GEOMAR REPORT

GEOMAR
Helmholtz-Zentrum für Ozeanforschung Kiel

Practical Guide for Environmental Monitoring of Conventional Munitions in the Seas

Results from the BMBF funded project UDEMM "Umweltmonitoring für die Delaboration von Munition im Meer"

Version 1.1

Berichte aus dem GEOMAR
Helmholtz-Zentrum für Ozeanforschung Kiel

Nr. 54 (N. Ser.)

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Version / Date	Contribution	Contributor
26 April 2019	First outline draft	UDEMM partners; GEOMAR, CAU, IOW
5 September 2019	First distributed draft V1.1	UDEMM partners; GEOMAR, CAU, IOW, BLANO, EGEOS
16 September 2019	Added: Biota analyses in section 2.3	GEOMAR
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Contents

Preface

This "Practical Guide for Environmental Monitoring of Conventional Munitions in the Sea" has been developed as part of the joint scientific project UDEMM (March 2016 - June 2019) funded by the Federal Ministry of Education and Research Germany with partners from GEOMAR Helmholtz-Centre for Ocean Research Kiel (GEOMAR), the Christian-Albrechts University in Kiel (CAU) and the Baltic Sea Research Institute in Warnemünde (IOW). Four research groups combined their expertise to test and develop new methodologies, develop a monitoring strategy and investigate the current environmental state of a munitions dumping ground. The detailed objectives were to:

- better understand the current state of munitions contamination in the munitions dumping ground at Kolberger Heide
- apply or newly develop state-of-the-art monitoring technologies for:
    a) highly detailed mapping of munitions on the seafloor with hydroacoustic and optical means
    b) the chemical analyses of munitions contaminants in water and sediments
    c) the uptake of munitions contaminants into organisms and the establishment of toxic thresholds
- setup and advance an existing oceanographic model of the Baltic Sea to extrapolate the distribution of munitions contamination
- verify the validity of assumptions and modelling during sampling campaigns in Kiel Bay and the entire German Baltic Sea

Four research groups worked on these objectives. The group of Prof. Greinert (GEOMAR) applied multibeam mapping technologies, visual investigations by towed camera, autonomous underwater vehicles (AUV) and divers as well as sediment sampling to map and classify munition and the specific habitat within the different study areas. These maps served as base information to guide water sampling and in-situ experiments for TNT dissolution rates that were undertaken by the group of Prof. Achterberg (GEOMAR). A second focus of Achterberg's group was to establish a workflow and analytical technologies for measuring munitions compounds (MC) in water samples with very low detection limits on the order of fg/L (10^{-15}g/L). In parallel the group of Prof. Maser (CAU) aimed at using mussels for biomonitoring of munitions contaminants Analytical advancements and toxicological interpretation of data were part of the group's work. Finally the group of Dr. Graewe (IOW) used the existing Baltic Sea Model (GETM; General Estuarine Transport Model) and implemented chemical and biological modules for the dissolution and turnover of explosive compounds in dependence of seasonally changing current and temperature conditions.

For logistic reasons, the area marked as explosives dumping ground (disused) located in the marine area Kolberger Heide, just off Schönberg (Plön County, Schleswig-Holstein (SH)) was selected as the main study area. This shallow area (7-19m water depth), only 12 nautical miles (nmi) from Kiel, was the ideal location for such scientific studies, easy to reach with GEOMAR vessels and shallow enough for divers and with reasonably good visibility due to the sandy sediment. From the very beginning it was clear that an integrated approach of geologists/geophysicists, chemists, toxicologists and physical oceanographers was needed to acquire and generate scientifically valid data to fulfil the objectives mentioned above.

The aim of this Practical Guide is to summarize the results of the UDEMM project, give an evaluation of the state of contamination in the Kolberger Heide, introduce the use of commonly available and newly developed technologies and present a blueprint for monitoring efforts with regards to the "Environmental Monitoring of Conventional Munitions in the Sea". Some, but not all of the presented results have been published in peer reviewed scientific journals. Several assumptions are presented although a final and scientifically sound proof cannot be given; this is because long-term monitoring still needs to be performed before conclusions can be drawn.

This guide is a living document, which we aim to update in the coming years as part of new projects and in-house investigations. Thus it should not be seen as a final product but rather as a work in progress. Nevertheless, we believe that substantial progress has been made in developing a monitoring strategy and the necessary technologies, and that these are now accessible to scientists, governmental bodies, NGOs, and companies who are asked to implement such monitoring activities.

1. Conventional munitions in the sea: Threats and problems

1.1 What are the threats?

Several threats exist with regards to munitions in the sea. The most important one today in Germany – and many other countries – is the risk of explosions during underwater construction work. In Germany the establishment of offshore wind-parks for power generation brought the problem of munitions in the sea again to the attention of politicians and the public. Secondly, findings of munitions along beaches and related accidents with munitions washed onshore, including findings of white phosphorous, highlight that munitions dumped after WWI and WWII are not 'safely stored away' but constitutes a constant threat that impacts beach visitors. Other threats exist, which are presented in Table 1; the risk levels assigned to these threats are how the UDEMM consortium sees them without claiming that scientifically valid data have been acquired as a basis of this assessment. Our assessment is mainly based on own experience and measurements in the field, through discussions with colleagues from other countries, as well as with authorities in Germany as there are: Ministry of Energy, Agriculture, the Environment, Nature and Digitalization in SH (MELUND), and the German Navy, the Kampfmittelräumdienst – Explosive Ordnance Disposal (EOD) service in SH, the German Federal Maritime and Hydrographic Agency (BSH). A thorough risk assessment was not possible as methods and workflows to generate the necessary data were not available at the beginning of the UDEMM project. Only after thorough monitoring efforts have been conducted, a reliable risk assessment can be made. This Practical Guide shows how we, the UDEMM consortium, think such monitoring can/should be done.

Table 1: Current threats as seen by the UDEMM consortium; see more details here[1].

Threats	**Risks in the Baltic Sea (regional to coastal scale)**	**Risks in Kiel Bay (local scale)**
	Marine Traffic	
Ships run on ground	**Low**: No reports of such instances; state of technology and safety features in ships is high.	**Low**: No reports of such instances; state of technology and safety features in ships is high.
	Construction	
General construction	**Medium**: Offshore wind parks are installed in the Baltic and other Seas. Thorough mapping and clearance of construction sites needs to be done prior constructions.	**Low**: Currently no large constructions planned in Kiel Bay, however thorough mapping and clearance of local construction sites needs to be done prior constructions.
Dredging	**Medium**: Most of the area. **Very high**: Spatially threats increase, thorough mapping, clearance or other precautionary measures strongly recommended.	**Low**: With the exceptions of central Hohwachter Bucht and some other restricted areas indicated in official sea charts.
Coastal protection	**Medium**: Most of the area. **Very high**: Spatially threats increase, thorough mapping, clearance or other	**Low**: With exceptions of small sections of beaches known to be contaminated with warfare material.

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[1] Only in German: https://www.schleswig-holstein.de/DE/UXO/Berichte/PDF/Berichte/aa_blmp_langbericht.pdf

	precautionary measures strongly recommended.	
Public & recreational activities		
Public awareness	**Medium**: Concerns are growing that seafood might be contaminated, continuous information is needed.	**High:** Concerns are growing that seafood might be contaminated, Kolberger Heide is in the news and people want to know if seafood is edible and the water quality is still good. Less concerns about the environment.
Tourism; explosives washed on shore	**Medium**: Encounters of warfare material and accidents with white phosphorous are reported annually along German Baltic Sea beaches. Especially white phosphorous mistaken for amber or chunks of explosives washed onshore containing TNT and hexyl brings humans in unintentional contact with hazardous material.	**High:** White phosphorous has been encountered in Laboe, Hohenfelde and Heiligenhafen; propellants and cartridges on beaches of the inner Kiel Fjord and chunks of explosives north and south of its mouth (Danish Wahld, Probstei).
Scuba diving	**Medium**: Recreational diving is generally of low risk, if certain areas are avoided. Due to unintentional relocation of military objects by bottom trawls, safe areas might change their status.	**High:** Inside and around the ports of Kiel, Lübeck and Neustadt/H., the restricted areas off Schönberger Strand (BKB04L), off Falshöft (BKB01L) and the central Hohwachter Bucht might as well be heavily contaminated with warfare material as their immediate vicinity is.
Environment and food		
Environmental pollution	**Medium**: UDEMM studies show that TNT contamination of is virtually ‘everywhere’ along the German Baltic Sea; concentrations are in pM to nM levels.	**High:** At certain hot spots like Kolberger Heide open explosives are in direct contact with sea water.
Uptake of toxic substances into fauna	**Medium**: Uptake of TNT in organisms has been proven at hot spots such as Kolberger Heide, but less uptake has been observed farther away.	**Medium**: Uptake of TNT into organisms has been proven, spatial extent of TNT uptake is greatest directly adjacent to munitions (meter scale).
Pelagic fishing	**Low**: Only traces of MCs measured in the water column.	**Low**: With exceptions of the immediate vicinity of restricted area off Schönberger Strand (BKB04L), the impact area of former firing range training north of Stoller Grund (BKB07L) and Falshöft triangle (BKB01L).
Benthic fishing	**Low**: Benthic fishing is generally of low risk, if certain areas are avoided carefully. Note: Due to unintentional relocation of military objects by ground trawls areas that are usually recognized as safe might change their status.	**Very high:** Inside and around restricted area off Schönberger Strand (BKB04L), the impact area of former firing range training north of Stoller Grund (BKB07L) and Falshöft triangle (BKB01L).
Others		
Terrorism (collection of Explosives/TNT)	**High:** Due to proximity to shore, lack of surveillance of dumping grounds and the easy recovery of munitions and explosive chunks.	**High:** Due to proximity to shore, lack of surveillance of dumping grounds and the easy recovery. Kolberger Heide is a hot spot!
Wrong risk assessment due to insufficient data and knowledge	**Very high:** Due to the lack of knowledge about the current state of the munitions integrity/corrosion, a detailed inventory of munitions occurrence, contamination of the environment, uptake by flora and fauna, distribution patterns of dissolved and particulate contaminants due to normal currents and storm events and no knowledge about temporal changes, detailed and reliable assessments are not possible.	

Risk scale

Low	Known occurrences/incidents are very rare or do not exist, it is very unlikely that circumstances change so that incidences become more likely.
Medium	Incidents can and have occurred and pollution was measurable. Good and scientifically correct media information is needed.
High	The threat is real, proximity to shore makes access easy; uninformed information and media-driven worst-case scenarios will heat up the discussion, human threats are seen as more important than environmental damage.
Very high	Incidents or threats are imminent; misinformation due to a lack of reliable and accurate data and understanding will lead to wrong decisions.

We identified that ***delaying the implemention of sustained monitoring programms is the largest threat.*** Started through the Bund-Länder Ausschuss (since 2018: Bund-Länder Arbeitsgemeinschaft) Nord- und Ostsee, Expertenkreis Munition im Meer (BLANO-Munition), the cooperation between the Federal Republic of Germany and its Federal States of Lower Saxony, Hamburg, Bremen, Schleswig-Holstein and Mecklenburg-Vorpommern needs to continue and should be intensified with one state taking a clear lead, like Schleswig-Holstein does since 2009. Resources for sample collection, analyses, and interpretation (including oceanographic modelling) need to be allocated. Further, an open cooperation between federal and state governmental bodies (BSH, Federal Waterways and Shipping Administration (Wasserstraßen- und Schifffahrtsverwaltung (WSV)), Ministries of Environment, Marine Protection, Economy and the Interior; the German Navy, cross-administration working groups like the BLANO[2] and research institutes/centres and universities (Thünen Institute, IOW, GEOMAR, AWI, CAU, …) is essential for establishing a strategy for monitoring munitions in the seas, to constantly improve technologies and to provide updates on risk assessments. A fundamental prerequisite is to accept the threat of environmental pollution from underwater munitions. Starting establishing one joint federated database portal, where data from all stakeholders can be accessed, needs to be part of a successful monitoring strategy. Data security with some of the data being very sensitive needs to be guaranteed and access rights need to be given accordingly. Without joint data management and data exploration capabilities, a comprehensive, correct and thus informed assessments cannot be made and subsequent decisions and actions might not be as effective as anticipated or even cause additional environmental damage.

NOT overcoming data sharing restrictions will make a conclusive environmental assessment impossible.

Doing nothing is NOT an option if a responsible evaluation of this international problem of munitions in the seas is the aim; Germany could take a leading role.

Reporting about munitions in the seas is a threat in itself, when thinking about misusing this data in one or the other way. Transparency towards the general public about the threats, results of investigation and monitoring progresses including potential consequences to food safety and human health issues is

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[2] https://www.meeresschutz.info/blano.html

important as this will show that the problem of munitions in the seas is taken seriously. However, to a certain extend some information needs to be disclosed from the public; this is particularly true for presenting exact locations of ammunition objects, exact numbers and state of corrosion. Because of this, all detailed maps in this report do not show coordinates. Exact sample locations should not be given in public documents, including scientific publications. UDEMM members, together with partners at the German Navy, the BLANO and Kampfmittelräumdienst Schleswig-Holstein, agreed on publishing coordinates with an accuracy of less than ~180 m (one digit for minute values of coordinates, e.g. *DDD°MM.m'*).

1.2 What are the methodological tasks and problems?

Even after overcoming financial, time, data management and responsibility issues, methodological tasks and related problems remain, which need to be considered for a scientifically sound monitoring. Three major tasks exist:

A. how to monitor munitions dumping grounds
B. how to define toxicity levels
C. how to evaluate the risks

This guide focuses on the first task of "how to monitor munitions dumping grounds" and gives insights into the definition of toxicity levels. Defining risks or developing decision workflows for evaluating the risks of munitions in the seas was not topic of UDEMM. The parallel running project DIAMON[3] focused on this task and presented a first version of a Decision Support Tool. This tool strongly depends on reliable and conclusive data. How to acquire such data was the goal of UDEMM and to focus efforts of such a complex task, one dumping ground type was studied in detail. Within the area of Kolberger Heide, large ammunition objects and chunks of explosives are distributed on the seafloor surface in relatively shallow water. For such and other scenarios the monitoring can be sorted according to five overarching topics:

A. the occurrence/distribution of ammunition objects and their redistribution/ migration over time
B. the dissolution flux of contaminants from solid explosives into the water, and the mechanisms and timescales of conversion into non-toxic substances
C. the spatial and temporal distribution of dissolved and particulate contaminants in the water column
D. the uptake and accumulation of contaminants by organisms and the occurrence within the food web
E. the consequences of munition-related contamination for specific habitats and the environment in general

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[3] https://www.daimonproject.com/

This guide deals with topics A to D and the respective results gained through the UDEMM project; ongoing studies will continue to advance knowledge for all topics. The involved processes are shown schematically in Figure 1. Schematic view of the pathways and effects of munitions in the marine environment, and the linkages between monitoring outputs and management outcomes. These processes have been identified and evaluated on different spatial and temporal scales within the Kolberger Heide study site. Work in UDEMM focused on contamination derived from the main charge (mainly Schießwolle 39/gun cotton 39) comprising especially the toxic (e.g., carcinogenic) compound TNT and its metabolites. Inorganic contaminants such as mercury and lead are potentially present in fuses, and are likely also subject to many of the processes shown in Figure 1.

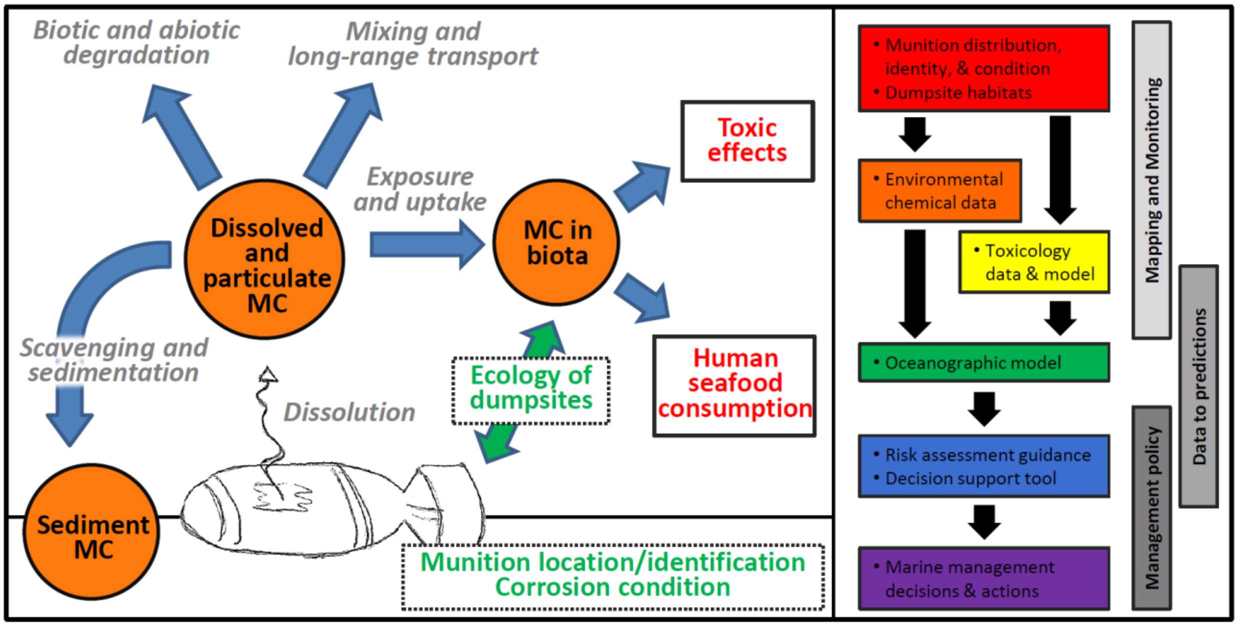


Figure 1. Schematic view of the pathways and effects of munitions in the marine environment, and the linkages between monitoring outputs and management outcomes.

Generally, the contamination and its spread into the environment occurs in **dissolved and particulate phase** from rusting ammunition objects such as mines, bombs, torpedoes, grenades, etc. In Kolberger Heide one location also shows chunks of open explosives of several decimetres in size and of different colour and texture. Depending on the explosive composition, **dissolution rates** are controlled by the surface area of the explosive material in contact with water (this will change through time and progressing dissolution), the water temperature and salinity and most likely the turbulence at the explosive surface. This means that dissolution rates are likely to vary seasonally due to temperature changes or increased bottom currents (e.g. storm events) and thus cannot be assumed to be constant.

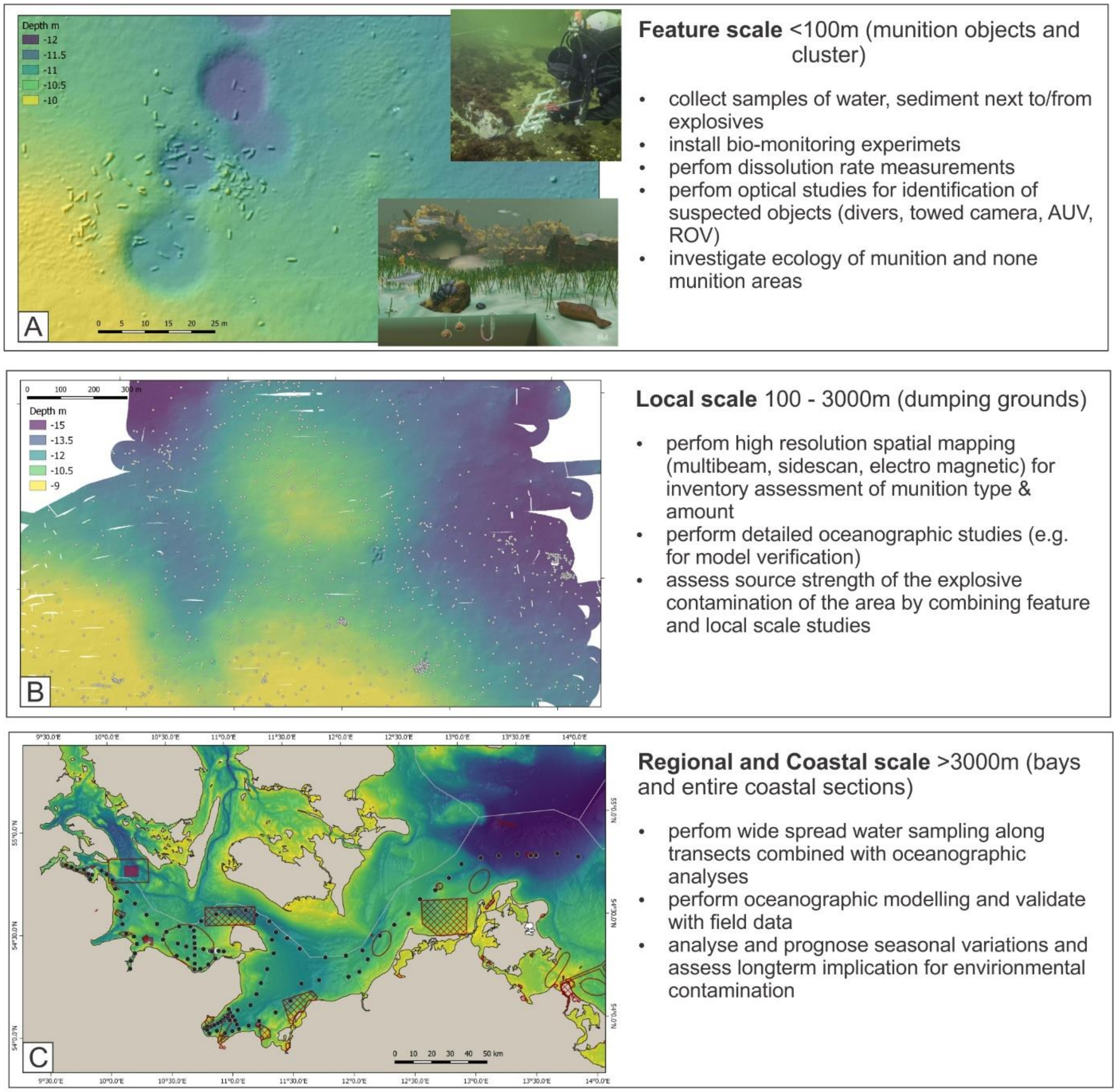
Dissolved explosive compounds (e.g. TNT, TNT metabolites, RDX) will be transported by water currents and will be **subject to biogenic** (microbial transformation or uptake by organisms) **and abiogenic** (e.g. photolytic) **conversion and final degradation or sequestration** (Beck et al., 2018). Particulate or surface-adsorbed explosives will be transported with the sediment, buried in sediment, or even washed onshore. The extent to which small particulate explosives are taken up by biota and accumulate into their tissue is still largely unknown. Rapid dissolution in the water column is likely to limit the redistribution and impact of intact explosive particles.

Dissolved explosive compounds are **transported by currents and are substantially diluted** during mixing. Knowing type, distance and source strength of the releasing location is of great importance to adequately interpret measured concentration values on **different spatial scales**. To illustrate the complexity of the problem, Figure 2**Error! Reference source not found.** shows three different spatial scales, the feature, local, and regional to coastal scale.

We define the **feature scale** (< 100 m) as the scale where individual ammunition objects or parts of explosives determine the observation/sampling methodology and interpretation. Positioning of sampling needs to be accurate in the centimetre range for e.g. determining dissolution rates of explosive material. Bio-monitoring experiments need to be positioned with at least decimetre accuracy near individual ammunition objects or within meter accuracy with respect to larger clusters of ammunition objects such as piles of sea mines, clusters of depth charges or boxes of munitions.

The **local scale** (100 - 3000 m) represents entire munitions dumping grounds, which typically show several clusters of dense munitions features. Within Kolberger Heide several feature hot spots were found with sizes ranging between 10 m and 40 m and distances between them are on the order of from 70 m to 500 m. On such scale, the location of individual ammunition objects within a cluster is less important, but the size and integrated source strength of the different clusters will determine the distribution of contaminants. On this scale the overall release strength of a dumping ground needs to be established. Habitat mapping exercises should be performed on such a spatial scale and are ideally compared to similar but uncontaminated areas in the vicinity. The local scale should be large enough to hold several cells of a regional ocean and TNT distribution model to allow for model verifications.

The **regional to coastal scale** relates to areas covering e.g. the entire exclusive economic zone (EEZ) of the German Baltic Sea with several munitions dumping grounds. Individual ammunition objects are of limited importance on this scale; larger clusters of objects and dump areas will influence the integrated TNT concentrations over several 100 to 1000 m distances (equivalent to a few grid cells of a coastal ocean model).



Feature scale <100m (munition objects and cluster)

- collect samples of water, sediment next to/from explosives
- install bio-monitoring experimets
- perfom dissolution rate measurements
- perfom optical studies for identification of suspected objects (divers, towed camera, AUV, ROV)
- investigate ecology of munition and none munition areas

Local scale 100 - 3000m (dumping grounds)

- perfom high resolution spatial mapping (multibeam, sidescan, electro magnetic) for inventory assessment of munition type & amount
- perform detailed oceanographic studies (e.g. for model verification)
- assess source strength of the explosive contamination of the area by combining feature and local scale studies

Regional and Coastal scale >3000m (bays and entire coastal sections)

- perfom wide spread water sampling along transects combined with oceanographic analyses
- perform oceanographic modelling and validate with field data
- analyse and prognose seasonal variations and assess longterm implication for envirionmental contamination

Figure 2: Overview of the different spatial scales that need to be considered during munitions studies. A) Shows the bathymetry of an area with explosion crates and dumped munitions (ground mines and torpedo heads) in the Kolberger Heide. B) Shows the bathymetry of the Kolberger Heide with ammunition objects marked with grey dots (total 1,136). C) Germany Baltic Sea with points indicating water sampling stations during POS530 (October 2018) and munitions dumping grounds (red), munitions occurrence areas (red pattern) and munitions suspected areas (red polygons).

Table 2 shows the typical studies and applications at different scales as they have been performed during the UDEMM project. Other methodologies and technical devices can be added to the portfolio of a monitoring strategy.

Table 2: Overview of different scales that need to be considered with their typical studies, methods and related problems.

Scale	**Typical studies and methods**	**Problems**
Feature scale single objects or clusters of objects spatial size: < 100 m temporal scale: minutes – months	**Hydro-acoustic** investigations aiming at object detection and inventory assessments; repeated surveys can investigate object migration and burrowing. **Optical investigations** aim at resolving objects with a resolution of only one to few pixel/mm. Repeated measurements can be used to detect changes over time. Date acquisition can be done by divers (e.g. small 3D photomosaic reconstructions), remotely operated underwater vehicles (ROVs) or AUVs (larger photomosaics). **Electromagnetic** investigations with towed or ROV/AUV deployed systems aiming at verifying ferro-magnetic objects. **Visual** inspection by divers aims at verifying ammunition type and degradation stage. **Bio-monitoring experiments** by placing mussels in bags on a weight in a certain distance from the target; making transects and having bags in different height above the seafloor (short mooring) helps to evaluate the spatial impact of contaminates. **Passive samples** can be placed in the same way. For both, divers are needed in the proximity to ammunition objects, at greater distance > 30 m moorings can be placed from the boat **Sampling** of water, sediment, and fauna to establish the extent of contaminant release at source, and to evaluate the extent of ecological exposure at the top high risk location. **Dissolution rate measurements** using syringe sampling or chambers. Accurate positioning is needed and due to the proximity to explosives this needs to be performed by divers.	**Diver orientation** and the weather dependence of diver operations are a typical problem. Generally **accurate underwater localization** and navigation is a challenging problem, even with USBL systems. Visual investigations suffer from **turbid water**. Different seasons and weather conditions need to be considered. Hydro-acoustic and electromagnetic measurements need **highest position accuracy** (RTK support for GNSS). Environmental samples collected near munitions require diver support due to the explosive hazard.
Local Scale Dump site areas spatial size: 100 - 3000 m temporal scale: minutes – years	**Hydro-acoustic** investigations aiming at mapping entire areas but keeping the same high resolution as for feature detection purposes. Data from multibeam systems (bathymetry, backscatter, snippets) or side-scans are further used for habitat mapping and seafloor classification purposes. With increasing depth AUV-based or deep-towed mapping has to replace ship-based investigation due to the decrease of resolution. **Optical investigations** with towed or AUV-based camera systems are used for habitat mapping and sediment classification purposes. **Electromagnetic investigations** on local scale aim detecting buried munitions that cannot be seen otherwise. **Oceanographic** measurements as moored ADCPs	Hydro-acoustic and electromagnetic measurements need **highest position accuracy** (RTK support for GNSS) and ships navigation (ideally dynamic positioning). Visual investigations suffer from **turbid water**. Different seasons and weather conditions need to be considered. Water sampling by pumps can be slow, so ship positioning is important for accurate spatial sampling on small scales. Rapid water collection with Niskin bottles

	(Acoustic Doppler Current Profiler) or CTDs (Conductivity Temperature Depth) record the local variability of physical parameters over longer time (months - years) in high temporal resolution. Such data are used to validate oceanographic model results and as input parameters e.g. in dissolution models. **Sampling of water** helps indicate the integrated local source strength, and the extent to which released contaminants are spread away from the source. Sample depths need to be adjusted to the actual stratification of the water column. Transects across and away from the dumping grounds should be considered, sample spacing can be linked to the model cell size. **Sampling of sediment** is needed to ground truth sediment classification (needed for munitions burial estimates), as well as for analyses of explosive compounds (evaluating the extent to which contaminants are accumulated in sediments). **Biota sampling** is necessary to determine the extent of ecological exposure outside the immediate contamination source, yet within the zone of elevated concentrations.	is preferred.
Regional Scale Coastal areas spatial size: > 3000 m temporal scale: days to decades	**Sampling of water** aims at quantifying the spread of contaminants outside of known dumping grounds. Changing distribution patterns with a focus towards sensitive areas (fishing grounds, tourist areas) will be analysed. Sample depths need to be adjusted to the actual stratification of the water column. **Bio-monitoring** at specific locations outside of dumping grounds will support the evaluation of contamination spread and uptake into the food web. **Oceanographic modelling** is to determine the integrated source strength of an area and predict spreading over time (warning system).	**“Large” amount of water analyses** accompanied by physical measurements are needed for gathering a comprehensive data set. With increasing knowledge and duration of monitoring, the amount of samples can most likely be reduced. **Oceanographic modelling** with combined ‘TNT’ dissolution and degradation modules is needed (high performance computing).

1.3 Further information and related regulations

The above short introduction does not claim to be complete in its methods, it is so far the first compilation of munitions monitoring recommendations publically available in Germany and, to our knowledge, in Europe. Ongoing research and monitoring results will contribute to this ‘Best Practices Guide’ and will constantly extend and improve it.

Yearly meetings of researchers, authorities and subcontractors, who execute the monitoring, shall lead to a yearly updated version of this document, results and progress of monitoring should be introduced and maintained under the Monitoring Handbook of BLMP[4].

This is the continuation of the work and discussions, which made sure, that the topic of sea-dumped munitions finally reached political levels. First efforts for Northern Europe started in 1974, when the Helsinki Convention introduced first guidelines for the protection of the marine environment of the

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[4] https://mhb.meeresschutz.info/de/start

Baltic Sea area (Carton and Jagusiewicz, 2009). This led to the federation of the bordering states and the European Economic Community, and the ratification of the HELCOM convention ('Baltic Marine Environment Protection Commission - Helsinki Commission') (Carton and Jagusiewicz, 2009). With signing the convention the parties agreed to prohibit sea-dumping of waste, including chemical and conventional munitions (Carton and Jagusiewicz, 2009; HELCOM, 2014). Equivalently, the OSPAR ('Oslo-Paris Convention for the Protection of the Marine Environment of the Northeast-Atlantic') convention applies for the North Sea area (OSPAR Commission, 2007). In addition, the European initiative of the Marine Strategy Framework Directive (MSFD) aims for establishing a good environmental status of European waters by 2020. Within the directive's descriptor 8, munitions disposal sites are explicitly named as a source for contamination and pollution (Law et al., 2010[5]).

