



Exposure status of sea-dumped chemical warfare agents in the Baltic Sea

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ABSTRACT

About 50 000 tons of chemical weapons (CW) were dumped to the Baltic Sea after the Second World War. Munitions are located in the deep areas of the Baltic Sea, and there they act as a point source of contamination to the ecosystem. Corroded munitions release chemical warfare agents (CWAs) to nearby water and sediments. In this study we investigated known dumpsites (Bornholm, Gotland and Gdansk Deep) and dispersed chemical munitions, to evaluate the extent of contamination of nearby sediments, as well as to assess the degradation process of released CWA. It was found that CWA-related phenylarsenic chemicals (Clark I, Clark II and Adamsite) and sulfur mustard are released to the sediments and undergo environmental degradation to chemicals, of which some remain toxic. The extent of pollution of released CWAs and their corresponding degradation products reaches more than 250 m from the CW objects, and seem to follow a power curve decrease of concentration from the source. Bornholm Deep is characterised with the highest concentration of CWAs in sediments, but occasional concentration peaks are also observed in the Gdansk Deep and close to dispersed munitions. Detailed investigation of spreading pattern show that the range of pollution depends on bottom currents and topography.

1. Introduction

Chemical weapons (CW) were extensively used during World War I, and their production and stockpiling continued before and during World War II. They were not used in the European theatre, which resulted in vast amounts of chemical munitions and chemical warfare agents (CWAs) in arsenals of both axis and allied forces (Glasby, 1997; Surikov et al., 2014). Sea dumping operations started on small-scale at the very end of the war, in the Little Belt area, and was performed by German Army, to prevent capture of most innovative weapons containing nerve gas tabun (Knobloch et al., 2013). After the fall of Germany, based on the Potsdam agreement, allies forces took control on German chemical arsenal, which contained roughly 65 000 tons of active agents (Surikov et al., 2014). Large amounts of the captured munitions were dumped in the Skagerrak Strait and Atlantic Ocean, on orders of British and American occupation authorities. In the Baltic Sea, at least 50 000 tons

of CWs were dumped – it is assumed that these contained roughly 15 000 tons of CWAs – under the Soviet Military Administration in Germany. The most important dumpsites in the Baltic Sea are the Little Belt, near the island of Bornholm, and in the Gotland Basin. In most cases, the CW was thrown overboard, either loose (both bombs and shells) or in containers, but some ships were also sunk. In most cases, those dumped materials contained explosives (bursting for the CWs) (Nawała et al., 2020), in some cases dumping of conventional munitions, was commenced in the same locations as CW. There are strong indications that part of the CWs were thrown overboard during transport to the Baltic dumpsites; how many tonnes were thus dumped is not known.

There is, though never verified, information that chemical munitions were also dumped in the Baltic Sea for many years after the last official recorded dumping in 1948 by the navy of the German Democratic Republic and the Soviet Navy. Unofficially, the dumping continued up to the 1980s. As those suspected operations were unofficial, little is known

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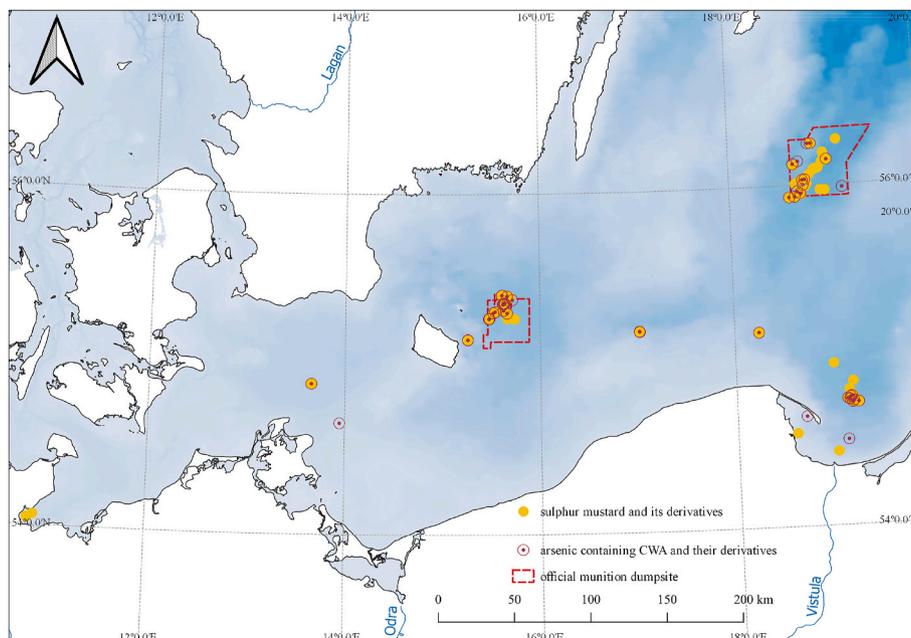


Fig. 1. Map of study sites, including detection of CWA-related chemical including sulfur mustard or phenyl arsenic chemicals, in the CHEMSEA and MODUM projects.

on the types of munitions or containers dumped (Neffe et al., 2011).

Areas included in this study include the Bornholm and Gotland Deep – the official sites – and an unofficial dumping site of the Gdańsk Deep, where presence of dumped chemical munitions was confirmed during the CHEMSEA project (Beldowski et al., 2016; Czub et al., 2018).

The most abundant chemical in the dumped stockpile was sulfur mustard (7027 tons in Bornholm Deep and 608 tons in Gotland Deep) (Knobloch et al., 2013). Most of the sulfur mustard was dumped as aircraft bombs (typically 250 kg bombs, called KC 250) and artillery shells (105 mm or 150 mm) (Knobloch et al., 2013). Other main agents in the dumped munitions and containers were Clark I (2000 and 180 tons; possibly also Clark II) and Adamsite (1400 and 120 tons), which are phenylarsenic-containing chemicals. In addition to the above two types of chemicals, also α -chloroacetophenone – a tear gas – (520 and 44 tons) and hydrogen cyanide (74 and 6 tons) were dumped.

Sulfur mustard is liquid in room temperature. However, the melting point of pure mustard is 14 °C and for technical mixtures little bit lower. For winter conditions, sulfur mustard was mixed with arsine oil to improve its usability especially in winter conditions. The German WWII winter-grade mustard, containing arsine oil i.e. technical grade Clark I, would be liquid down to –24 °C. The US and Soviet mustard could instead contain the additive Lewisite, another blistering agent. The addition of arsine oil and lewisite provided a more momentary effect on the victim and lowered the freezing point (www.chemsea.eu; Beldowski et al., 2014), but still at the temperatures on the sea floor at the dumpsites, it would be solid. Sulfur mustard is poorly soluble in water. During long storage time it can form water soluble salts and further polymerise into so-called mustard heel, the contents of the munitions may become totally solid over time. Depending on the marine conditions mustard heel can also hydrolyse to form cyclic degradation products.

Both Clark I and Adamsite are solid materials. Both are poorly soluble in water (DA 0.2 g/L (Green, and Perry, 2007) DM 0.064 g/L (Olajos and Stopford, 2004), but Clark I will hydrolyse relatively fast in contact with water. Both chemicals can form hydrolysis products, which dimerize easily, and go through oxidation. Arsine oil is technical Clark I (35%), which also contains blister agent phenyldichloroarsine (PDCA or “pfiffikus”) (about 50%), as well as triphenylarsine (5%) and arsenic trichloride (5%) (Franke, 1997). The two first components are liquids and hydrolyse easily in contact with water. The hydrolysis product for

arsenic trichloride is arsenous acid, which could also originate from other sources. The last component is solid and quite stable. α -Chloroacetophenone is a solid chemical and relatively stable in water. Its degradation in environment is not well known as it is not posing a major risk due its low toxicity. Hydrogen cyanide is very water soluble liquid and is not usually found in shells, which have corroded through or in sediment samples.

