Traffic lights for the release of chemical weapons from dumped ammunitions

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1. Introduction

It has been decided to establish simple non-numerical guidelines for assessing hazards from chemical weapons leaking out from dumped ammunition. These guidelines will act as starting points in the DAIMON Decision Support Software (DSS), and will be refined when more knowledge concerning the hazards from such dumped ammunition becomes available.

The method presented in this report gives simple three-colour codes, so called "traffic lights", to indicate whether the hazard to sediments, water, benthic organisms, pelagic organisms or humans are low (green), intermediate (yellow) or high (red). These traffic lights are based on experimental and estimated leakage rates from dumped ammunition, and available ecotoxicity of selected chemical warfare agents. The agents discussed in this paper are tabun, sulphur mustard, and arsenic containing warfare agents. A distinction is also given between effects on water and sediments close to the dumped ammunition (less than 20 m) and in the vicinity of the ammunition (between 20 m and 500 m) as well as benthic organisms living close to the dumped ammunition (less than 50 m) and away from the ammunition (more than 50 m). These distances are partly based on experiences from the Skagerrak dumping area and partly set due to the higher mobility of benthic organisms compared to sediments.

The assessment is based on the conditions at the dumping area at 600-700 m depth south-east of Arendal in Skagerrak, but could also be used for other dumping areas in relatively deep water. We have assumed that only one ammunition shell releases the content at a given time and that the released agent over time will be diluted and hydrolysed in water. The removal of agents by adsorption to the sediments has not been taken into account. Effects from physical contact with the dumped agents, e.g. skin damage, are not considered in the current assessment.

2. Physical and ecotoxicity data for selected compounds

Tabun [77-81-6] has a density of 1.09 g/cm^3 at 6 ˚C [1] and is therefore slightly heavier than sea water (density 1.028 g/cm^3) [2]. Tabun is soluble in sea water (98 g/l [3]) and is not expected to adsorb to suspended solids and sediment based upon the low estimated K_{OC} [1] (K_{OC}=39) [4]. Tabun also hydrolyse quickly in sea water with a half-life of 5 hrs at 7 °C [5]. Tabun will therefore dissolve easily in sea water when the ammunition is opened by corrosion, but will have a limited

[1] K_{OC} is the distribution coefficient between water and organic carbon and measures the mobility of a substance in soil. A very high value means it is strongly adsorbed onto soil and organic matter and does not move throughout the soil.

distribution caused by the rapid decomposition to relatively non-toxic compounds. Tabun has a Log K_{OW}=0.29 [2] and a BCF=3.16 [3] [6] and does therefore not expect to bioaccumulate.

Sulphur mustard [505-60-2] has a density of 1.27 g/cm^3 and is therefore heavier than sea water. The compound will with a K_{OC}=275 to some extent adsorb to suspended particles and sediments [7]. Sulphur mustard is also poorly soluble (< 1%) in water and it is observed that the hydrolysis is slowed down or completely prevented by formation of oligomeric and polymeric layers on the outside of the lumps laying on the sea floor. Sulphur mustard may therefore resist degradation in the sediments for several decades. As a consequence, the distribution will be concentrated to an area in the vicinity of the ammunition and the long term concentration in sea water will be low. A bioconcentration factor of 0.3 [8] and a Log K_{OW} = 1.37 [9] indicate that sulphur mustard does not bioaccumulate [10].

None of the dumped chemical warfare agents are predicted to bioaccumulate significantly (BCF< 5000) [11]. The arsenic containing agents, clark I [712-48-1] and adamsite [578-94-9] have the highest BCF values; BCF=600 (Log K_{OW} = 4.52), and BCF=262 (Log K_{OW} = 4.05), respectively [7]. The arsenic containing agents (except lewisite) are poorly soluble and heavier than sea water with densities from 1.42 g/cm^3 (clark I) to 1.65 g/cm^3 (adamsite). The arsenic containing agents (except lewisite) decompose very slowly in sea water and their decomposition products are still toxic to the marine environment. Both arsenic containing CWA and their decomposition products have in several studies been found in sediment samples around the dumped ammunition. These compounds are not homogeneously distributed around the wrecks, but most of the deposition will occur within a radius of 100 m from the source [12].

3. Experiments conducted to establish the leakage rate from a dumped bomb

Ammunition dumped at sea will corrode over time and the content will eventually be released to the environment. There are many factors affecting the corrosion rate in sea water, such as temperature, water current, salinity, oxygen content, pH and type and amount of sediment cover [3, 13, 14]. The corrosion rate will not be discussed in this paper. Leakages from a KC 250 chemical bomb with predefined corrosion openings of 10 cm^2, 5 cm^2 or 2.5 cm^2, laying on the sea floor have been simulated [15]. This type of aerial bomb was during the Second World War filled with sulphur mustard, phosgene or tabun according to the DAIMON Chemical Weapon Catalog (http://153.19.108.112/catalog/). Experiments were conducted at The Norwegian Defence Research Establishment (FFI) to measure leakage rates of a tabun simulant into sea water. The experiments were compared with numerical simulations of release rates from corrosion openings located at different positions on the bomb (top and bottom) [15]. Tabun was

[2] K_{OW} is the distribution coefficient between octanol and water and is a relative indicator of the tendency of an organic compound to adsorb to soil and living organisms. K_{OW} is also related to the ability of the compound to bioaccumulate.