To comply with the MSFD, Germany e.g. has established a monitoring program called BLMP (Bund/Länder Messprogramm). This programme has released a public report on Munitions in German Marine Waters - Stocktaking and Recommendations, concluding that the status of munitions within German waters remains unknown to a large extent (Böttcher et al., 2011). Even though the report is updated yearly, the situation in general remains the same, while an effective monitoring procedure has not yet been established. About 300,000 metric tons of conventional munitions and 5,000 metric tons of chemical warfare (CW) material have been brought into German waters of the Baltic Sea. The North Sea contains around 1,300,000 metric tons of conventional and 9,000 metric tons of chemical munitions (Böttcher et al., 2011). In addition of unexploded ordnance from combat and bombing (UXO), all kinds of munitions from onshore munitions depots have been dumped after World War II (WWII) in dedicated nearshore areas. Instead of shipping the munitions to the official dumping grounds, it was common practice to start dumping along the way to the designated areas – also known as 'on-route-dumping' (Böttcher et al., 2011; 2015). This and the dislocations of ordnance and initial relocations by fishery activities, make it difficult to estimate exact numbers of munitions inside those areas (Beddington and Kinloch, 2005; Böttcher et al., 2011; 2015; 2016). If not blown in place, defused munitions have been taken out of the water to a large extend (95 % of 21,000 objects reported since 2013) and has been disposed on land. A small fraction though could not be taken out (i.e. British ground mines) but where relocated by the Kampfmittelräumdienst (or EOD service – explosive ordnance disposal service) to a marine dumping ground instead. This is also done because WWII explosives, having rested underwater for seventy years by now, become increasingly unstable and the risk of a spontaneous detonation during transport, particularly onshore, has strongly increased (Pfeiffer, 2012). Due to this necessary time-consuming and costly practice, the number of ammunition objects in the sea is effectively not decreasing so far. Nautical charts indicate certain areas of the seafloor according to IMO-Standards for electronic nautical charts (ENS) as:

- Explosives dumping ground, individual mine or explosive (No. 23.1)
- Explosives dumping ground (disused), Foul (explosives) (No. 23.2) or
- Dumping ground for Chemical waste [including chemical waste from sea dumped chemical munitions] (No. 24).

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[5] https://mcc.jrc.ec.europa.eu/documents/201801085655.pdf

Despite this, their precise boundary, actual amount of munitions and the extent of munitions just outside the dumping grounds is barely known (Beddington and Kinloch, 2005; Böttcher et al, 2011 - 2018; United Nations Mine Action Service, 2014). Therefor the map published by Böttcher et al. 2011 indicated

- 15 munitions dumping grounds (dedicated areas)
- 56 munitions-contaminated areas (e.g. routes from operational ports to dumping grounds
- 21 munitions suspected areas in German territorial waters.

Due to their proximity to shore and thus densely populated areas as well as marine shipping routes, it is urgent to gain a better picture of the state of the different munitions under water. As the problem will not disappear but rather spread, it is necessary to establish monitoring procedures for long-term observations and risk assessments of those dumping grounds. Here, we present results of the German BMBF-funded project UDEMM (‘environmental monitoring for the delaboration of munitions in the sea’). For implementing the HELCOM guidelines from 2013 (HELCOM, 2013) and the MSFD, a monitoring workflow is developed, presenting a current state-of-the-art approach for mapping conventional munitions dumping grounds, including chemical, biological and toxicological investigations.

2. Case study Kolberger Heide and western German Baltic Sea

For the UDEMM project the Kolberger Heide was the main study area for about 20 cruises with different research vessels of GEOMAR and the Federal Ministry for Environment (see also UDEMM webpage[6]). The area served as test location to develop new methods and workflows which are described above and detailed further below. In this section, we give an overview of what has been done and what the first results of these studies showed.

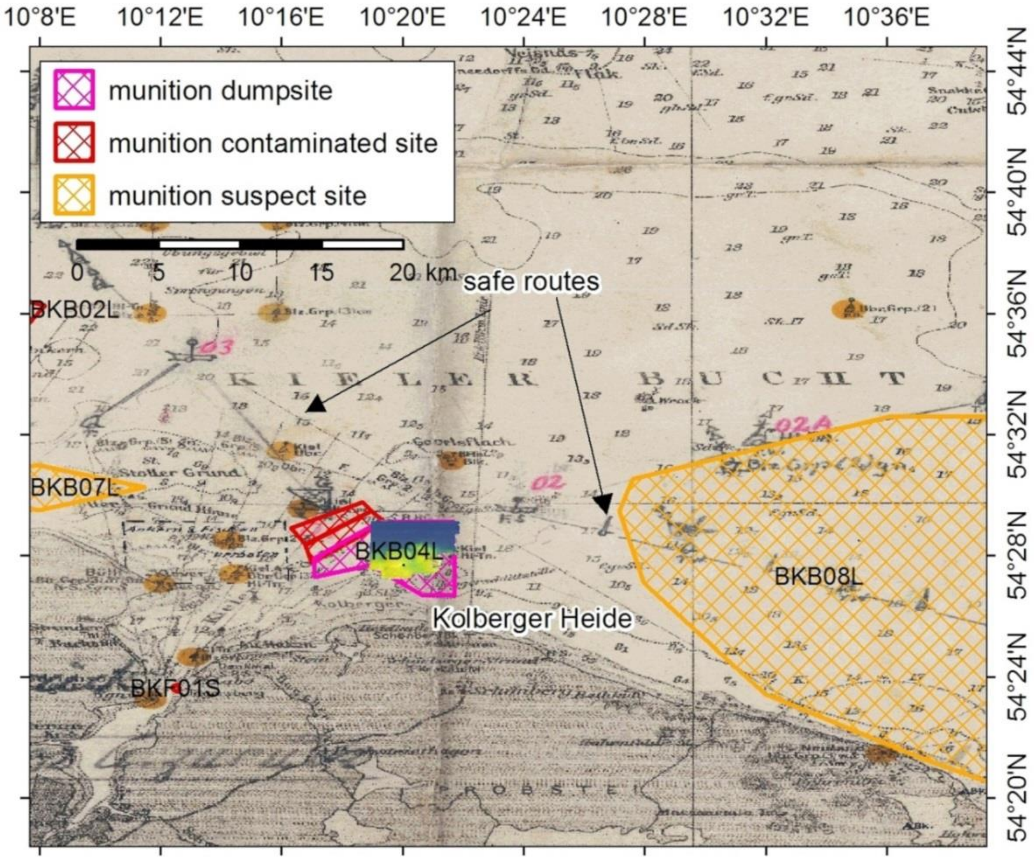

Figure 3: Section of a nautical chart of the western Baltic Sea, showing Kiel Bay and its munitions dumping grounds (munitions dumping grounds (pink); munitions-contaminated sites (red) and munitions suspected areas (orange)). The dumping ground *Kolberger Heide (BKB04L) was mapped with multibeam during UDEMM surveys. The underlying map originates from 1923 and was used during WWII for navigation purposes. Last changes were made in 1945. The yellow dots indicate positions of navigation marks and light ships (Library of Mürwik Naval School; EGEOS, AmuCad).*

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[6] https://udemm.geomar.de/home

In October 2018, the UDEMM consortium went on an additional cruise along the German Baltic coast with RV POSEIDON (cruise POS530 – MineMoni) and acquired a substantial set of water samples, dropped bio-monitoring moorings and used a high-resolution ship-based multibeam system and AUV-based camera observations to map selected areas in very high detail (Fehmarnsund and Bay of Lübeck; Figure 3).

The sequence of the next subsections is organized in such a way as we believe a monitoring of a new, largely unknown area should be done. During UDEMM itself, we did not follow the best methodology structure, as the respective approaches still needed to be developed. At a late stage of the project, we further got in contact with Uwe Wichert (Consultant BLANO, MELUND and HELCOM SUBMERGED) who is an expert in WWI and WWII maritime war activities doing research in various archives in Germany and the UK. Through his expertise we realized that an in depth historical survey of the type of ammunition and their amounts that are/might be present in an area is of great importance for a better interpretation of results. It also allows for a better informed comparison between different areas and their joint impact on the environment.

2.1 History of the study area Kolberger Heide

Responsible institute: BLANO & GEOMAR

Kampmeier et al. (in review) just recently presented an overview of the Kolberger Heide including its historical analyses. Documents of the provincial and federal archives in Schleswig and Freiburg (Germany) and the National Archive in Kew (UK) provide detailed information on the usage of the Kolberger Heide area in the past. With regards to war activities, the Kolberger Heide was firstly mentioned in the sea battle on 1 July 1644 during the Swedish-Danish war (1643-1645 CE). Before and during WWI, it was only used for commercial fishing, as it was too shallow for the German fleet to enter (Sections of nautical sea charts of the German Kriegsmarine, last changes in May 1945, Fachbibliothek Marineschule Mürwik). It is possible that 28 cm training grenades (steel housing without explosives) were introduced to the area during training exercises of the gun battery in Laboe. Apart from that, there are no records of additional munitions entering the area until WWII.

The first records from this period report the introduction of munitions in 1940, when the British Royal Air Force started bombing Kiel. Failed bombings, emergency overboard disposal and targeted attacks on vessels and watch units occurred along the Marine Traffic Route 1. This traffic route extended from Kiel to the eastern parts of the Baltic Sea (Figure 3) and was constantly surveyed and cleared by the German Kriegsmarine by mine clearing vessels and airborne mine clearing systems. It was the only 'safe' path vessels could use during times of war and was therefore an important target for the British Air Force. However, the route was protected by German forces with onshore and vessel-based 12.8 cm anti-aircraft guns. A number of these shells ended up as unexploded ordnance (UXO) in Kiel Bay and also in the Kolberger Heide area. To obstruct vessel traffic, the British mined the Traffic Route 1, with as many as 3,896 British mines, also targeting the Kolberger Heide (British Mining Operations 1939 - 1945). Because of the high number of mines and resulting losses, commercial fishing was prohibited in Kolberger Heide in 1942 (Bundesarchiv Militärarchiv Kriegstagebuch Sperrkommandant westliche Ostsee). Bombing and mining activities continued until the end of the war in May 1945. After the war, enormous quantities of captured arms and munitions were dumped into the sea, this was seen as the fastest and at that time safest method to secure and dispose of the weapons. The dumping grounds in German waters (North Sea and Baltic Sea) were chosen and approved on 29th July 1945, with Kolberger Heide mentioned as the first dumping ground (documents from the national archive of the UK in Kew).

Following this decision, continuous sea-dumping of munitions occurred at Kolberger Heide. This included torpedo heads and mines from the torpedo arsenals in Schleswig-Holstein. Documents from the federal state of Schleswig-Holstein describe the dumping of about 24,000 metric tons of all kinds of munitions in Kolberger Heide. Adding torpedo heads and mines, about 30,000 t of munitions have to be assumed to be present at the site (Landesarchiv SL Akten des Kampfmittelräumdienstes). This includes an array of ammunition types ranging from gun and pistol cartridges, artillery projectiles consisting of grenades and propulsion cartridges, as well as anti-aircraft ammunition of 2 cm up to 40.6 cm calibre. In addition, the Kolberger Heide site most likely contains explosive charges such as anti-tank and anti-personnel mines, rifle grenades or bursting and hollow charges. Furthermore, bombs ranging from 1 kg up to 500 and 1.000 kg in weight, rockets with diameters of up to 32 cm, as well as marine munitions such as moored and ground mines, torpedo heads, whole torpedoes, and depth charges are present. Some torpedoes that were formerly dumped in the area of Jägersberger Bridge were relocated to Kolberger Heide and re-dumped. Also, a barge loaded with 500 tons of chemical munitions (grenades of 10.5 and 15 cm calibre) were sunk in the Little Belt. According to records, it was recovered and re-sunk in the area of Kolberger Heide. In 1959, boxes with propellant charge powder stored on the upper deck of the barge were salvaged, until the chemical munitions were discovered. After that the chemical grenades were partially removed and the remainder relocated together with the barge to Geltinger Birk, where everything was encased in concrete and finally sunk in the North Atlantic (Landesarchiv SL Akten des Kampmittelräumdienstes).

As often when dealing with WWI and WWII dumped munition, the exact number and type of ammunition (and manufacturer) is unknown and therefore all common explosives and propellant charge powders used in WWII have to be assumed to be present at the Kolberger Heide site. This includes all sorts of filling powder, amatol, ammonite, ammonal, grenade filling 88 and marine explosives such as gun cotton (e.g. Schießwolle 36 and 39), special and testing explosives.

Since the munitions were manufactured from different kinds of material, it is not possible to predict the precise state of the munitions housings. Thin-walled moored mines and cartridges may already be heavily corroded, exposing explosive material to sea water; thick-walled artillery shells, bombs and ground mines may yet still be intact.

After WWII, the Allies intended to only dump defused munition; however it cannot be taken for granted that this was true for all dumped objects. Accidents including personal injuries and death occurred during the dumping work, and thus it needs to be assumed that at least some of the handled munitions were still armed. This is especially true for long-period delay detonators, mines with lead fuses or pendulum impact ignition.

Additional regions similar to Kolberger Heide were chosen as munitions dumping grounds by the Allies; these include areas offshore Schönhagen and Falshöft in the Bay of Lübeck/Bay of Neustadt. It is also known that light-weight munitions like grenades were thrown overboard in Friedrichsort, Stollergrund, Strande Bay, and en route to these dumping grounds. These actions are indicated by findings of fishermen and the EOD service (BLMP Bericht 2011 and Akten des Landesarchivs SL) and demonstrate the wide spread disposal of munitions in the south-western Baltic Sea that is now Germany territory.

Following WWII, Kolberger Heide was not used as a military training area anymore and is therefore not affected by contamination with further munitions. However, munitions that were subsequently found along marine traffic routes in Kiel Bay was defused and relocated to Kolberger Heide by the EOD service; this practice is still ongoing and its results have been noticed during the UDEMM project by comparing multibeam maps acquired at different times.

Table 3 Amunition type and explosive weights for dumped munitions in Kolberger Heide.

Mine type	**amount**	**shell weight kg**	**explosive weight kg**	**ratio explosive/shell**	**total explosives tones**
Sea mine large	316	220-280	300-350	0.51 - 0.61	102.70
Sea mine small	29	130	30	0.19	0.87
Ground mine A	1834	200-230	560-800	0.7 - 0.8	1,247.12
Ground mine B	181	900	200	0.18	36.20
Depth charges large	3000	80	60	ca. 58:42 %	180.00
Depth charges small	788	55	130	ca. 30:70 %	102.44
Bomb mine 1000	6	400	600	40:60 %	3.60
Bomb mine 250	31	125	125	50:50 %	3.88
British mine	110	200-400	90-500	0.18 - 0.71	32.45
Total					1709.255

2.2 Hydro-acoustic and visual mapping results

Responsible institute: GEOMAR

As part of the scientific work in UDEMM, we tested two different kinds of state-of-the-art multibeam systems, a NORBIT iWBMS and a RESON T50. Both systems performed well with respect to their capacity, but most of the mapping finally occurred with the T50, which has a higher resolution (0.5° along- and 1° across track). For high quality survey results, it was essential to properly reference all sensors to each other and use undisturbed RTK correction for the navigation. The presented results below have recently been submitted by Kampmeier et al. (in review).

For the compilation of the entire Kolberger Heide area 20 d of surveying were needed (Figure 3), that were performed between 2016 and 2018. Repeating surveys in Nov. 2015, Feb. 2018 and June 2018 aimed at identifying potential migration of objects. The restricted dumping ground is located in the south of the area in 5 - 14 m water depth on a shallow platform, which towards the north develops into a more horizontal plain in 19 - 20 m water depth. Patches of algae, covering the seafloor with varying density could be observed in underwater video profiles and show seasonal variability in their spatial distribution. Small scale ripples of 5 cm height and 20 cm width indicate sediment transport on the seafloor. Their crests are generally N-S oriented and thus perpendicular to the bottom current direction (Figure 4).

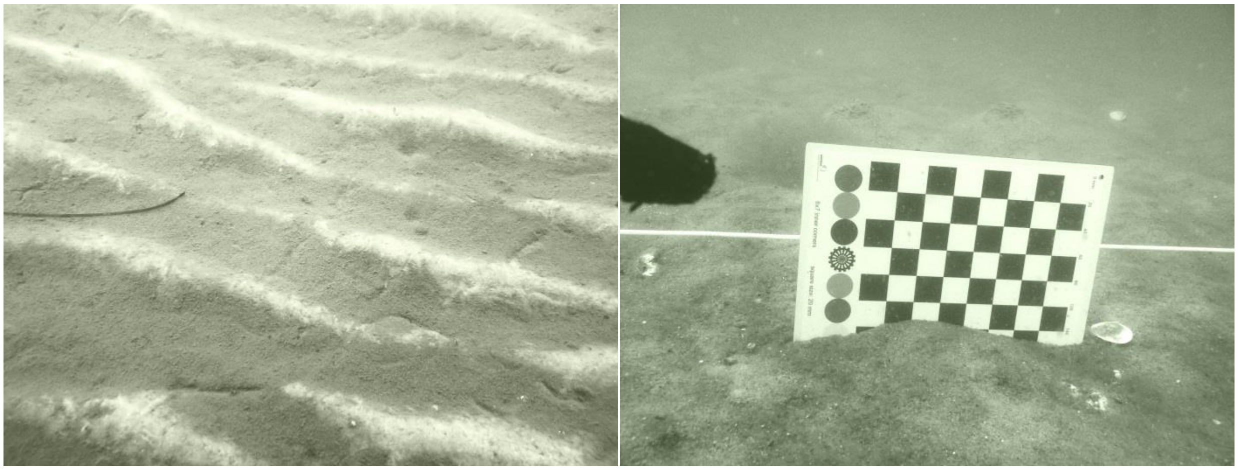

Figure 4 Left: a ripple field in Kolberger Heide. Right: Measuring the ripple height via a checker board. The black and white squares are of 2 cm size each. The observed ripples are ca 5 cm high and up to 20 cm wide. Their symmetric shape rather point to wave induced ripples, rather than formed by currents.

In 19 m water depth in the outer area of the dumping ground, otter trawling marks are clearly visible inside the soft sediments and indicate significant fishing activities. This fishing method uses two boards that are dragged across the seafloor to keep the trawling net open. Since 2004, the trawling is prohibited in the Baltic Sea for areas more shallow than 20 m water depth or within 3 miles to the coastline. Despite the ban, 10 - 100 h of otter board trawling were noted within this area in 2006 (Sell et al., 2011). Even though Kolberger Heide is not one of the main fishing grounds in Kiel Bay, bottom trawling seems to occur close to the official dumping ground and thus can potentially lead to object displacement.

On local scale the bathymetry is characterized by a shallow platform, which extends from the shore and declines with a slope of less than 1° towards the north. It builds a plain in 19 m water depth. Patches that show increased rugosity (height differences of 2 - 4 cm) and ripple-like structures are present in the feature-scale morphology. Those areas produce high backscatter intensities and contain increased amounts of rocks. As the underwater environment of Kolberger Heide is strongly affected by anthropogenic use, artificial objects and remnants of activities are present on local and feature-scale. There are explosion craters with average diameters of 20 m and depths of 1.5 m, which can be observed as clusters or isolated craters across the entire study area. Craters were formed by in-situ destructions that partially acted as tests for bubble curtain experiments. Bubble curtains significantly decrease the sound energy of detonations and thus particularly protect marine mammals (Würsig et al., 2000). Remnants of these bubble curtains in form of hoses and anchor stones were left on the seafloor; they can be reactivated if needed. Other types of feature-scale objects are all kind of UXO and dumped munitions in high numbers. Depending on the ammunition type, accurate identification is challenging to a varying degree. Three hot spot areas have been detected. The first area is composed of ~70 defused moored mines, piled up to a mound-like structure of 30 m length and 15 m width. Its height above the surrounding seafloor is about 1.5 m. The second highly contaminated area is located at a cluster of detonation craters (Figure 5). At this location around 90 munition objects of different types ranging from German and English ground mines over torpedo heads, water bombs to moored mines can be found.

Some of these objects have been brought to the dumping ground after being defused by the EOD service. The third area of around 150 m^2 in size shows ca. 100 objects of 1 m by 0.6 m.

Initial validation dives identified these objects as aerial bombs, possibly fused. A high number of additional suspicious objects can be found all over the research area. Moored mines occur as spherical shaped objects with ca 1.2 m diameter all over the existing bathymetric data set. Due to their size and elongated shape, ground mines and torpedoes can be identified rather easily. Smaller objects such as bombs and torpedo heads are not as easily identified and require validation by divers or underwater video. Joint observation of derivatives with bathymetric data, can greatly enhance the speed of detecting and identifying munition objects. Slope, surface area and curvature highlight distinct objects as rocks and munitions on the seafloor very clearly (Figure 5).

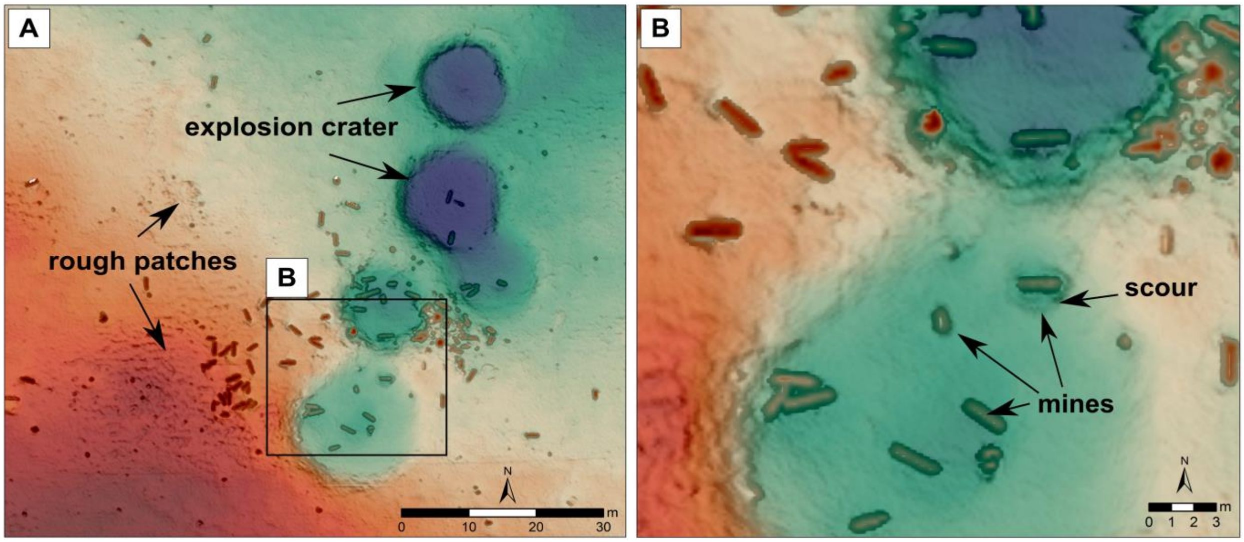

Figure 5 A) The high resolution bathymetry reveals morphological features like five explosion craters of around 25 m diameter. Furthermore, differences in the seafloor texture like patches of increased rugosity are visible. B) Close-up of ground mines in and around explosion craters (feature scale).

2.3 Munitions compounds in water, sediment and biota

Responsible institute: GEOMAR

Dissolved MC in the water column: Dissolved MCs were detectible in nearly all water column samples collected during the UDEMM project. Concentrations showed a range nearly exceeding nine orders-of-magnitude (Figure 6), most likely due to rapid mixing and dilution. Most of the samples showed TNT concentrations on the order of 1-10 pM, highlighting the critical need to use ultra-sensitive detection methods such as those developed during UDEMM. Previous results showed that MC distributions in the water column were highly variable in both space and time and that high resolution sampling is required to adequately monitor the regional magnitude and extent of contaminant plumes from underwater munitions dumping grounds. As a result, the sample collection and processing method that had been developed earlier during UDEMM (and published in Gledhill et al., 2019) were modified to reduce processing time and facilitate higher frequency sampling (see Section 4.7).

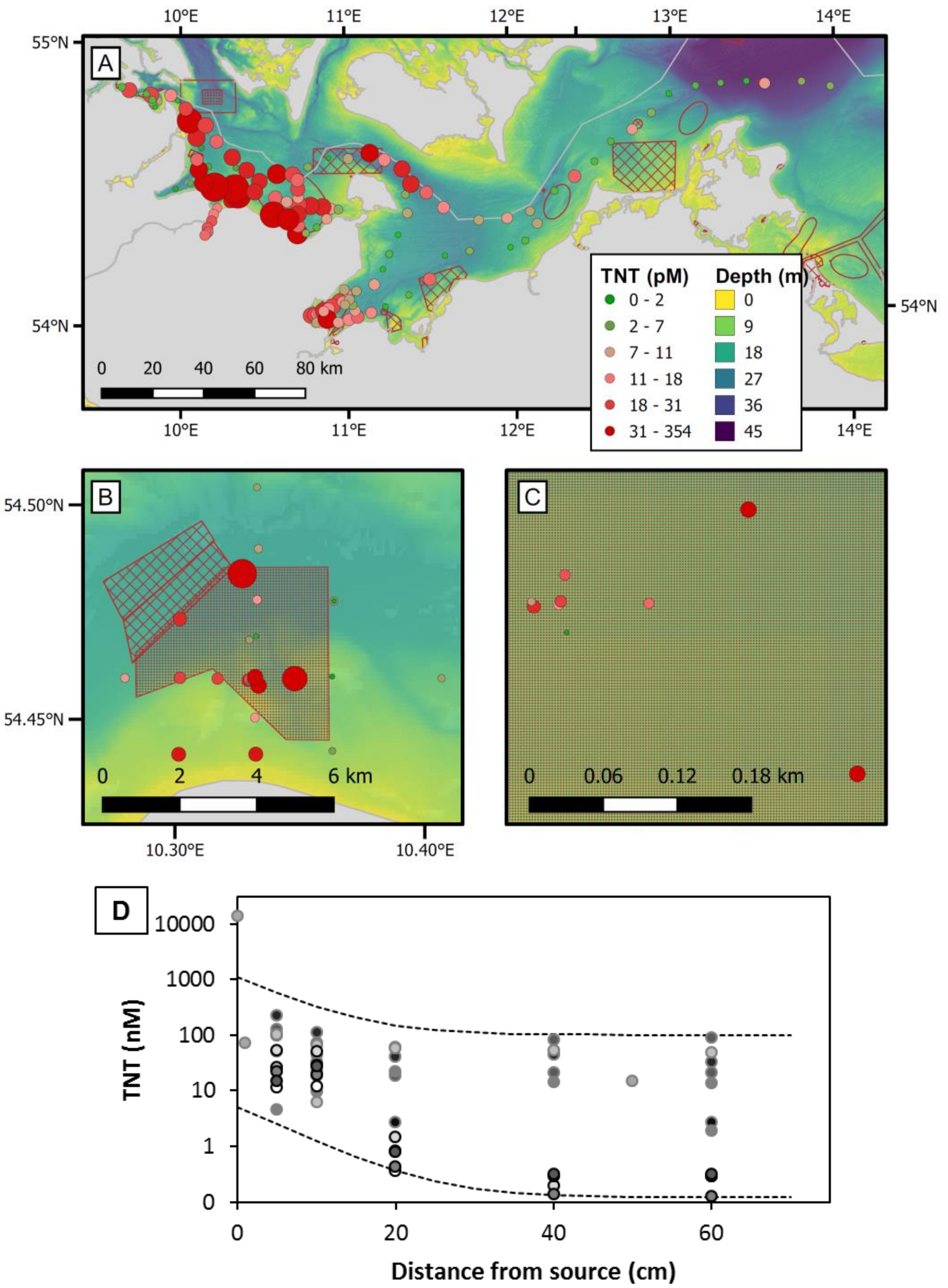

Figure 6: A) Regional-scale distribution of dissolved TNT in bottom waters throughout the south-western German Baltic Sea. B) Wide-local scale of dissolved TNT in bottom waters at Kolberger Heide. C) Narrow-local scale view of the cluster of overlapping points at centre in B. D) Feature-scale gradients within 1 m of munitions surfaces. Symbol colour and size in A-C) indicate concentration. Shading and marker line colour in D) distinguishes among 17 individual sample sets. Data shown in A-C) includes samples collected in October 2017 and 2018. Data in D) are redrawn from Beck et al. (2019) and include March, June, and October 2017. Additional data in D) are from October 2018. Note that the units in D) are on a log-scale and are 1000-fold higher than in A-C).

At the regional scale (Figure 6A), clear gradients were evident in TNT concentration. Areas with munitions dumping ground (e.g., Kolberger Heide; Bay of Lübeck) or known munitions contamination tended to show the highest concentrations (up to 354 pM for TNT). Nonetheless, there were marked differences among dumping ground, illustrated by the nearly order-of-magnitude difference between maximum concentrations observed in October 2018 in Kolberger Heide (354 pM) compared with the Bay of Lübeck (43 pM). This is the case, despite estimates that the Bay of Lübeck contains about double the amount present in Kolberger Heide (Böttcher et al., 2011). TNT concentrations were lowest in the Arkona Basin and the Mecklenburg Bight, likely as a result of their deeper water column and greater distance from munitions sites. Water exchange through the central channel and Belt Sea (north and northeast of Fehmarn) dilutes contamination originating close to coastlines, although samples collected north and northeast of Fehmarn showed substantial TNT enrichment.

The widespread presence of munitions on the Baltic seafloor make it challenging to link specific MC sources to plumes of dissolved MCs in the water column. Elevated concentrations oberved in the far western basin, and the wide dispersion of MCs on wide local scales (Figure 6B) imply long-range transport of MCs. This must occur on relatively short time scales, before loss by microbial or abiotic degradation or sorption and sedimentation with particles occur.

Loss of MCs through mechanisms such as degradation or sorption is likely to depend on site-specific characteristics such as temperature and salinity. Evaluating the impact of MC release on ecological systems requires constraint of potential long-range transport and chemical residence times. A number of simple experiements were conducted during UDEMM (see below) to provide an approximation of these controls and a quantitative constraint for modelling purposes.

On the local scale (0.05 - 5 km) in Kolberger Heide, water column TNT distributions show some indication of gradients around known munitions hotspots (Figure 6 and Figure 7). A general east-west increase in concentration cross the entire Kolberger Heide site may reflect enrichment of water traveling along the predominant current direction (Figure 7B. However, on the small local scale (10s to 100s of meters), gradients seem to be smoothed out by water mixing. For example, nine samples collected within 200 m around a pile of some 70 - 90 sea mines show no clear gradient in dissolved TNT (Figure 7c, Figure 8). This suggests that on such spatial scales, mixing is rapid relative to both input from the munitions source as well as removal mechanisms such as degradation.

A variety of explosive compounds in an even more extensive array of explosive mixtures exist, with more than 500 formulations manufactures (Haas and Thieme, 1996). Most organic explosives also undergo degradation or transformation to daughter compounds. Many of these daughter compounds are equally or more toxic than the parent, or toxicity is unknown. Such alteration can occur on a time scale of hours to days. It may thus be possible to have high influx, but low water column inventories of the parent MC. Monitoring only the parent MCs would underestimate the total chemical release. This emphasises the importance of multi-compound chemical analyses for evaluating chemical emission from underwater munitions.

The method developed during UDEMM (Gledhill et al., 2019) targets 17 compounds, including both a variety of explosives as well as several daughter product compounds. This was important, to elucidate chemical release trends across all spatial scales.

