aqueous and aqueous-alcoholic alkaline solutions as decontamination media for CWA

Bases may be present as active components of anhydrous or aqueous solutions for decontamination. With regard to the reaction of bases with CWA it is often described as the neutralisation of toxic properties or loss of the CWA under the influence of the bases. Reactivity of alkaline decontamination solutions depends on many factors. To correctly choose the chemicals and the decontamination environment, nucleophilicity and basicity should be considered as well as the impact of the type of solvent and catalyst contained in the decontamination solution. One can, however, ignore the impact of factors such as: temperature, concentration, solubility, etc. The nucleophilicity of the decontamination agent is its relative reactivity. The concept of nucleophilicity cannot be clearly defined and it is understood that the nucleophile has the capability of electron transfer to the carbon atom, which has a partial positive charge.

### 2. Aqueous hypochlorite solutions

Hypochlorite solutions (commonly known as bleach) are very efficient decontaminants for numerous CWAs, but they are corrosive. Although they meet the requirements for detoxifying contaminated material, the utility of the material after decontamination may be doubtful or problematic.

- **Common household bleach** is an aqueous solution of 2-6% sodium hypochlorite ( $\text{NaOCl}$ ). Usually it contains 5% sodium hypochlorite, but sometimes calcium hypochlorite is used. It can be used for decontamination of equipment. A dilute solution of bleach decontaminates through both oxidation and hydrolysis. The effectiveness of bleach solutions can be improved by introducing stronger oxidants to the system. Hypochlorite is effective when it is used in excess quantities and given sufficient reaction time.
- **High test hypochlorite (HTH)** is composed of calcium hypochlorite [ $\text{Ca(OCl)Cl} + \text{Ca(OCl)}_2$ ] as a solid powder or 7% aqueous slurry. The mixture contains approximately 70% available chlorine. Because **HTH** is a strong oxidizing agent, it is very corrosive. This composition is effective in destroying HD and G agents.

- **Super tropical bleach (STB)** is a mixture of 95% calcium hypochlorite [ $\text{Ca(OCl)}_2$ ] with a strong base calcium oxide ( $\text{CaO}$ ). STB contains at least 30% available chlorine.  $\text{CaO}$  in solution produces  $\text{Ca(OH)}_2$ . STB is prepared as a solid powder or as 7, 13, 40, or 70% by weight aqueous slurries. This bleach is more stable than common bleaches. Similar to HTH, STB is an effective decontaminant for HD and G agents. STB and HTH are standard U.S. Army field decontaminants. However, STB is extremely irritating, causes corrosion to metals and may ignite spontaneously when it comes in contact with certain materials.
- **Hydantoin (dichlorodimethylhydantoin or DCDMH)**, is an organic halamine. DCDMH was developed in the 1990s by the U.S. Army. Because it has greater chlorinating power than HTH or STB, it has been used to detoxify HD, nitrogen mustard, Lewisite, and phosgene (carbonyl chloride).
- **Dutch powder** contains  $\text{Ca(OCl)}_2$  and  $\text{MgO}$ . This powder has been used by some European countries.
- **Activated solution of hypochlorite (ASH)** was developed in the 1960s. The general formula ASH by weight percent is: calcium hypochlorite (0.5%), sodium dihydrogen phosphate buffer (0.5%), Triton X-100 surfactant (0.05%), and water (98.95%).
- **Self-Limiting Activated Solution of Hypochlorite (SLASH)** is 0.5% aqueous solution of calcium hypochlorite buffered with sodium citrate/citric acid and detergent. SLASH successfully eliminates chemical agents such as: HD, GA, GB and GD. Both ASH and SLASH are much less corrosive than STB.

### 3. Anhydrous alkoxide solutions as nucleophile decontaminants

In recent years, more attention has been paid to the universally active decontamination liquids; these liquids are a mixture of alkali alkoxides, alcohol and amines. Their composition is very different and depends on the type of used amines and alcohols. In general they contain from 0.5 to 1 mol of alkali alkoxides (lithium or sodium), which is obtained based on alcohol, aminoalcohol or alkoxialcohol. If the mixture does not have aminoalcohols, then the mixture must contain from 50 to 70% of amine or mixture of amines. Most preferred are polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine and propylenediamine. If amino alcohols are applied, then the polyamine remains at a high level. Most often amines are mixed with higher alcohols, such as hexylene glycol or propylene glycol monomethyl ether. Amine content should be at a high level, due to reaction with CWA (decreases their concentration) and because their efficiency is reduced due to the negative impact of carbon dioxide and water.

