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Evaluation of a chemical munition dumpsite in the Baltic Sea based on geophysical and chemical investigations

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ARTICLE INFO

Article history:

Received 10 February 2010

Received in revised form 22 April 2010

Accepted 29 April 2010

Available online xxx

Keywords:

Chemical munition dumpsite

Baltic Sea

Chemical analysis

Seismic-magnetic

ABSTRACT

This paper discusses the results of geophysical and chemical investigations carried out in a chemical munition dumpsite in the southern Baltic Sea, east of the island of Bornholm. After WW2 over 32,000 tons of chemical war material was dumped here including shells and bombs as well as small drums and containers. The geophysical investigations combined very-high-resolution seismics and gradiometric measurements. The results indicate the presence of a large number of objects buried just below the seafloor. The size of the objects and their distribution, with a marked increase in density towards the center of the dumpsite, suggests that we are dealing with dumped war material. Sediment and near-bottom water samples, taken within the dumpsite and in the surrounding area, were analysed for the presence of various chemical warfare agents (CWA) including Adamsite, Clark, sulphur mustard, tabun, chlorobenzene and arsine oil. The results indicate a widespread contamination that reaches far beyond the dumpsite boundary. CWA degradation products were found in most of the sediment samples. The contamination was mostly related to arsenic containing compounds; only one sample indicated the presence of sulfur mustard. Although the correlation between detected objects and CWA concentrations is not always straightforward, the overall results suggest that a lot of the dumped war material is leaking and that over the years the contamination has reached the seafloor sediments.

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1. Introduction

The problem posed by sea-dumped chemical warfare agents (CWA) deserves considerable international attention: the amount dumped in the North European seas alone since the end of World War I runs into hundreds of thousands of tons at least (Kafka, 1995; Stock and Lohs, 1997). The toxic war material, often dumped in relatively shallow waters and areas of active fishing, not only represents a serious possible threat to the marine environment but also to the often densely populated coastlines. Dumped chemical weapons regularly reappear in the human environment, for example when retrieved in fishing nets or when washed ashore on beaches (e.g. BSH, 1993; HELCOM, 1993a, 1993b, 1993c, 1993d; SOAEFD, 1996). Nevertheless, the problem has received little attention and has been neglected for a long time at the international level.

There are a number of reasons for the decades of delay in addressing this problem. Most importantly, the issue is politically sensitive as it raises the problem of accountability. Many dumping operations were carried out secretly and it is not always clear who can be held responsible. Some dumpsites are located in international

waters, although more often dumping operations were carried out in territorial waters near the borders of neighbouring states. The government bodies of both the states that carried out the operations and those bordering the dumping areas were long reluctant to tackle this sensitive problem (especially during the Cold War), but these political obstacles have mostly been removed by now.

Another critical factor is the complexity of the problem, which requires in-depth expertise in different scientific fields, and therefore involves a significant commitment of financial and technological resources. In recent years sea-dumped chemical weapons have been the subject of growing concern in a number of international conferences and workshops. Although the full extent of the dumping operations still remains unclear – often due to a lack of documentation and loss or destruction of records – an increasing number of dumpsites have been documented (e.g. BSH, 1993; SOAEFD, 1996; Granbom, 1996; MEDEA, 1997; Rapsch and Fisher, 2000; Missiaen and Henriët, 2002; Tørnes et al., 2002; Tørnes et al., 2006; Plunkett, 2003; ICAM, 2006).

One of the difficulties in managing the risk associated with chemical munition dumpsites is the uncertainty associated with their location. Indeed little is known about the exact location and distribution of the dumped munition. This is partly due to the lack of official records of the dumping operations, which often took place in chaotic circumstances right after the war. In many cases the

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dumped weapons are no longer exposed on the sea floor but have become buried under a cover of recent sediments, making “fast” tracking methods such as side-scan sonar or multibeam sonar imaging of little use. As a result a correct estimation of the location and the amount of dumped war material is still lacking. Yet this information forms a first and important step in order to carry out a reliable risk assessment of the dumpsite.

Knowing the exact location of the dumped CWA however does not provide any information on the current leaking process and possible contamination. Strategically chosen sample positions and careful chemical analysis of the water and sediment samples is therefore necessary. Because the concentrations of toxic chemicals are expected to be low, it is essential to optimize and validate the existing methods for CWA analysis in order to obtain an accurate evaluation of the present contamination and to produce reliable, repeatable and comparable analysis data which can be used as a sound basis for any follow-up study of the dumpsite status.

1.1. Aim and goal of the study

In this paper we will discuss the results of geophysical and chemical investigations carried out in a chemical munition dumpsite in the southern Baltic Sea, east of the island of Bornholm. The investigations were carried out in the framework of the EC-FP6 project “MERCW” (Modelling of Environmental Risks related to sea-dumped Chemical Weapons). The geophysical acquisition combined very high resolution seismics and magnetics. Recent studies in Belgium had demonstrated the importance of such a complementary geophysical approach (Henriet and Missiaen, 2005). The main goal of the geophysical investigations was to map the precise location and distribution of the dumped weapons, including their burial depth, and to image the internal structure of the dumpsite in the highest possible detail.

Based on the results of these geophysical surveys a detailed sampling survey was carried out. Sediment and near-bottom water samples were taken at well-chosen locations within the Bornholm dumpsite and in the surrounding area. The samples were analyzed for the presence of selected CWA and their degradation products based on review on literature. This semi-quantitative chemical analysis is aimed to prove the presence of dumped chemicals and/or their degradation products in the marine environment. Combined, the geophysical and chemical investigations form a crucial basis in (modeling the) risk assessment of the dumpsite.

2. Chemical munition dumpsite in the Bornholm Basin

After World War II approximately 32,000 tons of chemical weapons, containing about 11,000 tons of toxic agents, were dumped in the Bornholm Basin, east of the island of Bornholm in the southern Baltic Sea. The dumping operations were carried out in 1947 on the orders of the Soviet military administration in Germany. The transports were assembled in the harbors of Wolgast and Peenemünde and involved a wide variety of war material, ranging from shells, mines, grenades and bombs to wooden encasements, containers and small drums (see Table 1) (HELCOM, 1993e). By far the largest part of the dumped war material involves aircraft bombs and artillery shells. Although the latter are by far in the majority, the total amount of chemical warfare agents stored in aircraft bombs is much higher (see Table 2). Also of importance is the fact that aerial bombs have much thinner walls than shells and grenades.

The main toxic warfare agents dumped in 1947 in the Bornholm Basin involve sulfur mustard (63%), arsenic-containing compounds [totally 31%; including Clark and arsine oil (18%), and Adamsite (13%)] and α -chloroacetophenone (5%) (see Table 2) (for more details on the chemical warfare agents see Section 4). Mustard gas and α -chloroacetophenone were for the largest part stored in aircraft

Table 1
Number of objects dumped in Bornholm Basin in 1947 (HELCOM, 1993e).

Types of CW	S-mustard	Other As-cont.	Adamsite	CN	Others	Total
Aircraft bombs	65,779	8338	7388	4785	–	86,290
Artillery shells	302,926	–	29,639	49,702	–	382,267
High-explosive bombs	31,442	–	–	–	–	31,442
Mines	9590	–	–	–	–	9590
Encasements	487	1434	693	–	55	3166
Smoke grenade	–	–	32,250	–	–	32,250
Cans	–	–	–	–	7234	7234
Containers	–	924	–	–	–	924
Drums	–	–	6927	–	–	6927
Total	410,224	10,696	76,897	54,487	7786	560,090

bombs (this contradicts information from the Bornholms Marine District stating that α -chloroacetophenone was mainly dumped in wooden casings – Sanderson and Fauser, 2008). Clark and arsine oil were also dumped in containers and wooden encasements; Adamsite was mainly stored in bombs and wooden encasements (Table 2). During the dumping operation the munition was cast overboard either loose or packed in wooden chests. The chests were often seen drifting around before sinking to the bottom (HELCOM, 1993e). After reports of chests being washed ashore the order was given to shoot the drifting crates (Sanderson and Fauser, 2008). So far no official records were found of scuttled ships loaded with chemical weapons. One HELCOM report mentions eight naval vessels and one cargo vessel were sunk in the dumpsite area, but this information was classified as ‘not verified’ (HELCOM, 1996). According to the Bornholms Marine District no ships were sunk in 1947 (Sanderson and Fauser, 2008).

In addition to the dumping operation of 1947, some 200 to 300 tons of chemical weapons were dumped in the Bornholm Basin between 1952 and 1965 on the orders of the East German Authorities (BSH, 1993). During this dumping operation mainly bombs and shells filled with mustard gas, phosgene, Adamsite and Clark were dumped (Politz, 1994). According to documents discovered in the archives of the Ministry of Internal Affairs of the German Democratic Republic (DDR) one ship was scuttled in 1962 in the Bornholm Basin. The ship, a wooden barge filled with bombs and drums covered in concrete, was scuttled during operation “Hanno” (Politz, 1994) (Fig. 1).

The munition dumpsite is located in the southern part of the Bornholm Basin, east of the island of Bornholm, in water depths ranging from 70 m to over 96 m. The primary dumpsite area is marked by a circle with a radius of 3 nautical miles (Fig. 2 – black circle), but it is very likely that the chemical munition was dumped over a much larger area (HELCOM, 1994). This extended dumpsite is marked by a rectangular area roughly ranging between 55°07’N–55°26’N and 15°25’E–15°55’E (Fig. 2 – black rectangle). Further spreading of the dumped munition subsequently took place by fishing vessels during trawling (Fig. 2 – grey line). The retrieved munition was often thrown

Table 2
Amount of toxic agents (in tons) dumped in Bornholm Basin in 1947 (HELCOM, 1993e).

Types of CW	S-mustard	Other As-cont.	Adamsite	CN	Others	Total
Aircraft bombs	5920	906	591	479	–	7896
Artillery shells	671	–	61	36	–	768
High-explosive bombs	314	–	–	–	–	314
Mines	42	–	–	–	–	42
Encasements	80	203	693	–	74	1050
Smoke grenades	–	–	65	–	–	65
Containers	–	924	–	–	–	924
Drums	–	–	18	–	–	18
Total	7027	2033	1428	515	74	11,077



Fig. 1. Sinking of a barge filled with chemical weapons in Bornholm Basin in 1962 during operation “Hanno” (Photo Bornholms Museum).

overboard. However, munition may also have been dragged over the seabed over considerable distances without being retrieved in fishing gear. It is known that part of the munition was already thrown overboard during transport to the dumping area, but the quantities involved here are not known (HELCOM, 1996; Schulz-Ohlberg et al., 2002).

Magnetic surveys carried out in 1999 and 2000 enabled the identification of four shipwrecks in the dumpsite area (Gorodnitski and Filin, 2002). The large magnetic anomalies observed suggest a steel hull and not a wooden ship. All the wrecks are located in the primary dumpsite (see also Fig. 4). In 2001 multibeam and ROV (Remotely Operated Vehicle) surveys were performed over two of the wrecks (Paka and Spiridonov, 2002). Additional side-scan sonar data were obtained over all the wrecks in 2006 (Paka, 2006). The images indicate that the wrecks are extensively damaged, with the hull often deeply immersed into the bottom sediments. One wreck was

surrounded by what seemed fragments of artillery shells on the sea bed as well as a large bomb. Partly corroded artillery missiles were observed on the deck of another wreck (Paka and Spiridonov, 2002).