Over 70% of the objects dumped in Bornholm and Gotland deeps were aircraft bombs, which have a thin metal shell (Arison III, 2013). Only 7% of the dumped material was contained in artillery shells, which have a thicker outer casing. Remaining agents were dumped in containers or encasements. The rate of release of the payload due to corrosion depends on the type of the munition/container as well as on the thickness and material of the outer shell. The quality of the metal used in German bombs and shells became worse and very variable towards the end of the war, which would affect the corrosion rate.

Materials were mostly dumped by item-by-item from vessels (Arison III, 2013). Some of the aircraft bombs were dumped in their wooden transport boxes, which caused them to float away from the dumping sites. In the main dumping areas, different types of shells and munitions have been randomly deposited and partly sunk in the sediment. Therefore, sediment samples can be expected to contain residue from several types of munitions simultaneously. Additionally, there can be high and low concentration areas very close to each other despite setting designated dumping zones, i.e., primary or secondary dumping sites, because of the low accuracy of positioning systems available at the time, the dumped materials are distributed almost randomly across large geographical areas (Missiaen et al., 2010).

This paper gives an overview on contamination based on results of CHEMSEA and MODUM projects. We concentrate on these two projects related to studies of sea-dumped munitions in the Baltic Sea, even there have been one project MERCW (<https://cg.cs.uni-bonn.de/en/projects/mercw/>) (Missiaen et al., 2010) before these projects. The European Union (EU) project CHEMSEA (2011–2013) (Beldowski et al., 2014, Beldowski et al., 2016a) focused on the dumpsite at Gotland Deep even though the dumpsite east of Bornholm and the suspected unofficial dumpsite at Słupsk Furrow and Gdańsk Deep were included in the project. In these studies, sediment sampling was performed nearby objects identified with sonar scanning. The sampling was performed with

equipment guided from boat in possible contaminated areas as well as collected with remotely operated vehicle (ROV) guidance directed towards visible objects resembling munitions. Based on experience in previous projects like MERCW and review of current literature on known dumped agents and expected degradation products (Missiaen et al., 2010, www.chemsea.eu), target chemicals were selected and analysed.

NATO SPS project "Towards the Monitoring of Dumped Munition Threat" (MODUM) (<http://www.iopan.gda.pl/MODUM/>) addressed the uncertainty of the impact of sea-dumped chemical munition on the Baltic environment. The very limited datasets that exist nowadays, show that the degradation products of conventional and chemical munitions are present in the sediments close to sunk objects (Knobloch et al., 2013), and adverse chronic effects on fish are not excluded. Therefore, the MODUM project aimed at a cost-effective monitoring and survey methods for the explosives and chemical munitions dumping grounds, in order to control the magnitude of the leakage of pollutants associated with warfare material, and their impact on the Baltic ecosystem. It focused on improving survey and identification methods and assessing the risk associated with sea-dumped chemical weapons by means of chemical and biological measurements. The MODUM project also included hydrological measurements in areas of concern and modelling the possible transport of pollution from the dumpsites represented by particles and dissolved CWA (Beldowski et al., 2017).

The EU INTERREG Baltic Sea Region Programme 2014–2020 Decision Aid for Marine Munitions, DAIMON (<https://www.daimonproject.com/>), continued the studies of dumped munitions as the source of CWA related pollution and provided more controlled sampling solutions.

2. Material and methods

2.1. Study area

Studied sites included known dumpsites for chemical munitions, namely Bornholm Deep, Gotland Deep and Gdańsk Deep, as well as areas where either dumping was suspected, or in routes used for transportation of chemical munitions from the harbour of Wolgast to designated dumpsites. The location and division of sampling areas is depicted in Fig. 1. Study sites varied in terms of depth, distance from the shore, oxygen levels and type of chemical weapons dumped.

The area of primary Bornholm dumpsite was officially established as a target location for dumping the chemical armament in the Bornholm Deep (Neffe et al., 2011). The centre of the area was designated at 55°21' N and 15°37' E and the whole dumpsite was about to spread in a diameter of 6 NM. The mean depth of this area is 100 m, what was expected to prevent munition scattering and allocating towards the shallow zones and inhabited shores (Knobloch et al., 2013).

In fact, both CWAs and conventional weapons were scattered within relatively larger area, which was later assigned and marked on nautical charts among the area limited by the meridians 55°10' N and 55°23' N and by the parallels of 15°24' E and 15°55' E. The area is defined as the Bornholm secondary dumpsite. It is assumed, that the scattering of munitions sunken at the primary dumpsite was a result of the bottom currents and accidental trawling by draggers and trawlers.

The whole dumpsite located at the Bornholm Deep, can be characterised by depth in the range from 90 to 110 m, and temporary oxygen depletion. It is estimated that nearly 11 000 tonnes of CWAs were dumped in this region, including sulfur mustard, as well as phenylarsenic containing CWAs, such as Clark I and Adamsite.

The second officially designated dumping area is located close to the Gotland Deep, in the southern part of the Gotland Basin (Neffe et al., 2011). The Gotland dumpsite spreads within nearly 330 km², what makes it nearly twice as big as the Bornholm dumpsite. It is estimated, that 1000 tonnes of chemical munition was dumped at this site, in the areas from 70 to 120 m deep. Both the size of the area, and the number of dumped munitions, make the harmful objects much more scattered than in the case of Bornholm primary and secondary dumpsites. Periodical

oxygen deficiencies are observed in this area (Knobloch et al., 2013).

As for the Gdańsk Deep, there was no established official site designated for dumping of chemical nor conventional munitions. However, according to the HELCOM MUNI working group (Knobloch et al., 2013), even 12 000 tonnes of warfare could be deposited on the sea bottom in this location. Because the depths of this area can reach up to 120 m, this deep could have also been assumed as a proper dumping area, where the sunken munitions were expected to be isolated from other basins and shallow waters. This region also suffers from temporary anoxia (Knobloch et al., 2013).

A separate category, are the areas located in more shallow waters, closer to the shore. Based on the documents from Polish Navy's Hydrographic Office, some amounts of chemical weapon could have been dumped also on the routes from the harbours to the officially pointed dumping areas (Szarejko and Namieśnik, 2009; Radke et al., 2014). As a result, CWAs can be also detected in the areas of the Gulf of Gdańsk, Słupsk Furrow, beyond the secondary Bornholm dumpsite etc. Also in Kiel Bay and Bay of Mecklenburg chemical and conventional munitions were dumped. All of those areas relatively are shallow (from 15 to 70 m) and characterised by sandy sediments, due to high dynamics of the environments. Even though single episodes on anoxic conditions might occur in those places, no long-time oxygen depletions affect those regions, what may impact the possibility of oxidation of CWAs present in the environment. Since the munitions from those areas are located in large distance from themselves, they are referred in the text as "other".

2.2. Survey, inspection and sampling

Investigation in the studied area was conducted in the following way and consists of two actions: Area Wide Assessment (AWA) and Detail Survey and Investigation (DSI). The AWA procedure was carried out with towed side scan sonars and the autonomous underwater vehicles (AUVs). The side scan sonar survey was conducted to obtain big coverage of the interested region but at the cost of low resolution. The aim of this activity was to detect all big obstacles, such as shipwrecks and ghost nets, to avoid them in future AUV missions. When the preliminary survey was done, data were post-processed and the AUV missions were designed based on received sonar mosaics. After recovering the AUV from the water, recorded detail sonar and magnetometer data were processed to obtain high-resolution mosaics with overlaid layer of the magnetic field deviation, and then, targeting procedure was ran. Based on selected, most promising objects ROV missions were conducted in terms of DSI actions. With a usage of the ROV, a visual inspection of interesting targets was performed with High Definition (HD) cameras and BlueView sonar, simultaneously with sediment samples collection in close proximity from it.

