

REVIEW

Open Access



Effects of climate change on marine dumped munitions and possible consequence for inhabiting biota

Jörn Peter Scharsack^{*} , Daniel Koske, Katharina Straumer and Ulrike Kammann

Abstract

Marine environments are contaminated with enormous amounts of warfare agents due to military activity and exercise, and the disposal of unused ordnance. Due to corrosion of munition shells, substances are leaking from the warfare materials into the environment. It has to be expected that climate change will influence munition corrosion and distribution of their content. Although there is no doubt about the principle toxicity of many of the munition compounds, including their transformation/degradation products, the impact of munition compounds on marine environments, including their biota are yet only at the beginning to be understood. Recently the intake of munition compounds has been confirmed in mussels and fish collected from contaminated areas. It has become clear that dumped munitions are a continuous source of toxic substances leaking into the environment and that ongoing corrosion will worsen the problem. The present review intends to evaluate the available literature on how climate change might influence the contamination of marine environments and inhabiting biota with munition compounds. Direct testing (or modelling) of climate change scenarios in the context of the marine munition problems has yet not been undertaken. Nevertheless, it can be predicted that climate change effects such as rising temperature and higher frequencies of extreme weather events will accelerate the rates at which disposed ordnance corrodes and consequently accelerate the rate at which munition compounds are leaking out. Climate change will cause elevated stress to biota, ranging from temperature stress and lower availability of oxygen to shifts in salinity and pH. In combination, elevated release of munition related compounds and elevated environmental stress, will put biota under threat, in particular in areas with high munition contamination and limited water exchange, such as the Baltic Sea. On a positive side, biodegradation of organic munition compounds by biota and microorganisms is likely to be accelerated with rising temperature.

Keywords: Munition compounds, Climate change, Corrosion, TNT, Temperature, Pollution, Biota

Introduction

Climate change coincides with changes in temperature, precipitation and the frequencies of extreme weather events [33]. An increase of average temperatures by 1.5 °C by the middle of the twentieth century is predicted if the emission of greenhouse gases continues as

currently ongoing [51]. The mean atmospheric carbon dioxide (CO₂) concentration is increasing, from approximately 280 parts per million (ppm) in pre-industrial times [73] to a recent concentration of 413 ppm in the beginning of the year 2020 [58]. The rising atmospheric CO₂ level (350 to 380 ppmv, 1990–2010) contributes to climate change more than any other greenhouse gas and its implications are for instance global warming, sea-level rise (3.6 mm per years 2006–2015, 21–24 cm since 1880) and ocean acidification (pH 8.13 to 8.08, 1990–2010) [18, 22, 23].

*Correspondence: joern.scharsack@thuenen.de
Institute of Fisheries Ecology, Herwigstrasse 31, 27572 Bremerhaven, Germany
Daniel Koske and Jörn Scharsack are co-first authors.

Accordingly, it is likely that climate change will also affect pollutants that are already present in the marine environment. As climate change alters abiotic conditions, such as salinity, pH, temperature, precipitation and circulation of the water column in marine environments [28, 71], it has to be expected that the state, environmental fate and potential risk of the pollutants are affected. Such changes will also apply to munitions dumped in marine environments (Fig. 1).

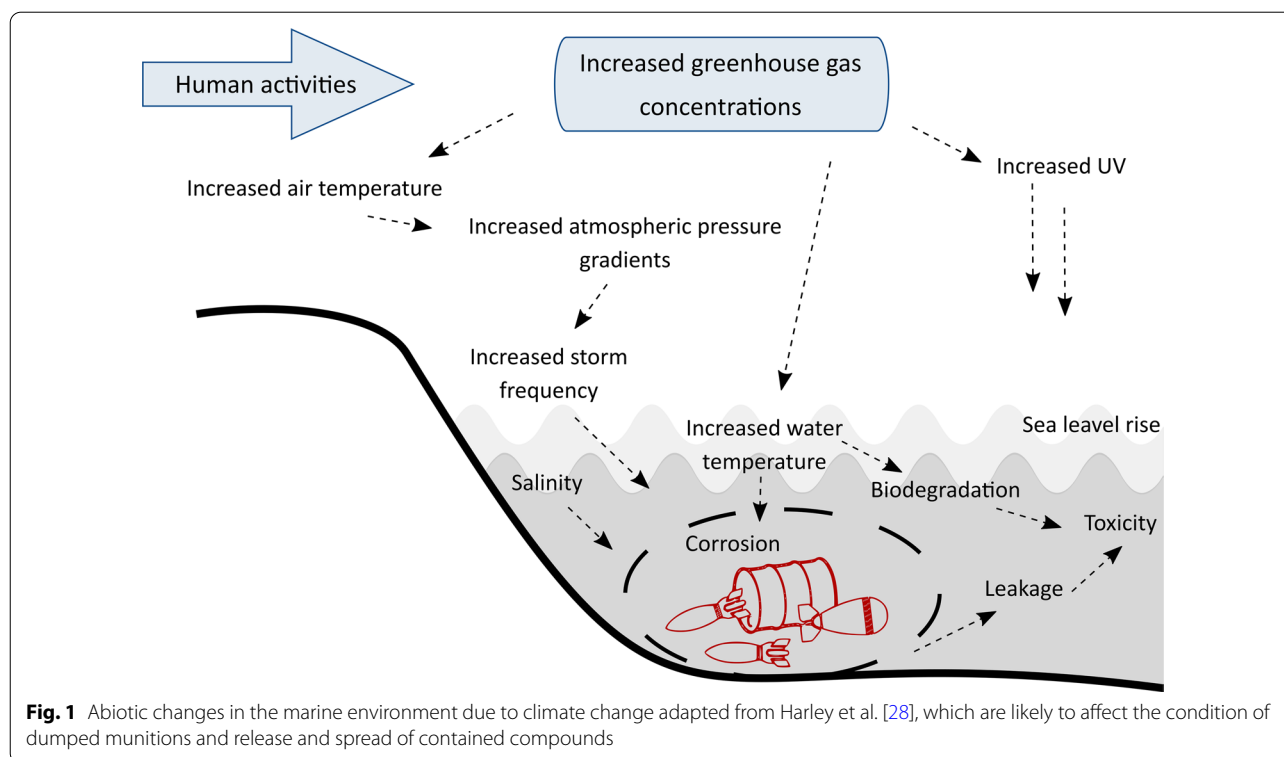
Contamination of marine environments with dumped munitions has become a global problem since the World Wars in the twentieth century. Munitions in the marine environment are often remains of military activities during wars and trainings, but the far majority was dumped intentionally as fast, economic and legal disposal practice until the 1970 [16]. Alone in German coastal waters of the North and Baltic Sea about 1.6 million metric tons of munition were dumped during and after World Wars I and II [11]. In addition to the explosion and security risk, these munitions contain cytotoxic, genotoxic, and carcinogenic chemicals associated with conventional explosives, chemical warfare agents, and munition structural components (e.g., mercury in fuses) [68, 82], reviewed in Ref. [6, 27]. Besides explosives and chemical warfare agents, also mercury from the dumped munition might be released in the environment. Some munition objects contained

mercury, either elementary or as mercury fulminate a common explosive primer [9].