3. Recent incidents and state of the dumped war material

Since 1984 fishing has been officially prohibited in the primary dumpsite. The extended dumpsite area is marked as “anchoring and fishing not recommended”. Yet the dumpsite has always remained a popular fishing area and fishermen have repeatedly found munition in their bottom-trawled nets (HELCOM, 1993a, 2005) (Fig. 2). Because Denmark compensates its fishermen for any contaminated catches, fairly reliable Danish statistics exist about reported finds of chemical warfare agents. Since 1960 over 720 finds of chemical munition were reported (Sanderson and Fauser, 2008). After 1992 the number of caught munition has decreased (on average 5–10 per year). The

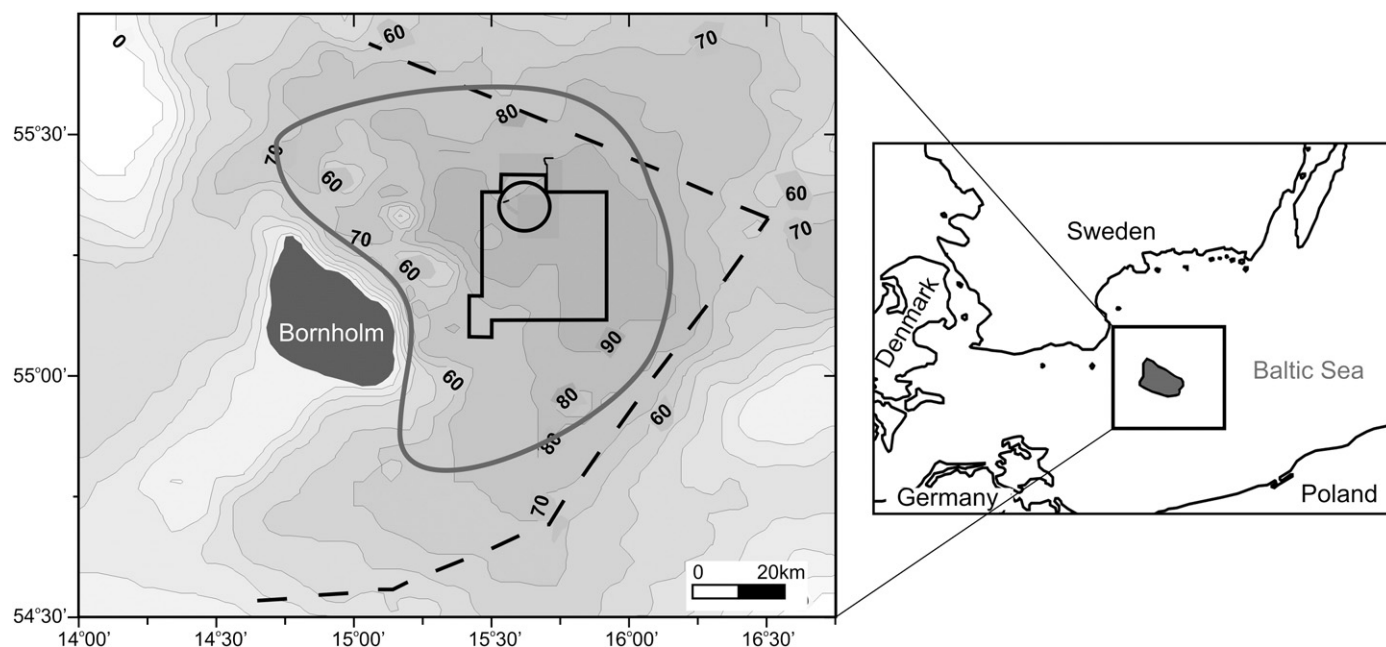


Fig. 2. Overview map showing the location of the chemical munition dumpsite in the Bornholm Basin, southern Baltic Sea (depth lines every 10 m). The black circle marks the primary dumpsite area. The black rectangle marks the larger dumpsite boundary. The thick grey line marks the zone where fishing incidents related to chemical weapons were reported (after BSH, 1993). The dashed line marks the border of the Danish economic zone.

reason for this decrease is uncertain, but it is possibly related to a decrease in fishing activity due to declining fish stocks.

Fishermen from other nations bordering the Baltic Sea are not obliged to notify the authorities of munition finds, and therefore only incomplete figures exist (HELCOM, 1996). Germany has reported 13 incidents in the dumpsite area east of Bornholm or in its immediate vicinity (HELCOM, 1993c). Sweden reported four incidents with mustard gas from the area east of Bornholm between 1980 and 1992, one involving a fishing vessel from Estonia (HELCOM, 1993d). In 2001–2002 two incidents were reported to the Swedish Coast Guard, one south of the Swedish coast near Nordersund (mustard gas), and one in the harbor of Simrishamn (mustard gas and Clark) (HELCOM, 2003a).

By far the largest part of the contaminated fish catches involves mustard gas, only a small part involves other chemical warfare agents such as Adamsite, Clark and α -chloroacetophenone (HELCOM, 2003b). This is not so surprising since mustard gas makes up the main part of the dumped munition (see Table 2). The mustard gas is either caught loose in lumps or still stored in the munition (aerial bombs). The large amount of caught mustard gas bombs may also be (partly) explained by the fact that these bombs were often stored in wooden crates which may have hindered them sinking deep in the bottom. In 1947 local newspapers reported hundreds of wooden bomb casings being washed upon the shores of Bornholm (Sanderson and Fauser, 2008).

Over the years, the corrosion of the munition has been steadily advancing. Before 1992 most of the caught munition was only partly corroded, but since 1992 nearly all munition is either empty or very heavily corroded (Sanderson and Fauser, 2008). We should however keep in mind that the caught munition was most likely exposed on the sea floor. According to information from local divers, munition that is buried in the sediment seem to be much more intact (Sanderson and Fauser, 2008). This agrees well with the findings at the Paardenmarkt dumpsite off the Belgian coast where buried munition from WW1 was still remarkably intact when recovered in the early seventies (Missiaen and Henriët, 2002).

Almost all of the caught mustard gas munition near Bornholm involve aerial bombs of type KC250. The weight of the active ingredients in these bombs is typical around 100 kg (Sanderson and Fauser, 2008). Caught mustard gas lumps vary in weight between 0.5 kg and 130 kg (HELCOM, 2003a). In recent years the lumps are increasingly hard and brittle (Fig. 3-left), whereas until 10 or 20 years ago they were often still semi-liquid inside. Although the dumped munition was not armed (i.e. not provided with a detonator) the finds often still contain both priming and bursting charges. The latter are mostly re-dumped for safety reasons (Sanderson and Fauser, 2008).

So far no bombs were caught that contain Adamsite or other arsenic-containing chemicals (Clark and arsine oil). These compounds

were only found stored in wooden encasements. The cases have largely decayed and unlike mustard gas the retrieved lumps are still sticky (Fig. 3-right) (Sanderson and Fauser, 2008). However this does not exclude that some of the empty munition may have contained Adamsite or Clark.

4. Chemical warfare agents and their breakdown products

4.1. Dumped chemical warfare agents

The chemical warfare agents that were dumped in significant amounts in the Bornholm Basin include sulfur mustard (H), phosgene (CG), α -chloroacetophenone (CN) as well as arsenic-containing compounds such as Adamsite (diphenylaminechloroarsine, DM), Clark I (diphenylarsine chloride, DA), Clark II (diphenylarsine cyanide, DC) and arsine oil (HELCOM, 1993e; Politz, 1994). Arsine oil is a technical mixture of Clark I (35%), phenyldichloroarsine (PDCA; 50%), trichloroarsine (TCA; 5%) and triphenylarsine (TPA; 5%). It is uncertain whether also nitrogen mustard (HN3) and tabun (GA) were dumped in the Bornholm Basin (BSH, 1993; HELCOM, 1996). Based on munition recovered from Wolgast harbor, however, the presence of tabun in the dumpsite area cannot be ruled out (Theobald, 2002). This is confirmed by local newspapers in 1948 reporting nerve gas cans having washed ashore in Sweden (Sanderson and Fauser, 2008). It was therefore decided to include tabun in the chemical analysis.

Most of the dumped chemicals were developed during World War I and were considered obsolete as warfare agents during World War II. Only sulfur mustard and tabun were considered as potential warfare agents at the time. α -Chloroacetophenone is still in use as tear gas, although it has been mostly replaced by less toxic agents. Many of the dumped chemical warfare agents also contained additives. One of these was chlorobenzene (CB) which was added to both sulfur mustard (10–30%, to lower its freezing point) and tabun (up to 5–20%, for easier dispersion) (Franke, 1977). Chlorobenzene is also a precursor of Clark I (Lohs, 1967) and therefore it might have been present as by-product after synthesis (no literature was found supporting the presence of CB in arsine oil). Chlorobenzene is potentially environmentally hazardous (HELCOM, 1994) and was therefore included in the chemical analysis. Also arsine oil was often mixed with sulfur mustard to lower the freezing point (Franke, 1977).

Phosgene is an irritant gas (classified as pulmonary agent), which causes damage to lungs, skin, eyes, nose and throat. α -Chloroacetophenone is a tear gas (also called lachrymators), which irritates mucous membranes. It is a solid agent, which is used as an aerosol (Franke, 1977). Sulfur and nitrogen mustard are blister agents (also called vesicants). Both are liquids, which absorb through skin, eyes and lungs. Mustard gases are spread as aerosols and they cause severe



Fig. 3. Left: Weathered mustard gas lump. Right: Caught Adamsite lump (Photos Bornholms Marine Distrikt).

chemical burns, which result in painful water blisters. The symptoms appear delayed after several hours from exposure (Franke, 1977).

Clark and Adamsite are solid chemicals which act as vomiting agents. Clark causes sneezing, coughing, headache, salivation, and vomiting. Adamsite causes, after some delay, irritation of the eyes, lungs and mucous membranes followed by headache, nausea and persistent vomiting. Phenyldichloroarsine (PDCA; also known as Pffikus) – a component of arsine oil – was used as vesicant in World War I (Lohs, 1967). In addition to vesicant properties, it has also vomiting agent properties. Tabun is a nerve agent. As all nerve agents it is a liquid, which is spread as an aerosol. It affects the transmission of neural signal with almost no delay in the case of inhaled agent. The final symptoms are convulsions and stopping of breathing.

4.2. Degradation of chemical warfare agents

Most of the chemical warfare agents degrade in the presence of water by hydrolysis (Munro et al., 1999). Appendix A gives a list of the chemicals that were involved in this study, with their degradation products and derivatives. Also, it is very common for both sulfur mustard and arsenic-containing chemicals to oxidize in environment.

In water, sulfur mustard degrades into thiodiglycol (TDG) (Munro et al., 1999), which can oxidize into thiodiglycol sulfoxide (TDG[ox]) (Black et al. 1992) (see Appendix A). Sulfur mustard has also many other degradation products, but TDG and TDG[ox] were considered most relevant when planning the project. In sea water, the rate of hydrolysis and dissolution is lower than in fresh water (Bizzigotti et al., 2009). Low temperatures, such as encountered at the bottom of the Bornholm Basin (3–4 °C), may change the liquid compound into solid form which may decrease the speed of dissolution and hydrolysis. Additionally, the surface of exposed mustard gas (e.g. when a corroded shell starts leaking) may start to form a shell of polymerized mustard finally forming hard and brittle lumps – the latter were found in the area (Sanderson and Fauser, 2008). This will slow down the dissolution and hydrolysis even more.