For detailed study of CWA spreading, samples were collected next to a wreck and between two objects 100 m from the wreck. Collection of samples included a shipboard deployed Van-Veen Grab, and cassette sampler. The cassette sampler was developed within the MODUM project, and included 6 scoop samplers mounted on a frame, with video camera supervision, and closed in sequential with a signal from the surface. The sampler was deployed from a rubber boat, positioned above the sampling point with a system of three anchors. The rubber boat was then allowed to drift over a sampling point while subsequent cassettes were closed, which enabled collection of 6 samples per dive, on a distance of approximately 20 m up-current and down-current from sampled object.

Besides of sediment samples collected with the use of ROV, GEMAX dual gravity corer, and box corer were used to collect sediments from the ship. In each case, distance to the object was assessed by means of Global Positioning System (GPS) position of the ship, and ultra short baseline (USBL) derived position of ROV next to an object.

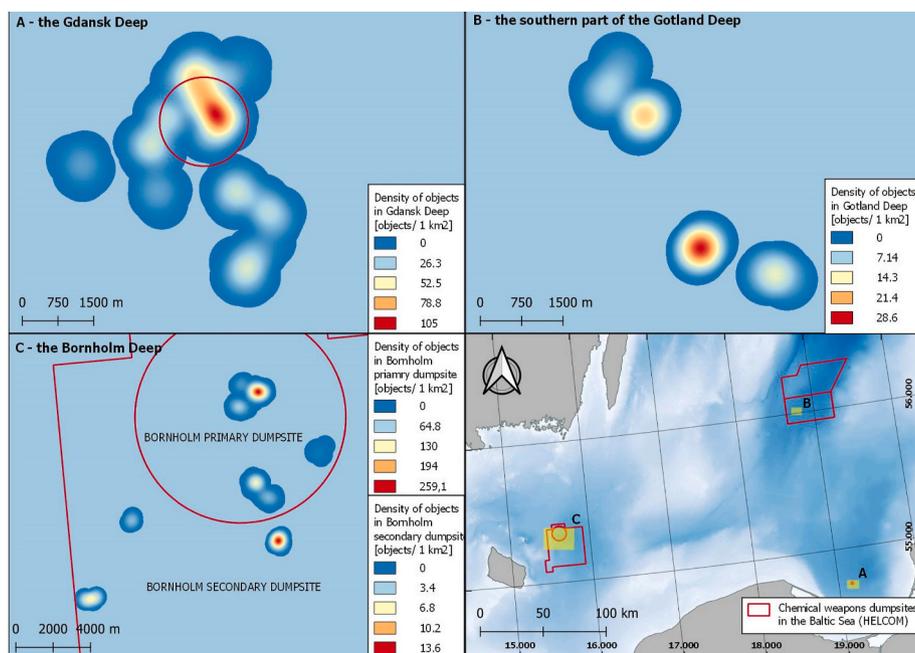


Fig. 2. Localization of survey areas with results of objects density calculations. A – the Gdansk Deep, B – the southern part of the Gotland Deep, C – the Bornholm Deep including primary and secondary dumping sites, D Overall picture of studied dumping sites.

2.3. Analysis of sediment and pore water samples

2.3.1. Chemicals

Analysis were performed in two reach-back laboratories, namely at the Swedish Defense Research Agency (FOI) and Finnish Institute for Verification of Chemical Weapons Convention (VERIFIN).

Sulfur mustard, thiodiglycol sulfoxide, 1,4,5-oxadithiepane, 1,2,5-trithiepane, 1,7-dioxa-4,10-dithiacyclododecane, Adamsite, Clark I, phenyldichloroarsine, α -chloroacetophenone, Lewisite I and Lewisite II was synthesized in-house at FOI. The following chemicals purchased by FOI from commercial sources: phenylarsonic acid and triphenylarsine (Alfa Aesar, Ward Hill, MA, USA), 5,10-dihydrophenoarsazin-10-ol 10-oxide; triphenylarsine oxide, 1,4-dithiane and 2,2'-thioacetic acid (Sigma-Aldrich, St. Louis, MO, USA).

VERIFIN had synthesized Clark I, Adamsite, phenyldichloroarsine and tabun in-house. Sulfur mustard, 1,4-dithiane, 4-oxathiane, 1,4,5-oxadithiepane and 1,2,5-trithiepane were received from Finnish Defence Research Agency (FDRA). Lewisite I and Lewisite II were received to VERIFIN from Spiez Laboratory Switzerland. The following chemicals purchased from commercial sources: thiodiglycol (Aldrich, Missprie, USA), triphenylarsine (Acros, France) and α -Chloroacetophenone (Fluka, Missouri, USA).

Additional references required for analyses after trimethylsilylation, oxidation or derivation with propane-1-thiol were prepared from the chemicals listed above using the same reactions as for the actual samples described by Söderström et al., 2018.

2.3.2. On-ship analysis

In some of the cruises, early screening of sediments was performed onboard, and if CWA degradation products were found, more detailed sampling was performed. In cruises where ship based analysis was not possible, sampling was based solely on AUV and ROV data, and collected samples were sent directly to reach-back laboratories.

On-ship analysis was based on previously published methods (Magnusson et al., 2016)). The samples were centrifuged to remove the pore water and the sediment phase is analysed using a HAPSITE® portable Gas Chromatograph/Mass Spectrometer with internal Tenax concentrator tube and an external Headspace Sampling System (HAPSITE®

Smart Plus Chemical Identification System, INFICON AG, Switzerland). The HAPSITE® GC-MS is designed for on-site chemical detection and identification of volatile organic chemicals and the dynamic head space method was optimized for the sulfur mustard degradation products i.e., 1,4-oxathiane, 1,3-dithiolane, 1,4-dithiane, 1,4,5-oxadithiepane, 1,2,5-trithiepane using 2-methyl-1,3-dithiolane as an internal standard. For further information, see Magnusson et al. (2016). The developed rugged and easy handled GC/MS instrument provided sensitive and selective on-ship-analysis for identification and semi-quantification of sulfur mustard degradation products (Magnusson et al., 2016). The obtained identifications are based on automatic data processing with Automated Mass Spectral Deconvolution & Identification System (AMDIS) and spectra matching will provide identification data with high confidence. The automated analysis will provide identification from a level of 15–80 $\mu\text{g}/\text{kg}$, which could be improved with manual interpretation and spectra matching in NIST-library to 1–10 $\mu\text{g}/\text{kg}$ (<https://chemdata.nist.gov/dokuwiki/doku.php?id=chemdata:downloads:start>). The intention with this data was to provide the crew on the ship with evidence of the presences of sulfur mustard degradation products in the analysed sample and a semi-quantitative estimate in order to identify “hot spots” of contamination. The taken samples were then be frozen and transported to reach-back laboratory for further analysis. The intention with this analysis was to provide the scientific data of the leakage of CWA-related chemicals into the environment.

