

# Risk Assessment of Sea Dumped Conventional Munitions

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**Abstract:** Energetic compounds from dumped ammunition are toxic to aquatic organisms. Leakage of ammunition residues will occur when the bombshells are broken and the energetic compounds come into contact with water. The munitions compounds have a complex behavior in the environment, particularly in the sediment-water phase, and the calculation of safety levels are dependent on choice of methodology. Estimated sediment quality benchmark levels combined with multi-increment sampling strategy provide

the most proper tool for performing ecological risk assessment at a dump site. Dumped munitions may be located in areas, where shellfish, invertebrates, and benthic or pelagic fish are consumed by humans. A monitoring program for early warning of potential contaminants in the vicinity of fish farms could be conducted by passive samplers for explosives. Further development of both sample procedures and analytical methods to increase the quality of the chemical analyses are encouraged.

**Keywords:** Dumped ammunition · Risk assessment · Energetic materials · Explosives · Aquatic toxicity

## 1 Introduction

Huge amount of ammunition, both conventional and chemical weapons, have been dumped in the oceans of the world during the last century. In particular, large amounts of ammunitions were dumped in the sea after the Second World War. It has been estimated that between 750000 and 1.5 million metric tons of conventional ammunition was dumped along the German North Sea coast [1]. In Norway, an estimate of approximately 200000 metric tons of ammunition were dumped after the Second World War. These figures do, not include disposal of ammunition in the two northernmost counties in Norway, which probably represented a similar amount [2]. Dumping in the oceans as well as in lakes and rivers was regarded as an accepted measure to dispose redundant ammunition, it was fairly efficient and considered as secure. In addition, there are large amount of UXOs across the world from military activity [3]. Although less in volume, ammunitions are still left behind as unexploded materials in waters during training.

Wastewater, soils, groundwater, and surface waters have become contaminated with a variety of energetic compounds arising from ammunition manufacture and processing [3–6]. Less is known about environmental spread of energetic compounds in dumped ammunition, but some concerns are raised that explosives and other toxic compounds from dumped ammunition can leak out to ambient water and sediments and expose various organisms. The energetic compounds in dumped ammunition were originally sealed into the bombshells and are in principle not subjected to considerable leakage. Leakage will first occur when bombshell is broken and the energetic compounds come into contact with water and air. The bombshells, which are made of different alloys of metals, will after dumping start

to corrode and sooner or later the explosives inside will be exposed. The problem of leakage of explosives from dumped ammunition appears to be greater in seawater than in fresh water, due to a higher corrosion rate [2]. Bearing in mind that large amount of dumped ammunition have been exposed to weathering for almost a century in saline water there are reasons to believe that leakage will increase significantly within a relatively short time frame.

Several studies have demonstrated the toxicity of energetic compounds on aquatic organisms [7–9]. In spite of the considerable amount of explosive residues that are dumped in the environment there are very little knowledge about the extent of and the potential effects they might have on both freshwater and marine organisms. Based on current knowledge it cannot be excluded that dumped conventional ammunition may pose a future threat to the environment. In the future there will probably be an increased pressure to take measures on contaminated sites both to protect the environment and economic interests, such as the aquaculture industry. This will require applicable site specific methods for risk assessment.

The current review discusses approaches for the calculation of screening benchmarks or safe environmental levels of energetics from dumped ammunition for aquatic organisms, with emphasis on benthic organisms. Strategies for risk assessment of dumped ammunition will be suggested. In addition a brief overview of the compounds in dumped

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munitions and their environmental fate is given. Metals might also be contaminants of concern from dumped munitions, but will not be covered by the current study. For more in-depth comprehensive information about the aquatic toxicology and risk assessment of energetic compounds we will recommend the following reviews [7–9].