The high amine content ensures high reactivity of the decontamination mixture. The U.S. Patent No. 3079346 recommends that decontamination solutions be composed of: recommended in U.S. Patent No. 3079346 that decontamination solutions be composed of:

- 1 to 10% of NaOH,
- 20 to 40% of methoxyethanol, and
- 50 to 79% of primary, secondary or tertiary amines, especially diethylenetriamine and ethylenediamine.

The most recommended decontamination solution has the following composition:

- 2% of NaOH,
- 28% of methoxyethanol ( $\text{CH}_3\text{O}-\text{CH}_2\text{CH}_2-\text{OH}$ ),
- 70% of diethylenetriamine ( $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}_2$ ) or 70% of ethylenediamine ( $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2$ )

This decontamination mixture is denoted by the symbol **DS-2** (Decontaminating Solution 2) and used in the armed forces of many countries, including the U.S. and Germany. This mixture does not need to be diluted and can be used after transportation by the extinguishing spray apparatus, whether there are small or large decontamination aggregates. Decontamination agent DS-2 mixed with water in any proportions and during mixing of the solution must be heated strongly. The Flash Point of DS-2 is about 80°C. DS-2 causes corrosion of aluminium containers and containers covered with a layer of cadmium, tin or zinc. Other metals do not corrode.

#### 4. Oxidizing systems as a CWA decontaminants

Adding 1% hydrogen peroxide to 0.1 M sodium hydroxide can sufficiently accelerate the reaction between sodium hydroxide and selected chemical warfare agents. The half-life for disappearance of some agents in the absence of the peroxide is many hundreds times greater. G-agents (Tabun, Sarin) would be rapidly hydrolyzed not only because of catalysis by the hydroperoxide anion but simply because of the high pH.

- **Fichlor** (*sodium N,N-dichloroisocyanurate*) is a stable oxidizer and hydrolysis catalyst. Fichlor reagent reacts in water to produce hypochlorous acid. It has been used extensively in the food and beverage industry as an antimicrobial detergent.
- **Chloramine-B** (*sodium N-chlorobenzenesulfonamide*) is a stable, water soluble, oxidizing compound. It has been used to decontaminate HD. Chloramine-B is less corrosive than other bleaches. It was developed as a towelette impregnated with chloramine-B used in conjunction with a sealed glass ampule containing a solution of 5%  $\text{ZnCl}_2$ , 45% ethanol, and 50% water for decontamination of skin and personal equipment. Chloramine-B dissolves in water and produces a caustic solution. However the presence of the  $\text{ZnCl}_2$  maintains the pH of the solution at between

5 and 6. Related decontaminants are chloramine-T (sodium paratoluenesulfochloramine), dichloramine-B (benzenesulfodichloramide) and dichloramine-T (paratoluenesulfochloramine).