2.3.3. Reach-back analysis

Extensive analysis of traces of dumped CWAs in environmental samples mainly sediment has been done during the CHEMSEA and MODUM-projects investigations in well-equipped laboratories. Sample preparation was based non-polar and polar extraction of dry sediment and analysis of CWAs thereafter (Söderström and Östin, 2017; Söderstrom et al., 2018; Nawala et al., 2016; Popiel et al., 2014). Flow-charts of sample preparation are given in Supplementary section (S-1, Figs. 1–3). Studied target chemicals are presented in Supplementary data S-2.

Sample analysis was performed using a gas chromatography–tandem mass spectrometric (GC–MS/MS) and liquid chromatography–tandem mass spectrometric (LC–MS/MS) methods. The off-site methods are

Table 1
Result of spatial analysis of detected CW-like objects.

Area	Number of detected objects in the area	Density (objects/1 km ²)		
		maximum	mean	median
Bornholm primary dumpsite	732	259,1	94,6	74
Bornholm secondary dumpsite	31	13,6	5,2	4
Gdansk Deep	577	105	36,3	29,5
The southern part of the Gotland Deep	76	28,6	11	10

Table 2
Sum of degradation products of sulfur mustard in different studies areas sediments. n = number of results, SD = standard deviation, N_{tot} = total number of samples.

	n	Mean µg/Kg	Median	Min	Max	SD	N _{tot}
Bornholm Primary	21	266	32	2	2887	642	27
Bornholm Secondary	18	28	3	1	274	64	20
Gdansk Deep	13	127	8	0	550	205	35
Gotland South	15	46	5	0	561	143	56
Gotland North	11	9	5	3	33	9	41
Other	19	49	4	0	749	170	37
Gdansk Bay	3	15	11	8	28	11	9

Table 3
Sum of degradation products of phenylarsenic related chemicals in different studies areas sediments. n = number of results, SD = standard deviation, N_{tot} = total number of samples.

	n	Mean µg/Kg	Median	Min	Max	SD	N _{tot}
Bornholm Primary	18	2316	751	19	18731	4409	27
Bornholm Secondary	14	156	21	3	1572	412	20
Gdansk Deep	8	188	103	4	560	187	35
Gotland South	6	110	39	2	333	144	56
Gotland North	5	16	13	1	44	18	41
Other	9	494	42	3	4026	1325	37
Gdansk Bay	2	95	95	79	111	22	9

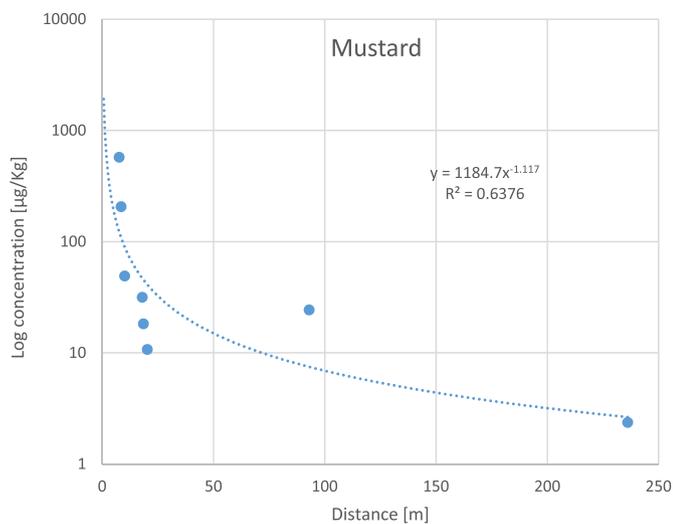


Fig. 3. Log-normalized concentration of sum of sulfur mustard degradation products versus distance (meters).

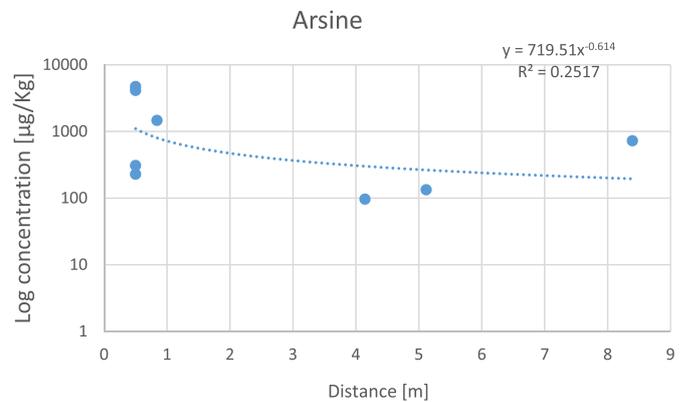


Fig. 4. Log-normalized concentrations of sum of degradation products of phenylarsenic based CWAs versus normalized distance (meters).

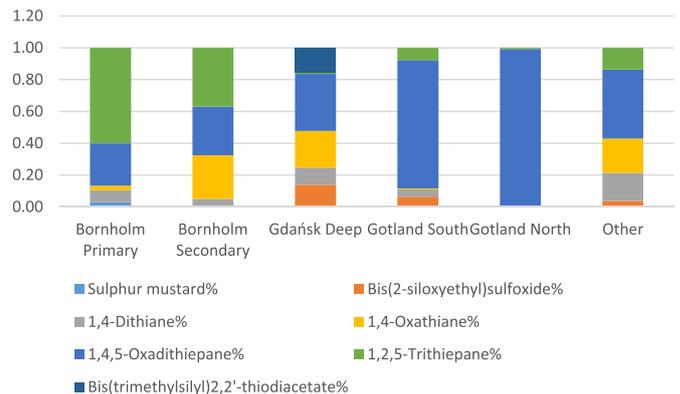


Fig. 5. Contribution of different degradation products of sulfur mustard related CWAs to measured total concentration.

described in detail elsewhere (Söderström and Östin, 2017; Söderström et al., 2018).

Some samples, which were analysed onboard, were also analysed at a reach back laboratory. In this type of reach-back laboratory with state-of-the-art analysis techniques like GC-MS/MS and LC-MS/MS the analysis data provides quantitative data of a broader range of compounds (see Supplementary section S-2). The analysis work was primarily focused on providing quantitative data which will be obtained with a LOQ in the range of 0.3–13 µg/kg dw for e.g. sulfur mustard, Arsine oil/Clark I & II, Adamsite related degradation products. The intact mustard gas could occasionally be detected at 0.03 µg/kg dw in the reach-back laboratory. On-ship and reach-back analysis at FOI were compared, showing relatively good correlation (See Supplementary info S-3, Tables S-2).

Analysis of sediment and pore water samples were mainly performed in laboratories for targeted chemicals using GC-MS, GC-MS/MS or LC-MS/MS in the selected ion monitoring (SIM) modes or multiple reaction monitoring modes (MRM), which allows selective and sensitive analysis of target chemicals. It also means that no other chemicals outside the list of selected target chemicals could be detected. The chemical analysis was mainly directed towards phenylarsenic based agents such as hydrolysis and oxidation products of Clark, Arsine oil and Adamsite to be analysed preferably with LC-MS/MS after oxidation with hydrogen peroxide or alternatively with GC-MS/MS after derivatisation with propanethiol. Sulfur mustard analysis was preferably done with GC-MS/MS analysis directed towards cyclic degradation products without derivatisation.