Typical of arsenic-containing chemicals is that several chemicals may form the same hydrolysis and oxidation product. For instance both Clark I (DA) and Clark II (DC) will degrade into diphenylarsinous acid (DPA) which easily reacts to form bis(diphenylarsinic)oxide (Haas et al., 1998; Hanaoka et al., 2005) (see Appendix A). Natural oxidation will further result in formation of diphenylarsinic acid (DPA [ox]). In aqueous environment, both DA and DC will degrade rapidly. According to Hanaoka, DA will degrade totally in 30 min in aqueous conditions (Hanaoka et al., 2005). Hydrolysis products of DA and DC are reported to have an equal toxicity as the parent chemicals, posing a long-lasting threat to the marine environment (Francken and Hafez, 2009). In this paper we will use Clark to refer to Clark I and Clark II together. This convention is used as all degradation products for Clark I could also be formed from Clark II.

Adamsite degrades in a similar manner as Clark I and II producing both hydrolyzed and oxidized products (Haas et al., 1998). Also phenylchloroarsine and trichloroarsine degrade in a similar manner. α -Chloroacetophenone (CN) hydrolyses slowly, but it produces non-toxic degradation products. The latter were therefore not included in this study. Phosgene will hydrolyze fast in sea water producing hydrochloric acid and carbon dioxide, which cannot be detected. Keeping in mind the low amount of dumped phosgene it was decided not to include phosgene in the present study.

Both triphenylarsine (TPA) and chlorobenzene (CB) are stable components and highly resistant to hydrolysis and oxidation and therefore studied only as intact chemicals. Tabun degrades via a couple of intermediates into phosphoric acid (Munro et al., 1999), which is also naturally occurring in the environment. The half-life of tabun in sea water (4.5 h at 20 °C) is shorter than in fresh water (Clark, 1989).

4.3. Physical properties and the environment

The physico-chemical parameters (e.g. melting point, boiling point and density) of intact target chemicals are given in Appendix B. There are two major parameters which we think best describe the distribution of the chemicals at the sea bottom: octanol water partitioning coefficient (K_{OW}) and organic carbon adsorption coefficient (K_{OC}). The former describes how easily the chemical is dissolved in water. The latter describes how well the chemical is adsorbed in soil containing organic carbon (e.g. sediment containing organic material).

All of the dumped chemical warfare agents are heavier than water (i.e. density $>1 \text{ g/cm}^3$) and therefore they are expected to remain fairly close to the sediment unless shifted by bottom currents. Most of the agents are water soluble and their solubility in the water increases when they are hydrolyzed and/or oxidized. The solubility of the chemicals is typically lower in low temperatures. The intact chemicals have also high K_{OC} values, making them easily adsorbed into the sediment, where they can be stored for a longer time. Especially, for the stable triphenylarsine the log K_{OC} value of 5.64 is very high. Chlorobenzene has clearly a lower log K_{OC} value (2.10), but it still readily adsorbs in the sediment.

5. Data acquisition

5.1. Geophysical data acquisition

Two geophysical surveys were carried out in the Bornholm dumpsite area. A first very high resolution (VHR) reflection seismic survey took place in June 2006 on board R/V “Shelf”. During this survey three acoustic sources with a distinct frequency range were used (multi-electrode sparker, Seistec boomer, parametric echosounder). One large-scale network (line spacing 750 m) and two small-scale networks (line spacing 50–100 m) were recorded in the primary dumpsite (Fig. 4). The main goal of this 2006 survey was to image the general geological framework and the internal structure of the dumpsite. The results are discussed in detail in Missiaen and Noppe (2009).

In July 2007 a second geophysical survey took place on board “Fritz Reuter”. During this survey the parametric echosounder was deployed simultaneously with a deep-towed magnetic array. The latter consisted of three cesium vapor magnetometers mounted on a triangular-shaped frame and was towed a few m above the seafloor. Two small grids of roughly $0.5 \times 2 \text{ km}$ were recorded with a line spacing of 10 m. Both grids are located in the primary dumpsite area (Fig. 4). The main aim of this second survey was the detection and identification of buried objects. In this paper we will focus on the results of this second survey. More details on the seismic and magnetic acquisition can be found in Missiaen and Feller (2008).

5.2. Sampling for chemical data acquisition

A first sampling campaign was carried out in June 2007 on board R/V “Professor Shtokman”. Sampling of the sediment and near-bottom water concentrated on the primary dumpsite area, in particular the areas surrounding the shipwrecks. In total 13 box cores and 65 Niemistö cores were taken. Only nine sediment samples of this set of samples were forwarded to VERIFIN for analysis, and it is only these samples (together with the samples taken during the second campaign) that are taken into account in this paper. The samples were divided in 1 cm slices and frozen on board.

A second sampling campaign was carried out in February 2008. In total 59 sediment samples and 61 near-bottom water samples were taken with a Niemistö bottom corer from 63 sampling stations. The cores were frozen on board. Sampling positions in the primary dumpsite were chosen based on the results of the seismic and

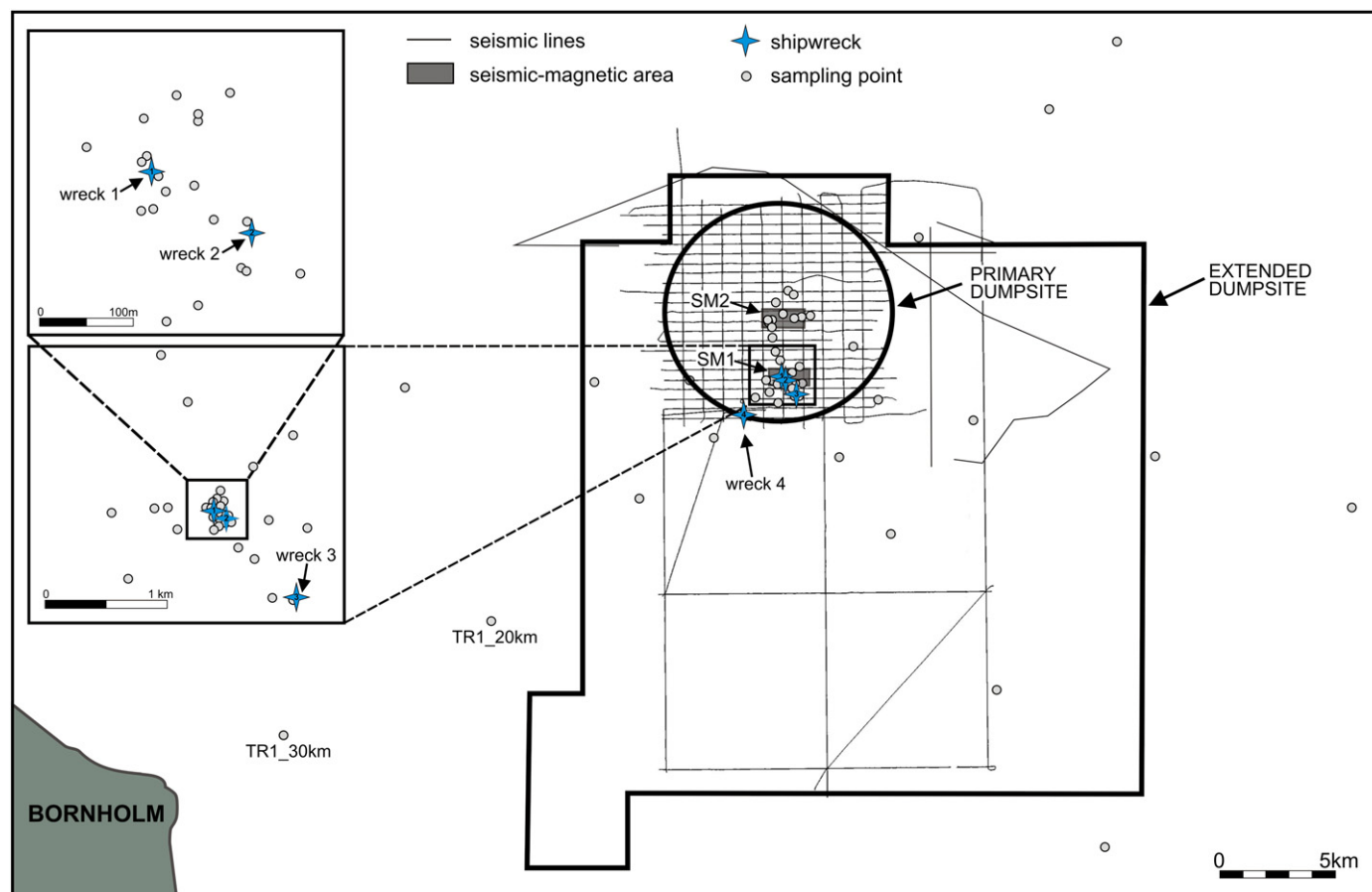


Fig. 4. Overview of the geophysical acquisition and sampling locations in the Bornholm Basin. Thick black lines mark the primary and extended dumpsite boundary. Thin black lines mark the seismic profiles. The two grey rectangles mark the seismic–magnetic areas SM1 and SM2. Blue stars mark the shipwrecks. Sampling locations are marked by small circles. The inset on the left shows a close-up of the sampling locations in the vicinity of wrecks 1 and 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

magnetic survey in July 2007. In order to investigate possible contamination outside the primary dumpsite it was decided to enlarge the sampling area. An additional number of sampling points were taken at steady intervals along 6 different radial transects starting from wreck 1 and reaching up to 30 km from the primary dumpsite area. An overview of the sampling locations (both from 2007 and 2008) is given in Fig. 4. All samples were taken in muddy bottom sediments except for the two samples near Bornholm (TR1_20km and TR1_30km, see Fig. 4) which involve a sandy bottom.

5.3. Chemical data acquisition

Two types of samples were received for laboratory analysis: sediment core samples (frozen) and near bottom water samples. Only the top 5 cm from the cores was used for analysis. Each sediment core sample was divided into sediment and pore water portions, which were treated for chemical analysis. The sediment samples were analyzed with i) gas chromatography–mass spectrometry (GC–MS; for intact volatile chemicals or derivatized chemicals) using selected ion monitoring (SIM), and ii) liquid chromatography–tandem mass spectrometry (LC–MS/MS; for intact water soluble chemicals or oxidized derivatives) using multiple reaction monitoring (MRM). The water samples were only analyzed with LC–MS/MS. Derivatisation prior to the analysis is required to make the degradation products volatile for GC–MS analysis or to improve sensitivity of intact chemicals for GC–MS or LC–MS/MS analysis. Conventional GC–MS methods for arsenic-containing chemicals based on alkanethiol derivatisation do not make any distinction between the intact,

hydrolyzed and oxidized chemical (Haas et al., 1998). However, the newly developed LC–MS/MS method is able to do so. In this method, the samples are first analyzed without any derivatisation and then after oxidation using hydrogen peroxide. The first run shows the intact chemical (only for Adamsite) and its naturally occurring hydrolysis and oxidation products (for Adamsite, Clark I and Clark II, PDCA). The second run shows the total amount of both intact chemical and all of its degradation products as all of these chemicals oxidize into the same oxidized derivative (for Adamsite, Clark I and Clark II, PDCA). The analyzed chemicals including the analytical derivatives are summarized in Appendix A.

Clark I, Clark II and their three degradation products will produce the same derivative propyl diphenylarsinothioite (DPA[SPr]) which is used for GC–MS analysis (Haas et al., 1998) as well as the same oxidation product diphenylarsinic acid (DPA[ox]). Therefore the term “diphenylarsine chemical” DPA is used for the derivatives instead of the original chemical. The derivatives are referred to as [SPr] (propanethiol derivatisation, for GC–MS method) and [ox] (hydrogen peroxide oxidation, for LC–MS/MS method).