- **Hydrogen peroxide** ( $\text{H}_2\text{O}_2$ ) is a less caustic agent. It has long been used in the medical community as a biological sterilizer. Solutions of  $\text{H}_2\text{O}_2$  with addition of peroxide activators such as carbonate, bicarbonate, and molybdate is used with cosolvents such as butanol, ethanol, isopropanol, and surfactants to produce rapid decontamination of CWAs such as HD, and G agents. Decontamination occurs via generation of the nucleophile peroxy anion,  $\text{OOH}^-$ . Addition of peroxyacetic acid to  $\text{H}_2\text{O}_2$  increases the oxidizing power of solution. Unfortunately hydrogen peroxide is unstable and breaks down into nontoxic products: water and oxygen. The diluted form of hydrogen peroxide 3-10%, is commercially available for home use. The professional decontamination solution contains mixtures of hydrogen peroxide (11-30%), activators such as sodium bicarbonate, and cosolvents such as t-butanol. Cosolvents increase the contact between  $\text{H}_2\text{O}_2$  and the chemical agents. The activators increase the effectiveness of  $\text{H}_2\text{O}_2$  and reaction speed. For example, the initial half-life for GB in neutral peroxide is 67 hours. When bicarbonate (0.037 M  $\text{NaHCO}_3$ ) is added to the solution, half-life for the reaction is <1 minute. The reaction proceeds with the initial loss of fluoride. Sulphur mustard (HD) is oxidized fairly slowly in a solution of 1.3 mL of 30%  $\text{H}_2\text{O}_2$  and 1.9 mL of t-butanol. The solutions of  $\text{H}_2\text{O}_2$  greater than 20%, with additions of t-butanol and bicarbonate (<1 M) decreases the reaction half-life to < 2 minutes. Solid urea peroxide can be used instead of peroxide solutions. When the molybdate is used instead of bicarbonate, the solution oxidizes the HD two orders of magnitude faster at the low temperature through generation of either singlet oxygen or peroxomolybdate such as  $\text{MoO}(\text{OO})_3^{2-}$  or  $\text{Mo}(\text{OO})_4^{2-}$ . The perhydrolysis of  $\text{H}_2\text{O}_2$ , however, occurs slower than hypochlorite oxidation, but selectively yields the non-vesicant sulfoxide.
- **Vaporized hydrogen peroxide (VHP)** is a patented process of oxidizing fumigation. The vapor is generated from concentrated peroxide solutions (>30%  $\text{H}_2\text{O}_2$ ). At present this technology is commercially used in the fumigation of cabinets and to disinfect surfaces. VHP is under experimental investigation as a CWA decontamination technology. Modified vaporous hydrogen peroxide (mVHP) contains low levels of ammonia gas. These technologies (both VHP and mVHP) have been tested in the laboratory for efficacy against CWA. At a concentration of 250 ppm and with a contact time of 24 hours, mVHP reduced many CWAs to a simple products. Although  $\text{H}_2\text{O}_2$  is not corrosive, concentrated vapor is toxic and interacts with many surfaces, including concrete.

- **Peroxygen Oxidants (Peroxy Acids)**

- o Oxone<sup>®</sup> is the commercial mixture of:  $2 \text{KHSO}_5 - \text{K}_2\text{SO}_4 - \text{KHSO}_4$ . The active ingredient of this mixture is potassium peroxymonosulfate ( $\text{KHSO}_5$ ). It is a relatively stable, commercially available compound. Oxone<sup>®</sup> dissolved in water produces an acidic solution. It can be used for detoxification of HD, but is not suitable for decontamination of G-agents. Oxone, has the pH of 2.3 at 20°C. Oxone was tested against HD. In a solution of 0.05 M HD, 0.1 M Oxone, and 15 vol % N-methyl-2-pyrrolidone (added to help dissolve the HD), HD was oxidized immediately to the sulfoxide, which converted within an hour to the sulfone. It has been observed that N-methyl-2-pyrrolidone at a level of ~ 20% does little to improve the solubility of HD and that it causes the Oxone to decompose. Oxone does not oxidize G-agents, but it is acidic enough to catalyze their slow hydrolysis. Oxone, like other peroxygen-containing oxidants (especially m-chloroperoxybenzoic acid and magnesium monoperoxyphthalate) are effective against HD. But it should be pointed out that organic peroxides tend to be dangerously unstable.

- o **Meta-Chloroperoxybenzoic acid (m-CPBA)**

is a strong oxidizing agent ( $\text{C}_7\text{H}_5\text{ClO}_3$ ) available as a powder. It is not particularly stable. m-CPBA can be used for the oxidation of HD (oxidation occurs at the sulphur atom).

- o **Magnesium monoperoxyphthalate (MMPP;  $[\text{HO}_2\text{CC}_6\text{H}_4\text{CO}_2]_2 \text{Mg}$ )** is a stable, water-soluble, solid peroxyacid that has been used as an antimicrobial. MMPP was active in oxidizing/detoxifying of HD.

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## CONCLUSIONS

Following large-scale use of chemical weapons in World War I, extensive preparations were made to further develop chemical warfare and increase its capacity. Even though never used on the European battlefield, large amounts of chemical weapons remained after the end of the war. The victors chose to take responsibility for the disposal any chemical munitions found in their area of oversight. In addition to being a cheap method of disposal, the belief was that the vast amounts of water in the oceans would neutralise and absorb the dangerous substances.