## 2 Compounds in Dumped Munitions

Ammunition consist essentially of the metal shell filled with the main charge or booster explosives, propellants, and the detonator, of which all the non-metals are considered potentially hazardous. The compounds in dumped munitions of most interest in terms of risk can be divided into four classes: the nitroaromatics, nitramines, nitrate esters, and perchlorate salts, which are used as propellants [10,11]; the nitroaromatics include 2,4,6-trinitrotoluene (TNT), 2,4- and 2,6-dinitrotoluene (DNT), 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB), 2,4,6-trinitrophenylmethylnitramine (tetryl) and 2,4,6-trinitrophenol (picric acid); the nitramines include hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); and the nitrate esters include pentaerythritol tetranitrate (PETN) and nitroglycerine. Other substances used in ammunition are nitroguanidine, diethylene glycol dinitrate (DEGDN) and ammonium nitrate. Frequently used initiators are lead azide, lead styphnate, and mercury fulminate. Furthermore, white phosphorus is used in smoke grenades and is very toxic to both humans and animals [12,13]. The

most widely used explosives in the main charge are TNT, RDX, and HMX. The high explosives in the main charges are often made in different mixtures and combinations. Cyclitol is 75% RDX and 25% TNT by weight. Composition B is 60% RDX and 40% TNT, desensitized with 1% wax. Octols are mixtures of HMX and TNT. Torpexes are mixtures of RDX, TNT, and aluminum. Minols are mixtures of TNT, aluminum, and ammonium nitrate [13].

## 3 Fate of Dumped Ammunition in the Aquatic Environment

Most studies on environmental fate of explosives have been performed on terrestrial and freshwater systems. A study by Brannon et al. [14] showed that studies on freshwater systems were applicable to saline environment and it is reasons to believe that several processes in the environmental fate of ammunition are common, irrespectively of where it is deposited. After dumping the metal shell of the ammunition starts to corrode and leakage of explosives starts when the outer shell breaks. The rate of corrosion is dependent on the steel quality (higher carbon content results in increased corrosion rate) and thickness of the shell. The rate of corrosion of the metal shell is, in addition, governed by salinity, oxygen content, temperature, and the speed of water currents.

In a Swedish study in freshwater it was calculated that it can take up to 1000 years before the casing corrode allowing the contents to start leaking [15], particularly at sites low in oxygen and if the ammunition is covered by mud. The yearly estimated corrosion rate of steal in saline water is 0.01–0.575 mm [16–18]. Leaching of dumped ammunitions at sea has been suggested to start after 25–265 years [18]. There are several processes a chemical may undergo in the environment. Environmental transport results from volatilization and dissolution from the source, water current, and sediment/soil sorption processes. Sediment type and redox conditions can also affect the dissolution rate of the compounds in water [19]. Transformation processes of the ammunition residues include photolysis, hydrolysis, oxidation, reduction, and biological transformation. The various compounds' solubility and the octanol-water partition coefficient ( $K_{ow}$ ) value indicate whether they will diffuse into surrounding water or adsorb to sediments [20]. With some exception, such as picric acid, most components of ammunition are not very water soluble, so that the concentration in the surrounding water will probably remain low. It is, however, expected that several of the energetics have high potential to accumulate in sediments due to their high affinity to organic carbon [21–23]. Yost et al. [21] investigated fate of TNT and other TNT-related compounds in slurries of marine sediments and found a rapid decrease in the aqueous phase concentrations of TNT. The decrease was particular prominent in a sediment with high content of organic materials.

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## 4 Bioaccumulation of Explosives

Concerns are raised if leakage of residues from dumped ammunition accumulates in exposed animals. For a compound to accumulate in the food chain the uptake of the compound must be higher than the secretion. Studies on terrestrial plants have revealed some uptake of explosive residues in the roots and the leaves, indicating a possibility for the remnants to be transferred further into the food chain [24–28]. However, estimated half-life values for some of the explosives in different mammals and fish do not indicate a potential for bioaccumulation [29–33]. Elimination half-life of TNT in different fish species have been estimated to an hour or even less than an hour [32,33].