The targeted chemicals that were involved in the analysis are sulfur mustard (H), Adamsite (DM), Clark I (DA), Clark II (DC), triphenylarsine (TPA), trichloroarsine (TCA), chlorobenzene (CB), α -chloroacetonephenone (CN), tabun (GA) and phenyldichloroarsine (PDCA) (intact compounds). Since sulfur mustard is easily hydrolyzed and further oxidized in aqueous matrices, also thiodiglycol (TDG) and thiodiglycol sulfoxide (TDG[ox]) were analyzed. In addition, the degradation products of DM, DA, PDCA and TCA were included in the analysis either as oxidized products (DM[ox], DPA[ox], PDCA[ox], TCA

[ox]) or as derivatives (DPA[SPr], TCA[SPr]). Three of the targeted chemicals (DA, PDCA and TCA) were not analyzed as intact chemicals, but only as derivatives as can be seen in Appendix A. The reason for this was that these chemicals are not stable in the GC–MS and they would degrade in the conditions used for LC–MS/MS if not already in the sample.

During the method validation the limits of quantitation (LOQ) were determined. Thanks to the sophisticated methods used (optimized sample preparation, SIM and MRM mass spectrometric techniques), quantification of the target chemical was possible at low concentration levels. This was essential since the expected concentrations in sediment and water samples were in the low range. For GC–MS, the LOQ in sediment was 0.18 µg/kg and 1.0 µg/l for water samples (for all chemicals). For LC–MS the LOQ for TDG[ox], DPA[ox] and DM[ox] was 0.089 µg/kg in sediment and 0.50 µg/l in water samples. LOQ values for LC–MS for TDG and PDCA[ox] were higher: 1.4 µg/kg in both sediment and water samples. The accuracy of the quantitation is the combined uncertainties of sample preparation and instrumental analysis: 9.3% for GC–MS and 16.8% for LC–MS/MS.

6. Geophysical results

The high resolution of the acoustic and magnetic data enabled the identification of a large number of objects. Nearly all objects are

buried (Fig. 5). Only four large objects were observed exposed on the sea floor in the vicinity of shipwrecks – possibly we are dealing with detached wreck parts. The buried objects are covered by no more than 1.5–2 m of sediment (over 80% of the objects are buried less than 70 cm deep). The low sedimentation rates in the Bornholm Basin can probably not account for the observed sediment cover and most likely it is due to sinking of the objects into the very soft muddy sediments. The size of the objects is in general less than 5 m, occasionally up to 10 m (over 60% of the objects have a size less than 2 m).

In most cases the buried objects appear scattered, although occasionally clusters of smaller objects are observed (Fig. 5C). The sea floor above some of the larger objects is often deformed, showing pit-like structures and an irregular morphology (Fig. 5B). This is probably caused by the impact of the dumped objects upon hitting the sea floor. The shallow pits are often (partly) filled with a layer of very soft or semi-liquid sediments. In a number of cases some minor sediment accumulation (maximum a few dm high) was observed on the sea floor above the buried objects (Fig. 5A). This could be linked to fluid mud accumulation deposited during a period of calm conditions after a near-bottom current event. However some relation to leaking toxic compounds cannot be entirely ruled out.

The shipwrecks stood out markedly on the magnetic and acoustic data. The wrecks are between 20 and 50 m in length and 5 to 10 m in width. The average height above the sea floor (not including long

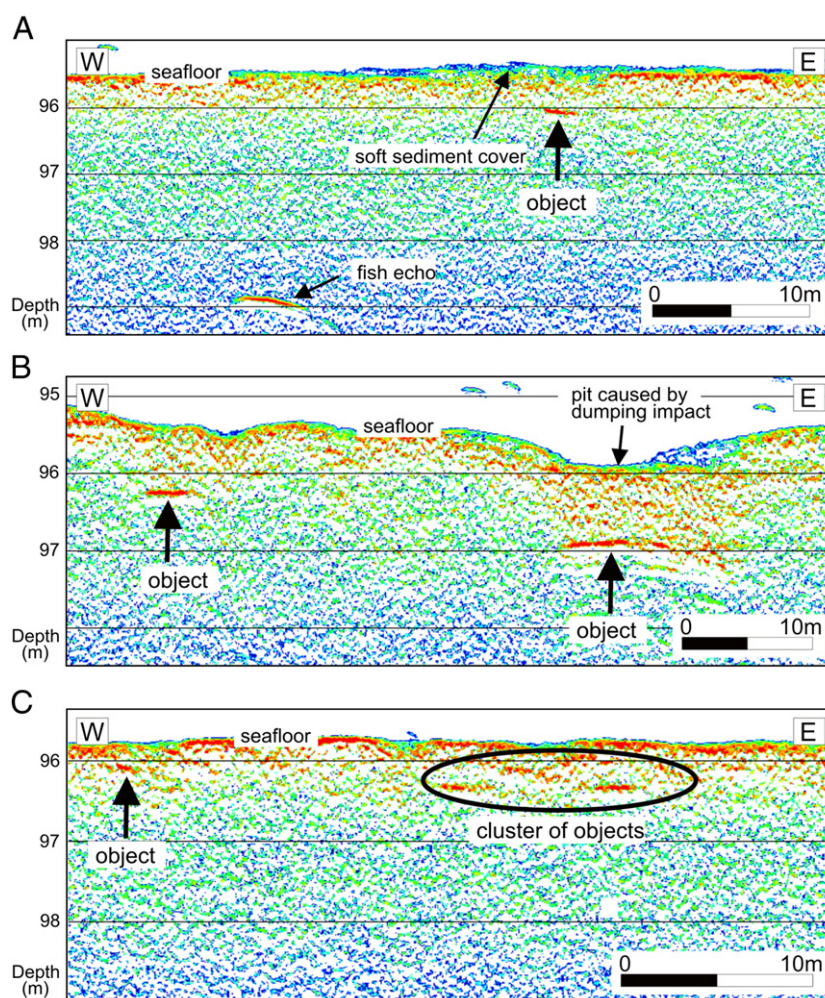


Fig. 5. Parametric echosounder profiles (100 kHz) showing the presence of different buried objects (marked by black arrows). A: Small buried object. The sea floor is marked by a local accumulation of soft sediments (blue/green colors). The object-like feature below on the left is an acoustic artefact caused by fish. B: Irregular seafloor morphology above large buried objects, most likely a result of the dumping impact. C: Small shallow object (left) and cluster of objects (ellipse). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

protruding parts) is no more than 2 m (Missiaen and Feller, 2008). This confirms the previous findings that the wrecks have largely submerged into the soft bottom sediments. The wrecks seem partly covered by a thin sediment layer of a few dm. Strong hyperbolic diffractions on the acoustic data indicate the presence of sharp protruding wreck parts (Missiaen and Feller, 2008).

Fig. 6 shows the distribution of identified magnetic and seismic objects in the two surveyed areas SM1 and SM2. Although there is often a good correlation between the two data sets (i.e. seismic objects coincide with magnetic objects), especially for the larger objects (>2 m), in many cases there seems to be no match between the two data sets (in grid SM1 13 of the 40 magnetic objects do not coincide with seismic objects, in grid SM2 this is the case for 160 of the 440 magnetic objects). This disagreement was largely due to the lateral deviation (sometimes up to 10 m or more) between the seismic and magnetic track lines, a direct result of the long tow distance – roughly 200 m – of the magnetic array behind the ship. Other reasons for the local mismatch between the seismic and magnetic data may be the fact that objects of limited size (<1 m) or objects oriented perpendicular to the track line (resulting in a small cross-section) may have failed to give a clear acoustic response.

The number of objects identified on the acoustic data is much higher than the number of magnetic anomalies (see Fig. 6). One possible reason for this is the extremely high resolution of the seismic data compared to the magnetic data. Indeed objects located only a few m apart can clearly be distinguished on the seismic data whereas they will often show up as one single magnetic anomaly (Missiaen and Feller, 2008). Furthermore a small increase in the object's burial depth (perhaps only a few dm) may seriously reduce the chance for magnetic detection (since the amplitude of the anomaly decreases with the third power of the distance to the sensor). This will particularly affect small objects – possibly also objects with a thin metal wall – which make up the largest part of the dumped objects. Last but not least, it is known that most of the munition caught by

fishermen nowadays is heavily corroded (HELCOM, 2005). An advanced state of corrosion will undoubtedly reduce the magnetic detectability of the object as it reduces the magnetic susceptibility. Although this effect is believed to be rather limited, it could render the magnetic detection of small objects more difficult.

Although there is no absolute certainty about the origin of the buried objects, the survey location and historical disposal evidence strongly suggest that we are dealing with dumped munition. The high diversity in shape and size of the detected objects confirms the existing information that a wide variety of war material was dumped in Bornholm Basin (see Tables 1 and 2). The difference in object density between the two surveyed areas is striking. In the southern grid SM1 only 40 magnetic objects and roughly 90 acoustic objects (including likely objects) were identified. In the northern grid SM2, on the other hand, 440 magnetic objects were observed and over 700 acoustic objects (again including likely objects). This difference in object density may partly be explained by the location. Indeed grid SM2 is located in the centre of the primary dumpsite which was the prime dumping target, whereas grid SM1 is located a few km towards the south, near the dumpsite boundary (see Fig. 4). But even so, the results suggest that the distribution of war material in the Bornholm dumpsite area is very heterogeneous and most likely characterized by areas of high object density alternating with zones where the objects are rare.

The total amount of war material dumped in the Bornholm Basin amounts to over 560,000 objects (see Table 1). This mainly involves artillery shells and aircraft bombs. If we assume 60% of the dumped war material to be located within the primary dumpsite area, we obtain a mean object density of roughly 3300 objects per square kilometer. This is almost four times higher than the object density in grid SM2, taking into account all likely objects. It seems to suggest that a large part of the dumped war material was not identified on the geophysical data. This may be due to several reasons: (1) small objects are not easily detected and these objects make up the largest part of