British and US military administrations have dumped their share of munition outside of Baltic Area (in Skagerrak and in the Atlantic Ocean). The Soviet Union dumped at least 50,000 tonnes of chemical munitions containing an estimated 15,000 tonnes of chemical warfare agents in the Baltic Sea, primarily in the Bornholm Basin. Other official dumping sites are the Little Belt area and the Gotland Deep. In addition to these sites, dumping took place *en route* from Wolgast, where vast amounts of chemical munitions were stored.

Surveys performed by CHEMSEA in the main area of interest, the Gotland Deep, recorded almost 40,000 objects, of which roughly 17,000 were later classified as probable munitions and 33 wrecks, which could potentially contain chemical weapons. Taking into account the visual confirmation of more than 250 of those targets, it appears that 50% of such objects may actually be regarded as chemical munitions.

Furthermore, CHEMSEA has found indications of chemical weapon dumping worth following up at the unofficial dumping sites of Slupsk Furrow and the Gdansk Deep.

Results from studies on cod health indicate no significant generic health effects on cod in CW dumpsites compared to reference sites. However, at lower organisational levels, such as organ, tissue, cellular and subcellular levels, some stress responses could be recorded in cod in CW dumpsites using the applied suite of biomarkers. Supporting this, higher stress responses were also observed in mussels deployed closer to the dumped CW (65 m) compared to the respective reference site and to mussels caged closer to the water surface (35 m).

The often anoxic conditions in the water bodies surrounding the dumped CW in the deep basins of the Baltic Sea limit the potential of common biological effect monitoring approaches in the field. If oxygen concentrations fall below 2 ml/L in the bottom water, marine organisms tend to migrate to more oxygenated waters. Therefore, a direct exposure of living organisms to the most polluted water bodies is unlikely to occur.

However, it is well known that species such as cod can be found in water layers with very low oxygen levels and thus at least a temporary risk of direct contact of cod or other species with munitions or released toxic compounds of CWA cannot be excluded.

It is necessary to extend research and monitoring activities both on a time scale, to reduce variability coming from changes in environmental conditions, and on a geographical scale, so that dumping areas without oxygen depletion (e.g. Skagerrak) can be included to create a comprehensive monitoring approach. Further, more efforts should be focused on laboratory exposure approaches using different ecologically relevant key species to assess biological effects and uptake mechanisms of toxic compounds leaking from dumped CWA on exposed organisms.

Different environmental factors like temperature, salinity, oxygen presence or depletion, sediment type and chemistry or presence of bacteria, as well as their combination affect chemical processes in the marine environment. Chemicals undergo constant transformations and change their structure and properties. Therefore the main objective in detecting chemical warfare agents in environmental samples was focused on their different degradation products. Derivatives or oxidation products of sulphur mustard, Adamsite, Clark I and Clark II, triphenylarsine, Lewisite I and Lewisite II were found in sediments. Despite differences between parent chemicals and derivatives, most CWA degradation products have similar toxic properties as the chemicals they originate from. Furthermore, remaining CWA derivatives have lower breakdown rates and can be considered as persistent pollutants. Nearly one third of samples collected in the CHEMSEA project contained at least one trace of chemical munitions. In comparison, sulphur mustard was only detected intact in one sample.

CWA pollution is most clearly visible in the Bornholm Deep. In this area nearly all analysed samples contained CWA derivatives. Arsenic containing CWA were found in 14 samples from a total of 21 collected in the Bornholm Basin area. Total arsenic concentrations were also elevated in that region compared to background levels. Only in samples taken on the transect within growing distance from the primary or secondary Bornholm dumpsite did concentrations of arsenic decrease and no arsenic containing CWA were found in the sediments.

In the Gotland Deep dumping area the situation is more diversified. A number of sediment samples did not contain CWA pollution and total arsenic concentrations did not show continuous spatial distribution despite high mean concentration. Based on this, it can be suggested that pollution of sediments with CWA is local and strongly dependant on spot environmental features. This also shows that the disposal of chemical weapon was more spread within the Gotland dumpsite.