For aquatic organisms it is relevant to estimate the so-called bioconcentration factor (BCF). A BCF is the ratio of the concentration of a chemical in an aquatic organism to that of the surrounding water, and is the most commonly used indicator of a compound's tendency to be concentrated in aquatic organisms [34]. Typically according to regulatory assessments, a chemical with a BCF above 1000 can be considered bioaccumulative [35]. An overview of BCFs of some energetics is made by Lotufo et al. [9]. The BCFs for TNT varies widely from 0.3 to  $9.7 \text{ mL g}^{-1}$  for various marine and freshwater invertebrates and fish species. Calculated BCFs for RDX and HMX are less than 3, and some of the TNT metabolites have similar BCF as TNT [9]. These figures indicate that munitions compounds cannot be considered particularly bioaccumulative.

## 5 Environmental Spread of Energetics from Dumped Ammunition

Munitions components from dumped ammunition will be heterogeneous spread on the sea and lake floors and the concentration in the surrounding water will probably remain low, both due to dilution effects and to the compounds relatively low water solubility. The highest concentrations will probably be found in the sediments, which are in close vicinity of the source. Very little is, however, known about how the energetics is dispersed into the sediment or overlaying water from a point source. It has been demonstrated low levels of explosives (RDX and picric acid) in shellfish outside areas with dumped munitions [36]. Norwegian clearance divers in cooperation with FFI have collected samples of water, sediment and biota close to encounters in shallow waters. The munitions were mainly remnants from the Second World War. Explosive residues were found in low concentrations in biota, sediment, and water samples. Water and sediment samples collected shortly after EOD operations, contained explosive residues [2].

In a study by Rosen and Lotufo [37] it was shown that dissolution from fragments of composition B was dependent upon the water turbulence and whether the fragments were covered with sediments. Fragments exposed to

water dissolve much faster than fragments covered with sediments. Similar has been reported by others [38,39]. The experiment was performed in 20 L aquaria in static conditions. Relatively high concentrations of TNT (ca.  $0.4 \text{ mg L}^{-1}$ ) and RDX (ca.  $1 \text{ mg L}^{-1}$ ) were measured in the overlaying water in the aquarium with fragments exposed to water. With flow renewal of the water at a rate of 0.5 per day the concentration of TNT and RDX dropped to approximately  $0.2 \text{ mg L}^{-1}$  and  $0.4 \text{ mg L}^{-1}$ , respectively. It was found sub lethal effects on the mussel embryo-larval development manifested as developmental abnormalities. A concentration of  $0.4 \text{ mg L}^{-1}$  TNT is also close to concentrations that are lethal to Rainbow trout [40]. In the experiments where the fragments were buried under static conditions, the water concentrations of TNT and RDX reached approximately  $0.03 \text{ mg L}^{-1}$  and  $0.08 \text{ mg L}^{-1}$ , respectively. The pore water concentrations of TNT ( $2\text{--}8 \text{ mg L}^{-1}$ ) and RDX ( $2\text{--}6 \text{ mg L}^{-1}$ ) were higher than in the overlaying water. The elevated concentrations found in the sediment pore water are acutely toxic for many aquatic organisms, but were only found in the close vicinity of the fragments. Some studies have been performed near production facilities for munitions compounds, which may give an indication of their potential for spread. For example, at Cornhusker Army Ammunition Plant near Grand Island, Nebraska, where the production of TNT ceased in 1973, TNT concentrations were measured at a range of  $1.0\text{--}350 \text{ } \mu\text{g L}^{-1}$  in the groundwater after disposal of munitions wastes [4]. The TNT contaminated area covered approximately  $0.1 \text{ km}^2$ .

