Leakage rate of the nerve agent tabun from sea-dumped munition

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1. Introduction

Large amounts of chemical ammunitions were dumped at sea in many locations worldwide just after the Second World War. Much of the German stocks were loaded on to condemned ships and sunk in the deepest part of Skagerrak, outside the Norwegian and Swedish territorial waters. Norwegian authorities gave permission to such dumping at 600–700 m depth, 25 nautical miles southeast of Arendal (Fonnun et al., 1997; Arison, 2013). Between 130 000 and 160 000 tonnes of chemical ammunition (gross weight) containing between 41 000 and 48 000 tonnes of chemical warfare agents may have been dumped in Skagerrak between 1945 and 1947 (Arison, 2013; Stock and Kaffka, 1996; Tørnes et al., 2002). The high number of public protests against dumping in Skagerrak caused the last ships to be scuttled at 1000 m depth in the Norwegian Sea, north of the 63rd latitude, in 1948. The load was described as “toxic ammunition” and the type and quantity of each chemical was not specified (Utenriksdepartementet, 1948). A detailed survey of the relevant area in the Norwegian part of Skagerrak by the HUGIN autonomous underwater vehicle was conducted in 2015–2016. In the search area, 36 wrecks possibly related to the scuttling of chemical warfare agents after Second World War were identified (Hansen et al., 2019a).

Ammunition dumped at sea will corrode over time and the content will eventually be released to the environment. There are many factors affecting the speed of corrosion in seawater, such as temperature, water current, salinity, oxygen content, pH and type and amount of sediment cover (e.g. (King, 1980; HELCOM, 2013; Silva and Chock, 2016)). Different metals in contact with each other have higher corrosion rates than a single metal alone (galvanic corrosion) (Loiska, 2017). Bacteria will also contribute to the corrosion process by forming biofilms on the surface (Silva and Chock, 2016). In addition, the metal in the ammunition produced in Germany close to the end of the Second World War was of variable quality due to shortage of resources (Jacobsen, 2017). These factors make it difficult to estimate corrosion rates based on theoretical considerations alone.

The Norwegian Research Establishment (FFI) carried out investigations of some of the scuttled wrecks south-east of Arendal by remotely operated vehicles in 1989 and in 2002. Aerial bombs pierced through by corrosion, with the content already leaked out, were observed close to the wrecks, both in 1989 and in 2002 (Tørnes et al., 1989, 2002). Sediment samples were collected near the wrecks and seven different chemical warfare agents and decomposition products were identified in the samples (Tørnes et al., 2006).

Investigations at a dumping site with similar sea depth (300–500 m) outside Hawaii, in which chemical warfare agent were disposed between 1933 and 1946, have been carried out from 2009 to 2014 (Silva and Chock, 2016). During one part of this Hawaii Undersea Military Munition Assessment (HUMMA) project, 1842 objects classified as discarded military munitions were observed. The integrity of these munitions ranged from intact and nearly pristine to very deteriorated. The state of corrosion varied within similar types of munitions found in the same area, indicating that the corrosion process is very complex and difficult to predict. The same is assumed to be the case for the ammunition dumped in Skagerrak.

Francken and Hafez (Franken and Hafez, 2009) have modelled the dispersion in sediments of the poorly soluble chemical warfare agents mustard (H), diphenylchloroarsine (Clark I) and diphenylcyanomarssine (Clark II) from ammunitions disposed at sea. The calculations are valid for ammunitions that are undisturbed by external activities, like sea currents or fishing activities. They found that leaking mustard will give toxic effects only up to a few centimetres outside the ammunition before the agent is degraded to non-toxic compounds. The arsenic containing agents Clark I and Clark II will decompose to other toxic decomposition products that could affect an area around the ammunition with radius 0.5 m in 10 years and 1.5 m in 100 years.

The calculations described by Francken and Hafez (Franken and Hafez, 2009) depend on the rate of which the toxic compounds leak out from the ammunition. It is therefore of interest to estimate how fast chemical warfare agents will be transported out from a sea-disposed chemical bomb or grenade when the casing has been breached by corrosion, and the bomb is not moved by external activities like sea currents or fishing. Chemical ammunition is likely to have thinner walls compared to conventional ammunition (HELCOM, 2013), and aerial bombs have thinner walls compared to artillery shells (Fabisiak et al.,
It is therefore assumed that chemical bombs will start leaking before other types of ammunition.