Looking at the overall amount of anthropogenic marine dumpings, munitions might only be a small fraction, but they are a ticking time bomb. Since their marine disposal, metal housings of munitions are subjected to corrosion [41, 74] and more and more munition shells deteriorate and munition compounds are leaking into the environment [6, 7, 86]. These processes are ongoing and it is difficult to estimate when a peak in the release of munition compounds is reached.

Since environmental factors such as water turbulence, temperature and salinity are influencing the corrosion of munition housings and the distribution of munition compounds [6], the future development of these parameters in marine environments is of great importance. In this respect, it has to be expected that climate change will influence the speed at which munition compounds are released. Furthermore, biota and their interaction with munition compounds, are dependent on environmental factors that are subject to climate change.

We hypothesise that climate change will increase the physicochemical pressure on marine munitions mainly through rising temperatures, but also by water turbulence due to more frequent extreme weather events. As a consequence, more munition compounds will be set free into the environment. Microorganisms might accelerate



the speed at which they metabolise organic munition compounds, but higher taxa will presumably suffer to higher extent from the toxic properties of many munition compounds and their degradation products. Particularly so, since climate change will coincide with elevated exposure of organisms to environmental stress, such as temperature shifts.

The marine dumped munitions problem is receiving increasing attention and has become a major concern to seafood consumers, environmentalists, politicians and scientists [5, 6, 43, 49, 50, 66, 76], but information on how climate change will affect dumped munitions and the associated effects on biota including fish is limited. Direct investigations of climate change effects on marine dumped munitions are extremely scarce. Indirect evidence, for example on temperature effects on the dissolvability of organic explosives, allows to discuss aspects of the marine munition problem in the light of climate change. With the present review, we have investigated the available literature for evidence about climate change effects on marine dumped munitions.

Chemicals contained in dumped munitions

With regard to the munition compounds released into the environment from dumped munitions, a fundamental distinction must be made between conventional munition and chemical weapons (CW). Munition dumped in German territorial waters are mainly conventional with about 1.3 mio t in the North Sea (90 t CW) and 0.3 mio t in the Baltic Sea (5000 t CW). Most CW of German origin were dumped outside German territorial waters, 170,000 t in the North Sea (Skagerrak, European North Sea, German Bight) and 42,000–65,000 t in the Baltic Sea (Bornholm Basin, Gotland Basin, Small Belt) [11].

Conventional munition compounds typically contain organic and metalloorganic explosives and metals from the casings. Heavy metals, such as mercury and lead are included in the compounds used to initiate detonations of secondary explosives [6]. Mercury fulminate ($\text{Hg}(\text{CNO})_2$) is a common explosive primer used for different munition objects. Beldowski et al. [9] estimated that about 300 t of mercury are present in dumped munition in the Baltic Sea.

The quantitatively most important conventional munition compounds are the explosives TNT (2,4,6-trinitrotoluene), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocin), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and tetryl (2,4,6-trinitrophenylmethylnitramine) [6].

Chemical warfare agents (CWAs) include a large number of different compounds that were already produced during World War I as riot control and blistering agents [55]. Prominent examples are the phenylarsenic CWAs

Adamsite, Clark I/II, Triphenylarsine or Lewisite and sulfur-based CWAs, such as mustard gas [8].

Environmental fate of munition compounds

The fate and behaviour of munition compounds, both conventional explosives and CWAs, in the marine environment strongly depends on environmental factors. For example, the solubility of TNT, HMX and RDX increases significantly with temperature and water turbulence [7]. Upon release from the casings, munition compounds spread and traces of both CWA and conventional explosives were discovered in marine organisms. In cod (*Gadus morhua*) collected from a CWA dumpsite near Bornholm in the Baltic Sea residuals of CWA were detected in muscle tissue at higher rates compared to a reference site [59].

Blue mussels (*Mytilus edulis*) exposed to a site contaminated with conventional munition (Kolberger Heide, Kiel Bay, Baltic Sea) had elevated concentrations of TNT and its metabolites in their tissues [79]. This particular area was also affected by “blast in place” (BiP) operations which often result in incomplete (low-order) detonation, leaving substantial quantities of the explosive material in the environment [49, 50]. Concentrations measured in mussel tissue depended on the distance at which the mussels were placed over the contaminated ground. In mussels placed at the ground, 103.75 ± 12.77 ng/g wet weight of 2-ADNT and 131.31 ± 9.53 ng/g wet weight 4-ADNT were recorded. TNT itself was measured with an average concentration of 31.04 ± 3.26 ng/g mussel wet weight. In mussels positioned one meter above ground TNT and 2-ADNT were not detected, but 4-ADNT with an average concentration of 8.71 ± 2.88 ng/g mussel wet weight [79]. Experimental exposures with blue mussels revealed that characteristic shell closing behaviour of bivalves at trigger concentration lead to non-linear responses to exposure concentrations [72]. Accordingly, measured concentrations of TNT and its derivatives in tissues in field exposed mussels might rather lead to an under-estimation of the abundant TNT.

In the same dumping area, significantly elevated concentrations of TNT and its metabolites were found in free ranging bottom dwelling flat fish, dab (*Limanda limanda*) [37]. Measurements were taken from bile fluid, with which detoxification products from the livers are expelled. TNT exceeded the limit of detection only marginally, but 2-ADNT (1.60 ng/mL bile) and 4-ADNT (17.06 ng/mL bile) were detected in significant amounts. This suggests that highly toxic TNT, if taken up by dab is metabolised to less toxic 2-ADNT and 4-ADNT [37]. This was supported by in vitro experiments with liver cells collected from dab (*L. limanda*), plaice (*Pleuronectes platessa*) and flounder (*Platichthys flesus*). TNT added to

the liver cell cultures was rapidly metabolised to 2-ADNT and 4-ADNT [36].