[3] Bioconcentration Factor (BCF) is an indicator of a chemical substance's tendency to accumulate in the living organism. A substance could bioaccumulate if the BCF>5000.

selected because of its high toxicity and high solubility in sea water, making this agent a worst case in terms of leakage rate.

Tabun is slightly denser than sea water. According to the conducted experiments and simulations, the time to empty a KC 250 bomb initially filled up with tabun is very dependent on the position of the corroded opening. If the opening is on the part facing upwards, tabun will hydrolyse to less toxic compounds while still inside the bomb. These decomposition products are water soluble and will be released to the sea water without causing any harm to the surrounding environment. If, on the other hand, the corrosion opening is on the side or bottom of the bomb, the release rate will be quick and most of the toxic content will be released to surrounding sea water in less than 24 hours [15].

4. Hazards associated with the release of the selected compounds

The hazards associated with release of tabun, sulphur mustard and arsenic containing chemical warfare agents are estimated and shown as colour codes (traffic lights): green, yellow and red. These three compounds have been selected as examples of dumped chemical warfare agents because of their different solubilities, decomposition rates and toxicities.

The hazard colour codes appears from a combination of the agent' solubility and decomposition rate in sea water, the elapsed time after release, the distance from the release, the distribution in the water body and subsequent dilution of the dissolved part over time. The combined colour codes are shown in Table 1, below. The distribution and dilution of the dissolved agent in sea water is similar for all the compounds and will therefore affect the traffic lights in the same way. These parameters are therefore not shown in this table.

Table 1 Hazard colour coding of the Traffic Lights. For explanation see text.

	Short time/ short distance	Medium time/ medium distance	Long time/ long distance
High solubility or low decomposition rate	Red	Yellow	Green
Medium solubility or medium decomposition rate	Yellow	Yellow	Green
Low solubility or high decomposition rate	Yellow	Green	Green

Green lights do not mean that no organisms could potentially be affected, but that the probabilities of such effects are very low.

The experiments referred to in Chapter 3, show that the chemical agents denser than sea water will stay inside the bomb shell if the corroded opening is located on the part facing upwards.

These compounds will therefore hydrolyse to less toxic compounds before leaking out to the surrounding waters. These situations are therefore given green lights.

If the openings are corroded on the part of the bomb facing sideways or downwards, or in case of a total collapse of the bomb, the content will leak out to the surroundings. Depending on the solubility in sea water, the compounds will be distributed and diluted by the bottom currents. Most of the dumped warfare agents will hydrolyse to much less toxic compounds over time. The nerve agent tabun will hydrolyse quickly with a half-life of 5 hours in sea water, while the time-limiting process for sulphur mustard is its low solubility rate in water. Once solved in water, the half-life of sulphur mustard is relatively short (less than three hours). Most of the arsenic containing warfare agents will hydrolyse quickly, but will produce other less toxic arsenic agents which may still affect the biota. An overview of solubilities and decomposition rates in sea water for the relevant agents are shown in Table 2.

Table 2. Solubilities and decomposition rates in sea water

Agent	Solubility in sea water [16] (g/l)	Decomposition rate in water
Tabun	98	$T_{1/2}$ = 300 min [1)]
Sulphur mustard	0.9	$T_{1/2}$ = 175 min [2)]
Diphenyl chloroarsin (clark I)	2	Slow
Diphenyl cyanoarsin (clark II)	2	Slow
Adamsite	0.4	Very slow

[1)] At 7 °C in sea water [5]

[2)] At 5 °C in sea water [1]

Decomposition products of sulphur mustard and arsenic containing agents like clark, adamsite and arsine oil have been found in sediment samples [6, 12, 17, 18, 19, 20]. Non-decomposed warfare agents like clark I, sulphur mustard and chloroacetophenone have also been found within 20 m of the scuttled wrecks with chemical ammunition [6]. The chemical warfare agents and their decomposition products are not evenly distributed around the wrecks, but most of the deposition will most likely occur within a radius of 100 m from the source [12]. Such compounds have not been found in water samples collected close to the bottom near the dumping sites, but arsenic containing decomposition products have been found in pore water from sediment samples in the Bornholm basin dumping area [18].

The nerve agent tabun is highly toxic, water soluble and decompose quickly in water. It is expected high concentration of this agent in water close to the leaking ammunition which will represent a high hazard to benthic organisms close to the bomb. It will, however, dilute and hydrolyse quickly in sea water, which leads to low hazard at some distance from the ammunition.

Sulphur mustard is less toxic than tabun, but is poorly soluble and will adsorb to sediments close to the dumped ammunition. When dissolved in sea water, sulphur mustard will decompose quickly. It is expected medium concentrations in water and sediments close to a leaking bomb, resulting in a medium hazard close to the ammunition. As some distance from the ammunition only low hazard is expected.