The chemical warfare agents dumped in largest amounts at sea after World War II are chloroacetophenone, Clark I, Clark II, adamsite, arsine oil,\(^1\) phosgene, sulphur-mustard, nitrogen-mustard and tabun (Arison, 2013; Tørnes et al., 2002). Some of the sea-dumped agents, like mustard and arsenic compounds, are heavier than water, poorly soluble in water, and will stay on the sea floor many decades after released from the ammunition. The nerve agent tabun (GA, ethyl N, N-dimethylphosphoramidocyanate) is more toxic, but also more soluble in water. Tabun will, within hours, be diluted to non-dangerous concentrations and decomposed to less toxic compounds. Until recently, it was assumed that no nerve agents were dumped in the Norwegian part of Skagerrak. Arison has, however, documented that two ships (Sperrbrecher and T-65) carrying in total 3220 US short tons\(^2\) of ammunition, containing tabun, sulphur mustard, phosgene and chloroacetophenone, was scuttled on July 1 and July 2, 1946 at 650 m depth in Skagerrak (Arison, 2013).

According to U.S. Army Chemical Material Destruction Agency, tabun was filled in 10.5 cm light howitzer shells, 15 cm type 39 artillery shells, 15 cm rockets, and 250 kg aerial bombs during World War II. The tabun in these ammunition types may have been added 20% chlorobenzene as stabiliser (U.S. Army Chemical Material Destruction Agency, 1998). Because of the high solubility in seawater (98 g/l (HELCOM, 2013)) and high toxicity of the nerve agent tabun, it is of particular interest to investigate the leakage rate of this agent into the seawater.

A majority of the chemical ammunition dumped at sea was aerial bombs. One commonly used example is the KC250 aerial bomb, shown in Fig. 1. The bombs containing 100 kg tabun were designated KC250 III Gr (DAIMON on-line munition catalog, 2020). The fill-percentage of a chemical bomb is difficult to specify accurately because of differences in purity of the technical grade agent at the time of filling and inaccurate measuring equipment during the Second World War. We have assumed that the bomb was filled completely full with tabun, as was normally the case (Koehler, 2018).

DAIMON (Decision Aid for Marine Munitions) was an international project consisting of partners from Poland, Germany, Sweden, Finland, Norway, Lithuania and Russia, and cooperating experts worldwide, united by the goal to solve the problem of underwater munitions. The project was part-financed by the EU INTERREG Baltic Sea Region Programme 2014–2020.

One of the activities in DAIMON was to evaluate the leakage rate of chemical warfare agents from a corroded bomb shell already pierced through by corrosion. A model of a fairly common chemical bomb, the KC250 aerial bomb, has been used in a laboratory experiment to simulate the leakage of the chemical warfare agent tabun into seawater. In addition, Computational Fluid Dynamics (CFD) simulations of the release have been conducted, and a simple analytical model for estimating the release rate developed. The investigation described here has been conducted as a part of the DAIMON project.

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1. Arsine oil: 50% phenyl dichloroarsine, 35% diphenylchloroarsine, 5% triphenylarsine and 5% trichloroarsine (Haas and Krippendorf, 1997).

2. 3220 US short tons equals 2921 metric tonnes.
2. Experimental

A bomb-model resembling a KC250 bomb was built of aluminium and plexiglass at the FFI Prototype workshop, see Fig. 2. The bomb-model had a total volume of 103.9 L and a total length of 119 cm, where 40 cm at one end was conical. The body diameter was 37 cm and the narrowest end of the cone had a diameter of 20 cm. The model had an opening in the centre of the non-conical part to simulate a corroded opening. The opening was circular with area 10 cm$^2$, and in addition, two plastic adapters with 5 cm$^2$ and 2.5 cm$^2$ opening sizes were made to simulate lesser degrees of corrosion.