Mercury is a contaminant entering the environment via various sources including war relicts [67]. It has been shown before that mercury as war emission is bioavailable over the water phase for organisms [80]. Beldowski et al. [9] observed increased concentrations of mercury in sediments from a munition dumpsite and also detected mercury fulminate in sediments indicating that that dumped munition may be a local point source of mercury. In addition, Uścińowicz et al. [83], observed high mercury concentrations in Baltic Sea sediments from specific munition dumpsites. In the environment, inorganic mercury can turn into methyl mercury, which bioaccumulates within the food chain. Lang et al. [38], reported higher disease prevalence in fish that exhibited elevated methyl-mercury levels.

It is still unclear if mercury released from dumped munition will significantly increase contamination of organisms, such as mussel or fish living there—or if mercury from diffuse sources may overlay the additional input from dumped munitions. However, mercury exposure originating from dumped munition may contribute to the overall mercury load of organisms.

Biodegradation of organic munition compounds

Organic munition compounds (i.e., TNT, HMX, and RDX) were originally believed to be recalcitrant to microbial biodegradation. More recently, it has been established that natural bacterial assemblages in coastal waters and sediment can metabolize these organic nitrogen sources and even incorporate their carbon and nitrogen into bacterial biomass [56, 75, 76]. Experimental studies suggest that under anaerobic conditions, substantial amounts of munition derived nitrogen is metabolised to aerobic nitrogen (N_2) which is released to the atmosphere [2]. Rates of biodegradation of organic munition compounds depends on the assemblage of micro-organisms [19, 77] and their activity is dependent on environmental factors, such as temperature and salinity [26].

Also, the habitat structures available for microbial colonisation, such as the grain size of sediments, influence biodegradation activity. Both, sorption and microbial degradation of organic munition compounds occurred faster in sediments with smaller grain size [76] and higher carbon content [3]. It is difficult to predict how climate change will alter sedimentation of organic materials. Extended vegetation periods in combination with fertilization may increase primary production and sedimentation of organic matter. Marine sediments, transferred to laboratory conditions, exhibited the highest rate of TNT disappearance under biotic conditions, but also exhibited high sorption affinity for TNT under abiotic conditions.

At higher temperature, kinetics of biotic processes outpaced abiotic processes, but at low temperature, kinetics of abiotic processes were more significant [17]. Consequently clearance rates for organic munition compounds in marine environments are suspected to be susceptible to climate change effects [56]. However, ocean warming might facilitate the biodegradation of organic munition compounds.

Weather conditions

Important factors that will affect the condition of dumped munitions are weather conditions, such as extreme winds, waves and storms, which are expected to intensify and become more frequent in the future [33]. It is likely that the dissolution of munition compounds in storm events will be enhanced by stronger water movements, most obviously in shallow areas. The deposition or burial of munition objects and distribution of particulate munition material by currents [53] is also likely to increase during extreme weather events. With a burial recording mine placed at a sandy shore lines of the Belgian North Sea at 7–10 m depth, storm events were observed to facilitate vertical relocation of the object deeper in the sediment [62]. This means that extreme weather events, may on the one hand cause burial of munition objects and reduce their release of munition compounds and on the other uncover them and accelerate leakage. In general, location of many munition objects can change over time and encounters of objects along traffic routes or beaches will continue to occur.

To which extent changes in water turbulences influence corrosion of unburied munition shells and the dissolution of their content in aquatic environments was not investigated yet. However, it might be possible that elevated water turbulence rather accelerates corrosion rates and dissolution of munition compounds. On the other hand, concentration gradients of dissolved munition compounds might be less stable in turbulent waters and locally high concentrations of munitions compounds might be less likely to occur.

Climate change will likely result in longer vegetation seasons which may result in higher primary production and enhanced delivery of organic matter to sediments. High organic matter in sediments is known to increase sorption and degradation of organic munition compound [3, 5]. Delivery of organic fine particulates to nowadays sandy bottom munition dumpsites might facilitate the sorption of explosives, but since the critical shear threshold of fine sediments of organic origin is low [40], this may also facilitate transport and spread of munition compounds.

Similar processes were suggested to play a role for the distribution of chemical warfare agents (CWA) via fine biogenic materials. Circulation models at the chemical warfare dumpsites in the Bornholm and Gotland basins of the Baltic Sea revealed that the bottom friction velocity was almost permanently below the resuspension thresholds for the suspended particulate matter and fine sand, and even the Major inflows could not violate the balance. Only occasionally the bottom friction velocity may exceed the resuspension threshold for the fine biogenic material (fluffy layer and cysts) almost everywhere in the deep Baltic basins [89].

Extended vegetation seasons are likely to alter marine habitats differentially. The Baltic Sea is an inland Sea with minor tidal influence and currents and reduced water exchange. With the freshwater inflow, communal and agricultural efflux reach the Baltic Sea that fertilize primary production and enhance formation of organic sediments [52]. Open Oceans are generally more turbulent, due to tides and currents, but fertilization and extended vegetation seasons might alter the marine munition problem here too.

Vegetation period and fertilization are connected with oxygen concentrations, which rise during photosynthetic primary production and decrease during the decomposition of biotic material [24] and regional hypoxia may occur [52]. For marine munition oxygen concentrations matter in the context of corrosion of munition shells [74]. Corrosion is a complex process in marine systems, but shifts in oxic and anoxic conditions are likely to accelerate corrosion [85]. Biodegradation of organic munition compounds occurs under aerobic and anaerobic conditions [4, 5] and the speed of degradation in sediments increased with low grain size, high carbon content [3]. Further research is needed to get a better understanding of how climate change, vegetation season, fertilization and oxygen concentrations interact on the fate of marine munitions.

In specific marine habitat situations, such as the semi-enclosed shallow Baltic Sea, more stable stratification is predicted as a result of ongoing climate change [32, 52]. This is explained by changes in re-stratification during spring caused by the increase of the mean temperature. In future, temperatures in the Baltic Sea are expected to be usually higher than the temperature of maximum density and thermally induced stratification will start without prior thermal convection [32]. Earlier and stronger spring blooms are a consequence which are facilitated by nutrient input to the Baltic Sea from inflowing freshwater systems. As a result, sedimentation of organic matter and its decomposing causes hypoxia in deeper water layers [52]. The Baltic Sea is a special marine habitat, but it teaches us, that we need to look at specific habitat/

local conditions, if we want to understand how marine munition will develop in future. In deeper zones of the Baltic, in which most munition was dumped, in future, more stable stratification and more stable (prolonged) hypoxic/anoxic conditions have to be expected. One might hypothesize that under such conditions corrosion of munition shells occurs slower as with convection and shifts between oxic and anoxic conditions.