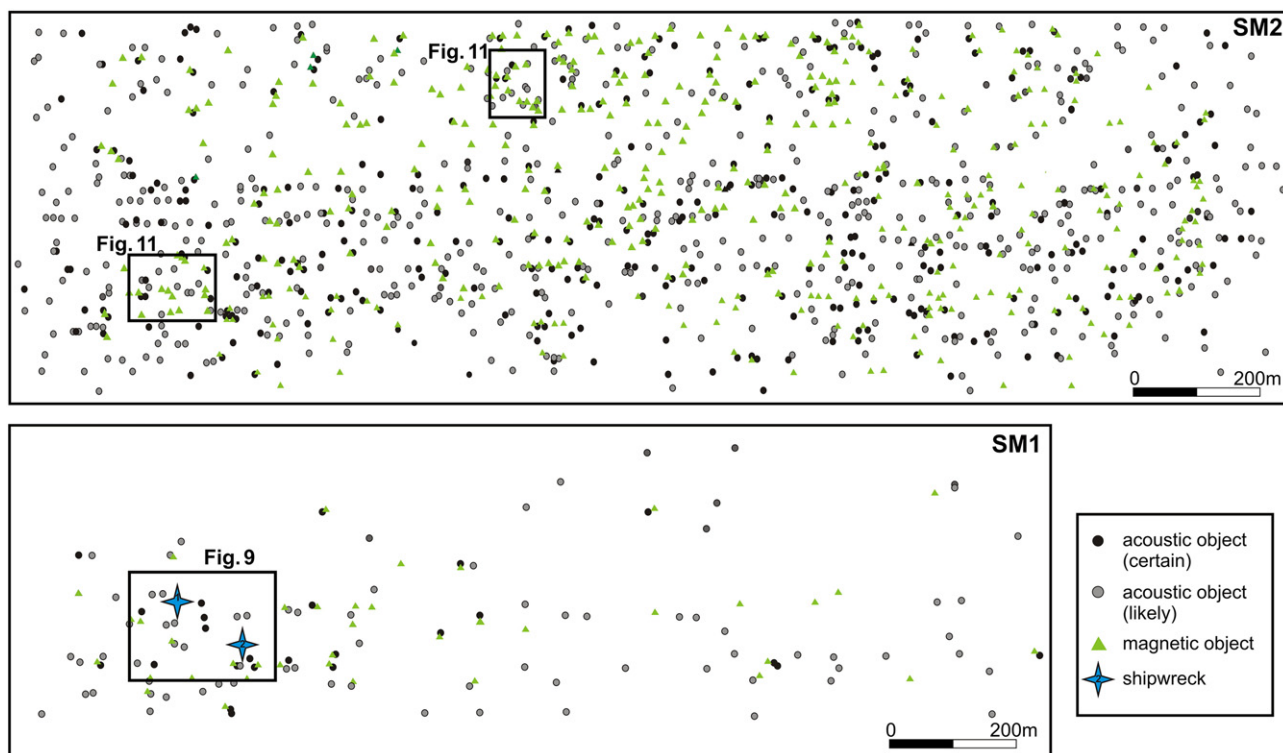


Fig. 6. Distribution of identified buried objects in the areas SM1 and SM2 (for location see Fig. 4). Triangles mark identified magnetic objects, circles mark identified acoustic objects. Shipwrecks are indicated by blue stars. The small black rectangles mark the areas shown in Figs. 9 and 11. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the dumped material; (2) objects located in between two tracklines are often not detected; and (3) objects cemented together will show up as one single object. However we should also keep in mind that the amount of war material located outside the primary dumpsite area could be much larger than was assumed here.

7. Chemical results

A first marked result of the chemical analyses is that no intact parent compounds – sulfur mustard (H), tabun (GA), Clark I (DA), Clark II (DC), Adamsite (DM) or α -chloroacetophenone (CN) – were found in any of the analyzed samples. This is not so surprising since the CWA degrade in the presence of water and the contamination spread from dumped war material is therefore more likely to be found as degradation products. Indeed the degradation products for sulfur mustard, Clark and Adamsite as well as components of arsine oil were found (for sulfur mustard and Adamsite only in the sediment portions of the sediment samples). A second marked result is that no contamination was found in the near-bottom water samples above the quantification level (it should be noted however that the limit of quantification is much lower in sediment samples than in water samples).

CWA degradation products were detected in the sediment portion of 56 of the 65 analyzed sediment core samples. Only in four samples the pore water contained degradation products of Clark and phenyldichloroarsine (PDCA). The highest concentrations in pore water were found in the same sample where the highest sediment concentrations were found. No traces of thiodiglycol or thiodiglycol sulfoxide (TDG[ox]) were found in the pore water samples. Fig. 7 shows the sediment concentrations of different CWA and their degradation products over the larger dumpsite area. The concentrations are presented as $\mu\text{g}/\text{kg}$ of wet sediment (i.e. weight of wet sediment after centrifugation).

It is clear from Fig. 7 that the CWA degradation products have contaminated large areas of the munition dumpsite. In general, the highest concentrations are found within the primary dumpsite with a clear spread also within the secondary dumpsite. This agrees well with the historic records. In many locations outside the secondary dumpsite area also increased concentrations are found. The samples taken between the extended dumpsite and Bornholm island all contain degradation products of either Adamsite or phenyldichloroarsine. Additionally, one sample north-east of the dumpsite contains degradation products of phenyldichloroarsine. This spreading of the contamination outside the dumpsite area is in good agreement with the munition finds by fishermen which reach almost up to Bornholm (see grey line on Fig. 2).

The highest found amounts of the degradation products of Clark in sediment were $4600 \mu\text{g}/\text{kg}$ (as DPA[ox], Fig. 7B) and $16,400 \mu\text{g}/\text{kg}$ (as DPA[SPr], Fig. 7F). The results produced by using different derivatives (e.g. DPA[SPr] and DPA[ox]) give different results probably due to different reactivity of the degradation products (in the case of degradation products of Clark there were at least three different degradation products present in the samples) towards the reagents. For Adamsite the highest concentration in sediment was $170 \mu\text{g}/\text{kg}$ (as DM[ox], Fig. 7A). Other arsine oil components were also found in high concentrations in the sediment: $39,000 \mu\text{g}/\text{kg}$ for triphenylarsine (as intact TPA, Fig. 7E) and $6000 \mu\text{g}/\text{kg}$ for phenyldichloroarsine (as PDCA[ox], Fig. 7C). It is striking that the highest concentrations of DPA [SPr], DPA[ox], TPA and PDCA[ox] were found in the same sample located between wrecks 1 and 2 (sample A in Fig. 8).

Only one sediment sample showed a trace of thiodiglycol ($1.6 \mu\text{g}/\text{kg}$ from an oxidized sample as TDG[ox]). This was very surprising, considering the fact that over 60% of all dumped CWA involves mustard gas (see Table 2) and most munition caught by fishermen concern mustard gas bombs. A possible explanation for this could be that the mustard gas has formed partly polymerized lumps, which are

not easily soluble in water. Previous studies of old buried or sea-dumped munition have reported mustard gas lumps to have solidified to a degree (Mazurek et al., 2001; Hanaoka et al., 2005).

Chlorobenzene (CB) contamination seems to be restricted to the primary dumpsite area (Fig. 7D). Remarkably, almost all samples which contained CB also showed increased concentrations of DPA [SPr], DPA[ox], TPA, and PDCA[ox]. One of these samples contained TDG[ox]. Different explanations are possible: (1) chlorobenzene was not only added to mustard gas but also to arsine oil – although there seems to be no support for this in literature; (2) both arsine oil and chlorobenzene were added to mustard gas (both are mentioned as being added separately; Franke, 1977); or (3) the contamination comes from separate objects that are close together (e.g. mustard gas bomb and encasement with arsine oil). However we should not forget that chlorobenzene has also been mentioned also as a precursor of Clark (Lohs, 1967) and some remnants of CB are likely to be traceable in the degradation products.

Only one sample was found to contain trichloroarsine (TCA) and several samples contained triphenylarsine (TPA) while both are components of arsine oil in similar amounts. Trichloroarsine degrades in water into water soluble inorganic arsenic chemicals. On the other hand, triphenylarsine is very stable and is easily absorbed into the sediment due to its high K_{OC} value. Therefore, TPA can be expected to be a better signature compound for arsine oil than TCA.

There are only seven samples which do not contain any of the targeted CWA or their degradation products. Many sample points – even in the primary dumpsite – contain most of the target chemicals but do not contain one or the other target chemical above the limit of quantitation. Often samples with high concentrations were surrounded by samples showing much less or even no contamination – for example the highest measured concentration sample has neighbouring stations where nothing was detected. This clearly indicates that the spreading of the contamination is not evenly distributed over the dumpsite area but instead it is very patchy. The latter agrees well with the results of the geophysical investigations which suggest a very heterogeneous distribution of buried objects in the dumpsite area.

8. Integration of geophysical and chemical data

8.1. Shipwreck area

8.1.1. CWA contamination

Fig. 8 shows the sampling locations and the measured concentrations of different CWA and their degradation and/or derivatisation products in the southern part of the primary dumpsite area, near shipwrecks 1 and 2 (for location see Fig. 7). Although some of the samples near the wrecks show high concentrations of arsenic-containing chemicals, still the found concentrations seem rather patchy and localized. It is surprising that the samples nearest to the wrecks do not necessarily show a high contamination. For example the sampling station nearest to wreck 1, roughly 10 m southeast of the wreck, does not show any contamination. At the same time the sample nearest to wreck 2, roughly 15 m northwest of the wreck, shows a relative high concentration.

Some of the highest concentrations of arsenic-containing chemicals were measured in samples located further away from the shipwrecks. The highest concentration of target chemicals was measured roughly 70 m east of wreck 1 (sample A on Fig. 8). This seems to suggest that the degradation products are not necessarily originating from the wrecks themselves. On the other hand we see that the main contamination takes place in an area less than 100 m away from the wrecks. Samples further away show very low or no contamination (except for one Adamsite sample 200 m southwest of wreck 2, see Fig. 8A). This would then suggest some relation between the contamination and the wrecks.

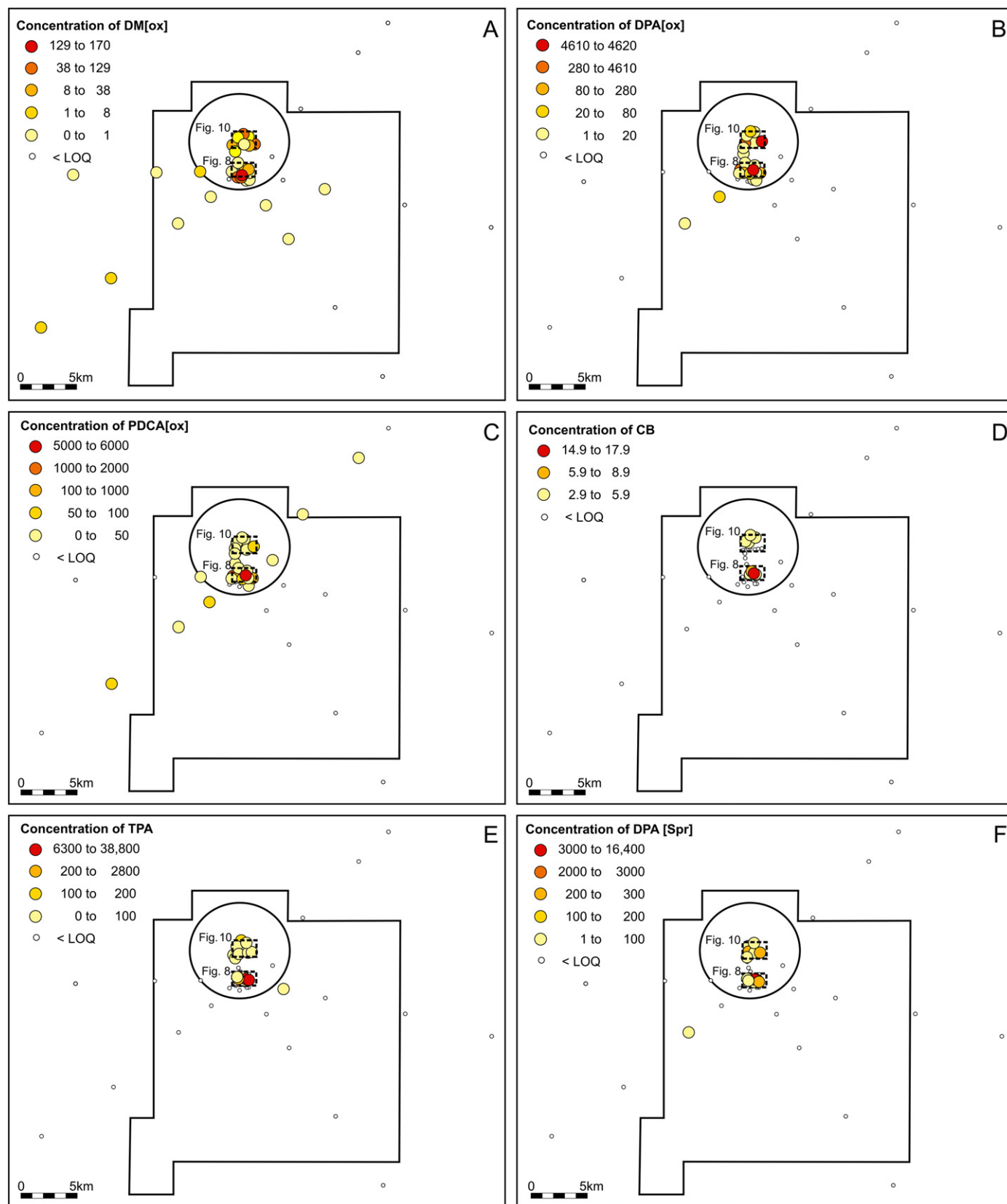


Fig. 7. Concentrations of CWA and their degradation product in the larger dumpsite area (in $\mu\text{g}/\text{kg}$ of wet sediment). LOQ = limit of quantitation. The black circle marks the primary dumpsite area. The black rectangle marks the extended dumpsite area. The two small striped rectangles mark the location of Figs. 8 and 10.