The model, with the opening facing upwards, was placed in the centre of a large tub (2 m × 1 m and 1 m high) filled with 1200 L seawater (Fig. 3). Fresh tap water was mixed with sodium chloride to obtain a mixture with density 1.028 g/cm$^3$. Water movement with a current of 0.02–0.03 m/s (similar to the conditions at 600–700 m depth in Skagerrak) was induced using an electric motor with a propeller (Yamaha, model M-15). A measuring device (Valeport Model 803 Electromagnetic Current Meter) was used to measure the horizontal water current.

The conditions in the tub were selected to simulate the conditions in Skagerrak as closely as possible. Some seawater parameters in Skagerrak (Norwegian Institute of Marine Research, 2014) have been investigated in the current work. Sugar enriched water with a density of 1.09 g/cm$^3$ was used as simulant for tabun. This is the density of tabun at 6°C (Blanch, Jan 2001). The volume of tabun simulant (sucrose) leaking out of the bomb-model is equal to the volume of sodium chloride solution leaking in. The release of the tabun simulant was determined by measuring the amount of chloride in


PSU: Practical Salinity Unit.

The leakage of a tabun simulant into seawater through the opening with area 10 cm$^2$ has been investigated in the current work. Sugar enriched water with a density of 1.09 g/cm$^3$ was used as simulant for tabun. This is the density of tabun at 6°C (Blanch, Jan 2001). The volume of tabun simulant (sucrose) leaking out of the bomb-model is equal to the volume of sodium chloride solution leaking in. The release of the tabun simulant was determined by measuring the amount of chloride in the bomb by potentiometric titration at an accredited laboratory (ALS Laboratory Group Norway AS, 2016).

Experiments with the release of fresh water (with density 0.997 g/cm$^3$) into seawater (with density 1.028 g/cm$^3$) were conducted with the same experimental setup. In these cases, experiments with openings on the bomb-model of 10 cm$^2$, 5 cm$^2$ and 2.5 cm$^2$ were used, simulating different degree of corrosion. The purposes of these experiments were twofold; firstly to investigate the release rate of the hydroslysis products that are lighter than seawater and secondly to calculate the release rate of tabun through a downward facing opening. If the opening is facing downward, tabun (which is denser than seawater) and heavy decomposition products will exit from the bomb, while seawater enters. The release of a light liquid into a dense liquid through an opening facing up is governed by the same physical processes as the release of a dense liquid into a lighter liquid through an opening facing down. Thus, the experiments with release of fresh water from an opening on top should be transferable to releases of tabun from a downward facing opening when scaled for the density differences. In these experiments, the amount of seawater entering the bomb model was measured by monitoring the change in conductivity inside the model by a conductivity/temperature meter (Cond 1970i from Wissenschaftlich-Technische Werkstaten GmbH, Weilheim, Germany). In all experiments, the water temperature in the tub was between 17°C and 20°C.

2.1. Numerical simulation

The CFD simulations were conducted using a Volume-of-Fluid code developed at Cascade Technologies Inc. (Palo Alto, CA, USA) and compared with the experimental results. The simulations are used as means to test the assumption that the experiments with the release of fresh water through an opening facing up can be used to estimate the leakage rate of tabun through an opening facing down.

One simulation of the release of fresh water into seawater through an upward facing opening, and one simulation of the release of tabun into seawater through a downward facing opening were conducted. The former simulation is compared with the corresponding experiment with the release of tabun simulant into seawater through an opening facing up. The latter simulation was compared against the experiment with the release of fresh water into seawater, scaled for the density differences.

Two geometrical models of the bomb with a 13 cm$^2$ opening facing straight up or facing down in an angle of 45° from the vertical axis respectively, were constructed. Except for the direction of the opening in the bomb, the models were identical. The walls of the bomb had no-slip boundary conditions, while the outside walls of the computational domain had slip conditions. The mesh size in the area of the opening was about 0.5 cm and increased in size away from the opening. The velocity field was modelled by Large Eddy Simulations using a dynamical Smagorinsky subgrid scale model. No external velocity field was invoked; all the motion is due to the density difference. The interior of the cylinder was initialised with fresh water and tabun respectively for the two simulations and the surroundings was initialised with seawater. Due to the necessary small time step needed to achieve numerical convergence, only a few minutes of the leakages were simulated.