In the Gdansk Deep area concerned as a potential dumping site, half of the samples analysed were confirmed for pollution with CWA and mean arsenic concentration was also elevated in comparison to the reference area.

In all areas of interest there is a visible relation between total arsenic concentration and the presence of arsenic



containing chemicals related to chemical weapons, although only in very few cases did arsenic contents exceed the biogeochemical background estimated for the whole Baltic Sea.

According to literature estimates for corrosion and leaching duration, the natural processes affecting CWA transformation as well as specific environmental conditions it is possible that the transition rate of toxic chemicals from the remaining weapons to the surrounding environment will constantly increase in time. Further monitoring of chemical pollution in dumping areas is necessary. It is important for estimating the status of chemical ammunition and containers and for further surveying threats of this pollution to the environment.

Accidents during the last decades have confirmed the risk of catch or extraction of CW in maritime areas marked on navigational charts as dumping sites, as fishing operations are still carried out in these areas, despite official bans. Chemical munitions continue to be a threat for fishermen. During the last ten years (2003 - 2012), there have been 44 reported incidents of CW catch. Even though the numbers are declining, the problem remains, as there are dangerous objects in the Baltic Sea both inside and outside known dumping locations. CHEMSEA has confirmed the hypothesis of munitions being thrown overboard while en route to designated dumping sites, which means the risk of contact with hazardous agents extends far behind the limits of official dumping sites.

Activities taking place on the seabed of the Baltic Sea need to acknowledge the presence of chemical munitions and the potential dangers they constitute. Additionally, there are environmental factors that need to be taken into account as chemical munitions remain on the seabed far longer than originally believed.

Nowadays, rapidly growing activity on the seafloor in the form of temporal or permanent facilities (e.g. monitoring stations, offshore wind farms, sea cables and pipelines, resource extraction) increases the risk of coming into contact with CW and bringing them onboard. Thus, the risk of contact and contamination is not limited to fishermen but applies also to offshore industry employees and other groups working at sea. These groups should be firstly aware of the risk existence and secondly ready to take precautionary actions to minimise the threat. CHEMSEA conducted wide area research in the context of awareness assessment resulting in the Awareness Training Program, ready to be carried out in the Baltic states.

**Hereby, CHEMSEA encourages national authorities to implement the Awareness Training Program as mandatory for selected target groups.**

This sea scenario, however, is not the only scenario expected. The last decades have confirmed that the threat posed by CW may easily reach coastlines in the form of munitions pieces washed ashore, creating a need to react

not only at sea but also on land.

Analysis of national contingency procedures and plans currently available in case of incidents involving chemical munitions revealed that although national procedures are well established, no transboundary response plans are in place and responsibilities within Baltic Sea countries are divided between different entities, depending on the country in question.

**In order to minimise discrepancies, CHEMSEA worked out a unified model contingency plan and encourages national authorities to implement it in the context of crisis management procedures.**

In order to continue the research on the state of chemical munitions in the Baltic Sea and continuously monitor the threat, **CHEMSEA supports the suggestion of HELCOM MUNI to create a database of incidents and a reporting system run by the Secretariat, using a jointly developed system (CHEMSEA/MUNI).**

Another aspect of the maritime industry are operations conducted directly on or in the sediment layer in the vicinity of chemical munitions. Such activities may damage the encasements of chemical munitions that have not yet lost their integrity, generating threats to humans and the environment.

Therefore, prior to any offshore operation an appropriate methodology of risk assessment must be followed. The model approach was introduced during the biggest investment of recent years in the Baltic Sea area, i.e. the Nord Stream pipeline construction. The documented experiences of the Nord Stream pipeline laying project between 2005 and 2011 could be a model for future project plans. In order to facilitate Wide Area Assessment and Detailed Survey phases within the model methodology, CHEMSEA worked out a framework of detection, classification and mapping of CWA that consists of:

- Desktop research of historical documents and munitions examples in order to define sizes and shapes of objects searched for
- Hydroacoustic detection with multiple survey tools
- Magnetometric detection
- ROV / visual confirmation
- Post-processing of data into a geospatial database and mapping

Based on CHEMSEA research, hydroacoustic surveys would be advised as the first step in both environmental impact assessment and work site selection in the area where suspected dumped munitions are located. It is advisable to perform sonar survey using side scan sonars, multi beam echosounders and sub-bottom profilers.