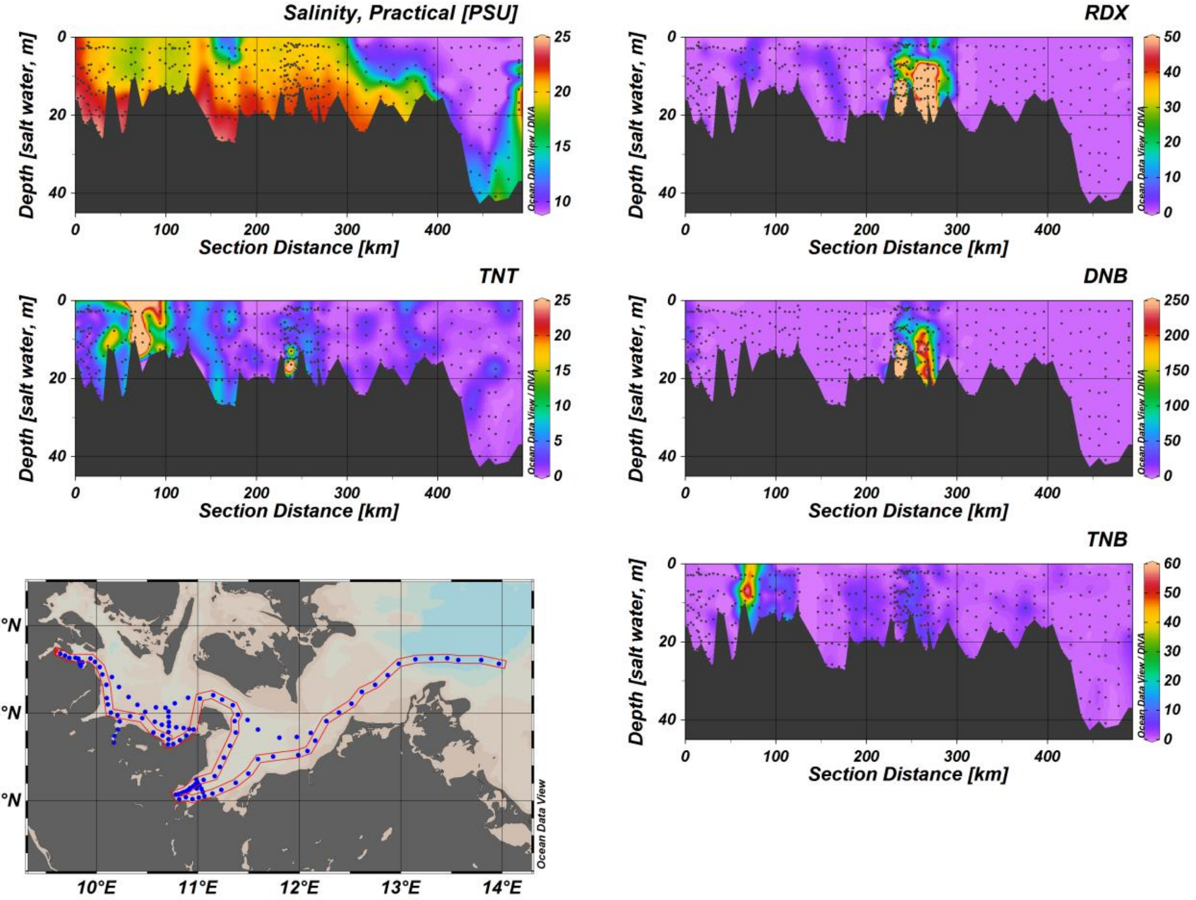

Figure 7. Sections showing the regional MC distribution with depth along the nearshore cruise track of POS530 highlighted in red (October 2018). The Kolberger Heide (located at ~75 km) and the Bay of Lübeck *(at ~250 km) are particular focal points of the MC load. Black dots show the positions of the individual samples used for contouring. TNT = Trinitrotoluene, RDX = Hexogen, DNB = Dinitrobenzene, TNB = Trinitrobenzene.*

At the regional scale, major differences were observed in the abundance of different explosive compounds. One of the most obvious difference was evident between Kolberger Heide and the Bay of Lübeck. The Bay of Lübeck is posited to have nearly double the quantity of munitions compared with Kolberger Heide (Böttcher et al., 2011). Dissolved TNT concentrations were nonetheless eight-fold lower in the Bay of Lübeck (43 vs. 354 pM; Figure 7). In contrast, the explosive compounds RDX and DNB were more than 30-fold higher in the Bay of Lübeck compared to Kolberger Heide. This suggests a major difference in the type of explosives dumped at the two sites. Whereas TNT inventories indicate lower MC contamination in the Bay of Lübeck, DNB and RDX suggest a contrary situation. Monitoring that targets only individual compounds can lead to vastly differing conclusions on the extent of explosives contamination.

At the feature scale, in situ benthic chamber incubations of individual exposed explosive solids at Kolberger Heide revealed clear compositional differences. The ratio of TNT, RDX and DNB released from three separate solids showed order-of-magnitude differences (Figure 8). This suggests that there is heterogeneity in explosives dumped at individual sites as well as among different sites. Strategies to monitor the overall chemical release from underwater munitions must therefore take into account spatial variability in the explosive source types.

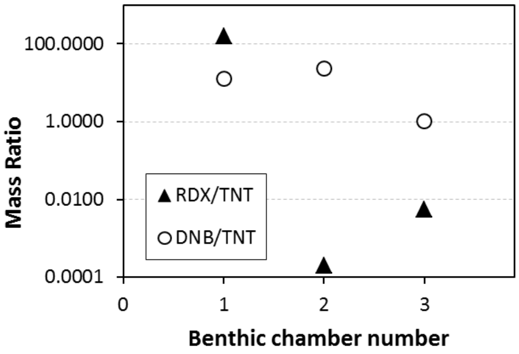

Figure 8: Mass ratio of RDX and DNB to TNT observed in three in situ benthic chamber incubations of different explosive solids.

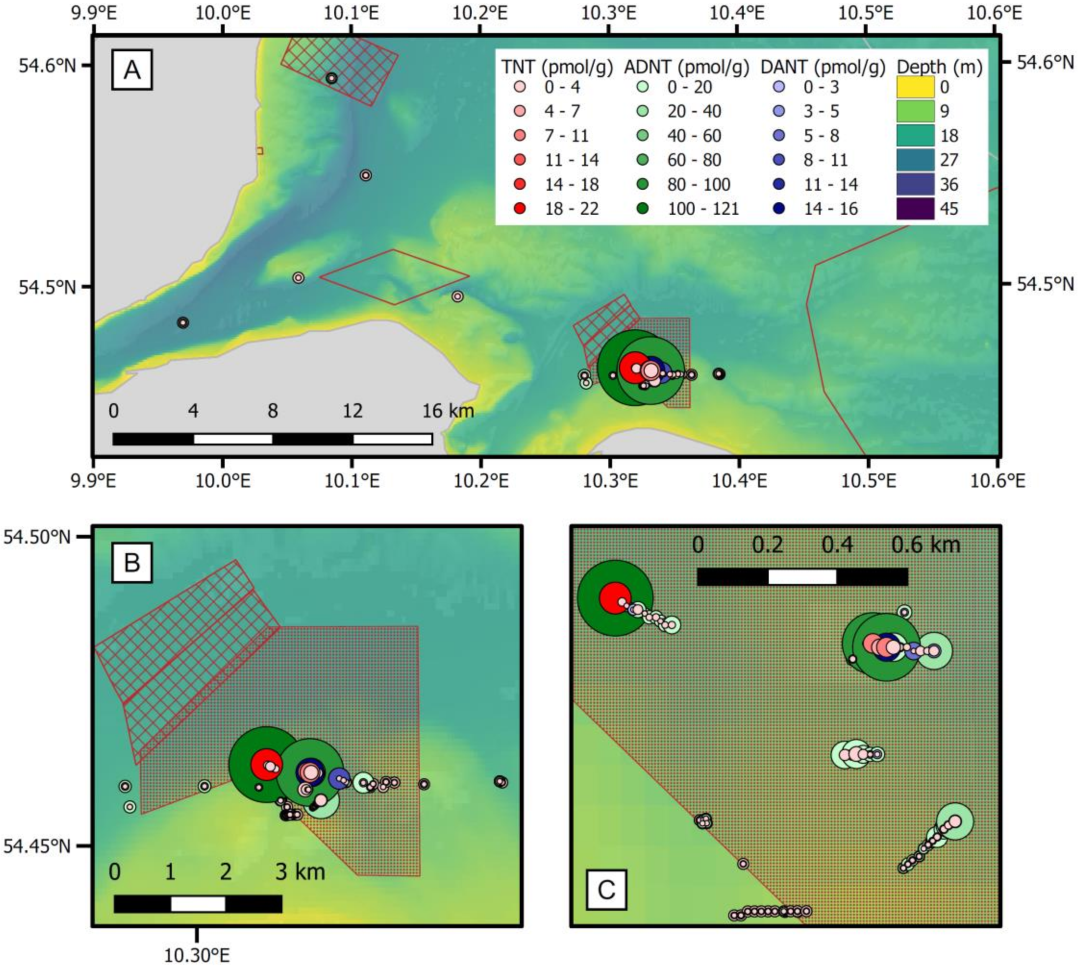

Figure 9: A) Regional-scale distribution of TNT, ADNT and DANT in surface sediments throughout the Kiel and Eckernförde Bights. B) Wide-local scale of TNT, ADNT and DANT in surface sediments at Kolberger Heide. C) Narrow-local scale view of the main Kolberger Heide site. The cluster of points near the centre is a transect across the mine mound as described above. Symbol shading and size indicate MC content and colour distinguishes among the three compounds.

Local retention of sediment MCs is consistent with the pattern observed at the km-scale (Figure 9b). Elevated concentrations were observed within kilometres of munitions hotspots identified by seafloor mapping, but declined rapidly away from the central source (Figure 9b). In contrast, enormous heterogeneity was observed at the sub-km scale (Figure 9c). Samples separated by 10s of meters showed as much variability as transects separated by several hundred meters.

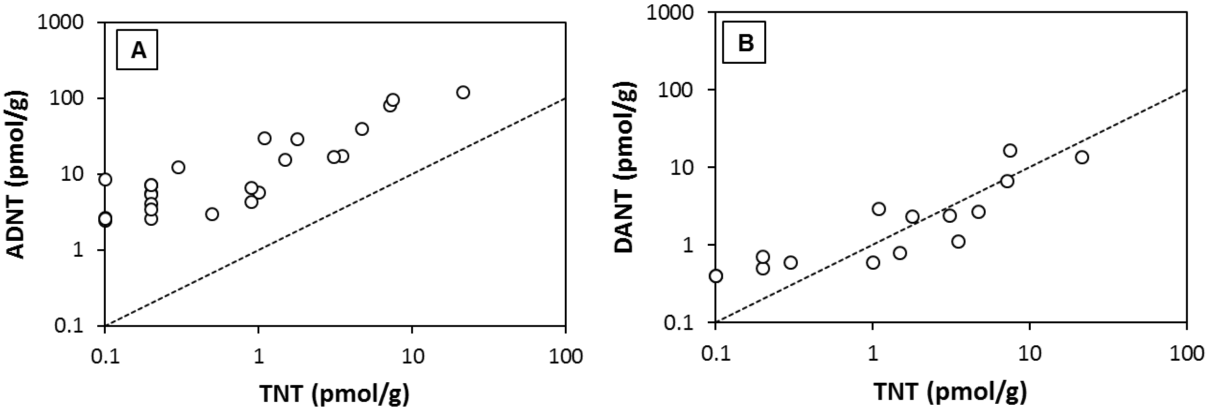

Figure 10: Covariation of (A) ADNT and (B) DANT with TNT in sediments. The dashed line indicates a 1:1 relationship.

No clear gradients were observed in feature-scale (< 2 m) sediment MC distributions around four individual mines investigated in 2017 (Figure 11). Concentrations varied from less than 1 to several hundred pmol per gram and maximum concentrations varied widely among mines. This is consistent with observations that munitions housing corrosion varies widely among objects at the Kolberger Heide dumping ground. Similar to regionally-collected sediments, ADNT and DANT tended to exceed their parent compound TNT. The relative quantities of TNT and its amino-derivatives ADNT and DANT indicate that transformation (likely microbially mediated) limits the persistence of TNT in sediments. This further underscores the importance of monitoring chemical residues, not only the original parent compounds. In the case of TNT and its daughter compounds, ADNT and DANT appear more stable and persistent in sediments, as also expected from their greater sorption potential (e.g. Sheremata et al., 1999). As a result, these may be the chemical forms exposed to biological receptors, consistent with ADNT accumulation observed in mussels (Appel et al., 2018; Strehse et al., 2017).

Sediment-associated MC levels are unlikely to respond rapidly to changes in MC release from underwater munitions. Nonetheless, they do provide a long-term indication of contamination at dumping ground, particularly from a regional perspective. Heterogeneity at local and feature scales suggests that random, statistically representative sampling is necessary to adequately establish contamination levels.

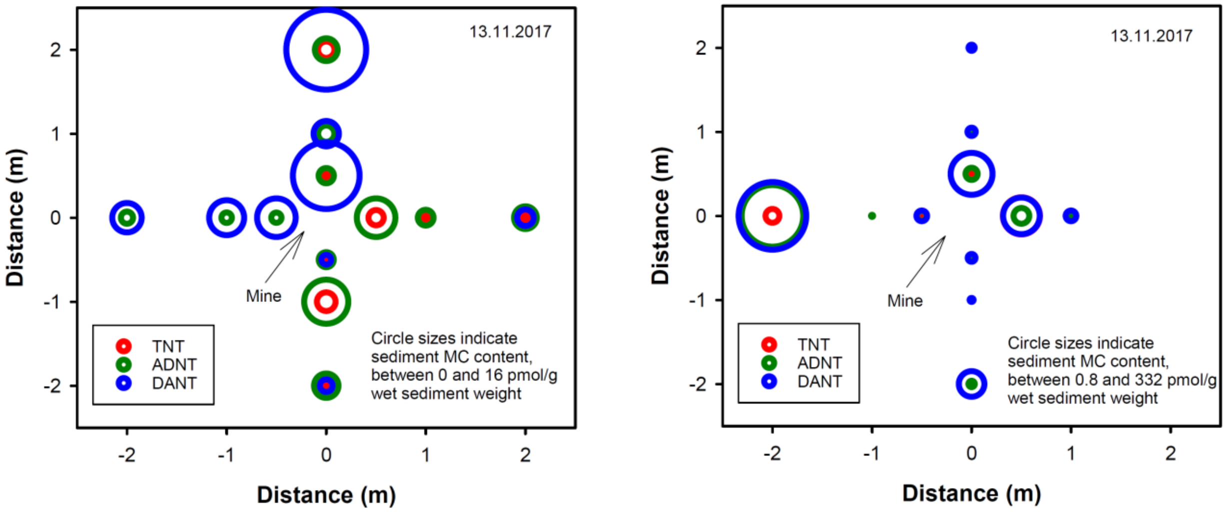

Figure 11: Examples of MC content in surface sediments collected radially around individual munitions. Colours indicate TNT (red), ADNT (green; a transformation product of TNT) and DANT (blue; a transformation product of ADNT). Circle sizes indicate MC content; note different scales among figures. Molar units are used to allow direct comparison of the different compound amounts.

Source term – Dissolution: Dissolution of solid explosives is the principle control factor on MC emission from underwater munitions. Dissolution rates are affected by physicochemical conditions such as temperature, salinity and mixing energy, as well as explosive chemical formulation (Lynch et al., 2001; Lever et al., 2005; Monteil-Rivera et al., 2010; Dontsova et al., 2006). All other conditions equal, MC release may therefore be highly site-specific. In UDEMM, multiple approaches were used to quantify dissolution fluxes. In situ dissolution was measured directly by MC release from exposed explosives enclosed within a benthic chamber (e.g. Figure 12). Feature-scale gradients (Figure 6d) were also fit with a simple steady-state model to estimate dissolution fluxes. These in situ methods revealed fluxes that were substantially lower when compared to laboratory experiments reported in the literature (Beck et al., 2019). The discrepancy most likely resulted from lower mixing energy in situ compared to laboratory conditions.

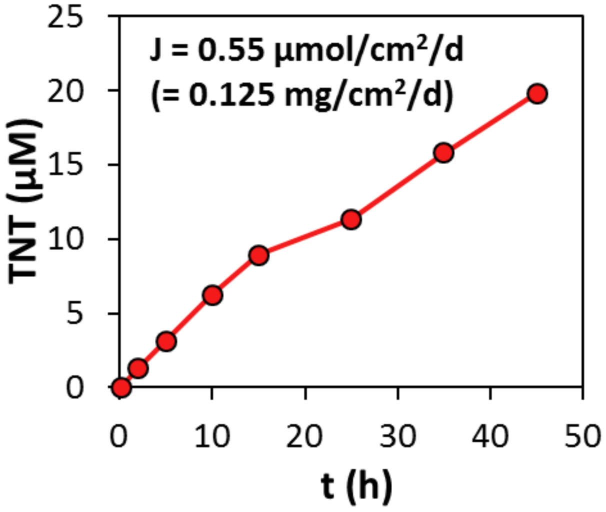

Figure 12: Increase of dissolved TNT in a benthic chamber enclosing an exposed explosive solid. The dissolution flux calculated from the observed trend is also indicated.

Salinity and temperature effects on dissolution were therefore tested under low mixing energy conditions in controlled laboratory experiments. The results confirmed the lower dissolution fluxes under mixing conditions more representative of the Baltic seafloor and revealed strong temperature and salinity effects on dissolution (Figure 13). Experimentation on solid explosives is logistically difficult, and while not necessarily a component of long-term monitoring, these results provide critical parameterization for model predictions.

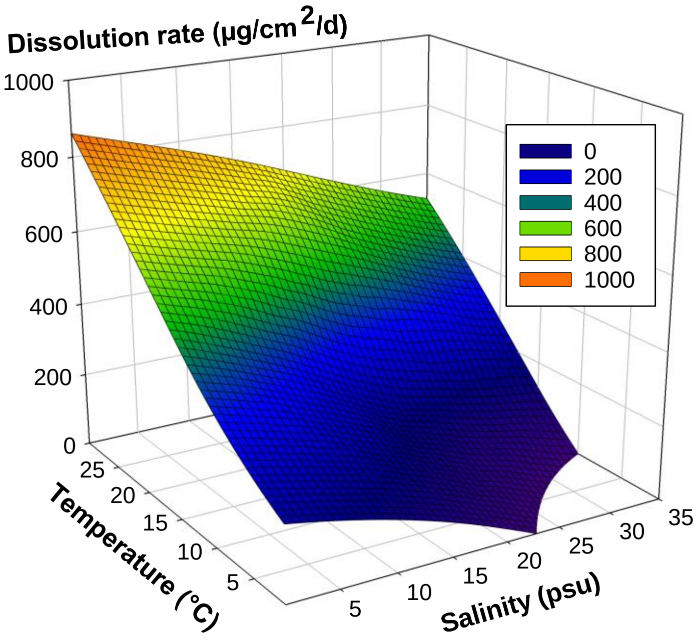

Figure 13: Effect of temperature and salinity on TNT dissolution from explosive solids. Low dissolution rates are observed at low temperature and high salinity, but are not visible here due to plotting artefacts.

Sink term – Degradation: Degradation of MCs determines the extent at which contamination can spread and affect ecological habitats. We conducted a series of incubation experiments to evaluate degradation rates and their dependence on temperature. Whole water MC degradation rates exceeded abiotic rates by a factor of about four, indicating microbial control (Figure 14). Similar to other microbially mediated reactions, TNT loss rates doubled with every 10 °C increase in temperature. The UDEMM numerical model combining these removal rates with dissolution fluxes predicts clear seasonal variation in water column MC.

Similar experiments using an axenic monoculture of the hydrocarbon-degrading bacterium *A. borkumensis* (S. Krause and A. Beck, unpublished) showed even higher rates of TNT removal, implying that microbial community composition is an important factor in site-specific removal. Indeed, microbial community composition is affected by factors such as salinity, which varies widely in estuarine systems such as the Baltic Sea. More work is necessary to establish whether a repetition of such experimentation is required as a component of monitoring or if existing data are sufficient to constrain the loss term for predictive modelling.

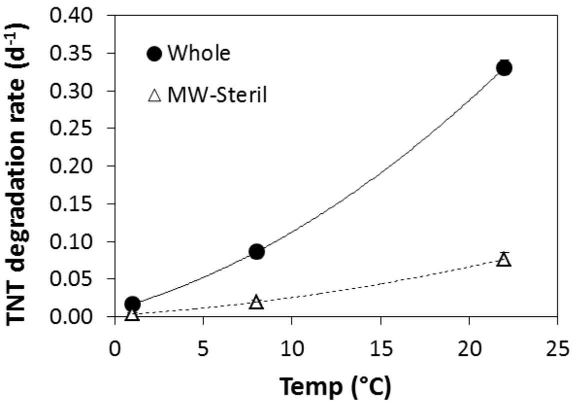

Figure 14: TNT degradation rates as a function of temperature in whole and microwave-sterilized Baltic Sea water (solid circles and hollow triangles, respectively). The microwave-sterilized treatment reflects abiotic degradation or adsorption onto suspended particles.

Metal contamination from munitions sources in the water column: Dissolved metals were measured during several cruises at the beginning of the UDEMM project in an attempt to determine contamination from primary explosives (e.g., Pb styphnate or Hg fulminate) or munitions housing (e.g., Fe or Zn). However, results showed no elevated enrichment (e.g. of Pb, Fe) in the vicinity of dense accumulations of munitions and concentrations were generally within the range expected for the Baltic Sea. As a result, samples for metals analysis were largely discontinued for the second half of the UDEMM project period.

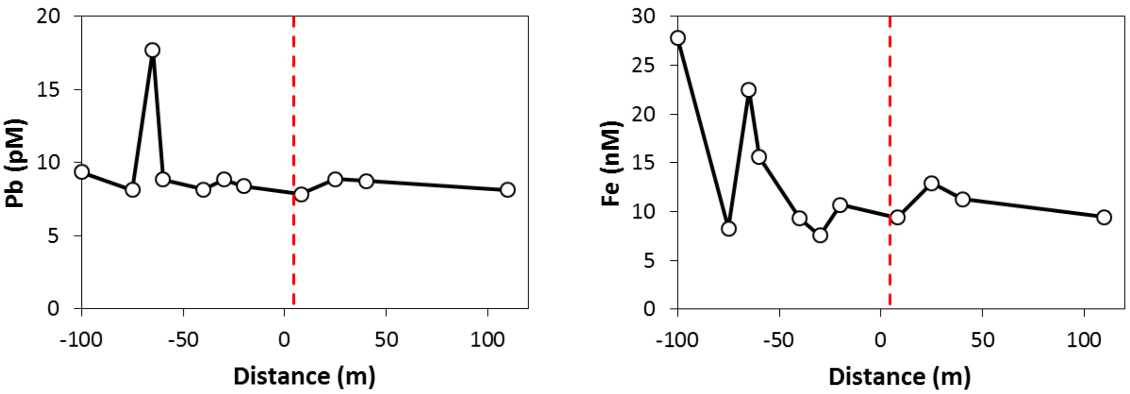

Figure 15: Dissolved Pb and Fe measurements in bottom-water samples from mine mound location (April 2016). Site distances are referenced relative to the mine mound.

Sediments: Surface sediments showed similar MC patterns as the water column, although a smaller set of samples was collected. On the regional scale, sediment MCs were higher at the Kolberger Heide dumping ground when compared with more distant sites (Figure 9a), suggesting that sediment-associated MCs are retained locally to some extent. Comparison of compounds in the TNT degradation chain (TNT -> ADNT -> DANT) showed no clear spatial gradient. ADNT and DANT were the most abundant compounds detected. Concentrations of the three compounds generally co-varied (Figure 10), but there were no obvious patterns in their spatial distribution.

Biota: Marine organisms were collected ad hoc throughout the UDEMM project period for detection of MCs in biotic tissue. Because they were not collected systematically on the spatial scales discussed in this report, the data cannot be reported in a similar manner to water and sediments. Here, the data are pooled into samples from the Kolberger Heide hotspot, and those collected elsewhere. Most biota samples were collected by hand by divers in the Kolberger Heide, and using a Van Veen benthic grab elsewhere. Plankton samples were collected using a small plankton net. Flatfishes (plaice and flounder) were collected by trawl by the Thünen Institute of Fisheries Ecology.

The biota samples measured here represent a range of trophic levels and approximate a reasonable, if incomplete, representation of the Baltic food web. Detection of different MCs was highly variable across species (Figure 16), although in many cases, an insufficient number of organisms were collected to be confident of the presence or absence of MCs in those organism types. Nonetheless, at least some of the target compounds were detected in individuals of all types of sampled organisms. This indicates widespread exposure to and uptake of MCs in the southwest Baltic Sea.

In most cases, MC concentrations in organisms from Kolberger Heide were higher than in organisms collected elsewhere. Macroalgae, tunicates, and sea stars from the Kolberger Heide contained the highest levels, which probably reflect their proximity to the hotspot source. In the case of sea stars, individuals collected from munitions surfaces had concentrations several orders of magnitude higher than other individuals. This may be due to sea star feeding on exposed explosive surfaces or it could be a potential artefact due to external adherence of explosive particles. The latter explanation is unlikely given the highly elevated levels of TNT transformation products in the sea stars (ADNT and DANT; Figure 16), which are not present to a significant extent in the solid explosives (our unpublished data).

In general, TNT and its transformation products, ADNT and DANT, were the most abundant MCs detected in biota, followed by DNB (Figure 16). The nitramine RDX was infrequently detected, which may reflect ring cleavage and elemental incorporation (Ballentine et al., 2016), rather than a lack of exposure. Indeed, the levels of all extracted MCs almost certainly underestimate the true exposure and body burdens due to unextractable residues (e.g., Smith et al., 2015).

No obvious trend of bioaccumulation or enrichment in successive trophic levels was evident, with similar levels in phytoplankton and macroalgae, benthic invertebrates and fish. This is consistent with previous studies showing low accumulation and little evidence of trophic transfer (Ballentine et al., 2015; Belden et al., 2005). This suggests that exposure occurs via the dissolved phase or by ingestion of particles with adsorbed MCs, but a gap remains in our understanding of how MCs enter marine organisms.

All of the MCs measured during UDEMM were detected in at least some individuals of commercially-exploited flatfishes (Figure 16), demonstrating the uptake into human seafood. The parent compound TNT was only rarely detected in all fish tissues (Figure 17). Similar to previous reports (e.g. Ownby et al., 2005), transformation products accumulate to a greater extent in fish tissue than the parent compound. Detection of ADNT was slightly more frequent than TNT and in both cases the highest occurrence was in samples from Kolberger Heide. In contrast, DANT was detected in virtually all samples, and all tissues. There was no significant difference between concentrations in organisms from Kolberger Heide compared to those collected elsewhere. This may reflect the widespread transport of TNT observed in the water column, coupled with the time required for microbial transformation to ADNT and then DANT. A major open question is whether DANT is taken up directly or if it is transformed within the fish tissues. Concentrations of DANT were significantly higher in fish liver tissue compared with other tissues. Concentrations of all three TNT-related compounds tended to be lowest in muscle tissue compared with other organs, which indicates a moderate risk to human seafood consumers.

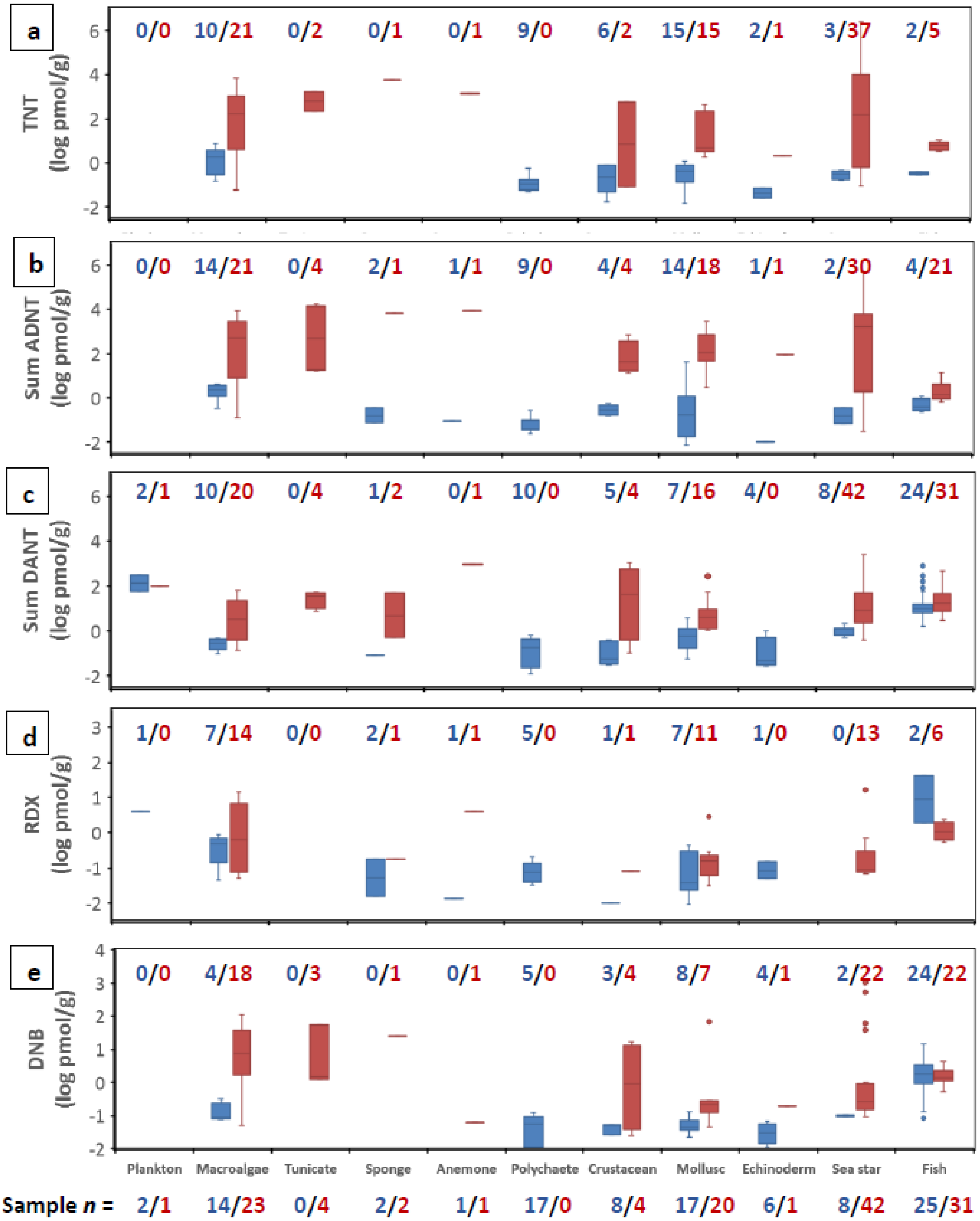

Figure 16: Tissue content (log-transformed pmol/g tissue) of a) TNT, b) ADNT, c) DANT, d) RDX, and e) DNB. Values reported for ADNT and DANT are the sum of the two differently substituted forms. Colours indicate samples collected at the Kolberger Heide site (red) or all other locations (blue). The

sample n shown below the organism type names on the abscissa indicates the total number of organisms that were collected ("non-KH/KH"). The numbers shown in each plot above the data boxes represent the number of samples of each type in which the corresponding MCs was actually detected (i.e. the number of data points included in each box-and-whisker set). Median MC content is indicated by the horizontal line within the boxes. Upper and lower bounds of the boxes indicate the upper and lower quartiles, and the whiskers indicate smallest and largest samples 1.5 times the interquartile range. Dots indicate data points outside this range.

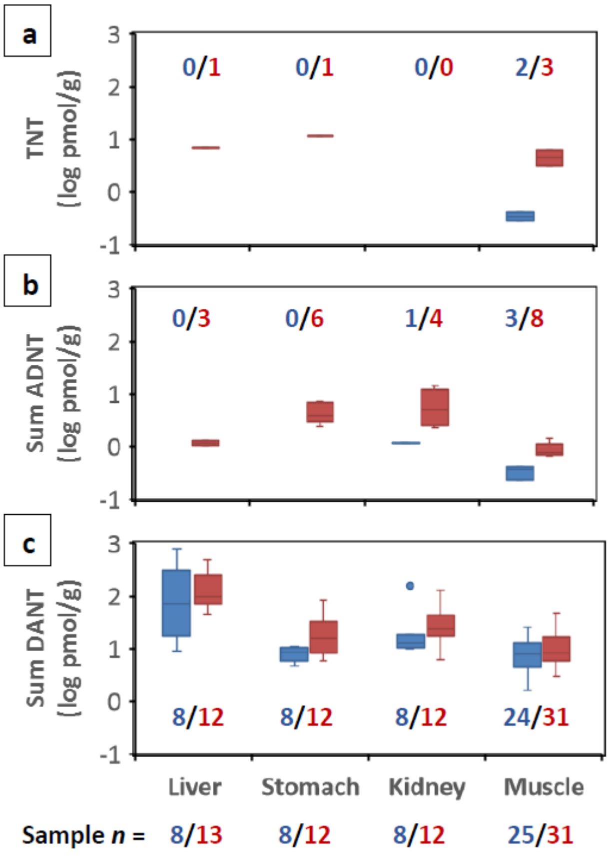

Figure 17: Tissue content (log-transformed pmol/g tissue) of a) TNT, b) ADNT, and c) DANT, in different organs in plaice and flounder. Values for ADNT and DANT are the sum of the two differently substituted forms. Colours indicate samples collected at the Kolberger Heide site (red) or all other locations (blue). The sample n shown below the tissue type names on the abscissa indicates the total number of organisms that were collected ("non-KH/KH"). The numbers shown in each plot above the data boxes represent the number of samples of each type in which the corresponding MCs was actually detected (i.e., the number of data points included in each box-and-whisker set). Median MC content is indicated by the horizontal line with the boxes. Upper and lower bounds of the boxes indicate the upper and lower quartiles, and the whiskers indicate smallest and largest samples 1.5 times the interquartile range. Dots indicate data points outside this range.