2.2. Analytical model

An analytical model of the release rates through one and only one opening is not straightforward, since the bomb contents leave the bomb and seawater enters the bomb through the same opening. However, the influence of the various governing parameters on the release rate is possible to determine.

The Buckinghams pi theorem (Buckingham, 1914) states that for a physical problem with M parameters and N units, a number of M-N independent dimensionless parameters can be derived to describe the problem. The following parameters are postulated to be important: the release rate, $q$ [kg/s]; the density difference, $\Delta \rho$ [kg/m$^3$]; the area of the...
Fig. 4. Pictures of corroded bombs on the sea floor in Skagerrak (Photo: FFI).

Fig. 5. Upper left: Experimental leakage rate, calculated rate with the analytical model and leakage rate from the CFD simulation through an upward facing opening area of 10 cm$^2$. The first 10 min of the leakage is shown (note that the CFD simulation is only conducted for 5 min). Upper right: Experimental and calculated leakage rates for the first 200 min of the experiment with 10 cm$^2$ opening. In addition, the mean results from the CFD-simulation is shown. Lower left: Experimental and calculated leakage rates from the first 200 min of experiments with 5 cm$^2$ and 2.5 cm$^2$ opening areas.
opening, $A$ [m$^2$]; and the gravitational acceleration, $g$ [m/s$^2$]. There are thus four parameters ($q$, $\Delta \rho$, $A$, $g$) and three units (kg, s, m), and one dimensionless parameter, $\Pi$, should describe the problem.

From the procedure of the theorem, the following dimensionless parameter is found:

$$\Pi = \frac{\Delta \rho A^{5/2} g}{q^2}$$  \hspace{1cm} (1)

and the release rate can thus be calculated from:

$$q = \beta \Delta \rho A^{5/4} \sqrt{g}$$  \hspace{1cm} (2)

where $\beta = \Pi^{-1/2}$ is a dimensionless model parameter.

As tabun exits and seawater enters the bomb, the density in the bomb, as well as in the water surrounding the bomb, will change, and consequently the density difference will vary with time. Since the water volume outside the bomb is much greater than the bomb volume, the density outside is assumed to be constant. The density of the liquid in the bomb is strongly dependent on the mixing within the bomb. For the present calculation, the initial liquid density in the bomb is used for the calculations. In reality, the liquid density in the bomb will decrease as seawater enters. In addition, hydrolysis will alter the average density in the bomb further. The assumption of constant density difference is conservative in the sense that lower density difference would lead to a lower release rate.

It should be noted that this is a simple model intended for an approximate calculation of the leakage rates. For a detailed and accurate calculation, the model should be refined. The authors however, did not have the resources to refine the model further during this work.

3. Discussion

The ammunition in Skagerrak is dumped at 600–700 m depth, where the ambient pressure is 60–70 bar. The pressure inside the intact bombs is assumed to be at atmospheric pressure. However, it is considered that this pressure difference will have a small impact on the release rate. The bombs are assumed to be filled with liquid toxic agents, and since liquids are almost incompressible, there is no space available for inducing motion. If, on the other hand, the bombs have large volumes of air (only partly filled up with liquid toxic agents), some movement of water into the bomb will occur. This movement has been disregarded in the following calculations and discussion.

3.1. Leakage of tabun simulant into seawater

In this scenario, the experiments were carried out with the opening facing upwards. Recent recordings of corroded aerial bombs laying on the seafloor at the bottom of Skagerrak, indicate that this is the predominant direction of the corroded openings (Fig. 4) (Ternes et al., 2006; Grabowski, 2018; Hansen et al., 2019b). It should be noted that these observations are made from a very small part of the dumping area, and should therefore not be considered as representative of the overall area.

The experiment with release of tabun simulant into seawater was conducted with the 10 cm$^2$ area opening. Hydrolysis of the tabun was disregarded. The bomb-model was completely filled with 103.9 L of simulant (sucrose) as the start of the experiment. The volume of tabun simulant leaking out of the bomb-model is equal to the volume of sodium chloride solution leaking in. The concentration of chloride inside the bomb was used to estimate the amount of tabun simulant leaking out.