The experiments by Rosen and Lotufo [37] show that munitions residues, such as TNT and RDX, if exposed to water, readily dissolve in the surrounding water if not protected by a layer of sediments. Their study was performed with sediment low content of organic matter and may represent a worst-case scenario since many energetics have high affinity to organic matter. As long as the contamination is not isolated within a limited volume of water, the high loads of water in the sea or lakes will dilute the chemicals into less toxic concentrations. Combined with the low bioaccumulation potential of the energetic materials, the approach of calculating safety levels in sediment rather than in water may therefore be reasonable.

## 6 Sample Strategies for Contaminated Sediment

Munitions components from dumped ammunition are heterogeneously distributed on the seabed. Very high and toxic concentrations may appear in the sediment and sediment pore water in close vicinity of an ammunition fragment, but only a short distance away the concentrations may drop to non-toxic and non-detected levels [37]. This requires sophisticated sampling strategies to evaluate the state of contamination in an area with dumped ammunition since the risk of sampling errors will be high. Common

characterization of polluted sediments includes randomly sampling of single and replicate samples of sediment and soil. This is a strategy that only characterizes the points, at which they are taken and often differ substantially from nearby points only a few meters or even centimetres away. This might lead to erroneous assessments of an area's level of contamination.

To reduce errors in sampling and even reduce the number of samples needed to be analysed a strategy of so-called multi-increment sampling should be used. Multi-increment sampling has been shown to increase reproducibility of replicate samples to within an order of magnitude. Multi-increment sampling is based on collecting many evenly distributed samples within a specific area, or decision unit (DU), and with similar mass from a randomly generated point within the area to be investigated [41,42]. The collected samples within the DU constitute an increment and, if performed correctly, will represent the state of contamination within the specific area. The level of contamination in the sediment within the selected area will then make the basis for further safety level evaluation of the munitions in sediment and water.

## 7 Calculation of Environmental Safety Levels of Energetics in Sediment

Some attempts have been made to provide estimates of a safe concentration level of explosives in sediments. One approach is to calculate sediment quality benchmarks (SQB), which are based on laboratory studies of aquatic toxicity on benthic invertebrates and equilibrium partitioning theory between water and sediment concentrations [7,43]. Another approach has been to calculate sediment toxicity values which are based on sediment spiking experiments and calculated NOEC (No Observable Effect Concentration) values [44].

The SQBs aim to give protection to the most sensitive organisms and use water toxicity studies that are relevant for benthic organisms. No sediment-spiking experiments are used. It is argued that the quantification of exposure concentrations in sediment spiking studies may be inaccurate due to chemical and biological transformation of the compounds. In addition, there might be uncertainty associated with the validation of the estimated equilibrium between water and sediment. This is outlined by Di Toro et al. [45]. SQB is calculated from a chronic toxicity value multiplied with the compounds partition coefficient between sediment and pore water,  $K_p$ . The partition coefficient,  $K_p$ , between sediment and pore water is calculated from the components  $K_{oc}$ , which is the particle organic carbon partition coefficient, and the mass fraction of organic carbon with the assumption that  $K_{oc}$  approximately equals the octanol-water partition coefficient ( $K_{ow}$ ) [45]. Organic carbon will be the dominant phase for chemical sorption in sediments and increased levels of OC makes the compounds

less available. The SQBs estimated by Pascoe et al. [43] was emphasized to be temporary, since most of the studies used in the calculations were done in fresh water. Nipper et al. [36] have suggested that marine organisms are more sensitive to explosives than freshwater organisms, as this has been found applicable for TNT. However, it has also been found that the toxicity values in freshwater of DNB, TNB, and RDX is lower than the toxicity values found in marine studies [43]. A study by Brannon et al. [14] showed that studies on freshwater system were applicable to saline environment and it is reasons to believe that several processes in the environmental fate of ammunition are common, irrespectively of where it is deposited. The calculated SQBs for most of the compounds were in the concentration range between 1 and 10  $\mu\text{g kg}^{-1}$  dry weight sediment and resembled the SQB calculated for some energetics by Talmage et al. [7]. Some of these values were close or even below the detection limits of the analytical methods that were used.