How weather conditions affect marine munition strongly depends on the location and the surrounding habitat conditions. The deeper they are located, the less likely direct weather impact becomes. In more shallow waters, exposure to waves and currents and the surrounding sediments form complex interactions which in concert will determine the fate of munition objects. To gain a better understanding of how marine munition will be affected by weather conditions, more habitat specific investigations are needed.

Salinity

Changing ocean salinity, for example depending on precipitation in certain regions [33], are expected during ongoing climate change. For ship wrecks, e.g., WWII relicts, it is established that salinity alters the speed of corrosion [46, 47] and generally abundance of salt accelerates the corrosion rates of shipwrecks [57].

Yet only limited information is available on how changes in salinity may influence corrosion of munition shells and the fate of organic munition compounds. Sorption of munition compounds to passive samplers did not vary with natural salinity gradients [87]. With an in situ study, Beck et al. [7] measured dissolution of TNT in a salinity range from 15.4 to 18.2 ppt and conclude that a salinity effects is rather small compared to other factors.

However, the photochemical degradation of dinitrotoluene (DNT), a degradation product of TNT was more strongly influenced by salinity and dissolved organic matter (DOM) as by nitrate, pH and temperature in their natural range [64]. Increasing salinity and increasing DOM enhanced the photochemical degradation of DNT [64]. In sum, specific information on the effects of salinity on the corrosion of munition shells is lacking. Sorption and dissolution of organic munition compounds does not seem to be altered strongly by salinity. However, increased salinity seems to enhance the photochemical degradation of organic munition compounds.

UV radiation

UV radiation is expected to increase in future by halogenated pollutants and rising greenhouse gas concentrations, which alter the spatial distribution of ozone that protects the earth's surface from excessive UV radiation [18, 71].

The photochemical sensitivity of conventional munition compounds is well known. UV radiation enhances their transformation and degradation and such effects are stronger in salt, compared to fresh water [44, 64].

Thus, it is clear that exposure of munition compounds to increased UV radiation will enhance degradation processes and the formation of degradation products. Since the intensity of UV radiation decreases with water depth, effects of UV radiation is particularly significant for munition objects lying in shallow water [6].

Exposure of aquatic organisms to pollution in combination with UV radiation can enhance the toxicity of pollutants [63]. There is also evidence that toxicity of explosive compounds increases through photoactivation and photolysis to other toxic compounds [21, 88]. In sum, elevated UV radiation coinciding with global climate change, will have two sided effects. On the one hand degradation of conventional munition compounds will be accelerated in shallow waters. On the other hand, organisms will be exposed to elevated amounts of toxic photodegradation products.

Water temperature

The average global sea surface temperature rose by 0.85 °C over the past 130 years and this trend is expected to accelerate in the future [28, 33]. When addressing the influence of rising water temperatures on the contamination of the marine environment by dumped munitions mainly corrosion and the solubility, sorption and degradation/transformation of the leaking compounds must be considered.

The progressive corrosion process of munition housings is suggested to be influenced by temperature [34], among other factors, but this relationship has not yet been investigated with a focus on marine dumped munitions. MacLeod [46, 47] investigated the in-situ corrosion of WW II shipwrecks over years and derived an influence of temperature on corrosion of steel. North and Macleod [60] investigated the complex relationship between corrosion of metals and temperature and estimated a doubled corrosion rate for every 10 °C in temperature increase. However, this only applies without any biological interaction, such as protective biological growth on the corroding surface [42]. The munition housings are commonly made out of iron steel, but can also contain copper and other non-ferrous metals for driving bands and fuses [6, 78, 82]. North and Macleod [60] calculated a corrosion rate of 0.11 mm/year for steel, copper might corrode twice as fast in marine environments.

A higher water temperature is likely to increase the solubility of compounds from dumped munitions [45]. An in situ study investigated the solubility of exposed conventional munition material in the Baltic Sea and did not

find substantial differences in the solubility during different seasons with changing water temperatures [7]. On the other hand, sorption of TNT to marine sediments, sand and silt was inversely correlated to temperature change [5]. In addition, the absorption of TNT and RDX in passive samplers was inversely correlated to temperature change [87].

Temperature rise will not only influence the abundance of dissolved munition compounds, but will also change the exposure conditions for marine organisms, for example fish. Processes that alter toxicokinetics, such as diffusion rates, ventilation, metabolic rates and feeding activity, may result in increased uptake of pollutants as water temperature rises. Change of single factors or multiple factors in concert, may lead to increased exposure rates and toxicity for the organisms. On the other hand, increased elimination and detoxification rate of pollutants in the organism can coincide with increased metabolic activity, which counteracts potential toxification of the organisms [13, 29, 48, 71].

Multiple studies reported increased toxicity at higher temperatures to aquatic organisms, and suggest that changes in toxicity are based on the altered substance-specific bioactivation and detoxification during biotransformation of xenobiotics [15, 25, 61, 65]. Experimental exposure of marine flatworms to the TNT derivate 4-ADNT revealed that its toxicity increases with temperature. After 12 day exposure of flatworms to ADNT (33.3 mg/L) at 30 °C mortality was 100% and at 21 °C mortality was close to 60%. In corresponding controls no mortality was recorded [10]. This observation clearly illustrates that toxicity of explosives is temperature dependent.

In fish, specific tests with munition compounds and temperature are lacking. However, Schartup et al. [70], explained an increase in tissue methyl-mercury concentrations in Atlantic bluefin tuna (*Thunnus thynnus*) with increases in seawater temperature. Buckman et al. [14] showed that increased water temperature shortened the half-life of PCBs in the water and simultaneously the biotransformation of PCBs in rainbow trout increased. Consequently, the concentrations for certain toxic, hydroxylated PCBs increased in the trout plasma with rising temperatures. The herbicide atrazine showed increased toxicity in catfish with increasing temperature, also in combination with lower oxygen level in the water [25]. Since the biotransformation of munition compounds is crucial for their toxicity, future rise in water temperature will also have consequences for exposed fish. Taking this into account, as a precautionary principle, higher toxicity to fish species exposed to munition compounds should be expected with rising temperatures.

Another possibility is that degradation products are more toxic than their original compounds, such as 1,2,5-trithiepane derived from mustard sulphur, which was extensively used in CWA [20]. In this case elevated degradation rates due to temperature increase might result in higher abundance of highly toxic degradation products.