The mean concentration of chloride in the bomb-model after a duration of 196 h (a little more than eight days) was measured by potentiometric titration to 36.9 ± 3.9 mg/l Cl$^-$ (ALS Laboratory Group Norway AS, 2016). This is equal to a sodium chloride concentration of 60.8 ± 6.43 mg/l, corresponding to an amount of 5.04 g NaCl or a volume of 0.125 l leaking into the bomb; the start concentration of sodium chloride (12.3 mg/l), taken as the concentration in fresh water (Nedre Romerike Vannverk and NRV, 2017), is subtracted in the calculation. This is only 0.12% of the initial content of the bomb-model. In comparison, the experimental duration of 196 h equals 39 half-lives of tabun, which is 5 h at 7 °C (Stock and Kaffka, 1996).

Although very little tabun simulant has leaked out, the available volume will be filled up with seawater, and this will lead to hydrolysis inside the bomb. Since the leakage rate out of the bomb is very slow, most of the tabun will hydrolyse inside the bomb and those decomposition products that are lighter than seawater will leak out to the surrounding water. The slow leakage rate of tabun is not unexpected, since tabun is denser than seawater.

In order to estimate the release rate of the hydrolysis products that are less dense than seawater, experiments with the release of fresh water into seawater from openings with different areas were conducted. The durations of the experiments were 20 h, 70 h and 215 h for the measurements with opening areas 10 cm$^2$, 5 cm$^2$ and 2.5 cm$^2$ respectively. In this case, the lighter fresh water exits due to buoyancy. Fig. 5 shows the release rates in the three experiments. All experiments have a high initial release rate before reaching a plateau at a lower release rate. Only the first 200 min of the experiments are therefore shown in the figure.

The model parameter, $\beta$, in the analytical model (Equation (2)) is determined from the experimental measurements from about 20 min after start of the releases to be $\beta = 0.29$ (the initial high release rate is disregarded). A CFD simulation of the release of fresh water through an upward facing opening has also been conducted. The analytical model results and the CFD simulation result are included in Fig. 5.
The experiments described in the previous section were conducted with the opening facing upward; however, openings may corrode also on other sites on the bombs. In order to estimate leakage rates from openings facing downward, we use the experiments with the release of fresh water through an opening facing upwards (Fig. 5). We assume that the leakage rate is driven by the same physical mechanism, buoyancy due to the difference in density, regardless of the position of the corroded opening. In addition, a CFD simulation of the release of tabun through an opening facing down is conducted and compared with the experimental results (scaled for the density differences).

The release rate of tabun through one downward facing opening with area of 1 cm², 2.5 cm², 5 cm² or 10 cm² is calculated with the analytical model (Equation (2)), using the density difference of tabun and seawater (instead of seawater and fresh water). An opening with area 1 cm² was included in these calculations to estimate the release rate from a smaller opening compared to the experimental work.

The mass of tabun in the bomb is corrected for hydrolysis:

$$m_t = m_0 e^{-\lambda t} \tag{3}$$

where \(m_0\) is the mass of tabun inside the bomb, \(m_t\) the initial mass of tabun, \(\lambda\) the half-life constant (using the half-life of 5 h (Stock and Kaffka, 1996)), and \(t\) the time. The correction for hydrolysis is conducted iteratively with a python script, where also the mass of hydrolysis products and seawater in the bomb are accounted for. In this script, it is assumed that the hydrolysis products have the same density as tabun.