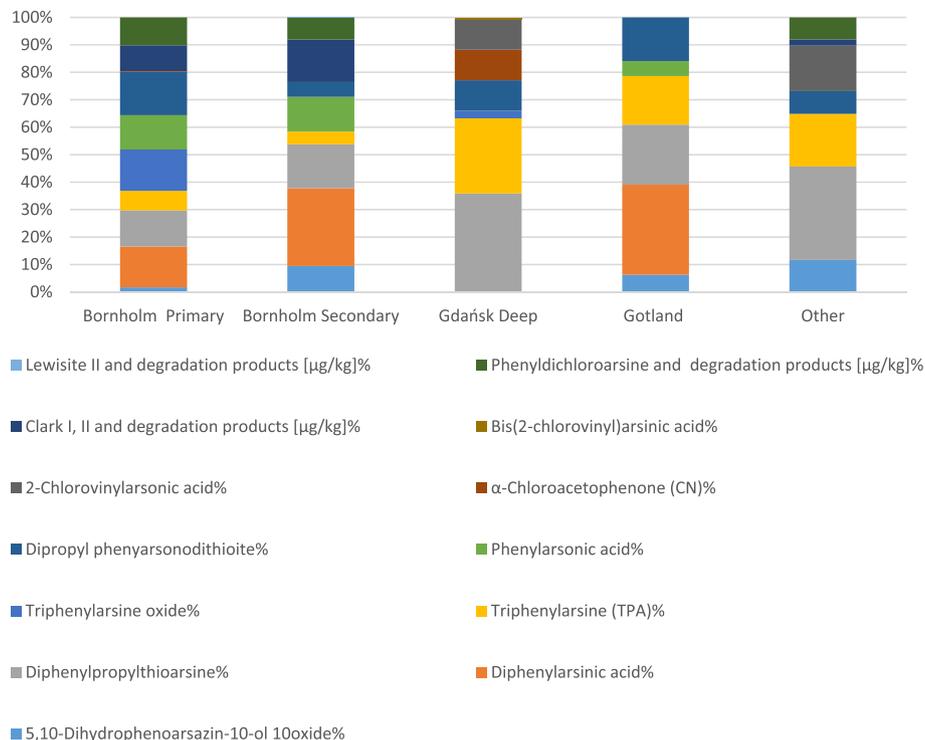


Fig. 6. Contribution of phenylarsenic based CWA degradation products to measured total concentration.

3. Results and discussion

3.1. Distribution of objects

Hydroacoustic surveys were conducted in selected CWs dumpsites of the Baltic Sea: the Gdansk Deep, the southern part of Gotland Deep and the Bornholm Deep (Fig. 2). The Bornholm Deep area was additionally divided into primary and secondary dumpsites. Based on collected and processed side scan sonar data, locations of CW-like objects were pointed and extracted into geographical coordinates format. Next, obtained points were entered into the Geographic Information System (GIS) software and spatial analysis was conducted. The numbers of detected objects and their densities (objects per square kilometer) were calculated for designated regions. Results of the spatial analysis are presented in Table 1.

The densities of objects were calculated with the heatmap technique, based on Kernel Density Estimation. The kernel shape for the analysis was Quartic.

The highest number of detected objects with the highest densities were observed in the area of Bornholm primary dumpsite. On the other hand, Bornholm secondary dumpsite is characterized by the lowest number of CW-like targets and also the lowest density, despite its proximity to the Bornholm primary dumpsite. The number of detected objects in the region of Gdansk Deep was 577 and it is comparable to Bornholm primary dumpsite. However, the density of targets in the area of Gdansk Deep is lower than in Bornholm. It suggests that CW-like objects in the region of Gdansk Deep are more scattered. The total quantity of detected targets in the southern part of Gotland Deep was 76, with a density of 28.6 objects per 1 square kilometer.

It is assumed, that the mean sedimentation rate in the areas of Bornholm Deep, Gotland Deep and Gdańsk deep equals 1 mm per year. Therefore, it could be roughly estimated, that the sunken ordnance at present could be covered by a layer of 6–7 cm thickness. As the bottom of the deeps consists mostly of the aleuritic mud, there is also a possibility that the weaponry dropped off into the soft sediments.

3.2. CWA detection

Even though a few indications of active agents at ppt ($\mu\text{g agent Kg}^{-1}$ sediment) levels were noted for sulfur mustard and Adamsite, the main indications for leakage of hazardous chemicals are based on hydrolysis/degradation products in the ppb range (ng agent Kg^{-1} sediment). From the number of 225 sediment samples collected in total, in 121 at least one CWA or its degradation product were detected, and 57 samples contained at least one target chemical. Chemicals related to sulfur mustard and arsenic-containing chemicals were found in 37 and 39 samples, respectively. Both types of chemicals were detected in 19 samples.

Comparing the distance between contaminated and non-contaminated samples leads to the conclusion, that the pollution of sediments with CWA is local and is strongly dependant on the type of seabed, the condition of the munitions and the prevailing bottom currents. Studies using mercury as a tracer of munitions showed only limited contamination in chemical weapons dumpsites, much lower than in conventional munition dumpsites (Beldowski et al., 2019). The Gotland Deep dumping activities were characterised by item-by-item dumping in a relative large area, what is reflected in 63% of the samples with positive detections of the dumped material. The Bornholm Deep dumping activities were performed in a relative small area including scuttling of ships packed with chemical munition as well as item-by-item dumping. In this region 80% of samples contained the remains of CWAs. Target chemicals were found in all studied areas. These results indicate that CWA also could have been dumped in the transport route between harbours and areas designated as the official dumping sites at Gotland and Bornholm Deep.

3.3. Differences between areas

3.3.1. Total concentration of studied CWAs

Total concentration of CWAs observed in sediments varied greatly between investigated dumpsites. For mustard related agents, Bornholm primary dumpsite displayed values up to almost $3000 \mu\text{g/kg}$, in extreme

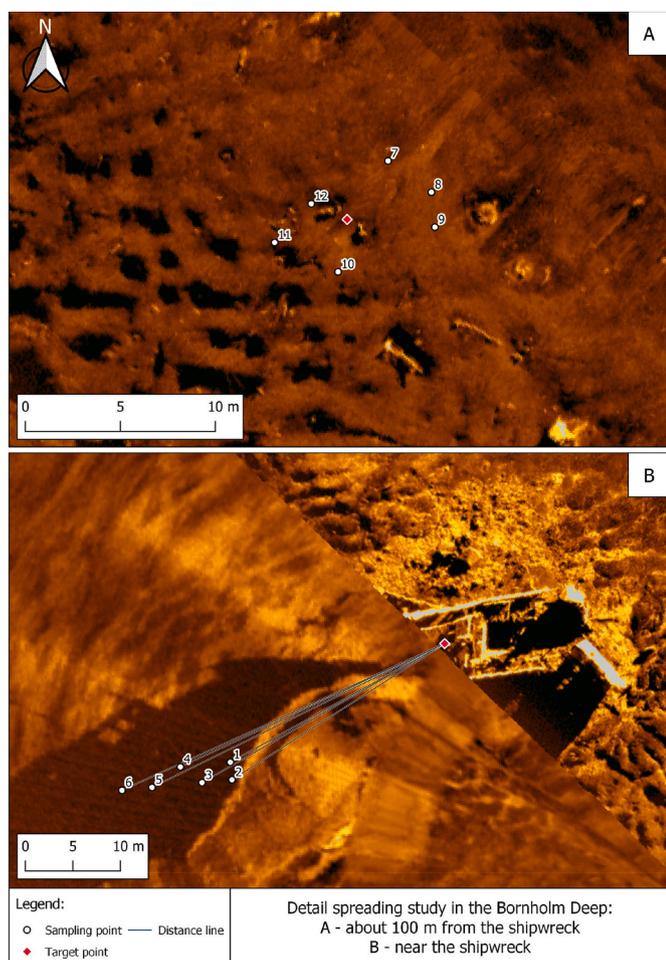


Fig. 7. Detailed spreading study performed in Bornholm Deep A - 100m from shipwreck, next to two munition objects; B at the shipwreck suspected of containing ammunition.

cases, while at other areas, including both dumpsites and single munitions from Kiel Bay, Bay of Mecklenburg and Słupsk Furrow extreme values did not exceed 1000 $\mu\text{g}/\text{kg}$ (see Table 2).