The most important contamination in the shipwreck area seems to be related to Clark and arsine oil. Adamsite concentrations are generally quite low (except for one sample in the south). Contam-

ination related to chlorobenzene is restricted to a few samples. Only one of these, sample A (see Fig. 8D), shows a high concentration. This sample does not indicate any thiodiglycol contamination. The only

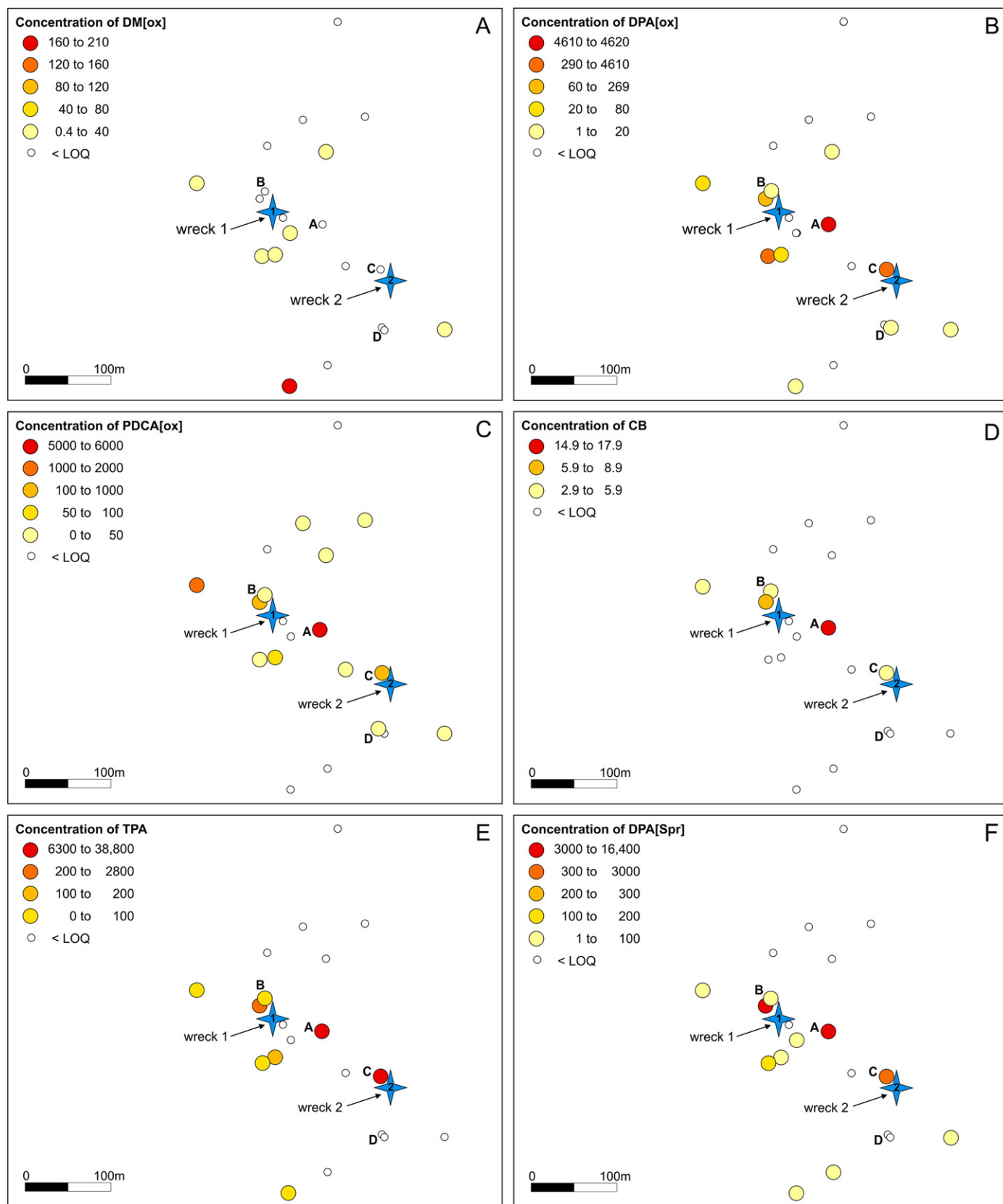


Fig. 8. Concentrations of CWA and their degradation products in the southern part of the primary dumpsite area near wrecks 1 and 2 (for location see Fig. 7). LOQ = limit of quantitation. The letters A to D indicate the sampling points discussed in Fig. 9.

sample showing thiodiglycol contamination is marked by low chlorobenzene concentration. As stated before, it is difficult to pinpoint the origin of the chlorobenzene (CB). A likely explanation

is that there has been mustard gas present (CB was a known additive). Mustard gas and chlorobenzene have almost the same $\log K_{OC}$ values (2.12 and 2.10, respectively) while mustard has slightly higher water

solubility ($\log K_{OW}$ for mustard is ca. 0.8 and for chlorobenzene 0.4). Thiodiglycol on the other hand is totally miscible in water. Thus, they would bind similarly to sediment, but mustard will slowly dissolve and degrade, leaving chlorobenzene (which does not degrade) intact in the sediment. Another possible explanation is that CB may have been added to arsine oil. This would also explain the increased concentrations of TPA, TCA, DPA[ox] and DPA[SPr].

8.1.2. Integration with geophysical data

Fig. 9 gives an overview of the sampling locations and detected objects near wrecks 1 and 2, together with some examples of echosounder profiles across identified seismic objects that coincide with four of the sampling locations (A to D). Due to the lack of dynamic positioning the sampling locations did not always coincide exactly with identified objects. In many cases however there is a good match between the geophysical and chemical data. Two locations show an overall low to medium contamination (D and B) whereas the other two show a high contamination (A and C). The latter both coincide with large objects. All of the objects are buried except for object C which seems to protrude above the seafloor.

Sampling location A shows a medium to very high contamination for all targeted chemicals except DM and TDG. The sample coincides with a large seismic object (Fig. 9, profile A). The diversity in CWA contamination and the fragmented appearance of the seismic object suggests that we may be dealing with several objects located very close together. Sampling location B shows medium contamination of all targeted chemicals except TCA, TDG and DM. It coincides with several buried objects of different size (Fig. 9, profile B). It is not sure whether the relatively high concentrations observed in the neighbouring sample (10 m to the south) can be linked to the same buried objects or to other nearby undetected objects.

Sampling location C near shipwreck 2 shows a generally high contamination for all targeted chemicals except DM, TDG and TCA. The sample coincides with a large seismic feature which possibly consists of several closely located objects (Fig. 9, profile C). At first it was believed that these objects were related to a detached (and broken up) wreck piece due to its proximity to wreck 2. However the high contamination (see Fig. 8) rather indicates a relation to dumped CWA. Sampling location D (2 samples) only shows a low contamination for DPA[ox] and PDCA[ox] (see Fig. 8B and C). There are 3 coinciding objects of diverse size (Fig. 9, profile D). The largest object is also clearly visible on the magnetic data. Possibly we are dealing with a large container and an encasement and/or aircraft bomb, all filled with arsenic-containing compounds.

Although sulfur mustard or its degradation products were not detected (except for one sample) it is possible that many detected objects may originally have contained sulfur mustard as very large number of these objects have been dumped in the area.

8.2. Central primary dumpsite area

8.2.1. CWA contamination

Fig. 10 gives an overview of the sampling locations and the measured concentrations of different CWA and their degradation and/or derivatisation products in the central part of the primary dumpsite area surrounding seismic–magnetic area SM2 (for location see Fig. 7). Thiodiglycol sulfoxide (TDG[ox]) and trichloroarsine were not detected above the limit of quantitation. A number of these sampling locations (E to H) fall within the seismic–magnetic network SM2.

There is a marked difference between this area and the southern part of the primary dumpsite area near the shipwrecks (see Fig. 8). Instead of the rather patchy and localized contamination pattern observed near the wrecks, we see now that almost all samples in the

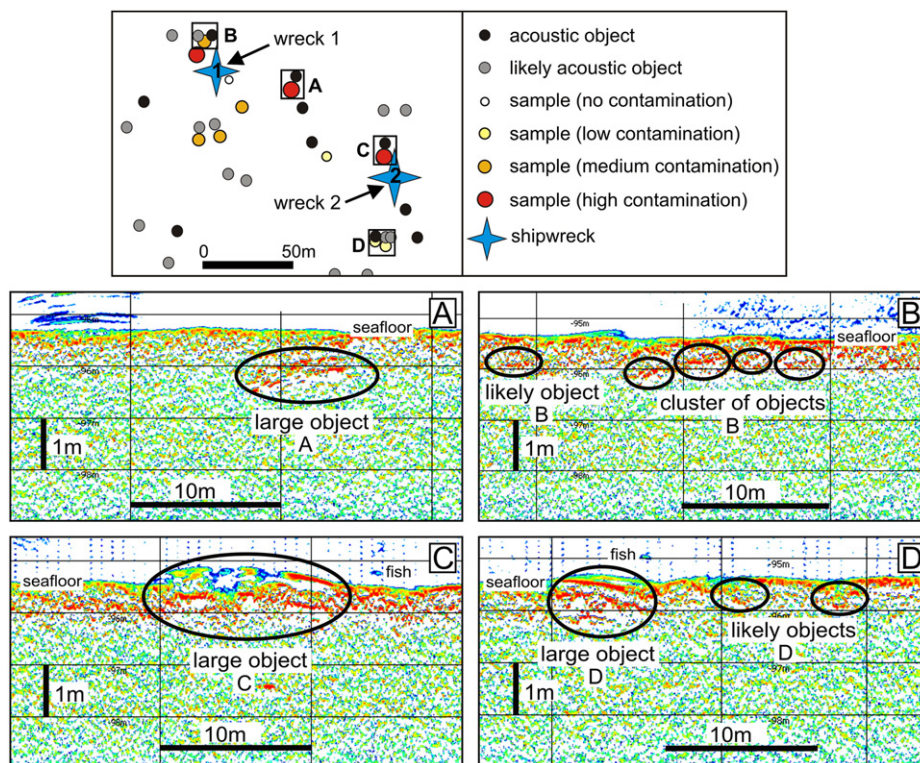


Fig. 9. Top: Sampling locations and identified objects in the southern part of the primary dumpsite area, near shipwrecks 1 and 2 (for location see Figs. 6 and 7). Boxes A to D mark sampling locations coinciding with objects shown below. For a detailed overview of the CWA concentrations at the sampling sites see Fig. 8. Bottom: Parametric echosounder profiles (100 kHz) across the different identified objects near sampling points A to B. The objects are buried except for object C which protrudes above the sea floor. Fish are occasionally observed in the water column. The acoustic noise in profile B is possibly due to a large school of fish. The large diffractions towards the left in profile A are caused by side-reflections related to wreck 1.