The other approach to calculate sediment safety values of munitions has been to use sediment spiking experiments and calculated NOEC values [44]. The calculated NOECs are recognized as the sediment safety level of a certain compound. With a few exceptions the spiked sediment NOECs were substantial higher than the SBQs calculated by Pascoe et al. [43]. For RDX and HMX the spiked sediment NOECs calculated by Lotufo et al. [44] were 17000 and 66000-fold higher than the SBQs calculated by Pascoe et al. [43]. Some of the differences may be attributed to the validity of the partition coefficients between water and sediment concentrations of the energetics used in the calculation of SBQs, the design of the sediment spiking experiments which might underestimate the toxicity, and loss of chemicals during the experiment due to transformation of the chemicals in the sediments and irreversible binding to organic matter.

As outlined by Di Toro et al. [45] the type of sediments used in experiments are essential for the toxicity of a chemical and the SBQ approach is designed to take this into consideration. The sediment-water partition coefficient calculated in the SBQ approach is a theoretical value. Bearing in mind that most of the munitions components have a very high affinity to organic materials the SBQ approach may overestimate their sediment toxicity. The validity of the toxicity values used in the calculation must also be considered with cautions. In the study by Rosen and Lotufo et al. [37] it was shown that the pore water concentration dropped very fast to nontoxic concentrations just a few centimetres from the fragments. This enables benthic organisms to avoid contact with the contaminants. The chemical tested in most toxicological studies on aquatic organisms which are used in risk assessment are homogenously mixed into the water and/or the sediments. The toxicity data used for the evaluation of safety levels in sediments may therefore only be valid immediately adjacent to the dumped munitions.



## 8 Approaches for Risk Assessment of Dumped Ammunitions

Evaluation of risk for aquatic organism to be exposed to energetics in dumped ammunition is challenging due to the heterogeneous spread of the ammunition, the behavior of the munitions compounds in the sediment-water interface and a relatively low persistency of the parent compounds in the environment. An overestimation of risk may lead to unnecessary and potentially dangerous clean-up measures at a dumping site, whereas an underestimation of the risk may potentially lead to unacceptable harm to organisms living in the area or economic losses by nearby aquatic industry. Due to dilution of munitions residues in the seawater it will probably not be possible to detect residues in the free water mass unless the ammunition is dumped in an area with little exchange of water, like a small lake or a threshold fjord. If explosives residues are detected in the free water mass there is a relatively high knowledge base of the water toxicity of munitions on aquatic organisms [9]. Water quality benchmark levels may be calculated according to species sensitivity distributions (SSDs) models as described in the USEPA protocol for estimating numerical water quality criteria [46] or similar methods [47,48].

Sediment living organisms are probably of highest risk of being exposed to harmful concentrations of munitions residues, which require a basis for estimating reliable sediment quality levels. Compared with toxicity studies using sediments spiked with explosives, the SQBs calculated by Pascoe et al. [43] may appear conservative. Some of the SQBs are even close to the detection limits for chemical analysis. The SQB values are based on theoretical concentrations of different munitions constituents in the sediment pore water and a thorough review of current knowledge of aquatic toxicity of munitions constituents. Albeit the values might overestimate the risk, the SQBs will protect the benthic fauna as well as the pelagic fauna near a dumping site and are valuable for screening purposes. Screening is very important when it comes to sea dumped munitions because it allows us to discriminate between no-measures sites and sites that need to be investigated further. Pollution from dumped munitions has a very heterogeneous distribution. If we take too few samples, there are risks of both underestimate and overestimate the concentration in the sediments. Many discrete samples can be too costly. Hence, the first approach is to define the assessment area, or in terms of multi-increment sampling, the DU. As reported by Rosen and Lofutu [37] the concentrations of TNT and RDX immediately adjacent to the munitions fragment may reach hazardous concentrations and will probably exceed calculated sediment quality criteria, regardless of the method used to estimate the benchmark levels. The ecological relevance of such small hot spots is probably of minor importance for the benthic community living in the area and will not defend any clean-up measures. The stake-

holders should not be concerned about very local effects, but the benthic and aquatic environment in a DU in general.