However, median values of mustard concentration for dumpsites showed less variability: Bornholm Primary dumpsite was four times higher than anywhere else, with Gdansk Deep and Gdansk Bay coming close. Results are given in Table 3. Although the dumpsite at Gdansk Bay is the smallest of investigated sites, the ammunitions there were dumped in 1954, which may suggest that the release of agents to the nearby sediments is at earlier, more potent stage, however another reason may be either different type of predominant ammunition dumped there or their environmental conditions. The smallest median values were observed for solitary munitions in Kiel Bay, Bay of Mecklenburg and Słupsk Furrow.

For phenylarsenic based CWAs the situation is different (see Table 3). There both Bornholm primary and secondary dumpsites are characterized with the highest maximum observed concentration. Isolated peaks are also observed next to dispersed munitions (Kiel Bay, Bay of Mecklenburg, Słupsk Furrow), but this could be an effect of random sampling next to a leaking munitions. Median values are showing similar trend to sum of sulfur mustard CWAs, with elevated values at Gdansk Deep site, probably resulting from similar reasons.

Literature overview of sediment and pore water concentrations in different areas is given in Supplementary info (S-4, Tables S-3). In Hawaii dumpsites, relative high sulfur mustard concentrations have been found (2.1–410 $\mu\text{g}/\text{kg}$ dw) for 30 positive samples (Briggs et al., 2016; Tomlinson et al., 2016) compared to few observations in the Baltic

Sea – 0.4 to 33 $\mu\text{g}/\text{kg}$ dw in this study, observed in 5 samples from Bornholm primary dumpsite. This might be due to the anoxic conditions in the Pacific Ocean. The 1.4 dithiane concentration in Hawaii dumpsite varied from 18 to 2100 $\mu\text{g}/\text{kg}$ dw for 22 positive samples (Briggs et al., 2016), which is higher than recorded in the Baltic (540 $\mu\text{g}/\text{kg}$ dw, this study), but lower than 2887 $\mu\text{g}/\text{kg}$ dw of sum of all mustard degradation products observed in Bornholm primary dumpsite). Another conclusion of the acquired data is that there are quite few studies on contamination of pore water or deep water fractions/portions. This would need more focus in the future studies and would be important for evaluation of risk to marine biota.

3.3.2. Range of contamination

Investigations regarding the range of contamination were performed at Bornholm Deep, since this was an area where availability of confirmed munitions allowed for collection of the samples in transects. Fitting the data on concentration versus distance from the object plot resulted in points fitting a power curve ($r^2 = 0,64$) for sulfur mustard derivatives (Fig. 3), while relationship for phenylarsenic based agents was not so clear (Fig. 4). The reason for this was combining several pairs of data. In some cases the transect was situated from 0.6 to 4 m, in others 10–18 m. To normalize and compare those transects instead of absolute distance from the munition, we have set the proximity samples to half a meter and remote samples to difference in transect range, following the formula:

$$X_i = A_{\text{dist}} \cdot (x_1 + 0,5)$$

Where: x_i is distance on the x axis; A_{dist} is the absolute distance from munition; x_1 is the distance of the closest object from munition object (Fig. 3).

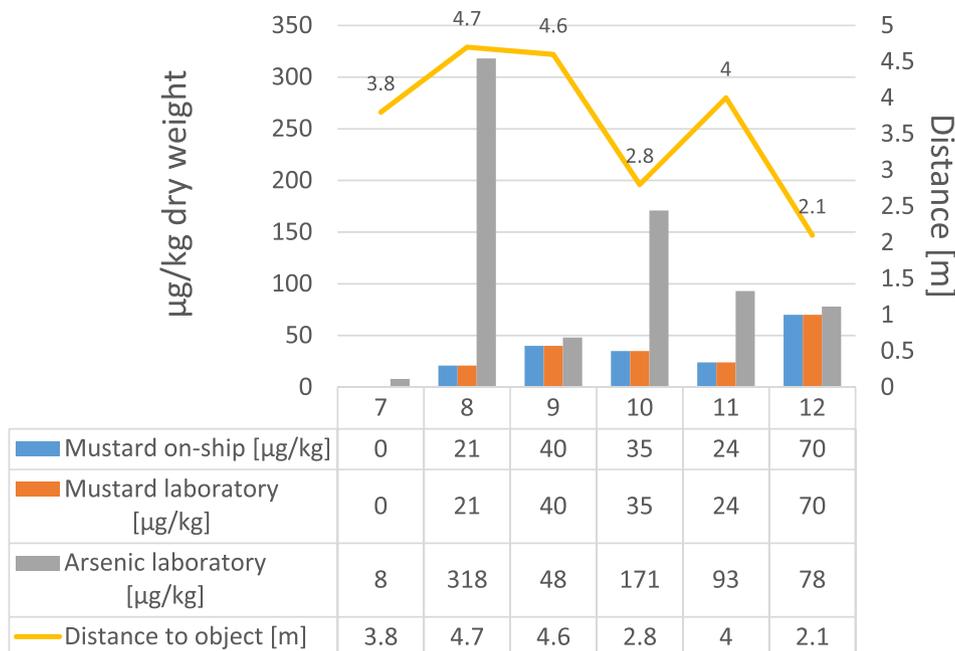
In case of phenylarsenic based CWAs the relationship with normalized distance could also be described with a power curve (Fig. 4), however the correlation is weaker than for sulfur mustard CWAs (0.25). This could either be the result of normalization procedure, or more complicated release process of phenylarsenic based warfare agents. Former studies has shown that arsenic levels are elevated in the whole Bornholm dumpsite (Beldowski et al., 2016b), which suggests long range spreading of degradation products. While mustard, upon exposure to seawater covers itself with a polymeric skin (Missiaen et al., 2010), phenylarsenic based CWAs are readily emitted to the environment directly after corrosion opens the containers, which would then make the magnitude of the source a function of corrosion and size of opening created by it, rather than time dependent. We know from previous studies, that corrosion rate is uneven in the Baltic (Knobloch et al., 2013), which could be responsible for observed spreading of As CWA (see Fig. 4).

3.3.3. Degradation

Degradation process of CWA is a function of environmental conditions, age of exposure and initial agent. In order to trace the environmental fate of CWAs, the degradation products were plotted for different investigated dumpsites and presented as contribution to sum of sulfur mustard related and phenylarsenic related CWAs in Figs. 5 and 6, respectively.