An important aspect of temperature change for the marine munition problem is that biodegradation of organic munition compounds leaking from corroded munition shells is positively correlated with temperature rise [17].

Crucial questions for the marine munition problem are, how the mentioned effects interact with one another will there be effects dominating over others? Possible predictions are that rising temperature increases corrosion of munition shells and the solubility of organic munition compounds, which will result in higher emission from dumped munitions. A further possible prediction is that sorption of organic munition compounds to sediments will decrease with rising temperatures. Accordingly, amounts of munition compounds available in the water column might increase.

If (how) elevated amounts of released munition compounds will be detrimental to the environment is difficult to estimate. This will to a large extent depend on the degradation speed of toxic munition compounds which is likely to increase with rising temperatures. On the other hand, toxicity of munition compounds is likely to increase with temperature too. Which of these processes will dominate might in the end also depend on other factors, such as the availability of carbon for biodegrading microorganisms.

Stress-on-stress responses

Climate change is expected to have strong impact on marine ecosystems [22]. Abiotic and biotic conditions change and this causes stress to inhabiting organisms (e.g., [54, 69]). Climate change induced stress is likely to interfere with the ability of marine organisms to cope with pollutants and their potential toxicity and accumulation [35]. The example of marine flatworms that showed higher mortality during experimental exposure to the TNT derivate 4-ADNT at 30 °C compared to 21 °C [10] suggests that multiple stressors amplify toxic effects of munition compounds.

An example for a fish species that is subjected to multiple stressors and clearly declines, is the Baltic cod (*Gadus morhua*). Fishing pressure plays a role [1], but also the expansion of areas/periods with hypoxic conditions in the Baltic Sea [81]. At one of the most important spawning sites of the eastern Baltic cod, the Bornholm basin [30, 31], about 50,000 t chemical weapons (CW) were

dumped after WW II [11, 84]. Indeed traces of chemical warfare agents (CWA) were detected in cod from the Bornholm Basin [59]. In Baltic mussels (*Mytilus trossulus*) exposed in the Bornholm Basin CWA were not detected, but a series of biomarkers indicated that the mussels suffered from stress at the dumpsite [39]. It was proposed that multiple stressors including CWA affect the health status of mussels and cod in the Baltic Sea [12].

In situations with multiple stressors it is extremely difficult to disentangle which stressors have more or less strong fitness effects and which stressors might amplify one another's effects. For the marine munition problem, experimental exposure studies with munition compounds and additional stressors are needed, to make more robust predictions how environmental stress triggered by climate change, interferes with toxic stress from munition compounds.

Conclusions

Climate change will influence a number of factors that determine the fate of munition compounds in marine environments. Direct effects concern mechanical impact through water turbulences which is likely to increase the leakage of toxic compounds from dumped munitions. Corrosion is a ticking time bomb, which will lead to increased leakage from dumped munitions. There is no doubt about this ongoing process, but it is likely that climate change will rather accelerate corrosion, than attenuate it. Organism confronted with munition compounds seem to be able to metabolise them to some extent, toxic effects of munition compounds might outweigh the benefits of metabolism and degradation, in particular when organisms are exposed to environmental stress due to climate change.

Outlook

The present review illustrates that the marine munition issues are extremely complex. We are only at the beginning to understand how environmental factors alter the fate of marine munitions. Given the complexity of the problem, a lot of information is still missing. Although general information about locations of munition dumps is often available, detailed data on types of munition and their state are often missing. Furthermore, it is often unknown if munition compounds are leaking out and what the effects on the environment are. More detailed investigations at multiple contaminated sites are urgently needed. For the question how climate change impacts on marine munition, in particular comparisons of data from dump sites across different climate zone would be very helpful. Such comparisons ask for standardised sampling methods to be applied to measure the (corrosive) state of munition objects, but also the amounts of leaking

compounds and their presence in and effects on biota. Furthermore, laboratory studies are needed in which variables affected by climate change (e.g., temperature, shifts in oxic–anoxic conditions) are tested on biota together with environmentally relevant concentrations of munition compounds. When more data about state and emission of marine munition become available, it would be extremely valuable to develop models that enable predictions of how climate variables will interact with marine munition.

Acknowledgements

We thank Katja Broeck who initiated the conceptualisation of the present manuscript.

Authors' contributions

The concept and idea of this review was developed by JPS and DK and UK. DK wrote a first draft, which was elaborated by JPS. UK and KS provided input on the drafted manuscript. All authors read and approved the final manuscript.

Funding

The positions of Katharina Straumer and Daniel Koske were financed by the EU INTERREG Baltic Sea Region Programme 2014–2020 within the DAIMON 2 project.

Availability of data and materials

Not applicable.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

There are no competing interests.