In addition, a CFD simulation of the release of tabun is conducted. This simulation is only performed for a few minutes real-time and is therefore not corrected for hydrolysis of tabun. The liquid density in the bomb will decrease as seawater enters, but the initial liquid density in the bomb is used for these calculations. Fig. 6 shows the calculated leakage rates corrected for hydrolysis, as well as the leakage rate from the CFD simulation. Fig. 6 left shows the leakage rate from the CFD simulations and the calculated leakage rate with the analytical model for the first 10 min, following the release through an opening with area 10 cm². CFD gives a higher release rate than the analytical model, as was also seen in the experiments with the opening facing up. The ratio between the rates from the CFD simulation and the model is roughly a factor of 2–3, both in Figs. 6 and 5. This might be due to the analytical model being tuned to the “steady-state” leakage rate, while initially the leakage rate is higher (as seen in Fig. 5). Fig. 6 (right) shows the calculated hydrolysis rates up to 600 min corrected for hydrolysis for areas of 1 cm², 2.5 cm², 5 cm² and 10 cm². During the leakage process, the total amount of tabun exiting into the sea for the four different opening areas calculated with the analytical model are given in Table 1. It is assumed that the bomb model is initially filled with 113.3 kg tabun. The ratios of the initial bomb contents to what is released and the time until all tabun is either leaked out or hydrolysed, are also given in the table.

Fig. 7 shows the mass of tabun in the bomb and the released mass as function of time for different opening directions, with and without correcting for hydrolysis. The size of the opening was 10 cm² in these calculations. The results for the opening pointing upwards are taken from the experimental measurements and the results for the downward facing openings are calculated with Equation (2).

In reality, more than one opening can corrode in a bomb. This will lead to an increase in the leakage rate, both because the total opening area will increase, but also because water can (primarily) enter through one (or more) openings and tabun and hydrolysis products exit through other openings, leading to a somewhat smoother flow.

### 4. Conclusions

Experiments simulating the leakage of tabun from a sunken aerial bomb have been conducted. In addition, a simple mathematical model for estimating the leakage rate was developed. This simple model is intended for an approximate calculation of the leakage rates. For a detailed and accurate calculation, the model should be refined. Both methods were used to estimate the leakage rates to the sea with openings at various positions on the bomb. The effect of decomposition due to hydrolysis of the agent has been included.

If the corroded opening is facing upwards, the leakage rate of the denser-than-water nerve agent is very low. According to the limited number of corroded bombs observed on the sea floor, it seems that the

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**Table 1**

<table>
<thead>
<tr>
<th>Area (cm²)</th>
<th>Total mass of tabun released (kg)</th>
<th>Ratio of released mass to initial mass in the bomb (%)</th>
<th>Time until all tabun is released or hydrolysed (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>25</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>39</td>
<td>34</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>54</td>
<td>48</td>
<td>5</td>
</tr>
</tbody>
</table>

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5. The original bomb was filled with 100 kg tabun (DAIMON on-line munition catalog, 2020), but 113.3 kg tabun-simulant was used in the simulations because the bomb model was slightly bigger than the KC250 III Gr bomb.
openings are most often located at the part facing upwards (Tønnes et al., 2006; Grabowski, 2018; Hansen et al., 2019b). The reason might be higher sea currents and less sediment cover at the upper parts of the bombs. In these cases, most of the nerve agent tabun will hydrolyse inside the bomb and only the relatively harmless decomposition products will leak out to the surrounding seawater.

If, on the other hand, the corroded openings are not facing upwards, both tabun and some of the decomposition products will leak out fairly rapidly due to their higher density compared to seawater. If the opening area in the bomb shell is 1 cm², the content of the bomb containing 113 kg tabun will be released within 16 h. Due to hydrolysis, however, only 12 kg tabun is expected to be released into the sea during this time. If the opening is larger, the release will be even quicker. For an opening of 10 cm², about 54 kg tabun (half the initial content) will leak out during about 5 h. The size of the hazardous area around a corroded bomb is therefore to a large degree determined by the size of the corroded opening and the half-life of tabun in seawater (5 h) (Stock and Kaffka, 1996).

CRedit authorship contribution statement

John Asulf Tønnes: Conceptualization, Methodology, Investigation, Writing - original draft. Thomas Vik: Investigation, Visualization, Writing - review & editing. Tomas Tungen Kjellstrøm: Investigation.

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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References

Fonnun, F., 1997. Investigation of the ships filled with chemical munitions which were sunk off the Norwegian coast after World War II. In: Stock, T., Lohn, K. (Eds.), Chapter 20, SIPR Chemical & Biological Warfare Studies, 16 the Challenge of Old Chemical Munitions and Toxic Armour Wastes. SIPRL.