As depicted in Fig. 5, sulfur mustard itself in low concentrations was observed only in Bornholm Deep. In both primary and secondary Bornholm dumpsite the degradation process goes in direction of 1,2,5 trithiepane and 1,4,5 oxadithiepane, although at secondary dumpsite 1,4 oxathiane was a significant part of total concentration. 1,4 Dithiane is present at all investigated dumpsites except the northern part of Gotland, although at low values from 5 to 18%. At Bornholm Deep no oxidation products of sulfur mustard are observed, suchlike thiodiglycol sulfoxide, which would suggest either ongoing oxidation or fast dissolution of those products and flux to the water column. Oxidation could also take place during sampling and transport. Main pathway of sulfur

A - about 100 m from the shipwreck



B - near the shipwreck

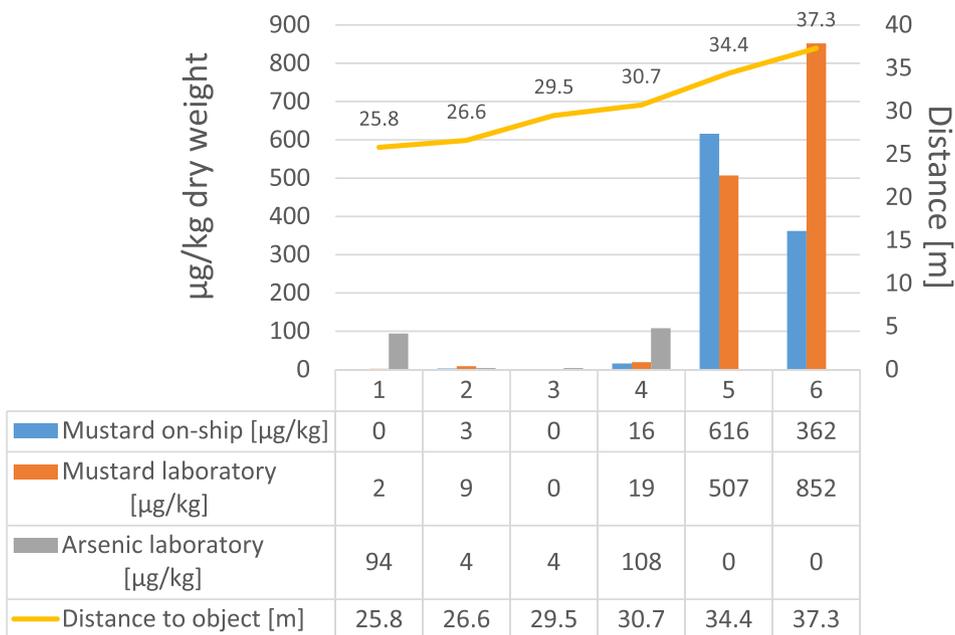


Fig. 8. CWA degradation products identified with chemical analysis in samples collected according to Fig. 7 nearby a wreck in the Bornholm deep dumpsite A) at objects 100 m from the wreck and B) nearby the wreck.

mustard degradation in the sediments is its hydrolysis and reaction with sulfides present, which suggests that anoxic conditions dominate in the dumpsite areas. Detected compounds are formed in other than oxidation reactions. Mostly, detected compounds are either contaminants, which are side products of mustard synthesis, or can be also formed during spontaneous degradation inside dumped munitions. In the Gdańsk Deep, one reach-back laboratory observed both hydrolysis products (i.e., thiodiglycol) and other oxidation products (i.e., thiodiglycol sulfoxide and thiodiglycolic acid). It suggests that in this area, mustard is continuously

released, and oxygen-rich conditions prevail. In isolated munitions from shallow areas, including Gdańsk Bay, Kiel Bay, Bay of Mecklemburg and Słupsk Furrow degradation is similar to that observed in the Gdańsk Deep, but with higher domination of oxidation products, which is probably related to more energetic environment, which together with higher oxygen concentration in nearbottom water in those sites promotes faster oxidation.

In samples from Gotland Deep only one sample contains oxidation product (thiodiglycol sulfoxide), in remaining 14 samples 1,4,5-

oxadithiepane dominates, which is caused by rather low oxygen concentration in this dumpsite, but not preventing partial oxidation of sulfur mustard related chemicals.

Fig. 6 represents contribution of phenylarsenic based CWA degradation products to measured total concentration. The group named “other” includes munitions from Gdansk Bay and isolated munitions from Kiel Bay, Bay of Mecklemburg and Słupsk Furrow. In case of phenylarsenic based agents situation is more complicated than in case of sulfur mustard derived degradation products. In all studied areas oxidation products were observed – namely end-products like arsenic and arsonic acids, which may suggest that oxidation of those agents is faster than sulfur mustard, and even episodic oxygen presence is sufficient for their oxidation. The phenylarsenic compounds are prone to oxidation during handling and transport and furthermore it was preferred to analyse the phenylarsenic compounds as their oxidised derivative due to instrumental limitations. Since oxidation products were the target of the analysis in case of phenyl arsenic based CWA, anoxic degradation pathway could not be identified based on analysed compounds.

3.3.4. Detailed spreading study

Sampling for the environmental analysis is performed on the sediment surrounding objects of interest in order to study potential leakage. However, the guidance of the sampling is most often difficult and a direct hit on the object containing high levels of toxic material could not be excluded. Furthermore, the operation towards deteriorated dumped objects makes it often unclear if the studied object is of relevant interest or not. This, while the sampling mission in a marine environment includes costly ship and personnel time. Therefore, it is of interest to be able to perform on-ship analysis to support the sampling team with an indication that relevant object is studied and to assist secure handling of the sample (see Chapter 3.2).

The collected samples was divided for on-ship analysis and laboratory analysis, respectively. The analysis on the deployable system provided evidence for the on-board crew that the site is contaminated with dumped sulfur mustard and thereby the study was performed on a relevant object.

In the laboratory analysis, a more detailed analysis study achievable providing data on additives to the dumped mustard gas (Arsine oil/Clark) well as for other types of dumped munition. Samples analysed direct on-ship, as indicated in Fig. 8 showed good performance as compared to the laboratory analysis. The laboratory analysis results given in Fig. 8 shows the sum of sulfur mustard degradation products while the phenylarsenic analysis shows the sum of arsine oil degradation products. During the investigation of Wreck 1 (Fig. 8B) the data demonstrates presence of arsine oil and sulfur mustard leakage. However, the sampling points closest to the wreck indicate lower detected concentrations while the amounts, especially of sulfur mustard degradation products, are higher 10 m from the wreck. This could be due to higher water current velocity close to the wreck or alternatively leaking objects outside the wreck, which is a more probable explanation.

At the sampling points 100 m from wreck 1 (Fig. 8A) at observed objects, remains of arsine oil/Clark and sulfur mustard are identified as well as Adamsite.

Sequential sampling will enhance the possibility to detect major leakage while overcoming uneven distribution around a wreck. Preferably, would the sampling be extended and combined with more stations to get sampling series “upstream” and “downstream” the wrecks. Control samples, collected 100 m from wreck with munitions, in other direction than two munition objects, where no objects were present at the sediment surface, still contained remains of phenylarsenic based CWA. A hundred meter distance was evidently not enough for a control sample. If there would have been possibility during each sampling campaign for onboard analysis this problems might have been avoided.

4. Conclusions

In this paper an overview of distribution of objects of sea-dumped CWAs is given including study areas primary and secondary Bornholm dumpsite, Gotland dumpsite and Gdansk deep. Analysis results obtained on-ship correlated well with results of reach-back laboratories and therefore proved to be a valuable tool for guiding sampling on dumpsites. Differences between areas in total concentration of leaked phenylarsenic and sulfur mustard, their degradation products and spreading in Baltic Sea were observed, which could also be the result of number of samples taken from the sites and success in finding CW munition. Nevertheless, it seems that degradation pathways of CWA differ in particular dumpsites, as a consequence of environmental conditions. It is important to extend these studies to get more data on status of leakage of sea-dumped CW munitions and to establish continuous monitoring programmes to keep eye on overall effects on marine biota. Detailed spreading study and mathematical models used show that the impact of dumped munitions is modified by bottom currents speed and direction, as well as bottom topography. Therefore, interpolation of CWA pollution cannot be performed by object-dependent pattern, but should include hydrodynamic modelling.

There are already evidence that phenylarsenic CWAs accumulate into marine biota (Niemikoski et al., 2017), and therefore continuous monitoring campaigns would be matter of importance. For environmental risk evaluation, also pore water and deep water samples should be included to the monitoring campaigns.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marenvres.2020.105112>.