Often some information about the dumped ammunition is needed in order to define a DU since the dumped ammunition may be heterogeneous scattered over a large area or concentrated within a limited area. Due to uncertainty about the distribution of explosives in an aquatic system from a point source, the DU should as a first step cover the area containing the dumped munitions, extending it with a zone of approximately 20 m in width. The distance of 20 m was chosen based on the following rationale: The distance from the source must be short enough to ensure that we are not diluting away the problem when doing sampling, but large enough to ensure that multi-increment sampling is feasible when the munitions on the seabed constitutes only a few, or one object. If the area containing dumped munitions is very limited compared with the area that we are interested in protecting it can be argued to extend the DU by extending the perimeter to the source. Samples should be taken, depending on the nature of the sediment, by a corer or a box corer. Samples to include in an increment should be taken from the upper 10–20 cm of the sediment, depending on the state of the top sediment and how deep the ammunition residues are buried. To reduce sample errors due to the heterogeneous distribution of the contaminants and to get a statistical representative estimate of the contaminant level in the DU, the number of increments should be at least 50 [49,50]. To minimize errors, 100 samples or more may, however, be required. For more details on sampling strategy as well as sample preparation and analytical methods see recently published works [41,42,49–52].

Some fish farms are located in the vicinity of seadumped munitions sites. There is a worry that stationary fish or other food organisms could accumulate explosives in an extent that would be unacceptable for the consumer. These values can be lower than the toxicity benchmarks for the organisms themselves. A cost-effective way to indicate accumulation of explosive residues in fish is to use passive samplers [53–55]. A few passive samplers (more than three) could be lowered in water next to a farming facility. A passive sampler accumulates both the parent compounds and metabolites over time ensuring enough material for analysis. It is also possible to calculate the concentration of explosives in the ambient water based on established algorithms for the specific passive sampler. Although the results from the passive sampler do not give an answer to the question whether the fish is consumable or not it will provide a warning that the fish farming industry should probably look closer at the population at stake.

## 9 Concluding Remarks and Future Work

Despite the low concentrations of explosives that have been identified in the natural environment, it can be argued that the presence of munitions in sea water may pose an ecological risk. Some attempts have been performed to make sediment quality benchmark of munitions in order to calculate levels of concentrations that are safe for sediment living organisms. The munitions compounds have a complex behavior in the environment, particularly in the sediment-water phase, and the calculation of safety levels appears to be very dependent on choice of methodology.

SQB values calculated for 25 different munitions compound by Pascoe et al. [43] are conservative but represents a thorough review of current knowledge and will probably protect both the benthic fauna as well as the pelagic fauna near a dumping site and are valuable for screening purposes. The SQBs could be improved if more studies on the sediment-water interface and their potential of spread from a source are performed. Nevertheless, combined with a multi-increment sampling strategy the SQBs provide the most proper tool for performing ecological risk assessment. Sampling of sediments in an aquatic environment is, however, challenging. Further developments of sample methodology at seas, which can overcome some of these challenges, are therefore encouraged. In addition, a monitoring program for early warning of potential contaminants from a dump site could be conducted by passive samplers for explosives.

Dumped munitions may be located in areas where shellfish, invertebrates, and benthic or pelagic fish are consumed by humans. Laboratory studies have shown some uptake of energetic in aquatic organisms, but apparently these chemicals are not particular prone to accumulation. As far as we know, there are no models that can predict the levels in different organisms, so tissue analysis will provide the best measure of the risk associated with consumption of explosive-containing organisms. Further development of both sample procedures and analytical methods to increase the quality of the chemical analyses are encouraged.

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## REVIEWS

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