Multi-beam echo sounders and side scan sonars provide a detailed picture of contours of the sea floor and of objects lying on the seabed, whereas sub-bottom profilers penetrate

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deep into the material on the sea bottom to show a cross-section of the seabed. To exclude natural or non-munitions objects, the sonar survey should be complemented with other techniques, such as magnetometry used for detecting ferrous items.

The aforementioned survey techniques generate an enormous amount of data, which then needs to be fused and processed using GIS computer software, widely available on the commercial market. The resulting output constitutes an enhanced graph display of the surveyed area in the form of detailed charts aimed to support decision-making processes in the area of human maritime activities. There is also a risk of retrieval of contaminated sediments during dredging operations. In the CHEMSEA Findings suggestions for how to incorporate sediments contaminated with chemical munitions into existing waste management procedures are included, pointing at specific risks associated with such material and available decontamination procedures.

The overall conclusion stemming from the CHEMSEA project is that chemical munitions dumpsites, although not representing an immediate danger, will continue to be a problem for the Baltic Sea. On one hand, they represent scattered point sources of pollution of unknown magnitude and difficult to control. On the other hand, they are a major economic impairment, making the Baltic Sea a less safe and potentially more costly area for investment. From an environmental point of view they present a risk for marine biota through chronic exposure, though not directly for consumers. However, the amount of available data does not enable predictions on the development of situation. If a steady pace of corrosion and leakage is maintained, the problem is long lasting but local, and eventually degradation processes will remove most of the associated threat. However, if leakage increases, the degradation processes will not balance the leakage and the problem may become severe. Further studies are needed, especially for time trends, including the magnitude of leakage and the rate of corrosion and transport of contaminants to determine which scenario is more probable.

## CHEMSEA POLICY PAPER SUBMITTED TO HELCOM

The CHEMSEA project, which comprises 11 research institutes from six Baltic Sea states, wishes to highlight the following items based on three years of research on chemical warfare agents (CWA) in the Baltic Sea:

- Detailed surveys of the well-known Gotland Deep dumpsite, the Gdansk Deep, and along the post-war transport routes revealed a previously unknown extent of dumped munitions containing CWA. Modelled and measured bottom currents and their directions show that sediments polluted by CWA degradation products can be transported outside of the dumpsites, thus creating diffuse sources of contaminants to the neighbouring areas.
- Studies on the possible impacts of CWA and their degradation products on Baltic Sea biota show negative health impacts on tested marine organisms in the vicinity of dumpsite areas, especially at Bornholm Deep. The observed effects include changes in disease prevalence, genotoxicity, and more alterations on cell and tissue levels compared to the reference site. It is nevertheless still not possible to definitively conclude that these effects are caused by CWA exposure. Further studies are currently being performed.
- Although established national contingency procedures and plans for dealing with chemical munitions incidents exist, no transboundary response plans that clearly clarify responsibilities among and within the Baltic Sea states are currently in place.
- Awareness of risks and emergency procedures among fishermen and other potentially affected groups on encounters with chemical munitions are generally low.
- Regulations for the management of dredged sediments do not specifically mention CWA degradation products as a factor to be examined during identification of hazardous waste.

CHEMSEA proposes the following:

- HELCOM takes into consideration to formally recognize the probability of further encounters with objects containing CWA in areas surrounding the Bornholm Basin dumpsite, the Gotland Deep dumpsite, the Little Belt area, the Gdańsk Deep, and along the transport routes from Wolgast Harbour as potential hazards.
- HELCOM member states consider to officially recognize that CWA degradation products exist as contaminants in the Baltic Sea marine environment, with multiple diffuse sources located on the seabed.
- HELCOM RESPONSE Group is requested to draw attention to the current discrepancies in national procedures and systems of compensation regarding CWA incidents, and the absence of an adequate transboundary dimension in the existing contingency plans.
- CHEMSEA fully supports the suggestion of HELCOM MUNI to create a database of incidents and reporting system run by the HELCOM Secretariat, using a jointly developed system (CHEMSEA/MUNI).
- Baltic Sea states are encouraged to include training of emergency procedures in case of accidental recovery of chemical munitions as part of mandatory trainings for fishermen and other groups potentially under risk when operating in the Baltic Sea region.