References

- Arison III, H.L., 2013. European Disposal Operations: the Sea Disposal of Chemical Weapons. CreateSpace Independent Publishing Platform.
- Beldowski, J., Klusek, Z., Szubska, M., Turja, R., Bulczak, A.I., Rak, D., Brenner, M., Lang, T., Kotwicki, L., Grzelak, K., Jakacki, J., Fricke, N., Ostin, A., Olsson, U., Fabisiak, J., Garnaga, G., Nyholm, J.R., Majewski, P., Broeg, K., Soderstrom, M., Vanninen, P., Popiel, S., Nawala, J., Lehtonen, K., Berglind, R., Schmidt, B., 2016a. Chemical munitions search & assessment-an evaluation of the dumped munitions problem in the Baltic Sea. *Deep-Sea Res Pt II* 128, 85–95.
- Beldowski, J., Szubska, M., Emelyanov, E., Garnaga, G., Drzewinska, A., Beldowska, M., Vanninen, P., Ostin, A., Fabisiak, J., 2016b. Arsenic concentrations in Baltic Sea sediments close to chemical munitions dumpsites. *Deep-Sea Res Pt II* 128, 114–122.
- Beldowski, J., Fabisiak, J., Popiel, S., Ostin, A., Olsson, U., Vanninen, P., Lastumaki, A., Lang, T., Fricke, N., Brenner, M., Berglind, R., Barsiene, J., Klusek, Z., Pączek, B., Söderström, M., Lehtonen, K., Szubska, M., Malejevas, V., Koskela, H., Michalak, J., Turja, R., Bickmeyer, U., Broeg, K., Olejnik, A., Fidler, J., 2014. CHEMSEA Findings, Gdańsk, vol. 86. Institute of Oceanology Polish Academy of Sciences, ISBN 978-83-936609-1-9.

- Beldowski, J., Been, R., Turmus, E.K., 2017. Towards the Monitoring of Dumped Munitions Threat (MODUM): A Study of Chemical Munitions Dumpsites in the Baltic Sea. Springer Netherlands.
- Beldowski, J., Szubska, M., Siedlewicz, G., Korejwo, E., Grabowski, M., Beldowska, M., Kwasigroch, U., Fabisiak, J., Łońska, E., Szala, M., Pempkowiak, J., 2019. Sea-dumped ammunition as a possible source of mercury to the Baltic Sea sediments. *Sci. Total Environ.* 674, 363–373.
- Briggs, C., Shjegstad, S.M., Silva, J.A.K., Edwards, H., 2016. Distribution of chemical warfare agent, energetics, and metals in sediments at a deep-water discarded military munitions site. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 128, 63–69.
- Czub, M., Kotwicki, L., Lang, T., Sanderson, H., Klusek, Z., Grabowski, M., Szubska, M., Jakacki, J., Andrzejewski, J., Rak, D., Beldowski, J., 2018. Deep sea habitats in the chemical warfare dumping areas of the Baltic Sea. *Sci. Total Environ.* 616, 1485–1497.
- Franke, S., 1977. *Lehrbuch der Militärchemie*, second ed., vol. 1. Militärverlag der DDR, Berlin.
- Glasby, G.P., 1997. Disposal of chemical weapons in the Baltic Sea. *Sci. Total Environ.* 206, 267–273.
- Green, D.W., Perry, R.H., 2007. *Perry's Chemical Engineers' Handbook*. McGraw-Hill Education, USA.
- Knobloch, T., Beldowski, J., Böttcher, C., Söderström, M., Rühl, N.-P., Sternheim, J., 2013. 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) Baltic Sea Environmental Proceedings. HELCOM, p. 129.
- Magnusson, R., Nordlander, T., Ostin, A., 2016. Development of a dynamic headspace gas chromatography-mass spectrometry method for on-site analysis of sulfur mustard degradation products in sediments. *J. Chromatogr. A* 1429, 40–52.
- Missiaen, T., Soderstrom, M., Popescu, I., Vanninen, P., 2010. Evaluation of a chemical munition dumpsite in the Baltic Sea based on geophysical and chemical investigations. *Sci. Total Environ.* 408, 3536–3553.
- Nawała, J., Czupryński, K., Popiel, S., Dziedzic, D., Beldowski, J., 2016. Development of the HS-SPME-GC-MS/MS method for analysis of chemical warfare agent and their degradation products in environmental samples. *Anal. Chim. Acta* 933, 103–116.
- Nawała, J., Szala, M., Dziedzic, D., Gordon, D., Dawidziuk, B., Fabisiak, J., Popiel, S., 2020. Analysis of samples of explosives excavated from the Baltic Sea floor. *Sci. Total Environ.* 708, 135198.
- Neffe, S., Beldowski, J., Fabisiak, J., Kasperek, T., Popiel, S., 2011. REPORT concerning the issues included in Decisions no. 23 and 24, made at the 1st Meeting of the Expert Group concerning updating and reviewing available information on chemical weapons dumped in the Baltic Sea "HELCOM MUNI 1/2010. In: HELCOM. Chief Inspectorate of Environmental Protection, Warsaw.
- Niemikoski, H., Söderström, M., Vanninen, P., 2017. Detection of chemical warfare agent-related phenylarsenic compounds in marine biota samples by LC-HESI/MS/MS. *Anal. Chem.* 89 (20), 11129–11134.
- Olajos, E.J., Stopford, W., 2004. *Riot Control Agents: Issues in Toxicology, Safety & Health*. CRC Press.
- Popiel, S., Nawała, J., Czupryński, K., 2014. Preparation and application of sol-gel acrylate and methacrylate solid-phase microextraction fibres for gas chromatographic analysis of organoarsenic compounds. *Anal. Chim. Acta* 837, 52–63.
- Radke, B., Jewell, L., Piketh, S., Namieśnik, J., 2014. Arsenic-based warfare agents: production, use, and destruction. *Crit. Rev. Environ. Sci. Technol.* 44 (14), 1525–1576. <https://doi.org/10.1080/10643389.2013.782170>.
- Söderström, M., Östin, A., 2017. Analysis of sediment samples for sea-dumped chemical weapons. In: Recommended Operating Procedures for Analysis in the Verification of Chemical Disarmament, pp. 631–649.
- Söderstrom, M., Ostin, A., Qvarnstrom, J., Magnusson, R., Rattfelt-Nyholm, J., Vaheer, M., Joul, P., Lees, H., Kaljurand, M., Szubska, M., Vanninen, P., Beldowski, J., 2018. Chemical analysis of dumped chemical warfare agents during the MODUM project. Towards the Monitoring of Dumped Munitions Threat (Modum): A Study of Chemical Munitions Dumpsites in the Baltic Sea, pp. 71–103.
- Surikov, B.T., Vries, J.G.d., Mikulin, A.I., Kossyi, I.A., Holsboer, J.H., Seward, R.C., Duursma, J.C., Alfred, H., Heineken, Duursma, E.K., 2014. *Dumped Chemical Weapons in the Sea - Options*. Drukkerij van Denderen BV, Amsterdam.
- Szarejko, A., Namieśnik, J., 2009. The Baltic Sea as a dumping site of chemical munitions and chemical warfare agents. *Chem. Ecol.* 25 (1), 13–26. <https://doi.org/10.1080/02757540802657177>.
- Tomlinson, M.S., De Carlo, E.H., 2016. Occurrence and possible sources of arsenic in seafloor sediments surrounding sea-disposed munitions and chemical agents near O'ahu, Hawai'i, Deep Sea Research Part II. *Topical Stud. Oceanogr.* 128, 70–84.