Arsenic containing chemical warfare agents are poorly soluble in water and will slowly hydrolyse to other arsenic containing agents. These arsenic agents will stay in sediments and biota for very long time and could accumulate and possibly also biomagnificate in biological organisms. Benthic organisms like hagfish will stay close to the leaking ammunition for some time and arsenic chemical warfare agent related products have recently been found in samples from benthic fish collected in the area [21]. This shows that these agents are taken up by marine biota living near the sea floor. It is therefore expected that arsenic agents represent medium hazards to benthic organisms in the vicinity of the ammunition, but also in greater distance from the ammunition.

It is not expected that pelagic organisms will stay long enough in the vicinity of dumped ammunition to reach significant levels of any chemical warfare related compounds. No chemical warfare agents have been found in samples from pelagic fish. It is not expected that dumped chemical warfare agents will affect humans by the consumption of fish and sea food.

A summary of the risk assessment and corresponding colour codes are shown in Table 3.

Table 3 Risk assessment for leakage from a single (KC250 aerial) bomb located on the sea floor

Risk assessment from leakage from a single bomb (250KC aerial bomb) lokated at the sea floor								
A: Tabun								
Position of opening	Water close to bomb (<20 m) immediately	Water within 20-500 m	Sediments close to bomb (<20 m)	Sediments (>20 m)	Benthic organisms close to bomb (<50 m)	Benthic organisms away from bomb (>50m)	Pelagic organisms in the area	Humans*)
Top	Hydrolysis before leakage	Hydrolysis products	Not leaked out	Not leaked out	No observed effects	No observed effects	No observed effects	No effects
Side	Leakage before hydrolysis	Mostly decomposed	No expected effects	No expected effects	Likely to be affected	No observed effects	No observed effects	No effects
Bottom	Leakage before hydrolysis	or diluted	No expected effects	No expected effects	Likely to be affected	No observed effects	No observed effects	No effects
B: Sulphur mustard								
Position of opening	Water close to bomb (<20 m) immediately	Water within 20-500 m	Sediment sclose to bomb (<20 m)	Sediments (>20 m)	Benthic organisms close to bomb (<50 m)	Benthic organisms away from bomb (>50m)	Pelagic organisms in the area	Humans*)
Top	Poorly soluble in water	Not leaked out	Not leaked out	Not leaked out	No observed effects	No observed effects	No observed effects	No effects
Side	Poorly soluble in water	Poorly soluble in water	Could adsorb to	No expected effects	No observed effects	No observed effects	No observed effects	No effects
Bottom	Poorly soluble in water	Poorly soluble in water	suspended particles	No expected effects	No observed effects	No observed effects	No observed effects	No effects
C: Arsenic containing CWA								
Position of opening	Water close to bomb (<20 m) immediately	Water within 20-500 m	Sediments close to bomb (<20 m)	Sediments (>20 m)	Benthic organisms close to bomb (<50 m)	Benthic organisms away from bomb (>50m)	Pelagic organisms in the area	Humans*)
Top	Not leaked out	Not leaked out	Not leaked out	Not leaked out	not leaked out	not leaked out	not leaked out	not leaked out
Side	Hydrolyses (slowly)	Could be	Could adsorb to	No expected effects	Decomposition products	Decomposition products	Decomposition products	Can biomagnificate
Bottom	in water	dispersed in water	suspended particles	No expected effects	found	found	found	Can biomagnificate
*) Assessed from consumed marine organisms and no fishing restriction, contact hazard has not been looked at								

5. Conclusions

Simple non-numerical guidelines for assessing hazards from the chemical warfare agents, tabun, sulphur mustard and arsenic containing agents leaking out from dumped ammunition, so called "traffic-lights", have been established. These traffic lights indicate if the hazard to sediments, sea water, benthic organisms, pelagic organisms and humans are low (green), intermediate (yellow) or high (red). The guidelines are based on the density, solubility, decomposition rate and toxicity of the agents and are given for ammunition dumped in deep water. They will act as starting points in the DAIMON Decision Support Software (DSS), and will be refined when more knowledge on the hazards from such dumped ammunition is available.

Different traffic lights are given for the nerve agent tabun, sulphur mustard and arsenic containing chemical warfare agents because of their different solubilities, decomposition rates and toxicities. Intact chemical warfare agents will not leak out from an upward facing opening. It is only a risk if the corroded opening on the bomb is facing sideways or downwards allowing the content to leak out before it is hydrolysed.

The risk is only assessed as high from the nerve agent tabun in water close to the leaking bomb and for benthic organisms living less than 50 m from the bomb. Intermediate risk is expected in water and sediments close to a bomb leaking sulphur mustard and within 20-500 m from a bomb leaking tabun. Because the arsenic agents will stay in sediments and biota for very long time, and that they could accumulate and possibly biomagnificate in biological organisms, the risk is assessed as intermediate in a larger area compared to tabun and sulphur mustard. Low risk is expected in sediments more than 20 m from a leaking bomb and for pelagic organisms and human consumers of sea food from all agents.

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