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2.4 Bio-Monitoring

Responsible institute: CAU-Toxicology

A total of nine cruises were carried out in the project at different times of the year and blue mussels *(Mytilus edulis)* were deployed and later retrieved at different positions. The bioconcentrations of 2,4,6-trinitrotoluene (TNT) and its main metabolites 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT) leaking from corroded munitions at a munitions dumping ground (Kolberger Heide, Germany) were measured in mussel tissue.

Analytical method: Two GC-MS/MS methods have been developed for the detection of explosive compounds in mussel tissue. The analytes TNT, 4-ADNT and 2-ADNT can be detected with a TG-SQC 5MS GC column (15 m × 0.25 mm × 0.25 µm) with an absolute detection limit of 0.5 - 1.5 pg. Separation of the diamino compounds is not possible with this column. After adapting the method and using a TG-5MS GC column (30 m × 0.25 mm × 0.25 µm), all five explosive compounds (TNT; 2-ADNT; 4-ADNT; 2,4-DANT; 2,6-DANT) could be detected with an absolute detection limit of 1.5 - 5 pg. Hexanitrodiphenylamine (a component of hexanite (German: “Schießwolle”)) could not be determined by gas chromatography due to its thermal instability. Instead, an HPLC method was developed, which allowed its detection in the pg-range. Due to the complex sample matrix it is not yet possible to detect hexanitrodiphenylamine in mussels. Liquid chromatography coupled to a mass detector (LC-MS) should overcome this problem, although a method has yet to be developed.

TNT metabolites in mussels near moored mines: With the help of divers, moorings with mussel bags were placed at varying positions near a pile of about 70 moored mines distributed over an area of approx. 70 × 30 square metres (Figure 18). To keep the mussel bags in place, moorings were constructed consisting of welded steel rods painted with a protective coating and two lifting bodies connected by a rope. Each mooring held two nets with 20 mussels each, one lying on the seafloor (0 m, position P0) the other positioned in a height of one meter (1m, position P1).

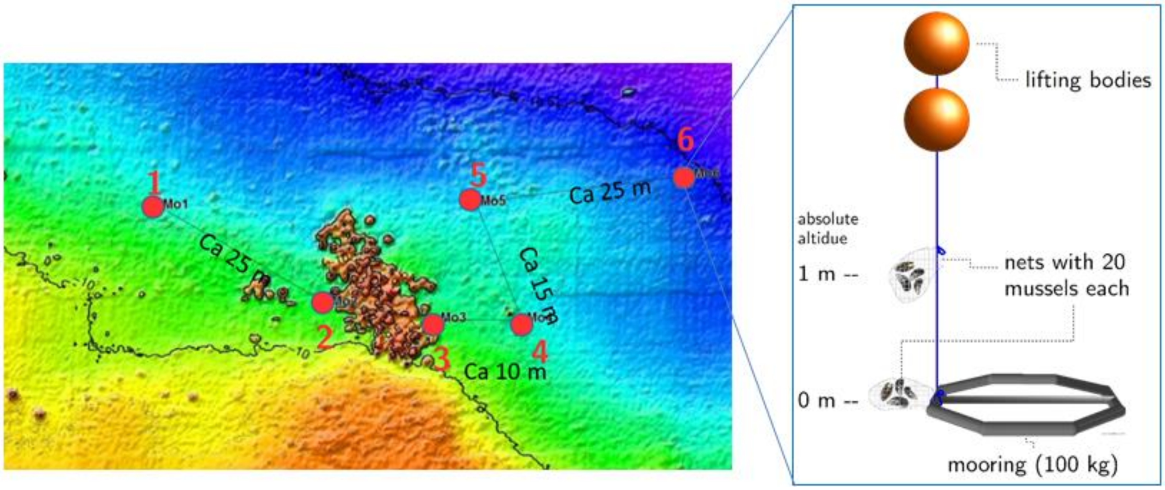
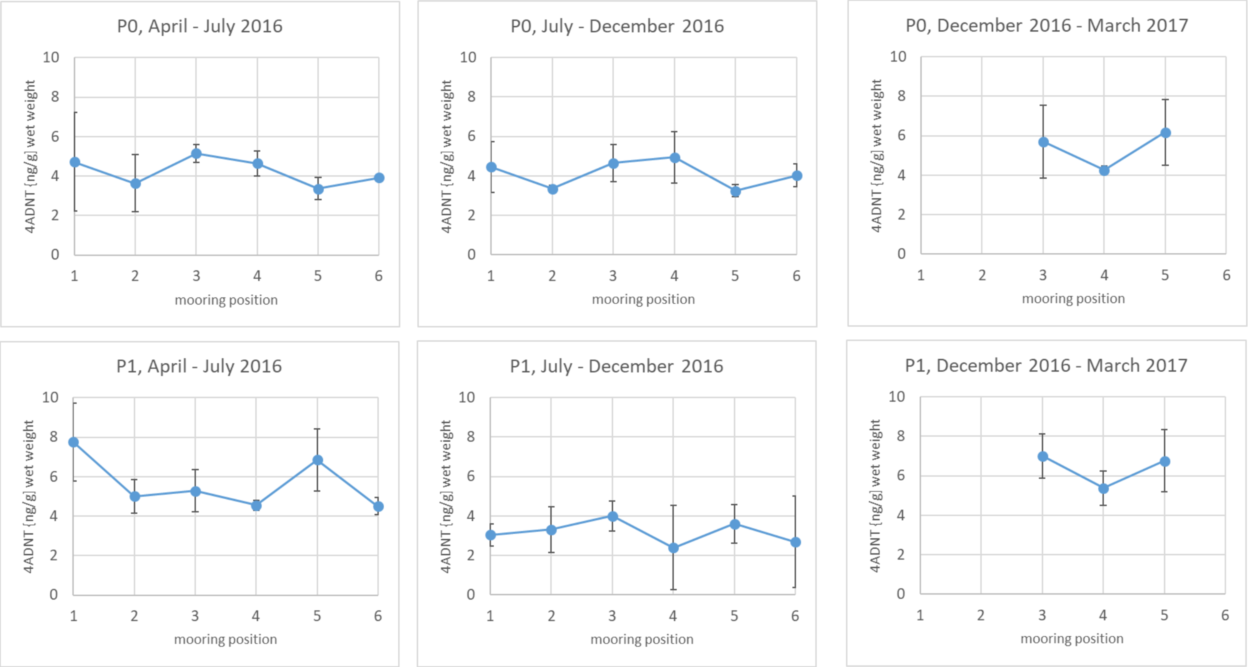


Figure 18: Map with Mussel-Moorings deployed in Kolberger Heide. On the right a schematic drawing of the mooring.

In order to monitor any differences resulting from changing seasons, three exposure time periods were chosen. First exposure period: April to July 2016 (106 d); second exposure period: July to December 2016 (146 d); third exposure period: December 2016 - March 2017 (92 d). We found amounts of 4ADNT in mussel tissue ranging from 2.40 ± 2.13 to 7.76 ± 1.97 ng/g (mussel wet weight). Neither TNT nor 2ADNT could be detected. Considering seasonal differences, orientation and distances of the moorings to the mine mound or seafloor, no correlation between levels of TNT or its metabolites in mussel tissue was evident (Figure 19).

When selecting exposure sites, we assumed to find greater amounts of TNT and its metabolites in mussels placed closely to the mines, and lower amounts in mussels placed at greater distance. However, there are hardly any differences of TNT metabolites in mussels among the locations. Even the mussels of mooring No. 6 with a distance of more than 20 m east of the mine pile have a similar 4-ADNT content as the mussels in the immediate vicinity of the mine pile (e.g. mooring 2 and 3, Figure 18 and Figure 19). A possible west-east current cannot explain this result, since the 4-ADNT contents of the mussels of mooring 1 are on a similar level. Apparently, dissolved explosive material is distributed relatively evenly like a diffuse cloud around the whole dumping ground.


P0, April - July 2016

P0, July - December 2016

P0, December 2016 - March 2017

P1, April - July 2016

P1, July - December 2016

P1, December 2016 - March 2017

Figure 19: 4ADNT-concentrations ± SD in mussels found at positions 1-6 after various exposure times and in different heights above the seafloor (P0, 0 m; P1, 1 m).

The concentrations of all other explosive compounds investigated were below the detection limit. The fact that we found no TNT indicates that conversion to (mainly) 4-ADNT happens rapidly. The reduction of TNT to the corresponding amino compounds is attributed to three different mechanisms: Photolysis, microbial alteration and metabolism catalysed by cytochrome P-450 enzymes within biota.

TNT metabolites in mussels near TNT lumps in direct contact to sea water: In the same area, several torpedo heads and mines have been destroyed by blasting. In the vicinity of the blast craters, unexploded material of various sizes (up to several decimetres) is lying openly on the seafloor. One mooring had been placed here with the lower mussel net sitting directly on a piece of explosive compound (position P0) and the other mussel net hanging one meter above (position P1, Figure 20). While only low 4ADNT concentrations were detected in mussels near a mound of sea mines (Figure 19), concentrations more than one magnitude higher were found in mussels from this position (Figure 21). Also, 2ADNT was detected in significant amounts. In addition, lower levels of TNT, which is otherwise rapidly reduced to amino derivatives (mainly: 4ADNT), were detected in this case. Much lower or zero concentrations were found in mussels from position P1, indicating high dilution rates (Figure 21). Adding the contents of all hazardous compounds of mooring 7 results in more than 50 times higher concentrations than in mussels at moorings 1-6 together.
Survival rates of mussels after a three-month exposure period near a mine mound were high (> 95 %). Even 18 out of 20 mussels in direct contact to unexploded material survived. No dead mussels were found in the net one meter above.

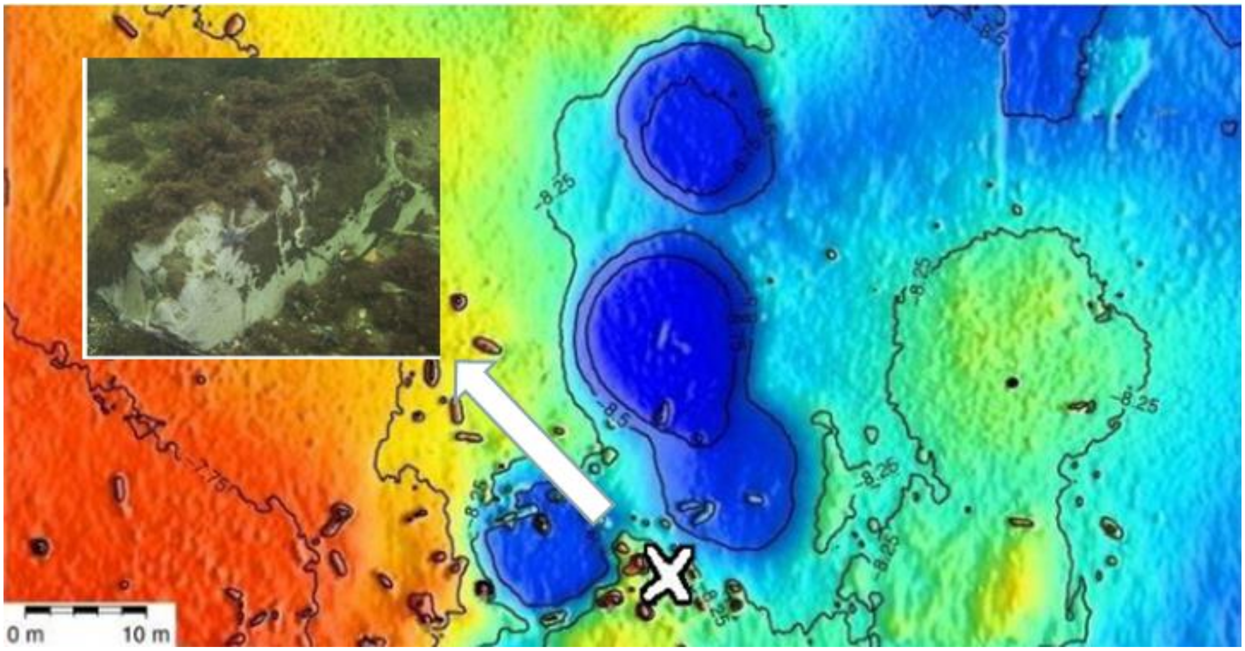


Figure 20: The white cross marks the position of mooring 7 located near blast craters on the seafloor. In the vicinity of blast craters unexploded material, a result of "low order detonations", is lying on the ground.

In the same area several torpedo heads and mines have been destroyed by blasting. In the vicinity of the blast craters unexploded material of various size is lying openly on the seafloor. One mooring had been placed here with the lower mussel net sitting directly on a piece of explosive compound (position P0) and the other mussel net hanging one meter above (position P1). While only low 4ADNT concentrations were detected in mussels near a mound of sea mines (Figure 19), concentrations more than one magnitude higher were found in mussels near from this position (Figure 21). Also, 2ADNT was detected in significant amounts. In addition, lower levels of TNT, which is otherwise rapidly reduced to amino derivatives (mainly: 4ADNT), were detected in this case. Much lower or zero concentrations were found in mussels from position P1, indicating high dilution rates (Figure 21). Survival rates of mussels after a three-month exposure period near a mine mound were high (> 95 %). Even 18 out of 20 mussels in direct contact to unexploded material survived. No dead mussels were found in the net one meter above.

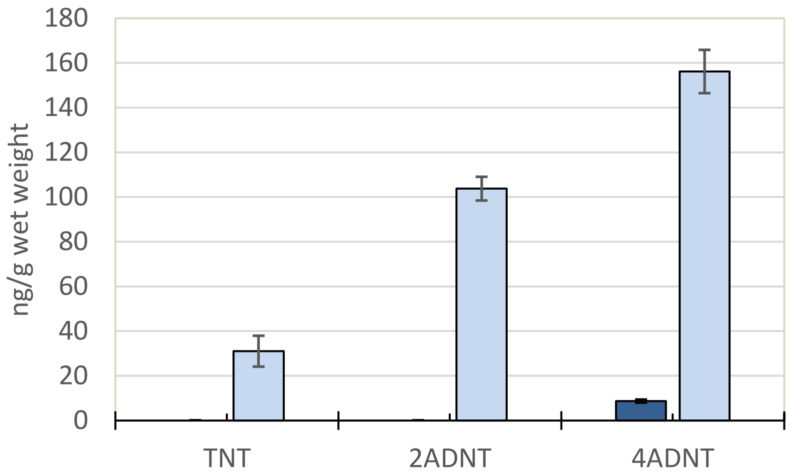


Figure 21: TNT, 2ADNT and 4ADNT concentrations in mussels in direct vicinity of a piece of unexploded material lying on the seafloor after an exposure period of 93 d. Data are given as mean values ± SD, n = 7-8 ng/g; light blue bars, position P0; dark blue bar, position P1. TNT and 2ADNT were not detected in mussels from position P1.

Since mussels from mooring 7, which were placed directly on a piece of hexanite, had such high STV concentrations in their tissues, we performed a study to investigate the dilution of hazardous compound accumulation in relation to distance. Mussels were exposed on the seafloor at 0, 30, 60 and 90 cm distance from the hexanite lump. As before, 4-ADNT was detected in highest concentrations, 2-ADNT and 2,4-diamino-6-nitrotol (2,4-DA-6-NT) were also detected, but no TNT (Figure 22).

Again, we found very high total concentrations of the different TNT metabolites, which were many times higher than the concentrations in mussels placed in immediate vicinity of dumped mines in different states of corrosion. Amazingly, no declining concentrations were detected in increasing distance of up to 90 cm to the piece of hexanite. Closer inspection of the ground revealed small pieces of explosive material scattered in the vicinity of the larger piece. Therefore, it was not possible to measure a gradient of TNT and its metabolites in the mussels placed on the sea ground.

Nevertheless, this unexpected result is a strong argument against the practice of blasting dumped munitions for clearing purposes. In case of low order detonations, a large area might be contaminated with unexploded material. While blue mussels tolerate quite high concentrations of toxic nitroaromatics, other benthic organisms could be much more sensitive. In addition, these compounds have the potential to enter the food chain. Already now mussels sitting in the vicinity of hexanite in contact with sea water are not fit for human consumption. This is of particular concern, since some nitroaromatic compounds are suspected carcinogens.

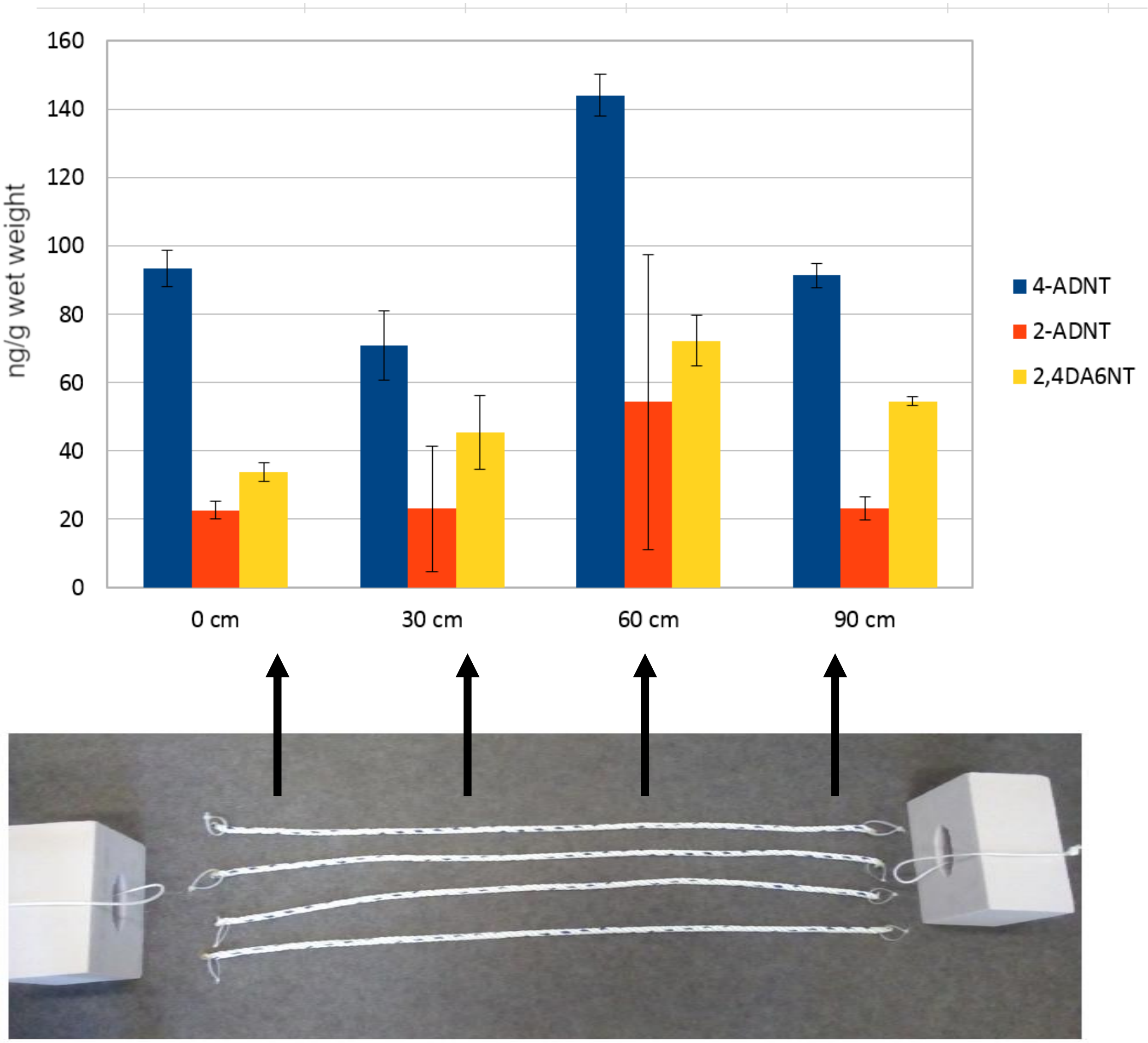


Figure 22*: Concentrations of 4-ADNT, 2-ADNT and 2,4-DA-6NT found in mussels near a piece of hexanite lying on the seafloor. Two stones and several ropes were used to held the mussel bags in place.*

References:

Appel D, Strehse JS, Martin HJ, Maser E. Bioaccumulation of 2,4,6-trinitrotoluene (TNT) and its metabolites leaking from corroded munition in transplanted blue mussels (M. edulis). Mar Pollut Bull. 2018 Oct; 135: 1072-1078.

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2.5 Oceanographic field measurements

Responsible institute: IOW

For the munitions dumping ground Kolberger Heide, currents, salinity, temperature and turbidity have been monitored by ADCP and SeaCat measurements between 2016 and 2018, to later on validate the modelled hydrodynamics. The currents close to the bottom are slower than those on the surface (0.04 m/s compared to about 0.3 m/s). The direction of the current is mainly west-northwest at the surface layer and varies between northwest and southeast at the bottom layer (Figure 23).

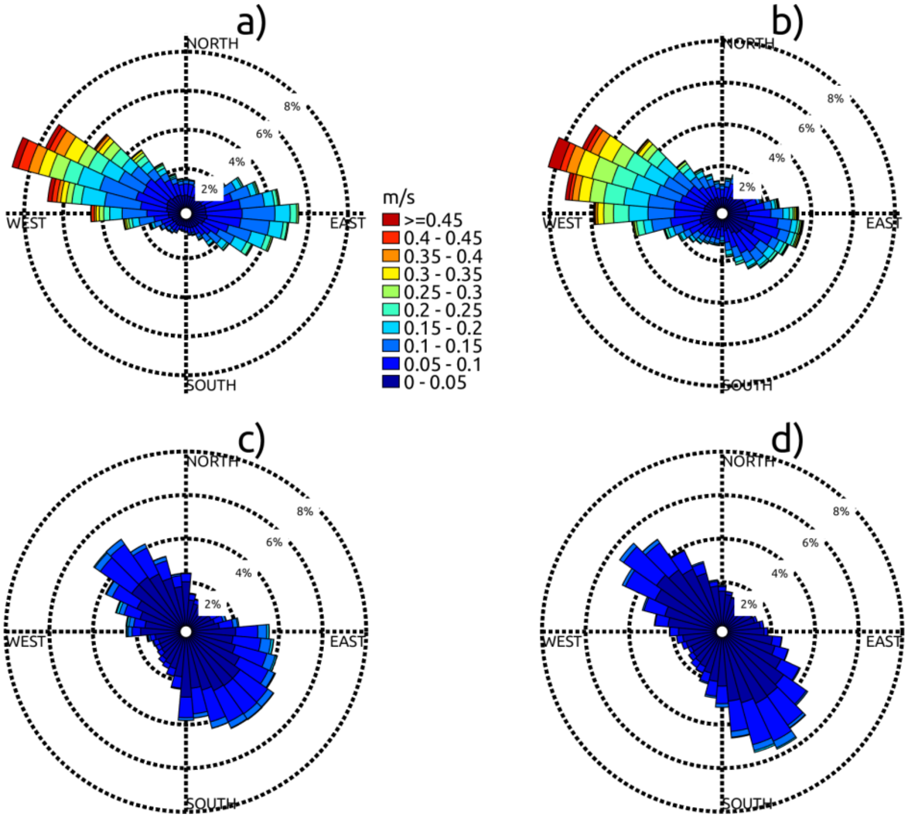

Figure 23: Distribution of current direction and velocity between September 2016 and June 2018 at the munitions dumping ground Kolberger Heide. On the left (a, c), we show the observed values and on the right (b, d) the modelled values. The upper row depicts the surface values and the lower row shows the current rose for the near bottom currents. The data was measured with the 1200kHz ADCP of the IOW.

The turbidity is low on average. The salinity and temperature points at minor small-scale inflow events are shown in Figure 24. The comparison of the measured temperature with the modelled temperature at the bottom layer at Kolberger Heide shows a high similarity (Figure 25). By contrast, the general trend of the modelled salinity is similar to the measured but the model underestimates the salinity by 1-2 g/kg.

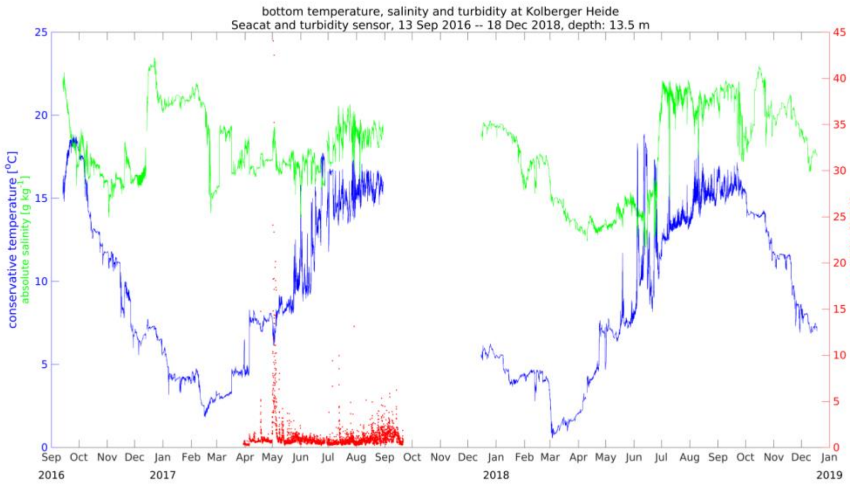

Figure 24: Time series of temperature (blue), salinity (green) and turbidity (red) close to the bottom.

This indicates an underestimated stratification, which is a general challenge for numerical ocean models in that region. A potential consequence could be an overestimation of the vertical diffusivity across the halocline. As a result, the upward transport of bottom placed hazardous substances in the model will be overestimated. Even with the use of terrain following vertical adaptive coordinates (Hofmeister et al., 2010; Gräwe et al., 2015) the stratification dynamics in the western Baltic Sea pose a challenge to state of the art ocean models (Klingbeil et al., 2018).

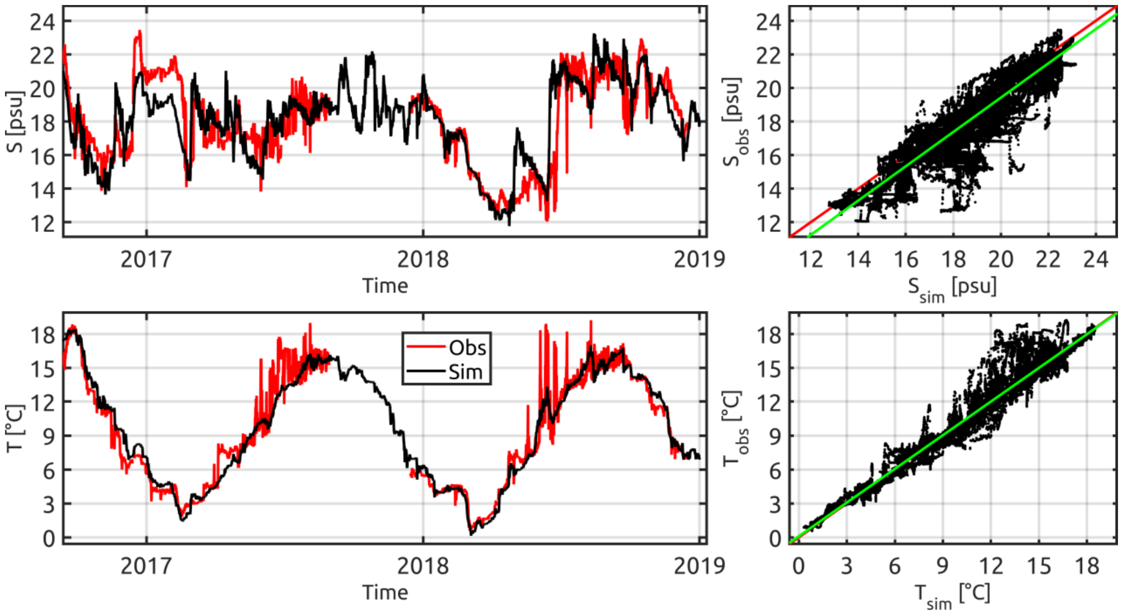

Figure 25: Comparison of modelled and measured salinity (upper row) and temperature (lower row) in the bottom layer at Kolberger Heide as time series and correlation plots. In the right column, we show the scatter plot or correlation plot. The red line indicates a line with a slope of unity. The green line indicates a linear fit.

2.6 Coupled TNT-GETM model

Responsible institute: IOW

The hazardous substances are modelled as TNT in form of open TNT surfaces at the bottom, dissolved TNT in the water column and TNT accumulation in benthic filter feeders (Figure 26). The TNT dynamics depend on temperature- and salinity-depending solubility, temperature-depending degradation rate in the water column and filter capacity of the benthic filter feeders (mussels). The TNT model is coupled via FABM (Framework for Aquatic Biogeochemical Models, Bruggeman and Bolding, 2014) to the GETM model. The parametrization is based on lab and field experiments in section 2.3(see Figure 13). For the mussels we assume a filter capacity of 1.5 m^3 m^{-2} d^{-1}, which corresponds to approximately 100 mussels per m^2 (personal communication Alexander Darr, IOW).

The source regions of TNT in the model are based on the munitions dumping grounds described in the database of BLANO-Expertenkreis “Munition im Meer” and the naval command of the German armed forces (Marinekommando der Bundeswehr – Abteilung Einsatz, Unterabteilung Geoinformation) (Figure 27).

In section 2.2 the amount of dumped munitions and the size of their open TNT surfaces is estimated based on hydroacoustic measurements and underwater video recordings at Kolberger Heide. About 100 corroded pieces of munition were found on an area of 1260 ha with an open TNT surface of about 50 × 50 cm^2. This estimate has been applied to all dumping grounds in the western Baltic Sea with the assumption that munitions-contaminated areas cover only 10 % of the open surfaces of the dumping grounds and munitions suspected areas only 1 % of the open surfaces.

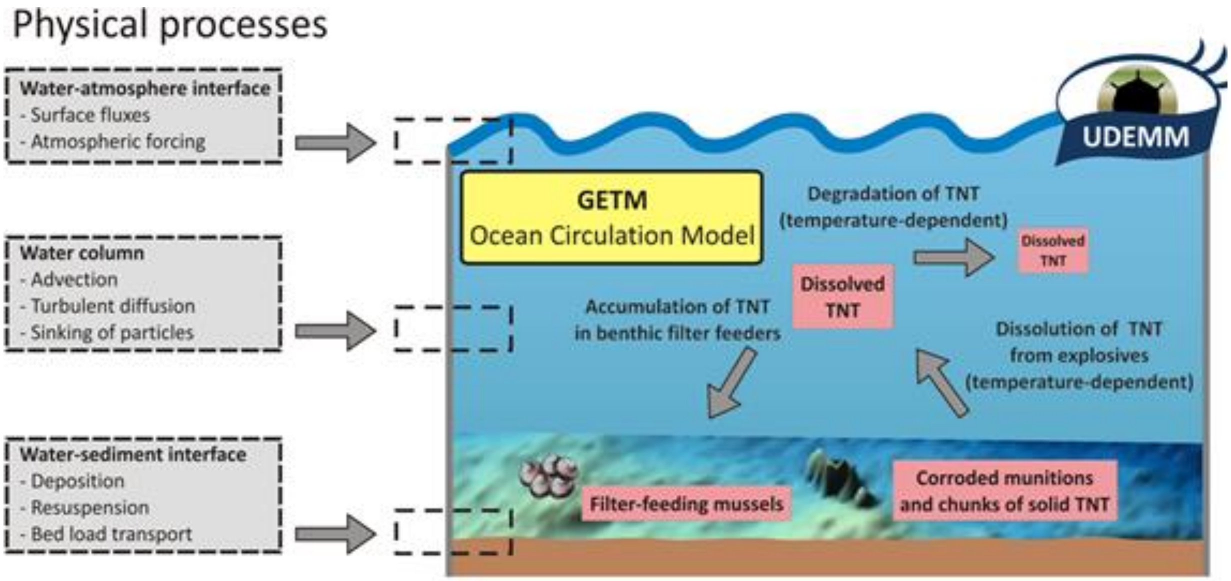

Figure 26: Schematic sketch of the concept of the coupled TNT-GETM model.