Received: 11 May 2021 Accepted: 31 July 2021

Published online: 28 August 2021

References

- Andersen KH, Farnsworth KD, Thygesen UH, Beyer JE (2007) The evolutionary pressure from fishing on size at maturation of Baltic cod. *Ecol Model* 204(1–2):246–252
- Ariyaratna T, Ballentine M, Vlahos P, Smith RW, Cooper C, Bohlke JK, Fallis S, Groshens TJ, Tobias C (2019) Tracing the cycling and fate of the munition, Hexahydro-1,3,5-trinitro-1,3,5-triazine in a simulated sandy coastal marine habitat with a stable isotopic tracer, N-15- RDX. *Sci Total Environ* 647:369–378
- Ariyaratna T, Ballentine M, Vlahos P, Smith RW, Cooper C, Bohlke JK, Fallis S, Groshens TJ, Tobias C (2020) Degradation of RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) in contrasting coastal marine habitats: Subtidal non-vegetated (sand), subtidal vegetated (silt/eel grass), and intertidal marsh. *Sci Total Environ* 745:1
- Ariyaratna T, Vlahos P, Smith RW, Fallis S, Groshens TJ, Tobias C (2017) Biodegradation and mineralization of isotopically labeled TNT and RDX in anaerobic marine sediments. *Environ Toxicol Chem* 36(5):1170–1180
- Ariyaratna T, Vlahos P, Tobias C, Smith R (2016) Sorption kinetics of TNT and RDX in anaerobic freshwater and marine sediments: batch studies. *Environ Toxicol Chem* 35(1):47–55
- Beck AJ, Gledhill M, Schlosser C, Stamer B, Böttcher C, Sternheim J, Greinert J, Achterberg EP (2018) Spread, behavior, and ecosystem consequences of conventional munitions compounds in coastal marine waters. *Front Mar Sci* 5:1
- Beck AJ, van der Lee EM, Eggert A, Stamer B, Gledhill M, Schlosser C, Achterberg EP (2019) In situ measurements of explosive compound dissolution fluxes from exposed munition material in the Baltic Sea. *Environ Sci Technol* 53(10):5652–5660
- NATO Science for Peace and Security Series C: Environmental Security (2018) In: Beldowski J, Long T, Söderström M, (eds) Towards the Monitoring of Dumped Munitions Threat (MODUM). Springer Dordrecht, Netherlands
- Beldowski J, Szubska M, Siedlewicz G, Korejwo E, Grabowski M, Beldowska M, Kwasigroch U, Fabisiak J, Łońska E, Szala M, Pempkowiak J (2019) Sea-dumped ammunition as a possible source of mercury to the Baltic Sea sediments. *Sci Total Environ* 674:363–373
- Bickmeyer U, Meinen I, Meyer S, Kroner S, Brenner M (2020). Fluorescence measurements of the marine flatworm *Macrostomum lignano* during exposure to TNT and its derivatives 2-ADNT and 4-ADNT. *Mar Environ Res* 161:105041
- Böttcher C, Knobloch T, Rühl NP, Sternheim J, Wichert U, Wöhler J (2011) Munitionsbelastung der Deutschen Meeresgewässer - Bestand-saufnahme und Empfehlungen (Stand 2011). BSH, Hamburg, Rostock
- Brenner M, Baude R, Broeg K (2012) Impact assessment of chemical warfare agents from dumping sites in the Baltic Sea on the health of cod (*Gadus morhua* L.) and blue mussels (*Mytilus edulis* L.). *Comp Biochem Physiol* 163(1):S12–S12
- Buchwalter DB, Jenkins JJ, Curtis LR (2003) Temperature influences on water permeability and chlorpyrifos uptake in aquatic insects with differing respiratory strategies. *Environ Toxicol Chem* 22(11):2806–2812
- Buckman AH, Brown SB, Small J, Muir DCG, Parrott J, Solomon KR, Fisk AT (2007) Role of temperature and enzyme induction in the biotransformation of polychlorinated biphenyls and bioformation of hydroxylated polychlorinated biphenyls by rainbow trout (*Oncorhynchus mykiss*). *Environ Sci Technol* 41(11):3856–3863
- Capkin E, Altinok I, Karahan S (2006) Water quality and fish size affect toxicity of endosulfan, an organochlorine pesticide, to rainbow trout. *Chemosphere* 64(10):1793–1800
- Carton G, Jagusiewicz A (2009) Historic disposal of munitions in u.s. and european coastal waters, how historic information can be used in characterizing and managing risk. *Mar Technol Soc J* 43(4):16–32
- Chappell MA, Porter BE, Price CL, Pettway BA, George RD (2011) Differential kinetics and temperature dependence of abiotic and biotic processes controlling the environmental fate of TNT in simulated marine systems. *Mar Pollut Bull* 62(8):1736–1743
- Coelho FJRC, Santos AL, Coimbra J, Almeida A, Cunha A, Cleary DFR, Calado R, Gomes NCM (2013) Interactive effects of global climate change and pollution on marine microbes: the way ahead. *Ecol Evol* 3(6):1808–1818
- Crawford RL (1995) Biodegradation of Nitrated Munition Compounds and Herbicides by Obligately Anaerobic Bacteria. In: Spain JC (ed) Biodegradation of Nitroaromatic Compounds. Springer US, Boston, MA, p 87–98
- Czub M, Nawala J, Popiel S, Dziedzic D, Brzeziński T, Maszczyk P, Sander-H, Fabisiak J, Beldowski J, Kotwicki L (2020) Acute aquatic toxicity of sulfur mustard and its degradation products to *Daphnia magna*. *Mar Environ Res* 161:105077
- Dave G, Nilsson E, Wernersson AS (2000) Sediment and water phase toxicity and UV-activation of six chemicals used in military explosives. *Aquat Ecosyst Health Manage* 3(3):291–299
- Doney SC, Ruckelshaus M, Duffy JE, Barry JP, Chan F, English CA, Galindo HM, Grebmeier JM, Hollowed AB, Knowlton N, Polovina J, Rabalais NN, Sydeman WJ, Talley LD (2012) Climate change impacts on marine ecosystems. *Ann Rev Mar Sci* 4:11–37
- Dore JE, Lukas R, Sadler DW, Church MJ, Karl DM (2009) Physical and biogeochemical modulation of ocean acidification in the central North Pacific. *Proc Natl Acad Sci* 106(30):12235
- Fennel K, Testa JM (2019) Biogeochemical Controls on Coastal Hypoxia. *Annual Review of Marine Science*, Vol 11. C. A Carlson and S J Giovannoni 11:105–130
- Gaunt P, Barker SA (2000) Matrix solid phase dispersion extraction of triazines from catfish tissues; examination of the effects of temperature and dissolved oxygen on the toxicity of atrazine. *Int J Environ Poll* 13(1–6):284–312