### **Institute of Oceanology of the Polish Academy of Sciences (IO PAN)**

The Institute of Oceanology of the Polish Academy of Sciences (IO PAN) conducts scientific research in shelf seas and coastal regions in the Baltic and European Arctic Seas. IO PAN was the lead partner in the CHEMSEA project.



### **Polish Naval Academy (PNA)**

The Polish Naval Academy (PNA) is a military university under the supervision of the Ministry of National Defence and a military unit carrying out missions related to national defence. It is also a military scientific institution, based in Gdynia, with expertise in operational oceanography, including underwater operations relating to dumped munitions.



### **Military University of Technology (MUT)**

The Military University of Technology (MUT) in Warsaw is a state military technical school at the university level. It is one of the most experienced entities regarding CWA security issues in Poland and is the operator of the largest Polish CWA laboratory. The Institute of Chemistry at MUT is a full-time organisational unit of the Faculty of New Technologies and Chemistry, established to conduct teaching and education, research and training of scientific staff in the disciplines of ecology and environmental monitoring, explosives and fireworks, hazardous materials and chemical rescue.



### **Swedish Defence Research Agency (FOI)**

The Swedish Defence Research Agency (FOI) is an assignment-based authority under the Swedish Ministry of Defence, specialising in research, methods and technology development, as well as studies in the context of defence and security. Both military and civil assignments include security policy studies and analyses in defence and security, assessment of different types of threats, systems for control and management of crises, protection against and management of hazardous substances, IT-security and studies concerning the potential of new sensors.



### **Swedish Maritime Administration (SMA)**

The Swedish Maritime Administration (SMA), located in Norrköping, is the safe shipping and nautical charting authority responsible for hydrographic surveying and fairway maintenance in Swedish waters as well as technical development in these fields. Their areas of activity include pilotage, fairway service, maritime traffic information, icebreaking, hydrography, maritime and aeronautical search and rescue and seamen services.



### **Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN)**

VERIFIN, the Finnish Institute for Verification of the Chemical Weapons Convention, is located in the Department of Chemistry at the University of Helsinki. VERIFIN is one of the world's leading institutes in the field of analysis of chemical warfare agents in environmental samples. During the last years the Institute has also focussed on method development and analysis of biomarkers for chemical warfare agents in various samples like human urine/plasma and fish and mussel tissue samples. VERIFIN is an accredited laboratory. It is also the designated laboratory of the Organisation for the Prohibition of Chemical Weapons (OPCW) and a National Authority of Finland defined by the Chemical Weapons Convention (CWC) working under the guidance of the Ministry for Foreign Affairs of Finland.



### **Finnish Environment Institute (SYKE)**

The Finnish Environment Institute (SYKE) is a state agency under the Finnish Ministry of Environment carrying most of the environmental research as well as the coordination of national environmental monitoring.



### **Thünen Institute of Fisheries Ecology (TI-FI)**

The Thünen Institute of Fisheries Ecology (TI-FI) is one of the 14 science institutes within the Johann Heinrich von Thünen Institute, Federal Research Institute for Rural Areas, Forestry and Fisheries, under the German Ministry of Food and Agriculture. It has expertise in agriculture, forest ecology and fisheries. TI-FI addresses issues related to the effects of anthropogenic pressures on marine ecosystems, with a focus on the effects in fish from the North and Baltic Seas. It is responsible for national chemical and biological monitoring with regards to hazardous substances and their biological effects on biota from offshore regions.



### **Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research (AWI)**

The Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research (AWI) in Bremerhaven is Germany's leading institute for polar and marine research. The AWI Department Ecological Chemistry has broad experience in the development of indicators and expert systems for integrated analysis of chemical and biological data including the assessment of contaminant impact on the marine environment.



### **European CBRNE Center**

The European CBRNE Center is a research consortium consisting of Umeå University, the Swedish Defence Research Agency, Västerbotten County Council, the City of Umeå, the Swedish Armed Forces National CBRN Defence Centre and the Swedish National Fortification Agency. The Center coordinates projects and exercises in the area of hazardous substances and conducts research and training concerning security and vulnerability relating to incidents with chemical, biological, radiological, nuclear and explosive subjects. The Center's work includes everything from smaller regional projects to larger international EU project and task assignments.