In a sensitivity study the size of the open TNT surfaces was varied between a factor 10 to 100 smaller and a factor 10 to 100 greater than the estimated open TNT surface of 50 × 50 cm^2. The sensitivity study has been compared to measured field TNT concentrations with the result that open TNT surfaces of 1 × 1 cm^2 per piece of ammunition are most realistic (Figure 28). The modelled TNT-concentrations show a seasonal cycle with values between 10 and 30 ng L^{-1} in summer (water temperatures between 5 °C and 20 °C) and about 1 ng L^{-1} in winter (water temperatures below 5 °C) which covers the measurements of 20 – 25µg/l close to the open surfaces and less than 1 ng L^{-1} in larger distances.

With the assumed filter capacity of 1.5 m^3 m^{-2} d^{-1} and open surfaces of 1 × 1 cm^2, mussels could accumulate 29 mg m^{-2} d^{-1} in winter and 151 mg m^{-2} d^{-1} in summer. With the assumption of 100 mussels per m^2 a single mussel ends up with 29-151 ng d^{-1}.

In Figure 28, we show some time series of modelled parameters at Kolberger Heide. In the upper panel, we show the water age (the time elapsed since last contact with the surface). The water age, sometimes also called “ventilation age”, is a good proxy for stratification. One can clearly see low values in winter (well mixed water column) and high values during summer. Since in summer the bottom layer is shielded by the thermocline and/or the halocline, the vertical exchange is limited and the water age increases, reaching values of up to 60 days. The near bottom concentration shows a similar pattern: low values in winter and high values in summer. This annual cycle is mainly caused by the temperature dependency of solubility of TNT. The effect of stratification and enrichment below the pycnocline adds to that effect. In the model, we can do bookkeeping of the TNT dissolved into the water. In the lower panel of Figure 28, we show the total dissolved amount of TNT at all dumping grounds. On average, 2 tons of TNT go into suspension every year. To get an approximation, we take the estimation of 300,000 tons of dumped munitions in the western Baltic and assume that it consist of 50 % TNT. Given the suspension of 2 tons of TNT per year, we estimate that it will take approximately 7000 years to bring all TNT into suspension. Although this is only a crude approximation, it should stress the importance to take action and remove the dumped munitions from the sea.

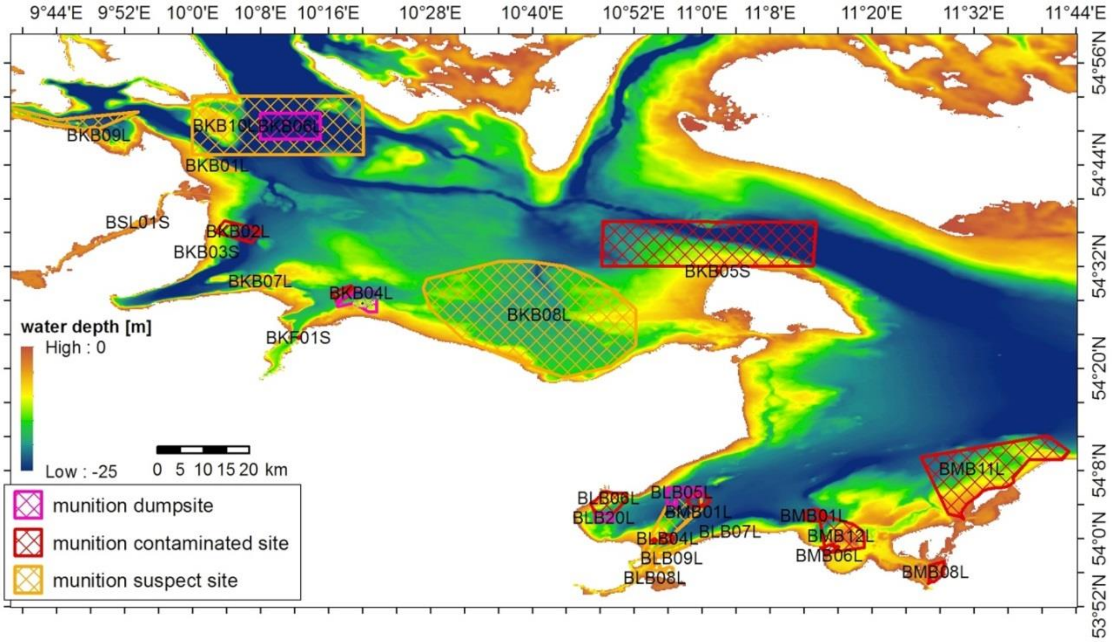

Figure 27: Munitions dumping grounds and the bathymetry of the western Baltic Sea. Dumping grounds are marked magenta, munitions-contaminated regions red and munitions suspected areas orange. The data are based on http://amucad.egeos.de.

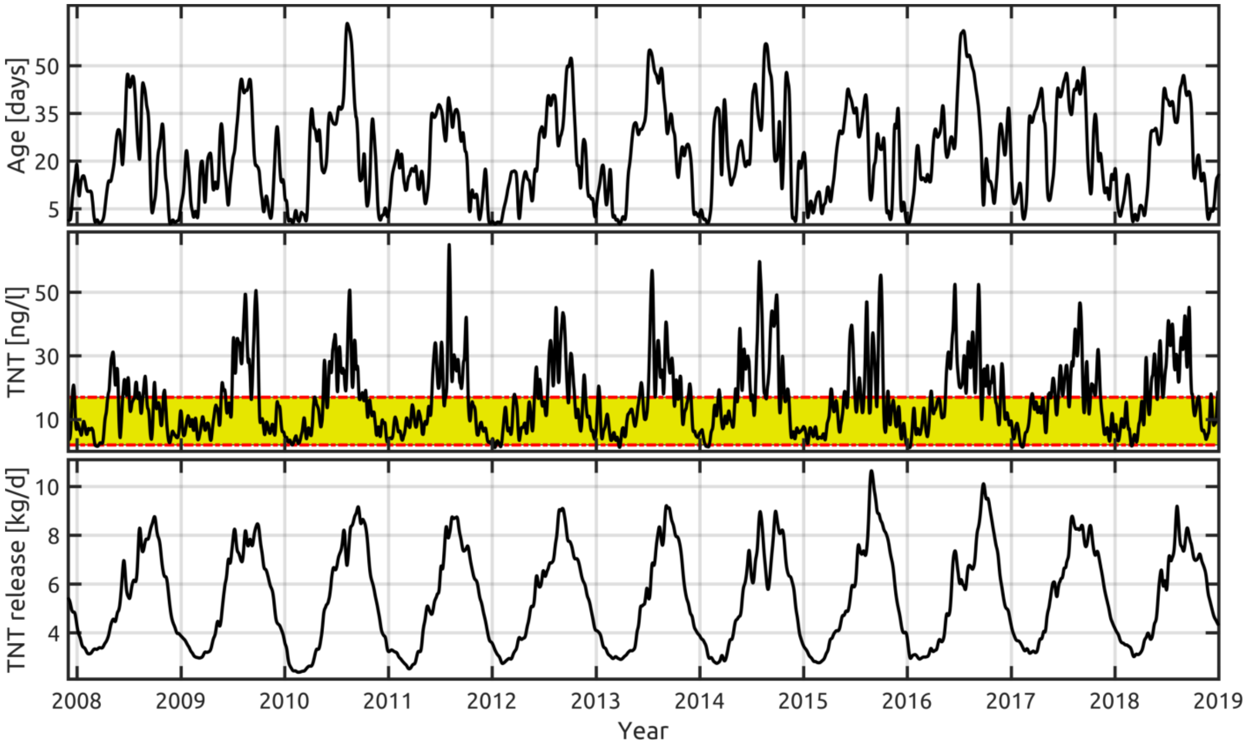

Figure 28: Time series of the modelled water age at Kolberger Heide (upper panel), TNT concentration in the bottom layer at Kolberger Heide (middle panel) and release of TNT into the water column for the entire western Baltic Sea, for the period 2008-2018. The yellow area in the middle panel indicates the span of the measurements.

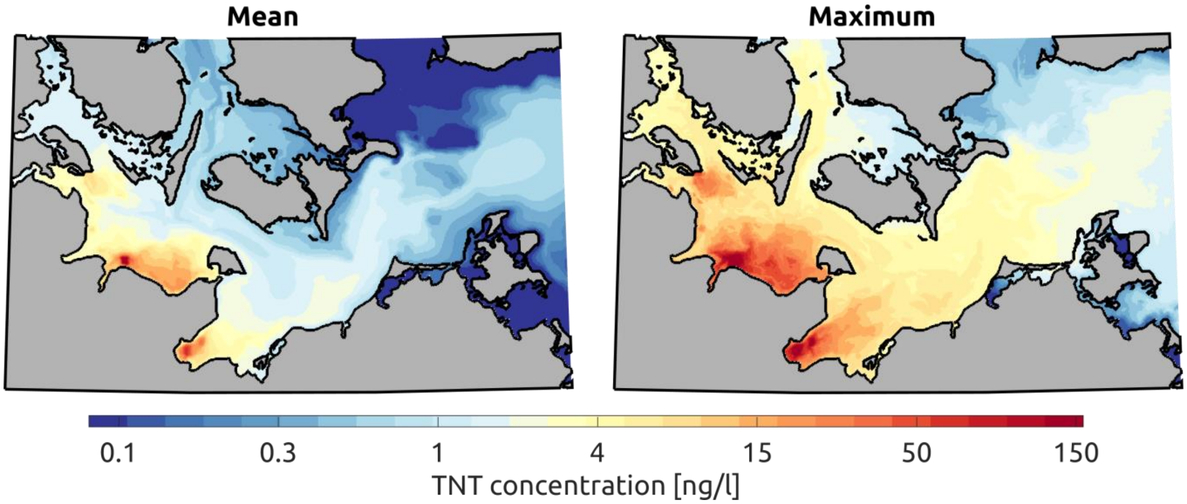

Figure 29 TNT concentration at the bottom layer. Left: annual mean concentration Right: annual maximum concentration during the period 2006 - 2018. Please note the non-linear colour scaling.

Figure 29 shows the mean and maximum TNT concentration during 2006 - 2018. The TNT concentrations mirror the locations of the dumping grounds, especially at Kolberger Heide and Bay of Lübeck. Near the dumping grounds, mean concentrations can reach values of 30-50 ng L^{-1}. However, some ten kilometres away, the concentration drops below 5 ng L^{-1}. The model results indicate that even in the Arkona Basin dissolved TNT can be found (< 1 ng L^{-1}). If one is focusing on maximum values, these occur likely in summer. The high water temperatures in combination with a thermocline and calm conditions can enhance the near bottom concentrations (like during the exceptionally warm summer in 2018). The maximum values are shown in Figure 29. TNT concentration can be as high as 100 ng L^{-1} and even exceed this value locally.

As a final exercise, we compare the measurements made during the MineMoni cruise with the modelled values. In Figure 30, we show the average near bottom concentration of TNT during the cruise (for comparison see section 2.3). As already seen in Figure 29, we can clearly identify the dumping grounds as hotspots of high TNT concentration. To get a better understanding of the complex vertical structure of the tracer fields, we show vertical transects in Figure 32, of temperature, salinity and TNT concentration in the Fehmarn Belt, the Kadetrinne and across the Darss Sill. In the TNT field, we see a multi-layer structure: Low bottom values in the Fehmarn Belt, overlaid by water masses with a higher TNT concentration. This structure is mirrored by the salinity field. An inflow of dense saline water with low TNT concentration is overlaid by less dense fresher water, but with higher TNT values, likely originating from the Bay of Lübeck.

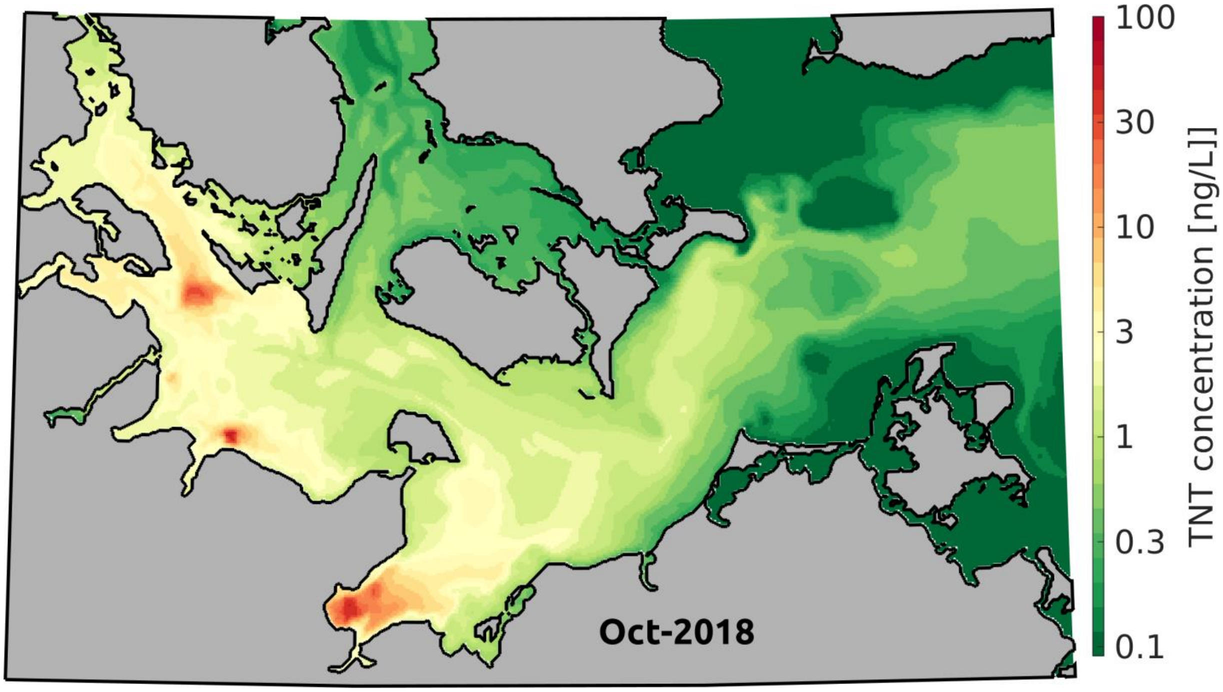

Figure 30 Distribution of TNT in the near bottom layer during the MineMoni Cruise.

To provide a performance measure of the implemented TNT module in GETM, we finally compare the measured TNT concentration during the MineMoni cruise (October 2018) with the model predictions. In Figure 31, we present the scatter plot of the data. Especially for TNT values smaller than 20 ng L^{-1}, the model shows good predictive skill. However, for large values, the model system underestimates the measured values. As one possible reason, it is very likely that not all sources of dumped munitions were included in the model. Furthermore, one still has to keep in mind that the model provides grid cell averages. Thus, the model system computes a mean concentration over a 600 × 600 m^2 grid cell. Hence, peak values are often underestimated.

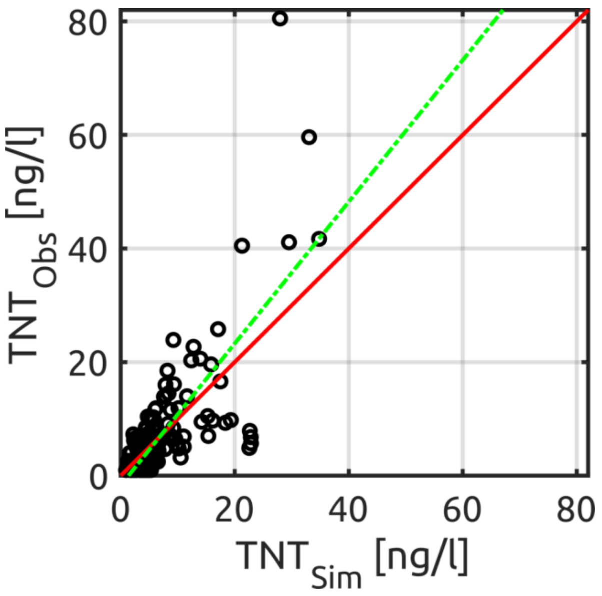

Figure 31 Comparison of measured and modelled TNT concentrations during the MineMoni cruise. The red line indicates a line with a slope of unity and thus perfect prediction. The green dashed-dotted line represents a linear fit.

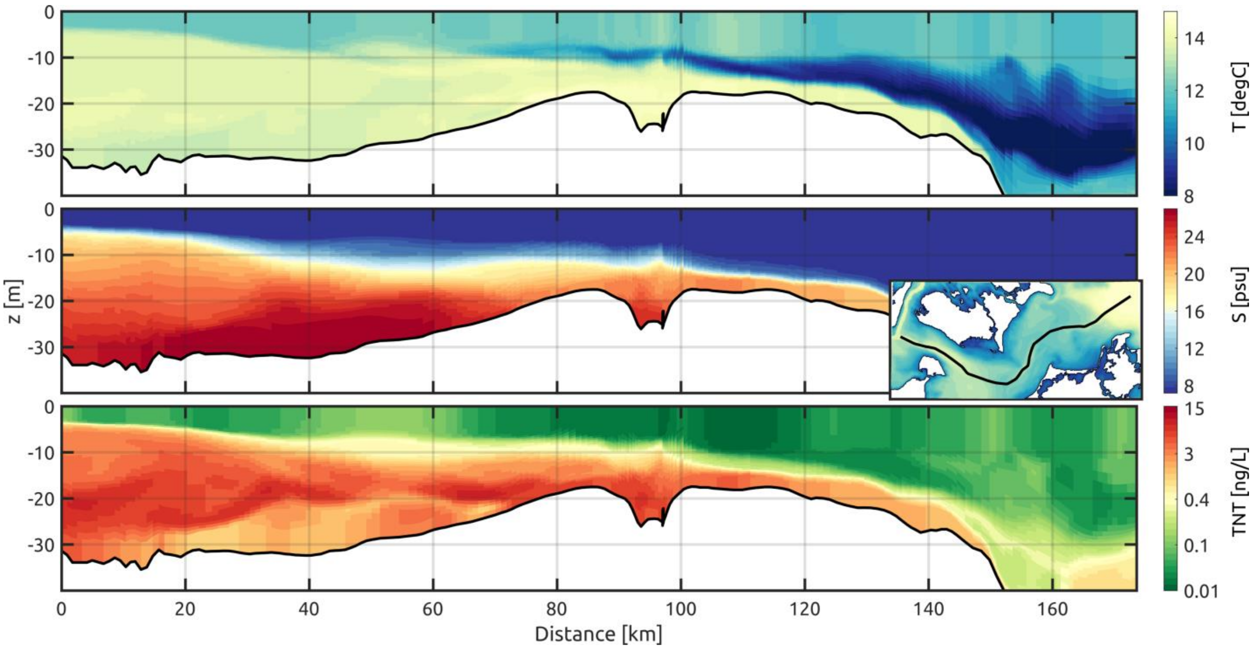

Figure 32 Transect through the Fehmarn Belt, Kadetrinne and Darss Sill during the MineMoni cruise POS530. Shown are the temperature (upper panel), salinity (middle panel) and TNT (lower panel). The insert shows a map with the route of the transect. For comparison, see the measured data in section 2.3.

The presented TNT-GETM model gives a first approximation of the distribution of TNT in the western Baltic Sea region. However, several aspects could influence the results and the performance of the model as an early-warning system:

1. The applied TNT parameterization is based on a limited number of observations and experiments that are extrapolated to all munitions dumping grounds, munitions-contaminated

areas and munitions suspicious areas with a scaling factor. On the one hand, the amount of dumped munitions in the other areas as well as the open surfaces could differ. On the other hand, the composition of the hazardous substances in the dumped munitions in the other areas could be different. Especially munitions produced at the end of WWII were filled with a mix of different substances, besides TNT. This was caused by the lack of material supply. TNT is one of the common compounds but there are others, not investigated in detail in this project. For instance, the seawater chemistry of RDX or HDX might be different from TNT.

2. The assumed scaling factor could be over- or underestimated. The lab measurements do not take into account the biofilm covering of the open surfaces, which is likely subject to an annual cycle. How this biofilm affects the solubility of TNT is still unknown. Moreover, until now, the effects of wind waves and currents on the solution of TNT are unknown. One can assume that an increased bottom stress, either due to wind waves or due to oceanic currents, will likely increase the solution of TNT on open surfaces. Moreover, it is likely, that under the influence of surface wind waves, the vertical mixing from the bottom boundary layer to the surface is increased. Especially in the Bay of Lübeck but also in the entire Baltic Sea, hypoxia poses a challenge to higher trophic levels. Along with low hypoxic or even anoxic conditions, the occurrence of hydrogen sulphide (H_2S) is likely. Until now, it remains unclear how H_2S interacts with munitions shells (increase or decrease of corrosion) or even TNT (faster/slower degradation). Anyhow, to support this hypothesis, dedicated lab experiments are needed to quantify the impact of varying bottom stress on the release rate of TNT.
3. Currently no information is available on the interaction of TNT and biogeochemistry. For instance, chlorophyll-a might increase or decrease the dilution of TNT. At present, we use only temperature to compute the degradation of TNT in the water column. Here, temperature is a good proxy for biological activity, but also microbiological effects. However, these effects need to be separated to account for individually.
4. The present implementation of the TNT chemistry only handles TNT. As shown by the biomonitoring (section 2.5), the TNT metabolites 2-ADNT or 4-ADNT, pose a similar threat to the environment as TNT. Thus, the implemented simple TNT chemistry needs to be expanded.
5. Furthermore, more data of open TNT surfaces of the dumped munitions in the different areas (dumping ground, munitions-contaminated and munitions suspected areas) are needed to tune the model more realistically.
6. Finally, the spatial resolution of GETM is 600 m, while Kolberger Heide is about 1,200 ha in size, which results in about three TNT sources per GETM-grid box modelled as point source. A more realistic view would be the modelling as a Gaussian shaped TNT source with declining concentration with distance and a higher spatial model resolution.
7. The impact on the filter feeder mussels also depends on some estimates. More data about their distribution as well as of the mechanism of how they accumulate TNT is needed.

To conclude, the coupled TNT GETM allows for a first overview of the possible consequences of sea dumped TNT munitions in the western Baltic Sea and can built the basis for further research.

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2.7 Conclusion, knowledge gaps and recommendations

2.7.1 In Conclusion

The Kolberger Heide and POS530 field studies, onshore analyses and related modelling clearly showed that the used techniques and new methodological approaches are very adequate to get a fast and conclusive inventory of the munitions in a certain area and the spread of contaminates into the environment. We could clearly show that munitions are releasing different kind of explosive compounds as dissolved phase into the water; TNT, metabolites of TNT, RDX, and DNP sometimes reach high concentrations. The uptake of TNT and TNT metabolites in mussels shows that fauna is being impacted to a higher degree in close proximity to open explosives, but even samples further away from open explosives were impacted. Table 4 shows the range of concentrations that have been measured in different types of samples.

Table 4: Summary of concentrations of selected explosive compounds in different sample types.

Sample type	Munition compounds				
	TNT	**2-ADNT**	**4-ADNT**	**RDX**	**DNB**
Water** inside Kolberger Heide (pM)	0.3 - 355	0.7 - 93	1.2 - 170	0.3 - 14	0 - 31
Water** outside Kolberger Heide (pM)	0 - 183	0 - 71	0 - 101	0 - 666	0 - 2000
Mussels from bio-monitoring [ng/g wet weight]	31*	104*	2,4 - 156	n.m.	n.m.
Biota (pmol/g dry or wet) (Plankton, macroalgae, tunicates, sponges, crustaceans, molluscs, echinoderms, polychaetes, anemones, sea stars, fish)***	0.01 - 2.45 × 10^6	0.007 - 2.37 × 10^5	0.007 - 2.77 × 10^5	0.009 - 42	0.01 - 1070
Sediment (pmol/g dry or wet)	0 - 184	0 - 87	0 - 74	0 - 7.2	0 - 78

* Detected only in mussels in direct contact with unexploded material.

** Data include only samples from the water column, not feature-scale samples collected adjacent to munitions.

*** See Figure 16 and Figure 17.

n.m.: not measured

2.7.2 Knowledge gaps

Knowledge gaps have been identified by the UDEMM consortium. This non- complete list is presented to highlight the topics and detailed needs to better understand the impact of marine munitions on the environment. We regard all of them as being important enough to be part of upcoming monitoring and particularly future financed research. They are grouped in different scientific disciplines.

Archive investigation knowledge gaps:

Extensive work has been done but massive amounts of archive documents still need to be carefully examined. Methods such as digital text recognition and machine learning could enhance the process and help with the identification and connection of information. This will lead to a more precise knowledge on the number of ammunition objects dumped into the sea and a better identification of so far unknown hot spots.

Physical knowledge gaps:

Environmental controls on munitions housing corrosion: Corrosion was not addressed in UDEMM.TNT release and distribution primarily depends on the source strength. The strength of this source depends on the corrosion state and exposure of the explosives to seawater. Environmental factors such as salinity and dissolved oxygen may affect corrosion rates, and most likely vary throughout the Baltic Sea.

Effect of sedimentological processes on munitions deposition: Sediment scours can form around ammunition objects due to water currents or waves initiating object displacement and burial. These processes are complex and coupled to sediment composition, slope, water depth, object shape and incident burial depth. Numerical models are still not able to include all parameters and therefore scour formation, as well as subsequent displacement and burial cannot be reliably predicted. Also the effect of vegetation overgrowth of objects on the fluid dynamic around the object and its influence on mixed grain size distributions need to be addressed to generate a good predictive numerical model on munitions re-deposition and long-term dumping ground stability.

Influence of hydrodynamic forces (current or wave induced) on TNT solubility and spreading: The influence of hydrodynamic forces acting on exposed explosives might increase their mechanic erosion and enhance solubility. Such processes should be incorporated into chemical models for predicting mixing and dissolution rates. Mechanical weathering and erosion of exposed explosives will modulate MC spreading and environmental contamination.

Chemical knowledge gaps:

Mixing energy effects on explosive dissolution rates: Results of laboratory and in situ dissolution experiments in UDEMM indicated low release rates and suggest that mixing energy may be the primary control on TNT dissolution rate. Regional differences or changes in waves and currents may therefore have a major effect on MC release from underwater munitions.

Effect of climate change on munitions and contaminant release: Climate change effects include increasing temperature, decreasing pH, and increasing intensity of storms. These changes will impact the rate of corrosion, chemical release, and movement of underwater munitions. Additional work on the relevant parameters will allow evaluating the climate induced consequences of MC release. Potential effects could already be tested with the oceanographic model developed in UDEMM.

Microbial and physicochemical degradation in relation to time and environmental parameters: The good match between measured and modelled TNT concentrations including microbial TNT transformation suggests that microbial activity is indeed a major control on the fate of TNT in the bottom water. More research is needed to evaluate the strong temperature dependence of microbial activity but at the same time quantify the sunlight effect on TNT transformation in surface waters. The effect of decreased oxygen concentrations (and dissolved sulphides) during hypoxia events may also be an important factor as some TNT transformation pathways occur only under strictly anoxic conditions.

Importance of MC mineralization vs transformation: Transformation products of TNT (ADNT, DANT) were identified to be important components of MC contamination in the environment. These daughter-compounds, as well as others, can be equally toxic as or more toxic than the parent compound. Quantitative mass balance analyses for MCs released from underwater munitions are important to understand the extent to which contaminants are removed from the environment (i.e., degraded to inorganic constituent compounds) or simply transformed to other forms.

Biological and toxicological knowledge gaps:

Pathways of contaminant accumulation in and out of the biota: MCs were measured in different organisms found in place and accumulation was observed in mussels deployed for biomonitoring. Questions still remain, if organisms accumulate MCs from the dissolved phase, particulate food they ingest (including particulate MCs) or both. It is important to determine the partitioning of MCs in different body tissues, particularly in relevant seafood organisms. Also the effect of potentially decreasing contaminant levels within organisms should be determined, to establish if contaminants can be fully degraded or ‘flushed’ from the organism.

MCs accumulation in food webs and human seafood: MCs were measured in UDEMM in a limited number of organisms throughout the food web, including seafood species. A systematic and statistically robust investigation is necessary to determine, whether MCs are transferred among trophic levels, and the extent to which commercial seafood is affected by environmental MC contamination already.

DMM as habitats: Ammunition objects provide hard substrate and shelter for sessile biota and actually act as artificial habitats and reefs. Since marine flora and fauna particularly live in such environments, a systematic comparison of dumping ground with uncontaminated marine habitats of very similar type is important to determine the importance of dumping ground as local ecosystems.

MCs as part of a multi-stressor environment: Marine organisms are exposed to a number of stressors, which influence their reproduction rate and fitness. Assuming that MCs do accumulate within marine organisms and do have a certain toxicity, it is important to analyse the role of these contaminants as part of the multi-stressor environment for individual groups of organisms. Effects of TNT on fish health might be e.g. smaller or greater compared to a parallel uptake of e.g. heavy metals like mercury. It might also be possible that negative effects of other stressors can be enhanced, when MC uptake is increased. A clear understanding of MCs on the organism health in a multi-stressor environment needs to be known.

Toxicity of different MCs: Toxicity levels for all MCs and its degradation products need to be established. This way, human seafood can be evaluated to be toxic or not more easily and recommendations can be given. The establishment of proper toxicity levels is the base for any recommendation to restrict seafood consumption or to close fishing grounds.

Monitoring knowledge gaps:

Spatial and temporal patterns observed in UDEMM and replicated in the computer model revealed widespread and seasonally-variable transport of MCs. Long-term monitoring at munitions hotspots and control sites is necessary to evaluate the persistence of these trends, and the extent to which hotspots differ from un-impacted locations.

Methodological knowledge gaps:

Validation and inter-comparison of analytical methods: Two analytical methods were used in UDEMM (GC-MS and LC-MS), but many others exist. It is critical to validate and ground truth these different methods. Intercomparison/intercalibration experiments are essential, as is the development of reference materials for water, sediment and biota.

Autonomous munitions detection: Depending on ammunition type and environment, different detection methods exist but typically a combination of different methods and validation via divers is needed. This requires extensive ship time and man power. Artificial intelligence could combine different methods in an objective way, even online, while data are still acquired. This would improve munitions detection and could allow setting standards for munitions detection and the clearance of areas. Several AUV platforms can be operated in parallel, which would reduce time and costs of surveying for UXO removal and environmental monitoring purposes alike.

2.7.3 Recommendation

We recommend overcoming political, administrative and technical problems for a better integrative data management of all relevant data. We propose to establish a federated data infrastructure with different access levels that allow viewing general information about munitions in the sea all the way to very detailed and restricted information such as exact munitions locations, planned disposal actions and plans for intervention. Data of public interest such as concentrations in the water column and fish should be presented openly with automatic updates originating from latest measurements.