26. Gorontzy T, Drzyzga O, Kahl MW, Bruns-nagel D, Breitung J, E. v. Loew and K. H. Blotevogel, (1994) Microbial degradation of explosives and related compounds. *Crit Rev Microbiol* 20(4):265–284
27. Greenberg MI, Sexton KJ, Vearrier D (2016) Sea-dumped chemical weapons: environmental risk, occupational hazard. *Clin Toxicol* 54(2):79–91
28. Harley CD, Randall Hughes A, Hultgren KM, Miner BG, Sorte CJ, Thornber CS, Rodriguez LF, Tomanek L, Williams SL (2006) The impacts of climate change in coastal marine systems. *Ecol Lett* 9(2):228–241
29. Heugens EHW, Hendriks AJ, Dekker T, N. M. v. Straalen and W. Admiraal, (2001) A review of the effects of multiple stressors on aquatic organisms and analysis of uncertainty factors for use in risk assessment. *Crit Rev Toxicol* 31(3):247–284
30. Hinrichsen HH, John MS, Lehmann A, MacKenzie BR, Koster FW (2002) Resolving the impact of short-term variations in physical processes impacting on the spawning environment of eastern Baltic cod: application of a 3-D hydrodynamic model. *J Mar Syst* 32(4):281–294
31. Hinrichsen HH, von Dewitz B, Lehmann A, Bergstrom U, Hussy K (2017) Spatio-temporal dynamics of cod nursery areas in the Baltic Sea. *Prog Oceanogr* 155:28–40
32. Hordoir R, Meier HEM (2012) Effect of climate change on the thermal stratification of the Baltic Sea: a sensitivity experiment. *Clim Dyn* 38(9–10):1703–1713
33. IPCC (2014) Climate Change 2014: Synthesis Report. In: Pachauri RK and Meyer LA (eds) Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC Core writing team: 151. Geneva, Switzerland
34. Jurczak W, Fabisiak J (2017) Corrosion of ammunition dumped in the Baltic Sea. *J KONBIN*. 41(1):227–246
35. Kibria G, Nuggeoda D, Rose G, Haroon AKY (2021) Climate change impacts on pollutants mobilization and interactive effects of climate change and pollutants on toxicity and bioaccumulation of pollutants in estuarine and marine biota and linkage to seafood security. *Marine Poll Bull* 167:1
36. Koske D, Goldenstein NI, Rosenberger T, Machulik U, Hanel R, Kammann U (2020) Dumped munitions: new insights into the metabolism of 2,4,6-trinitrotoluene in Baltic flatfish. *Mar Environ Res* 160:104992
37. Koske D, Straumer K, Goldenstein NI, Hanel R, Lang T, Kammann U (2020) First evidence of explosives and their degradation products in dab (*Limanda limanda* L.) from a munition dumpsite in the Baltic Sea. *Mar Poll Bull* 155:7
38. Lang T, Kruse R, Haarich M, Wosniok W (2017) Mercury species in dab (*Limanda limanda*) from the North Sea, Baltic Sea and Icelandic waters in relation to host-specific variables. *Mar Environ Res* 124:32–40
39. Lastumaki A, Turja R, Brenner M, Vanninen P, Niemikoski H, Butrimaviciene L, Stankeviciute M, Lehtonen KK (2020) Biological effects of dumped chemical weapons in the Baltic Sea: a multi-biomarker study using caged mussels at the Bornholm main dumping site. *Mar Environ Res* 161:1
40. Le Hir P, Monbet Y, Orvain F (2007) Sediment erodability in sediment transport modelling: can we account for biota effects? *Cont Shelf Res* 27(8):1116–1142
41. Li SX, George RD, Hihara LH (2016) Corrosion analysis and characteristics of discarded military munitions in ocean waters. *Corros Sci* 102:36–43
42. Lonska E (2017) Influence of marine microorganisms on corrosion of chemical munition shell dumped in the Baltic Sea. *J Ecol Saf* 11:188–202
43. Lotufo GR, Belden JB, Fisher JC, Chen SF, Mowery RA, Chambliss CK, Rosen G (2016) Accumulation and depuration of trinitrotoluene and related extractable and nonextractable (bound) residues in marine fish and mussels. *Environ Pollut* 210:129–136
44. Luning Prak DJ, Breuer JE, Rios EA, Jedlicka EE, O'Sullivan DW (2017) Photolysis of 2,4,6-trinitrotoluene in seawater and estuary water: Impact of pH, temperature, salinity, and dissolved organic matter. *Mar Pollut Bull* 114(2):977–986
45. Lynch JC, Myers KF, Brannon JM, Delfino JJ (2001) Effects of pH and temperature on the aqueous solubility and dissolution rate of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). *J Chem Eng Data* 46(6):1549–1555
46. MacLeod ID (2016) In-situ corrosion measurements of WWII shipwrecks in chuuk lagoon, quantification of decay mechanisms and rates of deterioration. *Front Mar Sci* 3:1
47. MacLeod ID (2016) In-situ corrosion measurements of WWII shipwrecks in chuuk lagoon, quantification of decay mechanisms and rates of deterioration. *Front Mar Sci* 3:38
48. Maruya KA, Smalling KL, Vetter W (2005) Temperature and congener structure affect the enantioselectivity of toxaphene elimination by fish. *Environ Sci Technol* 39(11):3999–4004
49. Maser E, Strehse JS (2021) Can seafood from marine sites of dumped World War relics be eaten? *Arch Toxicol* 95(7):2255–2261
50. Maser E, Strehse JS (2021) "Don't Blast": blast-in-place (BiP) operations of dumped World War munitions in the oceans significantly increase hazards to the environment and the human seafood consumer (vol 94, pg 1941, 2020). *Arch Toxicol* 95(7):2603–2603
51. IPCC (2018) Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. In: Masson-Delmotte V, Zhai P, Pörtner HO, Roberts D, Skea J, Shukla PR, Pirani A, Moufouma-Okia W, Péan C, Pidcock R, Connors S (eds) World Meteorological Organization. (In press)
52. Meier HEM, Hoglund A, Eilola K, Almroth-Rosell E (2017) Impact of accelerated future global mean sea level rise on hypoxia in the Baltic Sea. *Clim Dyn* 49(1–2):163–172
53. Menzel P, Schütt C, Wranik H, Paschen M, Drews A (2018) Towards a general prediction-model for the current-induced mobilisation of objects on the sea floor. *Ocean Eng* 164:160–167
54. Miller KA, Munro GR, Sumaila UR, Cheung WWL (2013) Governing marine fisheries in a changing climate: a game-theoretic perspective. *Can J Agric Econ* 61(2):309–334
55. Mohammed Abdullah Christensen I, Swayne Storgaard M, Fauser P, Foss Hansen S, Bastrup E, Sanderson H (2016) Acute toxicity of sea-dumped chemical munitions: luminating the environmental toxicity of legacy compounds. *Glob Sec* 1(1):39–50
56. Montgomery MT, Boyd TJ, Hall NS, Paerl HW, Osburn CL (2020) Ecosystem capacity for microbial biodegradation of munitions compounds and phenanthrene in three coastal waterways in North Carolina, United States. *ACS Omega* 5(13):7326–7341
57. Moore JD (2015) Long-term corrosion processes of iron and steel shipwrecks in the marine environment: a review of current knowledge. *J Marit Archaeol* 10(3):191–204
58. National Oceanic and Atmospheric Administration N (2020) Retrieved 2.13., 2020, Available via <https://esrl.noaa.gov/gmd/ccgg/trends/>
59. Niemikoski H, Straumer K, Ahvo A, Turja R, Brenner M, Rautanen T, Lang T, Lehtonen KK, Vanninen P (2020) Detection of chemical warfare agent related phenylarsenic compounds and multi-biomarker responses in cod (*Gadus morhua*) from munition dumpsites. *Mar Environ Res* 162:105160
60. North N, Macleod I (1987) Corrosion of metals. In: Pearson C (ed) Corrosion of Marine Archeological Objects. Butterworths, London, pp 68–98
61. Noyes PD, McElwee MK, Miller HD, Clark BW, Van Tiem LA, Walcott KC, Erwin KN, Levin ED (2009) The toxicology of climate change: environmental contaminants in a warming world. *Environ Int* 35(6):971–986
62. Papili S, Wever T, Dupont Y, Van Lancker V (2014) Storm influence on the burial of objects in a shallow sandy shelf environment. *Mar Geol* 349:61–72
63. Peachey RB (2005) The synergism between hydrocarbon pollutants and UV radiation: a potential link between coastal pollution and larval mortality. *J Exp Mar Biol Ecol* 315(1):103–114
64. Prak DJL, Milewski EA, Jedlicka EE, Kersey AJ, O'Sullivan DW (2013) Influence of pH, temperature, salinity, and dissolved organic matter on the photolysis of 2,4-dinitrotoluene and 2,6-dinitrotoluene in seawater. *Mar Chem* 157:233–241
65. Ratushnyak A, Andreeva MG, Trushin MV (2005) Effects of type II pyrethroids on *Daphnia magna*: dose and temperature dependences. *Riv Biol* 98(2):349–357
66. Rosen G, Lotufo GR, George RD, Wild B, Rabalais LK, Morrison S, Belden JB (2018) Field validation of POCIS for monitoring at underwater munitions sites. *Environ Toxicol Chem* 37(8):2257–2267
67. Rua-Ibarz A, Bolea-Fernandez E, Maaga A, Frantzen S, Valdersnes S, and Vanhaecke F (2016) Assessment of Hg pollution released from a WWII submarine wreck (U-864) by Hg isotopic analysis of sediments and cancer pagurus tissues. *Environ Sci Technol* 50(19):10361–10369