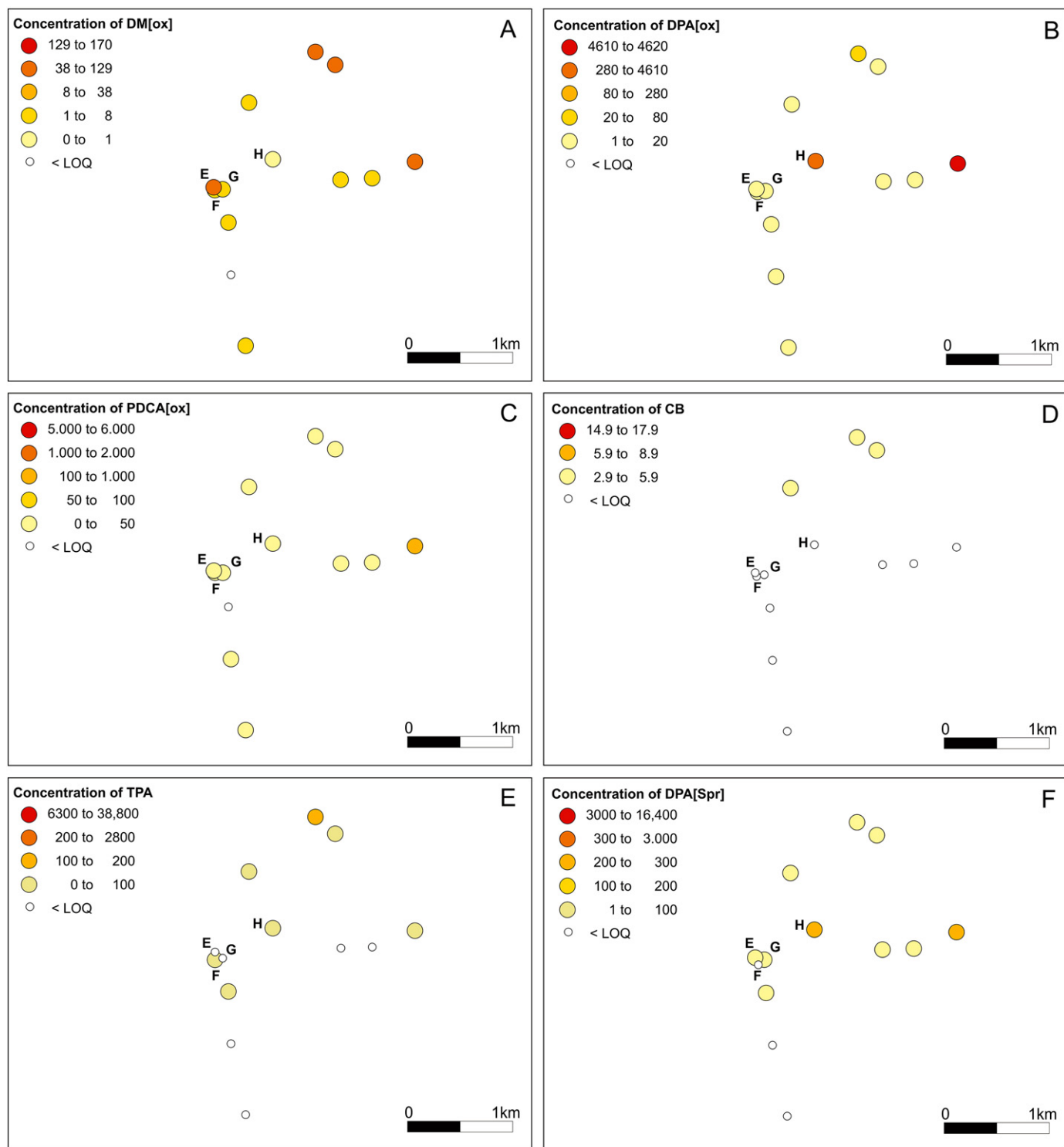


Fig. 10. Concentrations of CWA and their degradation products in the central part of the primary dumpsite area (for location see Fig. 7). LOQ = limit of quantitation. The letters E to H indicate the sampling points discussed in Fig. 11.

central part show some kind of contamination. The only exception seems to be chlorobenzene which shows low concentrations in only three sampling points towards the north (Fig. 10D). These observations agree well with the geophysical results which indicate an increased density of buried objects in the central part of the primary dumpsite area, as shown in Fig. 6.

The contamination related to Adamsite (DM[ox]) seems to be the most important in the central area, contrary to the shipwreck

area where the measured DM[ox] concentrations were mostly quite low. The latter may be partly explained by the increased concentration of dumped objects in the central area in addition to the high percentage of objects containing Adamsite (see Table 1). The contamination related to Clark and arsine oil is generally less pronounced though in the case of Clark it can be locally quite high. The lack of any thiodiglycol contaminated samples confirms the theory that mustard gas is most likely hard to detect due to the fact

that it tends to solidify into hard lumps which are not easily degraded in water.

8.2.2. Integration with geophysical data

In the following paragraphs we will focus on four different sampling points that are located within the seismic–magnetic area SM2 (samples E to H). Fig. 11 gives an overview of the sampling locations and nearby detected objects in two areas of SM2, together with some examples of echosounder profiles across identified seismic objects that coincide with four of the sampling locations (E to H). Due to the high object density in this area (see Fig. 6 top) most samples coincide – at least approximately – with buried seismic objects. Two sampling locations show an overall low contamination (F and G) and two show medium contamination (E and H). Surprisingly enough the highest concentrations do not coincide with the largest objects. All of the objects are buried.

Sampling stations E and F are located close together (25 m distance). Both samples show a similar contamination pattern for DM, DPA and PDCA (see Fig. 10) except for the overall higher concentrations for sample E. The most important contamination was measured for DM[ox] (Fig. 10A). The seismic data show much less similarity. Sampling location E coincides with two presumed buried objects (Fig. 11, profile E), whereas sample F coincides with a wide cluster of large objects (Fig. 11, profile F). The dumping impact of the latter is clearly visible in the seafloor depression, which has become partly filled up with recent soft sediments (blue color). The objects are buried quite deep (between 0.8 and 2 m), which could perhaps explain the relatively low concentrations measured here. The size of the objects at samples E and F and the measured concentrations suggest drums, encasements or containers filled with Adamsite, Clark and arsine oil.

Sampling location G shows an overall low contamination similar to sample F and coincides with two likely objects of small to medium size

(Fig. 11, profile G). Both objects are buried no more than 50 cm below the seabed. The fragmented appearance of the largest object, on the right, suggests that we may be dealing with a number of very small objects located very close together, possibly artillery shells or grenades filled with Adamsite. Sampling station H is the only location with an increased concentration related to Clark. The seismic data suggest a possible cluster of small seismic objects (Fig. 11, profile H). This would agree with the diverse contamination (not only Clark but also Adamsite and arsine oil) suggesting at least two different types of leaking objects.

9. Discussion and conclusions

The geophysical data indicate the presence of a large number of objects buried just below the seafloor, in most cases less than 70 cm deep. The diversity in shape and size of the objects seems to reflect the wide variety of dumped war material, ranging from shells, grenades and aerial bombs to encasements, drums and large containers. Most of the objects are relatively small (less than 2 m). Large objects (>3–4 m) can most likely be linked to small groups of objects crusted together or located too close to allow separate detection. The large variation in object density suggests a heterogeneous distribution of the dumped war material, with a marked increase in object concentration towards the centre of the primary dumpsite. The large discrepancy between the number of identified objects and the (presumed) amount of dumped objects suggests that a substantial part of the war material was not detected. These ‘missed’ objects can most likely be linked to artillery shells and grenades, who make up the largest part of the dumped material but whose small size (<40 cm) is at the limit of geophysical detection.

The chemical data indicate a widespread contamination which reaches far beyond the dumpsite boundary. This can only be interpreted in one way – the dumped war material is leaking. The

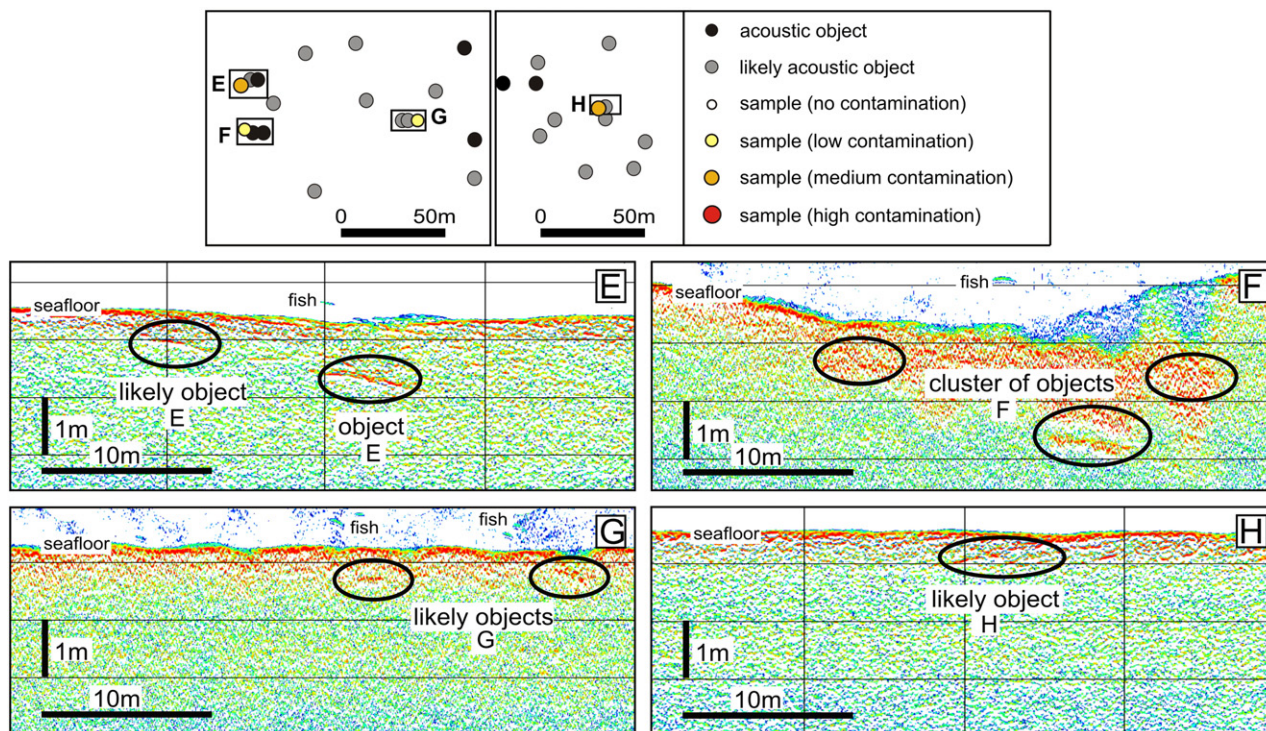


Fig. 11. Top: Sampling locations and identified seismic and magnetic objects in the central part of the primary dumpsite area (for location see Figs. 6 and 7). Boxes E to H mark sampling locations coinciding with objects shown below. For a detailed overview of the CWA concentrations at the sampling sites see Fig. 10. Bottom: Parametric echosounder profiles (100 kHz) across the different identified objects near sampling points E to H. All of the objects are buried. The irregular seafloor in figure F is most likely due to the dumping impact. Fish are occasionally observed in the water column.

highest concentrations are found within the primary dumpsite which agrees well with the historic data and geophysical results. The CWA contamination outside the extended dumpsite area reaches almost up to Bornholm – similar to the area of contaminated fish catches. The contamination pattern is very patchy (samples with high concentrations are often surrounded by low contaminated samples) which confirms the uneven distribution of the dumped objects. No intact parent compounds were found, which was to be expected in view of the degradation in sea water. However CWA degradation products were found in most of the sediment samples. No contamination was found in any of the near-bottom water samples, and only four pore water samples showed degradation products. This could partly be due to the level of quantification which is much higher in water samples compared to sediment samples. It may also be that over time the chemicals have been strongly bound to the sediment and are not likely to be dissolved into pore water. It is furthermore also possible that the chemicals dissolved to the pore water diffuse out of the sediment into near-bottom water.