Linked to data management concerns (standardisation) but also to keep comparability of measurements high, we recommend that MC data in environmental samples be reported in molar units (e.g. pM, picomole per litre; pmol/g, picomole per gram sediment or tissue) rather than mass units. This allows direct comparison among the parent and transformation products. For example, complete transformation of one pmol TNT produces 1 pmol ADNT, and eventually 1 pmol DANT. In contrast, transformation of 1 ng TNT produces 0.86 ng of ADNT and 0.74 ng of DANT. Two exceptions to this recommendation are when reporting measurements or rates of explosive solid dissolution and tissue concentrations for toxicological risk analysis. In the case of explosive solid dissolution, mass units provide a more direct relationship with solid loss, (i.e. in relation to explosive volume and density). In addition, reporting MC data in biota in mass units (e.g. picogram per gram dry weight or per gram wet weight) allows comparisons with toxicological limit values (e.g. maximum residue levels in food). Molar masses for the MCs reported in this document and unit conversions are listed in Table 5.

Table 5: Munitions compounds molecular masses, and mole- to mass-unit conversion factors.

Munitions compounds	**Molecular mass (g mol^{-1})**	**pmol ng^{-1}**
TNT	227.13	4.4
ADNT	197.15	5.1
DANT	167.168	6.0
RDX	222.117	4.5
DNB	168.11	5.9

3. Practical guidence for sampling and monitoring

3.1 Scientifically "best" monitoring

This section describes the our scientifically 'best practice' for sampling and monitoring munitions-contaminated areas in seas and oceans. This means that to our current knowledge the presented methods and approaches allow for a detailed assessment and the evaluation of the state of the environment. The acquired data are furthermore important for a long-term monitoring approach and allow for adjustments and refinements at any time. Generally, the 'best' monitoring should start as soon as possible, meaning **starting monitoring NOW, and** runs for a sufficient amount of time after which it can be assumed that no additional contamination will occur anymore. Based on our results and model based extrapolations we see a minimum time for monitoring to be **AT LEAST for 30 years** from now.

Three main purposes are seen for the monitoring, including the **baseline study**, the **long-term monitoring** and a short term **ad-hoc monitoring** that should take place before, during and after clearance and here particularly during blast-in-place operations. The baseline study should include a good knowledge about the history of the munitions dumping ground from historic records, to answer the questions of what types of munitions is present and what kinds of explosives are likely to be dominant. The baseline study should further include a habitat characterization as this will determine the needed/useful sampling (e.g. geophysical methods as sub-bottom profiling/electro-magnetic) and monitoring methods (e.g. biomonitoring through mussels and/or fish or the use of passive samplers instead). Already first results of the initial mapping will allow determining the size of the area that is contaminated and thus needs to be surveyed in detail. Not included in this guide are recommendations for sub-bottom mapping with acoustic and electro-magnetic sensors as these were not part of the UDEMM sensor portfolio. A respective knowledge about suitable systems, their application, processing and interpretation already exists in UXO survey and clearance companies(Frey et al., 2019). Recommendations for monitoring chemical warfare dumpsites have been released by the NATO project MODUM (Bełdowski et al., 2018) and incorporate the need of baseline studies for an area wide assessment and resulting selection of sepcific areas of interest. These recommendations can be adapted to conventional dumpsites. As highlighted in the chapters before, baseline studies need to include oceanographic and chemical studies of the water column with both types of investigations going hand in hand for a scientifically sound and meaningful data acquisition. Ideally, a well-established and validated oceanographic model supports these studies and is fully integrated in any risk assessment and prediction. All long-term monitoring builds on the comparison of data that have been acquired over long time with different sensors measuring the same parameter, with different analytical methodologies that over the time will become more accurate and with ever higher resolving acoustic and optical systems. A **good and sustainable data management** is thus of utmost importance with ideally one authority collecting, hosting and maintaining the respective data base.

How to prioritize the order in which specific areas will be monitored next, depends on several factors, including e.g. a) the amount of open explosives being in direct contact with water and thus are the strongest contamination hot spot, b) the need for underwater installations in a specific area, or c) ad-hoc observations before clearance. In all cases monitoring needs to be adjusted specifically to the spatial scale it is intended to address and all of the three described spatial scales need to be considered for a proper monitoring. The monitoring for each spatial scale varies in number of samples/monitoring sites and temporal resolution/sampling repetition. Below we describe A) Baseline studies that aim at evaluating the munitions content and potential chemical contaminations for the first time in an area, and B) long-term monitoring studies to establish a sound evaluation of changes over different time-scales, including long-term trends, and C) what should be done for ad-hoc monitoring in the case of munitions clearance.

Reference:

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3.2 Baseline Study

The baseline study is an essential part of any envisioned long-term monitoring. It consists of a spatially higher resolving and explorative set of studies than the routine monitoring.

Table 6: Description of tasks for a Baseline study.

Feature scale (baseline)		
Topic	**What to do**	**Comments**
Spatial mapping		
Multibeam mapping	Full high resolution mapping + habitat classification	State-of-the-art method to gain a good overview in relatively short time; only munitions on the seafloor detectable
SBP mapping	Mapping of the sub seafloor in hotspot areas	Time-consuming, very densely spaced profile lines required; also buried munitions detectable
Magnetic mapping	Mapping of the seafloor to detect buried and unburied munition; either full mapping, or detailed mapping in hotspot areas	Time-consuming, very densely spaced profile lines required; also buried munitions detectable
Visual mapping	Photomosaic/visual data of hotspots	Additional information about corrosion state, type and amounts of findings
Discrete sampling		
Water sampling	Collect water samples within 0.5 to 1 m of individual munitions objects. Multiple samples can be collected from 0 - 1 m at 10 cm intervals to capture concentration gradients. Samples must be collected by divers, with care to avoid water mixing that can obscure gradients.	In our experience, collection of samples directly adjacent to objects shows extremely high variability (five to six orders of magnitude). The source of this variability remains unclear, or exactly what these concentrations reflect. Nonetheless, there may be some value in collecting such samples, such as for estimating dissolution rates or evaluating maximum exposure levels.
Sediment sampling	For MC analysis: Collect sediment samples within 2 m of individual munitions objects. Multiple samples can be collected at intervals radiating away from ammunition	Precise underwater navigation can be an issue for divers. However, the exact sampling position should be known. To prevent sampling a wrong seafloor

	objects to capture concentration gradients. Samples must be collected by divers, with care to avoid contacting munitions that may be buried under shallow sediments. For seafloor classification ground truth: Collect as many sediment samples in each derived seafloor class as possible (min. five per class). Samples must be collected by divers or ROV.	class, make sure to plan sediment samples for ground truth in a wide homogeneous area. Also take pictures of the surrounding environment and add a brief description of seafloor properties (grain size distribution, vegetation, munition).
Biota	Collect biota samples representing different trophic levels near munitions objects. Multiple individuals from each trophic level should be collected.	
Bio-monitoring		
Mussel-Bags	Four moorings with mussel bags (20 mussels each) should be placed during summer season in about 1 m distance in the area around the objects. Retrieve after three months. Analyse by LC-MS or GC-MS.	Mussels are fairly robust, stationary and easy to handle. Other organisms might be better suited depending on the habitat. Nitroaromatic compounds are of highest toxicological concern. Heavy metals (Pb, Hg) seem to be less abundant.
Fish	Collect statistically robust number of individuals.	Multiple trophic levels should be sampled to the extent possible. Should focus on non-migratory, less mobile species, may include non-seafood species.
Oceanographic studies		
Oceanographic measurements	To quantify the physical environment, and changes in it, a longer term observation is needed. This would include measurements of temperature and oxygen, since both have the highest impact of the solution and degradation of TNT. Additionally, salinity measurements can be of further help. Near bottom measurements and hourly or 6-hourly sampling are likely to be sufficient. To further support the analysis current measurement (ADCP) would be of added value. The ADCP data could help also to extract information on stratification, but more important on bottom stress and general transport pattern.	This Is part of the local baseline study as well.
Oceanographic modelling	-	Is part of the local to regional baseline study
Local scale (baseline)		
Historical Analyses	A historical analysis of the area is required to choose a) the right mapping techniques and b) to define areas of special interest.	
Spatial mapping		
Multibeam mapping	Full high resolution mapping + habitat	State-of-the-art method to gain a good

	classification	overview in relatively short time; only munitions on the seafloor detectable
SBP mapping	Mapping of the sub seafloor in hotspot areas	Time-consuming, very densely spaced profile lines required; also buried munitions detectable
Magnetic mapping	Mapping of the seafloor to detect buried and unburied munition; either full mapping, or detailed mapping in hotspot areas	Time-consuming, very densely spaced profile lines required; also buried munitions detectable
Visual mapping	Photomosaic/visual data of hotspots	Additional information about corrosion state, type and amounts of findings
Discrete sampling		
Water sampling	Collect statistically representative number of samples in bottom water (< 3 m from seafloor) randomly throughout site. Seasonal sampling (winter/summer) should be conducted to capture extremes of dissolution and degradation.	
Sediment sampling	For MC analysis: Collect statistically representative number of samples randomly throughout site. For seafloor classification ground truth: Collect as many sediment samples in each derived seafloor class as possible (min. five per class). Samples must be collected by divers or ROV.	Precise underwater navigation can be an issue for divers. However, the exact sampling position should be known. To prevent sampling a wrong seafloor class, make sure to plan sediment samples for ground truth in a wide homogeneous area. Also take pictures of the surrounding environment and add a brief description of seafloor properties (grain size distribution, vegetation, munition).
Biota	Collect statistically representative number of samples randomly throughout site. Biota samples should represent different trophic levels. Multiple individuals from each trophic level should be collected.	
Bio-monitoring		
Mussel bags	One mooring with mussel bags (20 mussels each) should be placed during summer season in about 1 m distance near each suspected hotspot. Retrieve and analyse after three months. At least ten moorings are required.	The number of moorings should not depend on the availability of ships and divers to retrieve the mussels.
Fish	Collect statistically robust number of individuals	Multiple trophic levels should be sampled to the extent possible. Should focus on non-migratory, less mobile species. Should focus on seafood species, but may include non-seafood species.
Oceanographic studies		
Oceanographic measurements	At the local scale, measurements are of limited use. At this stage regional numerical ocean models are need to predict transport pathways and distribution pattern.	

Oceanographic modelling	Minimum requirements are an adequate vertical resolution in the near shore region, but also in the deeper straits. Here models with terrain-following vertical coordinates are superior. Moreover, state of the art turbulence closures are needed. A spatial resolution 300 - 600 m is likely to be sufficient. To quantify variability on different time scales, multi-annual model runs are needed. The model runs need to be supported with measurements to calibrate and validate the TNT module.	
Regional scale (baseline)		
Historical Analyses	A historical analysis of the area is required to choose a) the right mapping techniques and b) to define areas of special interest.	
Spatial mapping		
Multibeam mapping	Full high resolution mapping + habitat classification	State-of-the-art method to gain a good overview in relatively short time; only munitions on the seafloor detectable
SBP mapping	Mapping of the sub seafloor in hotspot areas	Time-consuming, very densely spaced profile lines required; also buried munitions detectable
Magnetic mapping	Mapping of the seafloor to detect buried and unburied munition; either full mapping, or detailed mapping in hotspot areas	Time-consuming, very densely spaced profile lines required; also buried munitions detectable
Visual mapping	Photomosaic/visual data of hotspots	Additional information about corrosion state, type and amounts of findings
Discrete sampling		
Water sampling	Collect samples in bottom water (below pycnocline, or preferably < 3 m from seafloor) throughout the region at a minimum of ten sites. Sites should be chosen with guidance from the oceanographic modelling results, in order to obtain representative sampling of different water masses. Seasonal sampling (winter/summer) should be conducted to capture extremes of dissolution and degradation.	
Sediment samples	For MC analysis: Collect statistically representative number of samples randomly throughout region. For seafloor classification ground truth: Collect as many sediment samples in each derived seafloor class as possible (min. five per class). Samples must be collected by divers or ROV.	Precise underwater navigation can be an issue for divers. However, the exact sampling position should be known. To prevent sampling a wrong seafloor class, make sure to plan sediment samples for ground truth in a wide homogeneous area. Also take pictures of the surrounding environment and add a brief description of seafloor properties (grain size distribution,

		vegetation, munition).
Biota	Collect statistically representative number of samples randomly throughout region. Biota samples should represent different trophic levels. Multiple individuals from each trophic level should be collected.	
Bio-monitoring		
Mussel bags	One mooring with mussel bags (20 mussels each) should be placed during summer season in about 1 m distance near suspected hotspots. Retrieve and analyse after three months.	The logistic effort for a reliable bio-monitoring on this scale may exceed what is feasible. To get an overview of a possible contamination, organisms living near suspected hotspots could be collected once and analysed for explosive compounds.
Fish	Collect statistically robust number of individuals.	Multiple trophic levels should be sampled to the extent possible. Can include migratory species. Should focus on seafood species, but may include non-seafood species.
Oceanographic studies		
Oceanographic measurements	The measurements are part of the MARNET station system and standard monitoring cruises of the IOW.	The standard oceanographic measurements are taken at hourly resolution at the MARNT stations Kiel Lighthouse, Fehmarn Belt and Darss Sill. During the regular monitoring cruises (4 - 8 times a year) a full set of biological measures are sampled.
Oceanographic modelling	To study the transport of TNT on a basin scale long-term stable numerical ocean models are needed. The spatial resolution should be at least 2 nm and a vertical resolution of 40 - 70 vertical levels is required. The model needs to reproduce the inflow dynamics, but also the summer three-layer stratification in the deeper parts. The model exercises should be done on decadal and multi-decadal time scales. The model runs need to be supported with measurements to calibrate and validate the TNT module.	

3.3 Long-term monitoring

The long-term monitoring approach depends on the findings of the base line study and is ideally integrated and becomes part of other monitoring schemes in the respective area. There is no need to schedule specific sampling cruises exclusively for munitions monitoring.

Table 7: Description of monitoring tasks during long-term monitoring.

Feature scale (long-term)		
Topic	**What to do**	**Comments**

	Spatial mapping	
Multibeam mapping	Mapping hotspots every five years	
SBP mapping	New data is only needed, if changes have been detected during multibeam mapping	Depending on the stability of the environment
Magnetic mapping	New data is only needed, if changes have been detected during multibeam mapping	Depending on the stability of the environment
Visual mapping	Photomosaic/visual data of hotspots every two years (+ if required because of changes detected through other measurements /observations)	Continuous information about corrosion state, type and amounts of findings
	Discrete sampling	
Water sampling	Collect water samples within 0.5 - 1 m of individual munitions objects. Multiple samples can be collected from 0 - 1 m at 10 cm intervals to capture concentration gradients. Samples must be collected by divers, with care to avoid water mixing that can obscure gradients.	
Sediment sampling	For MC analysis: Collect sediment samples within 2 m of individual munitions objects. Multiple samples can be collected at intervals radiating away from ammunition objects to capture concentration gradients. Samples must be collected by divers, with care to avoid contacting munitions that may be buried under shallow sediments. For seafloor classification ground truth: Collect as many sediment samples in each derived seafloor class as possible (min. five per class). Samples must be collected by divers or ROV.	Sediment-associated MC levels are unlikely to respond rapidly to changes in MC release from underwater munitions. Monitoring on five- to ten-year scale is probably sufficient. Precise underwater navigation can be an issue for divers. However, the exact sampling position should be known. To prevent sampling a wrong seafloor class, make sure to plan sediment samples for ground truth in a wide homogeneous area. Also take pictures of the surrounding environment and add a brief description of seafloor properties (grain size distribution, vegetation, munition).
Biota	Collect biota samples representing different trophic levels near munitions objects. Multiple individuals from each trophic level should be collected.	Depending on the organism (life-span, trophic level, migration behaviour), biota samples may need to be collected seasonally at multi-year intervals.
	Bio-monitoring	
Mussel-Bags	Four moorings with mussel bags (20 mussels each) should be placed during summer season in about 1 m distance in the area around the objects. Retrieve after three months. Analyse by LC-MS or GC-MS. Monitoring should be continued for at least five years.	In view of the ongoing corrosion of the munitions shells increasing concentrations of explosive compounds might be expected. Therefore, longer bio-monitoring periods are advisable.
	Oceanographic studies	
Oceanographic measurements	At this spatial scale, ADCP measurements would be of highest priority. With the help of ADCP data, the local vertical shear (but also horizontal shear) could be quantified. This is needed to compute diffusion	

	coefficients to estimate the spreading of the dissolved TNT. Additional temperature and oxygen measurements would help to correlate them with local munitions shell corrosion and dissolution of TNT.	
Oceanographic modelling	-	
Local scale (long-term)		
Spatial mapping		
Multibeam mapping	Mapping hotspots every 5 years	
SBP mapping	New data is only needed, if changes have been detected during multibeam mapping	Depending on the stability of the environment
Magnetic mapping	New data is only needed, if changes have been detected during multibeam mapping	Depending on the stability of the environment
Visual mapping	Photomosaic/visual data of hotspots every 2 years (+ if required)	Continuous information about corrosion state, type and amounts of findings
Discrete sampling		
Water sampling	Collect statistically representative number of samples in bottom water (< 3 m from seafloor) randomly throughout site. Seasonal sampling (winter/summer) should be conducted to capture extremes of dissolution and degradation.	
Sediment sampling	For MC analysis: Collect statistically representative number of samples randomly throughout site. For seafloor classification ground truth: Collect as many sediment samples in each derived seafloor class as possible (min. five per class). Samples must be collected by divers or ROV.	Sediment-associated MC levels are unlikely to respond rapidly to changes in MC release from underwater munitions. Monitoring on five- to ten-year scale is probably sufficient. Precise underwater navigation can be an issue for divers. However, the exact sampling position should be known. To prevent sampling a wrong seafloor class, make sure to plan sediment samples for ground truth in a wide homogeneous area. Also take pictures of the surrounding environment and add a brief description of seafloor properties (grain size distribution, vegetation, munition).
Biota	Collect statistically representative number of samples randomly throughout site. Biota samples should represent different trophic levels. Multiple individuals from each trophic level should be collected.	Depending on the organism (life-span, trophic level, migration behaviour), biota samples may need to be collected seasonally at multi-year intervals.
Bio-monitoring		
Mussel-Bags	One mooring with mussel bags (20 mussels each) should be placed during summer season in about 1 m distance near suspected hotspots. Retrieve and analyse after three months. At least ten moorings are required. Monitoring should be	

	continued for at least five years. At least ten moorings are necessary near hotspots. In addition, further moorings should be placed randomly at even distances, depending on the availability of ships and divers to retrieve the samples.	
Oceanographic studies		
Oceanographic measurements	The standard monitoring at the MARNET stations (Kiel Lighthouse, Fehmarn Belt and Darss Sill) provides sufficient observations to cover the hydrodynamic situation.	
Oceanographic modelling	At great time scales and on the local scales, the present knowledge about the TNT chemistry in seawater is too little to provide reliable long-term predictions.	
Regional to coastal scale (long-term)		
Spatial mapping		
Multibeam mapping	Mapping hotspots every 5 years	
SBP mapping	New data is only needed, if changes have been detected during multibeam mapping	Depending on the stability of the environment
Magnetic mapping	New data is only needed, if changes have been detected during multibeam mapping	Depending on the stability of the environment
Visual mapping	Photomosaic/visual data of hotspots every 2 years (+ if required)	Continuous information about corrosion state, type and amounts of findings
Discrete sampling		
Water sampling	Collect samples in bottom water (below pycnocline, or preferably < 3 m from seafloor) throughout region at minimum ten sites. Sites should be chosen guided through oceanographic modelling results to obtain representative sampling of different water masses. Water sampling sites should also be adjacent to bio-monitoring stations. Seasonal sampling (winter/summer) should be conducted to capture extremes of dissolution and degradation.	
Sediment sampling	For MC analysis: Collect statistically representative number of samples randomly throughout region. For seafloor classification ground truth: Collect as many sediment samples in each derived seafloor class as possible (min. five per class). Samples must be collected by divers or ROV.	Sediment-associated MC levels are unlikely to respond rapidly to changes in MC release from underwater munitions. Monitoring on five- to ten-year scale is probably sufficient. Precise underwater navigation can be an issue for divers but exact sampling position are needed. To prevent sampling a wrong seafloor class, take sediment samples for ground truth in wide homogeneous areas. Take pictures of the surrounding environment and add a brief description of grain size distribution, vegetation, munition).
Biota	Collect statistically representative number	Depending on the organism (life-span,

	of samples randomly throughout region. Biota samples should represent different trophic levels. Multiple individuals from each trophic level should be collected.	trophic level, migration behaviour), biota samples may need to be collected seasonally at multi-year intervals.
Bio-monitoring		
Mussel-Bags	One mooring with mussel bags (20 mussels each) should be placed during summer season in about 1 m distance near suspected hotspots. Retrieve and analyse after three months. Monitoring should be continued for at least five years. At least ten moorings are necessary near hotspots. In addition, further moorings should be placed randomly at even distances, depending on the availability of ships and divers to retrieve the samples.	
Oceanographic studies		
Oceanographic measurements	At present, no additional action is required. The MARNET stations provide a good long-term base for the physical environment.	
Oceanographic modelling	To monitor the transport of TNT on a basin scale, the implementation of TNT modules in operational forecast models are needed. This would help to forecast the far-field transport of dissolved TNT, its accumulation in the deeper basins and the spreading of dissolved TNT during major inflows.	

3.4 Monitoring during clearance activities

The monitoring for blow-in-place is an ad-hoc monitoring immediately before and after the blow-in-place operation one day to few hours before and as soon as possible after the detonation.

Table 8: Description of the monitoring tasks before, during and after delaboration.

Clearance		
Topic	**What to do**	**Comments**
Spatial mapping		
Multibeam mapping	Mapping before (if not buried) and after	Mapping can reveal the impact and formation of explosion crater
SBP mapping	Not required	
Magnetic mapping	Mapping before and afterwards	Mapping can reveal spreading of metal parts caused by the explosion
Visual mapping	Inspection before and afterwards	Mapping can reveal the impact onto the benthic seafloor and if any chunks of explosives are left.
Discrete sampling		
Water sampling	Water samples should be collected before clearance activities begin to establish baseline contaminations levels. Sampling	

	during and immediately after remediation (i.e. non- detonation clearance) to detect unintended release. Samples collected a long time (months to years) after clearance should be used to evaluate the applied clearance method's effect on long-term contamination levels.	
Sediment sampling	Sediment samples should be collected before clearance activities begin to establish baseline contaminations levels. Sampling during remediation (non-detonation clearance) and immediately after to detect unintended release. Samples collected a long time (months to years) after clearance should be used to evaluate the applied clearance method's effect on long-term contamination levels.	MC distribution during clearance is not unknown. The sampling scheme might be changed in future, based on actual results. Sediments collected immediately after remediation may be critical for observing low-order (incomplete) detonation solid residues, which, if present, would represent a major release of MCs to the environment.
Biota	Biota samples should be collected before clearance activities to establish baseline contamination levels. Samples collected months to years after clearance should be used to evaluate the applied clearance method's effect on long-term exposure.	Biomarkers of MC exposure are not yet well-developed, but may show a more rapid response to exposure than tissue MC burdens.
Bio-monitoring		
Mussel-Bags	Three months before the detonation four moorings with mussel bags (20 mussels each) should be placed in 50 m distance around the objects and retrieved and analysed after three months. As soon as possible new mussels should be placed in the same positions after the detonation and retrieved after three months.	Blue mussels can be used in water depths of up to 20 m. To determine background body loads, mussels should not be placed directly on unexploded material lying on the seafloor.
Oceanographic studies		
Oceanographic measurements	During clearance work, the deployment of at least one ADCP is needed. The measurements should cover at least one week before and one week after the delaboration work. Additional T/S profiles should be conducted. As clearance will most likely occur during calm weather conditions, a few deployments are enough to characterize the water stratification	
Oceanographic modelling	At present, only the BSH has the infrastructure and logistics to do operational forecasting. A forecast should be done if at all possible.	For a research institute, an operational forecast is not possible. However, with a delay of some days to weeks, a reconstruction of the physical state is possible. This, would allow a detailed analysis of the potential transport of leaked traces and an objective judgment of the performance of all employed sensors and equipment.

4. Methodologies

4.0 Historical Analysis

Responsible institute: BLANO & MELUND

Historical Analysis (German: Historisch-genetische Rekonstruktion – HGR) consists of several individual operations and phases. It is completed with a written summary of its results and forms the basis for subsequent steps in a project. First, the area to be considered is specified. A precise definition is necessary, in order to focus and to point possible problem areas. After determining the study area an overview of the history of the entry of munitions is created. This overview contains the assumed age of expected munitions, combat operations or periods of military trials. On the basis of this list, archive data for the corresponding area need to be found.

Starting with the local archives, municipal archives, district archives, state archives, federal archives and military archives, all available data are reviewed according to periods or events and, if necessary, scanned and saved. Found references to persons and involved military units, ships or authorities are particularly recorded and also considered and evaluated. If there are indications of possible data archiving in other archives, such as the Federal Archives of Economic Affairs, Armaments or Industry, these branches will also be examined.

In the same way, documents in the archives of other countries, especially the Allies of the Second World War, are examined. The research in these archives is much more difficult because e.g. Britain has a somewhat more complicated documentation in the existing files. Here, in all likelihood, an investigation of the involved units and persons must take place in parallel in order to find and evaluate the appropriate documents.

In addition, data collection and backup is also essential here. All collected documents must be reviewed and associated. A chronological order is created. Transport units are assigned the daily transport volume in tons and, if possible, the transported goods. The transport route is reconstructed with the statements in shipping diaries, harbor dossiers and/or other records and provided with the time and environmental factors (weather). The type of sinking, as "on-off dumping", en-route-dumping, manual dumping or dumping by a hopper barge are important facts and show, in connection with the number of crew members, the quantity of the dumped munitions. After collecting all facts, the result must be verified through a check of additional historic documents in the manner. If this confirmation agrees with the determined data, the result can with a high probability be regarded as a real result. These steps are created individually for each ship, unit or other entity and then combined for the area under review.

Historical datasets can act as a starting point for the definition and specification of monitoring activities. They indicate historic events (e.g. munitions dumping, war activities) and can be used to specify sampling strategies in terms of spatial distribution and suspected substances.

Collecting and revising historic data: Military charts, minelaying and minesweeping planes, reports and other historic data must be collected, digitized and constantly revisited during monitoring activities. The origin of geodesic dates must be verified and transformed into actual geodesic dates, to ensure positional accuracy and overlaying of actual and historic spatial information. This process should be carried out inside of a specifically designed digital system for visualisation and management of multiple information sources and measurement data.

Event description: Historic events have to be extracted from the collected data and described including all relevant information. Multiple independent sources per event should be included for verification and uncovering of different perspectives. Events should be spatially localized to identify spatial connections and dimension. Extensive metadata information of specific events (e.g. naval mining, naval combat, dumping activities) should be recorded including precise information about numbers of objects (e.g. naval mines), origin of objects and risk originating from objects. In addition, accidents and damages during transport and routes taken should be recorded. In specific circumstances detailed research has to be carried out regarding objects and their history e.g. figuring out the composition of MCs. Research and interpretation have to be carried out including contextual knowledge and data.

Contemporary datasets: Historic information has to be backed/verified by current high-resolution datasets from bathymetry, side scan sonar, sub-bottom profiler, geomagnetics, photo or video (and if necessary identification by divers). An assessment of the origin of the objects should be carried out by EOD specialists and all resulting datasets have to be analysed and managed in a digital system combined with the acquired historic data.

Evaluation: An ongoing evaluation process has to be established regarding the quality and information content of the combination of historic and contemporary datasets.

Tools: Management, analysis and visualisation of digitized historic and contemporary datasets should be generally carried out by functions provided by geographic information systems (GIS). A specifically designed system for the management of historic datasets in combination with actual measurements is the Ammunition Cadastre Sea (AmuCad) which in addition includes databases for munitions and chemicals and incorporates actual research results (DAIMON, North Sea Wrecks).

4.1 Acoustic mapping and monitoring

Responsible institute: GEOMAR

The preferably used mapping technique is highly dependent on the dumping ground characteristics, such as type of ammunition and seafloor properties.

Multibeam echosounder surveys are recommended for unburied objects of a minimum size of 0.5 × 1 m^2 in shallow waters of less than 30 m. As the aim of monitoring is to detect changes over time, very high precision in positioning is required. To reliably quantify object and sediment movements, MBES surveys shall always be conducted in conjunction with the use of RTK (real time kinematics) services, increasing GPS accuracies to 5 cm. To perform high resolution multibeam mapping in order to fulfil the IHO special order (IHO, 2008), a frequency of at least 400 kHz and beam opening angles of maximum 0.5° × 1° are recommended. Lateral resolutions of min. 20 cm should be achieved. Equidistant mode ensures same resolution across the entire swath. Swath widths should not exceed 120° and survey speed not more than 3.5 knots. Although it is time consuming, the surveys shall be conducted with 100 % overlap. For high data quality it is absolutely necessary to have static offsets, which are well measured and a patch test performed after each movement of the multibeam relative to the systems components (IMU or GPS antenna). Sound velocity profiles shall be performed at least twice a survey day. The MBES provides one tool for three different applications:

1. Detailed bathymetry of the dumping ground for object detection and monitoring
2. Detailed backscatter map of the dump for seafloor classification and monitoring
3. Automated object and change detection

In a first run the dumping ground have to be mapped in its total extent. Based on the bathymetric and backscatter data in combination with ground truth, a seafloor classification map needs to be created. In combination with detected objects this will then serve as a basis for planning further monitoring activities. Areas of special interest have to be defined. Those can be areas with a high number of objects, objects close to ship traffic or beaches or areas where sediment mobilization can be expected. These areas will need to be monitored at least every five years. Best time of the year is in spring, after heavy winter storms.

Multibeam mapping is a standard technique at present to acquire bathymetric information from the seafloor with a parallel recording of backscatter data (Lamarche and Lurton, 2017; 2018). When aiming to detect proud and buried munitions (ground mines, moored mines, torpedoes, or water charges) towed side-scan sonar and magnetometer surveys in conjunction with sub-bottom profiler information are performed and have been successfully applied e.g. to detect buried chemical munitions in the Baltic Sea (Missiaen and Feller, 2008). Very detailed and sophisticated methodologies have been developed by naval forces as well as EOD companies (Lim, 2015; SERDP, 2018). However, much of this information is disclosed and the time needed to perform such surveys (unless they are completely undertaken by AUV) is rather long.

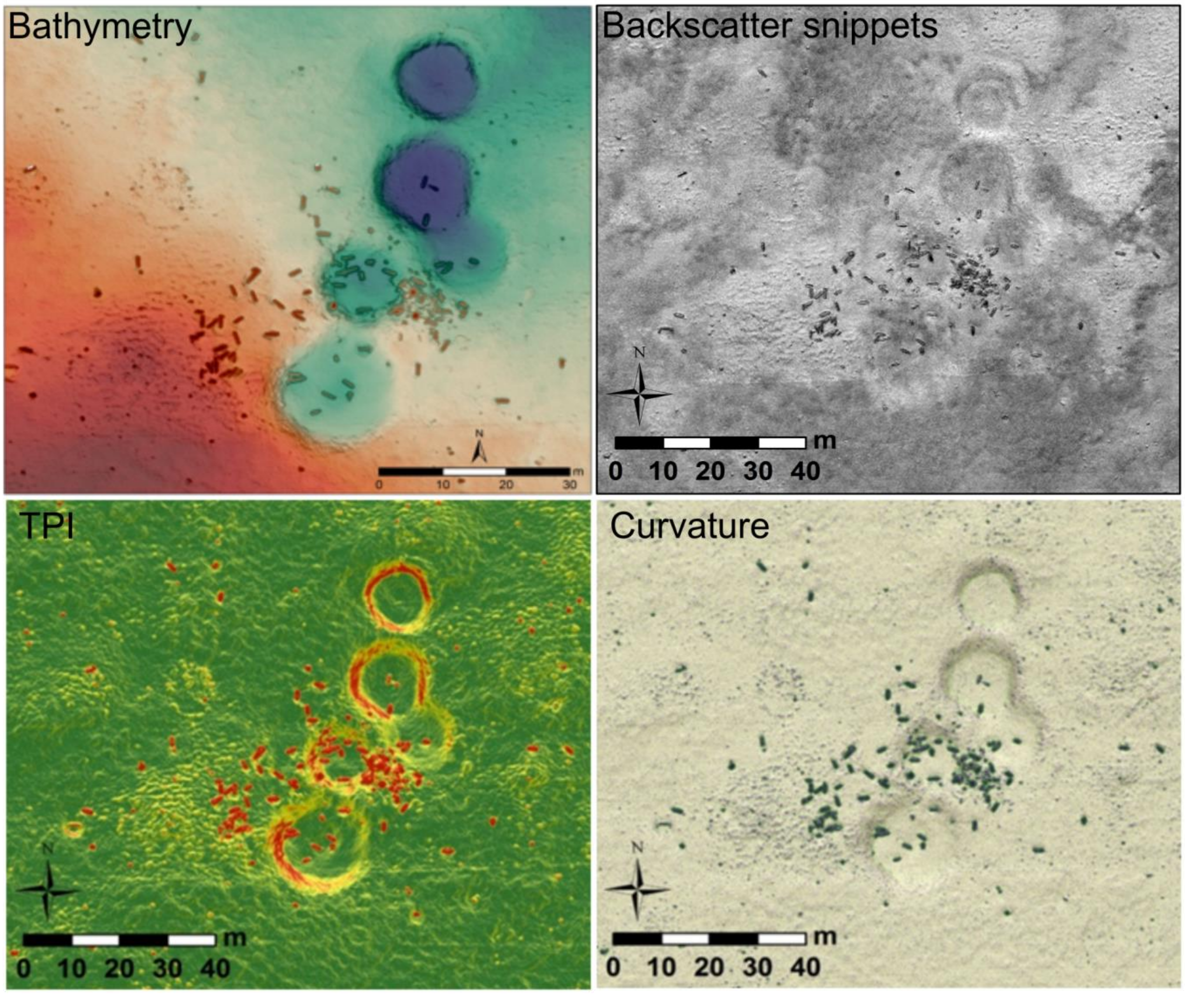

Figure 33: Bathymetric and backscatter snippet data from a munitions dumping ground next to explosion craters in the Kolberger Heide (Kiel Bay; data GEOMAR – UDEMM project). Mines can be well displayed using derivatives based on the bathymetry such as slope and curvature. (note, all detailed bathymetric maps that show munitions are presented without coordinates due to security regulations).