### **Lithuanian Environmental Protection Agency (LEPA)**

The Lithuanian Environmental Protection Agency (LEPA) is charged with organising, coordinating and performing environmental monitoring and implementation of the Lithuanian policy on control of hazardous substances. The LEPA Marine Research Department has experience with assessments of the environment state at chemical munitions dumpsites in the Lithuanian economic zone and in publishing guidelines for fished munitions in Lithuania.



### **Biuro Projektów Fidler**

Biuro Projektów Fidler is a Berlin-based consulting company specialised in application and management of international projects funded by EU donor programmes. They are mainly active in Central-Eastern Europe and Scandinavia, covering such programmes as INTERREG and ENPI Cross-border Cooperation Programmes, Life+, BONUS and the Framework Programmes for Research and Technological Development.

## ASSOCIATED PARTNERS

In addition to the CHEMSEA partners, several other organisations declared their strong interest in the project and their willingness to become Associated Organisations with a clearly defined commitment and an active role in the project. They are also important in terms of granting permits for scientific activities in the respective national waters.

In Poland, the **General Inspectorate for Environment (GIOS)** will make sure that project guidelines and other results find application in the realisation of the Baltic Sea Strategy. The **Maritime Office Gdynia**, the authority managing the Polish territorial waters, also supported the project and intends to implement CHEMSEA guidelines and other results and tools. The project also had the support of the **Marshall Office of Pomorskie Voivodeship and the Department of Security and Crisis Management of Pomeranian Voivodeship**, who will ensure a policy impact on a regional level in Poland. Importantly, the **National Sea Fisheries Institute in Gdynia** will link project results to the Polish fishery sector.

In Sweden, CHEMSEA was supported by the **Swedish Coast Guard**, who is the competent authority for response to harmful substances at sea. Even though the **Swedish Navy, MWDC (Mine Warfare Data Center)** is not an official Associated Partner, they took an active role in the assessment and characterisation work, providing expertise on CWA-detection methods. The **Swedish Geological Survey (SGU)** aided the project by providing geological, environmental and spatial planning information.

In Finland, CHEMSEA had the support of the **Ministry of Environment**.

In Lithuania the **Nature Research Center (NRC)** provided their expertise on environmental genotoxicity of CWAs.

CHEMSEA was also supported by the **Atlantic Branch of the Shirshov Institute of Oceanology of the Russian Academy of Sciences (AB SIO RAS)**. AB SIO RAS is the leading source of data on underwater munitions in the Baltic Sea. In cooperation with IO PAN, they provide their data and expertise on the localisation and other parameters of CWAs.

Additionally, **IDUM**, the International **Dialogue on Underwater Munitions** and **SIPRI**, the **Stockholm International Peace Research Institute**, an independent institute dedicated to research and monitoring of munitions related issues, both shared their experience and networks with the CHEMSEA project. IDUM has been also actively involved in the project activities, interpretation of the data and preparation of Guidelines.

Last but not least, the **HELCOM** secretariat was aware of and highly supportive of the CHEMSEA project. Project objectives and activities were well in line with the **HELCOM MUNI** group as well as the **HELCOM Response** group activities. CHEMSEA cooperated closely with the HELCOM MUNI working group in order to create the most synergies and ensure the largest possible impact of produced results.



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At least 50,000 metric tonnes of chemical munitions have been dumped in the Baltic Sea since the World War II, many of them containing toxic substances. Uncertainty still exists about the location of all dumping areas, the content and condition of the munitions or how they behave under Baltic Sea conditions. CHEMSEA (Chemical Munitions, Search and Assessment) is a flagship project of the Baltic Sea Region Strategy, financed by the EU Baltic Sea Region Programme 2007-2013. It has a budget of € 4.5M, part-financed by the European Union through the European Regional Development Fund. The project seeks to close existing knowledge gaps about dumped chemical warfare agents (CWA) in the Baltic Sea by mapping and characterizing dumping sites, developing guidelines in order to reduce potential threats to the environment and fishermen and by preparing a region-wide joint blue print of contingency plan for cases of CWA leakages.

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