Of all CWA, Adamsite contamination seems to have spread the furthest, not only in the primary and extended dumpsite area but also outside. The second important CWA to have spread far is arsine oil (especially phenyldichloroarsine PDCA). Historic data (see Tables 1 and 2) suggest that Adamsite and arsine oil were for the largest part stored in aircraft bombs and wooden encasements (arsine oil was also stored in containers). According to local newspapers a lot of wooden encasements containing Adamsite and arsine oil were washed ashore in Bornholm in December 1947 (Sanderson and Fauser, 2008). This indicates that these cases may have drifted far from the dumpsite before actually sinking. This could possibly (partly) explain the far-reaching contamination of Adamsite and arsine oil.

All samples were taken from the upper 5 cm of the core. When we take into account the burial depth of the objects, this implies that over the years the contamination has spread upwards over quite some distance (a few m) and was able to reach the uppermost seafloor sediments. Close comparison of seismic and chemical data indicates that objects buried just below the seafloor as well as objects buried more deeply coincide with contaminated samples. Most of the contaminated samples are related to arsenic-containing CWAs such as Adamsite, Clark and arsine oil. Only one sediment sample showed a trace of thiodiglycol, the main degradation product of sulfur mustard. This was rather surprising in view of the large amount of dumped mustard gas (60% of all dumped CWA). A likely explanation is that mustard gas tends to form polymerized lumps which are not easily soluble in water.

Recent modeling studies carried out in Belgium suggest that the toxic effects of mustard gas remain limited to a small sphere (few cm radius) surrounding the leaking munition (Francken and Hafez, 2009). The study only applies to a small artillery shell, but it is reasonable to believe that larger quantities of mustard gas (such as stored in aerial bombs and encasements) will increase the radius but most likely the affected area will remain limited. In other words, the chance for a contaminated sample would be very low. For Clark, the study suggests a contaminated volume with a radius between 0.5 m (10 years) and 1.5 m (100 years) for a shell containing an estimated 44 g of arsenic (Francken and Hafez, 2009). Again, it is expected that the contaminated area will increase for larger quantities of CWA. This agrees well with the results from the Bornholm dumpsite area which indicate a spreading radius of at least a few m.

The source of the chlorobenzene (CB) contamination remains uncertain. The contamination is restricted to the primary dumpsite area. One sample also shows thiodiglycol (TDG) contamination, which is not so surprising since CB was a known additive to sulfur mustard. Since the latter will dissolve only very slowly, the chance of finding chlorobenzene (which does not degrade) is much higher. Almost all

samples showing increased CB concentrations also showed contamination related to Clark and arsine oil. A possible explanation could be that both arsine oil and chlorobenzene were added to mustard gas. But it is more likely that the contamination comes from separate objects located close together (for example a mustard gas bomb and encasement filled with arsine oil). Last but not least, chlorobenzene is also known to be a precursor of Clark I and some remnants of CB are therefore likely to be present along with the degradation products. In any case, the K_{OC} value for CB is probably higher than for the more water soluble degradation products of arsenic containing chemicals. This means that CB will stay adsorbed in the sediments better than the other chemicals (except for triphenylarsine, which has higher K_{OC} than CB).

The relation between the shipwrecks and the dumped CWA remains ambiguous. The contamination in the wreck area is very patchy and samples nearest the wrecks do not necessarily show a high contamination. On the other hand, most of the contamination seems to be contained in an area less than 100 m away from the wrecks, with samples further away showing no or very low contamination. This would suggest some relation to the wrecks. Especially the high concentrations related to Clark and arsine oil are striking. However if we assume that the wrecks actually contain CWA it remains difficult to explain the large spreading distance of the contamination. Seismic data furthermore indicate the presence of buried objects in the close vicinity of most contaminated samples. So for the moment we are inclined to relate the contamination to single dumped war material, but in the future more sampling is needed to provide a definite answer.

The correlation between detected objects and CWA concentrations is not entirely straightforward. First of all there will always be some uncertainty regarding the exact core position on the sea floor in view of the large water depth (over 90 m). Secondly, the diverse contamination measured in a lot of samples suggests that many objects, possibly due to their small size, were not detected. The fact that some contaminated samples did not coincide with any object at all further confirms this. These 'missed objects' agree well with earlier geophysical findings. Furthermore the size of the objects and their occurrence (single object or group of objects) did not always match up with the measured contamination level. Small single objects were sometimes found to coincide with high concentrations, whereas clusters containing large objects can coincide with moderate/low contamination.

If we assume a fairly restricted contamination zone surrounding the leaking objects (a scale of meters rather than tens of meters, as suggested by Francken and Hafez (2009)), this would imply that (positive) core samples were taken almost exactly above or very close to the buried objects. Keeping in mind the positioning uncertainty of the samples and the random distribution of sampling locations, this strongly suggests that a lot of the dumped war material (if not all) is actually leaking. The fact that objects of all sizes and shapes were found to coincide with contaminated samples seems to confirm this.

10. Final remarks

The study presented here is by no means complete. Due to the sheer size of the extended dumpsite area (close to 1000 km²) and in view of the limited time and available budget, only a small part could be investigated thoroughly. Detailed seismic and magnetic data were only obtained from two small areas with a total size of 2 km². Compared to the total area of the studied site the number of analyzed sediment cores was very small. Especially further away from the primary dumpsite the sampling points were very random as they are 5 km apart from each other. Nevertheless, the fact that most of the sampling points were positive indicates that the contamination is widely spread. However, there are large areas between the transects

which are totally uncharted. Therefore the total level of contamination cannot be estimated accurately at this moment.

It would be valuable to conduct further studies at the Bornholm dumpsite to get a better view of the total spread of the dumped objects and the contamination, and to evaluate the development of the situation at the dumpsite. This would require a much wider area for seismic–magnetic investigations and a considerably higher number of samples over a long period of time.

Only the Bornholm dumpsite was selected for this study. There are other less studied dumpsites in the Baltic Sea which equally deserve attention (for instance the dumpsites in the Gotland Basin and Skagerrak). The diverse conditions (e.g. water depth, bottom sediments, currents, type of dumped war material, mode of dumping and fishing activities) at different dumpsites may lead to totally different risk assessment results.

Acknowledgements

This study has been carried out in the framework of the EC-FP6 project “MERCW” (Modelling of Environmental Risks related to sea-dumped Chemical Weapons) (Contract Nr. INCO-CT2005-013408). The work at VERIFIN was partially financed by the Ministry for Foreign Affairs of Finland. The captains and crews of R/V “Shelf” and M/S “Fritz Reuter” are gratefully acknowledged. The authors would furthermore like to thank the following persons for their assistance during the geophysical data acquisition and sampling: Koen De Rycker, Lieselot Noppe, Ewald Frederickx, Albert Monjoie, Samuel Willems, Vadim Paka, Anu Hirvonen, Yuri Savin and Fidaev Dzhuraboy. Also the work of Tomi Hämäläinen, Terhi Taure-Gesterberg, Heikki Björk, Olli Kostianen, Marja-Leena Kuitunen and Mia Halme at VERIFIN is acknowledged.

Appendix A. Summary of analysed chemicals and the derivatives

Name	Structure of the intact chemical	Technique	Analysed as		
			Intact	Derivative for GC-MS [SPr]	Derivative for LC-MS/MS [ox]
Sulfur mustard (H)		GC-MS		-	-
Thiodiglycol (TDG)		LC-MS/MS		-	
Thiodiglycol sulfoxide (TDG[ox])		LC-MS/MS		-	-
Adamsite (DM)		LC-MS/MS		-	
Clark I (DA) Clark II (DC)		GC-MS LC-MS/MS	- -		-
Triphenylarsine (TPA)		GC-MS		-	-
Phenyldichloroarsine (PDCA)		LC-MS/MS	-		
Trichloroarsine (TCA)		GC-MS	-		-
Tabun (GA)		GC-MS		-	-
α -Chloroacetophenone (CN)		GC-MS		-	-
Chlorobenzene (CB)		GC-MS		-	-

Appendix B. Physico-chemical parameters of intact target chemicals

Chemical	CAS	Acronym	Melting point (°C)	Boiling point (°C)	Density (g/cm ³)	Log K _{ow}	Solubility in water (g/l)	Log K _{oc}
Sulfur mustard	505–60–2	H	13–14	215–217	1.27–1.33	1.37–2.41	0.8–1	2.12–2.44
Adamsite	578–94–9	DM	195	410	1.65	4.05	0.0004	3.70
Clark I	712–48–1	DA	44	333	1.39	4.52	0.003–2	4.28
Clark II	23525–22–6	DC	31.5	346	1.33	3.29	2	3.84
Triphenylarsine	603–32–7	TPA	59–61	360*	1.22	5.97	Insoluble	5.64
Trichloroarsine	7784–34–1	TCA	–16	130	2.16	1.61	2.3	1.54
Chlorobenzene	108–90–7	CB	–46	132	1.11	2.64–2.84	0.4	2.10
α-Chloroacetophenone	532–27–4	CN	58–59	244–245	1.32–1.19	1.93	0–1.64	1.95
Tabun	77–81–6	GA	–50	220–246	1.07–1.08	0.38–0.29	98–120	1.35–2.02
Phenyldichloroarsine	696–28–6	PDCA	–15.6	257	1.66	3.06	0.64	2.91
Thiodiglycol	111–48–8	TDG	–16	168–282*	1.18	–0.62–0.77	Miscible	0.96

*Chemical decomposes at this temperature.

Log K_{oc}, log organic carbon partition coefficient, an estimate of the tendency of a chemical to adsorb to the organic carbon phase in soil or sediment.

Log K_{ow}, log octanol/water partition coefficient, an estimate of a chemical's tendency to bioaccumulate in organisms.

Sources: Eagleson, 1994; EPA, 1988; EPA, 2009; Merck, 2009; CBWinfo, 2009; Oxford, 2009; Munro et al., 1999; NIOSH, 2009; NOAA, 2009; Sanderson et al., 2007; Stock, 1995; Tørnes et al., 2002.

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