Within the frame of this study we are exclusively concerned about munitions lying on the seafloor as such occurrences have the greatest potential to release toxic chemicals into the water column and the food chain. Modern high frequency multibeam system (> 200 kHz) with beam opening angles of 0.5° have the necessary resolution to map large ammunition objects as ground charges, torpedoes, sea mines in the bathymetric data, and are even higher resolving and more sensitive to the strong backscattering, in the snippet information (Figure 33).

The technical performance of MBES has strongly improved over the last years, making them a cost-effective and state-of-the-art tool for precise and high-resolution seafloor mapping (Lamarche et al., 2011; Herkül, Peterson and Paekivi, 2017). The advantage of MBES is the precise positioning of seafloor soundings down to an accuracy of 0.1 m, when RTK-GPS navigation is used. In conjunction with the possibility of automated seafloor classification (supervised and unsupervised) and object detection specific backscatter analysing techniques and machine learning methodologies are applied to arrive at objective quantitative assessments of seafloor grain sizes, number of habitats and their spatial distribution (Alevizos et al., 2015; 2018). In addition, they help to detect munitions either via supervised classification based on a classification dictionary (Figure 34) or machine learning algorithms as Random Forest, Artificial Neural Networks, or Supported Vector Machines. Such calculations can be done in GIS environments (e.g. ArcGIS, SAGA) or other software packages like MatLab.

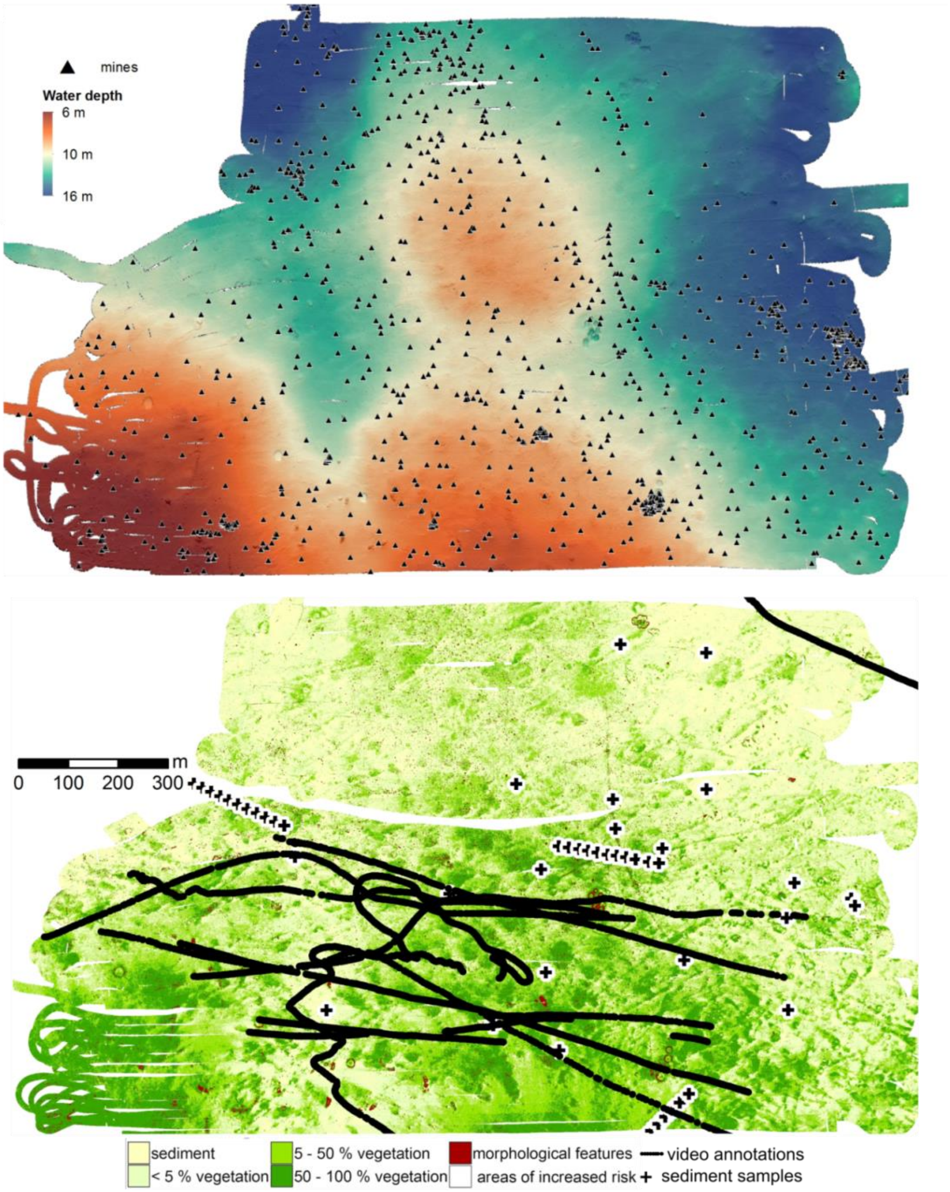

Figure 34: Results from a hydroacoustic survey in the area of Kolberger Heide. Top: Bathymetric map of the central Kolberger Heide with all identified mines marked with triangles; below: Seafloor Classification map based on the multibeam backscatter distribution and ground truth data (video and sediment samples).

Bathymetric derivatives such as slope (Figure 33), bathymetric positioning index (BPI), curvature, rugosity, or concavity (Figure 33), have been proven to be correlated to different kinds of habitats (McGonigle et al., 2009). In addition, backscatter data and their statistics also show close correlation and are jointly used for a statistically valid seafloor classification with respect to sediment grain size (Alevizos et al., 2015; 2017).

During the UDEMM project, several multibeam surveys have been conducted in the area of the munitions dumping ground Kolberger Heide and based on the generated multibeam map sampling/monitoring locations were planned. Several sites of interest were identified for further investigation with geochemical and bio-monitoring methods. In combination with ground truth data a seafloor classification map was generated, that provides information about the seafloor coverage by algae. In the Kolberger Heide, large amounts of conventional munitions in form of moored mines (1.5 m diameter), ground mines (2.5 m length) and water bombs (1 × 0.5 m) can be found.

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SERDP (2018) FINAL REPORT SERDP Workshop on Acoustic Detection and Classification of Munitions in the Underwater Environment April 2018.

4.2 Visual observations and mapping

Responsible institute: GEOMAR

Photo and video acquisition: In addition to the acoustic data, ground truth is required to identify habitats and validate findings of munitions and proud explosives. This can be achieved by using a towed camera system (OFOS), camera observations made by divers or AUV observations. It is important that the position precision is similar to the acoustic mapping data. We therefore recommend using USBL (ultra-short-baseline) navigation for a towed camera system (Figure 35).

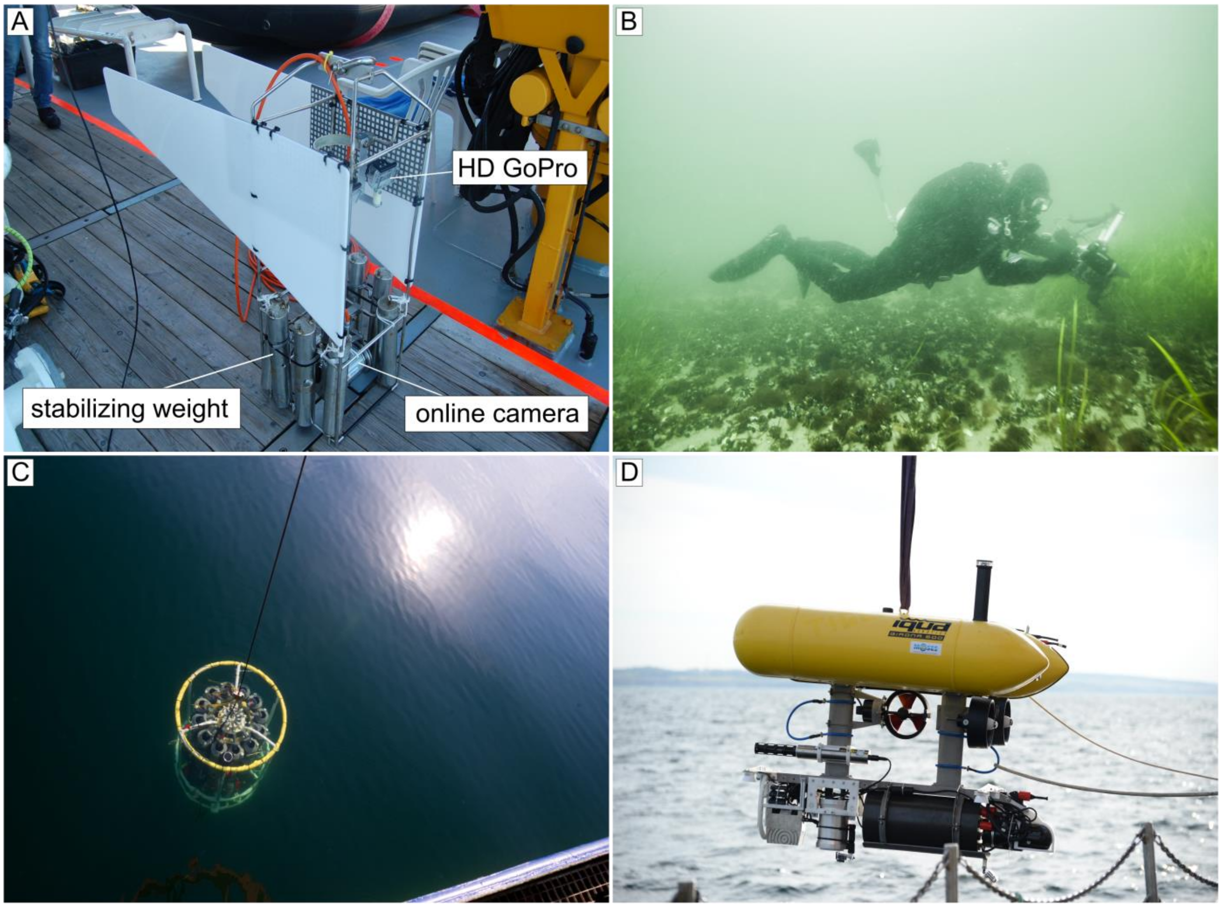
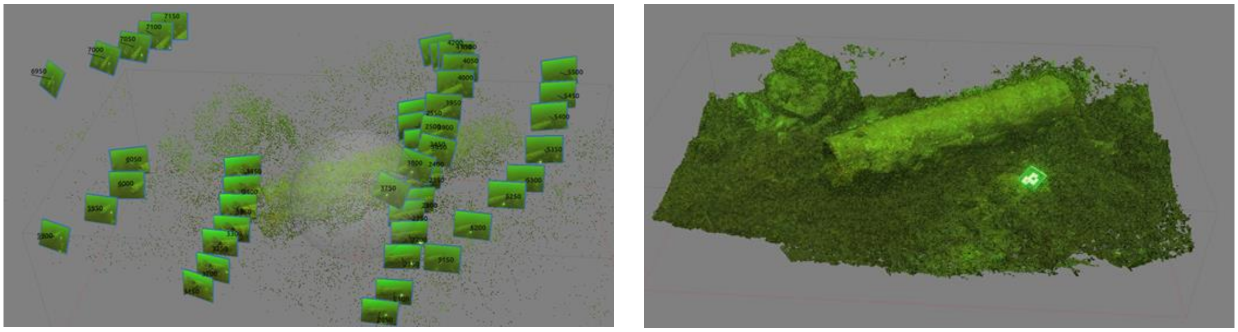


Figure 35: During UDEMM, four different types of platforms were used for visual inspection. A: An online camera mounted in a towing frame. The weight and fins stabilize the frame in the water column. HD videos are recorded with an additional GoPro camera. B: Detailed photo and video footage was recorded by scientific divers (credit: Jana Ulrich). C: A video CTD equipped with Niskin bottles for water sampling and additionally with an HD video camera and LED lights. A reduced resolution video is streamed online. D: The Girona-500 AUV is able to hover, which enables stable autonomous video and photo surveys of predefined areas.

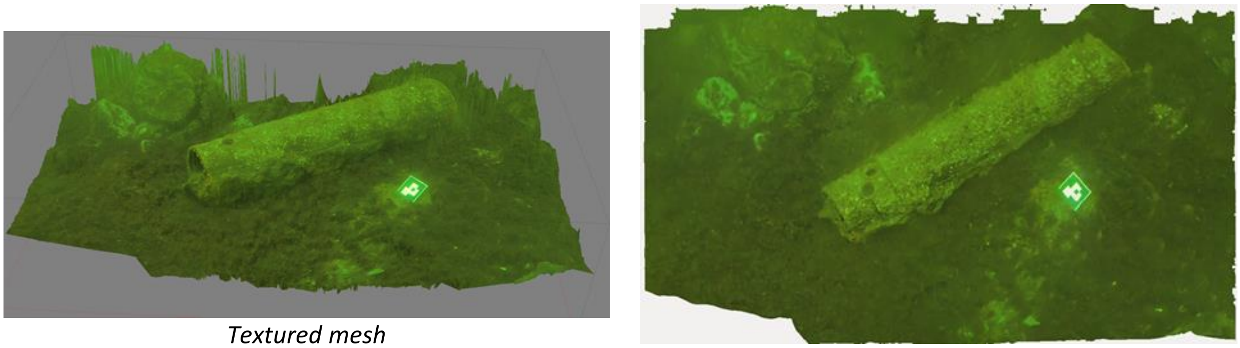
As a first step, a towed camera system can be used to identify habitat classes and their transitions. Long profiles should be planned based on the seafloor backscatter and morphology, crossing different habitats. Cross profiles enable for navigation precision evaluation. Besides the underwater video, the navigation string must be recorded. The videos have to be annotated and the annotations must be fitted to the right position. For highest precision, the annotation should be done by using a downward-facing camera. For online navigation, a second, forward-facing, camera can be used.

Areas of further interest, have to be examined in detail by using an AUV. The AUV survey should be planned carefully. Visibility and object height define the survey depth above the ground and thus the camera footprint. Distances between AUV profiles have to be defined to gain overlapping images. Also the survey speed and frames per second have to be well coordinated. The resulting images can then be used for building a 3D photomosaic. Covering landmarks, which can be found inside the acoustic data, helps to geo-reference the mosaic. A photomosaic provides detailed information about areas of interest and allows for repeated surveys above the same spot. This can be helpful to monitor the behaviour (dissolution) of MCs or the migration of objects.

Another method is to work with camera footage acquired by divers. The advantage is that the diver can take detailed footage of corrosion state or other object characteristics, which are useful for the identification. Due to its low positioning precision, this method is not adequate for large scale documentation of seafloor properties.



Images alignment and sparse point cloud *Dense point cloud*



Textured mesh *Orthomosaic*

Figure 36: Processing steps of the photogrammetric workflow to derive a textured 3D mesh and a 2D orthomosaic.

3D Photomosaicing: For visual mapping over larger areas photogrammetry methods are able to create a 3D reconstruction and merged large photomosaic from single images (Figure 36). To reconstruct the 3D model, the standard photogrammetry processing pipeline is implemented within commercial software such as Agisoft PhotoScan. In general, the workflow can be summarized by the following steps:

1. **Load the images and align the images.** This step extracts feature (key) points from images and tries to match the feature points between images. The matching results will then be used to estimate the exact camera position and orientation of each image and generate the sparse point cloud from the feature points.
2. **Build the dense point cloud.** The subsequent dense matching algorithm tries to find the corresponding matches for each pixel within the following image in order to generate a dense point cloud. Each dense matching result is stored in a depth map form. Afterwards, all depth maps are fused into a unified dense point cloud model.
3. **Georeference the point cloud.** Due to the lack of any reference information (absolute position), the dense point cloud is still unscaled and not georeferenced. There are two common ways to georeference the model, one is to record position date (e.g. GPS, USBL) with the images when they were captured and provide them while loading the images. Another way is give at least three known coordinates within the dense point cloud when it is generated.
4. **Build the mesh model from the dense point cloud.** Software specific to PhotoScan, one chooses surface type as “Height field (2.5D)” to build the polygonal (triangle) mesh from the dense point cloud.
5. **Build model texture and generate the orthomosaic.** PhotoScan projects all the meshes into a virtual ortho-view plane and each projected mesh is textured by the patch from the original images. This results in the final photomosaic.

One drawback when dealing with underwater images is that all photogrammetric software packages that are currently on the market focus on in non-aquatic applications. Due to several water effects, in both geometry and radiometry aspects, the refracted geometry and attenuated colour information in underwater images make the 3D reconstruction more difficult than the application in air. Thus, additional efforts are needed to make the current software applicable for underwater uses, especially for large scale AUV mapping purposes. GEOMAR thus developed an iterative refinement approach to link with PhotoScan for underwater reconstruction tasks. This approach utilizes the initial reconstruction results from PhotoScan to correct the water effects in the images, and then feeds these corrected images as input to the next reconstruction iteration until the reconstruction results between two iterations converged. More details about this iterative approach have been recently published by Song et al. (2019) . A large scale reconstruction of underwater munitions boxes (reconstructed from 1,059 images) taken by an AUV in the Bay of Lübeck, is shown in Figure 37 and Figure 38.

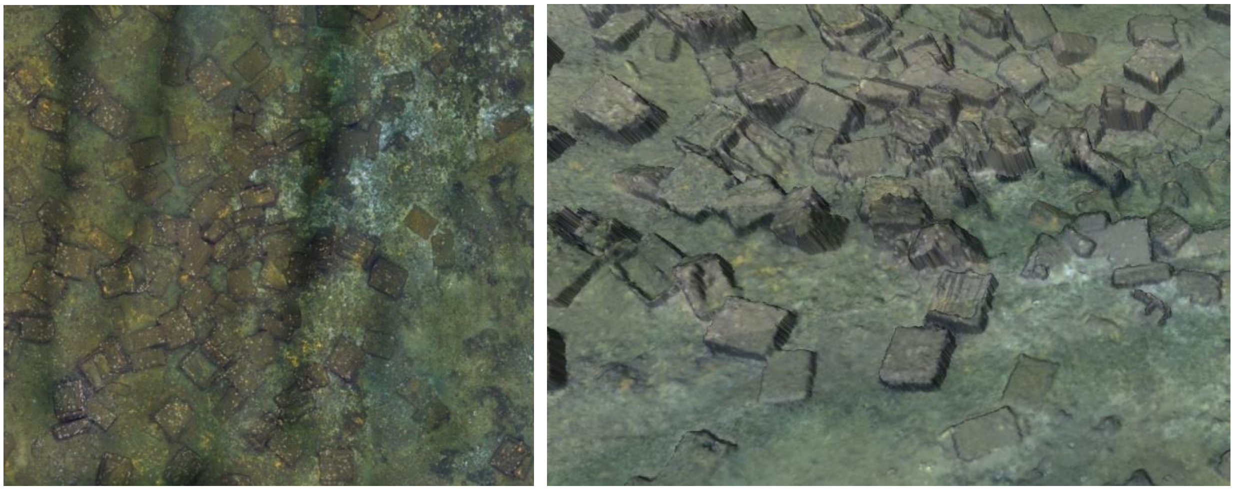


Figure 37: On the left side: A photomosaic of munitions boxes was created based on photo profiles run by the GIRONA-500 AUV from GEOMAR. Right side: 3D model calculated from the photomosaic.

Top and side view of original 3D mesh output from PhotoScan

Top and side view of refined 3D mesh

Figure 38: Photogrammetric reconstruction of images acquired in the Bay of Lübeck. The upper two images show the original PhotoScan results. The lower two images show the iteration approach developed by GEOMAR, now with a flat and correct seafloor.

Reference:

Song, Y., Köser, K., Kwasnitschka, T., and Koch, R. (2019) ITERATIVE REFINEMENT FOR UNDERWATER 3D RECONSTRUCTION: APPLICATION TO DISPOSED UNDERWATER MUNITIONS IN THE BALTIC SEA, Int. Arch. Photogramm. Remote Sens. Spatial Inf. Sci., XLII-2/W10, 181-187, https://doi.org/10.5194/isprs-archives-XLII-2-W10-181-2019.

4.3 Field sampling of sediment and biota

Responsible institute: GEOMAR

Sediment and biota can be collected using a Van Veen-type surface grab or coring apparatus in areas where there is no risk of encountering submerged munitions. **Where there is a risk of hitting submerged munition, samples must be collected by properly trained divers only.**

Sediment samples are performed for grain size analyses and other sediment properties. The sediment grain size allows to assess the acoustic properties of the sediment . In combination with the underwater footage it is the base for a habitat map. The positioning precision of the sample has to be as close as possible to the acoustic positioning precision. Otherwise it is impossible to correlate it with the right habitat. For grain size analysis the sample size is dependent on the grain size. The coarser a sample, the larger it needs to be, to give representative results. The sampling spot should additionally be documented via photo and a brief description. The sample does not necessarily have to be cooled. In the lab it has to be sieved or analysed by a laser particle analyser according to the sediment classes proposed by Blott and Pye (2012).

Sediment sampling for later TNT analysis is done as for regular sediment samples, but samples must be stored frozen at -18 °C until further processing. Samples for total metal content measurements should be stored frozen as well. If sediment mineral phases are to be determined (e.g. authigenic oxide or sulphide minerals), samples cannot be stored long term even if frozen, and must be processed immediately.

Biota (e.g. algae clumps, sea stars, mussels) can be collected manually by divers. If aggregations of algae or mussels are transferred immediately to fine mesh or plastic bags, associated organisms such as worms and crustaceans can also be obtained. Sediment infauna are collected from surface grabs. A 0.5 mm sieve can be used to separate organisms from the sediment matrix. Like sediments, biota samples should be stored frozen.

4.4 Habitat mapping

Responsible institute: GEOMAR

To describe the seafloor properties of the monitored dumping ground, the creation of a habitat map is needed. This will give information about sediment composition and floral distribution within this area. Both is needed, to evaluate the best areas for deploying monitoring moorings and to identify areas, which need special observation. Depending on the seafloor, different methods might be chosen for mine detection.

As input raster set a combination of seafloor backscatter and morphological derivatives have to be created. Which data is used, depends on the seafloor of the area. If the variability is mostly defined by changes within sediments, the backscatter is more important than morphological derivatives. (Brown et al., 2011) On the other hand, if topographic features dominate, derivatives, which best describe these, have to be developed. This can be done by the use of GIS programs like e.g. SAGA GIS, QGIS or ArcGIS. All input rasters have to have the same spatial extent and cell size.

There are different seafloor classification methods. One example is an unsupervised classification, using the ArcGIS 'ISO Cluster and Maximum Likelihood Classification' tool, which classifies the data based on the raster values and creates classes of similar value distributions (Calvert et al., 2015). The resulting classes have to be compared to the ground truth data (video, images, sediment samples, seafloor description) in order to identify habitats. Ground truthing should be planned based on the classification map, in order to sample each class multiple times.

Another method is to perform a supervised classification. For this, for known habitats (validated by the ground truth), the individual raster values will be analysed and assigned to a specific habitat. The habitats can then be spatially extrapolated (Hasan, Ierodiaconou and Monk, 2012). This method guarantees that each ground truth identified habitat will be mapped. On the other hand, a high number of ground truth samples is required, in order not to miss a distinct habitat.

With the unsupervised classification, ground truthing can be planned specifically, which saves survey time.

Which method is preferably used depends on the heterogeneity of the survey area. The more small scale variability can be found, the more ground truth data is needed. In order to make sure not to miss a certain habitat, unsupervised classification should be the first choice in that case.

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4.5 Oceanographic monitoring

Responsible institute: IOW

To characterize the physical/hydrodynamic environment, in situ measurements of currents, bottom salinity and bottom temperature at the munitions dumping ground are needed. For this purpose an ADCP, for shallow waters up to 12 m depth a 1,200kHz ADCP, or otherwise a 600kHz ADCP for deeper waters, and a SeaCat should be used. The positioning of the instruments should be at the deepest point of the munitions dumping ground to provide the broadest possible overview of the water column for current measurements. To ensure exactly vertical measurements, the ADCP should be mounted in a gimbaled frame, with the SeaCat besides it, such that the SeaCat does not interfere with the beams of the ADCP. To avoid munitions contact, divers should deploy this frame. The SeaCat and the ADCP should provide one measurement every 15 min, whereby the ADCP measurement should be a mean value of a

200-ping ensemble. Vertically the resolution should be 25 cm for 1200 kHz ADCPs or 50 cm for 600 kHz ADCP. These settings lead to a battery life of 3 months for the ADCP. Whilst changing the battery, the data can be exported and the compass should be re-calibrated (after the battery change, on land and away from magnetic interference of the ship). During quality control of the recorded data, spikes and noisy data close to the sea surface are removed.

To provide additional information, the deployment of an oxygen sensor would be beneficial. This would help to quantify the duration of hypoxic and/or anoxic events. For this purpose slow oxygen sensors will be sufficient. The entire oceanographic monitoring should be embedded into existing monitoring programs. For the dumping ground Kolberger Heide, the Belt Sea and the Danish Straits, the MARNET[7] program provided additional excellent data.

4.6 Modelling of currents, TNT distribution including its bio-degradation

Responsible institute: IOW

The basis of the modelling of the distribution of TNT in the water column is a state of the art, high resolution hydrodynamic model, that is validated by in situ measurements. The General Estuarine Transport Model (GETM, Klingbeil and Burchard, 2013) developed at the Leibniz Institute for Baltic Sea Research provides such basis for the western Baltic Sea. It has a horizontal spatial resolution of 600 m. The spatial resolution was chosen in such a way that the baroclinic Rossby radius was resolved. Fennel et al. (1991) estimate the baroclinic Rossby radius to be 3 - 6 km in the central Baltic Sea.

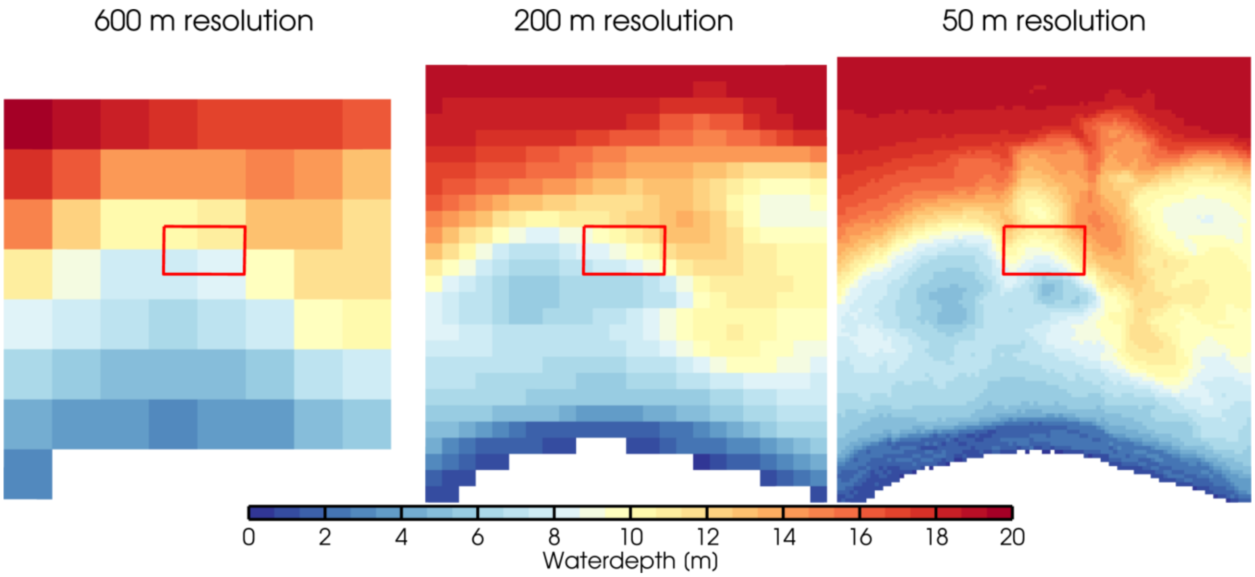

Figure 39 Impact of spatial model resolution on the resolution of topographic features. The red rectangle indicates the dumping ground Kolberger Heide. The spatial resolution varies from 600 m resolution (left panel), 200 m resolution (middle panel), and 50 m resolution (right panel).

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[7] https://www.bsh.de/EN/TOPICS/Monitoring_systems/MARNET_monitoring_network/_Module/Karussell/_documents/measuring_stations_baltic_sea_node.html

Given that at least 4 - 6 grid points are needed to resolve an eddy, the present resolution of 600 m is sufficient to characterize the model as eddy resolving. Although we have access to super computers (HLRN), and thus ten-thousands of CPUs, to increase the model resolution, there is still a balance between spatial resolution and covered simulation period. Since the aim was to study the large scale distribution of TNT, sensitivity of model parameters and climatology, we decided for the coarser resolution. In Figure 39 we show the impact of spatial resolution on the resolution of topographic features in the Kolberger Heide.

A vertical resolution of 42 layers in terrain-following adaptive coordinates with adaptation towards stratification (Hofmeister et al., 2010) with a maximum surface layer thickness of 50 cm was chosen. Lateral diffusion of momentum, salinity and temperature was carried out along these model layers with a harmonic Smagorinsky diffusivity and a turbulent Prandtl number of 3. Vertical diffusivities were obtained from GOTM (General Ocean Turbulence Model, Umlauf et al., 2005), based on a k-epsilon model with the algebraic second-moment closure of Canuto (2001). The second-order Superbee scheme with reduced numerical mixing (Klingbeil et al., 2014) was chosen for the advection of all prognostic quantities (including turbulent kinetic energy and dissipation rate). To account for ice coverage, for the present study GETM was extended by a thermodynamic ice model (fast growing ice) according to Winton (2000). A similar choice was made in the numerical experiments of Fennel et al. (2010).

The hazardous substances are modelled as TNT, a typical WWII MC, in form of open TNT surfaces at the bottom, dissolved TNT in the water column and TNT accumulation in benthic filter feeders. The TNT dynamics depend on temperature-depending solubility, temperature-depending degradation rate in the water column and filter capacity of the benthic filter feeders (mussels). The TNT model is coupled via FABM (Framework for Aquatic Biogeochemical Models, Bruggeman and Bolding, 2014) to the GETM model. The parametrization of temperature-depending TNT solubility as well as filter capacity of the benthic filter feeders is based on lab and field experiments.