68. Sanderson H, Fauser P, Stauber RS, Christensen J, Løfstrøm P, Becker T (2017) Civilian exposure to munitions-specific carcinogens and resulting cancer risks for civilians on the Puerto Rican island of Vieques following military exercises from 1947 to 1998. *Global Sec* 2(1):40–61
69. Scavia D, Field JC, Boesch DF, Buddemeier RW, Burkett V, Cayan DR, Fogarty M, Harwell MA, Howarth RW, Mason C, Reed DJ, Royer TC, Sallenger AH, Titus JG (2002) Climate change impacts on US coastal and marine ecosystems. *Estuaries* 25(2):149–164
70. Schartup AT, Thackray CP, Qureshi A, Dassuncao C, Gillespie K, Hanke A, Sunderland EM (2019) Climate change and overfishing increase neurotoxicant in marine predators. *Nature* 572(7771):648–650
71. Schiedek D, Sundelin B, Readman JW, Macdonald RW (2007) Interactions between climate change and contaminants. *Mar Pollut Bull* 54(12):1845–1856
72. Schuster R, Strehse JS, Ahvo A, Turja R, Maser E, Bickmeyer U, Lehtonen KK, Brenner M (2021) Exposure to dissolved TNT causes multilevel biological effects in Baltic mussels (*Mytilus* spp.). *Mar Environ Res* 167:1
73. Siegenthaler U, Sarmiento JL (1993) Atmospheric carbon dioxide and the ocean. *Nature* 365(6442):119–125
74. Silva JAK, Chock T (2016) Munitions integrity and corrosion features observed during the HUMMA deep-sea munitions disposal site investigations. *Deep-Sea Res* 128:14–24
75. Smith RW, Vlahos P, Bohlke JK, Ariyaratna T, Ballentine M, Cooper C, Fallis S, Groshens TJ, Tobias C (2015) Tracing the Cycling and Fate of the Explosive 2,4,6-Trinitrotoluene in Coastal Marine Systems with a Stable Isotopic Tracer, N-15- TNT. *Environ Sci Technol* 49(20):12223–12231
76. Smith RW, Vlahos P, Tobias C, Ballentine M, Ariyaratna T, Cooper C (2013) Removal rates of dissolved munitions compounds in seawater. *Chemosphere* 92(8):898–904
77. Spain JC (1995) Biodegradation of nitroaromatic compounds. *Ann Rev Microbiol* 49(1):523–555
78. Srinivasan R (2016) ECS Meeting
79. Strehse JS, Appel D, Geist C, Martin HJ, Maser E (2017) Biomonitoring of 2,4,6-trinitrotoluene and degradation products in the marine environment with transplanted blue mussels (*M. edulis*). *Toxicology* 390:117–123
80. Sun R, Hintelmann H, Liu Y, Li X, Dimock B (2016) Two centuries of coral skeletons from the Northern south China sea record Mercury missions from modern chinese wars. *Environ Sci Technol* 50(11):5481–5488
81. Teschner EC, Kraus G, Neuenfeldt S, Voss R, Hinrichsen HH, Koster FW (2010) Impact of hypoxia on consumption of Baltic cod in a multispecies stock assessment context. *J Appl Ichthyol* 26(6):836–842
82. Tornero V, Hanke G (2016) Chemical contaminants entering the marine environment from sea-based sources: a review with a focus on European seas. *Mar Pollut Bull* 112(1):17–38
83. Uścińowicz S (2011) Geochemistry of Baltic Sea surface sediments. Polish Geological Institute-National Research Institute, Warsaw
84. Vanninen P, Ostin A, Beldowski J, Pedersen EA, Soderstrom M, Szubska M, Grabowski M, Siedlewicz G, Czub M, Popiel S, Dziedzic D, Jakacki J, Paczek B, Nawala J (2020) Exposure status of sea-dumped chemical warfare agents in the Baltic Sea. *Mar Environ Res* 161:1
85. Videla HA (2000) An overview of mechanisms by which sulphate-reducing bacteria influence corrosion of steel in marine environments. *Biofouling* 15(1–3):37–47
86. Voie ØA, Mariussen E (2017) Risk assessment of sea dumped conventional munitions. *Propel Expl Pyrotechn* 42(1):98–105
87. Warren JK, Vlahos P, Smith R, Tobias C (2018) Investigation of a new passive sampler for the detection of munitions compounds in marine and freshwater systems. *Environ Toxicol Chem* 37(7):1990–1997
88. Woodley C, Downs C (2014) Ecological Risk Assessment of Munitions Compounds on Coral and Coral Reef Health
89. Zhurbas V, Vali G, Golenko M, Paka V (2018) Variability of bottom friction velocity along the inflow water pathway in the Baltic Sea. *J Mar Syst* 184:50–58

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Submit your manuscript to a SpringerOpen[®] journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► [springeropen.com](https://www.springeropen.com)