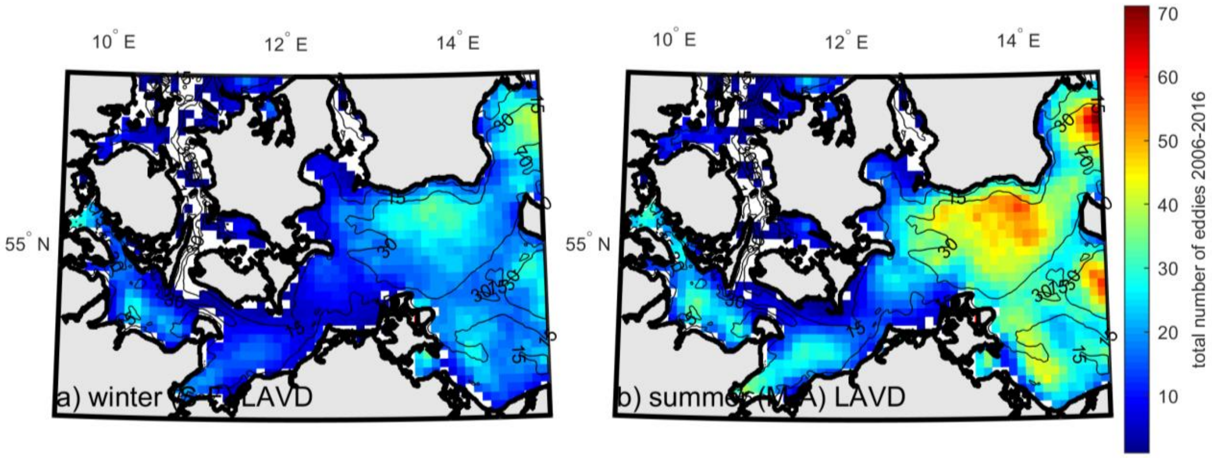

Figure 40 Total number of detected eddies living longer than 15 h in 12 × 12 km2 boxes within the period 2006 - 2016 applying LAVD based tracking. a) Total number of eddies in the season of cooling and mixing (September to February), b) Total number of eddies in the season of warming and stratification (March to August).

The source regions of TNT in the model are based on munitions dumping grounds described in the database of BLANO-Expertenkreis “Munition im Meer” and the naval command of the German armed forces (Marinekommando der Bundeswehr (Abteilung Einsatz, Unterabteilung Geoinformation)) (Figure 27). The amount of dumped munitions with open surfaces in these dumping grounds is unknown as well as the size of the open surfaces. The size of the open surfaces is depended on the type and amount of dumped munition, its degree of corrosion and if controlled detonations have taken place in this region. Hydroacoustic measurements and underwater video recordings can be used to estimate the size of the open surfaces. More precise estimates result in a more realistic model. Furthermore, there are differences in the amount of dumped munitions and their open surfaces in dumping grounds, munitions-contaminated areas and munitions suspected areas, that should be quantified in the model.

To estimate the lifetime of hydrodynamic structures, that mix the dissolved TNT in the water column, an analysis of front and eddy distribution in the western Baltic Sea is needed. There are several eddy and front detection tools available. It is important for the analysis that the applied tools use a definition of front resp. eddy, that take into account the physical impact of the hydrodynamic structure on the hydrodynamic in the region. For this purpose, we used a method that relies on the separation of regions of different dynamical behaviour by the eddy boundary resp. the front. The Lagrangian averaged vorticity deviation (LAVD) developed by Haller (2016) is used to detect eddies. LAVD detect separatrices between the eddy’s inside and outside defined as eddy boundary. The western Baltic Sea is characterized by short living hydrodynamic structures as fronts and eddies that separate, mix and in case of eddies transport water masses. A ten-years perspective (2006 - 2016) of the dynamics of eddies in the upper ten meters of the water column shows that 87 % of the detected eddies live shorter than 48 h and only 2 % longer than 100 h. Thereby most of the eddies stay close to their place of origin (89 % within a range of 10 km) and only 0.5 % travel longer distances of more than 30 km. The spatial distribution of the number of eddies in the season of cooling and mixing (September to February) and the season of warming and stratification (March to August) does not show different pattern (Figure 40), but the number of eddies within the pattern varies due to the influence of mixing and stratification processes. For fronts no long-term trend of their spatial distribution could be found. They act more as a temporal separation of water masses for some hours up to one day. In conclusion, eddies could act as seasonal transporters (Vortmeyer-Kley et al., 2019) of TNT-contaminated water masses in specific regions, while fronts as short-term separatrices hinder the exchange or mixing of water masses on regional scales.

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4.7 Water sampling

Responsible institute: GEOMAR

All samples should be protected from heat and light, as the target MCs are sensitive to both and may undergo transformation or degradation. Water samples are collected using either a pump system or Niskin bottles. Munitions act as point sources of MCs, which are rapidly diluted upon release. As a result, it is preferable, to collect water samples with Niskin bottles, to avoid ship drifting out of the munitions plume during pumping. Water samples may also be collected by divers in closer proximity to the munitions. More than 99 % of MCs in the water column appear to be in the dissolved phase (< 0.2 µm), so sample filtration does not appear necessary. However, degradation experiments indicate that sterile filtered samples are stable at 8 °C for up to 10 d, while unfiltered samples must be extracted and the MCs frozen immediately after collection. Suspended particles are collected with 0.2 µm Sterivex filters (filtrate can be reserved for dissolved MC analysis). Solvent-resistant membrane material (e.g. PTFE, PVDF) should be used, to allow MC extraction directly within the filter capsule.

TNT and other MCs can be adsorbed by plastic sampling materials, which indeed forms the basis for passive sampling of MCs in natural waters (e.g., Warren et al., 2019; Lotufo et al., 2019). In tests with plastic sampling materials used in UDEMM (amber HDPE bottles, PP centrifuge tubes) negligible adsorption of target within the short holding time was observed (Beck et al., 2019). Nonetheless, care should be taken, to ensure that samples for MC analysis are not stored in plastic containers for extended periods of time.

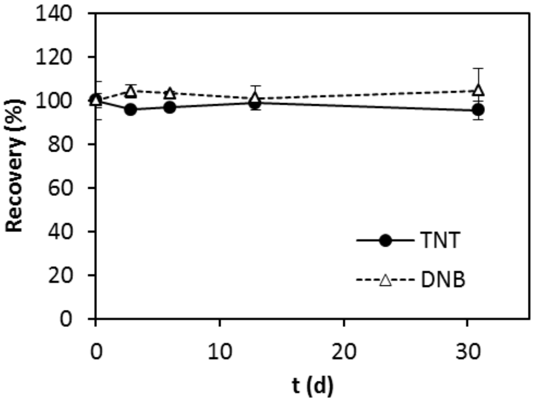

Figure 41: Recovery of stable isotope-labelled TNT and DNB. Error bars represent standard deviation of the mean of triplicate incubations (from Beck et al., 2019).

Previous results showed that MC distributions in the water column were highly variable in both space and time, and that high resolution sampling is required to adequately monitor the regional magnitude and extent of contaminant plumes from underwater munitions dumping grounds. As a result, the sample collection and processing method developed earlier during UDEMM (and published in Gledhill et al., 2019) was modified to reduce processing time and facilitate higher frequency sampling.

In the adapted method, 1 L water samples were collected using standard oceanographic Niskin bottles, spiked with stable isotope labelled MCs (TNT and DNB), and extracted on-board the research vessel. Samples were filled into medical-grade, UV-protected infusion bags, and passed by gravity through solid-phase extraction columns for pre-concentration. Glass fibre filters could also be placed ahead of the column, to collect particles for measuring adsorbed MCs. This allowed simultaneous processing of an unlimited number of samples, and eliminated the need to transport large-volume water samples to land-based laboratories. Columns with extracted MCs were stored frozen for transport to laboratories, or could be processed further on board.

Figure 42: (Left) Mini-Niskin bottle rosette for collecting vertical profile water samples. (Right) Gravity setup for MC extraction from seawater.

Water sampling for trace metals (e.g., Fe, Zn, Pb) and Hg must follow strict protocols for contamination control. Detailed methods can be found in the GEOTRACES Cookbook (Cutter et al., 2017). A brief description is included here. For metals, sample bottles should be made of low-density polyethylene, and cleaned according to Achterberg et al. (2001). Bottles are rinsed with methanol or acetone to remove oils, and soaked in an alkaline detergent for one week. After a deionized water rinse, bottles are rinsed again with ultrapure water (UHP; e.g., MilliQ 18MΩ-cm) under a HEPA-filtered laminar flow bench, and then placed in a 6M HCl bath for two weeks. Bottles are then rinsed again with UHP water, soaked in a 3M HNO3 bath for two weeks, rinsed with UHP water, and then filled with UHP water and acidified with 1 mL ultrapure HCl for storage. Bottles are stored and handled double-bagged in polyethylene zip closure bags.

For mercury, borosilicate bottles (e.g. Schott) are used, and cleaned according to Hammerschmidt et al. (2011). For total Hg, glass bottles are cleaned by a one week soak in alkaline detergent, followed by one-week soak in HCl, and an addition one-day soak in 0.5 % BrCl, with UHP water rinses between baths. A similar process is used for organic Hg species, but omitting the BrCl step.

Water is collected with either peristaltic or teflon diaphragm pumps, or with metal-clean Go-Flo bottles. Go-Flos and pump tubing must be deployed on a non-metal or plastic coated cable. Water is filtered through 0.2 µm PES Sartobran or Acropak capsule filters under a HEPA-filtered laminar flow bench, and filled directly into clean bottles. Metals samples are acidified to pH <2 with ultrapure HCl. Total Hg samples are preserved with 0.1 % BrCl (Cutter et al., 2017), and organic Hg samples are acidified with 0.6 - 1 % v/v H_2SO_4 (Bowman and Hammerschmidt, 2011).

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4.8 Bio-Monitoring with mussels

Responsible institute: CAU

Mussels for bio-monitoring purposes were not sampled in the field but were bought from a mussel farm near Kiel. A subset of the mussels should be screened for any contamination prior to being deployed for monitoring. Care shall be taken to keep the mussels alive and healthy until deployment (cold, circulating water of the right level of salinity).

Replacement of mussels during a field exposure experiment

Materials needed:

- Nets (common laundry net bags, 8 mm mesh size, knotless polyester, colourfast, 40 × 60 cm^2)
- Cable ties (98 × 2.5 mm; 290 × 4.8 mm; 360 × 4.8 mm)
- Plastic key chains in different colours
- Freezer bags
- Calliper anchorings must be selected according to the circumstances in the test area, based on the strength of the currents

For long term use moorings (ca. 100 kg) are recommended. In our case they consisted of steel rods painted with a corrosion-preventing varnish, which were welded together to a ring of approximately 1 m diameter. For a field experiment with a duration of a few weeks, calcareous sandstones (24 × 11 × 17.5 cm^3) are sufficient (Figure 43).

For marking and positioning of mussel bags above the ground a rope (e.g. polyethylene 10 mm diameter, 3-strands, breakload 1110 daN) and a trawl float (e.g. diameter 280 mm, buoyancy 8.4 kg) are needed.

Figure 43: Moorings used for bio-monitoring with blue mussels. (Left) A mooring used for shorter time periods together with lifting body, mussel net and three stones as anchor (6,6 kg each). Tow passive samplers are fixed to the rope above the net. (Middle) A mooring used for longer time periods hanging upside down on a ship crane, together with two lifting bodies, a steel anchor (100 kg), two mussel nets with mussels and a piece of wood inside the nets, to allow the mussels to attach themselves. (Right) Mooring on the seafloor, in direct vicinity to two moored mines.

A species which can naturally be found in the test area, in our case the mussel *M. edulis*, should be used for biomonitoring purposes.

Live mussels were bought from a commercial mussel farm. A big plastic bag (e.g. a common Ikea bag) can be used for transport. To prevent mussels against warmth and dehydration, they are covered for up to 6 h by a thick jute or linen bag soaked with sea water. For longer periods of time they are hung in seawater, either at the harbour or on the ship.

Each mussel is inspected to make sure that the mussel shells are intact and the byssus gland is present. Twenty mussels, preferably not smaller than 5 cm, are put in each bag. The exact size of each mussel is measured with a calliper before and after recovery. The growth during the exposure period gives an indication of the general mussel fitness. After the insertion of ten mussels, the net is separated in two parts with a cable tie and ten more mussels are put in the second part of the net. Bags are closed with a cable tie. To label the nets, a key chain with a number is fixed on every net. Different key chain colours facilitate identification. Nets intended to be placed at the sea bottom are held in place by a small stone of about 5 cm in diameter.

After recovery, the mussels should be unpacked as soon as possible and put in insulated bags on dry ice. For longer periods of time the mussels may be stored at -20°C in a freezer, until used.

4.9 Chemical analyses of water, sediment and organic matter

Responsible institutes: GEOMAR & CAU

4.9.1 Sample preparation

4.9.1.1 Water

Dissolved MCs: Samples were stored at 4°C and pre-concentrated as soon as possible after collection. Solid phase extraction was used for matrix removal and pre-concentration. Optimal pre-concentration conditions included a column preconditioning step with 4 mL acetonitrile (ACN) followed by 4 mL MQ-H_2O (gravity flow), sample loading (1 L) at a flow rate of 8 mL min^{-1} with the automated pre-concentration system or by gravity, rinsing with 10 mL MQ-H_2O under gravity flow, and sample elution with 3.5 mL ACN. For sample elution, ACN was first loaded onto the column and left for approximately 5 min, prior to elution into a vial via gravity flow. A 1.75 mL sample aliquot was evaporated to near dryness (ca. 50 µL) under vacuum after addition of 50 µl of MQ-H2O with a centrifugal evaporator. The evaporite was diluted to 0.5 mL with 50:50 MQ-H_2O:MeOH (v/v) and mixed for approximately 20 sec with a vortexor. Samples were transferred to an amber HPLC vial and kept at 4°C prior to analysis.

Particle-associated MCs: Filter-retained particles are extracted directly in the intact filter cartridges using 5 mL of LCMS grade acetonitrile. The acetonitrile is allowed to permeate the filter membrane, and then left in contact for 15 min. The acetonitrile is then forced through the filter into a sample vial. Samples are diluted to 30 % with MilliQ water, and analysed directly.

4.9.1.2 Mussel Condition Index

To compare general mussel fitness between different groups of exposed mussels, the Condition Index (CI) is calculated. Before sample preparation the shells and meat are weighed separately. The CI is calculated as follows: CI = [wet meat weight (g)/shell weight (g)] × 100.

4.9.1.3 Biota - Wet homogenization/extraction

Up to eight mussels are thawed, the whole meat put in a 50 mL polypropylene tube and homogenized using a T25 Ultra-Turrax. Tissues are aliquoted in 1.0 g portions, put in 50 mL polypropylene tubes and 5 mL acetonitrile are added per tube. Each sample is mixed for 1 min using a vortex mixer. After that, tubes are centrifuged for 5 min at 3000 rpm (20 °C). Supernatants are decanted and filled up with acetonitrile to a total volume of 10.0 mL, followed by GC-MS analysis.

4.9.1.4 Sediment and Biota - Lyophilization and dry homogenization/extraction

Sediment and biota samples are frozen and then lyophilized. Biota is ground to a coarse powder using a stainless steel grinder. For MCs, approximately 10-500 mg of tissue samples are extracted in one or two millilitres of acetonitrile. The smaller volume of ACN is used when available sample mass is less than 150 mg. Approximately 2 g of sediment are extracted in 10 mL ACN. Samples are sonicated for 15 min, and extracts filtered through 0.2 µm PTFE syringe filters (Whatman GD/X). Extracts are diluted with MQ-H2O to 30 % ACN for analysis.

For metals and Hg analysis extraction follows Hammerschmidt and Fitzgerald (2001) and Tseng et al. (1997). Briefly, dried solid samples (0.1-1 g dry weight) are placed in 15 mL polypropylene centrifuge tubes. 8 mL of 4M ultrapure HNO_3 is added to the samples and analytes are extracted in an ultrasonic bath at 55°C for 15 min. Microwave-assisted extraction is also appropriate (Tseng et al., 1997). Samples are centrifuged, and the supernatant retained for analysis.

4.9.2 Analysis

4.9.2.1 MC analysis by GC-MS

For GC-MS/MS analysis samples were injected in a Trace 1310 gas chromatograph (Thermo Fisher Scientific Inc., Waltham, MA, USA) and eluted analytes were ionized with electron ionization (EI) or negative chemical ionization (CI) with methane as the reagent gas and analysed with a TSQ 8000 EVO Triple Quadrupole Mass Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in MRM-mode. For details, see appendix.

4.9.2.2 MC analysis by LC-ESI-MS

Pre-concentrated MCs from the dissolved phase are analysed in a matrix of 50 % (vol.) LCMS-grade methanol or 33 % LCMS-grade ACN. Additional method detail is found in Gledhill et al. (2019). Briefly, samples are analysed with a biocompatible ultra-high performance liquid chromatographic system (UHPLC, Ultimate 3000, Thermo) consisting of a binary high pressure pump, a temperature controlled autosampler, a column oven and a UV-visible diode array detector. Analytes are separated using a 150 × 2.1 mm Explosives E2 column. The eluent from the UV detector is injected via a divert valve into a heated electrospray ionisation source and then into a high resolution quadrapole/orbitrap mass analyser (HESI-MS, Q Exactive, Thermo). The UHPLC-HESI-MS is controlled with Xcalibur and Chromeleon software.

4.9.2.3 ICP-MS

Dissolved metals are analysed after automated solid-phase pre-concentration, following Rapp et al. (2017). Briefly, 10 mL subsamples are buffered to pH 6.4 using ultrapure ammonium acetate, pre-concentrated on WAKO resin at 3 mL/min, and eluted with 1 mL of ultrapure 1M HNO_3. The eluate is analysed directly by ICPMS. Sediment and tissue extracts are analysed by ICPMS for both metals and Hg. Dilution of the digest solution may be necessary, to avoid injecting strong acid solutions into the ICPMS.

4.9.2.4 CV-AFS

For total Hg samples are analysed by purge-and-trap thermal desorption CV-AFS (Cutter et al., 2017). Samples are neutralized with 0.05 % v/v hydroxylamine hydrochloride, reduced with stannous chloride or sodium borohydride, and the Hg trapped on gold-coated sand columns. Trapped Hg on the column is desorbed at 600-800 °C, and flushed into a CV-AFS detector for quantification. For Methyl-Hg, the sample is digested with H_2SO_4 for 12 h, and buffered to pH 5 with sodium acetate. Methyl-Hg is ethylated with Na-tetraethylborate, sparged from solution, and trapped on a Tenax column (Bowman and Hammerschmidt, 2011). The Tenax column is heated to 90 - 250°C, and organic species separated on an isothermal GC column, pyrolyzed at 600 - 800°C and detected by CV-AFS.

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5. Appendix

5.1 Analysis of nitroaromatic compounds in mussel tissue (blue mussels)

Materials needed:

Standard compounds (acquired from AccuStandard Inc., New Haven, USA)

- 2,4,6-trinitrotoluene (TNT) (1 mg/mL)
- 2-amino-4,6-dinitrotoluene (2-ADNT) (1 mg/mL)
- 4-amino-2,6-dinitrotoluene (4-ADNT) (1 mg/mL)
- 2,4-diamino-6-nitrotoluene (2,4-DANT) (0.1 mg/mL)
- 2,6-diamino-4-nitrotoluene (2,6-DANT) (0.1 mg/mL)

Acetonitrile, gradient grade

Conical polypropylene tubes, 50 mL

Homogenizer (Ultra-Turrax®, Ika Works Inc., Staufen im Breisgau, Germany)

Vortex mixer (Vf2, Ika Works Inc., Staufen im Breisgau, Germany)

Centrifuge, capable to process 50 mL conical tubes (Heraeus Megafuge 11R, Thermo Fisher Scientific Inc., Waltham, MA, USA)

Sample preparation

Up to eight mussels are thawed, the whole meat put in a 50 mL polypropylene tube and homogenized using a T25 Ultra-Turrax®. Tissues are aliquoted in 1.0 g portions, put in 50 mL polypropylene tubes and 5 mL acetonitrile are added per tube. Each sample is mixed for 1 min using a vortex mixer. After that, tubes are centrifuged for 5 min at 3000 g (20 °C). Supernatants are decanted and filled up with acetonitrile to a total volume of 10.0 mL, followed by GC-MS analysis.

GC-MS/MS analysis

Short column

The detection limit (signal to noise ratio > 3) for TNT, 4-ADNT and 2-ADNT was 0.5 ng/g wet weight in case of the 15 m column. For GC-MS/MS analysis one microliter of the samples is injected with a splitless liner in a Trace 1310 Gas Chromatograph (Thermo Fisher Scientific Inc., Waltham, MA, USA) and analytes are separated on a TG-SQC GC column (15 m × 0.25 mm × 0.25 µm, Thermo Fisher Scientific Inc., Waltham, MA, USA). Helium is used as carrier gas with a carrier flow rate of 1.5 mL/min and a split flow rate of 20 mL/min. The oven temperature program is as follows (Figure 44):

1. 1 min at 120°C
2. heating to 220°C with a heating rate of 30°C/min
3. heating to 300°C with a heating rate of 50°C/min
4. 300°C held for 0.5 min

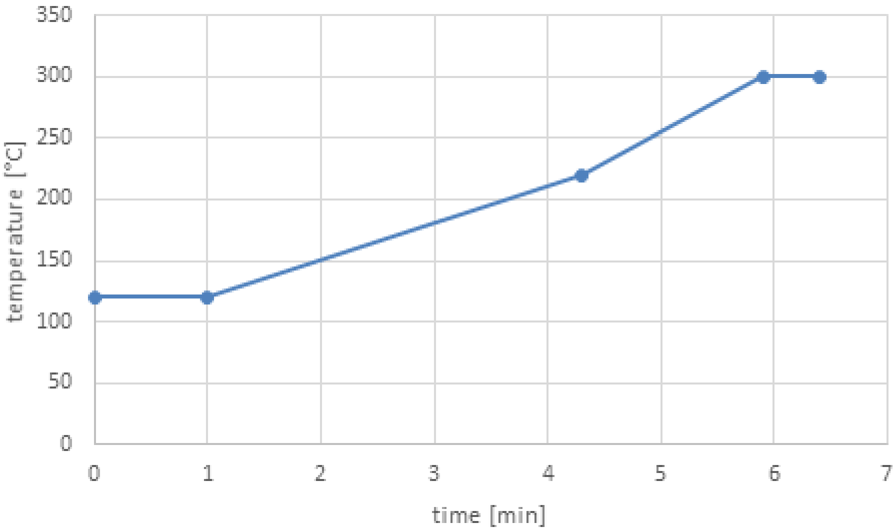

Figure 44: GC temperature program, short column.

This setup results in the following retention times (Figure 45):

- TNT, 3.5 min
- 4-ADNT, 4.3 min
- 2-ADNT, 4.5 min

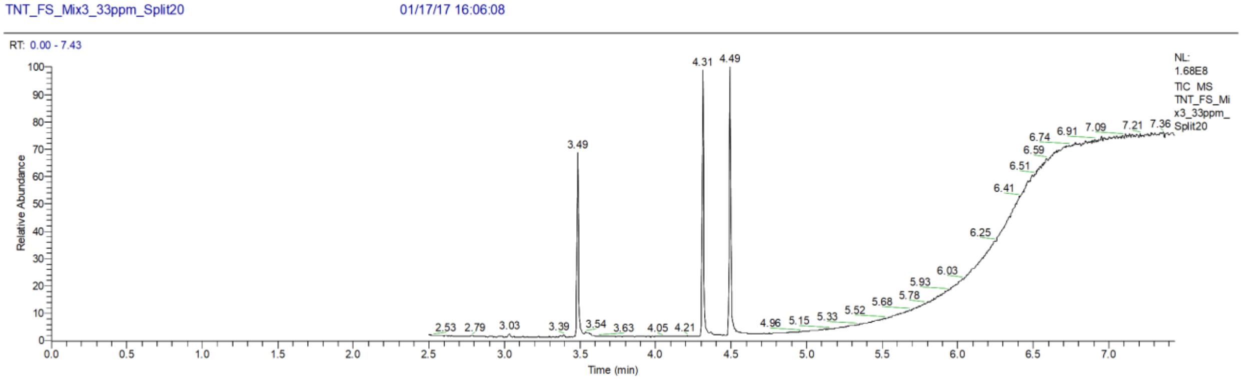

Figure 45: Total ion chromatogram (full scan mode) of a TNT, 2-ADNT, 4-ADNT standard mixture, 3.5 ng each.

Eluted analytes are ionized with electron ionization (EI) or negative chemical ionization (CI) with methane as the reagent gas and analysed with a TSQ 8000 EVO Triple Quadrupole Mass Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in MRM-mode. MRM specifics can be found in Table 9 and Table 10.

Long column

The detection limit (signal to noise ratio > 3) for TNT, the mono- and diamino compounds was 5 - 30 ng g^{-1} wet weight in case of the 30 m column. For GC-MS/MS analysis one microliter of the samples is injected with a splitless liner in a Trace 1310 Gas Chromatograph (Thermo Fisher Scientific Inc., Waltham, MA, USA) and analytes are separated on a TG-5MS GC column (30 m × 0.25 mm × 0.25 µm, Thermo Fisher Scientific Inc., Waltham, MA, USA). Helium is used as carrier gas with a carrier flow rate of 1.5 mL/min and a split flow rate of 20 mL/min. The oven temperature program is as follows (Figure 46):

1. 1 min at 120°C
2. heating to 230°C with a heating rate of 4°C/min
3. 230°C held for 1 min
4. heating to 300°C with a heating rate of 40°C/min
5. 300°C held for 1 min

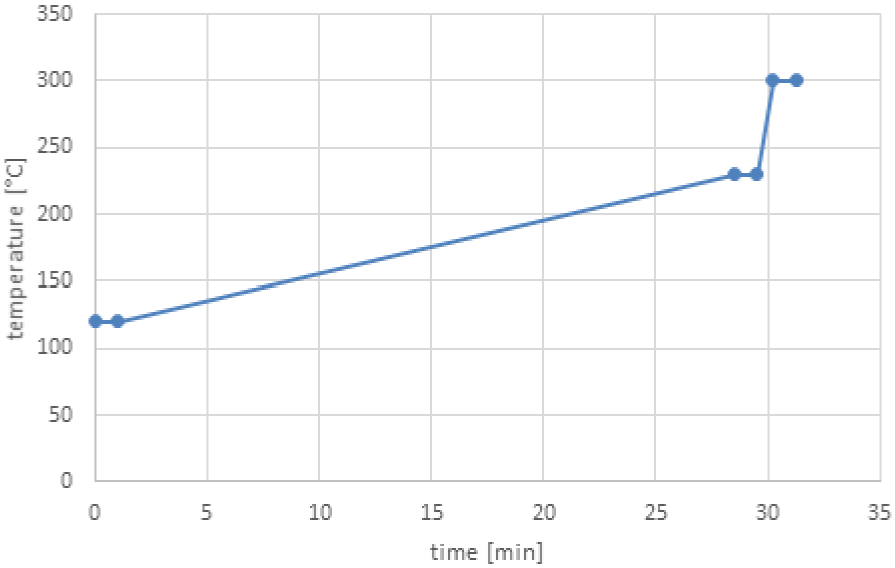

Figure 46: GC temperature program, long column.

This setup results in the following retention times (Figure 47):

- TNT, 13.5 min
- 2,4-DANT, 18.1 min
- 4-ADNT, 19.0 min
- 2,6-DANT, 19.9 min
- 2-ADNT, 20.2 min

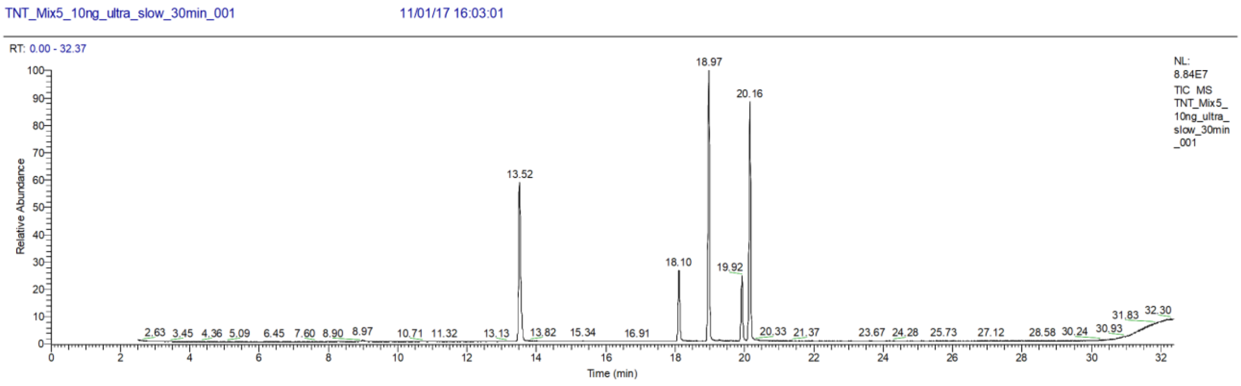

Figure 47: Total ion chromatogram (full scan mode) of a TNT, 2,4-DANT, 4-ADNT, 2,6-DANT, 2-ADNT standard mixture, 1 ng each.

Eluted analytes are ionized with electron ionization (EI) and analysed with a TSQ 8000 EVO Triple Quadrupole Mass Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in MRM-mode. MRM specifics can be found in Table 11.

Table 9: Multiple reaction monitoring transitions (m/z) values used for the detection of TNT and its metabolites with electron ionization (EI) (CE, collision energy; V, voltage).

Compound name	Quantitative transition		Qualitative transition 1		Qualitative transition 2		Qualitative transition 3	
	Precursor > product	CE (V)	Precursor > product	CE (V)	Precursor > product	CE (V)	Precursor > product	CE (V)
2,4,6-trinitrotoluene	210.0 > 164.1	6	210.0 > 193.0	8	180.0 > 76.1	12	164.0 > 90.1	10
4-amino-2,6-nitrotoluene	180.0 > 78.0	16	104.1 > 77.1	8	180.0 > 163.1	8	163.0 > 78.0	14
2-amino-4,6-nitrotoluene	197.0 > 180.1	6	104.1 > 77.0	8	180.0 > 133.0	6	180.0 > 67.0	12

Table 10: Multiple reaction monitoring transitions (m/z) values used for the detection of TNT and its metabolites with chemical ionization, short column (CI) (CE, collision energy; V, voltage).

Compound name	Quantitative transition		Qualitative transition 1		Qualitative transition 2	
	Precursor > product	CE (V)	Precursor > product	CE (V)	Precursor > product	CE (V)
2,4,6-trinitrotoluene	210.0 > 152.1	6	227.0 > 210.0	8	210.0 > 124.0	8

4-amino-2,6-nitrotoluene	197.0 > 46.0	12	167.0 > 46.0	26	167.0 > 137.1	8
2-amino-4,6-nitrotoluene	197.0 > 46.0	16	197.0 > 152.1	8	197.0 > 180.0	8

Table 11: Multiple reaction monitoring transitions (m/z) values used for the detection of TNT and its metabolites with electron ionization, long column (EI) (CE, collision energy; V, voltage).

compound name	quantitative transition		qualitative transition 1		qualitative transition 2		qualitative transition 3	
	Precursor > product	CE (V)	Precursor > product	CE (V)	Precursor > product	CE (V)	Precursor > product	CE (V)
2,4,6-trinitrotoluene	193 > 163	6	210 > 193.0	8	180.0 > 76	12	164.1 > 90.1	8
4-amino-2,6-nitrotoluene	181.0 > 78.0	16	104.1 > 77.1	8	180.1 > 163.1	6	197.1 > 180.1	6
2-amino-4,6-nitrotoluene	197.1> 180.1	6	104.1 > 77.0	8	180.1 > 133.1	6	180.1 > 67.1	12
2,4-DANT	150.1 > 95.1	6	167.1 > 95.1	12	167.1 > 150.1	4	121.1 > 94.1	6
2,6-DANT	121.1 > 77.1	12	94.1 > 67.1	6	104.1 > 77	6	167.1 > 121.1	12

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